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

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Biomass-based sustainable materials

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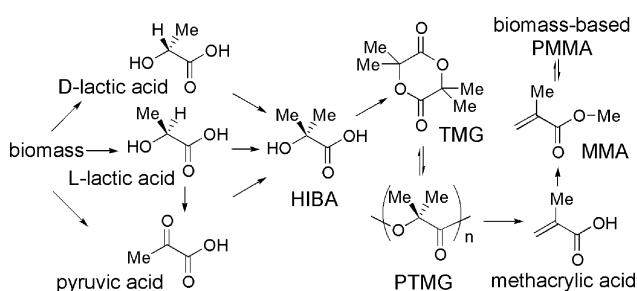
ABSTRACT. Racemization-free and depolymerization-controllable poly(tetramethyl glycolide) (PTMG) was synthesized from renewable resources: D/L-lactic acids and pyruvic acid. PTMG overcomes the undesirable properties of poly(lactic acid) such as low heat-resistance and racemization causing the decrease in crystallinity. PTMG was shown to have a higher melting point than 200 °C and to be a superior recyclable material capable of being depolymerized controllably into cyclic dimer tetramethyl glycolide (TMG) or methacrylic acid (MA) by using specific catalysts. PTMG can be reversibly synthesized from the depolymerized TMG. Moreover, biomass-based poly(methyl methacrylate) (PMMA) was prepared from the recovered MA.

KEYWORDS. Polylactic acid • Renewable resources • Ring-opening polymerization • Retro reactions • Depolymerization

The development of biomass-based polymers is one strategic step towards 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.¹ PLLA shows good physical properties such as crystallinity, thermoplasticity, transparency, and a high melting point (T_m) of around 170 °C.² It also has the excellent quality of being easily reproduced from the depolymerization product: L,L-lactide.³ 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,⁴ low impact resistance,² hydrolyzability,⁵ and racemization.⁶ PLLA readily causes racemization from an L to a D-unit in a chain under heating.⁷ Such racemization proceeds by the mechanism of ester-semiacetal tautomerization, causing a decrease in optical purity and crystallinity.⁸ 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 whilst 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 \pm -hydroxyisobutyric acid (HIBA).⁹ HIBA itself has also required preparation over many steps from petroleum using the cyanhydrin method for methyl methacrylate production.¹⁰ 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.¹¹ PTMG shows a high T_m at 185-190 °C⁹ and a characteristic thermal degradability into methacrylic acid, TMG, acetone, etc.¹² However, the derivation of PTMG from biomass and its controlled depolymerization into monomers, which will become 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.



Scheme 1. Total synthetic processes of PTMG and its depolymerization.

Table 1. Synthesis of \pm -hydroxy isobutyric 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 [°C/h]	Yield ^a [%]
1-1	methyl pyruvate	MeMgBr	1.0/1.0	r.t. / 1	50
1-2	HPEL ^c	LiTMP /MeI	1.0/1.2/2.0	-84 / 4	54
1-3 ^b	HPEL	LDA/MeI	1.0/1.3/2.0	-84 / 4	75

^aCalcd. from GC. ^bUnder the same conditions at reference.¹³ ^cEthyl D/L-lactate protected by a methoxymethyl group.

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 \pm -hydrogen on a chiral carbon: the other was the methylation of an \pm -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,¹³ 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-, L/D-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 90000) as shown in Table S1.

Previously, Deibig et al.⁹ 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.

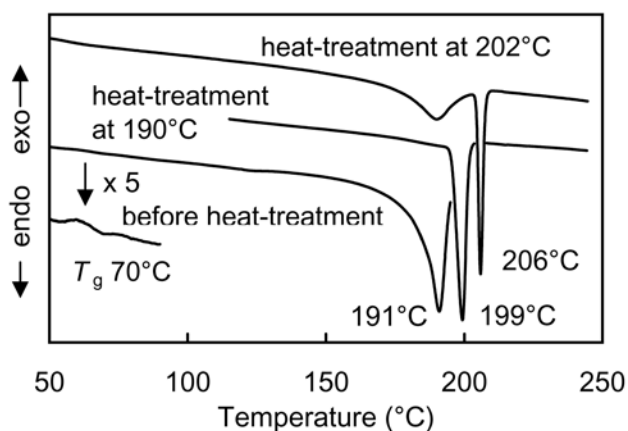


Figure 1. DSC profiles of heat-treated PTMG. Heating rate: 10 °C min⁻¹ under a nitrogen flow of 20 mL min⁻¹. Heat-treatment: 10 min.

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.^{12,14-17} 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 70000 and M_w 238000) 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.

Table 2. Catalytic thermal depolymerization of PTMG.

Run	Catalyst ^a	Temp. ^b [°C]	Volatile products [%] ^c		
			TMG	Methacrylic acid	Acetone
2-1	-	283	2.9	57.1	40.0
2-2	Sn(Oct) ₂	265	80.8	19.2	0
2-3	MgO	235	17.7	80.6	1.6

* PTMG: M_n 22000, M_w 32000. ^aCatalyst 1wt%. ^bIsothermal heating. ^cfrom ¹H NMR analysis.

In conclusion, the biomass-based and racemization-free polyester: PTMG was synthesized from lactic and pyruvic acids as renewable resources. The high T_m (~206 °C) and T_g (70 °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.

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

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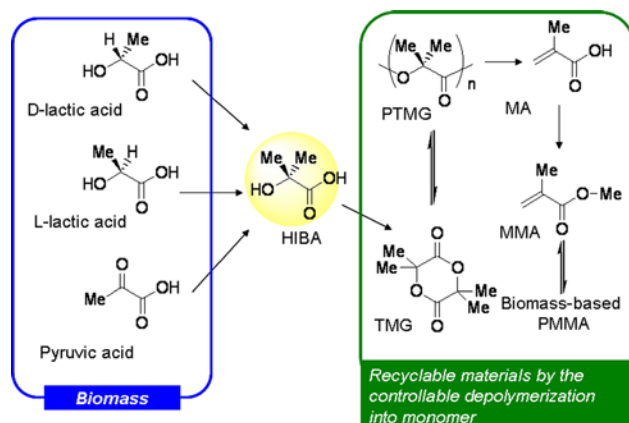
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