Fully-Renewable and Degradable Thermoplastic Elastomers

A DISSERTATION
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF THE UNIVERSITY OF MINNESOTA
BY

Carolyn Leigh Wanamaker

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Marc A. Hillmyer, William B. Tolman

January, 2009
Acknowledgements

I would like to acknowledge a number of people whose help and encouragement made this work possible. First I would like to thank my advisors, Marc Hillmyer and Bill Tolman, for their guidance and support. I appreciate their enthusiasm and encouragement throughout my graduate career.

It has also been a pleasure to come to lab every day and work beside so many generous, friendly and thoughtful people. Many thanks to the members of the Hillmyer and Tolman groups. In particular, I would like to thank Seth Friese, Jessica Imholte, Marc Rodwogin, Louis Pitet, and Mark Amendt. Thank you for all of the laughs, support, and advice. You made these years enjoyable and memorable. Thank you also to Mandy Schmit for your support and friendship.

Most importantly I would like to thank my husband, Tim. Thank you for your reassurance and understanding. This would have never become a reality without your love and support. I am ever grateful to all of my parents; Sue, Steve, Dick, Kris, Craig and Kristi, and to my sister, brothers, extended family and friends. You are constant blessings in my life, and I am thankful for your encouragement.
Abstract

The most common polymers derived from renewable feedstocks, poly(3-hydroxybutyrate), polyglycolide, and polylactide (PLA), have high stiffness and tensile strength, but are inherently brittle, thus limiting the potential for these polymers to replace elastic and ductile polymers derived from fossil fuels. The work described in this thesis was directed toward expanding the properties of renewable resource polymers through the investigation of completely-biorenewable thermoplastic elastomers. Polymenthide (PM), a soft biorenewable polymer derived from (−)-menthol, is immiscible with PLA and was utilized as the middle block in a PLA-containing ABA triblock copolymer. Tensile measurements demonstrated impressive elongations and elastomeric properties typical of thermoplastic elastomers, however, the materials were relatively weak. The tensile properties of the polymers were found to be highly dependent on the molecular weight and crystallinity of the polylactide blocks. Substituting the amorphous PLA with semi-crystalline PLLA or PDLA significantly improved the strength of the material. Blends of the enantiomeric triblock copolymers further increased the strength through stereocomplexation of the enantiomeric polylactide segments. These results led to the investigation of stereocomplexed micelles as nucleating agents for PLLA. Quantifiable improvements in the nucleation efficiency of PLLA were observed when blending PLLA with PDLA-containing triblock copolymers. Finally, potential applications of these all-biorenewable triblock copolymers were investigated through hydrolytic degradation and adhesion studies. During hydrolytic degradation, the triblock copolymers were able to maintain a significant amount of their mechanical properties for many weeks.
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Background

1.1 Introduction

The world’s fossil fuel supply is being exhausted by population growth and energy demand, and predictions indicate that the peak and subsequent decline in the world’s oil production will occur in the next few decades.\textsuperscript{1,2} Oil prices are volatile and subject to supply, production, and socio-political influences. Moreover, the emission of green-house gases during production and incineration of fossil fuels has unpredictable and irreversible consequences on the global climate.\textsuperscript{3} The utilization of fossil fuels in the manufacturing of plastics accounts for approximately 7\% of worldwide oil and gas.\textsuperscript{4} Synthetic polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC) are all plastics derived from fossil fuels. These materials cause serious environmental pollution due to wasted and undegraded polymers.\textsuperscript{4} The non-renewability, emission of green-house gases, and staggering waste problem are making a serious dent in the versatility of these materials.\textsuperscript{5} For these reasons, it is no surprise that a thriving area of new research today focuses on the subject of polymeric materials derived from biomass, i.e., plant derived resources.\textsuperscript{6}
Chapter 1: Background

Biorenewable polymers are those synthesized from renewable feedstocks such as corn, sugarcane, soybeans, wheat, and switchgrass. The use of bio-based polymer products will reduce the chemical industry’s dependence on fossil fuels. In contrast to petroleum-based products, the material costs of biorenewable products are relatively low while the processing costs are relatively high. As scientists and engineers develop more efficient processing technologies, the overall costs of bio-based products will drop significantly, making these products highly competitive with petroleum-based products.

Unfortunately, there are a limited number of polymers that are derived from renewable feedstocks, and only a fraction of these have the potential to replace petroleum-based products. These include poly(3-hydroxybutyrate), polyglycolide, and polylactide, all of which have high stiffness and tensile strength, but are inherently brittle and cannot replace the commodity plastics that are tough and flexible such as polyethylene and polypropylene. In order for bio-based polymers to replace petroleum-based polymers in the future, the properties “palette” of these polymers needs to be expanded.

The overall goal of expanding and improving the properties “palette” of these polymers can be accomplished through modification of current biorenewable polymers. Modification strategies include blending other molecules and polymers and synthesis of block copolymers. This chapter summarizes efforts towards improving the mechanical properties of the biorenewable polymer, polylactide, through the synthesis of polylactide block copolymers with biorenewable and non-biorenewable
components. The research contained in this thesis is aimed towards improving the toughness and flexibility of polylactide through the synthesis of new completely-biorenewable block copolymers.

1.2 Biorenewable and Biodegradable Polymers

Recently, there has been a drive toward designing processes and products that are both derived from biorenewable resources and can be degraded. Biorenewable and biodegradable polymers, illustrated in Figure 1.1 are polymers that are not only derived from renewable resources, but are also compostable. Natural polymers such as starch, proteins, cellulose and natural rubber are prime examples of degradable materials derived from biomass. Polyhydroxyalkanoates (PHAs) are a family of linear, biodegradable polyesters synthesized by a wide variety of bacteria through the fermentation of sugars, lipids, among others. The most representative member of this family is poly(3-hydroxybutyrate) (P3HB), a highly crystalline polymer with a melting temperature of 180 °C. P3HB is biocompatible and currently is used in biomedical applications such as biodegradable sutures.

Synthetic, biodegradable, and biorenewable polyesters are becoming more attractive for use in industrial applications. The simplest aliphatic polyester, polyglycolide (PGA) is prepared from the starting material glycolic acid, and is commonly used in biomedical applications such implants and sutures. One of the most popular biorenewable polymers, polylactide (PLA), will be discussed in detail in Section 1.3. More recent efforts have been placed on the development of new
biorenewable, biodegradable monomers. These include macrolactones derived from ricinoleic acid, \textsuperscript{14} 3-hydroxypropionic acid, \textsuperscript{15} and 9-hydroxynonanoic acid. \textsuperscript{16}

![Figure 1.1](image)

**Figure 1.1** A simplified cycle for biologically degradable materials derived from renewable resources

There are also many polymers that are partially-derived from renewable sources. Although not ideal, these polymers have a wide range of properties and uses. For example, polymers such as poly(butylene succinate) (PBS) and poly(trimethylene terephthalate) (PTT) are partially-derived from renewable resources; and PBS is biodegradable, whereas PTT is not. \textsuperscript{17} PBS is synthesized through a condensation polymerization from the C-4 compounds succinic acid and 1,4-butandiol, \textsuperscript{18} and is reported to have a melting point of around 114 °C. \textsuperscript{19} Zhang et al. have also
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synthesized a new monomer that is partially derived from lactic acid and contains lactic acid and oxetane subunits.\textsuperscript{20}

One of the most studied degradable aliphatic polyesters, poly(\(\varepsilon\)-caprolactone) (PCL), is derived from non-renewable resources. PCL is a semicrystalline polymer \((T_m \approx 60 \, ^\circ C)\) with a low glass transition temperature \((T_g \approx -60 \, ^\circ C)\).\textsuperscript{21} The PCL chain is flexible and exhibits high elongations with low strength. Other non-renewable resource degradable polymers include poly(1,5-dioxepan-2-one) (PDXO) and poly(1,3-trimethylene carbonate) (PTMC).\textsuperscript{22,23} New functionalized cyclic esters have also been synthesized that contain lactide or caprolactone backbones.\textsuperscript{24} Table 1.1 summarizes the thermal and mechanical properties of some of these biodegradable polymers.

1.3 Renewable Resource Polymers: Polylactide and Polymenthide

Polylactide (PLA) has attracted significant attention as it is a commercially produced biodegradable polymer derived from biomass.\textsuperscript{25} This aliphatic polyester can be synthesized via polycondensation of lactic acid\textsuperscript{26} or the ring-opening polymerization (ROP) of lactide (Figure 1.2).\textsuperscript{13} Lactide is the cyclic dimer of lactic acid, which is produced by fermentation from biomass such as corn and sugar beets.\textsuperscript{27,28} Lactide ROP using a metal catalyst is the more commonly used route to produce PLA,\textsuperscript{29} and is the synthetic route used commercially by Natureworks.\textsuperscript{25}
<table>
<thead>
<tr>
<th></th>
<th>P3HB\textsuperscript{5,30}</th>
<th>PGA\textsuperscript{30,31}</th>
<th>PBS\textsuperscript{5}</th>
<th>PTT\textsuperscript{5}</th>
<th>PCL\textsuperscript{5,23,30}</th>
<th>PDXO\textsuperscript{22,30}</th>
<th>PTMC\textsuperscript{23,32}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Density</strong></td>
<td>1.18–1.25</td>
<td>1.50–1.69</td>
<td>1.26</td>
<td>1.35</td>
<td>1.06–1.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Melting point (°C)</strong></td>
<td>164–175</td>
<td>220–225</td>
<td>114–115</td>
<td>225</td>
<td>60</td>
<td>---</td>
<td>36</td>
</tr>
<tr>
<td><strong>Tensile modulus (MPa)</strong></td>
<td>1,400</td>
<td>80–1,000</td>
<td></td>
<td></td>
<td>270–400</td>
<td>3–6</td>
<td></td>
</tr>
<tr>
<td><strong>Tensile strength (MPa)</strong></td>
<td>24–27</td>
<td>4,000–14,000</td>
<td>32</td>
<td>68</td>
<td>24</td>
<td>0.5–3</td>
<td></td>
</tr>
<tr>
<td><strong>Elongation at break (%)</strong></td>
<td>6–9</td>
<td>15–20fibers</td>
<td></td>
<td></td>
<td>300–1000</td>
<td>160–1000</td>
<td></td>
</tr>
<tr>
<td><strong>Biorenewable</strong></td>
<td>yes</td>
<td>yes</td>
<td>partially</td>
<td>partially</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>
Due to the chirality of the lactic acid molecule, lactide has three enantiomers, L-lactide with two S-stereocenters, D-lactide with two R-stereocenters, and meso-lactide with one S-stereocenter and one R-stereocenter. The stereochemistry of the monomers in the feed significantly influences the thermal and mechanical properties of polylactide.\(^{33}\) Polymerization of a mixture of D- and L-lactide typically results in atactic, amorphous \((T_g \approx 60 \degree C)\) poly(D,L-lactide), PLA, whereas polymerization of L-lactide or D-lactide results in isotactic, semicrystalline \((T_m \approx 180 \degree C)\) poly(L-lactide), PLLA, or poly(D-lactide), PDLA (Figure 1.3).\(^ {34}\)

Blending of PLLA and PDLA leads to the formation of stereocomplex crystallites with a different crystalline structure than that of the semi-crystalline homopolymers.\(^ {31,35}\) Ikada and Tsuji et al. have investigated the influence of the blending ratio of the two isomeric polymers,\(^ {41,36}\) the molecular weight of the isomeric polymers,\(^ {41,36-37}\) the optical purity of the isomeric polymers,\(^ {38-39}\) and the blending mode of the polymers\(^ {41,36-39}\) on the formation and properties\(^ {40}\) of the stereocomplex. The stereocomplex crystals have a melting temperature of approximately 230 °C, 50 °C higher than the \(T_m\) of the PLLA or PDLA components.\(^ {31,41}\) The higher melting temperature is attributed to strong van der Waals interactions that cause a specific
Figure 1.3 The lactide and polylactide enantiomers
energetic interaction-driven packing. Stereocomplexed PDLA/PLLA has higher stiffness and elongations than PLLA or PDLA homopolymer. The effect of stereochemistry on the mechanical properties of polylactide is summarized in Table 1.2.

**Table 1.2 Physical properties of polylactides**

<table>
<thead>
<tr>
<th></th>
<th>poly(D,L-lactide) (PLA)</th>
<th>poly(L-lactide) (PLLA)*</th>
<th>stereocomplexed polylactide*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.27</td>
<td>1.25–1.29</td>
<td></td>
</tr>
<tr>
<td>Glass transition</td>
<td>50–60</td>
<td>50–65</td>
<td>65–72</td>
</tr>
<tr>
<td>temperature (°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>---</td>
<td>170–190</td>
<td>220–230</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>1.5–1.9</td>
<td>7–10</td>
<td>8.6</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>40–50</td>
<td>120–2,300</td>
<td>880</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>5–10</td>
<td>12–26</td>
<td>30</td>
</tr>
</tbody>
</table>

* oriented fibers

As mentioned earlier, polylactide is a biodegradable polymer. It degrades by hydrolytic cleavage of the backbone ester bonds to eventually form lactic acid, which then is converted through metabolic processes to carbon dioxide and water. PLLA is even recycled industrially by hydrolysis to lactic acid. The rate at which PLA degrades is significantly dependent on the tacticity of the polymer. Isotactic PLLA and PDLA exhibit relatively slow hydrolysis rates relative to that of atactic PLA.
Chapter 1: Background

PLLA films allowed to degrade under biological conditions (pH 7.4, phosphate buffer at 37 °C) reached 50% of their initial molecular weights at around 53 weeks with no significant mass loss observed until 104 weeks, whereas atactic PLA, under the same conditions, reaches 50% of its initial molecular weight between 7 and 12 weeks with significant mass loss observed between 8 and 13 weeks.\textsuperscript{21,46,47}

Because of polylactide’s susceptibility to hydrolytic degradation and biocompatibility,\textsuperscript{30,48} it has been employed in biomedical applications including tissue engineering,\textsuperscript{49} drug delivery,\textsuperscript{50} and medical implants.\textsuperscript{51} Polylactide also possess high stiffness and tensile strength comparable to PET, as well as processing characteristics of PS, making it marketable for use in a variety of fiber and packaging products.\textsuperscript{25} While the stiffness of PLA is considered an asset in some applications, a property issue that has limited PLA’s use on a broader scale is its low impact strength or brittleness.\textsuperscript{52} Under tension, polylactide fractures at very low strains (see Table 1.2),\textsuperscript{31} and is therefore unsuitable for use in many applications where elasticity and ductility are essential. Numerous strategies have been implemented to alter the properties of PLA’s and will be discussed subsequently.

In our work, a soft complement to PLA was needed, and inspiration was taken from previous work on polymenthide. (−)-Menthol is a natural product extracted from the plants \textit{Mentha Arvensis} and \textit{Mentha Canadensis}, both known as cornmint, and is used in the pharmaceutical, confectionery, and flavor and fragrance industries.\textsuperscript{53} Over 12,000 metric tons of (−)-menthol are produced each year, most of which is cultivated from India and China.\textsuperscript{54} More recently, multistep processes were developed to make
synthetic (−)-menthol starting from the readily available terpenes (+)-citronellal, (−)-piperitone, and (+)-pulegone.\(^{54}\) The readily available ketone derivative of (−)-menthol, (−)-menthone, can also be found in cornmint oil and is an intermediate in the industrial synthesis of (−)-menthol from (+)-pulegone.\(^{54}\) (−)-Menthone can be converted to a seven membered lactone menthide through a Baeyer-Villiger reaction (Figure 1.4).\(^{55}\)

![Synthesis and polymerization of menthide from (−)-menthol](image)

**Figure 1.4** Synthesis and polymerization of menthide from (−)-menthol

Analogous to the well-established chemistry of related cyclic esters,\(^{29}\) the ring-opening polymerization of menthide was first reported in 1958.\(^{56}\) In this paper, the authors polymerized menthide using Na at 170 °C for 2 h, yielding a “thick white hygr. gel”.\(^{56}\) Besides this observation, no further characterization of polymenthide was performed. In 2005 in our laboratories, Zhang polymerized menthide using a well-defined zinc-alkoxide catalyst\(^{57}\) to form the aliphatic polyester.\(^{58}\) Full characterization ensued using NMR spectroscopy, size exclusion chromatography (SEC), and matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS). Polymenthide is a totally amorphous polymer with a glass transition around −20 °C.\(^{58}\) The rate constant for the polymerization reaction, \(k_p\), was found to be several orders of magnitude
slower than for the related polymerization of lactide\(^{57}\) due to the significant steric congestion around the ester functionality in menthide.\(^{58}\) The simple conversion of a readily available natural product\(^{54}\) to a monomer that is easily polymerized to yield a potentially useful material\(^{58}\) represents an important starting point for the development of a library of new biorenewable polymers.

### 1.4 Modifying the Mechanical Properties of Polylactide

Numerous techniques have been developed in efforts aimed at altering the mechanical properties of a polymer. The molecular weight, stereochemistry, level of crystallinity, crystalline orientation, and method of processing a homopolymer can be varied. Another technique to modify the mechanical properties involves blending plasticizers with the homopolymer. Plasticizers mixed with a glassy polymer decrease its glass transition temperature and improve its ductility and flexibility.\(^{59}\) Blending of two or more homopolymers is a widely-employed industrial technique for modifying the properties of a homopolymer. Another useful technique involves the synthesis of block copolymers. All of these strategies have been utilized for modifying the biorenewable and biodegradable polymer polylactide.

The amount of literature focused on the blending of plasticizers and polymers with polylactide is sizable. Recently, comprehensive overviews have been written summarizing the literature surrounding these PLA blends.\(^{34,60}\) This section will focus on a summary of biodegradable block copolymers containing polylactide, with emphasis on their mechanical properties.
Chapter 1: Background

The mechanical properties discussed in this chapter are the ultimate elongation ($\varepsilon_B$), tensile strength ($\sigma_B$), and tensile modulus (E). These properties are measured in a tensile test in which a material is pulled in opposite directions and the response of the material is measured. Figure 1.5 shows an example of the stress-strain curve obtained during the tensile testing of a material. The tensile modulus, or Young’s modulus, is a measure of the stiffness of the polymer and is determined from the slope of the linear portion at the beginning of the stress-strain curve. In general, the goal in improving the mechanical properties of polylactide is to increase the ultimate elongation while maintaining the tensile strength and tensile modulus. These mechanical properties can be obtained by synthesizing various random and block copolymers.

The synthesis of random or statistical copolymers is a strategy to obtain a product with a particular combination of desirable properties using more than one monomer. The copolymer composition depends on the composition of the monomers in the feed as well as the reactivity ratios of the monomers. Depending on the reactivity ratios of the monomers, the copolymer could have an alternating, random, or “blocky” structure. Alternating copolymers have properties that are a combination of the two monomers, while random copolymers tend to have properties that are an average of the two monomers (assuming the composition of the feed is 50:50). “Blocky” copolymers tend to have properties similar to the homopolymer blends without macrophase separation.

One of the most common strategies for improving the flexibility of a polymer while maintaining its strength is the synthesis of thermoplastic elastomers.
Figure 1.5 Representative stress-strain curve obtained after tensile testing
Thermoplastic elastomers are polymers that behave like elastomers in that they can be repeatedly stretched without distortion of the original shape, but are true thermoplastics. These characteristics arise because the polymers are physically crosslinked, whereas vulcanized rubbers are chemically crosslinked. The advantage of thermoplastic elastomers is that the stress-strain properties are similar to vulcanized rubbers, but the materials can be processed like conventional thermoplastics. The most common architectures of thermoplastic elastomers are linear ABA triblock copolymers and linear AB multiblock copolymers. In order to achieve thermoplastic elastomeric behavior, the A and B blocks should be immiscible, where A is a “hard”, high \( T_g \) or semicrystalline polymer and B is a “soft”, low \( T_g \) polymer. The mechanical properties of this class of polymers are a result of the microphase separation of the soft and hard blocks in which the soft, rubbery matrix phase is physically cross-linked by the hard phase (Figure 1.6), thus providing both strength and elasticity. These block copolymers are readily prepared by (a) sequential addition of monomers using living polymerization techniques, (b) chain extension of prepolymers with functional end groups, and (c) coupling of polymers with functional end groups.

### 1.4.1 Completely Biorenewable, Biodegradable Block Copolymers

As mentioned earlier, there are a limited number of readily available polymers derived completely from renewable resources. The most common renewable resource polymers found in block copolymers include polylactide (PLA), polyglycolide (PGA) and poly(3-hydroxybutyrate) (P3HB). Random and block copolymers of these
Figure 1.6 Schematic of ABA triblock copolymer thermoplastic elastomers
Chapter 1: Background

materials have been synthesized and characterized, but only a few reports discuss their mechanical properties.\textsuperscript{30} PLA–P3HB–PLA triblock copolymers in which the middle block was polymerized from a non-renewable resource starting material are discussed in Section 1.4.2.4.\textsuperscript{64}

By far, the most well known all-biorenewable copolymers are PLA/PGA copolymers due to their uses in drug delivery and orthopedic devices.\textsuperscript{65,66} These devices are random copolymers of lactide and glycolide. Polyglycolide has a much faster degradation rate than polylactide. As a result, the composition of the monomer feed is tailored to the degradation and tensile properties required for the final product.\textsuperscript{65} Table 1.3 summarizes the mechanical properties of the PLA/PGA copolymers currently used in biomedical devices. Also listed in the table are degradation times which it takes to reach complete resorption in the human body.

Table 1.3 Tensile and degradation properties of PLA/PGA copolymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Ref.</th>
<th>E (GPa)</th>
<th>$\sigma_B$ (MPa)</th>
<th>$\varepsilon_B$ (%)</th>
<th>Degradation time$^a$ (months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-\textit{co}-PGA (85/15)</td>
<td>67</td>
<td>2.0</td>
<td>3–10</td>
<td>5–6</td>
<td></td>
</tr>
<tr>
<td>PLA-\textit{co}-PGA (75/25)</td>
<td>67</td>
<td>2.0</td>
<td>3–10</td>
<td>4–5</td>
<td></td>
</tr>
<tr>
<td>PLA-\textit{co}-PGA (65/35)</td>
<td>67</td>
<td>2.0</td>
<td>3–10</td>
<td>3–4</td>
<td></td>
</tr>
<tr>
<td>PLA-\textit{co}-PGA (50/50)</td>
<td>67</td>
<td>2.0</td>
<td>3–10</td>
<td>1–2</td>
<td></td>
</tr>
<tr>
<td>PLLA-\textit{co}-PGA$^b$</td>
<td>65</td>
<td>600</td>
<td></td>
<td>1–2</td>
<td></td>
</tr>
<tr>
<td>PLLA-\textit{co}-PGA (88/12)</td>
<td>68</td>
<td>65</td>
<td></td>
<td>&gt;5</td>
<td></td>
</tr>
<tr>
<td>PLLA-\textit{co}-PGA (73/27)</td>
<td>68</td>
<td>66</td>
<td></td>
<td>&gt;5</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ time to complete resorption  \hspace{1em} $^b$ unknown composition
1.4.2 Biodegradable Block Copolymers Containing Polylactide and Non-biorenewable Components

Triblock copolymers synthesized from PLLA and the partially-biorenewable polymers such as poly(butylene succinate) (PBS)\textsuperscript{69,70} and poly(sebacic acid ester-anhydride)\textsuperscript{71} have been synthesized and their degradation profiles have been examined. However, the mechanical properties of these materials not been investigated. Other studies have been reported in which the mechanical properties of completely biodegradable copolymers containing a renewable resource polymer and a non-renewable resource polymer are presented, as described in the following subsections.

1.4.2.1 Polylactide/Poly(\(\varepsilon\)-caprolactone) Copolymers

Poly(\(\varepsilon\)-caprolactone) is the most common biodegradable polymer to copolymerize with polylactide. Relative to PLA, PCL is stable towards hydrolytic degradation; for example, PCL has been reported to lose only 30\% of its initial molecular weight after 45 weeks with no indication of mass loss after 60 weeks.\textsuperscript{72} A variety of PCL/PLA copolymers including AB diblock copolymers, AB multiblock copolymers, and random copolymers can be found in literature.

The first PLA–PCL block copolymers were synthesized in 1983 by Feng et al. using racemic PLA.\textsuperscript{73} Utilizing triethyl aluminum and an alcohol initiator, caprolactone and lactide were sequentially polymerized. Only the tensile strengths of the diblocks were reported.\textsuperscript{73}
Cohn et al. synthesized a series of PLLA–PCL–PLLA triblock copolymers by polymerizing differing amounts of \(\text{L-}\text{lactide}\) off of a difunctional PCL of 2,000 g mol\(^{-1}\) molecular weight.\(^74\) These triblock copolymers were then coupled to give PLLA–PCL multiblock copolymers.\(^74\) The tensile behavior of these thermoplastic elastomers was highly dependent on the morphology and composition of the copolymers. For all compositions, the tensile strength remained around 32 MPa, while the modulus ranged from 30 MPa to 800 MPa, and the elongation ranged from \(\sim 1600\%\) to \(\sim 200\%\) with increasing PLLA content.\(^74\) The influence of hydrolytic degradation on the properties of the multiblock copolymers was investigated. In vitro degradation (pH = 7.4, 37 °C) of the multiblock copolymers revealed significant loss of mechanical strength and elongation at break after about 8–9 weeks for all samples.\(^74\)

Statistical PCL/PLA and PCL/PLLA copolymers with varied compositions were synthesized by Hiljanen-Vainio et al.\(^75\) The polymerization of PCL is much slower than that of PLA, and as a result the statistical copolymers were more “blocky” with minor amounts of random structure (3-20% random structure). Higher average sequence lengths and higher crystallinity resulted in higher tensile modulus and tensile strength.\(^75\) The copolymers ranged from weak elastomers (Young’s modulus = 2.8 MPa, elongation >100%) to tougher thermoplastics (Young’s modulus = 52 MPa, elongation = 30%).\(^75\)

Block copolymers of statistical PCL/PLLA-\(b\)-PLLA were prepared by first by polymerizing CL and LLA for 3 h followed by the addition of LLA.\(^76\) The resultant polymers were similar to a-symmetric ABA triblock copolymers (with random
structure between the blocks) due to the relative reactivities of LLA and CL. All of the block copolymers were approximately 30 wt% PCL/PLLA statistical block, containing 50 wt% PCL, and 70 wt% PLLA. A series of these copolymers were synthesized, and only the temperature of the polymerizations was varied. Most likely a more “blocky” triblock copolymer was obtained at high temperatures due to the full conversion of LLA and CL in the statistical block before the addition of more LLA. Ultimate tensile strengths of approximately 30 MPa were reported with increasing elongation from 90% to 1500% corresponding to increasing reaction temperature used in the copolymer syntheses.

Amsden et al. synthesized PCL/PLA photo-cross-linked star statistical copolymers for use as biodegradable implants. The elastomers displayed relatively low values of Young’s modulus and tensile strength of under 6 MPa. The in vitro and in vivo degradation of the polymers revealed that the mechanism of degradation depends on the cross-link density. The polymer with high cross-link density degraded in a manner consistent with a surface erosion mechanism, while the polymer with low cross-link density degraded in a manner consistent with a bulk erosion mechanism. The elastomers lost all mechanical integrity after only 8 weeks of degradation.

Statistical copolymers containing CL, LLA, and GA units end-capped with diacrylate groups were synthesized and photo-cross-linked for potential use as tissue scaffolds. The networks had elongations of over 50%, and the modulus varied from 12.3 to 1.7 MPa. During 10 weeks of hydrolytic degradation, the strength and
stiffness of the polymers decreased at a constant rate while the elongations remained the same.\textsuperscript{78}

Shirahama et al. investigated the mechanical properties of stereocomplexed statistical and diblock PCL/PLLA and PCL/PDLA copolymers.\textsuperscript{79} Stereocomplex formation between the PLLA and PDLA blocks was evinced by the presence of a melting endotherm between 200 and 220 °C.\textsuperscript{79} The tensile modulus of the stereocomplexed diblock copolymers was much higher than that of the statistical copolymers. Also, it was found that dissolving and reprecipitating the stereocomplex a second and third time led to increased tensile strength and stiffness.\textsuperscript{79}

Table 1.4 summarizes the results from a large portion of the above studies. Samples are labeled according to the architecture of the polymer and the composition of the components in units of wt\%. Of the PCL copolymers, the multiblock and stereocomplexed diblocks seem to be the most promising copolymers for improving flexibility while maintaining stiffness.

1.4.2.2 Polylactide/Poly(1,3-trimethylene carbonate) Copolymers

Poly(1,3-trimethylene carbonate) (PTMC) is a non-renewable polyester with thermal and mechanical properties similar to polycaprolactone. ABA triblock copolymers, multiblock copolymers and random copolymers containing PTMC and PLA have been synthesized. TMC has also been copolymerized with CL to obtain statistical copolymers that are used as the soft block in ABA triblock copolymers and AB multiblock copolymers with PLA A-blocks.
Table 1.4 Summary of reported mechanical properties for PLA/PCL copolymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Note</th>
<th>Ref.</th>
<th>E (MPa)</th>
<th>σ_B (MPa)</th>
<th>ε_B (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-\textit{b}-PCL (12/88)</td>
<td></td>
<td>73</td>
<td>22.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLLA-\textit{b}-PCL (75/25)</td>
<td>multiblock</td>
<td>74</td>
<td>800</td>
<td>33</td>
<td>200</td>
</tr>
<tr>
<td>PLLA-\textit{b}-PCL (60/40)</td>
<td>multiblock</td>
<td>74</td>
<td>380</td>
<td>31</td>
<td>400</td>
</tr>
<tr>
<td>PLLA-\textit{b}-PCL (21/79)</td>
<td>multiblock</td>
<td>74</td>
<td>30</td>
<td>31</td>
<td>1600</td>
</tr>
<tr>
<td>PLLA-\textit{co}-PCL (98/2)</td>
<td></td>
<td>79</td>
<td>480</td>
<td>13</td>
<td>31</td>
</tr>
<tr>
<td>PLLA-\textit{co}-PCL (82/18)</td>
<td></td>
<td>79</td>
<td>162</td>
<td>14</td>
<td>140</td>
</tr>
<tr>
<td>PLLA-\textit{co}-PCL (60/40)</td>
<td></td>
<td>75</td>
<td>30</td>
<td>3.0</td>
<td>87</td>
</tr>
<tr>
<td>PLLA-\textit{co}-PCL (60/40)</td>
<td></td>
<td>75</td>
<td>2.8</td>
<td>0.080</td>
<td>&gt;100</td>
</tr>
<tr>
<td>PLLA-\textit{co}-PCL (20/80)</td>
<td></td>
<td>75</td>
<td>52</td>
<td>1.9</td>
<td>30</td>
</tr>
<tr>
<td>PLLA-\textit{co}-PCL (20/80)</td>
<td></td>
<td>75</td>
<td>30</td>
<td>1.6</td>
<td>&gt;100</td>
</tr>
<tr>
<td>(PLLA-\textit{co}-PCL)-\textit{b}-PLLA (30/70)\textsuperscript{a}</td>
<td></td>
<td>100 °C\textsuperscript{b}</td>
<td>76</td>
<td>30</td>
<td>90</td>
</tr>
<tr>
<td>(PLLA-\textit{co}-PCL)-\textit{b}-PLLA (29/71)\textsuperscript{a}</td>
<td></td>
<td>120 °C\textsuperscript{b}</td>
<td>76</td>
<td>31</td>
<td>250</td>
</tr>
<tr>
<td>(PLLA-\textit{co}-PCL)-\textit{b}-PLLA (34/66)\textsuperscript{a}</td>
<td></td>
<td>140 °C\textsuperscript{b}</td>
<td>76</td>
<td>31</td>
<td>1500</td>
</tr>
<tr>
<td>x-linked star-(PLA-\textit{co}-PCL)</td>
<td>1,250 g/mol\textsuperscript{c}</td>
<td>77</td>
<td>5.3</td>
<td>4.4</td>
<td>79</td>
</tr>
<tr>
<td>x-linked star-(PLA-\textit{co}-PCL)</td>
<td>7,800 g/mol\textsuperscript{c}</td>
<td>77</td>
<td>0.59</td>
<td>1.7</td>
<td>530</td>
</tr>
<tr>
<td>PLA-\textit{co}-PCL-co-PGA (20/60/20)</td>
<td></td>
<td>78</td>
<td>3.4</td>
<td>2.8</td>
<td>130</td>
</tr>
<tr>
<td>PLA-\textit{co}-PCL-co-PGA (40/20/40)</td>
<td></td>
<td>78</td>
<td>1.7</td>
<td>2.4</td>
<td>180</td>
</tr>
<tr>
<td>PLLA-\textit{co}-PCL (98/2) / PDLA-\textit{co}-PCL (92/8)</td>
<td>1:1 blend</td>
<td>79</td>
<td>520</td>
<td>20</td>
<td>230</td>
</tr>
<tr>
<td>PLLA-\textit{co}-PCL (82/18) / PDLA-\textit{co}-PCL (79/21)</td>
<td>1:1 blend</td>
<td>79</td>
<td>314</td>
<td>24</td>
<td>480</td>
</tr>
<tr>
<td>PLLA-\textit{b}-PCL (96/4) / PDLA-\textit{co}-PCL (94/6)</td>
<td>1:1 blend</td>
<td>79</td>
<td>1300</td>
<td>15</td>
<td>40</td>
</tr>
<tr>
<td>PLLA-\textit{b}-PCL (36/64) / PDLA-\textit{co}-PCL (34/66)</td>
<td>1:1 blend</td>
<td>79</td>
<td>100</td>
<td>23</td>
<td>650</td>
</tr>
</tbody>
</table>

\textsuperscript{a} (xx/xx) = (wt\% of 50/50 statistical copolymer / wt\% PLLA) \textsuperscript{b} Temperature of polymerization \textsuperscript{c} before cross-linking
A series of symmetric ABA triblock copolymers containing PLA, PLLA, and PDLA hard blocks were synthesized by first polymerizing TMC with a difunctional initiator followed by the addition of lactide. The triblock copolymers containing less than 10 mol% PLLA or PDLA and less than 15% PLA were able to reach elongations of over 1800%, while triblock copolymers containing ~45% PLLA or PDLA had tensile moduli over 400 MPa and elongations around 350%. Blending of equal amounts of PLLA–PTMC–PLLA and PDLA–PTMC–PDLA of similar molecular weights resulted in increased elongation by ~80%. More impressive was the significantly lower creep rate of the stereocomplexed triblock copolymers over their counterparts. Also, after 3,000 cycles of pulling the samples to 10% strain and back, the stereocomplexed copolymer had 0% permanent deformation whereas the PLLA triblock copolymer had around 0.5% permanent deformation.

Kim et al. investigated the physical and mechanical properties of PLLA/PTMC multiblock copolymers. In a similar fashion as Zhang et al., PLLA–PTMC–PLLA triblock copolymers were first synthesized followed by chain extension using 1,6-diisocyanatohexane to form the multiblock elastomers. The polymers were partially crystalline and exhibited well phase-segregated morphologies. Tensile testing of a low and high molecular weight elastomer revealed the materials to be both tough and elastic, with tensile stresses over 12 MPa and elongations over 180%.

Statistical PLA/PTMC copolymers for use as flexible materials for tissue engineering were synthesized using tin octanoate in bulk. Consistent with PLA/PCL copolymers, PLA/PTMC statistical copolymers were weak with lower elongations
relative to PLA/PTMC block copolymers of similar composition. The statistical
copolymers displayed tensile moduli of under 5 MPa and elongations of 600 to
1200%.32

ABA triblock copolymers synthesized from L-lactide (or D-lactide), 1,3-
trimethylene carbonate, and ε-caprolactone were investigated by Zhang et al.81 The
soft, B block was a statistical copolymer of PTMC and PCL synthesized using 1,6-
hexane diol as initiator. The difunctional middle block was then used as a
macroinitiator in the polymerization of L-lactide or D-lactide, and the enantiomeric
triblock copolymers were blended to form stereocomplexes.81 Similar to the PLA–
PTMC–PLA stereocomplexed copolymers,32 the creep-resistance was extremely low
for the PLA–(PTMC-co-PCL)–PLA stereocomplexed copolymers.81

Kricheldorf et al. synthesized PLLA–(PTMC-co-PCL) multiblock copolymers.82
Using tetraethylene glycol as the difunctional initiator and bismuth(III) n-hexanoate, a
compound with extraordinarily low toxicity, as the catalyst, CL and TMC were
copolymerized in bulk followed by LLA. Chain extension of the triblock copolymers
proceeded by the addition of 1,6-hexamethylene diisocyanate.82 Tensile strengths of
the multiblocks ranged from 12 to 42 MPa with elongations of 100 to 900%.82 Table
1.5 summarizes a large portion of the results from the above studies. The polymers are
labeled according to the type of copolymer and the copolymer’s composition.
### Table 1.5 Summary of reported mechanical properties for PLA/PTMC and PLA/PTMC/PCL copolymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Ref.</th>
<th>E (MPa)</th>
<th>σ_B (MPa)</th>
<th>ε_B (%)</th>
<th>creep rate$^{a}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-$b$-PTMC-$b$-PLA (7/86/7)</td>
<td>32</td>
<td>0.94</td>
<td>0.06</td>
<td>&gt;1800</td>
<td></td>
</tr>
<tr>
<td>PLLA-$b$-PTMC-$b$-PLLA (9/82/9)</td>
<td>32</td>
<td>21</td>
<td>1.4</td>
<td>120</td>
<td>3.0 E–6</td>
</tr>
<tr>
<td>PLLA-$b$-PTMC-$b$-PLLA (21/68/21)</td>
<td>32</td>
<td>410</td>
<td>20</td>
<td>330</td>
<td></td>
</tr>
<tr>
<td>PLLA-$b$-PTMC-$b$-PLLA (9/82/9) / PDLA-$b$-PTMC-$b$-PDLA (7/86/7)</td>
<td>32</td>
<td>28</td>
<td>&gt;3.3</td>
<td>170</td>
<td>1.0 E–6</td>
</tr>
<tr>
<td>PLLA-$b$-PTMC (52/48) multiblock</td>
<td>80</td>
<td>12.5</td>
<td>310</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLLA-$b$-PTMC (57/43) multiblock</td>
<td>80</td>
<td>21</td>
<td>180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLA-$co$-PTMC (22/78)</td>
<td>32</td>
<td>4.2</td>
<td>2.9</td>
<td>1140</td>
<td></td>
</tr>
<tr>
<td>PLA-$co$-PTMC (44/54)</td>
<td>32</td>
<td>3.8</td>
<td>1.3</td>
<td>650</td>
<td></td>
</tr>
<tr>
<td>PLLA-$b$-(PTMC-$co$-PCL)-$b$-PLLA (11/79/11)</td>
<td>81</td>
<td>15</td>
<td>1.0</td>
<td>60</td>
<td>4.0 E–6</td>
</tr>
<tr>
<td>PLLA-$b$-(PTMC-$co$-PCL)-$b$-PLLA (11/79/11) / PDLA-$b$-(PTMC-$co$-PCL)-$b$-PDLA (10/80/10)</td>
<td>81</td>
<td>22</td>
<td>1.1</td>
<td>80</td>
<td>0.9 E–6</td>
</tr>
<tr>
<td>PLLA-$b$-(PTMC-$co$-PCL) multiblock (56/(22/22))</td>
<td>82</td>
<td>12</td>
<td>840</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLLA-$b$-(PTMC-$co$-PCL) multiblock (83/(8/8))</td>
<td>82</td>
<td>42</td>
<td>120</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{a}$ at constant stress of 0.2 MPa
1.4.2.3 Polylactide/Poly(1,5-dioxepan-2-one) Copolymers

As mentioned earlier, poly(1,5-dioxepan-2-one), PDXO, is a non-renewable resource degradable polyester. PDXO is totally amorphous and is therefore valuable for copolymerization to improve the elasticity of a polymer over the semicrystalline soft blocks PCL and PTMC. Albertsson et al. has investigated the synthesis of the DXO monomer and routes to obtain high molecular weight PDXO.

More recent efforts have focused on the synthesis of PLLA–PDXO–PLLA thermoplastic elastomers and their hydrolytic degradation. 1,1,6,6-Tetra-n-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane prepared from dibutyltin oxide and ethylene glycol initiated the controlled ring-opening polymerization of DXO followed by the addition and polymerization of LLA. A multiblock was synthesized by direct polycondensation of the triblock copolymer with succinyl chloride. The triblock and multiblock copolymers were very elastic with elongations over 500% and tensile strengths over 20 MPa. After 60 days of hydrolytic degradation, the elastomers lost over half of their initial strength while maintaining their elongations.

Albertsson et al. have also synthesized copolymers based on TMC, LLA, and DXO for potential applications in soft tissue engineering. Using the same tin alkoxide initiator as the PLLA–PDXO–PLLA triblock copolymers, statistical copolymers of DXO and TMC were synthesized followed by the polymerization of LLA to give PLLA-\(b\)-(PDXO-\textit{co}-PTMC)-\(b\)-PLLA thermoplastic elastomers. The mechanical properties of the triblock copolymers were then compared to PLLA–PDXO and PLLA–PTMC diblock copolymers. The triblock copolymers had high
stiffness (tensile moduli over 53 MPa) and impressive elongations of up to 1100%. The compositions and mechanical properties of the PLLA/PDXO copolymers are listed in Table 1.6.

1.4.2.4 Polylactide/Poly(3-hydroxybutyrate) Copolymers

As discussed earlier, poly(3-hydroxybutyrate) are produced by bacterial fermentation and by transgenic microorganisms and plants. For the purpose of copolymerization with LLA, Hiki et al. have utilized synthetic P3HB. Synthetic P3HB has been synthesized from the ring-opening polymerization of a four-membered \(\beta\)-butyrolactone, a monomer derived from a non-renewable resource. Syndiotactic-rich (R,S)-P3HB, an elastomeric polymer due to low crystallinity, was utilized as the soft (B) segment in a PLLA-containing triblock copolymer. Copolymers of around 50% P3HB displayed tensile moduli ranging from 30 to 130 MPa, tensile strengths around 12 MPa, and elongations of 200% or lower (Table 1.7).

1.4.2.5 Polylactide/Poly(ethylene glycol) Copolymers

Despite the fact that polyethylene glycol (PEG) is not a renewable resource polymer and does not degrade hydrolytically, it is included in this summary because of its use in biomedical hydrogels. PEG is a hydrophilic polymer and speeds up the degradation of PLA/PEG copolymers because it is able to bring water into the polymer. PLA/PEG copolymers have been utilized as drug-delivery carriers and medical devices. More recently, PLA–PEG–PLA triblock copolymer
Table 1.6 Summary of reported mechanical properties for PLLA/PDXO and PLLA/PDXO/PTMC copolymers

<table>
<thead>
<tr>
<th>Material</th>
<th>LLA:DXO&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Ref</th>
<th>$E$ (MPa)</th>
<th>$\sigma_B$ (MPa)</th>
<th>$\varepsilon_B$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA-$b$-PDXO-$b$-PLLA (8/84/8)</td>
<td>100:300</td>
<td>83</td>
<td>33</td>
<td>910</td>
<td></td>
</tr>
<tr>
<td>PLLA-$b$-PDXO-$b$-PLLA (14/73/14)</td>
<td>150:300</td>
<td>83</td>
<td>42</td>
<td>830</td>
<td></td>
</tr>
<tr>
<td>PLLA-$b$-PDXO-$b$-PLLA (18/65/18)</td>
<td>200:400</td>
<td>83</td>
<td>23</td>
<td>560</td>
<td></td>
</tr>
<tr>
<td>PLLA-$b$-PDXO (34/66) multiblock</td>
<td>3 x 60:120</td>
<td>83</td>
<td>26</td>
<td>830</td>
<td></td>
</tr>
<tr>
<td>PLLA-$b$-PDXO</td>
<td>200:400</td>
<td>86</td>
<td>49</td>
<td>9.8</td>
<td>560</td>
</tr>
<tr>
<td>PLLA-$b$-PTMC</td>
<td>200:400&lt;sup&gt;b&lt;/sup&gt;</td>
<td>86</td>
<td>62</td>
<td>36</td>
<td>590</td>
</tr>
<tr>
<td>PLLA-$b$-(PDXO-co-PTMC)-$b$-PLLA</td>
<td>200:300:100&lt;sup&gt;c&lt;/sup&gt;</td>
<td>86</td>
<td>53</td>
<td>4.9</td>
<td>690</td>
</tr>
<tr>
<td>PLLA-$b$-(PDXO-co-PTMC)-$b$-PLLA</td>
<td>200:200:200&lt;sup&gt;c&lt;/sup&gt;</td>
<td>86</td>
<td>66</td>
<td>5.9</td>
<td>1100</td>
</tr>
<tr>
<td>PLLA-$b$-(PDXO-co-PTMC)-$b$-PLLA</td>
<td>200:100:300&lt;sup&gt;c&lt;/sup&gt;</td>
<td>86</td>
<td>68</td>
<td>4.5</td>
<td>920</td>
</tr>
</tbody>
</table>

<sup>a</sup> Monomer ratio in the feed. <sup>b</sup> LLA:TMC monomer ratio in the feed.
<sup>c</sup> LLA:DXO:TMC monomer ratio in the feed.

Table 1.7 Properties of PLLA-$b$-($R,S$)-P3HB-$b$-PLLA triblock copolymers<sup>64</sup>

<table>
<thead>
<tr>
<th>Composition (LLA/3HB)</th>
<th>Crystallinity by DSC (%)</th>
<th>$E$ (MPa)</th>
<th>$\sigma_B$ (MPa)</th>
<th>$\varepsilon_B$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>44/56</td>
<td>9</td>
<td>30</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td>53/47</td>
<td>10</td>
<td>130</td>
<td>14</td>
<td>150</td>
</tr>
<tr>
<td>69/31</td>
<td>23</td>
<td>160</td>
<td>15</td>
<td>86</td>
</tr>
</tbody>
</table>
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Stereocomplexes have been investigated as drug-delivery devices because of their improved thermal and hydrolytic stability.\(^\text{90}\)

Cohn et al. have synthesized multiblock PEG/PLLA thermoplastic elastomers and have investigated the changes in the mechanical properties when the polymers are wetted.\(^\text{91}\) As we have seen in many examples, the multiblocks were prepared from the coupling of PLLA–PEG–PLLA triblock copolymers. The hydrophilicity of the products was adjusted by adjusting the molecular weights of the blocks. Chain extension of the triblocks involved using hexamethylene diisocyanate.\(^\text{91}\) These copolymers absorbed between 70% and 120% water, and even though the strength of the hydrated polymers was typically about one third that of their respective dry counterparts (Table 1.8), these multiblock copolymers were still stronger than other biodegradable elastomers.\(^\text{91}\)

<table>
<thead>
<tr>
<th>Composition (LLA/EG)</th>
<th>E (MPa)</th>
<th>σ_B (MPa)</th>
<th>ε_B (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dry</td>
<td>wet</td>
<td>dry</td>
</tr>
<tr>
<td>450/1000</td>
<td>8.5</td>
<td>3.5</td>
<td>1000</td>
</tr>
<tr>
<td>1300/3200</td>
<td>17.5</td>
<td>9.5</td>
<td>30.0</td>
</tr>
<tr>
<td>2600/6000</td>
<td>13.5</td>
<td>8.5</td>
<td>31.0</td>
</tr>
<tr>
<td>3600/10,000</td>
<td>214.0</td>
<td>10.4</td>
<td>30.0</td>
</tr>
</tbody>
</table>
1.5 Summary of Polylactide Copolymers

The synthesis of block copolymers is an effective strategy towards altering polylactide’s tensile properties. As discussed above, the most common copolymer architectures utilized for this purpose include statistical copolymers, ABA triblock copolymers, and AB multiblock copolymers, where the A block is polylactide and the B block is a soft, low $T_g$ polymer. The tensile properties of these copolymers generally have higher elongations than homopolylactide and lower stiffness and strength. The many biodegradable polyesters that have been polymerized with polylactide include those derived from renewable and non-renewable resources.

Unfortunately, very few examples exist of all-biorenewable copolymers. The polyglycolide/polylactide copolymers described above were synthesized for the purpose of adjusting the degradation profiles rather than the tensile properties. Many more examples exist of copolymers containing polylactide and the non-biorenewable polyesters PCL, PTMC, PDXO, and P3HB.

Polycaprolactone, a non-renewable polyester, is one of the more common copolymers with polylactide. PCL/PLLA multiblock thermoplastic elastomers maintained relatively high stiffness while achieving elongations of up to 1600%, whereas the “blocky” statistical copolymers sacrificed considerable amounts of stress to reach elongations of under 150%. Most impressive were the stereocomplexed diblock and statistical PCL/PLA copolymers that had impressive stiffness and elongations. Due to the similar thermal properties of PTMC to PCL, the thermoplastic elastomers and statistical copolymers synthesized from TMC and lactide exhibited
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tensile properties similar to those of the PCL/PLA copolymers. Copolymers containing PLLA and PDXO, an amorphous polyester, resulted in tensile moduli around 60 MPa and elongations over 500%. Finally, synthetic (R,S)-P3HB/PLLA triblock copolymers had relatively low tensile strengths around 12 MPa, and elongations of 200% or lower.

1.6 Thesis overview

The challenge of preparing PLA block copolymers that retain completely renewable origins and improve the flexibility of polylactide is evident. The work described in the subsequent chapters builds on the previously discussed strategies to create polylactide block copolymers that are derived completely from renewable materials and degrade into the environment. Chapter 2 describes the synthesis and full characterization of PLA/PM triblock copolymers, creating completely biorenewable thermoplastic elastomers. Chapter 3 examines the hydrolytic degradation behavior of PLA–PM–PLA triblock copolymers and their homopolymer counterparts over a period of 45 weeks. Emphasis is placed on the degradation rates of the copolymers relative to the homopolymers and the tensile properties of the swollen copolymers. Chapter 4 investigates the relationship between polylactide stereochemistry and the triblock copolymers’ mechanical properties. Triblock copolymers containing PLA, PLLA, and PDLA segments of various molecular weights are synthesized and characterized. Blends of PLLA and PDLA triblock copolymers of similar molecular weight are made and the thermal and tensile properties of the stereocomplexed
triblock copolymers are evaluated. Chapter 5 examines the ability of PDLA–PM–PDLA triblock copolymer micelles to nucleate the crystallization of PLLA. The efficiency of the triblock copolymers to nucleate PLLA is determined from the crystallization temperature and the kinetics of crystallization of the blend compared to pure PLLA. The final chapter, Chapter 6, reports the adhesive properties of the totally amorphous PLA–PM–PLA thermoplastic elastomers and their potential use as biodegradable pressure-sensitive adhesives. Through this work, we have demonstrated the potential utility of new biorenewable thermoplastic elastomers to replace petroleum derived elastomers.

1.7 References


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Design and Synthesis of Renewable Resource Thermoplastic Elastomers based on Polylactide and Polymenthide*

2.1 Introduction

As discussed in Chapter 1, polylactide is an attractive biodegradable polyester that possesses many desirable properties such as nontoxicity, hydrolyzability, and biocompatibility,\(^1\) contributing to polylactide’s potential for use in the biomedical and pharmaceutical fields.\(^2,3\) Polylactide is most commonly synthesized by the ring-opening polymerization of lactide, the cyclic dimer of lactic acid.\(^4\) The thermal and mechanical properties of polylactide are significantly influenced by the stereochemistry of the monomers in the feed. Polymerization of racemic D,L-lactide typically results in atactic, amorphous \((T_\text{g} \approx 60\, ^\circ\text{C})\) poly(D,L-lactide), PLA, whereas polymerization of L-lactide or D-lactide results in isotactic, semicrystalline \((T_\text{m} \approx 180\, ^\circ\text{C})\) poly(L-lactide), PLLA, or poly(D-lactide), PDLA.\(^5\) One drawback of polylactide is its brittleness, making it unsuitable for use in numerous applications where elasticity and ductility are essential. Strategies developed to modify polylactide include plasticization,\(^6\) blending,\(^7\) and incorporation into block copolymers.\(^8\) These

modifications are used to enhance polylactide’s portfolio of properties, thus widening its applicability.

With the aim of enhancing the utility of polylactide, we have been interested in polylactide-containing ABA triblock copolymers. As discussed in Chapter 1, ABA triblock copolymers containing immiscible segments where A is a “hard”, high $T_g$ or semi-crystalline polymer and B is a “soft” amorphous, low $T_g$ polymer can behave as thermoplastic elastomers (TPEs). The strength and elasticity of thermoplastic elastomers are due to physical crosslinking of the hard blocks that results from microphase separation of the immiscible polymer segments. The stress-strain properties of TPEs are similar to vulcanized rubbers, but the materials can be processed like conventional thermoplastics.

Polylactide containing ABA triblock copolymers with non-biodegradable, non-renewable mid-blocks such as polyisoprene (PI) and polyisobutylene (PIB) have been synthesized. Frick et al. has shown that polylactide-b-polyisoprene-b-polylactide triblock copolymers exhibit high elongations (650 ± 70% for a sample with cylindrical morphology) and good elastomeric recovery, but this system has drawbacks and cannot be used for such applications as biomedical devices because it is inherently only partially renewable and biodegradable. The synthesis of all biodegradable triblock copolymer systems containing an aniline pentamer, poly(3-hydroxybutyrate), PHB, poly(1,3-trimethylene carbonate), PTMC, poly(1,5-dioxepan-2-one), PDXO, poly(ε-caprolactone), PCL, or poly(ethylene oxide), PEO, middle blocks and PLA, PLLA, or PDLA end blocks has also been investigated. The triblock copolymer
series PLLA-\textit{b}-PHB-\textit{b}-PLLA showed an improved initial modulus relative to the elastomeric homopolymer PHB but demonstrated low ultimate elongations of less than 200\%.\textsuperscript{14} The triblock copolymers PLLA-\textit{b}-PTMC-\textit{b}-PLLA and PDLA-\textit{b}-PTMC-\textit{b}-PDLA exhibited impressive elongations of $>1800\%$ when containing 10 mol\% PLLA or PDLA, and low creep rates were obtained by stereocomplex formation between enantiomeric poly(lactide) segments of the triblock copolymers in blends.\textsuperscript{16}

Completely biodegradable ABA triblock copolymers such as those described above will expand the potential utility of thermoplastic elastomers to be used in applications such as drug delivery matrices, flexible implants, substrates for cell culture and scaffolds for tissue engineering.\textsuperscript{2,19} We are interested in using a potentially biodegradable polyester, polymenthide (PM),\textsuperscript{20} as the soft, low $T_g$ segment of a PLA containing ABA triblock copolymer. PM is one of a variety of new polymers derived from biorenewable resources.\textsuperscript{21} The ring-opening polymerization of menthide (\textit{M}, Scheme 2.1), a derivative of (−)-menthol, was investigated by Zhang et al.,\textsuperscript{20} who showed that \textit{M} can be polymerized in a controlled fashion with molecular weights up to 91 kg/mol. PM is a non-crystalline, amorphous polymer that exhibits a $T_g$ of $-25$ °C, making it a suitable candidate for a soft segment in thermoplastic elastomers. At moderate molecular weight, a blend of PM (30 kg/mol) and PLA (30 kg/mol) exhibits two glass transition temperatures corresponding to each of the homopolymers, evidence that PM and PLA homopolymers are immiscible at moderate molecular weight and have the potential to microphase separate once incorporated in block copolymers.
Chapter 2: Synthesis of Renewable Resource Thermoplastic Elastomers

This Chapter reports the synthesis of PLA-\(b\)-PM-\(b\)-PLA thermoplastic elastomers and their full characterization, including by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy, size exclusion chromatography, differential scanning calorimetry, react infrared spectrometry, and small-angle X-ray scattering. We also synthesized a PLA-\(b\)-PM-\(b\)-PLA triblock copolymer on a 2 gram scale for mechanical testing, the results of which demonstrated its elastomeric behavior.

2.2 Experimental Section

2.2.1 Materials

All air- or moisture-sensitive compounds were handled under a nitrogen atmosphere in a glovebox, as indicated. Toluene used for polymerizations was purified by passing through activated alumina-based columns (Glass Contour, Laguna Beach, CA) followed by distillation from sodium. D,L-Lactide (Purac) was purified by recrystallization from toluene followed by repeated (2x) vacuum sublimation. Diethylene glycol (Sigma Aldrich) was distilled under reduced pressure from sodium. Molecular sieves (4 Å) were dried under vacuum at 180 °C for a minimum of 16 hours. All other solvents and reagents were used as received from the commercial source indicated without further purification. All glassware used in polymerizations was treated with a solution of \(\text{Me}_2\text{SiCl}_2\) (10% in \(\text{CH}_2\text{Cl}_2\)) and oven dried at 200 °C for a minimum of 3 h before use.
2.2.2 Measurements

$^1$H and $^{13}$C NMR spectra were collected on a Varian INOVA-300, VXR-300 or Varian INOVA-500 spectrometer. Samples of the polymers were prepared by dissolving approximately 30 mg of polymer in 1 mL of CDCl$_3$ (Cambridge). Molecular weights ($M_n$ and $M_w$) and polydispersity indices ($M_w/M_n$) were determined by size exclusion chromatography (SEC) using polystyrene standards. Samples were analyzed at 40 °C using a Hewlett-Packard high-pressure liquid chromatograph equipped with three Jordi poly(divinylbenzene) columns of $10^4$, $10^3$, and 500 Å pore sizes and a HP1047A differential refractometer. FT-IR spectra were collected on a Thermo Nicolet Avatar 370 FT-IR spectrometer. The kinetics of selected polymerizations were monitored by a Mettler Toledo ReactIR 4000 equipped with a diamond probe. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q1000 with nitrogen as the purge gas. An indium standard was used for calibration, and the scan rate was 10 °C/min. Samples weighing 3.0–8.0 mg were loaded into aluminum hermetic pans and the pans were sealed prior to measurement. Measurements for small angle X-ray scattering (SAXS) were performed at the University of Minnesota Twin Cities Characterization Facility beamline. Cu Kα X-rays ($\lambda = 1.542$ Å) were generated by a Rigaku RU-200BVH rotating anode fitted with a $0.2 \times 2$ mm$^2$ microfocus cathode and Franks mirror optics. Temperature control inside the evacuated sample chamber was accomplished with water-cooling and electrically heating the brass-block sample holder. All samples were heated to 160 °C and annealed for 10 min in the sample chamber prior to SAXS.
measurements at 80–160 °C. Two-dimensional diffraction images were recorded using a Siemens area detector located at the end of a 2.30 m evacuated flight tube and corrected for detector response before analysis. The two-dimensional images were azimuthally integrated and reduced to the one-dimensional form of scattered intensity versus the spatial frequency \( q \). Tensile deformation experiments were carried out at room temperature using a Rheometrics Scientific Minimat instrument operated at a cross-head speed of 5 mm/min. The sample gage length was 5 mm, the gage width was 3 mm, and the gage thickness was 1 mm.

### 2.2.3 General Procedure for the Synthesis of HO–PM–OH

As previously reported,\textsuperscript{20} menthide (\( M \)) was synthesized from (−)-menthone using meta-chloroperbenzoic acid.\textsuperscript{22} \( M \) was readily obtained on a 100-gram scale in > 70% yield by recrystallization from hexanes and sublimation of the crude product. Initial monomer concentrations were kept at 1 M. A stock solution of diethylene glycol (DEG) ([DEG] = 0.10 M in THF) was stored in the glovebox at –30 °C. The amount of catalyst and diethylene glycol used varied depending on the desired molecular weight of the resulting polymers. A representative procedure was as follows. In the glovebox, a volume of diethylene glycol (1.84 mL, 0.184 mmol) was injected into the reaction flask followed by the addition of diethylzinc (Sigma Aldrich, 1.0 M in hexanes) (918 µL, 0.918 mmol). The reaction flask was then charged with menthide (\( M \)) (2.500 g, 14.68 mmol), toluene (11.93 mL) and a stirbar. The reaction flask was sealed and taken out of the glovebox to stir at 100 °C for 4.5 h (73%
Chapter 2: Synthesis of Renewable Resource Thermoplastic Elastomers

conversion of monomer). Exposure to air and addition of water (3.0 mL) quenched the reaction. The majority of the solvent was evaporated, and the polymer was washed with methanol at 0 °C and dried at 90 °C in a vacuum oven (1.7 g recovered, 93% yield). $^1$H NMR (CDCl$_3$) $\delta$ 4.73 (m, 161H), 4.23 (t, $J = 4.5$ Hz, 4H), 3.69 (t, $J = 4.5$ Hz, 4H), 3.34 (m, 1H), 2.30 (dd, $J_{AB} = 15.3$ Hz, $J = 5.4$ Hz, 161H), 2.07 (dd, $J_{AB} = 14.4$ Hz, $J = 8.4$ Hz, 161H), 1.94 (m, 161H), 1.82 (m, 161H), 1.53 (m, 322H), 1.33 (m, 161H), 1.18 (m, 161H), 0.94 (d, $J = 6.6$ Hz, 482H), 0.89 (d, $J = 6.9$ Hz, 964H);

$^{13}$C{1H} NMR (CDCl$_3$) $\delta$ 173.2, 78.6, 42.2, 32.9, 31.4, 30.6, 28.7, 20.0, 18.9, 17.7.

2.2.4 General Procedure for the Synthesis of PLA-_{PM}-b-PLA Triblock Copolymers

Initial D,L-lactide concentrations were kept at 1.0 M. The amount of D,L-lactide used varied depending on the molecular weight of the macroinitiator. Each macroinitiator copolymerization series was performed under identical initial conditions (exception: PLA-PM-PLA (3.3–28–3.3)). The time allowed for each block copolymerization in the series was tailored to the product molecular weights desired. A typical procedure was as follows. In the glovebox, a reaction flask was charged with PM (10) (Table 2.1, 0.1250 g, 0.0125 mmol) and toluene (0.988 mL) followed by the addition of AlEt$_3$ (Sigma Aldrich, 1.0 M in heptane) (12.5 µL, 0.0125 mmol). The reaction flask was sealed and removed from the glovebox to stir at 90 °C. After 30 min, the reaction flask was brought into the glovebox and D,L-lactide (0.144 g, 1.00 mmol) was added. The resultant mixture was heated at 90 °C with stirring outside the
glovebox for 50 min (41% conversion of monomer). The reaction flask was then exposed to air and 10% HCl solution was added (3.0 mL) to quench the reaction. Minimal toluene was added (ca. 1 mL) and the organic layer was precipitated into an excess of methanol at 0 °C (300 mL). The product was isolated and dried in a vacuum oven at 80 °C overnight (70% yield assuming complete recovery of the PM block). ¹H NMR (CDCl₃) δ 5.19 (m, 66H), 4.73 (m, 161H), 4.23 (t, J = 4.5 Hz, 4H), 3.69 (t, J = 4.2 Hz, 4H), 2.30 (dd, J_AB = 14.4 Hz, J = 5.4 Hz, 161H), 2.08 (dd, J_AB = 14.7 Hz, J = 8.7 Hz, 161H), 1.94 (m, 161H), 1.82 (m, 161H), 1.60 (m, 196H), 1.53 (m, 322H), 1.33 (m, 161H), 1.18 (m, 161H), 0.94 (d, J = 6.3 Hz, 482H), 0.89 (d, J = 6.6 Hz, 964H); ¹³C(¹H) NMR (CDCl₃) δ 173.1, 169.3, 78.4, 69.2, 42.1, 32.8, 31.3, 30.5, 28.6, 19.9, 18.8, 17.7, 16.8.

2.2.5 Kinetic Experiments

A ReactIR 4000 spectrometer was used to monitor the polymerization reactions in situ. The glassware used was oven dried at 200 °C for at least 3 h. The ReactIR probe and the reaction flask containing a solution of monomer, catalyst, and initiator were assembled in the glovebox and quickly attached to the spectrometer outside the glovebox. The consumption of M was monitored to over 5 half-lives at 1274 and 1048 cm⁻¹. A nonlinear fit of the curve to $A_t = (A_o - A_\infty)\exp(-k_{obs}t) + A_\infty$ gave the observed rate constant ($k_{obs}$). On the basis of previous kinetic experiments, the dependence on [ZnEt₂] was assumed to be first order. ²⁰,²⁴ The second order rate constant, $k_p$, was therefore calculated by using the equation $k_{obs} = k_p[ZnEt₂]_0$. 
2.2.6 Synthesis of PM (29)

In the glovebox, a volume of 0.10 M diethylene glycol (1.60 mL, 0.160 mmol) was injected into a reaction flask followed by the addition of diethylzinc (801 µL, 0.801 mmol). The reaction flask was then charged with M (6.00 g, 35.2 mmol) and toluene (32.84 mL) and a stirbar was added. The reaction flask was sealed and taken out of the glovebox to stir at 100 °C for 5.25 h. Exposure to air and the addition of 10% HCl solution (ca. 20 mL) quenched the reaction. The solution was shaken and the emulsion was precipitated into an excess of −78 °C methanol (ca. 300 mL). The polymer was isolated, dissolved in minimal CH$_2$Cl$_2$ and precipitated into a second flask of −78 °C methanol (ca. 300 mL). The second isolation was performed and the majority of the solvent was evaporated under a stream of N$_2$. The product was dried at 40 °C in a vacuum oven overnight (70% yield). SEC (THF) $M_n = 21.1$ kg/mol, $M_w = 26.7$ kg/mol, $M_n / M_w = 1.26$; $M_n$ ($^1$H NMR) = 29.4 kg/mol; $^1$H NMR (CDCl$_3$) $\delta$ 4.73 (m, 170H), 4.23 (t, $J = 4.5$ Hz, 4H), 3.69 (t, $J = 4.5$ Hz, 4H), 3.34 (m, 1H), 2.30 (dd, $J_{AB} = 15.3$ Hz, $J = 5.4$ Hz, 170H), 2.07 (dd, $J_{AB} = 14.4$ Hz, $J = 8.4$ Hz, 170H), 1.94 (m, 170H), 1.82 (m, 170H), 1.53 (m, 340H), 1.33 (m, 170H), 1.18 (m, 170H), 0.94 (d, $J = 6.6$ Hz, 510H), 0.89 (d, $J = 6.9$ Hz, 1020H); $^{13}$C ($^1$H) NMR (CDCl$_3$) $\delta$ 173.2, 78.6, 42.2, 32.9, 31.4, 30.6, 28.7, 20.0, 18.9, 17.7.

2.2.7 Synthesis of PLA-PM-PLA (7.8–29–7.8) Triblock Copolymer

In the glovebox, a reaction flask was charged with PM (29) (Table 2.1, 1.50 g, 0.0510 mmol), toluene (5.15 mL) and molecular sieves and allowed to stir overnight.
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AlEt$_3$ (0.0510 mL, 0.0510 mmol) was added to the reaction flask, which was sealed and removed from the glovebox to stir at 90 °C. After 30 min, D,L-lactide (0.750 g, 5.20 mmol) was added to the reaction flask in the glovebox. The resultant mixture was heated at 90 °C with stirring for 4.5 h. The reaction flask was then exposed to air and 10% HCl solution was added (ca. 6 mL) to quench the reaction. Minimal toluene was added (ca. 1 mL) and the solution was shaken and precipitated into an excess of −78 °C methanol (ca. 300 mL). The polymer was isolated and precipitated into a second flask of −78 °C methanol (ca. 300 mL). The resulting polymer was dissolved in minimal dichloromethane and filtered to remove the molecular sieves. The product was dried in a vacuum oven at 50 °C overnight (75% yield assuming complete recovery of the PM block). SEC (THF) $M_n = 29.5$ kg/mol, $M_w = 36.9$ kg/mol, $M_n/M_w = 1.25$; $M_n$ (1H NMR) = 45.0 kg/mol; 1H NMR (CDCl$_3$) $\delta$ 5.19 (m, 108H), 4.73 (m, 170H), 4.23 (t, $J = 4.5$ Hz, 4H), 3.69 (t, $J = 4.2$ Hz, 4H), 2.30 (dd, $J_{AB} = 14.4$ Hz, $J = 5.4$ Hz, 1H), 2.08 (dd, $J_{AB} = 14.7$ Hz, $J = 8.7$ Hz, 170H), 1.94 (m, 170H), 1.82 (m, 170H), 1.60 (m, 324H), 1.53 (m, 340H), 1.33 (m, 170H), 1.18 (m, 170H), 0.94 (d, $J = 6.3$ Hz, 510H), 0.89 (d, $J = 6.6$ Hz, 1020H); 13C{1H} NMR (CDCl$_3$) $\delta$ 173.1, 169.3, 78.4, 69.2, 42.1, 32.8, 31.3, 30.5, 28.6, 19.9, 18.8, 17.7, 16.8.
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2.3 Results and Discussion

2.3.1 Preparation of HO–PM–OH

Difunctional polymenthide (HO–PM–OH) was prepared using the difunctional initiator diethylene glycol (DEG) (Scheme 2.1). Diethyl zinc (ZnEt$_2$) was used as the catalyst due to its availability and low cost.$^{23}$ To guarantee the polymerization of M a [ZnEt$_2$]:[OH] ratio of 2.5 was employed. All polymerizations of M were performed at 100 °C in toluene ([M]$_0$ = 1.0 M) under an inert atmosphere.

Scheme 2.1

The rate of polymerization of M using DEG and ZnEt$_2$ was determined by monitoring the decay of the absorbance of the peaks at 1274 and 1048 cm$^{-1}$ by in situ
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FTIR spectroscopy (Figure 2.1). The decay of $[M]$ over time ($[M]_t$) was found to be exponential, characteristic of first order dependence on $[M]$ described in equation 2.1 and equation 2.2:

$$[M]_t = [M]_0 * e^{-k_{obs} t}$$  \hspace{1cm} (2.1)

$$k_{obs} = k_p * [\text{ZnEt}_2]_0$$  \hspace{1cm} (2.2)

where $[M]_0$ is the initial concentration of $M$, $t$ is time, and $k_p$ is the propagation rate constant. Based on previous kinetic experiments, the dependence on $[\text{ZnEt}_2]$ was assumed to be first order. The propagation rate constant $k_p$ for varied ZnEt$_2$ loadings was $(3.5 \pm 0.35) \times 10^{-3}$ M$^{-1}$ s$^{-1}$ at 100 °C (Equation 2.2). At a typical concentration of $[\text{ZnEt}_2]_0$ of 0.023 M, the half life for this polymerization is about 140 min.

The molecular weights of HO–PM–OH were controlled by varying the monomer to initiator ratios and controlling the conversion of $M$ (Table 2.1). Polymerizations were quenched by exposure to air and water at approximately 75% conversion of $M$ (confirmed by NMR spectroscopy). The molecular weights determined by SEC (versus polystyrene standards) of HO–PM–OH were generally controlled, as demonstrated by the increase of the apparent molecular weight of HO–PM–OH with the decrease of DEG in the feed. A linear increase in molecular weight with $([M]_0 - [M]_t)/[I]_0$ was observed with a y-intercept near zero, consistent with the controlled polymerization of $M$ (Figure 2.2). All SEC traces were unimodal and the PDIs for HO–PM–OH obtained by this method were relatively narrow (PDI ≈ 1.3).
Figure 2.1 Representative kinetic data for the decay of the absorbance of the peak at 1048 cm⁻¹ (corresponding to M) monitored by FTIR spectroscopy with a first order exponential fit (black line). Conditions: toluene, 100 °C, [M]₀ = 1.0 M, [Zn]₀ = 2.00×10⁻² M. Result: $k_{\text{obs}} = 7.49\times10^{-5}$ s⁻¹, $k_p = 3.75\times10^{-3}$ M⁻¹ s⁻¹, $R^2 = 0.99$. 
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\(^1\)H NMR spectroscopy was employed to verify end functionalization, confirm the connectivity of DEG in the polymer chain, and determine the \(M_n\). All proton signals of the PM repeating units agree with those found in previous literature (section 2.2.3).\(^{20}\) Figure 2.3a shows the typical expanded \(^1\)H NMR spectrum from \(\delta 3.0-4.4\) ppm of the difunctional PM. The two methylene resonances attributed to the internal DEG unit appear at \(\delta 3.68\) ppm (H\(_a\)) and 4.22 ppm (H\(_b\)), and the resonance of the methine protons \(\alpha\) to the hydroxyl chain end is apparent at \(\delta 3.35\) ppm (H\(_c\)).

The resonance from the HO–PM–OH methine protons \(\alpha\) to the hydroxyl chain end (Figure 2.3a, H\(_c\)) was used to determine the \(M_n\) of the polymer chain (assuming exactly two end groups per chain). The \(M_n\) values were calculated from the integral ratio of these protons relative to the main chain methine resonance at \(\delta 4.70\) ppm. We observed excellent agreement between the calculated \(M_n\) and the \(M_n\) based on conversion of monomer (Table 2.1), confirming the average chain end functionality (\(F_n\)) to be 2. We observed a ratio of 1:1 when comparing the resonances of the protons on the DEG unit (Figure 2.3a, H\(_a\) and H\(_b\)). However, the integration ratio of the HO–PM–OH terminal methine protons (Figure 2.3a, H\(_c\)) to the resonance from the protons on the DEG unit (Figure 2.3a, H\(_a\) and H\(_b\)) gave \(F_n\) values greater than 2 (Table 2.1). Based on these high \(F_n\) values we conclude that there is an inconsistency between the number of DEG units expected in the polymer chain and the number of DEG units observed, while the observed number of terminal methine protons (Figure 2.3a, H\(_c\))
Table 2.1 Data for ring-opening polymerization of menthиде

<table>
<thead>
<tr>
<th>Sample</th>
<th>[M]₀: [DEG]₀</th>
<th>Conv. b (%)</th>
<th>Time (h)</th>
<th>Mₙ b (conv.) (kg/mol)</th>
<th>Mₙ b (EG) (kg/mol)</th>
<th>Mₙ (SEC) (kg/mol)</th>
<th>PDI</th>
<th>F₀ c (NMR)</th>
<th>Tₙ d (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM (10)</td>
<td>80</td>
<td>73</td>
<td>4.5</td>
<td>9.9</td>
<td>10</td>
<td>20</td>
<td>1.28</td>
<td>2.4</td>
<td>−26</td>
</tr>
<tr>
<td>PM (28)</td>
<td>220</td>
<td>76</td>
<td>7.0</td>
<td>28</td>
<td>29</td>
<td>35</td>
<td>1.31</td>
<td>2.6</td>
<td>−26</td>
</tr>
<tr>
<td>PM (43)</td>
<td>310</td>
<td>81</td>
<td>10.3</td>
<td>43</td>
<td>38</td>
<td>55</td>
<td>1.28</td>
<td>2.7</td>
<td>−25</td>
</tr>
</tbody>
</table>

a Conditions: [M]₀ = 1.0 M, [Zn]₀ = 0.063 M (PM (10)); 0.023 M (PM (28)); 0.016 M (PM (43)), toluene, 100 °C, [M]ₚₑₒ = 0.120 ± 0.063 M. b Molecular weights by conversion of menthide (conv.) and end group analysis (EG) calculated from ¹H NMR spectroscopy. c Chain end functionality calculated from relative integrations of HO–PM–OH end groups and DEG in the ¹H NMR spectrum. d Determined by DSC.
Figure 2.2 Plot of $([M_0-[M_i])/[M_0]$ (calculated from conversion of monomer in the $^1$H NMR spectrum) vs. molecular weight (calculated from end group analysis in the $^1$H NMR spectrum) for various polymerizations of $M$ initiated by DEG and diethyl zinc. Best fit line: $y = 0.162 * x + 0.061$, $R^2 = 0.97$. 
Figure 2.3 Expanded $^1$H NMR spectra for (a) HO–PM–OH (• methine proton of residual M) and (b) PLA–b–PM–b–PLA
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per polymer chain is as expected (because of the agreement between the calculated $M_n$ based on the integration of the terminal methine protons and the $M_n$ based on conversion of monomer). The reason for this inconsistency in the number of DEG units per polymer chain exists is unclear. $^{13}$C{$^{1}$H} NMR and IR spectroscopic data for the HO–PM–OH samples were consistent with previous data reported, and DSC revealed $T_g$’s of the PM samples of approximately $-25 \, ^oC$. No crystallinity was detected up to 100 °C.

2.3.2 Synthesis and Characterization of PLA-\textit{b}-PM-\textit{b}-PLA Triblock Copolymers

The set of HO–PM–OH samples in Table 2.1 were used as macroinitiators in the metal-catalyzed ring-opening polymerization of D,L-lactide. Aluminum alkoxides formed from AlEt$_3$ and HO–PM–OH were targeted as the initiators. To avoid the formation of gels, [OH]$_0$/[Al]$_0$ = 2 was chosen. All polymerizations were performed at 90 °C in toluene ([lactide]$_0$ = 1) and quenched by exposure to air and dilute HCl. A linear increase in molecular weight with ([L]$0$–[L]$_t$)/[I]$_0$ was observed with a y-intercept near zero, consistent with the controlled polymerization of LA (Figure 2.4). Triblock copolymers containing 20, 30, 40, and 50% PLA by mass were targeted. These series of triblock copolymers are summarized in Table 2.2.

The PLA-\textit{b}-PM-\textit{b}-PLA triblock copolymers were characterized by $^{1}$H NMR spectroscopy. The percent conversion of D,L-lactide in solution was measured by integration of the resonance from the methine protons corresponding to the polylactide chain ($\delta$ 5.18 ppm) and the resonance from the methine protons
Table 2.2 Results of the block copolymerization of D,L-lactide initiated with HO–PM–OH

<table>
<thead>
<tr>
<th>Triblock</th>
<th>[LA]&lt;sub&gt;0&lt;/sub&gt;/ [PM]&lt;sub&gt;0&lt;/sub&gt;</th>
<th>LA conv.&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>Time (min)</th>
<th>PLA-PM-PLA &lt;br&gt; &lt;i&gt;M&lt;/i&gt;&lt;sub&gt;n&lt;/sub&gt; (NMR) (kg/mol)</th>
<th>% PLA&lt;sup&gt;c&lt;/sup&gt;</th>
<th>&lt;i&gt;M&lt;/i&gt;&lt;sub&gt;n&lt;/sub&gt; (SEC) (kg/mol)</th>
<th>PDI</th>
<th>Yield&lt;sup&gt;d&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-PM-PLA (1.3–10–1.3)</td>
<td>80</td>
<td>21</td>
<td>20</td>
<td>1.3–9.9–1.3</td>
<td>20.2</td>
<td>24.0</td>
<td>1.22</td>
<td>65</td>
</tr>
<tr>
<td>PLA-PM-PLA (2.3–10–2.3)</td>
<td>80</td>
<td>41</td>
<td>50</td>
<td>2.3–9.9–2.3</td>
<td>31.6</td>
<td>29.9</td>
<td>1.19</td>
<td>70</td>
</tr>
<tr>
<td>PLA-PM-PLA (3.8–10–3.8)</td>
<td>80</td>
<td>58</td>
<td>60</td>
<td>3.8–9.9–3.8</td>
<td>42.8</td>
<td>32.2</td>
<td>1.22</td>
<td>69</td>
</tr>
<tr>
<td>PLA-PM-PLA (4.6–10–4.6)</td>
<td>80</td>
<td>79</td>
<td>100</td>
<td>4.6–9.9–4.6</td>
<td>48.0</td>
<td>35.5</td>
<td>1.22</td>
<td>54</td>
</tr>
<tr>
<td>PLA-PM-PLA (3.3–28–3.3)</td>
<td>62</td>
<td>79</td>
<td>60</td>
<td>3.3–28–3.3</td>
<td>18.9</td>
<td>48.0</td>
<td>1.29</td>
<td>66</td>
</tr>
<tr>
<td>PLA-PM-PLA (6.6–28–6.6)</td>
<td>220</td>
<td>38</td>
<td>45</td>
<td>6.6–28–6.6</td>
<td>31.8</td>
<td>54.1</td>
<td>1.28</td>
<td>75</td>
</tr>
<tr>
<td>PLA-PM-PLA (9.7–28–9.7)</td>
<td>220</td>
<td>66</td>
<td>90</td>
<td>9.7–28–9.7</td>
<td>40.7</td>
<td>50.5</td>
<td>1.40</td>
<td>53</td>
</tr>
<tr>
<td>PLA-PM-PLA (14–28–14)</td>
<td>220</td>
<td>86</td>
<td>120</td>
<td>14–28–14</td>
<td>49.9</td>
<td>66.9</td>
<td>1.34</td>
<td>86</td>
</tr>
<tr>
<td>PLA-PM-PLA (6.5–43–6.5)</td>
<td>400</td>
<td>19</td>
<td>35</td>
<td>6.5–43–6.5</td>
<td>23.1</td>
<td>64.1</td>
<td>1.29</td>
<td>89</td>
</tr>
<tr>
<td>PLA-PM-PLA (10–43–10)</td>
<td>400</td>
<td>33</td>
<td>60</td>
<td>10–43–10</td>
<td>32.1</td>
<td>71.2</td>
<td>1.30</td>
<td>75</td>
</tr>
<tr>
<td>PLA-PM-PLA (15–43–15)</td>
<td>400</td>
<td>54</td>
<td>60</td>
<td>15–43–15</td>
<td>41.2</td>
<td>69.8</td>
<td>1.39</td>
<td>84</td>
</tr>
<tr>
<td>PLA-PM-PLA (23–43–23)</td>
<td>400</td>
<td>74</td>
<td>85</td>
<td>23–43–23</td>
<td>51.5</td>
<td>90.8</td>
<td>1.41</td>
<td>75</td>
</tr>
</tbody>
</table>

<sup>a</sup>Conditions: [LA]<sub>0</sub> = 1.0 M, toluene, 90 °C.  <sup>b</sup>Calculated from <sup>1</sup>H NMR spectroscopy.  <sup>c</sup>Mass percent PLA calculated from <sup>1</sup>H NMR spectroscopy and composition of the triblock copolymers.  <sup>d</sup>Isolated yield.
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Figure 2.4 Plot of ([LA]₀–[LA]ₜ)/[I]₀ (calculated from conversion of monomer in the ¹H NMR spectrum) vs. molecular weight (calculated from end group analysis in the ¹H NMR spectrum) for various polymerizations of lactide using HO–PM–OH as the initiator. Best fit line: y = 0.159 * x + 0.049, R² = 0.98.
corresponding to D,L-lactide (δ 5.05 ppm). The resonance for the methine protons α to the hydroxyl functionality at the chain ends of HO–PM–OH (δ 3.35 ppm) was absent in the PLA-b-PM-b-PLA triblock copolymers (Figure 2.3b). This resonance was replaced by the resonance of the methine protons of the chain ends of the triblock copolymers (δ 4.36 ppm). We determined the percent PLA in the triblock copolymer by comparing the resonance from the methine protons corresponding to the PLA blocks and the resonance from the methine protons corresponding to the PM block. We observed excellent agreement between the calculated percent PLA based on the conversion of monomer in solution and the determined percent PLA in the product. 

Triblock copolymer formation was detected by the shift of the SEC traces relative to the respective homopolymer traces; a representative series is given in Figure 2.5. As the PLA composition increases for each series of triblock copolymers, a shift towards higher molecular weight occurs. The molecular weight distributions of the unimodal SEC chromatograms corresponding to the triblock copolymers were relatively narrow (PDI = 1.2–1.4).

2.3.3 Thermal Properties and Morphology of PLA-b-PM-b-PLA Triblock Copolymers

Microphase separation of the polylactide and polymenthide blocks in the PLA-b-PM-b-PLA triblock copolymers is essential to achieving the physical properties associated with thermoplastic elastomers. DSC and SAXS characterization were used to determine the immiscibility and ordered morphology of the triblock copolymers,
Figure 2.5 SEC data for PM (10) and the corresponding triblock copolymers
respectively. DSC analysis of all triblock copolymers revealed two glass transition temperatures, consistent with microphase separation (Table 2.3). For each series the $T_g$ values corresponding to the PM blocks were relatively invariant (ca. $-22 ^\circ C$) while the $T_g$ values corresponding to the PLA blocks ranged from 20 to 51 °C depending on the molecular weight of the PLA block. Figure 2.6 shows representative DSC thermograms of the PM (28) triblock copolymer series.

### 2.3.4 Small Angle X-ray Scattering of PLA-b-PM-b-PLA Triblock Copolymers

Small angle x-ray scattering was used to examine the spatial distribution of microphase-separated domains in these PLA-b-PM-b-PLA triblock copolymers. Figure 2.7 shows the SAXS results for each sample at 80 °C. All of the PLA-b-PM-b-PLA triblock copolymers exhibited a principal reflection, $q^*$, followed by several higher order reflections (Figure 2.7b,c,f). In some samples, broad oscillations in intensity (Figure 2.7e,g,h,i,j,k) followed the principal reflection consistent with microphase separated domains that do not exhibit long range order. Based on the positions of the higher order reflections, lamellar morphologies were observed for PLA-PM-PLA (4.6–10–4.6) and PLA-PM-PLA (14–28–14), and hexagonal morphologies were observed for PLA-PM-PLA (2.3–10–2.3), PLA-PM-PLA (3.8–10–3.8), and PLA-PM-PLA (6.6–28–6.6). We could not definitively determine the exact nature of the microphase-separated domains for the balance of the triblock copolymers and, thus, denote them as micellar (Table 2.3). Based on the SAXS data for three of the triblock copolymers in the lowest molecular weight series (Figure 2.7b,c,d), we
Table 2.3 Thermal and morphological properties of PLA-PM-PLA triblock copolymers

<table>
<thead>
<tr>
<th>Triblock %</th>
<th>PLA&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Morphology&lt;sup&gt;b&lt;/sup&gt;</th>
<th>D(Å)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>T&lt;sub&gt;g&lt;/sub&gt;(PM)&lt;sup&gt;d&lt;/sup&gt; (°C)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt;(PLA)&lt;sup&gt;d&lt;/sup&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-PM-PLA (1.3–10–1.3)</td>
<td>20.2</td>
<td>disordered</td>
<td>135</td>
<td>-22</td>
<td>21</td>
</tr>
<tr>
<td>PLA-PM-PLA (2.3–10–2.3)</td>
<td>31.6</td>
<td>cylindrical</td>
<td>178</td>
<td>-22</td>
<td>38</td>
</tr>
<tr>
<td>PLA-PM-PLA (3.8–10–3.8)</td>
<td>42.8</td>
<td>cylindrical</td>
<td>209</td>
<td>-22</td>
<td>42</td>
</tr>
<tr>
<td>PLA-PM-PLA (4.6–10–4.6)</td>
<td>48.0</td>
<td>lamellar</td>
<td>194</td>
<td>-21</td>
<td>44</td>
</tr>
<tr>
<td>PLA-PM-PLA (3.3–28–3.3)</td>
<td>18.9</td>
<td>micellar&lt;sup&gt;e&lt;/sup&gt;</td>
<td>231</td>
<td>-22</td>
<td>34</td>
</tr>
<tr>
<td>PLA-PM-PLA (6.6–28–6.6)</td>
<td>31.8</td>
<td>cylindrical</td>
<td>259</td>
<td>-22</td>
<td>46</td>
</tr>
<tr>
<td>PLA-PM-PLA (9.7–28–9.7)</td>
<td>40.7</td>
<td>micellar&lt;sup&gt;e&lt;/sup&gt;</td>
<td>471</td>
<td>-22</td>
<td>46</td>
</tr>
<tr>
<td>PLA-PM-PLA (14–28–14)</td>
<td>49.9</td>
<td>lamellar</td>
<td>367</td>
<td>-22</td>
<td>50</td>
</tr>
<tr>
<td>PLA-PM-PLA (6.5–43–6.5)</td>
<td>23.1</td>
<td>-</td>
<td>-</td>
<td>-22</td>
<td>48</td>
</tr>
<tr>
<td>PLA-PM-PLA (10–43–10)</td>
<td>32.1</td>
<td>micellar&lt;sup&gt;e&lt;/sup&gt;</td>
<td>314</td>
<td>-21</td>
<td>51</td>
</tr>
<tr>
<td>PLA-PM-PLA (15–43–15)</td>
<td>41.2</td>
<td>micellar&lt;sup&gt;e&lt;/sup&gt;</td>
<td>357</td>
<td>-21</td>
<td>53</td>
</tr>
<tr>
<td>PLA-PM-PLA (23–43–23)</td>
<td>51.5</td>
<td>micellar&lt;sup&gt;e&lt;/sup&gt;</td>
<td>455</td>
<td>-22</td>
<td>53</td>
</tr>
</tbody>
</table>

<sup>a</sup>Mass percent PLA calculated from <sup>1</sup>H NMR spectroscopy and composition of the triblock copolymers. <sup>b</sup>Based on SAXS data from 80–160 °C. <sup>c</sup>Determined by SAXS from the primary reflection (D= 2π/q<sup>*</sup>) at 80 °C. <sup>d</sup>Determined by DSC. <sup>e</sup>The SAXS data of these samples consist of a strong primary reflection followed by several low-amplitude, broad peaks due to the form of the microphase separated domains.
Figure 2.6 DSC analysis data for PLA-PM-PLA (3.3–28–3.3); PLA-PM-PLA (6.6–28–6.6); PLA-PM-PLA (9.7–28–9.7); PLA-PM-PLA (14–28–14)
Figure 2.7. Small angle x-ray scattering of the triblock copolymers at 80 °C. (▼) Peak positions calculated based on \( q^* \) are labeled by their Miller indices (hk for the two-dimensional hexagonal lattice, h for the one-dimensional lamellar lattice). For samples with little or no lattice order, only \( q^* \) is indicated. PLA-PM-PLA (a) (1.3–10–1.3), (b) (2.3–10–2.3), (c) (3.8–10–3.8), (d) (4.6–10–4.6), (e) (3.3–28–3.3), (f) (6.6–28–6.6), (g) (9.7–28–9.7), (h) (14–28–14), this sample exhibits ordered lamellar morphology above 140 °C. (i) (10–43–10), (j) (15–43–15), (k) (23–43–23).
suspect that the higher molecular weights of samples shown in Figures 2.7e–2.5h kinetically thwart the attainment of long range order.

A crude estimate of the effective interaction parameter between PLA and PM was made based on the change in lamellar domain spacing of PLA-PM-PLA (4.6–10–4.6) as a function of temperature. Equation 2.3 describes the domain spacing of strongly-segregated lamellar mesostructures.\textsuperscript{25}

\[ D = 1.10bN^{2/3}\chi^{1/6} \]  

(2.3)

where \( b \) is the statistical segment length, \( N \) is the number of segments, and \( \chi \) is the effective interaction parameter and is customarily given the functional form \( \chi = A/T+B \). For simplicity, the average statistical segment length was assumed to be 8 Å and \( N \) equal to the overall degree of polymerization. Figure 2.8 depicts the measured lamellar domain spacing \( (D = 2\pi/q^*) \) divided by \( 1.10bN^{2/3} \) and raised to the 6\(^{th} \) power vs. inverse temperature. The line-of-best-fit represents the estimate of \( \chi \). The effective interaction parameter that results from this analysis for this compositionally symmetric triblock copolymer is \( \chi = 364/T–0.50 \). Our assumptions for \( b \) and \( N \) amount to using an unknown segment reference volume for each. \( \chi \) represents interaction per segment volume, thus meaningful comparison with \( \chi \) for other block copolymer systems cannot be made. However, we feel this analysis will give a reasonable estimate of \( \chi \) between PM and PLA.
Figure 2.8 \((D/1.10bN^{2/3})^6\) vs. \(1/T \times 10^3\) for the lamellar PLA-PM-PLA (4.6–10–4.6).

The line of best fit represents the estimate for \(\chi\): \(\chi(T) = 364/T - 0.50\).
2.3.5 Mechanical Properties for PLA-\textit{b}-PM-\textit{b}-PLA Triblock Copolymers

For the purpose of mechanical testing and evaluation of thermoplastic elastomer (TPE) behavior, we targeted the synthesis a triblock copolymer on a larger scale (2 g) with hexagonally packed cylinders of PLA in a PM matrix. TPEs within hexagonally packed cylinders typically display impressive recoveries and high elongations at break.\(^9\) Successful large-scale synthesis of PLA-PM-PLA (7.8–29–7.8) was achieved by utilizing molecular sieves during the lactide triblock polymerization to eliminate water and by performing multiple precipitations of the product to remove residual HCl (section 2.2.7); the larger scale syntheses were not successful without these precautions. The final product was a rubbery solid with SEC traces and $^1\text{H}$ NMR spectra typical of the triblock copolymers previously synthesized. DSC revealed two $T_g$s at $-25$ °C and 44 °C, and, taking into consideration the relative fractions of PLA and PM, SAXS measurements were consistent with hexagonally packed cylinders of PLA in a matrix of PM.

The tensile properties of the PLA-\textit{b}-PM-\textit{b}-PLA triblock copolymer were characteristic, for the most part, of traditional TPEs. Representative stress-strain plots for the triblock copolymer pulled to ultimate tensile failure are shown in Figure 2.9. At low strains a linear response was observed in the stress-strain curve for all of the trials. However, the Young’s modulus observed (1.4 ± 0.3 MPa) was significantly reduced when compared to commercial polystyrene-\textit{b}-polybutadiene-\textit{b}-polystyrene TPEs (>6.0 MPa).\(^9\) Beyond the low strain elastic region the triblock copolymer shows yielding behavior indicative of a semicontinuous PLA phase dispersed in a PM matrix.\(^{26}\) The
Figure 2.9 Three representative stress-strain curves for PLA-PM-PLA (7.8–29–7.8) pulled to ultimate failure
ultimate tensile strength was 1.7 ± 0.1 MPa, which is also low compared to commercial polystyrene-\textit{b}-polybutadiene-\textit{b}-polystyrene TPEs (20–40 MPa). However, high elongations (960 ± 60\%) were achieved for every trial. These ultimate elongations are comparable to commercial TPEs\textsuperscript{9} and are higher than the largest elongations observed for the PLA-\textit{b}-PI-\textit{b}-PLA triblock copolymer series (650\%) and the PLLA-\textit{b}-PHB-\textit{b}-PLLA triblock copolymer series (200\%).\textsuperscript{11,14}

We investigated the elastic behavior or recovery of the triblock copolymer by subjecting the sample to cycles of loading and unloading at a strain of 300\%. Recovery was measured by observing the residual strain after a sample was unloaded. Residual strain was measured in two separate trials. In the first trial, a sample was subjected to consecutive cycles of loading and unloading, resulting in a residual strain of 30\% after four cycles. The second trial involved subjecting a separate sample to four cycles and allowed 6 minutes between each cycle for maximum recovery, resulting in a residual strain of only 16\% after four cycles (Figure 2.10).\textsuperscript{9} In both trials the residual strain increased with each cycle and then remained constant after the third cycle. This could be due to an alignment of the cylinders induced by the applied strain; as a result, the aligned polymer would not fully recover.\textsuperscript{11,27} Once this putative alignment was achieved, the subsequent cycles display identical stress-strain behavior (Figure 2.10, third and fourth cycles). The lack of complete recovery can also be explained by a slippage of trapped entanglements in the soft block during deformation.\textsuperscript{9} This slippage results in a delay of the failure of the hard domains in the TPE resulting in elongated samples. The overall recovery of the samples is affected
Figure 2.10 Four loading (filled symbols) and unloading (open symbols) cycles for PLA-PM-PLA (7.8–29–7.8) pulled to 300% with 6 minute delays between cycles: first cycle, squares; second cycle, diamonds; third cycle, triangles; forth cycle, circles
because the slippage of chains is not instantaneously reversible. Most likely the lack of recovery displayed by PLA-PM-PLA (7.8–29–7.8) is the result of both induced alignment and slippage of the PM block.

A separate sample of PLA-PM-PLA (7.8–29–7.8) was pulled to 200% to align the sample, released to zero strain and immediately pulled to ultimate failure (Figure 2.11). Ultimate tensile failure was not observed due to the sample slipping out of the grips at 1100%, which can be viewed as a lower limit. This value is significantly higher than the samples that were pulled once to failure (Figure 2.9).

### 2.4 Summary

A series of all biorenewable ABA thermoplastic elastomers comprised of soft PM and hard PLA blocks were obtained with varied composition and morphology. The synthesis involved the ring-opening polymerization of menthide by diethylene glycol and diethyl zinc to give the dihydroxy macroinitiator HO–PM–OH, followed by the ring-opening polymerization of lactide to yield the desired PLA-\(b\)-PM-\(b\)-PLA triblock copolymer. We were able to control the molecular weights of HO–PM–OH by varying the menthide-to-initiator ratio. These HO–PM–OH materials were characterized by NMR spectroscopy, SEC and DSC, and then subsequently used as difunctional macroinitiators for \(D,L\)-lactide polymerization. Three series of triblock copolymers with varied lactide composition were obtained. SEC traces of all of the samples showed unimodal signals and a gradual shift to the high molecular weight region when the PLA block length increased. Microphase separation of the blocks was
Figure 2.11 PLA-PM-PLA (7.8–29–7.8) pulled to 200% (gray line), released, and immediately pulled to ultimate failure (black line). The sample slipped out of the grips at 1100% elongation and did not reach ultimate failure.
confirmed by SAXS. Tensile measurements demonstrated impressive elongations and
elastomeric properties of the PLA-\textit{b}-PM-\textit{b}-PLA TPEs. These results demonstrate that
PLA-\textit{b}-PM-\textit{b}-PLA triblock copolymers are potentially suitable for numerous
applications in the biomedical and pharmaceutical fields.

2.5 Acknowledgments

This work was supported primarily by the MRSEC program of the National
Science Foundation under Award Number DMR-0212302. We also acknowledge the
Petroleum Research Fund (grant no. 45891-AC7), the National Science Foundation
(grant no. CHE-9975357) and Cargill, Inc. for partial support of this work.

2.6 References

85–92.


1846.

6147–6176.


Chapter 2: Synthesis of Renewable Resource Thermoplastic Elastomers


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3

Hydrolytic Degradation Behavior of a Renewable Thermoplastic Elastomer*

3.1 Introduction

Aliphatic polyesters derived from lactide (LA), glycolide (GA), and ε-caprolactone (CL) are an important class of degradable polymers for biomedical applications including tissue engineering,¹ drug delivery,² and medical implants.³ As discussed in Chapter 1, polylactide (PLA) is perhaps the most popular polyester in biomedical applications due to its many favorable characteristics, such as its high strength,⁴ susceptibility to hydrolytic degradation, and biocompatibility.⁵ The thermal, mechanical, and degradation properties of PLA are influenced significantly by its tacticity.⁶⁻⁸ Isotactic poly(L-lactide) (PLLA) or poly(D-lactide) (PDLA) is semi-crystalline (Tₘ ≈ 180 °C) and exhibits a relatively slow hydrolysis rate.⁷,⁹ PLLA films allowed to degrade in pH 7.4 phosphate buffer at 37 °C reached 50% of their initial molecular weights at around 53 weeks with no significant mass loss observed until 104 weeks.⁹ Atactic poly(D,L-lactide) is amorphous (Tₘ ≈ 60 °C) with a much faster

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hydrolysis rate than PLLA, reaching 50% of initial molecular weights between 7 and 12 weeks with significant mass loss observed between 8 and 13 weeks.\textsuperscript{7,10,11}

In addition to adjusting the tacticity of polylactide, copolymerization with other degradable polyesters such as CL has been used to obtain polymers with a wide range of properties and degradation rates.\textsuperscript{12-19} Poly(\(\varepsilon\)-caprolactone) (PCL) is a semicrystalline polymer (\(T_m \approx 60\) °C) with a low glass transition temperature (\(T_g \approx –60\) °C) that exhibits high elongations at break and a low modulus.\textsuperscript{7} Relative to PLA, PCL is stable towards hydrolytic degradation; for example, PCL has been reported to lose only 30% of its initial molecular weight after 45 weeks with no indication of mass loss after 60 weeks.\textsuperscript{12} Ye et al. studied PLA–PCL diblock copolymers with the aim of taking advantage of the degradability of PLA and the permeability to drugs of PCL,\textsuperscript{13} and Jeong et al. and Garkhal et al. used random copolymers of PLLA or PLA and PCL to exploit these flexible materials as scaffolds for tissue engineering.\textsuperscript{14,15} These investigations focused on the effects of composition and molecular weight on the degradability of the copolymers,\textsuperscript{13–15} but whether these PLA-containing block copolymers maintained their mechanical properties was not reported.

Mechanical properties play a vital role in determining the in vivo performance of biomedical systems, an illustrative example being the effects on healing of the stress induced on surrounding tissue by an implanted device.\textsuperscript{20} Cohn et al. reported the synthesis, characterization, and degradation of PLLA/PCL multiblock copolymers, focusing on the influence of composition and degradation on the mechanical properties of the materials.\textsuperscript{16} These copolymers were reported to behave as
thermoplastic elastomers in which the hard PLLA blocks microphase separated from the soft PCL blocks and acted as physical crosslinks resulting in properties similar to vulcanized rubbers.\textsuperscript{21} PLLA/PCL multiblock copolymers displayed widely varying stiffness (Young’s modulus up to 800 MPa) and flexibility (ultimate strains from 200 to 1600\%). Unfortunately, in vitro degradation (pH = 7.4, 37 °C) of these materials revealed significant loss of mechanical strength and elongation at break after about 8–9 weeks for all samples.\textsuperscript{16} Studies of the polymerization and degradation behavior of block copolymers containing PLLA or PLA and other degradable monomers such as glycolide,\textsuperscript{17} 1,5-dioxepan-2-one (DXO),\textsuperscript{22-24} trimethylene carbonate (TMC),\textsuperscript{25} and others,\textsuperscript{26} have been reported, but again, little emphasis has been placed on the effects of degradation on copolymer mechanical properties.\textsuperscript{22} One thermoplastic elastomer, poly(L-lactide-\textit{b}-1,5-dioxepan-2-one-\textit{b}-L-lactide) (PLLA–PDXO–PLLA), containing 73\% PDXO showed a decrease in ultimate tensile strength from 43 MPa to ~20 MPa during 8–9 weeks of in vitro degradation while maintaining high elongations (800\%),\textsuperscript{22} in contrast to the dramatic decrease in elongation seen for the PLLA/PCL multiblock copolymers.\textsuperscript{16}

Biodegradable thermoplastic elastomers such as those described above and in Chapter 1 will expand the range of chemical and mechanical attributes available for biomedical and other applications. As discussed in the previous chapters, we are interested in biodegradable ABA triblock copolymers using polymenthide (PM), an amorphous polyester ($T_g = –25$ °C), as the soft B segment.\textsuperscript{27} Unlike the soft blocks mentioned above, PM is one of a variety of polymers derived from renewable
resources. In Chapter 2, we synthesized α,ω-difunctionalized polymenthide (HO–PM–OH) and used it as a macroinitiator for the polymerization of D,L-LA to yield PLA–PM–PLA samples of controlled molecular weight and composition. Microphase separation of the blocks was confirmed by small-angle x-ray scattering (SAXS) and differential scanning calorimetry (DSC). Tensile measurements of one of the triblock copolymers demonstrated relatively low stiffness (tensile modulus = 1.4 ± 0.3 MPa) but impressive elongations (strain at break = 960 ± 60%) and elastomeric properties (high degree of recoverable strain after 300% elongation).

For use in biomedical and other applications, the hydrolytic degradation behavior of these renewable thermoplastic elastomers needs to be evaluated with particular focus on the influence degradation has on mechanical properties. In this Chapter, we report the results of studies aimed at addressing this requirement. The in vitro degradation behavior of a set of PLA-PM-PLA triblock copolymers was evaluated in phosphate buffer solution (pH 7.4) at 37 °C, and compared with that of the corresponding PLA and PM homopolymers. Changes in water uptake, molecular weight, mass, polymer composition and thermal properties during degradation are reported. Importantly, we determined the relationship between the copolymer composition and mechanical properties both prior to and during hydrolytic degradation. From these studies we conclude that the degradation rates of the triblock copolymers may be purposefully controlled and that their elastomeric properties are retained for prolonged periods as they degrade, thus making them potentially useful in biomaterial applications.
3.2 Experimental

3.2.1 Materials

Toluene used for polymerizations was purified by passage through activated alumina-based columns (Glass Contour, Laguna Beach, CA) followed by distillation from sodium. D,L-Lactide (Purac) were purified by recrystallization from toluene followed by repeated (2x) vacuum sublimation. Diethylene glycol (Sigma Aldrich) was distilled under reduced pressure from sodium. Molecular sieves (4 Å) were dried under vacuum at 180 °C for a minimum of 16 h. All other solvents and reagents were used as received from the commercial source indicated without further purification. The polymenthide and triblock copolymers were synthesized by the methods reported previously in Chapter 2. Poly(D,L-lactide) (PLA) was synthesized by the ring-opening polymerization of D,L-lactide with triethylaluminum (Et$_3$Al) and ethanol (EtOH) in toluene as follows. In a glovebox, 13.0 g of D,L-lactide (0.0902 mol), 89.9 mL toluene, 46.2 µL EtOH (0.791 mmol), and 0.396 mL Et$_3$Al (1.0 M in hexanes, 0.396 mmol) were placed into a 150 mL high-pressure vessel. The solution was stirred in an oil bath at 90 °C for 2.5 h. The polymerization was terminated with approximately 3.0 mL of 1.0 M HCl. The polylactide was precipitated into methanol and dried in a vacuum oven for 18 h at 80 °C (7.5 g, 67% conversion of lactide).

3.2.2 Hydrolytic Degradation

The triblock copolymers were pressed into dogbone-shaped bars of approximately 10 mm length, 5 mm width, and 1 mm thickness (0.15 g) and PLA (11)
Chapter 3: Hydrolytic Degradation of a Renewable Thermoplastic Elastomer

was pressed into rectangular bars of similar dimensions (0.20 g). PM (29), being a soft, viscous material at room temperature, was divided into samples of approximately 0.18 g. The polymers were subjected to hydrolytic degradation by immersing the samples into small vials containing a stir bar and filled with approximately 10 mL of 0.01 M, pH 7.4 phosphate buffered saline solution. To prevent microbial growth 0.04 wt% NaN$_3$ was added to the solution. The vials were placed in oil baths at 37 °C with constant stirring. The medium was changed once a week. The samples were removed from the buffer solution at the prescribed intervals and washed with deionised water. All tensile testing was performed on the samples within minutes of removing from the solution and patting dry. Samples were dried under vacuum for 18 h. Mass loss was calculated according to the following equation

\[
\text{Mass Loss} \% = \frac{m_i - m_t}{m_i} \times 100
\]

(3.1)

where $m_i$ and $m_t$ represent the initial mass and the dry mass at time $t$. The water uptake was calculated according to the following equation

\[
\text{Water Uptake} \% = \frac{m_s - m_t}{m_s} \times 100
\]

(3.2)

where $m_s$ and $m_t$ represent the swollen mass prior to vacuum drying and the dry mass at time $t$. The water uptake and mass loss values reported for the triblock copolymers are averages of measurements on 3 separate samples.
3.2.3 Measurements

$^1$H and $^{13}$C NMR spectra were collected on a Varian INOVA-300, VXR-300 or Varian INOVA-500 spectrometer to determine the molecular weights of polymer samples. Samples of the dried polymers were prepared by dissolving approximately 30 mg of polymer in 1 mL of CDCl$_3$ (Cambridge). Molecular weights ($M_n$ and $M_w$) and polydispersity indicies ($M_w/M_n$) were determined by size exclusion chromatography (SEC) in methylene chloride using polystyrene standards. Samples were analyzed at 40 °C using a Hewlett-Packard high-pressure liquid chromatograph equipped with three Jordi poly(divinylbenzene) columns of $10^4$, $10^3$, and 500 Å pore sizes and a HP1047A differential refractometer. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q1000 with nitrogen as the purge gas. An indium standard was used for calibration, and the scan rate was 10 °C/min. Samples weighing 3.0–8.0 mg were loaded into aluminum hermetic pans and the pans were sealed prior to measurement. Tensile testing experiments were carried out at room temperature using a Rheometrics Scientific Minimat instrument operated at a cross-head speed of 5 mm/min. The sample gage length was 5 mm, the gage width was 3 mm, and the gage thickness was 1 mm.

3.3 Results and Discussion

3.3.1 Synthesis and Characterization

Polylactide–polymenthide–polylactide triblock copolymers of various compositions were prepared via a two-step process as described in Chapter 2.\textsuperscript{29} The
triblock copolymers listed in Table 3.1 are labeled according to the number average molecular weights (determined by NMR spectroscopy) of each block in kg mol\(^{-1}\). Consistent with the triblock copolymers synthesized in Chapter 2, clean triblock formation was indicated by the shift of the SEC peak of the triblock copolymer relative to that of the parent PM homopolymer. The copolymers were prepared on a multigram scale and were free of significant PM or PLA homopolymer as determined by SEC and \(^1\)H NMR spectroscopy. Polymethide homopolymer (PM (29)) was synthesized as described in Chapter 2 (Section 2.2.3). Poly(D,L-lactide) (PLA (11)) was synthesized by the ring-opening polymerization of D,L-lactide catalyzed by triethylaluminum and ethanol in toluene. All polymers exhibited narrow molecular weight distributions (PDI = 1.05–1.31). The triblock copolymers were pressed into ~1 mm thick sheets and punched into dog bone-shaped samples for mechanical testing during the degradation study. Polylactide was pressed into rectangles of similar thickness.

The thermal properties of the polymers and the ordered morphology of the triblock copolymers were investigated by DSC and SAXS, respectively. All of the polymers were amorphous with glass transitions corresponding to their respective components (Table 3.1). SAXS analysis of PLA-PM-PLA (7.6–33–7.6) at 45 °C exhibited a principal reflection, \(q^*\), followed by broad oscillations in intensity consistent with microphase-separated domains and no long-range order (Figure 3.1). In contrast, SAXS analysis of PLA-PM-PLA (12–32–12) at 45 °C exhibited several higher-order reflections following the principal reflection consistent with hexagonally
Table 3.1 Characterization data for polymer samples used in the degradation study

<table>
<thead>
<tr>
<th>polymer</th>
<th>$M_n$ (NMR) (kg/mol)</th>
<th>% PLA$^a$ (NMR)</th>
<th>$M_n$ (SEC) (kg/mol)</th>
<th>PDI</th>
<th>$T_{g, PM}^b$ (°C)</th>
<th>$T_{g, PLA}^b$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-PM-PLA (7.6–33–7.6)</td>
<td>7.6–33.0–7.6</td>
<td>31.6</td>
<td>41.0</td>
<td>1.31</td>
<td>−23</td>
<td>47</td>
</tr>
<tr>
<td>PLA-PM-PLA (12–32–12)</td>
<td>11.6–32.2–11.6</td>
<td>41.9</td>
<td>54.0</td>
<td>1.19</td>
<td>−22</td>
<td>51</td>
</tr>
<tr>
<td>PM (29)</td>
<td>29.3</td>
<td>0</td>
<td>47.2</td>
<td>1.10</td>
<td>−24</td>
<td>42</td>
</tr>
<tr>
<td>PLA (11)</td>
<td>11.1</td>
<td>100</td>
<td>22.0</td>
<td>1.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Mass percent poly(D,L-lactide) calculated from $^1$H NMR spectroscopy and composition of the triblock copolymers. $^b$ DSC program: cool at 100 °C min$^{-1}$ to −60 °C, equilibrate, heat at 10 °C min$^{-1}$ to 200 °C. The $T_g$ values were determined from the final heating ramp data.
Figure 3.1 SAXS analysis at 45 °C of PLA-PM-PLA (7.6–33–7.6) and PLA-PM-PLA (12–32–12)
packed cylinders of PLA in a matrix of PM (Figure 3.1). As expected, the domain spacing of the triblock copolymers increased from 22.3 nm (PLA-PM-PLA (7.6–33–7.6)) to 28.2 nm (PLA-PM-PLA (12–32–12)) with increasing molecular weight of the PLA component.

### 3.3.2 Degradation: Visual Aspects and Mass Loss

The triblock copolymers and homopolymers were subjected to hydrolytic degradation by immersion of the samples into phosphate buffered saline solution (pH = 7.4) at 37 °C for 45 weeks. Initially, the copolymers and homopolymers appeared translucent and homogeneous. As the degradation proceeded, the PLA (11) samples appeared cloudy and increased to about four times their original size by week 15 followed by transformation into a fine white powder (Figure 3.2a). This burst-like behavior is characteristic of inner autocatalyzed degradation, and has been reported previously. The copolymer samples appeared increasingly cloudy during the course of the degradation experiment and began slowly increasing in size after week 29 (Figure 3.2b). No significant changes in appearance were observed for PM (29) homopolymer during the course of the experiment (Figure 3.2c).

Figure 3.3 shows the percent mass loss profile (Equation 3.1) for the polymers as a function of degradation time. The mass loss observed for the polymers in the first weeks is attributed to diffusion of low molecular weight compounds, e.g. residual monomer, into the buffer solution. Besides this initial loss of low molecular weight compounds, relatively little mass was lost during the first 11 weeks of degradation for
Figure 3.2 Representative images of a) PLA (11) before degradation and at weeks 1 and 21, b) PLA-PM-PLA (7.6–33–7.6) before degradation and at weeks 3, 29, and 37, and c) PM (29) before degradation and at weeks 21 and 37
Figure 3.3 Mass loss profiles of the polymers during degradation
all polymers. After week 11, a significant mass loss was observed for PLA (11), reaching over 80% mass loss at week 21. At week 21, a slight increase in mass loss was observed for PLA-PM-PLA (7.6–33–7.6), reaching 25% mass loss at week 37, whereas an abrupt loss in mass was observed at week 37 PLA-PM-PLA (12–32–12). A small mass loss of 8% by week 45 was observed for PM (29).

The final mass loss for the triblock copolymers at week 45 was 27% for PLA-PM-PLA (7.6–33–7.6) and 37% for PLA-PM-PLA (12–32–12), values similar to the mass percent of polylactide in the triblock copolymers (Table 3.1). These data suggest that the mass loss is due to the degradation and loss of the polylactide blocks. To evaluate this hypothesis, the compositions of the PLA-PM-PLA triblock copolymers were monitored by \(^1\)H NMR spectroscopy (Figure 3.4). Consistent with the mass loss profile (Figure 3.3), the composition of the triblock copolymers did not change during the first 15 weeks. The onset of the decrease in content of PLA in the triblock copolymers coincided with the start of mass loss. By week 45, the PLA content in the triblock copolymers was 3% (PLA-PM-PLA (7.6–33–7.6)) and 14% (PLA-PM-PLA (12–32–12)). Therefore, the released oligomers contained large amounts of PLA and the remaining materials were enriched in the PM component, consistent with the mass loss profile (Figure 3.3).

### 3.3.3 Thermal Properties

The thermal behavior of the samples was monitored by DSC analysis of the glass transition temperatures, \(T_g\)’s (Figure 3.5). The PLA glass transition temperature
Figure 3.4 The composition of the triblock copolymers determined by $^1$H NMR spectroscopy as a function of degradation time
Figure 3.5 Glass transition temperatures detected by DSC for all polymers. PLA $T_g$: open symbols, PM $T_g$: closed symbols
for PLA (11) homopolymer and the copolymers changed as degradation progressed from a distinct transition to a broad and ill-defined transition that was difficult to measure and had significant error (hence the apparent jump in $T_g$ for PLA-PM-PLA (12–32–12) at week 45). This change in the polylactide glass transitions coincides with the mass loss increases (Figure 3.3), providing further evidence of the hydrolytic degradation and mass loss of the PLA blocks in the PLA-PM-PLA triblock copolymers. For PM (29) and the block copolymers, the polynemthide glass transition remained unchanged during the entire degradation study (Figure 3.5).

### 3.3.4 Molecular Weight and the Rate of Degradation

The hydrolytic degradation of PLA-PM-PLA (7.6–33–7.6), PLA-PM-PLA (12–32–12), PLA (11), and PM (29) was monitored by SEC. Figure 3.6 displays the normalized number-average molecular weight ratio, $(M_n)_t / (M_n)_0$, as a function of degradation time. Based on SEC measurements, hydrolytic degradation of PM (29) was extremely slow, retaining 96.5% of its original molecular weight by week 45. The degradation rate of polynemthide is similar to that observed for PCL. The degradation profile observed for PLA (11) is consistent with those seen for other degradation studies that report a 50% decrease in molecular weight at ~10 weeks under the same conditions. The hydrolytic degradation of the triblock copolymers was clearly dependent on the initial molecular weight of the polylactide blocks. Based on SEC, degradation of the lower molecular weight PLA triblock copolymer, PLA-PM-PLA (7.6–33–7.6), began shortly after immersion of the sample into the buffer solution,
Figure 3.6 Molecular weight profile of the polymers during degradation as measured by SEC.
whereas significant degradation of PLA-PM-PLA (12–32–12) began at week 15 (Figure 3.6).

SEC measurements showed that both the polylactide and the polymenthide blocks in the triblock copolymers degraded. Figure 3.7 shows the SEC chromatograms of the polymenthide precursor, PLA-PM-PLA (7.6–33–7.6), and PLA-PM-PLA (7.6–33–7.6) after 15, 29 and 45 weeks of degradation. As degradation proceeds the peaks shift towards lower molecular weight. Importantly, the polymenthide precursor is higher molecular weight than the molecular weight for the triblock copolymer at weeks 29 and 45 (Figure 3.7). This is evidence for some chain scission of polymenthide in the triblock copolymers. If such chain scission did not occur during degradation, we would expect the SEC chromatograms to approach the chromatogram of the polymenthide precursor, and have molecular weights above or equal to that of the precursor. The apparently enhanced chain scission of the PM block in the triblock copolymers may be the result of carboxylic acid terminated PLA oligomers present in the degrading triblock samples.

Comparison of the molecular weight profile (Figure 3.6 and 3.7) and mass loss profile (Figure 3.3) for polylactide and the triblock copolymers provide insight into the relationship between hydrolytic degradation and mass loss. Hydrolysis begins (see Figure 3.6 and 3.7) before significant mass loss is observed (Figure 3.3). The onset of mass loss occurs once $(M_n)_t / (M_n)_0$ reaches 0.80 for the triblock copolymers. Based on the mass loss (Figure 3.3) and composition (Figure 3.4) profiles the mass loss of the triblock copolymers is due to the degradation and loss of the polylactide blocks.
Figure 3.7 Evolution of SEC chromatograms of the triblock copolymer PLA-PM-PLA (7.6–33–7.6) during hydrolytic degradation. The gray SEC trace corresponds to the PM precursor of PLA-PM-PLA (7.6–33–7.6)
However the polymenthide block is degrading through chain scission, but not being lost (Figure 3.7). Evidently, a higher degree of chain scission than observed is required for significant mass loss of polymenthide to occur in the triblock copolymers.

### 3.3.5 Water Uptake

All of the above data was acquired on samples that were removed from the degradation solution and dried. During the degradation experiment, the polymer samples absorbed water, and Figure 3.8 presents the water uptake profiles of the polymers during hydrolytic degradation. The data in Figure 3.8 is a measure of the fraction of water in the sample at the time it was removed from the degradation solution and not relative to the initial sample mass (see Equation 3.2). Polylactide is generally a hydrophobic polymer, but due to its relatively low molecular weight PLA (11) took up significant amounts of water by week 15. After week 15, the swollen PLA (11) burst into a powder. Polymenthide (PM (29)) absorbed minimal water during the course of the degradation experiment, due to its hydrophobic nature. Water uptake for the copolymers was intermediate between that of the two homopolymers. The rate of water uptake was more gradual for the copolymers compared to polylactide. Noticeable increases in water uptake occur for PLA-PM-PLA (7.6–33–7.6) at week 29 and for PLA-PM-PLA (12–32–12) at week 37, the same weeks that we observe significant loss in mass (Figure 3.3).

The initial molecular weight of the polylactide blocks in PLA–PM–PLA triblock copolymers significantly influences the degradation and water uptake rates of
Figure 3.8 Water uptake profiles of the polymers during degradation. We estimate an error in the water uptake values of ± 5%.
the copolymer. During the first 30 weeks of the degradation experiment PLA-PM-PLA (7.6–33–7.6) is less hydrophobic than PLA-PM-PLA (12–32–12) as evidenced by the water uptake profiles (Figure 3.8). As a result, hydrolytic degradation is faster for PLA-PM-PLA (7.6–33–7.6) than for PLA-PM-PLA (12–32–12) (Figure 3.6). A similar dependence of the rate of degradation on the molecular weight of the polylactide blocks was reported previously for PCL/PLA copolymers and PLLA–PDXO–PLLA triblock copolymers.\textsuperscript{15,16,23} In contrast, the investigation of random copolymers of PDXO and PLLA showed that an increase in the amount of lactide in the polymer resulted in faster degradation.\textsuperscript{24}

### 3.3.6 Mechanical Properties

The tensile properties of the triblock copolymers were tested both before and during hydrolytic degradation. Before degradation, both triblock copolymers were highly elastic (Table 3.2); we observed residual strain of 1.1\% for PLA-PM-PLA (7.6–33–7.6) and 3.0\% for PLA-PM-PLA (12–32–12) after subjecting the samples to 20 consecutive cycles of loading and unloading at a strain of 50\%. Consistent with previous work,\textsuperscript{29} the initial mechanical properties of the triblock copolymers before degradation were characteristic of thermoplastic elastomers.\textsuperscript{21}
Table 3.2 Tensile properties of the triblock copolymers prior to degradation

<table>
<thead>
<tr>
<th>polymer</th>
<th>$E$ (MPa)</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-PM-PLA (7.6–33–7.6)</td>
<td>0.78 ± 0.02</td>
<td>4.0 ± 0.3</td>
<td>1330 ± 40</td>
</tr>
<tr>
<td>PLA-PM-PLA (12–32–12)</td>
<td>3.13 ± 1.08</td>
<td>4.4 ± 0.5</td>
<td>580 ± 50</td>
</tr>
</tbody>
</table>

During the in vitro degradation of PLA-PM-PLA (7.6–33–7.6) and PLA-PM-PLA (12–32–12) the tensile properties of the water-swollen samples were tested regularly as a function of degradation time (Figure 3.9). At the onset of the experiment, we observed decreases in the Young’s modulus, tensile strength and elongation of the samples, associated with the small amount of water uptake observed during the first 5 weeks (Figure 3.8). Even though PLA-PM-PLA (7.6–33–7.6) and PLA-PM-PLA (12–32–12) had similar levels of water uptake, the tensile strength of PLA-PM-PLA (12–32–12) decreased to a larger extent as compared to PLA-PM-PLA (7.6–33–7.6). After week 5, the ultimate strain and Young’s modulus remained rather constant for both samples, while a gradual decrease in the tensile strength was observed (Figure 3.9). Once mass loss began for the triblock copolymers (see Figure 3.3), the tensile properties decreased considerably. This behavior is similar to that observed for the PCL-PLA multiblock copolymer system discussed previously.\(^\text{16}\) In that study, the mechanical properties of the PCL-PLA multiblocks were also found to be heavily dependent on the change in molecular weight, and after 7–8 weeks of degradation the copolymers lost all their initial mechanical strength.\(^\text{16}\) Similarly, photo-cross-linked star PCL/PLA copolymers exhibited dramatic decreases in the
Figure 3.9 Mechanical properties of the PLA-PM-PLA triblock copolymers as a function of degradation time
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elongation, tensile modulus, and ultimate strength during in vitro and in vivo degradation, and after only 8 weeks lost all their mechanical integrity.\(^{18}\)

In contrast to the PCL/PLA systems, the PLA-PM-PLA triblock copolymers retained a significant fraction of their tensile strength, stiffness and elongation for much longer periods of time. For example, only on PLA–PCL–PLA triblock copolymer of the five studied displayed any significant mechanical properties after 13 weeks; ultimate strain, tensile strength, and modulus were \(\sim20\%\), \(\sim3\) MPa, and \(\sim25\) MPa, respectively, values significantly lower than the initial mechanical properties of \(1600\%\), \(30\) MPa, and \(30\) MPa.\(^{16}\) Even after 21 weeks in the degradation solution the ultimate strain, tensile strength, and modulus for the PLA-PM-PLA (12–32–12) samples were \(450\%\), \(0.60\) MPa, and \(0.74\) MPa, respectively. We attribute this behavior to the increased hydrophobicity of the PM block that limits the water uptake in these materials. Nonetheless, we anticipate complete degradation and loss of mechanical integrity for the triblock samples at long times given that the PM block does undergo slow hydrolytic degradation.

3.4 Summary

As part of our efforts to develop biodegradable, biorenewable thermoplastic elastomers, we have investigated the hydrolytic degradation of PLA-PM-PLA samples, with a particular view towards understanding how mechanical properties are influenced during the degradation process. We compared the degradation of PLA (11), PM (29), PLA-PM-PLA (7.6–33–7.6) and PLA-PM-PLA (12–32–12) performed at 37
°C in a phosphate buffer solution at pH 7.4. Hydrolysis of PLA (11) and the triblock copolymers was characterized by a decrease in molecular weight followed by a mass loss that began once 20% of the original molecular weight was lost. The rate of degradation of the triblock copolymers was influenced by the molecular weight of the polylactide blocks and was intermediate to that of PLA and PM homopolymers. Most importantly, prior to the onset of significant mass loss, these versatile polymers are able to maintain a significant amount of their mechanical properties for approximately 21 weeks. This is a significant improvement over previously reported PLA-containing block copolymers, and establishes their potential utility in biomaterial applications.

### 3.5 Acknowledgments

We thank the donors of the American Chemical Society Petroleum Research fund (grant 45891-AC7) and Cargill, Inc. for financial support. Portions of this work were performed in the Institute of Technology Characterization Facility, University of Minnesota, which receives partial support from NSF through the NNIN program.

### 3.6 References


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4

Consequences of Polylactide Stereochemistry on the Properties of Polylactide-Polymenthide Triblock Thermoplastic Elastomers

4.1 Introduction

Polylactide (PLA) is a biorenewable and biodegradable polyester\(^1\) that has many applications, particularly in the biomedical and pharmaceutical fields because of its nontoxicity and biocompatibility.\(^2\) As mentioned in Chapter 1, the thermal and mechanical properties of PLA are influenced significantly by its tacticity,\(^3\) which may be controlled by the stereoisomeric form of lactide (LA) used in ring-opening polymerization processes.\(^4\) Atactic, amorphous poly(D,L-lactide) (PLA, \(T_g \approx 60^\circ C\)) is derived from polymerization of racemic D.L-lactide (D,L-LA), whereas isotactic, semi-crystalline (\(T_m \approx 180^\circ C\)) poly(L-lactide) (PLLA) or poly(D-lactide) (PDLA) results from polymerization of L- or D-lactide, respectively. Blending of PLLA and PDLA leads to the formation of stereocomplex crystallites with a different crystalline structure (\(T_m \approx 230^\circ C\)) than that of the semi-crystalline homopolymers.\(^5\) Stereocomplex formation is favored by stoichiometric blending of low molecular weight, enantiopure PLLA and PDLA homopolymers.\(^5-7\)
The potential applications of PLA are limited by the fact that it is brittle and subject to fracture at relatively low strain (5-30% elongation at break), so there is great interest in broadening its utility by various property modification protocols, including incorporation into block copolymers. Block copolymers represent an interesting class of self-organizing soft materials with wide ranging utility. In particular, ABA triblock copolymers that contain immiscible segments where A is a “hard”, high $T_g$ or semi-crystalline polymer (e.g., polylactide) and B is a “soft” amorphous, low $T_g$ polymer are of tremendous value as thermoplastic elastomers. Thermoplastic elastomers (TPEs) have stress-strain properties comparable to vulcanized rubbers, but can be processed like conventional thermoplastics. In previous work, we synthesized and characterized a series of all-renewable ABA triblock copolymers with amorphous PLA as the hard segment and polymenthide (PM), a biorenewable polymer derived from (+)-menthol, as the soft ($T_g = -25$ °C) segment (Scheme 4.1). Using a difunctional initiator, we synthesized the $\alpha,\omega$-dihydroxy functionalized polymenthide (HO–PM–OH), which is an effective macroinitiator for the subsequent ring-opening polymerization of D,L-LA to yield triblock PLA–PM–PLA samples of controlled molecular weight and composition. Small-angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC) data evinced microphase separation in these triblocks, and tensile measurements on one sample of copolymer revealed impressive elastomeric properties (strain at break = 960 ± 60% with a high degree of recoverable strain at modest elongations).
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Scheme 4.1

\[
\begin{align*}
\text{HO-} & \text{O} \quad \text{O} \quad \text{HO} \\
\text{O} & \text{O} \\
\text{m} & \text{H}
\end{align*}
\]

\[
\begin{array}{c}
\text{Scheme 4.1} \\
\text{HO-PM-OH} \\
\text{PLA-PM-PLA}
\end{array}
\]

\[
\begin{align*}
(\text{rac-PLA}) \text{-PM-(rac-PLA)} & \quad X = \text{[O} \quad \text{O} \quad \text{O} \quad \text{O}]_n \text{H} \\
\text{PLLA-PM-PLLA} & \quad X = \text{[O} \quad \text{O} \quad \text{O} \quad \text{O}]_n \text{H} \\
\text{PDLA-PM-PDLA} & \quad X = \text{[O} \quad \text{O} \quad \text{O} \quad \text{O}]_n \text{H}
\end{align*}
\]
Chapter 4: Consequences of Stereochemistry on the Properties of PLA–PM–PLA

The triblock copolymer tested in Chapter 2 exhibited a low tensile modulus (1.4 ± 0.3 MPa) and ultimate tensile strength (1.7 ± 0.1 MPa) compared to, for example, commercially available polystyrene based TPEs.\textsuperscript{11} Since the mechanical strength is provided in large part by the physical interactions among the hard segments,\textsuperscript{10} we hypothesized that (a) substituting the amorphous PLA blocks with semi-crystalline PLLA or PDLA blocks would result in greater strength, and (b) this effect could be enhanced further by stereocomplex formation between isotactic PLLA and PDLA blocks in triblock copolymer blends. Precedence for these notions includes the observation of two-fold increases in Young’s modulus and tensile strength for symmetric PLLA/PDLA blends when compared to homopolymer PLLA\textsuperscript{14} and the identification of stereocomplex formation in PLLA and PDLA-containing block copolymers,\textsuperscript{15} such as for the preparation of biodegradable hydrogels,\textsuperscript{16} scaffolds for tissue engineering\textsuperscript{17} and carriers for drug delivery.\textsuperscript{18} Less attention has been focused on the mechanical properties of TPEs with PLLA or PDLA segments, but recent reports are promising.\textsuperscript{19,21} For example, blends of PLLA–poly(trimethylene carbonate)–PLLA and PDLA–poly(trimethylene carbonate)–PDLA triblocks exhibited low creep rates\textsuperscript{19} and increases of around 50\% in the Young’s modulus when compared to the pristine triblock copolymers.\textsuperscript{20} Also, the elongation at break and Young’s modulus of enantiomeric blends of diblock copolymers containing PLA and poly(\textit{e}-caprolactone) were significantly improved compared with pure diblock samples.\textsuperscript{21}
Herein, we report the synthesis, characterization, and the mechanical properties of semi-crystalline triblock copolymers PLLA–PM–PLLA and PDLA–PM–PDLA. Comparison of the mechanical properties among these copolymers, their blends (both symmetric 50:50 and asymmetric 95:5), and analogs comprising amorphous PLA segments revealed a significant influence of isotacticity in the polylactide components on the mechanical strength relative to the atactic (amorphous) analogs.

4.2 Experimental

4.2.1 Materials

All air- or moisture-sensitive compounds were handled under a nitrogen atmosphere in a glovebox, as indicated. Toluene used for polymerizations was purified by passage through activated alumina-based columns (Glass Contour, Laguna Beach, CA) followed by distillation from sodium. D-Lactide and L-lactide (Purac) were purified by recrystallization from toluene followed by repeated (2x) vacuum sublimation. Diethylene glycol (Sigma Aldrich) was distilled under reduced pressure from sodium. Molecular sieves (4 Å) were dried under vacuum at 180 °C for a minimum of 16 h. All other solvents and reagents were used as received from the commercial source indicated without further purification. All glassware used in polymerizations was treated with a solution of Me₂SiCl₂ (10% in CH₂Cl₂) and oven dried at 200 °C for a minimum of 3 h before use. All triblock copolymers were synthesized by the methods reported previously using D,L-lactide, D-lactide or L-lactide on a 4 gram scale.
4.2.2 Measurements

$^1$H and $^{13}$C NMR spectra were collected on a Varian INOVA-300, VXR-300 or Varian INOVA-500 spectrometer. Samples of the polymers were prepared by dissolving approximately 30 mg of polymer in 1 mL of CDCl$_3$ (Cambridge). Molecular weights ($M_n$ and $M_w$) and polydispersity indices ($M_w/M_n$) were determined by size exclusion chromatography (SEC) using polystyrene standards. Samples were analyzed at 40 °C using a Hewlett-Packard high-pressure liquid chromatograph equipped with three Jordi poly(divinylbenzene) columns of $10^4$, $10^3$, and 500 Å pore sizes and a HP1047A differential refractometer. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q1000 with nitrogen as the purge gas. An indium standard was used for calibration, and the scan rate was 10 °C/min. Samples weighing 3.0–8.0 mg were loaded into aluminum hermetic pans and the pans were sealed prior to measurement. Measurements for small angle x-ray scattering (SAXS) were performed at the Advanced Photon Source (APS) on beamline 5 ID-D, which is maintained by the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT). The x-ray source operated at a wavelength of 0.8856 Å with a sample to detector distance of 8552 mm calibrated with silver behenate. Temperature control was performed by electrical heating of the sample stage under ambient pressure in air. The flight tube was evacuated. Two-dimensional diffraction images were recorded using a Mar 165 mm CCD x-ray detector at a resolution of 2048 x 2048. The two-dimensional images were azimuthally integrated and reduced to the one-dimensional form of scattered intensity versus the spatial frequency $q$. All wide-
angle X-ray scattering (WAXS) measurements were performed using a Siemens D500 X-ray diffractometer with Cu K radiation. Tensile deformation experiments were carried out at room temperature using a Rheometrics Scientific Minimat instrument operated at a cross-head speed of 5 mm/min. The sample gage length was 5 mm, the gage width was 3 mm, and the gage thickness was 0.2 mm. Transmission Electron Microscopy (TEM) was performed with a JEOL 1210 instrument operating at 120 keV in the bright field mode located in the University of Minnesota Institute of Technology Characterization Facility. Samples were stained according to established procedures\textsuperscript{22} to obtain sufficient electron mass density contrast between the different blocks. Briefly, solvent-cast PLLA–PM–PLLA samples were cryo-microtomed at −120 °C on a Reichart ultramicrotome fitted with a Microstar diamond knife to create a flat surface. These specimens were then exposed to RuO\textsubscript{4} vapors for 4 h at room temperature. Stained thin sections (70-90 nm thickness) were then cryo-microtomed at −120 °C and collected on copper grids (Ted Pella) for subsequent TEM analysis.

4.2.3 Polymer Blending

All PLLA–PM–PLLA/PDLA–PM–PDLA blends were prepared using a solution blending method similar to the procedure used by Ikada et al.\textsuperscript{14} The respective triblock copolymers were dissolved separately in dichloromethane (1 g/dL) then admixed and rapidly stirred for 15 min. The solution was poured into an aluminum pan, covered by a beaker, and allowed to dry overnight. The product was further dried under reduced pressure for 18 h at about 80 °C to remove residual solvent.
4.3 Results and Discussion

4.3.1 Synthesis and Characterization of Triblock Copolymers

Polylactide–polymenthide–polylactide triblocks of various composition containing either atactic or isotactic polylactide blocks were successfully prepared in a two-step process as described previously (Scheme 4.1). The triblock copolymers listed in Table 4.1 are labeled according to the stereochemistry of the polylactide blocks followed by the number average molecular weights (determined by $^1$H NMR spectroscopy) of each block in kg mol$^{-1}$. All copolymers exhibited PDI values between 1.1 and 1.4, and the molecular weights and compositions were easily controlled by adjusting the monomer-to-initiator ratios used in the polymerizations. Efficient triblock formation was consistent with the shift of the SEC data relative to the respective PM homopolymer data. All triblocks were prepared on a multigram scale and were free of significant PM or PLA homopolymer as determined by SEC and $^1$H NMR spectroscopy. Samples of the triblock copolymers were dissolved in dichloromethane (1 g/dL), poured into an aluminum pan to dry overnight, and further dried under reduced pressure for 18 h at approximately 80 °C. All subsequent characterization and mechanical tests were performed on the solvent-casted films.

Differential scanning calorimetry was used to elucidate the microphase separation and evaluate the degree of crystallinity of the triblock copolymers (Table 4.2, Figure 4.1). Samples were cooled to –60 °C followed by heating at 10 °C min$^{-1}$ to 250 °C. The data for the first heating is shown in Figure 4.1. The data reveal a glass transition corresponding to PM ($T_g$) and either a broad, low intensity glass
Table 4.1 Molecular characterization of polylactide–polymenthide–polylactide triblock copolymers

<table>
<thead>
<tr>
<th>polymer</th>
<th>$M_n$ (NMR) (kg/mol)</th>
<th>% polylactide&lt;sup&gt;a&lt;/sup&gt; (NMR)</th>
<th>$M_n$ (SEC) (kg/mol)</th>
<th>PDI (SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-PM-PLA (7.6–33–7.6)</td>
<td>7.6–33.0–7.6</td>
<td>31.6</td>
<td>41.0</td>
<td>1.31</td>
</tr>
<tr>
<td>PLA-PM-PLA (12–32–12)</td>
<td>11.6–32.2–11.6</td>
<td>41.9</td>
<td>54.0</td>
<td>1.19</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (6.9–28–6.9)</td>
<td>6.9–27.5–6.9</td>
<td>33.5</td>
<td>85.1</td>
<td>1.16</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>6.8–27.5–6.8</td>
<td>33.3</td>
<td>76.4</td>
<td>1.21</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (11–33–11)</td>
<td>11.3–32.8–11.3</td>
<td>40.8</td>
<td>75.8</td>
<td>1.15</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>11.1–32.8–11.1</td>
<td>40.3</td>
<td>73.6</td>
<td>1.16</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (13–33–13)</td>
<td>12.9–33.1–12.9</td>
<td>43.8</td>
<td>65.5</td>
<td>1.20</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>15.4–33.1–15.4</td>
<td>48.2</td>
<td>68.3</td>
<td>1.23</td>
</tr>
</tbody>
</table>

<sup>a</sup> Mass percent polylactide calculated from $^1$H NMR spectroscopy.
Table 4.2 Morphological and thermal properties of polylactide–polymethylene–polylactide triblock copolymers

<table>
<thead>
<tr>
<th>polymer</th>
<th>( D^a ) (nm)</th>
<th>( T_{g, PM}^b ) (°C)</th>
<th>( T_{g, PLA}^b ) (°C)</th>
<th>( T_{m, PLA}^b ) (°C)</th>
<th>( \Delta H_f^b ) (J/g)</th>
<th>( X_{PLA}^c ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-PM-PLA (7.6–33–7.6)</td>
<td>22.3</td>
<td>–22</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLA-PM-PLA (12–32–12)</td>
<td>28.2</td>
<td>–24</td>
<td>51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLLA-PM-PLLA (6.9–28–6.9)</td>
<td>28.7</td>
<td>–21</td>
<td>53</td>
<td>143, 150</td>
<td>18</td>
<td>57</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>30.5</td>
<td>–21</td>
<td>52</td>
<td>149, 154</td>
<td>17</td>
<td>54</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (11–33–11)</td>
<td>32.1</td>
<td>–21</td>
<td></td>
<td>142, 151</td>
<td>21</td>
<td>54</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>34.0</td>
<td>–21</td>
<td></td>
<td>151, 160</td>
<td>18</td>
<td>49</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (13–33–13)</td>
<td>26.7</td>
<td>–20</td>
<td></td>
<td>162</td>
<td>24</td>
<td>59</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>28.6</td>
<td>–21</td>
<td></td>
<td>165</td>
<td>22</td>
<td>49</td>
</tr>
</tbody>
</table>

\( a \) Determined by SAXS from the primary reflection \((D = 2\pi/q^* )\) at 45 °C. \( b \) DSC program: cool at 100 °C min\(^{-1}\) to –60 °C, equilibrate, heat at 10 °C to min\(^{-1}\) 200 °C. The data were determined from the final heating ramp. \( c \) \( X_{PLA} \) = % crystallinity of the PLA blocks, calculated as described in ref. 23.

\( d \) not observed due to broadness
Figure 4.1 DSC analysis data for the semi-crystalline polylactide–PM–polylactide triblock copolymers. DSC program: cool from 40 °C at 100 °C min^{-1} to −60 °C, equilibrate, heat at 10 °C to min^{-1} 200 °C. The data were determined from the final heating ramp.
transition \( T_{g,PLA} \) or a melting endotherm \( T_{m,PLA} \) or both depending on the nature of the polylactide end blocks (Table 4.2). Similar to previous findings\(^{11}\), the \( T_{g,PM} \) values are relatively invariant (ca. \(-21^\circ C\)), while the \( T_{g,PLA} \) values increase with increasing molecular weight of the polylactide block. Overall, the results are consistent with phase separation into distinct polylactide and PM rich domains, which is essential for achieving TPE behavior. The shape of and area under the endothermic \( T_{m,PLA} \) peak for the semi-crystalline triblock copolymers varied as a function of the molecular weight of the PLLA or PDLA segments (Figure 4.1), with increasing molecular weights corresponding to both higher melting temperatures and heats of fusion. From the latter we calculated degrees of crystallinity for the PLLA or PDLA segments between 49 and 59\%.\(^{23}\) As expected, similar melting behavior was observed for the triblock copolymers of similar molecular weights containing enantiomerically pure PLLA or PDLA blocks.\(^{24}\)

Bimodal melting endotherms were observed for the triblock copolymers PLLA-PM-PLLA (6.9–28–6.9), PDLA-PM-PDLA (6.8–28–6.8), PLLA-PM-PLLA (11–33–11), and PDLA-PM-PDLA (11–33–11). This behavior may be due to the presence of multiple crystal forms or to fractionated crystallization of the polylactide microdomains.\(^{25,26}\) PLA homopolymer (PLLA or PDLA) is known to form four kinds of crystal structures, and the structure(s) that form is(are) dependent on the crystallization temperature and molecular weight.\(^{27}\) The bimodal peaks observed in Figure 4.1 may be attributed to the presence of multiple PLLA or PDLA crystalline structures. Specifically, we hypothesize that the bimodal peaks are due to fractionated
crystallization of the microdomains.\textsuperscript{26} The microstructuring of block copolymers containing one or more crystallizable components is due to either crystallization of one block and expulsion of the other block from the crystalline structure or microphase separation due to chemical incompatibility between the two blocks. When the microstructure adopted by a block copolymer is due solely to crystallization of one block, the crystallizable component can be subdivided into microdomains, whose number is much larger than the number of usually active heterogeneities.\textsuperscript{28} Thus, several fractions are evident with broadly distributed crystallite sizes, resulting in the observation of multiple endotherms in the DSC thermograms. This phenomenon is seen in Figure 4.1 for samples PLLA-PM-PLLA (6.9–28–6.9), PDLA-PM-PDLA (6.8–28–6.8), PLLA-PM-PLLA (11–33–11), and PDLA-PM-PDLA (11–33–11). The thermograms for the higher molecular weight triblock copolymers, PLLA-PM-PLLA (13–33–13) and PDLA-PM-PDLA (15–33–15), do not exhibit this characteristic. The multiple melting endotherms for the lower molecular weight samples is likely due to a fractionated crystallization of the semicrystalline polylactide domains during solvent evaporation during preparation of the films. New samples were heated to 180 °C to ensure no degradation took place followed by cooling to −60 °C and heating again to 200 °C. Multiple endotherms were observed upon the second heating (Figure 4.2), indicating that fractionated crystallization of the semicrystalline polylactide domains also occurred during cooling of the samples.
Figure 4.2 DSC analysis data for the semi-crystalline polylactide–PM–polylactide triblock copolymers. DSC program: cool from 40 °C at 100 °C min\(^{-1}\) to −60 °C, equilibrate, heat at 10 °C min\(^{-1}\) to 200 °C, cool at 10 °C to −60 °C, equilibrate, heat at 10 °C min\(^{-1}\) to 200 °C. The data were determined from the final heating ramp.
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SAXS was used to determine the ordered morphology of the triblock copolymer films (Table 4.2, Figure 4.3). In the melt at 180 °C (above the melting transition of the semicrystalline polylactide), SAXS patterns for PLLA-PM-PLLA (6.9–28–6.9), PDLA-PM-PDLA (6.8–28–6.8), and PDLA-PM-PDLA (11–33–11) display a broad principal reflection, $q^*$, followed by broad oscillations consistent with a disordered state (Figure 4.3a). Cooling these samples from the melt leads to crystallization induced phase separation, consistent with the bimodal peaks observed in the DSC thermograms upon second heating. The samples PLLA-PM-PLLA (11–33–11), PLLA-PM-PLLA (13–33–13), and PDLA-PM-PDLA (15–33–15) exhibit a principal reflection, $q^*$, followed by several higher-order reflections, consistent with hexagonally packed cylinders of PLLA in a matrix of PM for sample PLLA-PM-PLLA (11–33–11) and a gyroid morphology for sample PLLA-PM-PLLA (13–33–13). For the triblock PDLA-PM-PDLA (15–33–15), the data indicated the coexistence of lamellae of PDLA and PM with domain spacing of 27.4 nm and hexagonally packed cylinders of PDLA in a matrix of PM with a domain spacing of 28.7 nm (Figure 4.3a). According to the self-consistent field theory for ABA triblock copolymers of around 40% A block, the $\chi N$ (where $\chi$ is the interaction parameter and $N$ is the number of segments) at the order-disorder transition is 18. We estimated $N$ to be 507 segments based on a reference volume of 108 Å³, giving us a $\chi$ value of 0.036 at the order-disorder transition. Thus, at 180 °C our system is ordered and $\chi$ is greater than 0.036.
Figure 4.3 SAXS patterns of the semicrystalline triblock copolymers at a) 180 °C and b) 45 °C
SAXS analysis was also performed on the as-cast triblock copolymers at 45 °C. SAXS patterns of PLLA-PM-PLLA (6.9–28–6.9), PDLA-PM-PDLA (6.8–28–6.8), PLLA-PM-PLLA (11–33–11), and PDLA-PM-PDLA (11–33–11) exhibit a broad reflection followed by weak oscillations in intensity consistent with a disordered state (Figure 4.3b). The SAXS pattern for PLLA-PM-PLLA (13–33–13) at 45 °C displays a reflection at 0.24 nm\(^{-1}\) with a slight shoulder. The large reflection and shoulder correspond to the principal peak and higher-order reflection of the gyroid morphology with a domain spacing of 26.7 nm. The small peak around 0.14 nm\(^{-1}\) may be due to the presence of semi-crystalline domains of PLLA that contain alternating lamellae of crystalline and amorphous regions and exhibit relatively large domain spacing. Upon heating this sample above the \(T_m\), the peak at 0.14 nm\(^{-1}\) disappears (Figure 4.3a). For the triblock PDLA-PM-PDLA (15–33–15), the SAXS pattern at 45 °C is broad and difficult to interpret. In general, the domain spacing increases with increasing PLLA and PDLA molecular weight in the semi-crystalline triblock copolymers PLLA-PM-PLLA (6.9–28–6.9), PDLA-PM-PDLA (6.8–28–6.8), PLLA-PM-PLLA (11–33–11), and PDLA-PM-PDLA (11–33–11), with a slight decrease in the domain spacing with increasing PLLA and PDLA molecular weight in the cases of PLLA-PM-PLLA (13–33–13) and PDLA-PM-PDLA (15–33–15). We are not certain as to why this decrease in domain spacing occurs.

Figure 4.4 shows representative TEM images that illustrate the microphase-separated morphology of PLLA-PM-PLLA (11–33–11). The polymer sample used in the TEM experiment was prepared by dissolving the polymer in dichloromethane and
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Figure 4.4 Representative TEM images of PLLA-PM-PLLA (11–33–11) (a and b), and a schematic representation of the point of view of the images (c)
allowing two weeks for the solvent to evaporate. The sample was cryo-microtomed at
–120 °C then stained with RuO$_4$ for TEM analysis. The TEM images of PLLA-PM-
PLLA (11–33–11) show crystalline PLLA domains surrounded by the preferentially
stained amorphous regions containing PM and amorphous fractions of PLA (Figure
4.4). The images exhibit regions of order corresponding to either lamellar or
cylindrical morphology. Approximately half of the TEM images obtained displayed
smaller domain spacings (Figure 4.4a) and the other half displayed larger domain
 spacings (Figure 4.4b). On the basis of these images, we calculate an average domain
spacing in Figure 4.4a of 17 nm and an average domain spacing in Figure 4.4b of 28
nm. The second value correlates with the domain spacing calculated from SAXS at 45
°C of 32.1 nm (see Table 4.2). Because the domain spacing of 17 nm is related to the
spacing of 28 nm by a factor of $\sqrt{3}/2$, we hypothesize that the two images represent the
different spacing corresponding to a cylindrical morphology (see Figure 4.4c). 31 Taken
together, the evidence suggests that PLLA-PM-PLLA (11–33–11) consists of
cylinders of PLLA in a matrix of PM.

4.3.2 Mechanical Properties of Triblock Copolymers

Mechanical testing for all triblock copolymers was performed on “dog-bone”
tensile bars originating from solvent-cast films. The mechanical properties of the
triblock copolymers are summarized in Table 4.3, with representative stress–strain
plots for the triblock copolymers pulled to ultimate tensile failure shown in Figure 4.5.
We previously determined a Young’s modulus of 1.4 ± 0.3 MPa, an ultimate tensile
Table 4.3 Mechanical properties of polylactide–polymenthide–polylactide triblock copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>% PLA&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Young’s modulus $E$ (MPa)</th>
<th>tensile strength $\sigma_B$ (MPa)</th>
<th>strain at break $\varepsilon_B$ (%)</th>
<th>residual strain&lt;sup&gt;a&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-PM-PLA (7.6–33–7.6)</td>
<td>32</td>
<td>0.8 ± 0.1</td>
<td>3.8 ± 0.2</td>
<td>872 ± 6</td>
<td>1.1</td>
</tr>
<tr>
<td>PLA-PM-PLA (12–32–12)</td>
<td>42</td>
<td>2.4 ± 0.2</td>
<td>3.7 ± 0.7</td>
<td>530 ± 58</td>
<td>3.0</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (6.9–28–6.9)</td>
<td>34</td>
<td>1.5 ± 0.1</td>
<td>13.6 ± 1.4</td>
<td>900 ± 76</td>
<td>2.0</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>33</td>
<td>1.6 ± 0.3</td>
<td>12.6 ± 0.4</td>
<td>849 ± 40</td>
<td>2.1</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (11–33–11)</td>
<td>41</td>
<td>5.4 ± 0.9</td>
<td>15.2 ± 0.2</td>
<td>703 ± 111</td>
<td>3.6</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>40</td>
<td>3.9 ± 0.6</td>
<td>12.3 ± 0.5</td>
<td>667 ± 65</td>
<td>4.1</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (13–33–13)</td>
<td>44</td>
<td>26.8 ± 2.1</td>
<td>19.5 ± 1.1</td>
<td>765 ± 40</td>
<td>10.1</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>48</td>
<td>25.0 ± 3.8</td>
<td>18.7 ± 0.6</td>
<td>731 ± 98</td>
<td>8.8</td>
</tr>
</tbody>
</table>

<sup>a</sup> Residual strain after 20 consecutive cycles of loading to 50% and unloading to 0%.
Chapter 4: Consequences of Stereochemistry on the Properties of PLA–PM–PLA

![Graph a)](image1)

- PLA-PM-PLA (7.6–33–7.6)
- PLLA-PM-PLLA (6.9–28–6.9)
- PDLA-PM-PDLA (6.8–28–6.8)

![Graph b)](image2)

- PLA-PM-PLA (12–32–12)
- PLLA-PM-PLLA (11–33–11)
- PDLA-PM-PDLA (11–33–11)
Figure 4.5 Representative stress–strain curves for the polylactide-polymethylene-polylactide triblocks
Chapter 4: Consequences of Stereochemistry on the Properties of PLA–PM–PLA

strength of 1.7 ± 0.1 MPa, and an elongation of 960 ± 60% for an amorphous PLA-PM-PLA (7.8–29–7.8) triblock. We prepared a comparable sample PLA-PM-PLA (7.6–33–7.6), and solvent cast samples of this material gave similar mechanical properties. Increasing the PLA weight fraction to 42% in PLA-PM-PLA (12–33–12) results in a three-fold increase in the Young’s modulus, a similar ultimate tensile strength, and a somewhat reduced strain at break (Table 4.3).

Next, we examined the effects on the mechanical properties of the triblock copolymers when substituting isotactic polylactide blocks for the atactic analogs. Zhang et al. observed 20–30 fold increases in Young’s Modulus and ultimate tensile strength and lower strains at break when substituting semicrystalline PLLA blocks for amorphous PLA blocks in PLA–poly(trimethylene carbonate)–PLA triblock copolymers. This significant change in mechanical behavior was attributed to enhanced phase separation and more extensive physical cross-linking in the case of semi-crystalline block copolymers. Figure 4.5a compares the stress–strain curves for the amorphous and semi-crystalline triblock copolymers that have a PLA weight fraction ≈ 30%. The semi-crystalline triblock copolymers exhibited a linear response at low strain followed by yielding and strain-hardening before breaking. The data in Figure 4.5a reveal a three-fold increase in tensile strength and a two-fold increase in Young’s modulus upon replacement of the atactic PLA blocks with PLLA or PDLA segments of similar size (Table 4.3). A similar increase in mechanical properties relative to the amorphous triblocks is evident in the data for the set having a polylactide weight fraction ≈ 40% (Figure 4.5b). These results are attributed to more
extensive physical cross-linking in the semi-crystalline polylactide phase of the semi-crystalline block copolymers compared to the amorphous analogs, which stems from the stronger inherent interaction between chains having identical stereochemical configuration.\(^1^9\)

Further changes in mechanical strength occurred upon increasing the molecular weight of the semi-crystalline blocks. The Young’s moduli of the semicrystalline PLLA-PM-PLLA (11–33–11) and PDLA-PM-PDLA (11–33–11) samples are approximately four-fold greater than the PLLA-PM-PLLA (6.9–28–6.9) and PDLA-PM-PDLA (6.8–28–6.8) triblocks. The ultimate tensile strengths were essentially invariant, and the strain at break for the higher molecular weight materials was moderately reduced (Table 4.3). The relationship between molecular weight, microstructure, and mechanical properties of semicrystalline–rubbery–semicrystalline triblock copolymers was investigated by Koo et al.\(^3^2\) As noted previously, block copolymers containing crystallizable components undergo either crystallization-induced phase separation from the melt upon cooling (or from a solution upon concentration) or melt microphase separation due to the incompatibility between the two blocks followed by crystallization of one of the components within the domains dictated by the melt-segregated structure upon cooling (or concentration). By controlling the molecular weight of model triblock polymers, Koo et al. observed low tensile strengths for samples that underwent crystallization-induced phase segregation and high tensile strengths for samples that were microphase separated prior to crystallization.\(^3^2\) Notably, we observed a significant increase in mechanical strength
for PLLA-PM-PLLA (13–33–13) and PDLA-PM-PDLA (15–33–15) relative to their 11–33–11 and 7–28–7 congeners. This increase in mechanical properties may be attributed to a transition from crystallization-induced phase segregation to phase separation due to incompatible blocks as evidenced by DSC and SAXS.

We investigated the recovery or “true elasticity” of the triblock copolymers by subjecting the samples to consecutive cycles of loading and unloading at a strain of 50%. The level of recovery after every cycle was measured by observing the residual strain after a sample was unloaded. Figure 4.6 shows the stress–strain behavior for cycles 1, 2, 4, 8, and 20 of PLLA-PM-PLLA (13–33–13). The residual strain for cycles 8 and 20 are nearly identical, suggesting that the triblock copolymer reaches a truly elastic state after about 7 cycles (Table 4.3). The yielding behavior in the first few cycles is supplanted by behavior reminiscent of traditional thermoplastic elastomers. All of the semi-crystalline triblock copolymers display identical stress–strain behavior after 6–9 cycles (versus only three cycles for the amorphous triblock copolymers). The residual strain after twenty cycles for all of the triblock copolymers is given in Table 4.3, and is slightly higher for the semi-crystalline block copolymers compared to their amorphous counterparts due to some plastic deformation that occurs at low strain.

4.3.3 Preparation and Characterization of Copolymer Blends

With the aim of inducing enantiomerically pure polylactide segments to self-assemble into stereocomplex crystallites, solutions of PLLA-PM-PLLA and PDLA-
**Figure 4.6** Loading and unloading cycles 1, 2, 4, 8, and 20 for PLLA-PM-PLLA (13–33–13) pulled to 50% with no delay between cycles
PM-PDLA of similar molecular weight were mixed in 50:50 or 95:5 (wt%) ratios and cast into films. Wide angle X-ray scattering (WAXS) was used to confirm the presence of stereocomplex crystallites (Figure 4.7). The diffraction peaks corresponding solely to stereocomplex crystallites (2θ at 12, 21, and 24°), as opposed to those characteristic of homo-crystallites (2θ at 17, 19, and 23°) were observed for all of the 50:50 blends, whereas diffraction peaks corresponding to both types of crystallites were seen in the 95:5 blends.

DSC was used to assess the thermal properties of the blends (Table 4.4, Figure 4.8). Similar to the pure triblock copolymers, the glass transitions corresponding to the PM blocks were relatively invariant (between –21 and –18 °C), while the thermal signatures associated with the \( T_g \) values corresponding to the polylactide blocks were weak and could not be ascertained for most of the blends (likely due to the intense melting endotherms). The endothermic peaks observed close to 160 and 220 °C (Figure 4.8) are assigned to melting of PLLA homo-crystallites and PLLA/PDLA stereocomplex crystallites, respectively. The relative intensity ratios of these peaks depends on the enantiomeric ratio of the blended copolymers; the high temperature feature associated with stereocomplex crystallites is the only peak seen for the 50:50 blends, whereas that associated with homocrystallites is dominant for the 95:5 blends, with the stereocomplex feature nonetheless evident. The extent of crystallinity attributed to the 50:50 blends were calculated from the heats of formation of the stereocomplex and fall between 40 and 48%. The percent crystallinity of the stereocomplex in the 95:5 blends was 21% for 95 PLLA-PM-PLLA (11–33–11) + 5
Figure 4.7 X-ray diffraction patterns of (a) PLLA-PM-PLLA (13–33–13), (b) 50:50 (13–33–13), and (c) 95:5 (13–33–13)
Figure 4.8 DSC analysis data for the copolymer blends. DSC program: cool at 100 °C min\(^{-1}\) to –60 °C, equilibrate, heat at 10 °C to min\(^{-1}\) 250 °C. The data were determined from the final heating ramp.
PDLA-PM-PDLA (11–33–11) and 50% for 95 PLLA-PM-PLLA (13–33–13) + 5 PDLA-PM-PDLA (15–33–15). In these asymmetric blends, we anticipated that the stereocomplexes would induce increased nucleation of PLLA homocrystallites compared to the pristine analog, and thus result in a higher fraction of homocrystallite crystallinity, as seen in asymmetric homoPLLA/homoPDLA blends.\(^{34}\) However, we did not observe a significant change in the percent crystallinities for the homocrystallites in the asymmetric blends as compared to the non-blended samples.

**Table 4.4** Thermal properties of blends of PLLA-PM-PLLA and PDLA-PM-PDLA

<table>
<thead>
<tr>
<th>polymer blend</th>
<th>(T_{m, \text{PLA}}^{a}) (^{\circ}\text{C})</th>
<th>(T_{m, \text{stereo}}^{a}) (^{\circ}\text{C})</th>
<th>(\Delta H_f^{a}) (J/g)</th>
<th>(X_{\text{PLA}}^{b}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA-PM-PLLA (6.9–28–6.9) + PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>213</td>
<td>25</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>PLLA-PM-PLLA (11–33–11) + PDLA-PM-PDLA (11–33–11)</td>
<td>209, 221</td>
<td>25</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>PLLA-PM-PLLA (13–33–13) + PDLA-PM-PDLA (15–33–15)</td>
<td>214, 227</td>
<td>33</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>95 PLLA-PM-PLLA (11–33–11) + 5 PDLA-PM-PDLA (11–33–11)</td>
<td>142, 153</td>
<td>205</td>
<td>19 / 1(^c)</td>
<td>51 / 21(^c)</td>
</tr>
<tr>
<td>95 PLLA-PM-PLLA (13–33–13) + 5 PDLA-PM-PDLA (15–33–15)</td>
<td>162</td>
<td>211</td>
<td>22 / 3(^c)</td>
<td>55 / 50(^c)</td>
</tr>
</tbody>
</table>

\(a\) DSC program: cool at 100 \(^\circ\text{C}\) min\(^{-1}\) to \(-60\) \(^\circ\text{C}\), equilibrate, heat at 10 \(^\circ\text{C}\) to min\(^{-1}\) 250 \(^\circ\text{C}\). The data were determined from the final heating ramp. \(b\) \(X_{\text{PLA}} = \%\) crystallinity of the PLA blocks, calculated as described in ref. 23. \(c\) Values represent: \(\Delta H_f, \text{PLLA} / \Delta H_f, \text{stereocomplex}\) or \(X_{\text{PLA}} / X_{\text{stereocomplex}}\).
4.3.4 Mechanical Properties of Copolymer Blends.

The results of tensile testing of the PLLA-PM-PLLA and PDLA-PM-PDLA copolymer blends are summarized in Table 4.5, and plots of the tensile properties versus the percent PLA are provided in Figure 4.9. Overall, the stress–strain curves for the blends were similar in form to those of the semi-crystalline triblock copolymers. In the 50:50 blends, as the molecular weight of the polylactide block increased, we observe a linear increase in both the Young’s modulus and the strain at break. Relative to the pure semi-crystalline TPEs, PLLA-PM-PLLA (6.9–28–6.9) and PDLA-PM-PDLA (6.8–28–6.8), as well as PLLA-PM-PLLA (11–33–11) and PDLA-PM-PDLA (11–33–11), the blends PLLA-PM-PLLA (6.9–28–6.9) + PDLA-PM-PDLA (6.8–28–6.8) and PLLA-PM-PLLA (11–33–11) + PDLA-PM-PDLA (11–33–11) exhibit fourfold increases in the Young’s moduli. An increase in Young’s modulus of about 40% was observed for the PLLA-PM-PLLA (13–33–13) + PDLA-PM-PDLA (15–33–15) samples compared to either PDLA-PM-PDLA (15–33–15) or PLLA-PM-PLLA (13–33–13). This relationship between the molecular weight of the polylactide block and the Young’s modulus is similar to the behavior reported previously for homopolylactide stereocomplexes of similar molecular weight.\textsuperscript{14} The strain at break values for the 50:50 blends were similar to those of the parent samples at lower molecular weights and were slightly higher at increasing molecular weights, as seen previously for other systems.\textsuperscript{14,20} We then investigated the elasticity of the 50:50 blends and found that after about seven cycles of consecutive loading and unloading from 50% to 0% the blends reached an elastic-like state. The residual strains for the
### Table 4.5 Mechanical properties of PLLA-PM-PLLA/PDLA-PM-PDLA blends

<table>
<thead>
<tr>
<th>Polymer Blend</th>
<th>Young’s modulus $E$ ± sd (MPa)</th>
<th>Tensile strength $\sigma_B$ ± sd (MPa)</th>
<th>Strain at break $\varepsilon_B$ ± sd (%)</th>
<th>Residual strain$^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA-PM-PLLA (6.9–28–6.9) + PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>5.6 ± 1.3</td>
<td>11.1 ± 0.5</td>
<td>754 ± 52</td>
<td>2.7</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (11–33–11) + PDLA-PM-PDLA (11–33–11)</td>
<td>17.7 ± 2.8</td>
<td>14.0 ± 0.3</td>
<td>681 ± 17</td>
<td>4.5</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (13–33–13) + PDLA-PM-PDLA (15–33–15)</td>
<td>36.5 ± 2.4</td>
<td>17.8 ± 0.7</td>
<td>994 ± 43</td>
<td>10.0</td>
</tr>
<tr>
<td>95 PLLA-PM-PLLA (11–33–11) + 5 PDLA-PM-PDLA (11–33–11)</td>
<td>8.7 ± 0.6</td>
<td>13.8 ± 0.2</td>
<td>740 ± 50</td>
<td>4.3</td>
</tr>
<tr>
<td>95 PLLA-PM-PLLA (13–33–13) + 5 PDLA-PM-PDLA (15–33–15)</td>
<td>29.2 ± 2.9</td>
<td>21.8 ± 0.8</td>
<td>990 ± 62</td>
<td>9.8</td>
</tr>
</tbody>
</table>

$^a$ Residual strain after 20 consecutive cycles of loading to 50% and unloading to 0%.
Figure 4.9 Mechanical properties vs. % PLA for the triblock copolymers and their blends
50:50 blends (Table 4.5) are slightly higher than the semi-crystalline block copolymers of similar composition (Table 4.3), which is most likely due to the larger Young’s modulus observed in the blends.

The 95:5 blends, having only a small fraction of stereocomplex crystallites present, exhibited an increase in Young’s moduli compared to their parent materials relative to their semi-crystalline TPE components, illustrating the effectiveness of the stereocomplex at increasing the Young’s modulus of these thermoplastic elastomers even though the overall level of crystallinity for the PLLA phase was about the same ($X_{\text{PLLA}} = 54\%$ for PLLA-PM-PLLA (11–33–11) and $X_{\text{PLLA}} = 51\%$ for the 95:5 blend). Interestingly, the strains at break for the 95:5 blends were nearly identical to the 50:50 blends. The elasticity behavior of the asymmetric blends was similar to the behavior seen for the symmetric blends (Table 4.5).

Finally, we note the outstanding strength and similar elasticity of the PLLA-PM-PLLA (13–33–13) + PDLA-PM-PDLA (15–33–15) copolymer blend relative to the amorphous PLA-PM-PLA copolymers.\textsuperscript{11} Increasing the molecular weight of the amorphous triblocks (i.e., (PLA-PM-PLA (12–32–12)) leads to somewhat improved properties compared to those reported earlier,\textsuperscript{11} but the properties are still far behind commercially relevant samples.\textsuperscript{10} A key finding of this study is that the mechanical properties of the PLA–PM–PLA triblock copolymers are greatly improved upon substitution of the amorphous PLA blocks with semi-crystalline PLLA (PDLA) blocks. Lastly, with enatiomeric blending we can achieve moduli of about 30 MPa, tensile strengths of about 20 MPa and ultimate elongations of about 1000%. These
results compare very favorably to commercially relevant samples\textsuperscript{10} and represents a tremendous improvement over the amorphous samples.

4.4 Summary

We prepared and analyzed a series polylactide–polymethide–polylactide thermoplastic elastomers of varying compositions, tacticities and morphologies. Thermal and morphological characterization was conducted to determine the purity, crystallinity, and morphology of the triblock copolymers. Tensile measurements of the all biorenewable triblock copolymers demonstrated elongations and elastomeric properties characteristic of TPEs. The semi-crystalline PLLA–PM–PLLA and PDLA–PM–PDLA triblock copolymers exhibited enhanced physical cross-linking of the semi-crystalline polylactide blocks over their amorphous counterparts. The noteworthy performance of the PLLA-PM-PLLA (13–33–13) and PDLA-PM-PDLA (15–33–15) samples (Young’s moduli of ca. 25 MPa, ultimate tensile strengths of about 20 MPa, and elongations of around 750%) may be attributed to microphase separation preceding crystallization. All of the copolymers exhibited highly elastic behavior. Blends of the enantiomeric triblock copolymers were obtained in order to further enhance physical cross-linking through self-assembly of the enantiomeric polylactide segments. WAXS and DSC results confirmed the presence of stereocomplexes in the blends. These thermoplastic elastomer blends combined remarkable stiffness (Young’s modulus up to 37 MPa), strength (up to 21 MPa) and enhanced extendability (elongations up to 1000%) over their amorphous and semicrystalline counterparts. The
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95:5 blends, having only a small fraction of stereocomplex crystallites present, exhibited impressive increases in Young’s moduli by over 60%. These biorenewable materials combine the well-known ABA TPE architecture with stereocomplex formation between enantiomeric polylactides to demonstrate the superior tensile properties of fully biorenewable self-assembled thermoplastic elastomers.

4.5 Acknowledgments

We thank the donors of the American Chemical Society Petroleum Research fund (grant 45891-AC7) and Cargill, Inc. for financial support. Portions of this work were performed in the Institute of Technology Characterization Facility, University of Minnesota, which receives partial support from NSF through the NNIN program. We also acknowledge Purac for the generous donation of D-lactide.

4.6 References

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2005, 6, 2843–2850.

875.


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(23) Calculated from $[\Delta H_{f}(\text{measured})/\Delta H_{f}(\text{PDLA or PLLA})]^{*}1/(f_{w}^{\text{PLA}})$, where

$\Delta H_{f}(\text{measured}) = \text{area under melting endotherm, } \Delta H_{f}(\text{PDLA or PLLA}) = 99 \text{ J/g (from ref. 22a), and } f_{w}^{\text{PLA}} = \text{weight fraction of PLA in the copolymer. For the stereocomplexes (Table 4), } \Delta H_{f}(\text{PDLA/PLL}) = 155 \text{ J/g. For the 95:5 blends, } f_{w}^{\text{PLL}} = \text{PLL} \text{ wt fraction x 0.9 and } f_{w}^{\text{stereocomplex}} = \text{PLL} \text{ wt fraction x 0.1 (a)}$


(24) We ascribe the slightly lower crystallinity for the PDLA copolymers to the presence of a minor contaminant in the D-LA feedstock.


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(30) Calculated from \( N = \frac{M_W}{\rho_{PLA} \cdot \upsilon_{ref}} \), where the molecular weight of the triblock copolymer (MW) is 63,000 g/mol, the density of PLA at 140 °C (\( \rho_{PLA} \)) is 1.15 g/mL, and the reference volume (\( \upsilon_{ref} \)) is 108 Å³.


5

Poly(D-lactide)–Polymenthide–Poly(D-lactide) Triblock Copolymers as Nucleating Agents for PLLA

5.1 Introduction

As discussed in previous chapters, polylactide can be synthesized using D,L-lactide, L-lactide or D-lactide. The polymers that result from the polymerization of L-lactide or D-lactide, poly(L-lactide) (PLLA) or poly(D-lactide) (PDLA), are both isotactic and semi-crystalline with identical properties. Blending PLLA and PDLA results in co-crystallization to form stereocomplex crystalites with thermal properties distinct from PLLA and PDLA. As discussed in Chapter 4, the stereocomplex crystals have a melting temperature of approximately 230 °C, 50 °C higher than the $T_m$ of the PLLA or PDLA components. The higher melting temperature is attributed to strong van der Waals interactions that cause a specific energetic interaction-driven packing. Ikada and Tsuji et al. were the first to report the formation of the polylactide stereocomplex, and have investigated the influence of the blending ratio of the two isomeric polymers, the molecular weight of the isomeric polymers, the optical purity of the isomeric polymers, and the blending mode of the polymers on the formation and properties of the stereocomplex. More recently, efforts have focused
on the mechanism of formation,\textsuperscript{11} spherulite growth,\textsuperscript{12,13} and crystal density\textsuperscript{12,14} of stereocomplex crystallites. Brochu et al. found that PLLA crystallization takes place epitaxially on PLLA/PDLA stereocomplex crystallites when the content of PDLA was as low as 10 wt\%.\textsuperscript{15} In other words, stereocomplex crystallites can act as nucleation sites for PLLA. Pure PLLA is slow to crystallize and nucleating agents are required in order to make use of industrially relevant processing techniques.\textsuperscript{16} Common PLLA nucleating agents such as talc\textsuperscript{16} and clay\textsuperscript{17} increase the rate of crystallization, but have been known to reduce the toughness in some systems.\textsuperscript{18}

The ability of PDLA/PLLA stereocomplex crystallites to nucleate the crystallization of PLLA has been studied.\textsuperscript{15-24} Schmidt and Hillmyer\textsuperscript{19} and Yamane and Sasai\textsuperscript{21} confirmed that the addition of homoPDLA is effective in increasing the number of PLLA spherulites in a PLLA sample, which results in an increase in the overall crystallization rate. Schmidt and Hillmyer observed significant changes in the crystallization rate of PLLA when only 0.5 wt\% of PDLA was present,\textsuperscript{19} and found that the nucleation efficiency was the highest when PDLA of moderate molecular weight (15 kg mol\textsuperscript{-1}) was added.\textsuperscript{20} Tsuji et al. noted the formation of stereocomplex crystallites in melt-quenched PLLA,\textsuperscript{22} indicating that in the melt of an asymmetric blend of PLLA and PDLA (190 °C) a dispersion of PLLA/PDLA stereocomplex crystallites within the PLLA matrix are present. Anderson and Hillmyer investigated the nucleation efficiencies of polylactide stereocomplex crystallites prepared in the melt.\textsuperscript{23} Nucleation efficiencies near 100\% and fast crystallization kinetics in isothermal crystallization experiments at 140 °C were observed.\textsuperscript{23}
Chapter 5: PDLA–PM–PDLA Copolymers as Nucleating Agents for PLLA

We hypothesize that melt blending (190 °C) a small wt% of PDLA–PM–PDLA block copolymers with homoPLLA will result in the formation of stereocomplex crystallites at the corona of PDLA–PM–PDLA micelles, and cooling will lead to nucleation of the PLLA matrix by the stereocomplex crystallite corona (see Figure 5.1). In Chapter 4, symmetric enantiomeric blends of PLA–PM–PLA triblock copolymers formed racemic crystallites, or stereocomplexes. The formation of the stereocomplex was preferred relative to homopolymer crystallization as demonstrated by the formation of racemic crystallites in asymmetric blends containing only 5% PDLA–PM–PDLA (see Chapter 4). Schmidt has demonstrated that polyisoprene–PLLA diblock copolymers can form spherical micelles in a melt of PLLA with core radii of approximately 12-14 nm and micelle densities of about 10^{15} micelles cm^{-3}. Because of the size and number densities of block copolymer micelles at low concentrations, PDLA block copolymer micelles could dramatically enhance the crystallization of PLLA.

In this chapter we explore the ability of the PDLA–PM–PDLA triblock copolymers to act as nucleating agents for PLLA. First, we evaluated the ability of the triblocks to form micelles when mixed with atactic PLA through SAXS analysis. The nucleation efficiency of the stereocomplexed micelles was assessed using a nucleating efficiency scale that allows for the quantitative evaluation of nucleating agents. In addition, isothermal crystallization experiments were performed at 140 °C to determine the ability of the all-biorenewable stereocomplexed block copolymer micelles to increase the crystallization rate of PLLA. Quantifiable
Figure 5.1 Schematic representation of the nucleation of PLLA using PDLA–PM–PDLA micelles
improvements in nucleation efficiency were observed when blending PLLA with PDLA-containing triblock copolymers as compared to PDLA homopolymers. This new approach to the nucleation of PLLA with all-biorenewable PDLA block copolymers increases the nucleation efficiency while decreasing the amount of nucleating agent required to obtain these high efficiencies. Finally, the tensile properties of the blends were investigated.

5.2 Experimental Section

5.2.1 Materials

All air- or moisture-sensitive compounds were handled under a nitrogen atmosphere in a glovebox, as indicated. Toluene used for polymerizations was purified by passing through activated alumina-based columns (Glass Contour, Laguna Beach, CA) followed by distillation from sodium. D-Lactide and L-Lactide (Purac) was purified by recrystallization from toluene followed by repeated (2x) vacuum sublimation. D,L-Lactide (Purac) was purified by recrystallization. Diethylene glycol (Sigma Aldrich) was distilled under reduced pressure from sodium. Molecular sieves (4 Å) were dried under vacuum at 180 °C for a minimum of 16 hours. All other solvents and reagents were used as received from the commercial source indicated without further purification. All triblock copolymers were synthesized by the methods reported previously (see Chapter 2).\textsuperscript{25} Commercial grade poly(L-lactide) was supplied by Toyota Motor Corporation.
5.2.2 Measurements

$^1$H and $^{13}$C NMR spectra were collected on a Varian INOVA-300, VXR-300 or Varian INOVA-500 spectrometer. Samples of the polymers were prepared by dissolving approximately 30 mg of polymer in 1 mL of CDCl$_3$ (Cambridge). Molecular weights ($M_n$ and $M_w$) and polydispersity indices ($M_w/M_n$) were determined by size exclusion chromatography (SEC) using polystyrene standards. Samples were analyzed at 40 °C using a Hewlett-Packard high-pressure liquid chromatograph equipped with three Jordi poly(divinylbenzene) columns of $10^4$, $10^3$, and 500 Å pore sizes and a HP1047A differential refractometer. Tensile deformation experiments were carried out at room temperature using a Rheometrics Scientific Minimat instrument operated at a cross-head speed of 5 mm/min. The sample gage length was 5 mm, the gage width was 3 mm, and the gage thickness was 1 mm.

5.2.3 Blend Preparation

Prior to blending, the PLLA pellets and the triblock copolymer were manually pre-mixed in the desired compositions in a vial. Melt blending was performed in a Haaka Rheomix 600 batch mixer. The pre-mixed material was added to the chamber of the mixer, which was heated to 190 °C (under a constant stream of nitrogen gas) with the blades rotating at a speed of 100 rpm. Once all of the material was in the chamber, the plunger was lowered to enclose the chamber. After 15 min the blades were stopped and the blends were obtained through a channel die and removed from
the chamber using a spatula. The hot blend was placed in a vial and allowed to cool to room temperature on the bench top.

5.2.4 Preparation of PLA/PDLA–PM–PDLA and SAXS Analysis

Poly(D,L-lactide) (PLA) was synthesized by the ring-opening polymerization of D,L-lactide with tin octanoate (Sn(oct)$_2$) in toluene as follows. In the hood, 40.0 g of D,L-lactide (0.278 mol), ~100 mL toluene, 57.8 µL EtOH (0.990 mmol), and 0.200 mL Sn(oct)$_2$ were placed into a 150 mL high-pressure vessel, which was sealed. The solution was stirred in an oil bath at 90 °C for 30 h. The polymerization was terminated with approximately 3.0 mL of 1.0 M HCl. The polylactide was precipitated 2 times into methanol and dried in a vacuum oven for 18 h at 80 °C (36.0 g, 90% yield). The amorphous PLA was melt blended with 0.5 to 15 wt% PDLA-PM-PDLA (15–33–15) triblock copolymer using the procedure described in Section 5.2.3.

Measurements for small angle x-ray scattering (SAXS) were performed at the University of Minnesota Twin Cities Characterization Facility beamline. Cu Kα X-rays were generated by a Rigaku Ultrex 18 kw generator. Temperature control inside the evacuated sample chamber was accomplished with water-cooling and electrically heating the brass-block sample holder. All samples were heated to 180 °C and annealed for 5 min in the sample chamber prior to SAXS measurements at 180 °C. Two-dimensional diffraction images were recorded using a Bruker Hi-Star multi-wire area detector located at the end of a 4.38 m evacuated flight tube and corrected for detector response before analysis. The two-dimensional images were azimuthally
integrated and reduced to the one-dimensional form of scattered intensity versus the spatial frequency $q$.

### 5.2.5 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q1000 with nitrogen as the purge gas and an indium calibration standard. Samples weighing 4.0–7.0 mg were loaded into aluminum hermetic pans and the pans were sealed prior to measurement. The melting and glass transition temperatures reported in Table 5.1 were determined by heating the sample from –60 °C at 10 °C min$^{-1}$. The percent crystallinity was calculated using the following equation

$$
\text{% Crystallinity} = 100 \times \frac{\Delta H_f}{f \Delta H_f^\infty}
$$

where $\Delta H_f$ is the measured heat of fusion, $f$ is the weight fraction of the component in question and $\Delta H_f^\infty$ is the enthalpy of fusion for a crystal having infinite crystal thickness. In chapter 4 we used a $\Delta H_f^\infty$ (PLLA) of 99 J g$^{-1}$ and a $\Delta H_f^\infty$ (stereocomplex) = 155 J g$^{-1}$, but for this chapter, a $\Delta H_f^\infty$ (PLLA) of 94 J g$^{-1}$ and $\Delta H_f^\infty$ (stereocomplex) = 142 J g$^{-1}$ has been used to make direct comparisons with previous literature.$^{23,29,30}$

Nonisothermal temperature programs were used to evaluate the effect of PLLA nucleation. Temperature program A (Figure 5.2) was used for the PLLA self nucleated samples to determine the nucleation efficiency scale. Temperature programs B (Figure 5.3) and C (Figure 5.4) were used to determine the nucleation efficiency of the
Figure 5.2 Graphical representation of temperature program A. The gray bar represents the partial melting zone.
Figure 5.3 Graphical representation of temperature program B. The gray bar represents the partial melting zone (172-178 °C).
Figure 5.4 Graphical representation of temperature program C. The gray bar represents the partial melting zone (172-178 °C).
PLLA/triblock copolymer blends. The temperature of crystallization \( (T_c) \) and the corresponding heat of crystallization \( (\Delta H_c) \) values were acquired directly from the nonisothermal crystallization steps (steps A2 and A4 from Figure 5.2, step B4 from Figure 5.3 and step C2 from Figure 5.4). An isothermal temperature program was used to evaluate the crystallization half-time \( (t_{1/2}) \). Here, the samples were directly heated to 185 °C at 200 °C min\(^{-1}\), held at 185 °C for 5 min, then quenched to 140 °C at 200 °C min\(^{-1}\). The samples were held at 140 °C for 15 to 90 min.

**5.3 Results and Discussion**

**5.3.1 Formation of PDLA–PM–PDLA/PLLA Stereocomplex Crystallites in Asymmetric Blends**

Full characterization of the PDLA–PM–PDLA triblock copolymers and PLLA homopolymer used to prepare the melt blends are given in Table 5.1. Additionally, we investigated blends containing PLLA homopolymer and a PLLA–PM–PLLA triblock copolymer (Table 5.1). PLLA blends containing 0.5% to 15% triblock copolymer were prepared by hand mixing the polymers at room temperature followed by melt blending in a Haake Rheomix mixer at 190 °C (see Section 5.2.3).

The formation of the stereocomplex was confirmed by DSC traces obtained on the as-prepared melt blended samples that were cooled to –60 °C and heated at 10 °C min\(^{-1}\) to 250 °C (Table 5.2). The first heating cycles for PLLA/PDLA–PM–PDLA melt blends prepared using PDLA-PM-PDLA (15–33–15) are shown in Figure 5.5. In most cases, the DSC signal corresponding to the glass transition temperature for
Table 5.1 Characterization of polylactide homopolymer and polylactide-containing triblock copolymer samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight Percent PLA&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$T_{g, PM}$&lt;sup&gt;b&lt;/sup&gt; (°C)</th>
<th>$T_{g, PLA}$&lt;sup&gt;b&lt;/sup&gt; (°C)</th>
<th>$T_{m, PLA}$&lt;sup&gt;b&lt;/sup&gt; (°C)</th>
<th>PLLA / PDLA Crystallinity (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>$M_n$&lt;sup&gt;c&lt;/sup&gt; (kg/mol)</th>
<th>PDI&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
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<tr>
<td>PLLA&lt;sup&gt;d&lt;/sup&gt;</td>
<td>100.0</td>
<td>---</td>
<td>53</td>
<td>174</td>
<td>43</td>
<td>65</td>
<td>1.95</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>18.4</td>
<td>-23</td>
<td>---</td>
<td>143</td>
<td>58</td>
<td>50</td>
<td>1.18</td>
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<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>33.3</td>
<td>-21</td>
<td>52</td>
<td>149, 154</td>
<td>57</td>
<td>71</td>
<td>1.28</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>40.3</td>
<td>-21</td>
<td>---</td>
<td>151, 160</td>
<td>48</td>
<td>74</td>
<td>1.16</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
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<td>-21</td>
<td>59</td>
<td>165</td>
<td>49</td>
<td>68</td>
<td>1.23</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (15–31–15)</td>
<td>48.3</td>
<td>-21</td>
<td>61</td>
<td>166</td>
<td>43</td>
<td>65</td>
<td>1.31</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated from $^1$H NMR spectroscopy. <sup>b</sup> Determined from DSC. <sup>c</sup> Determined by SEC versus polystyrene standards.

<sup>d</sup> PLLA supplied by Toyota Motor Company.
Table 5.2 First heating DSC data for homopolymer PLLA and melt blends

<table>
<thead>
<tr>
<th>Additive</th>
<th>Additive wt%</th>
<th>$T_{g, PM}$ (°C)</th>
<th>$T_{g, PLA}$ (°C)</th>
<th>$T_{m, PLA}$ (°C)</th>
<th>PLLA Crystallinity (%)</th>
<th>$T_{m, Stereo}$ (°C)</th>
<th>Stereocomplex Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.0</td>
<td>---</td>
<td>53</td>
<td>174</td>
<td>46</td>
<td>---</td>
<td>---</td>
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<td>60</td>
<td>174</td>
<td>49</td>
<td>212</td>
<td>34</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>1.0</td>
<td>---</td>
<td>60</td>
<td>174</td>
<td>49</td>
<td>207</td>
<td>36</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>3.0</td>
<td>---</td>
<td>60</td>
<td>173</td>
<td>51</td>
<td>211</td>
<td>33</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>8.0</td>
<td>–22</td>
<td>58</td>
<td>173</td>
<td>52</td>
<td>211</td>
<td>34</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>15.0</td>
<td>–22</td>
<td>58</td>
<td>172</td>
<td>54</td>
<td>212</td>
<td>24</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>0.5</td>
<td>---</td>
<td>60</td>
<td>174</td>
<td>52</td>
<td>213</td>
<td>25</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>1.0</td>
<td>---</td>
<td>60</td>
<td>174</td>
<td>51</td>
<td>211</td>
<td>34</td>
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<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>3.0</td>
<td>---</td>
<td>60</td>
<td>173</td>
<td>51</td>
<td>212</td>
<td>37</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>0.5</td>
<td>---</td>
<td>61</td>
<td>174</td>
<td>54</td>
<td>214</td>
<td>16</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>1.0</td>
<td>---</td>
<td>62</td>
<td>174</td>
<td>52</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>3.0</td>
<td>---</td>
<td>60</td>
<td>173</td>
<td>54</td>
<td>215</td>
<td>38</td>
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<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>8.0</td>
<td>---</td>
<td>58</td>
<td>173</td>
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<td>216</td>
<td>44</td>
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<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>15.0</td>
<td>–21</td>
<td>59</td>
<td>172</td>
<td>47</td>
<td>215</td>
<td>44</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>0.5</td>
<td>---</td>
<td>60</td>
<td>174</td>
<td>53</td>
<td>214</td>
<td>48</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>1.0</td>
<td>---</td>
<td>60</td>
<td>174</td>
<td>53</td>
<td>216</td>
<td>60</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>3.0</td>
<td>---</td>
<td>60</td>
<td>173</td>
<td>52</td>
<td>218</td>
<td>51</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>8.0</td>
<td>---</td>
<td>57</td>
<td>166</td>
<td>47</td>
<td>218</td>
<td>49</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>15.0</td>
<td>---</td>
<td>58</td>
<td>173</td>
<td>45</td>
<td>216</td>
<td>49</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (15–31–15)</td>
<td>0.5</td>
<td>---</td>
<td>60</td>
<td>174</td>
<td>50</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (15–31–15)</td>
<td>1.0</td>
<td>---</td>
<td>61</td>
<td>174</td>
<td>51</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (15–31–15)</td>
<td>3.0</td>
<td>---</td>
<td>59</td>
<td>173</td>
<td>50</td>
<td>---</td>
<td>---</td>
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</tbody>
</table>

$^a$ Calculated according to Equation 5.1 with $\Delta H_f^{\infty}$(PLLA) = 94 J g$^{-1}$, and $\Delta H_f^{\infty}$(stereocomplex) = 142 J g$^{-1}$. $^b$ see a $T_c$
Figure 5.5 DSC heating scans of PLLA melt blended with varying weight percents of PDLA-PM-PDLA (15–33–15)
polymenthide was not intense enough to accurately measure a $T_g$ due to the small fraction of polymenthide present in the blends. The glass transition temperature for PLLA was around 60 °C for all samples. Endotherms indicative of both PLLA homopolymer melting and stereocomplex melting were observed for all PLLA/PDLA–PM–PDLA melt blends except 99/1 wt% PLLA/PDLA-PM-PDLA (11–33–11) (Table 5.2). The melting peak from the PLLA homopolymer is present around 174 °C, while the stereocomplex melting peak is around 215 °C. For all of the blends, the level of crystallinity according to Equation 5.1 was approximately 50% for the PLLA endotherms (not accounting for the cold crystallization) and ranged from 16 to 60% for the endotherms corresponding to the stereocomplex.

5.3.2 SAXS Characterization of PLA/PDLA–PM–PDLA Micelles

A/A-B-A blends containing low levels of the triblock copolymers in Table 5.1 are expected to phase separate into disordered spherical micelles comprised of a B block core and A block corona swelled by the A block matrix (Figure 5.6). Poly(D,L-lactide)/PLLA-PM-PLLA (15–31–15) melt blends containing 0.5 to 15 wt% triblock copolymer were prepared to explore the micellization behavior of the PLLA/PDLA–PM–PDLA blends in the melt. Each sample was transparent, consistent with microphase separation. Using a Percus-Yevick (PY) analysis, the characteristic scattering obtained from these systems can be modeled. The use of SAXS and the PY analysis to obtain quantitative information of spherical micelles has been demonstrated and is described below.
Equation 5.2 describes the scattering intensity of radiation, \( I(q) \), from an array of particles,

\[
I(q) = (\Delta \rho)^2 N P(q) S(q) \quad (5.2)
\]

where \( q \) is the scattering wavevector, \( \Delta \rho \) is the electron density difference between the particles and their surroundings, \( N \) is the number of scattering particles, \( P(q) \) is the form factor, and \( S(q) \) is the interference factor.\(^{31}\) The electron density of the corona and the matrix in a PLA/PDLA–PM–PDLA melt blend are equivalent at 180 °C (i.e., both amorphous polylactide) so the scattering will stem entirely from the micelle cores. The intraparticle scattering for a dilute array of spheres is dependent on the size of the particle and is expressed through the form factor given in equation 5.3,

\[
P(q, R, \sigma) = \int_0^\infty \frac{1}{\sigma \sqrt{2\pi}} \exp \left( \frac{-(R - R_c)^2}{2 \sigma^2} \right) \left[ \frac{3(\sin(qR_c) - qR_c \cos(qR_c))}{(qR_c)^3} \right] \, \partial R \quad (5.3)
\]

where \( V \) represents the volume of the sphere, \( R_c \) is the radius of the micelle core, and \( \sigma \) is the standard deviation of \( R_c \) (Figure 5.6).\(^{31}\)

Figure 5.6 Schematic illustration of a single “wet brush” A-B-A triblock copolymer micelle where A is denoted by solid lines and B is denoted by the gray core
Schmidt calculated the maxima in the spherical form factor (Equation 5.3) to occur at:

\[ qR_c = 5.76, 9.10, \ldots \]  \hspace{1cm} (5.4)

The SAXS patterns at 180 °C for the PLA/PDLA–PM–PDLA melt blends (Figure 5.7) contain broad peaks and have a narrow range of q due to the limitations of the instrument. Therefore, it is difficult to determine if the peaks correspond to the intraparticle scattering peak maxima. However, assuming this is the case, the initial \( R_c \) value at 180 °C was calculated for the melt blends using Equation 5.4 (Table 5.3). The values of \( R_c \) obtained are in agreement with previously reported \( R_c \) measurements.

The micelle density of the blends were calculated based on the \( R_c \) and the amount of polymethide in the blend (Table 5.3), and ranged from \( 10^{14} \) to \( 10^{15} \) micelles cm\(^{-3}\), values much higher than the densities inferred from crystallization work with PLLA/PDLA crystallites of \( 10^7 \) to \( 10^9 \) micelles cm\(^{-3}\). The higher nucleation densities of the micelles suggest that the micelles will have faster nucleation rates and higher nucleation efficiencies relative to the PLLA/PDLA crystallites.

<table>
<thead>
<tr>
<th>Additive Additive Wt %</th>
<th>Additive Wt %</th>
<th>( R_c ) (nm)(^a)</th>
<th>micelle density (μmels cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDLA-PM-PDLA (15–33–15) 0.5</td>
<td>17.1</td>
<td>1.25 × 10(^{14})</td>
<td></td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15) 1.0</td>
<td>17.2</td>
<td>2.43 × 10(^{14})</td>
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</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15) 3.0</td>
<td>17.2</td>
<td>7.30 × 10(^{14})</td>
<td></td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15) 8.0</td>
<td>17.6</td>
<td>1.81 × 10(^{15})</td>
<td></td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15) 15.0</td>
<td>18.2</td>
<td>3.08 × 10(^{15})</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Calculated according to Equation 5.4.
Figure 5.7 SAXS data from PLA/PLLA-PM-PLLA (15–31–15) blends containing between 0.5 and 15 wt% triblock copolymer acquired at 180 °C. ▼ denotes the intraparticle scattering peak.
5.3.3 Determination of the Nucleation Efficiency Scale

In order to determine the effectiveness of a nucleating agent, we first need to create a nucleation efficiency scale by examining the melting behavior of pure PLLA. Following the example set forth by Wittman et al., Schmidt and Hillmyer were the first to construct a calorimetric nucleation efficiency (NE) scale for PLLA, employing nonisothermal DSC experiments. A nucleation efficiency scale for a polymer is determined by cooling a polymer sample from the melt and observing the temperature at which the sample crystallizes. Minimum nucleation efficiency occurs when there is an absence of nucleation sites in the melt. Upon cooling pure PLLA from the melt, the minimum efficiency crystallization temperature, $T_{c_{min}}$, is obtained. The range of temperatures in which there exists both melted PLLA and semicrystalline PLLA is called the partial melting zone (pmz). Maximum efficiency occurs at the the highest nucleation concentration, which is at the lowest temperature in the pmz. Cooling the polymer from this lowest temperature would give us the maximum efficiency crystallization temperature, $T_{c_{max}}$.

The four step temperature program A (Figure 5.2) was utilized to determine the $T_{c_{min}}$ and $T_{c_{max}}$ for melt blended pure PLLA (190 °C, 100 rpm, 15 min). In step A1, PLLA was heated to 200 °C and held for five minutes to erase the thermal history. The sample was then cooled at a rate of 5 °C min$^{-1}$ to 80 °C in step A2, and the observed exothermic peak was the $T_{c_{min}}$. The sample was then heated to a temperature within the partial melting zone and held for five minutes (step A3). The lower limit of the partial melting zone ($T_{pmz}^{min}$) is defined as the temperature at which there is a saturation of
stable crystal fragments.\textsuperscript{26} Below $T_{pmz}^{\min}$ insufficient melting occurs and the sample begins to crystallize. Figure 5.8 shows nonisothermal DSC traces obtain from step A4 at varied $T_{pmz}$’s. Using temperature program A, we determined $T_{pmz}^{\max}$ to be 178 °C and $T_{pmz}^{\min}$ to be 172 °C. From this analysis, $T_c^{\min} = 105.5$ °C and $T_c^{\max} = 136.6$ °C. These results are reproducible and are close to previous findings by Anderson et al. who determined $T_c^{\min} = 104.3$ °C and $T_c^{\max} = 142.9$ °C for the same PLLA sample melt blended at 190 °C at 50 rpm for 15 min. The NE of a nucleating agent is calculated using the following equation\textsuperscript{26,27}

\begin{equation}
NE = \frac{T_c - T_c^{\min}}{T_c^{\max} - T_c^{\min}} \times 100
\end{equation}

where $T_c$ is the crystallization temperature of the blend, $T_c^{\min} = 105.5$ °C and $T_c^{\max} = 136.6$ °C. An effective nucleating agent will cause the crystallization temperature to increase and result in a NE value that approaches 100%.

### 5.3.4 Nucleation Efficiency of PLLA/PDLA–PM–PDLA Crystallites

The nucleation efficiency of the PLLA/PDLA–PM–PDLA stereocomplexed micelles was determined using two temperature programs. Temperature program B is modeled after the program used by Schmidt et al. (Figure 5.3).\textsuperscript{19} In temperature program B, step B1 erased the thermal history of the sample followed by the formation of stereocomplex and homopolymer crystals in step B2. Samples were then heated to 185 °C (well above the $T_{pmz}^{\max}$ for PLLA) and held for 5 minutes to melt the PLLA homopolymer, leaving only the stereocomplexed block copolymer micelles (or block
Figure 5.8 Crystallization exotherms from nonisothermal DSC experiments conducted on self-nucleated PLLA at varied $T_{pmz}$’s using program A (Figure 5.2). For each exotherm, the $T_{pmz}$ is listed to the right and the peak $T_c$ values and $\Delta H_c$ are shown below each exotherm.
copolymers in the case of PLLA/PLLA–PM–PLLA melt blends). The final step, B4, allowed the determination of the NE of the preformed stereocomplex by measuring $T_c$ upon cooling at a rate of 5 °C min$^{-1}$ and using Equation 5.5 (Table 5.4 and 5.5). The final cooling cycles (B4) for PLLA and PLLA/PDLA–PM–PDLA (15–33–15) melt blends are shown in Figure 5.9. We observe an increase in $T_c$ and $\Delta H_c$ values for all blends, indicative of enhanced NE and crystallinity (Table 5.4). However, the shape of the DSC exotherm traces appears broad and bumpy in all samples, indicative of degradation of the samples prior to cooling. Most likely this degradation occurs during step B1 in which the samples are heated to 240 °C. To remedy this problem, we employed a second temperature program to determine the NE of the blends.

Temperature program C was utilized to obtain the NE of the blends without potentially degrading the samples (Figure 5.4), and is modeled after the program used by Anderson et al.$^{23}$ Step C1 quickly heated the samples to 185 °C (well above the $T_{pmz}^{max}$ for PLLA). At 185 °C the homopolymer PLLA is completely melted and more stereocomplex crystallites can form between the melted PLLA and free PDLA blocks of the triblock copolymer micelles. After 5 min at 185 °C the samples were cooled at 5 °C min$^{-1}$ and the $T_c$ and area of the crystallization exotherm ($\Delta H_c$) were recorded (Table 5.4). The cooling cycles for PLLA homopolymer and PLLA/PDLA-PM-PDLA (15–33–15) melt blends are shown in Figure 5.10. The DSC exotherm traces are relatively narrow when compared to those observed from temperature program B (Figure 5.9), suggesting that degradation has not occurred with these samples.
Table 5.4 Nonisothermal DSC results for self-nucleated PDLA–PM–PDLA/PLLA melt blends (cool rate = 5 °C min\(^{-1}\))

<table>
<thead>
<tr>
<th>Additive</th>
<th>Additive wt %</th>
<th>PDLA wt%</th>
<th>Temperature Program B</th>
<th>Temperature Program C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(T_c) (°C)</td>
<td>NE(^a) (%)</td>
</tr>
<tr>
<td>None</td>
<td>0.0</td>
<td>0.0</td>
<td>105</td>
<td>0</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>0.5</td>
<td>0.1</td>
<td>116</td>
<td>34</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>1.0</td>
<td>0.2</td>
<td>122</td>
<td>53</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>3.0</td>
<td>0.6</td>
<td>124</td>
<td>59</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>8.0</td>
<td>1.5</td>
<td>122</td>
<td>53</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>15.0</td>
<td>2.8</td>
<td>108</td>
<td>8</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>0.5</td>
<td>0.2</td>
<td>114</td>
<td>27</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>1.0</td>
<td>0.3</td>
<td>117</td>
<td>37</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>3.0</td>
<td>1.0</td>
<td>120</td>
<td>47</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>0.5</td>
<td>0.2</td>
<td>108</td>
<td>8</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>1.0</td>
<td>0.4</td>
<td>118</td>
<td>40</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>3.0</td>
<td>1.2</td>
<td>120</td>
<td>47</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>8.0</td>
<td>3.2</td>
<td>122</td>
<td>53</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>15.0</td>
<td>6.0</td>
<td>120</td>
<td>47</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>0.5</td>
<td>0.2</td>
<td>113</td>
<td>24</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>1.0</td>
<td>0.5</td>
<td>116</td>
<td>34</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>3.0</td>
<td>1.4</td>
<td>125</td>
<td>63</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>8.0</td>
<td>3.9</td>
<td>120</td>
<td>47</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>15.0</td>
<td>7.2</td>
<td>123</td>
<td>56</td>
</tr>
</tbody>
</table>

\(^a\)NE values obtained from Equation 5.5

\(^b\)Calculated according to Equation 5.3 with \(\Delta H_f^\infty\) (PLLA) = 94 J g\(^{-1}\).
Table 5.5 Nonisothermal DSC results for self-nucleated PLLA–PM–PLLA/PLLA melt blends (cool rate = 5 °C min\(^{-1}\))

<table>
<thead>
<tr>
<th>Additive</th>
<th>Additive wt %</th>
<th>(T_c, ^{(°C)})</th>
<th>(NE^{a}, (%))</th>
<th>(\Delta H_c, (J/g))</th>
<th>(X_{PLLA}^{b}, (%))</th>
<th>(T_c, ^{(°C)})</th>
<th>(NE^{a}, (%))</th>
<th>(\Delta H_c, (J/g))</th>
<th>(X_{PLLA}^{b}, (%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.0</td>
<td>105</td>
<td>0</td>
<td>35</td>
<td>37</td>
<td>105</td>
<td>0</td>
<td>35</td>
<td>37</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (15–31–15)</td>
<td>0.5</td>
<td>101</td>
<td>-14</td>
<td>30</td>
<td>32</td>
<td>104</td>
<td>-4</td>
<td>31</td>
<td>33</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (15–31–15)</td>
<td>1.0</td>
<td>102</td>
<td>-11</td>
<td>34</td>
<td>36</td>
<td>102</td>
<td>-10</td>
<td>28</td>
<td>30</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (15–31–15)</td>
<td>3.0</td>
<td>102</td>
<td>-11</td>
<td>34</td>
<td>37</td>
<td>101</td>
<td>-14</td>
<td>26</td>
<td>28</td>
</tr>
</tbody>
</table>

\(^a\)NE values obtained from Equation 5.5  
\(^b\)Calculated according to Equation 5.3 with \(\Delta H_f^{\infty}(PLLA) = 94\, J\, g^{-1}\).
Figure 5.9 Selected crystallization exotherms of PLLA/PDLA-PM-PDLA (15–33–15) melt blends cooled (5 °C min⁻¹) from 185 °C (Temperature program B (figure 5.3)). The composition of triblock copolymer is listed on the right, and the $\Delta H_c$ values (J g⁻¹) are recorded next to each exotherm.
Figure 5.10 Selected crystallization exotherms of PLLA/PDLA-PM-PDLA (15–33–15) melt blends cooled (5 °C min⁻¹) from 185 °C (Temperature program C (figure 5.4)). The composition of triblock copolymer is listed on the right, and the $\Delta H_c$ values (J g⁻¹) are recorded next to each exotherm.
Using temperature programs B and C, we observe an increase in $T_c$ values for all blends, indicative of enhanced nucleation efficiency (Table 5.4). However, the $T_c$ values obtained using temperature program C are significantly higher relative to the $T_c$ values obtained using temperature program B (see Table 5.4). The lowest NE value (Equation 5.5) obtained using temperature program C was 35% for the 95.5/0.5 wt% PLLA/PDLA-PM-PDLA (3.8–34–3.8) melt blend that contained less than 0.1 wt% PDLA. By increasing the triblock copolymer content to 99/1 wt% (less than 0.2 wt% PDLA) a nearly two-fold increase in NE was observed. Increases in NE were observed with increasing additive content for the PLLA/PDLA–PM–PDLA as illustrated in Figure 5.11. The most dramatic increases in NE are observed when the additive wt% is increased from 0.5% to 1.0%. A gradual increase in NE is observed when the additive wt% is increased to 3% and 8%, and a slight decrease or increase is observed when increasing the additive wt% to 15%.

Similar to previous findings, the nucleation efficiency is dependent on the molecular weight of the PDLA in the PLLA blends. All PLLA/PDLA-PM-PDLA (3.8–34–3.8) blends have lower NE values than the blends containing triblock copolymers of higher PDLA-block molecular weight and identical wt% (Figure 5.11, Table 5.4). PLLA/PDLA-PM-PDLA (15–33–15) melt blends have the best nucleation efficiencies at all compositions. The NE of the melt blend containing 0.5% triblock copolymer was 72% and increased to nearly 100% for the sample containing 15 wt% triblock copolymer, suggesting that the stereocomplex micelles behaved as a nearly ideal nucleating agents. Schmidt et al. and Anderson et al. also saw an improvement in
Figure 5.11 Plot of nucleation efficiency versus triblock copolymer content in the blends for all samples
the NE value when using approximately 15 kg mol$^{-1}$ homoPDLA compared to
to molecular weights of approximately 5 and 50 kg mol$^{-1}$.
At low PDLA block copolymer concentrations, the NE of PLLA/PDLA–PM–PDLA melt blends are
similar to those observed for PLLA/homoPDLA of higher wt% PDLA. For example, a
nucleation efficiency of 67% was obtained for the PLLA/homoPDLA (4.8) melt blend
containing 0.5 wt% PDLA. The 99/1 wt% PLLA/PDLA-PM-PDLA (3.8–34–3.8)
blend of significantly lower wt% PDLA (0.18 wt% PDLA) has a nucleation efficiency
of 65%. We attribute this enhancement in NE with lower wt% PDLA in the blends to
the superior nucleating ability of the stereocomplexed triblock copolymer micelles
over the randomly dispersed PLLA/PDLA stereocrystallites. Non-stereocomplexed
triblock copolymer micelles obtained when adding PLLA-PM-PLLA (15–31–15) as
nucleating agents for PLLA lower the $T_c$ when compared to melt blended PLLA,
resulting in NE values of less than zero (see Table 5.5).

The PLLA $\Delta H_c$ values for all of the PLLA/PDLA–PM–PDLA melt blends were
higher than the homopolymer PLLA. The $\Delta H_c$ of the melt processed PLLA was 35 J
g$^{-1}$, corresponding to a PLLA crystallinity of 37% (Equation 5.1). For the 99.5/0.5
wt% PLLA/PDLA-PM-PDLA(11–33–11) blend, the $\Delta H_c$ was determined to be 43 J g$^{-1}$
resulting in a PLLA crystallinity of 46% after accounting for a loss of 0.70% of the
sample due to the triblock copolymer and stereocomplex formation. Therefore,
crystallinity increased by approximately 15% upon addition of the stereocomplexed
nucleating micelles. This is consistent with the melt blend data of Anderson and
Hillmyer and solution blend data of Yamane et al., and contrary to the solution blend
data (using temperature program B) of Schmidt and Hillmyer.\textsuperscript{19,21,23} This discrepancy is most likely due to the degradation that may have occurred for Schmidt and Hillmyer when using temperature program B.\textsuperscript{19}

Yamane et al. investigated the nucleation efficiencies of PLLA/PDLA solution blends using a cooling rate of 2 °C min\(^{-1}\),\textsuperscript{21} therefore, the nucleation efficiencies of PLLA/PDLA–PM–PDLA and PLLA/PLLA–PM–PLLA melt blends were evaluated at a cooling rate of 2 °C min\(^{-1}\). First, the self-nucleation experiment was performed using the new cooling rate for steps A2 and A4 in temperature program A. From this analysis, \(T_{c_{\text{min}}} = 111.2\) °C and \(T_{c_{\text{max}}} = 143.0\) °C. Using temperature program A at a cooling rate of 2 °C min\(^{-1}\), Anderson et al. determined \(T_{c_{\text{min}}} = 111\) °C and \(T_{c_{\text{max}}} = 146\) °C.\textsuperscript{23} The \(T_c\), \(\Delta H_c\), and NE values for the PLLA/PDLA–PM–PDLA and PLLA/PLLA–PM–PLLA melt blends were then determined using temperature programs B and C with the new cooling rate for steps B4 and C2 and are given in Tables 5.6 and 5.7. The crystallization exotherms of PLLA and PLLA/PDLA–PM–PDLA (15–33–15) melt blends cooled at a rate of 2 °C min\(^{-1}\) are shown in Figure 5.12. For all blends, higher \(T_c\), \(\Delta H_c\), and NE values were obtained using the slower cooling rate, especially for all 99.5/0.5 wt% blends. For the 85/15 wt% PLLA/PDLA–PM–PDLA (15–33–15) melt blend, we calculated the highest NE value of 101\%, suggesting the stereocomplexed micelles in the blend were more effective at nucleating the crystallization of PLLA than even the PLLA crystallites from the self-nucleation experiment. Similar results were observed for Anderson et al.\textsuperscript{23} Consistent with the results observed for the 5 °C min\(^{-1}\) cooling rate, the PLLA/PDLA–PM–PDLA (15–33–15) melt blends exhibited the
Figure 5.12 Selected crystallization exotherms of PLLA/PDLA-PM-PDLA (15–33–15) melt blends cooled (2 °C min⁻¹) from 185 °C (Temperature program C (Figure 5.4)). The composition of triblock copolymer is listed on the right, and the $\Delta H_c$ values (J g⁻¹) are recorded next to each exotherm.
Table 5.6 Nonisothermal DSC results for self-nucleated PDLA–PM–PDLA/PLLA melt blends (cool rate = 2 °C min
-1)

<table>
<thead>
<tr>
<th>Additive</th>
<th>Additive Wt %</th>
<th>PDLA wt%</th>
<th>Temperature Program B</th>
<th>Temperature Program C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T_c$ (°C)</td>
<td>NE$^a$ (%)</td>
<td>$\Delta H_c$ (J/g)</td>
</tr>
<tr>
<td>None</td>
<td>0.0</td>
<td>0.0</td>
<td>111</td>
<td>0</td>
<td>32</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>0.5</td>
<td>0.1</td>
<td>128</td>
<td>52</td>
<td>55</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>1.0</td>
<td>0.2</td>
<td>131</td>
<td>61</td>
<td>57</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>3.0</td>
<td>0.6</td>
<td>131</td>
<td>61</td>
<td>55</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>8.0</td>
<td>1.5</td>
<td>125</td>
<td>43</td>
<td>49</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>15.0</td>
<td>2.8</td>
<td>112</td>
<td>2</td>
<td>39</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>0.5</td>
<td>0.2</td>
<td>128</td>
<td>52</td>
<td>58</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>1.0</td>
<td>0.3</td>
<td>130</td>
<td>58</td>
<td>56</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>3.0</td>
<td>1.0</td>
<td>130</td>
<td>58</td>
<td>55</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>0.5</td>
<td>0.2</td>
<td>126</td>
<td>46</td>
<td>52</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>1.0</td>
<td>0.4</td>
<td>127</td>
<td>49</td>
<td>58</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>3.0</td>
<td>1.2</td>
<td>127</td>
<td>49</td>
<td>56</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>8.0</td>
<td>3.2</td>
<td>127</td>
<td>49</td>
<td>48</td>
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<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>15.0</td>
<td>6.0</td>
<td>126</td>
<td>46</td>
<td>39</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>0.5</td>
<td>0.2</td>
<td>125</td>
<td>43</td>
<td>55</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>1.0</td>
<td>0.5</td>
<td>128</td>
<td>52</td>
<td>52</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>3.0</td>
<td>1.4</td>
<td>131</td>
<td>61</td>
<td>55</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>8.0</td>
<td>3.9</td>
<td>132</td>
<td>65</td>
<td>46</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>15.0</td>
<td>7.2</td>
<td>132</td>
<td>65</td>
<td>42</td>
</tr>
</tbody>
</table>

$^a$ NE values obtained from Equation 5.5
$^b$ Calculated according to Equation 5.3 with $\Delta H_f^\infty$ (PLLA) = 94 J g$^{-1}$. 

Chapter 5: PDLA–PM–PDLA Copolymers as Nucleating Agents for PLLA
Table 5.7 Nonisothermal DSC results for self-nucleated PLLA–PM–PLLA/PLLA melt blends (cool rate = 2 °C min\(^{-1}\))

<table>
<thead>
<tr>
<th>Additive</th>
<th>Additive wt %</th>
<th>(T_c) (°C)</th>
<th>NE(^a) (%)</th>
<th>(\Delta H_c) (J/g)</th>
<th>(X_{PLLA}^b) (%)</th>
<th>(T_c) (°C)</th>
<th>NE(^a) (%)</th>
<th>(\Delta H_c) (J/g)</th>
<th>(X_{PLLA}^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.0</td>
<td>105</td>
<td>0</td>
<td>35</td>
<td>37</td>
<td>105</td>
<td>0</td>
<td>35</td>
<td>37</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (15–31–15)</td>
<td>0.5</td>
<td>108</td>
<td>-10</td>
<td>36</td>
<td>39</td>
<td>109</td>
<td>-6</td>
<td>36</td>
<td>38</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (15–31–15)</td>
<td>1.0</td>
<td>109</td>
<td>-7</td>
<td>38</td>
<td>41</td>
<td>110</td>
<td>-5</td>
<td>36</td>
<td>39</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (15–31–15)</td>
<td>3.0</td>
<td>109</td>
<td>-7</td>
<td>38</td>
<td>41</td>
<td>109</td>
<td>-8</td>
<td>33</td>
<td>37</td>
</tr>
</tbody>
</table>

\(^a\)NE values obtained from Equation 5.5  \(^b\)Calculated according to Equation 5.3 with \(\Delta H_f^{\infty}(PLLA) = 94\) J g\(^{-1}\).
highest nucleation efficiencies at all compositions. Yamane et al. reported their lowest $T_c$ value to be 107 °C for pure PLLA, and their highest $T_c$ value to be 128 °C in a 95/5 wt% PLLA/PDLA solution blend.\textsuperscript{21} Our highest $T_c$ values of 147 °C when cooling at a rate of 2 °C min$^{-1}$ and 136 °C when cooling at a rate of 5 °C min$^{-1}$ are significantly higher than those obtained by Yamane et al.\textsuperscript{21} Using the same temperature programs on PLLA/PLLA–PM–PLLA melt blends, we observe nucleation efficiencies of less than zero and similar crystallinities to that of pure PLLA (Table 5.7).

### 5.3.5 Isothermal Crystallization

The effectiveness of a nucleating agent can also be assessed by measuring the crystallization half-time in an isothermal crystallization experiment. In this test, the polylactide melt blends were held for 5 minutes at 185 °C and quenched to 140 °C. The crystallization at 140 °C was monitored by DSC. From the integration of the resultant crystallization exotherms, a relative percent crystallinity based on the total area of the crystallization exotherm can be calculated at a given time, with 100% crystallinity corresponding to the total area of the peak. Figure 5.13 gives a representative example of the observed crystallization exotherm and the calculated relative crystallinity. From the relative crystallinity curve, the time it takes to reach 50% crystallinity, the $t_{\frac{1}{2}}$, can be determined. For example, from Figure 5.13, the $t_{\frac{1}{2}}$ is approximately 1.7 min. The $t_{\frac{1}{2}}$ values are given in Table 5.8 for PLLA and all of the melt blends.
Figure 5.13 Representative isothermal DSC trace taken at 140 °C (gray line) and corresponding curve (black line) for determining the crystallization half-time, $t_{1/2}$.
### Table 5.8 Isothermal DSC data for PLLA/PDLA–PM–PDLA melt blends

<table>
<thead>
<tr>
<th>Additive</th>
<th>Additive wt%</th>
<th>PDLA wt%</th>
<th>$t_{(1/2)}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.0</td>
<td>0.0</td>
<td>44.3</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>0.5</td>
<td>0.1</td>
<td>9.5</td>
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<tr>
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<td>0.2</td>
<td>3.4</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
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<td>0.6</td>
<td>2.9</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>8.0</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (3.8–34–3.8)</td>
<td>15.0</td>
<td>2.8</td>
<td>2.3</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
<td>0.5</td>
<td>0.2</td>
<td>3.9</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
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<td>0.3</td>
<td>3.4</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (6.8–28–6.8)</td>
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<td>1.0</td>
<td>2.6</td>
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<tr>
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</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
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<td>1.2</td>
<td>2.7</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
<td>8.0</td>
<td>3.2</td>
<td>1.9</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (11–33–11)</td>
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<td>6.0</td>
<td>1.9</td>
</tr>
<tr>
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<td>0.2</td>
<td>2.7</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
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<td>0.5</td>
<td>2.4</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>3.0</td>
<td>1.4</td>
<td>2.4</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>8.0</td>
<td>3.9</td>
<td>1.7</td>
</tr>
<tr>
<td>PDLA-PM-PDLA (15–33–15)</td>
<td>15.0</td>
<td>7.2</td>
<td>1.3</td>
</tr>
<tr>
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<tr>
<td>PLLA-PM-PLLA (15–31–15)</td>
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<td>23.5</td>
</tr>
<tr>
<td>PLLA-PM-PLLA (15–31–15)</td>
<td>3.0</td>
<td>0.0</td>
<td>30.7</td>
</tr>
</tbody>
</table>
A significant decrease in the $t_{1/2}$ values was observed in the melt blends when PDLA–PM–PDLA triblock copolymers were added. As the wt% of additive in the melt blends increased, the $t_{1/2}$ values decreased. The $t_{1/2}$ values for the PLLA/PDLA–PM-PDLA (15–33–15) melt blends were significantly smaller than the other blends, in agreement with NE data (Table 5.6). The shortest $t_{1/2}$ value of 1.3 minutes was obtained with the 85/15 wt% PLLA/PDLA-PM-PDLA (15–33–15) melt blend. The $t_{1/2}$ values obtained were very similar to those seen by Schmidt et al. The smallest $t_{1/2}$ at 140 °C was 75 seconds for a solution blend with 10% PDLA incorporation. Even lower values of less than 1 min were observed for PLLA/PDLA melt blends by Anderson et al. Interestingly, adding PLLA-PM-PLLA (15–31–15) did in fact lower the half-time of crystallization of PLLA, but the $t_{1/2}$ values obtained were much larger than those for the PLLA/PDLA–PM–PDLA melt blends.

5.4 Summary

Herein, we presented work using block copolymer micelles as novel nucleating agents for PLLA. Melt blends of 0.5 to 15 wt% PDLA–PM–PDLA triblock copolymers with PLLA formed triblock copolymer micelles in which the PDLA corona formed stereocomplexes with PLLA. The PM core radius was approximately 18 nm with nucleation densities of approximately $10^{15}$ micelles cm$^{-3}$, densities much higher than those obtained using PLLA/PDLA crystallites of $10^7$ to $10^9$ micelles cm$^{-3}$. The nucleation efficiency of the stereocomplexed micelles was evaluated and remarkable increases in the nucleation efficiency were observed. In addition, in
isothermal experiments the $t_{1/2}$ values were relatively low indicating a significant enhancement in the PLLA crystallization rate. The blends containing PDLA-PM-PDLA (15–31–15) stood out as having the highest nucleation efficiencies and the lowest $t_{1/2}$ values. Most surprising, blends containing low molecular weight PDLA blocks at low concentrations (ex. 99/1 wt% PDLA-PM-PDLA (3.8–34–3.8)) successfully nucleated PLLA with impressive NE values. This study demonstrates the feasibility of using PDLA block copolymers at low levels as stereocomplexed micelle nucleating agents for PLLA.

5.5 Acknowledgments

This work was supported primarily by the MRSEC program of the National Science Foundation under Award Number DMR-0212302. We also acknowledge the Petroleum Research Fund (grant no. 45891-AC7), the National Science Foundation (grant no. CHE-9975357) and Cargill, Inc. for partial support of this work.

5.6 References


(33) Calculated using the equation: $\# \text{micelles cm}^{-3} = \frac{V_{PM}}{V_{\text{micelle}}}$ where $V_{PM}$ (per cm$^{-3}$) = $(\text{wt\% additive in blend}) \times (\text{wt\% PM in additive}) / (4 \text{ g})$ and $V_{\text{micelle}} = 4/3 \pi R_c^3$. 
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Appendix 1

Biodegradable Pressure-Sensitive Adhesives

A1.1 Introduction

A pressure-sensitive adhesive (PSA) is a material that exhibits permanent tack at room temperature and can adhere to a variety of substrates with very light pressure.\textsuperscript{1} The function of PSAs is to achieve instantaneous adhesion to a surface without activation such as a treatment with solvents or heat, and also by having sufficient internal strength, or cohesive strength, so that the adhesive material will not break up before the bond between the adhesive material and the surface ruptures.\textsuperscript{1-3} PSAs have been in wide use since the late 19\textsuperscript{th} century, and are used in products ranging from self adhesive tapes and labels to biomedical devices.\textsuperscript{2} PSAs are generally composed of an elastomeric polymer, tackifying resins, plasticizers and fillers in various amounts depending on the application.\textsuperscript{1-4} The elastomeric polymers mainly come from three families: acrytics, polystyrene block copolymers, and natural rubber.\textsuperscript{5} Thermoplastic elastomers such as styrenic block copolymers are the latest PSAs to be studied because of their unique structures.\textsuperscript{1,5-7} These microphase separated materials are physically
Appendix 1: Biodegradable Pressure-Sensitive Adhesives

crosslinked by the polystyrene domains, which gives these materials superior resistance to creep, or flow.\textsuperscript{8}

Unfortunately, PSA films are a nuisance when it comes to recycling the material to which they are attached. For example, during the paper recycling process, the paper and adhesive are broken into fibers in an aqueous environment. Most of the PSA is removed at pressure screens, and the adhesive not removed is introduced into the paper making process.\textsuperscript{9} The adhesives create specks and holes on the produced paper and leave sticky deposits in the machines.\textsuperscript{10,11} The most cost-effective way to eliminate the impact of PSAs on paper recycling is to design adhesives that can be removed early in the recycling process, ideally using the existing equipment.\textsuperscript{9} This can be achieved by designing PSAs that inhibit fragmentation and are removed with pressure screens,\textsuperscript{9,12} redesigning paper using commercial additives to enhance the removal of PSAs,\textsuperscript{13} or using water soluble PSAs, among other strategies.\textsuperscript{14}

In this chapter, I describe the results of efforts aimed at exploring the potential for PLA–PM–PLA triblock copolymers to be used as renewable resource, biodegradable pressure-sensitive adhesives. As discussed in chapter 3, PLA–PM–PLA degrades under hydrolytic conditions. In paper recycling mills that use high temperatures, it is most likely that PLA–PM–PLA will hydrolytically degrade during the recycling process. Thus, we targeted for synthesis amorphous PLA–PM–PLA triblock copolymers with low wt% PLA in order to obtain soft and tacky samples. A blend was also made with a triblock copolymer and a rosin ester tackifier. The viscoelastic response of the copolymers and blend were investigated using rheology.
Peel, tack and shear strength are measured for all samples. We conclude that the most important variable to control and achieve the optimum balance of peel, tack and shear properties is the molecular weight of the triblock copolymer blocks.

**A1.2 Experimental Section**

**A1.2.1 Materials**

All air- or moisture-sensitive compounds were handled under a nitrogen atmosphere in a glovebox, as indicated. Toluene used for polymerizations was purified by passing through activated alumina-based columns (Glass Contour, Laguna Beach, CA) followed by distillation from sodium. D,L-Lactide (Purac) was purified by recrystallization from toluene followed by repeated (2x) vacuum sublimation. Diethylene glycol (Sigma Aldrich) was distilled under reduced pressure from sodium. The tackifier used was Aquatac, comprised of mostly a pentaerythritol ester (Arizona Chemical). Molecular sieves (4 Å) were dried under vacuum at 180 °C for a minimum of 16 h. All other solvents and reagents were used as received from the commercial source indicated without further purification. All glassware used in polymerizations was treated with a solution of Me₂SiCl₂ (10% in CH₂Cl₂) and oven dried at 200 °C for a minimum of 3 h before use. All triblock copolymers were synthesized by the methods reported previously (see Chapter 2). The backing for the adhesive was a Canon type E transparency sheet.
Appendix 1: Biodegradable Pressure-Sensitive Adhesives

A1.2.2 Measurements

$^1$H and $^{13}$C NMR spectra were collected on a Varian INOVA-300, VXR-300 or Varian INOVA-500 spectrometer. Samples of the polymers were prepared by dissolving approximately 30 mg of polymer in 1 mL of CDCl$_3$ (Cambridge). Molecular weights ($M_n$ and $M_w$) and polydispersity indices ($M_w/M_n$) were determined by size exclusion chromatography (SEC) using polystyrene standards. Samples were analyzed at 40 °C using a Hewlett-Packard high-pressure liquid chromatograph equipped with three Jordi poly(divinylbenzene) columns of $10^4$, $10^3$, and 500 Å pore sizes and a HP1047A differential refractometer.

Measurements for small angle x-ray scattering (SAXS) on PLA-PM-PLA (2.5–34–2.5) were performed at the University of Minnesota Twin Cities Characterization Facility beamline. Cu Kα X-rays were generated by a Rigaku Ultrex 18 kw generator. Temperature control inside the evacuated sample chamber was accomplished with water-cooling and electrically heating the brass-block sample holder. Two-dimensional diffraction images were recorded using a Bruker Hi-Star multi-wire area detector located at the end of a 4.38 m evacuated flight tube and corrected for detector response before analysis. SAXS measurements for samples PLA-PM-PLA (7.6–33–6) and PLA-PM-PLA (6.1–99–6.1) were performed at the Advanced Photon Source (APS) on beamline 5 ID-D, which is maintained by the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT). The x-ray source operated at a wavelength of 0.8856 Å with a sample to detector distance of 8552 mm calibrated with silver behenate. Temperature control was performed by electrical heating of the sample stage.
Appendix 1: Biodegradable Pressure-Sensitive Adhesives

Under ambient pressure in air. The flight tube was evacuated. Two-dimensional diffraction images were recorded using a Mar 165 mm CCD x-ray detector at a resolution of 2048 x 2048. The two-dimensional images were azimuthally integrated and reduced to the one-dimensional form of scattered intensity versus the spatial frequency \( q \).

Tensile deformation experiments were carried out at room temperature using a Rheometrics Scientific Minimat instrument operated at a cross-head speed of 5 mm/min. The sample gage length was 5 mm, the gage width was 3 mm, and the gage thickness was 0.2 mm. Rheological testing was performed on the as-synthesized samples with an ARES (Rheometric Scientific, Piscataway, NJ) with 8-mm parallel plates. The dynamic moduli were measured as a function of temperature at frequency of 1 rad/s, a strain around 1\%, and at a ramp rate of 3 °C min\(^{-1}\). Low-temperature measurements were performed by heating the sample above the order-disorder transition or glass transition of the PLA, increasing the distance between the parallel plates to around 5 mm thereby stretching the sample, and subsequently cooled to the test temperature. This allowed for the measurement of the moduli in the glassy region, in which the stiffness of the sample would have otherwise caused compliance errors and transducer resonance.

### A1.2.3 Adhesion Measurements

Solutions of the PSAs in ethyl acetate (40-50 wt\% polymer) were coated on Canon type E transparency films and dried in a 90 °C oven for 10 minutes. The film
Appendix 1: Biodegradable Pressure-Sensitive Adhesives

thickness target was 1 mil (1 milli-inch = 25.4 µm). The films were then transferred to a room with controlled temperature and humidity of 22 °C (±1.5 °C) and 50% (± 2% room humidity) and remained in the room for at least 3 h before testing.

PSA sample performance was evaluated using three tests. The peel strength of the PSAs was measured using an IMASS Inc. (Accord, MA) 180° Slip/Peel Tester Model SP101B at a peel rate of 12 inches min⁻¹. One inch wide polyester backed films were peeled from Pressure-Sensitive Tape Council, PSTC-grade polished stainless steel panels (ChemInstruments). Test laminates were rolled with a 5.0 lb ASTM quality manual roller. The average peel force and standard deviation from at least three tests were reported for each sample. Shear test strips were prepared with a contact area of 0.5 x 0.5 inches between PSTC-grade polished stainless steel panels and the adhesive. Samples were rolled with a 5 lb ASTM quality manual roller. 500 gram weights were attached to the bottom of the test strips. The average time in minutes for the weight to pull the polyester-backed films from the plate for at least three tests was reported for each sample. Tack was measured using the IMASS Inc. (Accord, MA) 180° Slip/Peel Tester Model SP101B with a 10 N load cell. A stainless steel cylindrical probe with a diameter of 5 mm contacted the film, was held at a constant force for 15 sec, and was then raised from the surface at a fixed rate. The resulting maximum force was recorded. The probe was cleaned with a dry Kimwipe before each test. The average tack force and standard deviation from at least 15 tests were reported for each sample.
A1.3 Results and Discussion

A1.3.1 Synthesis and Characterization

PLA–PM–PLA triblock copolymers of various compositions were prepared via a two-step process as described in Chapter 2. The triblock copolymers listed in Table A1.1 are labeled according to the number average molecular weights (determined by $^1$H NMR spectroscopy) of each block in kg mol$^{-1}$. Consistent with the triblock copolymers synthesized in previous chapters, clean triblock formation was indicated by the shift of the SEC peak of the triblock copolymer relative to that of the respective PM homopolymer. The copolymers were prepared on a multigram scale and were free of significant PM or PLA homopolymer as determined by SEC and $^1$H NMR spectroscopy. All polymers exhibited narrow molecular weight distributions ($\text{PDI} = 1.05–1.31$). The tackifier, Aquatac (20.1 kg mol$^{-1}$ as measured by SEC), was blended with 80 wt% PLA-PM-PLA (6.1–99–6.1) for adhesive testing.

The thermal properties of the polymers and the ordered morphology of the triblock copolymers were investigated by DSC and SAXS, respectively. All of the polymers were amorphous with glass transitions corresponding to their respective components (Table A1.1). The tackifier had two glass transitions at –16 °C and 36 °C. The glass transition at –16 °C corresponds to the pentaerythritol ester, which is the majority component of the tackifier. The higher glass transition is most likely a surfactant that is also present in the tackifier. Adding 20 wt% of tackifier to 80 wt% PLA-PM-PLA (6.1–99–6.1) resulted in broadening of the glass transition temperature of the PM block relative to pure PLA-PM-PLA (6.1–99–6.1), suggesting the tackifier
Table A1.1 Characterization of polylactide-\textit{b}-polymenthide-\textit{b}-polylactide triblock copolymers

<table>
<thead>
<tr>
<th>polymer</th>
<th>$M_n$ (NMR) (kg/mol)</th>
<th>% PLA\textsuperscript{a} (NMR)</th>
<th>$M_n$ (SEC) (kg/mol)</th>
<th>PDI</th>
<th>$T_{g, PM}$\textsuperscript{b} (°C)</th>
<th>$T_{g, PLA}$\textsuperscript{b} (°C)</th>
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<tbody>
<tr>
<td>PLA-PM-PLA (2.5–34–2.5)</td>
<td>2.5–33.5–2.5</td>
<td>12.8</td>
<td>39.5</td>
<td>1.18</td>
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<td>33</td>
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<td>1.31</td>
<td>–23</td>
<td>47</td>
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<td>PLA-PM-PLA (6.1–99–6.1)</td>
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<td>10.9</td>
<td>86.3</td>
<td>1.24</td>
<td>–23</td>
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<tr>
<td>80 PLA-PM-PLA (6.1–99–6.1) + 20 tackifier</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>–20</td>
<td>24</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Mass percent PLA calculated from $^1$H NMR spectroscopy and composition of the triblock copolymers. \textsuperscript{b} DSC program: cool at 100 °C min\textsuperscript{–1} to –60 °C, equilibrate, heat at 10 °C min\textsuperscript{–1} to 200 °C. The $T_g$ values were determined from the final heating ramp data.
is miscible with the PM block (Figure A1.1). The PM glass transition of the blend increased by 3 °C, approaching the $T_g$ of the tackifier (Table A1.1). We observed a decrease in the glass transition of the PLA blocks in the blend compared to pure PLA-PM-PLA (6.1–99–6.1). This difference is most likely due to the error in estimation of the broad PLA $T_g$ for both the pure polymer and the blend. However, it is possible that the tackifier is miscible with the PLA block, which would also result in a lower PLA glass transition. SAXS analysis of PLA-PM-PLA (7.6–33–7.6) and PLA-PM-PLA (6.1–99–6.1) at 25 °C and 45 °C exhibited a principal reflection, $q^*$, followed by broad oscillations in intensity consistent with microphase-separated domains and no long-range order (Figure A1.2), whereas PLA-PM-PLA (2.5–34–2.5) exhibited intensity patterns consistent with a disordered state. As expected, the domain spacing of the triblock copolymers PLA-PM-PLA (7.6–33–7.6) and PLA-PM-PLA (6.1–99–6.1) increased with increasing molecular weight from 22.2 nm to 23.0 nm, respectively. For unknown reasons, the domain spacing of PLA-PM-PLA (6.1–99–6.1) was slightly lower than anticipated.

A1.3.2 Tensile Testing and Rheology of PLA–PM–PLA PSAs

For the purpose of evaluation of the triblock copolymers as pressure-sensitive adhesives, we tested the mechanical properties of PLA-PM-PLA (7.6–33–7.6) pulled to failure. The tensile properties of the PLA-\textit{b}-PM-\textit{b}-PLA triblock copolymer were characteristic of traditional TPEs. Representative stress-strain plots for the triblock copolymer PLA-PM-PLA (7.6–33–7.6) pulled to ultimate tensile failure are shown in
Figure A1.1 DSC traces of the triblock copolymers and blend. Procedure: Heat to 120 °C, cool at 10 °C min$^{-1}$ to −100 °C, heat at 10 °C min$^{-1}$ to 120 °C. The traces were taken from the final heating data.
Figure A1.2 SAXS analysis at 25 °C of PLA-PM-PLA (2.5–34–2.5) (University of Minnesota), at 45 °C of PLA-PM-PLA (7.6–33–7.6) (Advanced Photon Source), and at 25 °C of PLA-PM-PLA (6.1–99–6.1) (Advanced Photon Source)
Figure A1.3. At low strains a linear response was observed in the stress-strain curve with a relatively low Young’s modulus of 0.78 MPa. Beyond the low strain elastic region the triblock copolymer shows yielding behavior followed by strain-hardening before ultimate failure (ultimate tensile strength = 3.8 MPa, ultimate elongation = 870%). Strain-hardening fulfills the typical requirement of an adhesive to fail without leaving a sticky residue on the surface.\(^5\) Multiple attempts to make tensile bars of the other samples failed due to their soft and adhesive nature.

Rheology measurements of PLA-PM-PLA (2.5–34–2.5), PLA-PM-PLA (7.6–33–7.6), PLA-PM-PLA (6.1–99–6.1) and 80 PLA-PM-PLA (6.1–99–6.1) + 20 tackifier blend are shown in Figure A1.4. In all systems, the storage modulus, \(G'\), and the loss modulus, \(G''\), at low temperature are high, and the material is glassy. The first drop in the storage modulus corresponds to the glass transition of the rubbery matrix. The next transition, \(T_g\) of the polylactide phase, is present in all samples. The final transition shown in Figures 6.4c and d corresponds to the order-disorder transition (ODT), where we observe a terminal drop in the modulus, and the material behaves as a typical homopolymer. At high temperature and low modulus the instrument loses sensitivity and \(G'\) appears to plateau (see 6.4b and 6.4d) rather than continue to drop (see 6.4c).

The dynamic moduli versus temperature for PLA-PM-PLA (6.1–99–6.1) and 80 PLA-PM-PLA (6.1–99–6.1) + 20 tackifier blend (Figure A1.4c and d) reveal the effect of the tackifier on the rheological characteristics of the block copolymer. The first drop in the storage modulus corresponding to the glass transition of the rubbery matrix
Figure A1.3 Representative stress-strain curves of the mechanical failure of the PLA-PM-PLA (7.6–33–7.6)
Figure A1.4 Dynamic moduli as a function of temperature at 1 rad s\(^{-1}\) and at a ramp rate of 3 °C min\(^{-1}\) for (a) PLA-PM-PLA(2.5–34–2.5), (b) PLA-PM-PLA (7.6–33–7.6), (c) PLA-PM-PLA (6.1–99–6.1) and (b) 80 PLA-PM-PLA (6.1–99–6.1) + 20 tackifier
(polymenthide for the pure triblock copolymer in Figure A1.4c and the polymenthide/tackifier blend in Figure A1.4d) broadens in the blend due to the tackifier, with the drop in $G'$ shifting from approximately $-23 \, ^\circ C$ (Figure A1.4c) to approximately $-18 \, ^\circ C$ (Figure A1.4d). These shifts will result in improved performance of the blend at short timescales, such as those required for peeling. The next transition, $T_g$ of the polylactide phase, is nearly the same value for both the pure triblock copolymer and the blend, evidence that the tackifier is miscible only with the polymenthide matrix and will dilute the entanglements in that phase so that crack propagation can be controlled and minimized.\textsuperscript{1-3,5} The order-disorder temperature is lower in the blend than in the pure triblock copolymer. The $T_{ODT}$ is $100 \, ^\circ C$ for the pure homopolymer (Figure A1.4c) and $85 \, ^\circ C$ for the blend (Figure A1.4d).

All three of the triblock copolymers at room temperature exhibit a plateau modulus above the Dahlquist criterion for tack ($G' \leq 3 \times 10^5 \, Pa$) (Figures 6.4a-c).\textsuperscript{16} The plateau modulus at room temperature for PLA-PM-PLA (6.1–99–6.1) is reduced from $3.4 \times 10^5 \, Pa$ to $1.4 \times 10^5 \, Pa$ for the PLA-PM-PLA (6.1–99–6.1)/tackifier blend, which is below the Dahlquist criterion (Figure A1.5). Below the Dahlquist criterion, good wetting and contact can occur between the adhesive and the substrate.\textsuperscript{16} The plateau modulus can also be used to calculate the entanglement molecular weight ($M_e$) of the polymenthide matrix. The Guth-Smallwood equation\textsuperscript{17} for filled systems has been applied previously\textsuperscript{7,18} to calculate the $M_e$ for phase-separated triblock copolymer systems:

$$G_N^0 = \rho RT(1 + 2.5V + 14.1V^2) / M_e$$

(6.1)
Figure A1.5 Storage moduli for PLA-PM-PLA (6.1–99–6.1) and 80 PLA-PM-PLA (6.1–99–6.1) + 20 tackifier as a function of temperature at 1 rad s\(^{-1}\) and at a ramp rate of 3 °C min\(^{-1}\).
where \( \rho \) is the density of the rubbery phase, \( R \) is the gas constant, \( T \) is the temperature, and \( V \) is the volume fraction of polylactide. For the blend, the density of the rubbery phase is assumed to be the same as the triblock copolymer. Applying this method to the triblock copolymer PLA-PM-PLA (6.1–99–6.1) indicates a \( M_e \) value of 13 kg mol\(^{-1}\), the first \( M_e \) recorded for polymnthide. The \( M_e \) for the blend increased to 31 kg mol\(^{-1}\), suggesting improved tack properties for the blend.

### 6.3.3 Adhesion Testing

Adhesive tests including those that evaluate 180° peel, tack and shear were performed for all samples (Table A1.3, Figures 6.6-6.8). For comparison, 180° peel and tack were tested on Post-it notes, Scotch tape, and electrical tape (Table A1.3). Peel strength is the force required to remove a PSA-coated material from a surface. Depending on the mode of failure, the peel strength is a measure of the adhesive or cohesive strength.\(^2\)\(^-\)\(^4\) For example, during the 180° peel test residue from the PLA-PM-PLA (2.5–34–2.5) adhesive was left on the plate. Therefore, the peel strength of PLA-PM-PLA (2.5–34–2.5) is a measure of the cohesive strength of the sample. Most likely this cohesion failure is due to the absence of physical crosslinks in the disordered structure. As the cohesive strength of the elastomer increases, the peel strength improves. However, an optimum exists past which increasing cohesion will eventually reduce peel strength by reducing the ability to wet the substrate.\(^2\)\(^-\)\(^4\) For example, increasing the molecular weight of the PLA blocks from 2.5 kg mol\(^{-1}\) to 7.6 kg mol\(^{-1}\) increased the glass transition of the PLA blocks (Table A1.2), thereby improving the
Table A1.3 Adhesion properties of the triblock copolymers and blend

<table>
<thead>
<tr>
<th>polymer</th>
<th>180° peel strength (N)</th>
<th>Tack (N)</th>
<th>Shear Strength (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-PM-PLA (2.5–34–2.5)</td>
<td>0.15 ± 0.02</td>
<td>0.75 ± 0.06</td>
<td>20 ± 10</td>
</tr>
<tr>
<td>PLA-PM-PLA (7.6–33–7.6)</td>
<td>0.01 ± 0.00</td>
<td>0.20 ± 0.03</td>
<td>3.3 ± 1.7</td>
</tr>
<tr>
<td>PLA-PM-PLA (6.1–99–6.1)</td>
<td>0.03 ± 0.01</td>
<td>0.17 ± 0.01</td>
<td>10,000+</td>
</tr>
<tr>
<td>80 PLA-PM-PLA (6.1–99–6.1) + 20 tackifier</td>
<td>0.17 ± 0.01</td>
<td>0.22 ± 0.07</td>
<td>2,500+</td>
</tr>
<tr>
<td>Post-it note</td>
<td>0.01 ± 0.00</td>
<td>0.09 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Scotch tape</td>
<td>0.37 ± 0.04</td>
<td>0.55 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>electrical tape</td>
<td>0.54 ± 0.04</td>
<td>0.41 ± 0.07</td>
<td></td>
</tr>
</tbody>
</table>

Figure A1.6 Effect of adhesive composition on the peel strength
Appendix 1: Biodegradable Pressure-Sensitive Adhesives

Figure A1.7 Effect of adhesive composition on the tack

Figure A1.8 Effect of adhesive composition on the shear strength
Appendix 1: Biodegradable Pressure-Sensitive Adhesives

ability of the blocks to physically cross-link at room temperature and improving the cohesive strength. At the same time, however, the adhesive strength decreased, as evinced by the decreased peel strength. Synthesis of a block copolymer with lower PLA molecular weight and higher PM content (sample PLA-PM-PLA (6.1–99–6.1)) improved the peel strength only slightly. Finally, adding only 20 wt% of tackifier to PLA-PM-PLA (6.1–99–6.1) increased the peel strength by almost 6-fold (Table A1.3).

The tack of PSAs is another measure of the adhesive strength (or cohesive strength depending on the mode of failure). Tack is the resistance of the adhesive film to detach from a substrate; it is the ability to form an instant bond when brought into low pressure contact with a substrate. Triblock copolymer PLA-PM-PLA (2.5–34–2.5) was the only sample that did not separate cleanly from the probe surface, again resulting in measurement of the cohesive strength rather than the adhesive strength. Overall, the tack of the triblock copolymers was consistent with the peel strength.

The shear test is a measurement of the resistance to flow under an applied load. In this test, all samples except PLA-PM-PLA (7.6–33–7.6) failed cohesively within the film rather than at the interface between the adhesive and stainless steel surface. Extremely low values of shear were obtained for PLA-PM-PLA (2.5–34–2.5) and PLA-PM-PLA (7.6–33–7.6). Impressive shear values of over 10,000 minutes were achieved for PLA-PM-PLA (6.1–99–6.1); these tests were stopped because of the limits of the timer and not cohesive failure. Adding tackifier to PLA-PM-PLA (6.1–99–6.1) results in a significant decrease in the shear strength compared to PLA-PM-
Appendix 1: Biodegradable Pressure-Sensitive Adhesives

PLA (6.1–99–6.1). However, relative to commercial PSAs, the shear value of 2500 minutes for the tackifier blend is competitive.²

A1.4 Summary

PLA–PM–PLA thermoplastic elastomers are environmentally friendly alternatives to the current PS–PI–PS triblock copolymers used in PSAs. Model PSAs were prepared from three PLA–PM–PLA triblock copolymers of varied wt% PLA. All copolymers displayed a plateau modulus above the Dahlquist criterion for tack. A tackifier was employed and blended with PLA-PM-PLA (6.1–99–6.1), and increased the $T_g$ of the matrix while simultaneously increasing $M_e$ and decreasing $T_{ODT}$. Furthermore, the tackifier successfully lowered the plateau modulus to below the Dahlquist criterion for tack. Adhesive properties were measured through 180° peel, tack, and shear tests. PLA-PM-PLA (2.5–34–2.5) displayed low cohesive strength and high adhesive strength whereas PLA-PM-PLA (7.6–33–7.6) had high cohesive strength and low adhesive strength. A balance between cohesion and adhesion was obtained with the synthesis of a triblock copolymer with PLA blocks long enough to ensure physical cross-linking and a PM mid-block large enough to maintain a PLA wt% of approximately 10%. This polymer, PLA-PM-PLA (6.1–99–6.1), displayed shear strength over 10,000 minutes (over 7 days). The 180° peel and tack increased considerably with the addition of the tackifier while the shear strength remained relatively high (2,500 min). These results demonstrate the potential use of PLA–PM–PLA triblock copolymers as a biodegradable pressure-sensitive adhesive.
A1.5 Acknowledgments

This work was supported primarily by the MRSEC program of the National Science Foundation under Award Number DMR-0212302. We also acknowledge the Petroleum Research Fund (grant no. 45891-AC7), the National Science Foundation (grant no. CHE-9975357) and Cargill, Inc. for partial support of this work. We also acknowledge Dr. Steve Severtson and Dr. Jiguang Zhang (University of Minnesota) for assistance with the solvent coating and adhesion testing.

A1.6 References


Appendix 1: Biodegradable Pressure-Sensitive Adhesives


