

## Aliphatic Polyester Block Polymers: Renewable, Degradable, and Sustainable

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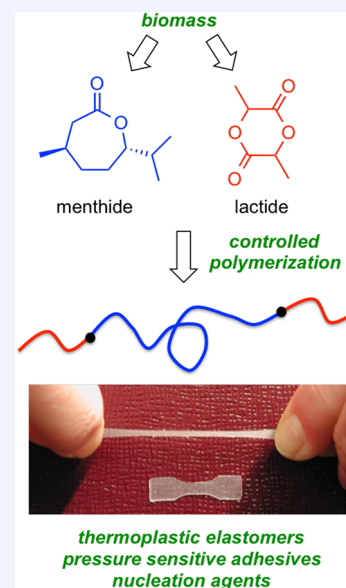
**CONSPECTUS:** Nearly all polymers are derived from nonrenewable fossil resources, and their disposal at their end of use presents significant environmental problems. Nonetheless, polymers are ubiquitous, key components in myriad technologies and are simply indispensable for modern society. An important overarching goal in contemporary polymer research is to develop sustainable alternatives to “petro-polymers” that have competitive performance properties and price, are derived from renewable resources, and may be easily and safely recycled or degraded. Aliphatic polyesters are particularly attractive targets that may be prepared in highly controlled fashion by ring-opening polymerization of bioderived lactones. However, property profiles of polyesters derived from single monomers (homopolymers) can limit their applications, thus demanding alternative strategies. One such strategy is to link distinct polymeric segments in an A–B–A fashion, with A and B chosen to be thermodynamically incompatible so that they can self-organize on a nanometer-length scale and adopt morphologies that endow them with tunable properties. For example, such triblock copolymers can be useful as thermoplastic elastomers, in pressure sensitive adhesive formulations, and as toughening modifiers. Inspired by the tremendous utility of petroleum-derived styrenic triblock copolymers, we aimed to develop syntheses and understand the structure–property profiles of sustainable alternatives, focusing on all renewable and all readily degradable aliphatic polyester triblocks as targets.

Building upon oxidation chemistry reported more than a century ago, a constituent of the peppermint plant, (–)-menthol, was converted to the  $\epsilon$ -caprolactone derivative menthide.

Using a diol initiator and controlled catalysis, menthide was polymerized to yield a low glass transition temperature telechelic polymer (PM) that was then further functionalized using the biomass-derived monomer lactide (LA) to yield fully renewable PLA–PM–PLA triblock copolymers. These new materials were microphase-separated and could be fashioned as high-performing thermoplastic elastomers, with properties comparable to commercial styrenic triblock copolymers. Examination of their hydrolytic degradation (pH 7.4, 37 °C) revealed retention of properties over a significant period, indicating potential utility in biomedical devices. In addition, they were shown to be useful in pressure-sensitive adhesives formulations and as nucleating agents for crystallization of commercially relevant PLA.

More recently, new triblocks have been prepared through variation of each of the segments. The natural product  $\alpha$ -methylene- $\gamma$ -butyrolactone (MBL) was used to prepare triblocks with poly( $\alpha$ -methylene- $\gamma$ -butyrolactone) (PMBL) end blocks, PMBL–PM–PMBL. These materials exhibited impressive mechanical properties that were largely retained at 100 °C, thus offering application advantages over triblock copolymers comprising poly(styrene) end blocks. In addition, replacements for PM were explored, including the polymer derived from 6-methyl caprolactone (MCL).

In sum, success in the synthesis of fully renewable and degradable ABA triblock copolymers with useful properties was realized. This approach has great promise for the development of new, sustainable polymeric materials as viable alternatives to nonrenewable petroleum-derived polymers in numerous applications.



### ■ BACKGROUND AND CONTEXT

Polymers, the molecules of plastic, are predominantly derived from fossil feedstocks and are annually produced on the teragram scale. They are inexpensive, in general, and are remarkably useful; lightweight, durable, protective, conductive, and self-healing are just a few of the many attributes of modern polymers that render them critical in countless technologies. Yet, such polymers are “challenged” with respect to sustainability. The Earth harbors finite carbon-based feedstocks that are being rapidly depleted by our increasing energy demand. Moreover, environmental impacts from the indis-

criminate disposal of polymers after their (often brief) use can be severe. In the long term, current paradigms for the generation and disposal of polymers are simply unsustainable. The key to shifting to sustainable alternatives will be to prepare both existing and new low-cost polymers with competitive performance properties from renewable feedstocks. In addition, to address the end-of-life issue, we must also develop polymers that can be more easily recycled, autonomously degraded to

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innocuous byproducts over reasonable time scales, or safely incinerated to recover their embedded energy.<sup>1–4</sup> In fact, many strategies to prepare commodity polymers like polyethylene, polypropylene, polystyrene, and polyethylene terephthalate from renewable feedstocks are being pursued commercially. In this Account, we focus our attention on a class of advanced polyesters that can meet key sustainability and performance requirements.

Among the sustainable polymers that may be considered, aliphatic polyesters present many attractive attributes. They can be prepared from renewable biomass-derived resources and can be recycled, composted, and incinerated with low environmental impact. They can be synthesized with exquisite molar mass, topological, and stereochemical control through ring-opening transesterification polymerization (ROTEP) of cyclic monomeric esters (lactones) using a variety of metal and organic catalysts.<sup>5–10</sup> Poly(lactide) (PLA) is an illustrative example.<sup>11</sup> Industrially produced on  $10^8$  kg year<sup>-1</sup> scale through the ROTEP of lactide,<sup>12</sup> PLA is now being used in numerous fiber, food packaging, and durable goods applications. These applications depend on the specific properties of PLA homopolymers, which vary with tacticity, among other factors.<sup>13</sup> However, the property profile of PLA is relatively narrow such that its broader use in diverse applications is limited. One strategy for addressing this issue focuses on the preparation of PLA-rich polymer blends.<sup>14</sup> A strategy that has even greater appeal because of the ability to precisely control properties involves the preparation of aliphatic polyester block polymers. While there are examples of such block polymers in the literature,<sup>15–17,33</sup> the goal of wholly renewable and degradable examples still represents a significant challenge. Furthermore, establishing foundational structure–property relationships in such materials is still needed. There is no doubt that this class of biorenewable multiphase polymers holds tremendous promise for the future.<sup>16,18,19</sup>

Styrenic ABA triblock copolymers represent the most useful, highest volume, and least expensive class of block polymers available today. These hybrid macromolecules are characterized by glassy poly(styrene) end blocks (A) and rubbery (i.e., low glass transition temperature) midblocks (B) such as poly(butadiene) or poly(isoprene). Key to the success of ABA triblocks in thermoplastic elastomers, pressure-sensitive adhesives, and toughening modifiers is the incompatibility between the A and B blocks that leads to self-organization in which relatively pure A and B domains are established on a molecular (i.e., nanoscopic) length scale.<sup>20</sup> The primary determinate of the ordered morphology adopted in the solid state is the composition of the material. Small fractions of the glassy poly(styrene) end blocks lead to a rubbery matrix consisting of majority poly(diene) midblock reinforced with nanoscopic spherical poly(styrene) domains. As the fraction of poly(styrene) increases, cylindrical or lamellar poly(styrene) domains can form. In the extreme of high poly(styrene) fractions, spherical inclusions of poly(diene) are dispersed through the glassy matrix. This range of morphologies leads to dramatic differences in the physical properties; strong and soft elastomers or rigid and tough plastics can be generated depending on the fraction of poly(styrene).

In addition to composition, the degree of incompatibility, typically parametrized by the Flory–Huggins interaction parameter  $\chi$ , between the blocks is an important characteristic. Ordered structures can be adopted at lower molar masses if the blocks are highly incompatible (relatively large values of  $\chi$ ), as

in the case of amphiphilic block polymers. More chemically similar blocks must be of higher molar mass in order to self-assemble. Thus, the balance between order and disorder depends on the product of molar mass and  $\chi$ . Moreover, the magnitude of  $\chi$  is inversely proportional to temperature. As a result, the order–disorder transition (ODT) can be accessed by changing temperature, which has important implications because processing is more facile in the disordered state, but physical properties are optimal in the ordered state. Understanding these thermodynamic aspects of block polymer self-assembly are critically important for materials design.<sup>21</sup>

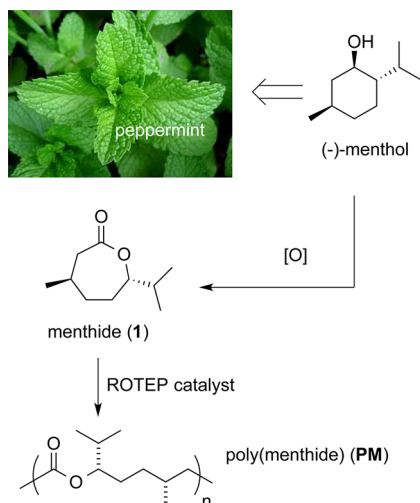
We have taken on the challenge of synthesizing and characterizing ABA triblocks that incorporate biorenewable, degradable, and otherwise higher performing sustainable blocks. Our work in sustainable ABA triblocks began over a dozen years ago by replacing the poly(styrene) end blocks with poly(lactide) in poly(lactide)-*block*-poly(isoprene)-*block*-poly(lactide) triblocks.<sup>22,23</sup> In that work, we established the utility of these materials, inspiring us to move to all polyester, all renewable, and all readily degradable triblocks that could compete with the ubiquitous styrenic block polymers. In this Account, we describe our successful efforts toward this goal, which included development and study of the catalytic polymerization of a “new” renewable monomer, its use in the controlled construction of polyester triblock copolymers, characterization of the new materials, and studies of their degradation and uses as thermoplastic elastomers and in pressure-sensitive adhesive formulations. Through this work, we have developed a class of sustainable polymers with useful properties and have laid a foundation for future efforts to prepare new members that may find numerous applications.

## ■ A MONOMER FROM MINT

In order to prepare discrete block polymers, controlled polymerizations are typically needed. Thus, to access an ABA triblock with glassy poly(lactide) (or semicrystalline poly(glycolide) or poly(trimethylene carbonate)) end blocks and a rubbery low glass transition temperature ( $T_g$ ) midblock, ROTEP of a cyclic ester that will give a noncrystalline midblock is a requisite first step. Such low  $T_g$  aliphatic polyesters that are derived from renewable resources are not readily available. Reasoning that an established key to avoiding crystallization is to incorporate bulky aliphatic substituents on the polymer chain, we sought bioderived lactones with two key characteristics: (a) large aliphatic pendant groups and (b) ring strain sufficient to render ROTEP thermodynamically favorable. Initially, we identified (–)-menthede (**1**, Scheme 1), which can be derived from (–)-menthol, a natural product used extensively in the flavor, fragrance, pharmaceutical, and confectionary industries that is well-known for its “cooling” properties when applied to the skin or inhaled. Interestingly, Baeyer and Villiger first reported the synthesis of **1** in 1899 via the oxidation of (–)-menthone as an example of their newly discovered transformation.<sup>24</sup> We noticed an early report by Hall et al.<sup>25</sup> (6 decades later) that reported that reaction of **1** with metallic sodium at 170 °C gave a “thick white hydr. gel” consistent with conversion of **1** to poly(menthede) (PM).

Initially using a discrete zinc catalyst that we had previously identified as being particularly active for ROTEP,<sup>26</sup> we closely examined the polymerization of toluene solutions of **1** to yield PM (Scheme 1).<sup>27</sup> Analysis of size-exclusion chromatography (SEC), matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS), and NMR spectroscopy data

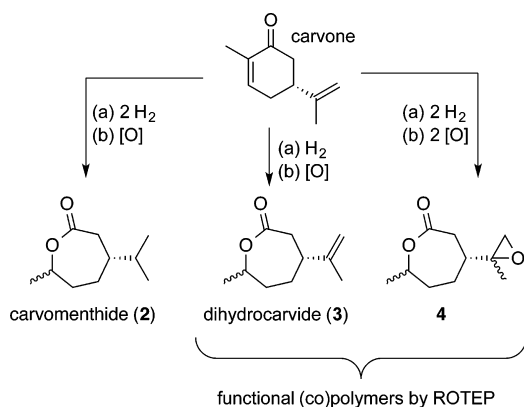
Scheme 1. Synthesis of Poly(menthede) (PM)



revealed the polymerization to be controlled, yielding polymers with molar masses approaching  $100 \text{ kg mol}^{-1}$ . Differential scanning calorimetry (DSC) analysis of the material gave a  $T_g \approx -25 \text{ }^\circ\text{C}$  and no crystallinity despite the stereochemical purity of the monomer. These findings indicated that the bulkiness of the substituents prevent this isotactic sample from crystallizing, akin to isotactic polyolefins with bulky substituents.<sup>28</sup> Measured thermodynamic parameters of  $\Delta H_p^\circ = -16.8 \pm 1.6 \text{ kJ mol}^{-1}$  and  $\Delta S_p^\circ = -27.4 \pm 4.6 \text{ J mol}^{-1} \text{ K}^{-1}$  corresponded to relatively low equilibrium monomer concentrations of  $0.031 \pm 0.018 \text{ M}$  at  $25 \text{ }^\circ\text{C}$  and  $0.120 \pm 0.063 \text{ M}$  at  $100 \text{ }^\circ\text{C}$ . Taken together, the results show that noncrystalline, low  $T_g$  samples of PM of defined molar mass and low dispersity are readily accessible through ROTEP of **1**.

In later work, we showed that more versatile monomers related to **1** could also be readily prepared and polymerized (Scheme 2).<sup>29,30</sup> Dihydrocarvone and carvomenthone, which

Scheme 2. Biorenewable Monomers and Polymers Derived from Carvone



are hydrogenated versions of the natural product carvone, served as starting materials for the synthesis of carvomenthide (CM, **2**), a regioisomer of **1**, further-functionalized dihydrocarvide (D, **3**), and epoxy-lactone **4**. The homopolymers PCM and PD derived from ROTEP of **2** and **3**, respectively, featured similar  $T_g$  values as PM (range  $-20$  to  $-27 \text{ }^\circ\text{C}$ ). The olefin functionality in **3** offers intriguing opportunities for post-polymerization modifications, which we explored through (a)

cross-linking of PCM with dithiols and radical initiators<sup>30</sup> and (b) the use of  $\epsilon$ -caprolactone/3 copolymers for the synthesis of oligomeric polyols, which in turn were used to prepare novel polyurethane block polymers featuring a significant biorenewable component.<sup>31</sup> In addition, copolymerization of  $\epsilon$ -caprolactone and **4** yielded cross-linked materials derived from ring-opening of the lactone and epoxide groups.<sup>29</sup> These sustainable materials exhibited excellent shape memory properties of possible utility for biomedical applications, for example.

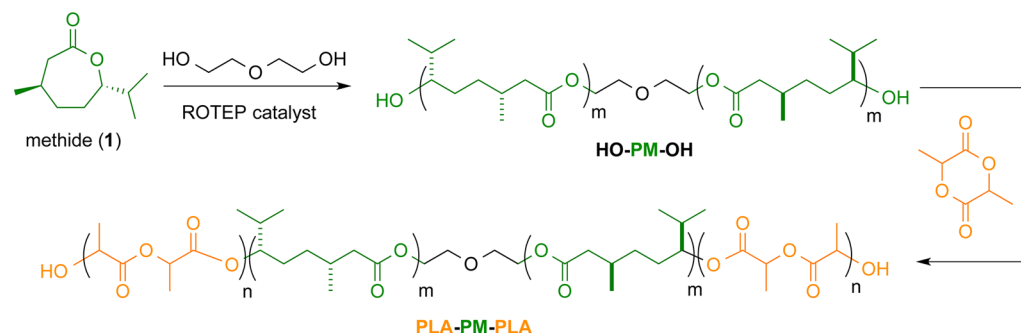
## ■ PLA–PM–PLA TRIBLOCK COPOLYMERS

We took advantage of the successful homopolymerization of **1** (Scheme 1) to build ABA triblock copolymers comprising PM as the midblock (B) segment, with PLA segments chosen as end blocks (Scheme 3).<sup>32</sup> Using diethylene glycol as initiator, ROTEP of **1** using the simpler and more readily available  $\text{ZnEt}_2$  as catalyst yielded  $\alpha,\omega$ -functionalized HO–PM–OH. After isolation and characterization, HO–PM–OH was used as an initiator for ROTEP of ( $\pm$ )-lactide catalyzed by  $\text{AlEt}_3$  to yield triblocks PLA–PM–PLA, with initially prepared samples having PM segment  $M_n = 10\text{--}43 \text{ kg mol}^{-1}$  and PLA content of  $20\text{--}52 \text{ wt } \%$ .<sup>33–35</sup> Key improvements subsequently implemented included development of (a) a green synthesis of **1** using aqueous oxone as oxidant instead of *m*-CPBA in  $\text{CH}_2\text{Cl}_2$  in the Baeyer–Villiger oxidation of ( $-$ )-menthone,<sup>35</sup> (b) a method for purification of **1** using crystallization rather than sublimation that enabled convenient larger scale synthesis ( $>100 \text{ g}$ ) of higher purity monomer in shorter time,<sup>36</sup> and (c) a one-pot synthesis procedure for PLA–PM–PLA wherein the commercially relevant tin octanoate was used as a catalyst for both polymerizations, performed in sequence under melt conditions at  $\sim 135 \text{ }^\circ\text{C}$ .<sup>35</sup> This later advance is particularly relevant to the practical synthesis of these materials under industrially relevant conditions.

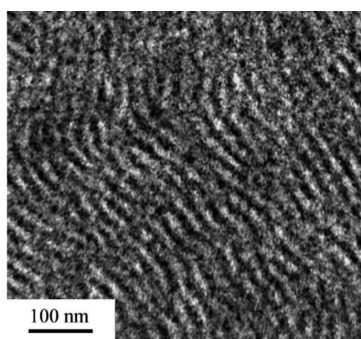
Using NMR spectroscopy, SEC, small-angle X-ray scattering (SAXS), and DSC, we confirmed the indicated block structures for the copolymers and showed that the PM and PLA segments were microphase-separated, a key characteristic required for thermoplastic elastomeric behavior.<sup>32,33,35</sup> The fidelity of the triblock architecture was not compromised by transesterification, as shown by  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy. Distinct glass transition temperatures consistent with microphase separation were evident in DSC traces, with the values for PM being essentially invariant ( $-21 \text{ }^\circ\text{C}$ ) and the poly(lactide)  $T_g$  values ranging from about  $45$  to  $60 \text{ }^\circ\text{C}$ . Triblocks with enantiomerically pure PLLA or PDLA segments also exhibited melting endotherms from which degrees of crystallinity of  $49\text{--}59\%$  were determined. Self-assembled morphologies such as lamellar and cylindrical structures that varied as a function of relative segment lengths were confirmed using SAXS, and the Flory–Huggins interaction parameter between PLA and PM was estimated to be  $\chi = 364T^{-1} - 0.50$  from analysis of the domain spacing of a lamellar sample of PLA–PM–PLA ( $4.6\text{--}10\text{--}4.6$ ) as a function of temperature. Transmission electron microscopy images for a sample of PLLA–PM–PLA ( $11\text{--}33\text{--}11$ ) were consistent with SAXS results and show crystalline PLLA domains (light) and preferentially stained amorphous regions (dark) that we infer contain predominantly PM (Figure 1).

Tensile testing results of the PLA–PM–PLA triblock copolymers verified their mechanical integrity and elastomeric nature. The highest performing samples from the standpoint of ultimate strength, elongation at break, and elastic recovery were those that contained semicrystalline poly(lactide) end blocks.



Scheme 3. Synthesis of PLA–PM–PLA Triblock Copolymers<sup>a</sup>

<sup>a</sup>The stereochemistry for lactide and the PLA segments is not indicated.

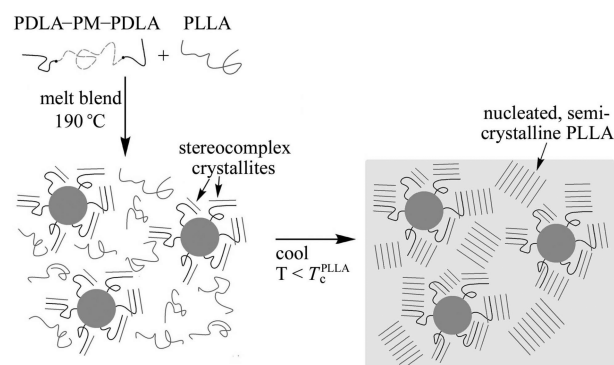


**Figure 1.** Representative TEM image of PLLA–PM–PLLA (11–33–11). Reproduced with permission from ref 33. Copyright 2009 American Chemical Society.

For example, PLLA–PM–PLLA (13–33–13) exhibited a Young's modulus  $E$  of  $26.8 \pm 2.1$  MPa, tensile strength  $\sigma_B$  of  $19.5 \pm 1.1$  MPa, and strain at break  $\varepsilon_B$  of  $765 \pm 40\%$ .<sup>33</sup> We were also able to improve upon these properties in mixtures of PLLA–PM–PLLA and PDLA–PM–PDLA containing only a minority of the enantiomeric PDLA–PM–PDLA. In these samples, poly(lactide) stereocomplex crystallites were formed in the end block domains. The semicrystalline samples behaved similarly to commercial styrenic ABA triblock polymers and hold promise as renewable surrogates for these widely useful materials.

With the semicrystalline triblocks in hand, we turned our attention to the nucleating ability of these hybrid macromolecules at low levels for the commercially relevant PLLA (Figure 2).<sup>34</sup> PLLA is slow to crystallize, and nucleating agents are often added to enhance the crystallization rate and degree of crystallinity.<sup>37</sup> We previously demonstrated that PDLA homopolymers were very effective nucleating agents,<sup>38,39</sup> and we hypothesized that by melt blending PDLA–PM–PDLA triblocks into a PLLA homopolymer the block polymers would form micelles and significantly increase the nucleant density. In fact, we showed that, compared to PLLA/PDLA homopolymer blends, nucleation efficiencies were higher. Thus, this “triblock nucleant” strategy has merit for future studies aimed at increasing the crystallization rate for PLLA.

Consideration of further applications of the PLA–PM–PLA triblocks required evaluation of their degradation characteristics. In a study aimed at assessing hydrolytic degradation, the behavior of PLA–PM–PLA and PLA and PM homopolymer samples immersed in phosphate buffered saline solution (pH 7.4, 37 °C) was compared over a 48 week period.<sup>40</sup> In all samples, a 20% decrease in molar mass preceded significant



**Figure 2.** Schematic representation of the nucleation of PLLA using PDLA–PM–PDLA triblock copolymers. Reproduced with permission from ref 34. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA.

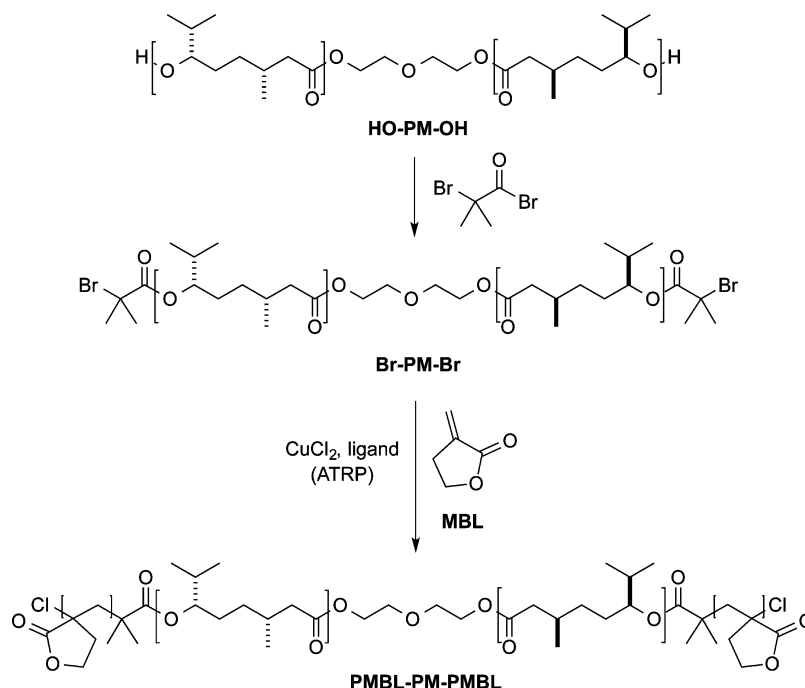
mass loss, with the level of mass loss of the triblocks being intermediate between PLA and PM homopolymers. The triblocks retained a significant amount of their tensile properties over the first half of the studied period, which is a key finding for potential biomedical applications.

In view of their degradation characteristics and the fact that ABA triblock polymers can be used as elastomers for pressure-sensitive adhesives (PSA), we reasoned that PLA–PM–PLA triblocks would be good candidates for renewable and degradable PSAs. We were able to show that by blending a high molar mass PLA–PM–PLA triblock with a commercially available and renewable rosin ester tackifier, PSAs were obtained with competitive tack and peel adhesion characteristics.<sup>41</sup> The shear strength of these materials was not as high as that of other commercial systems such as permanent tapes like Scotch tape, but these properties were at the level associated with removable PSAs. Again, these studies confirmed that the all renewable PLA–PM–PLA triblocks were quite good substitutes for styrenic-based systems in varied applications.

## ■ OTHER TRIBLOCK COPOLYMERS FEATURING PM MIDSEGMENTS

Seeking further improvements in the properties of renewable triblock copolymers, and in particular more competitive PSA behavior, we focused on alternatives to PLA end blocks while retaining the PM midblock. The renewable poly( $\alpha$ -methylene- $\gamma$ -butyrolactone) (PMBL)<sup>42</sup> drew our attention, as it was known to be a rigid, durable, and chemically/physically resistant thermoplastic ( $T_g = 195$  °C).<sup>43</sup> We anticipated that it would display the requisite incompatibility with PM and

Scheme 4. Synthesis of a Triblock Copolymer with PMBL End Blocks



because of its high  $T_g$  could be used in relatively small amounts as an end block and might yield thermoplastic elastomers that would retain their mechanical properties at high temperatures. PMBL may be prepared by free radical<sup>44</sup> and anionic<sup>45</sup> polymerization of  $\alpha$ -methylene- $\gamma$ -butyrolactone (MBL), which is found naturally in the common tulip and can be prepared readily from  $\gamma$ -butyrolactone.<sup>46</sup> Precedent for the suitability of PMBL came from reports of its use as hard segments in triblock copolymers with poly(*n*-butyl acrylate).<sup>44,47,48</sup>

We prepared the desired triblock copolymer, PMBL-PM-PMBL, by first derivatizing HO-PM-OH with 2-bromoiso-butyl bromide (Scheme 4).<sup>49</sup> Subsequent atom transfer radical polymerization (ATRP) with MBL led to PMBL-PM-PMBL, with samples with high molar mass PM (100 kg/mol) and low percentages of PMBL (6–20 wt %) being the primary targets because of their anticipated utility as PSAs. Microphase separation was evident from DSC, SAXS, and atomic force microscopy analyses. Most encouraging were the mechanical properties of the PMBL-PM-PMBL triblocks. We observed Young's modulus values ( $E = 17.3 \pm 0.85$  MPa for 9 wt % PMBL sample) comparable to related commercial poly(styrene)-*block*-poly(butadiene)-*block*-poly(styrene) (SBS),<sup>20</sup> strains in excess of 1600%, and tensile strengths similar to that of PLA-PM-PLA samples with high PLA fractions (>30 wt %).<sup>33</sup> Notably, only modest reduction of mechanical behavior at higher temperatures (100 °C) was found,<sup>49</sup> a significant improvement, with potential application advantages over triblock copolymers comprising poly(styrene) end blocks ( $T_g \sim 100$  °C).

## NEW DIRECTIONS

From our work on the synthesis and evaluation of poly(menthane)-containing triblock copolymers, it has become clear that poly(lactide) blocks flanking a low glass transition aliphatic polyester midblock can lead to interesting self-assembling block polymers with property profiles that can compete with the commercially relevant styrenic thermoplastic elastomers.

Importantly, we established that “clean” triblock architectures can be prepared using a difunctional initiator by sequential ROTEP steps as a result of limited transesterification between the growing poly(lactide) chain ends and the poly(menthane) midblock backbone when using simple, commercially available catalysts. Moreover, that these materials can be prepared under melt polymerization conditions bodes well for scale-up using commercial processes. Although we have not explored processing requirements, long-term performance attributes, or other practical issues associated with introduction of a new material into the marketplace, a clear limitation of the poly(menthane) systems is the cost of the menthane starting material, as it is derived from the oxidation of menthol, a molecule produced on large scale but at costs of  $\sim$ \\$20 per kilogram.<sup>50</sup> This limitation motivated the search for more practical low glass transition temperature, noncrystalline aliphatic polyesters that could be prepared by ROTEP and that could be readily incorporated into triblock polymers with poly(lactide) end blocks. To this end, we explored the use of poly(6-methyl caprolactone) as a midblock.

The cyclic ester 6-methyl caprolactone (MCL) can be prepared from the BV oxidation of methyl cyclohexanone, a readily available, low cost, albeit petroleum derived, compound. In fact, we showed that bulk polymerization of MCL followed by lactide using commercially relevant catalysts gave the corresponding triblock polymers with targeted molar masses and low dispersity.<sup>17</sup> Even the incorporation of one methyl group to the parent  $\epsilon$ -caprolactone resulted in an aliphatic polyester that is noncrystalline and resistant to transesterification. The triblocks microphase separated, and both cylindrical and lamellar morphologies were identified. In this system, the Flory-Huggins interaction parameter was determined from order-to-disorder transition temperatures for two symmetric triblocks, and PMCL and PLA were more compatible than poly(menthane) and poly(lactide) ( $\chi(T) = 61.2T^{-1} - 0.1$ ). In fact, the magnitude of the interaction parameter was nearly identical to that for poly(styrene) and poly(isoprene). Tensile

testing results showed that these materials had exceptional elastomer properties rendering them quite attractive for block copolymer-based applications. Finding a temperature that allows for facile processing (i.e., above the ODT) but limits depolymerization, thermal degradation, and transesterification between blocks will be a key challenge going forward.

## SUMMARY AND CONCLUSIONS

Aliphatic polyester triblock copolymers with poly(lactide) end blocks, low glass transition temperature, and noncrystalline midblocks are attractive and practical alternatives to commodity block polymers based on poly(styrene) and poly(diene)s. The former are produced through melt polymerization of cyclic esters in a sequential addition manner under much less stringent conditions than those of the solvent-based anionic polymerizations used to prepare styrenic block polymers. Poly(lactide) and poly(styrene) are essentially at price parity. Thus, the identification of aliphatic polyester midblocks that (i) have controlled architecture triblock polymers with poly(lactide) end blocks, (ii) are incompatible with poly(lactide), (iii) are noncrystalline, (iv) can be polymerized to high conversions, (v) are derived from renewable resources, (vi) are degradable, and (vii) are cost-competitive has laid the foundation for the development of new materials that could be potentially disruptive to the thermoplastic elastomer market. We are currently pursuing these targets and will build on the experience and foundations established in our previous work to realize this important end goal in sustainable polymers research.

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### Notes

The authors declare no competing financial interest.

### Biographies

**Marc A. Hillmyer** received his B.S. in Chemistry from the University of Florida in 1989 and his Ph.D. in Chemistry from the California Institute of Technology in 1994. After completing a postdoctoral research position in the University of Minnesota's Department of Chemical Engineering and Materials Science, he joined the Chemistry faculty at Minnesota in 1997. He is currently a Distinguished McKnight University Professor of chemistry and leads a research group focused on the synthesis and self-assembly of multifunctional polymers. He also serves as an Associate Editor for the ACS journal *Macromolecules* and is the director of the Center for Sustainable Polymers at the University of Minnesota, a National Science Foundation Center for Chemical Innovation.

**William B. Tolman** is a Distinguished McKnight University Professor at the University of Minnesota, Twin-Cities. He received a B.S. degree from Wesleyan University, CT, in 1983, and a Ph.D. from the University of California, Berkeley, in 1987. After a postdoctoral period, 1987–1990, at the Massachusetts Institute of Technology, he joined the faculty at the University of Minnesota. He is a member of the

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