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# Poly(tetramethyl glycolide) from Renewable Carbon, a Racemization-Free and Controlled Depolymerizable Polyester

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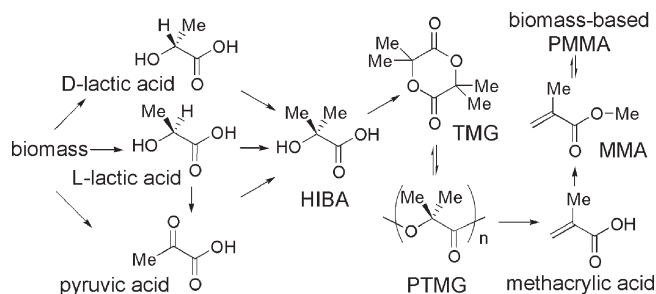
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The development of biomass-based polymers is one strategic step toward achieving a sustainable social system. A typical biomass-based polymer is poly(L-lactic acid) (PLLA), which through a combination of biological fermentation and chemical reaction can be synthesized from naturally abundant biomasses such as starch or cellulose.<sup>1</sup> PLLA shows good physical properties such as crystallinity, thermoplasticity, transparency, and a high melting point ( $T_m$ ) of around 170 °C.<sup>2</sup> It also has the excellent quality of being easily reproduced from the depolymerization product: L,L-lactide.<sup>3</sup> Hence, the likelihood that PLLA will become the plastic material of choice for sustainable systems has been attracting much interest from researchers. However, in practical applications, PLLA does have some drawbacks, such as slow crystallization,<sup>4</sup> low impact resistance,<sup>2</sup> hydrolyzability,<sup>5</sup> and racemization.<sup>6</sup> PLLA readily causes racemization from an L-unit to a D-unit in a chain under heating.<sup>7</sup> Such racemization proceeds by the mechanism of ester–semiacetal tautomerization, causing a decrease in optical purity and crystallinity.<sup>8</sup> This is a serious problem in the reproduction of practical materials via thermal depolymerization and repolymerization. A fundamental and complete solution to this problem requires a modification of the chemical structure of lactic acid.

In this study, in order to overcome the problems associated with PLLA while preserving its superior properties, a biomass-based and racemization-free polymer: poly(tetramethyl glycolide) (PTMG) possessing superior depolymerizability for the reproduction is developed. Previously, PTMG has been synthesized from petroleum by wholly chemical processes involving the ring-opening polymerization of tetramethyl glycolide (TMG), which is a cyclic dimer of  $\alpha$ -hydroxyisobutyric acid (HIBA).<sup>9</sup> HIBA itself has also required preparation over many steps from petroleum using the cyanhydrin method for methyl methacrylate production.<sup>10</sup> The methyl methacrylate production has been improved by some novel production processes such as the AVENEER method. Recently, a biosynthesis method of HIBA from renewable carbons has been achieved.<sup>11</sup> PTMG shows a high  $T_m$  at 185–190 °C<sup>9</sup> and a characteristic thermal degradability into methacrylic acid, TMG, acetone, etc.<sup>12</sup> However, the derivation of PTMG from biomass and its controlled depolymerization into monomers, which will become

Scheme 1. Total Synthetic Processes of PTMG and Its Depolymerization



required for many commonly used polymers in a future, are newly proposed in this study.

Renewable resources: D-/L-lactic acids and pyruvic acid derived from biomasses are employed as starting materials for the synthesis of HIBA in this study, which is an acyclic monomer of PTMG. The biomass-based HIBA is prepared by methylation of the acids and then converted into the cyclic dimer: TMG by a cyclic esterification. The following synthesis of polymer PTMG is carried out by a ring-opening polymerization of TMG. Moreover, the controlled depolymerization of PTMG is performed either to return to TMG or to convert to methacrylic acid depending on the use of a specific catalyst for each monomeric product.

Two synthetic routes of HIBA from the renewable resources were performed. One was the direct methylation of D-/L-lactic acid derivatives after the abstraction of  $\alpha$ -hydrogen on a chiral carbon: the other was the methylation of an  $\alpha$ -keto group of a pyruvic acid derivative by the Grignard reaction, which is an oxidized form of corresponding D-/L-lactic acid derivatives. Although the direct methylation has been reported in our recent research,<sup>13</sup> the methylation of the pyruvic acid derivative is a new finding introduced in this study. Results of the methylation are listed in Table 1. The methylation of methyl pyruvate by the Grignard reaction showed a 50% yield at room temperature. On the other hand, the direct methylation of the hydroxyl-group protected ethyl D-/L-lactate (HPEL), with protection provided by a methoxymethyl group, gave relatively high yields of 54–75% at –84 °C. These methylation reactions have the advantage of using multiple renewable resources: pyruvic acid and L-, D-, and D-/L-lactic acids without the need of high optical purity.

HIBA was obtained by the hydrolytic deprotection of methylated products with high yields of >74%. The cyclic dimerization of HIBA proceeded smoothly in the presence of the dehydration catalyst methane: sulfonic acid to isolate the cyclic dimer: TMG in a 67% yield. The ring-opening anionic polymerization of TMG that followed was achieved by using three initiators: EtOLi, *n*-BuLi, and *t*-BuLi, resulting in the preparation of a high molecular weight PTMG ( $M_n$  90 000) as shown in Table S1.

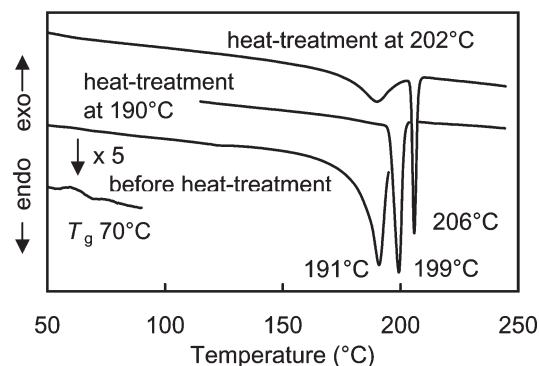
Previously, Deibig et al.<sup>9</sup> showed  $T_m$  of PTMG in a range of 180–190 °C, but no glass transition ( $T_g$ ) temperature was reported. The isolated PTMG showed  $T_m$  and  $T_g$  at 191 and 70 °C (Figure 1), respectively, about 15 °C higher than those of PLLA. The  $T_g$  transition signal was very weak, and the  $T_m$  peak shifted into higher temperatures of up to 206 °C with a corresponding increase in the heat treatment temperature. The weak  $T_g$  signal and high  $T_m$  value of PTMG suggest superior crystallization and heat resistance, respectively.

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**Table 1.** Synthesis of  $\alpha$ -Hydroxyisobutyric Acid (HIBA) Esters from Methyl Pyruvate and Hydroxyl Group Protected Ethyl Lactate (HPEL)

run	substrate (S)	reagent ( $R_1/R_2$ )	S/ $R_1/R_2$ [molar ratio]	temp/time [ $^{\circ}\text{C}/\text{h}$ ]	yield <sup>a</sup> [%]
1-1	methyl pyruvate	MeMgBr	1.0/1.0	rt/1	50
1-2	HPEL <sup>c</sup>	LiTMP/MeI	1.0/1.2/2.0	-84/4	54
1-3 <sup>b</sup>	HPEL	LDA/MeI	1.0/1.3/2.0	-84/4	75

<sup>a</sup> Calculated from GC. <sup>b</sup> Under the same conditions at ref 13. <sup>c</sup> Ethyl D-/L-lactate protected by a methoxymethyl group.

**Figure 1.** DSC profiles of heat-treated PTMG. Heating rate: 10  $^{\circ}\text{C min}^{-1}$  under a nitrogen flow of 20 mL  $\text{min}^{-1}$ . Heat treatment: 10 min.

An additional interesting result is the controllable depolymerization behavior of PTMG into TMG and methacrylic acid (MA). In the thermal degradation of PTMG, it has been reported that TMG, methacrylic acid, acetone, etc., are recovered as volatile products without any catalyst needed for the reaction control.<sup>12,14–17</sup> In this study, by using appropriate catalysts for the selective depolymerization, the thermal degradation of PTMG was controlled successfully to generate TMG or methacrylic acid as shown in Table 2. Recovered TMG can be used to reproduce PTMG. Another selectable product: MA was converted into a methacrylic ester: methyl methacrylate (MMA) after an esterification reaction. From the obtained MMA, a biomass-based poly(methyl methacrylate) (PMMA) with high molecular weight ( $M_n$  70 000 and  $M_w$  238 000) was produced by free-radical polymerization in bulk. This is an early report on the preparation of biomass-based PMMA.

These results reveal PTMG as a superior recyclable material by the virtue of its controllable conversion into each monomer.

In conclusion, the biomass-based and racemization-free polyester PTMG was synthesized from lactic and pyruvic acids as renewable resources. The high  $T_m$  ( $\sim 206$   $^{\circ}\text{C}$ ) and  $T_g$  (70  $^{\circ}\text{C}$ ) values of PTMG were confirmed, and the superior resource recyclability of PTMG was demonstrated showing selective reduction to TMG or methacrylic acid. Moreover, the preparation of biomass-based PMMA was reported.

**Table 2.** Catalytic Thermal Depolymerization of PTMG<sup>a</sup>

run	catalyst <sup>b</sup>	temp <sup>c</sup> [ $^{\circ}\text{C}$ ]	volatile products [%] <sup>d</sup>		
			TMG	methacrylic acid	acetone
2-1		283	2.9	57.1	40.0
2-2	Sn(Oct) <sub>2</sub>	265	80.8	19.2	0
2-3	MgO	235	17.7	80.6	1.6

<sup>a</sup> PTMG:  $M_n$  22 000,  $M_w$  32 000. <sup>b</sup> Catalyst 1 wt %. <sup>c</sup> Isothermal heating. <sup>d</sup> From  $^1\text{H}$  NMR analysis.

**Supporting Information Available:** Experimental details and the characterization data of  $^1\text{H}$  NMR, GPC, and DSC. The material is available free of charge via the Internet at <http://pubs.acs.org>.

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