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Enhancement of T_g of Poly(L-lactide) by Incorporation of Biobased Mandelic-Acid-Derived Phenyl Groups by Polymerization and Polymer Blending

Satoshi Otsugu, Yoshiharu Kimura, Hajime Nakajima,* and Katja Loos*

A high-molecular-weight polyester of poly(mandelate-co-lactate) (PML) is prepared by ring-opening polymerization of stereo-configuration controlled cyclic diester monomers of methyl-6-phenyl-1,4-dioxane-2,5-dione (MPDD) and lactide. The attained PML shows excellent glassy properties, although the original stereo-configuration of MPDD is not preserved. The intrinsic high glass transition temperature (T_g) of PML is promising, and it is able to be further enhanced by thermal treatment to as high as 90 °C. Interestingly, the enhanced high T_g is attained by only 15 mol% of mandelate content in the polymer chain which is far lower than the ones suggested by theoretical calculation. The enhancement in T_g is also attained by polymer blending of PML and poly(L-lactide) (PLLA). The T_g of the polymer blend also reaches 90 °C which is almost 20 °C higher than the ones suggested by theoretical calculations. These results indicate that the rigid mandelate unit consisting of phenyl groups in PML chain effectively interact with PLLA chains in amorphous domain to restrict their chain mobility. The thermal and glassy properties are sufficient to explore new applications in engineering fields.

(PLA: also abbreviation for polylactide),^[6–8] succinate related polymers,^[9–11] poly(hydroxy alkanate)s (PHAs),^[12–14] biobased polyurethanes,^[15–17] and polysaccharides.^[18–21] Although the impact of these successful examples is promising, we still face limited possibilities of application expansion of biobased polymers, mainly because of their inferior thermal durability to petroleum-derived polymers, especially if we aim for semi-engineering and engineering applications. For sufficient thermal durability for these applications, one of the key strategies is the introduction of bulky and rigid functional groups, such as phenyl into the main or side chains of biobased polymers for high glass transition temperatures (T_g). In fact, many high thermally durable petroleum-derived semi- and engineering polymers such as polystyrene (PS), poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), poly(ether-ether ketone) (PEEK), and others

have phenyl groups in their main chain. Many established pathways for the production of phenyl containing monomers from petroleum exist, but the negative environmental impacts from these petroleum-derived phenyl-containing monomers are not negligible. Although it is still very challenging, it is important to develop a new production process of purely biobased phenyl containing monomers and polymers. Here, mandelic acid (ma), which is able to be extracted from plant feedstocks such as almond, is reported as a promising phenyl containing biobased monomer. In addition to the biobased nature of ma, the nontoxicity of ma is also attractive, as it is practically used in the current food, cosmetics, and pharmaceutical industries.^[22–24] A homo-polymer of ma and its derivatives were reported to be active against HIV-1,^[25] but the resultant polymers have insufficient molecular weight for general and engineering applications of polymeric materials. The first high-molecular-weight polyester consisting of ma was reported by Baker et al.,^[26] which is based on ring-opening polymerization (ROP) of a cyclic diester of meso-mandelide (mMN). The reported high-molecular-weight poly(meso-mandelide) (PmMA) from mMN shows excellent amorphous properties, such as high transparency and high T_g that are comparable to those of conventional glassy polymers, such as PS. There is no doubt that these properties of PmMA are adequately high for an application in the semi-engineering field.

1. Introduction

Large public concerns have been raised on the environmental issues caused by the consumption of huge amounts of petroleum-derived polymers. The mass consumption of fossil resources, which causes an increase of the atmospheric content of heat latent carbon dioxide, is hypothesized to be one of the major driving-force of the global warming. A promising solution for this issue is the replacement of fossil resources by sustainable resources, such as biomass feedstocks for the production of biobased polymers.^[1–5] The on-going proactive social, academic, and industrial R&D activities on biobased polymers have led to great achievements, especially in biodegradable applications of polymers, such as poly(lactic acid)

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A stereo-configuration controlled poly(mandelic acid) (sc-PM) was also reported.^[27] Because of the controlled stereo-configuration, the sc-PM shows semi-crystalline properties with high T_g of 90 °C and melting temperature (T_m) of 300 °C, respectively. However, as the proposed synthetic scheme of monomers of both PmMA and sc-PM are too complicated, these are not realistic pathways for a practical production system in the current chemical industry. Therefore, if we seriously aim to develop a realistic production of ma-derived polyester, it is necessary to develop moderate processing conditions of the polymers and realistic synthetic pathways for the monomers at the same time without losing the amorphous properties such as high transparency and high T_g . One of the practical solutions to tackle this is a moderation of thermal properties by a copolymerization of ma with other biobased α -hydroxy aliphatic acids. Recently, we have reported that cyclic diester monomer, which consists of ma and glycolic acid and poly(mandelate-co-glycolate), was prepared by ROP of the cyclic diester.^[28] The mandelate and glycolate units are excellently miscible in the resultant polymers, and these copolymers also showed excellent amorphous properties, such as high transparency and high T_g . A poly(mandelate-co-lactate) (PML) was also prepared by a similar approach to our previously reported method.^[29] The molecular weight, transparency, weatherability of the PML are promising for thinking about future new applications of ma consisting polymers; however, its T_g around 75 °C should be improved even more if we seriously aim for engineering applications. In these previous reports, 50 mol% content of mandelate unit was required to induce the high T_g ; however, it is not easy to keep such a high content of ma in a process of polymerization in the practical plastic industry. Stereo-configuration controlled cyclic diester monomers of methyl-6-phenyl-1,4-dioxane-2,5-dione (MPDD) consisting of ma and la were prepared. These esters were used for ROP of homo-polymerization of MPDD or copolymerization of MPDD and L-lactide (L-LAC) to prepare PML which has superior amorphous properties to previously reported ones. It is also found that the T_g of PML can

be further enhanced by an annealing, and the resultant T_g after the annealing is comparable to petroleum-derived polymers. The obtained PML is also blended with PLLA by solvent casting, and it is found that adequately high T_g which is higher than 90 °C is attained by lower mandelate content than those calculated by theoretical method. It is the first report of successful enhancement of PLLA by a polymer blending with mandelate consisting polymers.

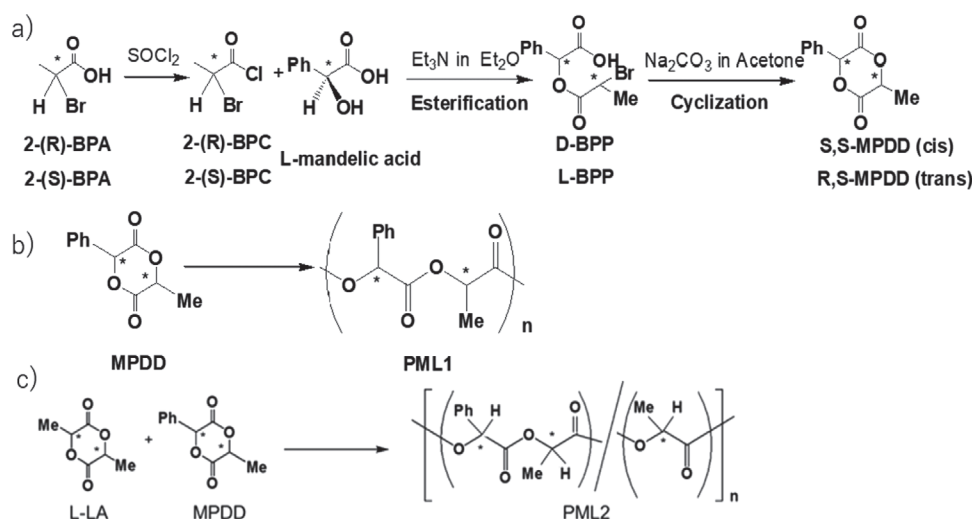
2. Results and Discussion

2.1. Synthesis and Characterization of Monomers

All the synthesis and polymerization steps are summarized and displayed in **Scheme 1**. It was recently reported that MPDD is synthesized with high yield and stereo-selectivity,^[30] and the chemical strategies used in this report were carefully applied for the syntheses in this study. The cyclic diester monomers of MPDD were synthesized by the process which is displayed in Scheme 1a. The optically active 2-BPC obtained by chlorination of 2-BPA was first reacted with L-ma to prepare L-BPP.

Although 2-BPC which is used as the starting material for the synthesis is toxic and not biobased, the resultant chemical structure of this unit is completely analogous to biobased lactic acid units. Theoretically, 2-BPC can also be prepared from biobased propionic acid via several synthetic steps, and this will be explored in our future studies.

L-BPP was then treated by Na_2CO_3 for cyclization with Walden inversion of the 2-BPC unit. Although the crude yield of both S,S-MPDD and R,S-MPDD are higher than 94.0%, the isolated final yield of both monomers was as low as 13.3% for S,S-MPDD and 7.7% for R,S-MPDD, respectively. This is because oligomerization of these was likely to occur during recrystallization. ^1H NMR of S,S-MPDD and R,S-MPDD, with TMS used as an internal standard, are displayed in **Figure 1**. The peak assignments are summarized in the subsequent experimental part, and it was found that the initially designed



Scheme 1. Reaction steps; a) synthesis of MPDD, b) ROP of MPDD for PML1, and c) ROP for PML2.

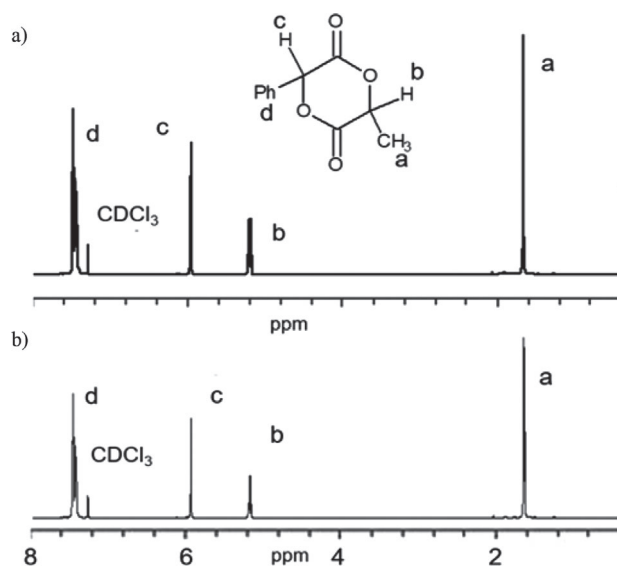


Figure 1. 500 MHz ^1H NMR spectrum of a) S,S-MPDD, b) R,S-MPDD in CDCl_3 .

structure of MPDD was successfully attained. Although the difference in stereo-configuration does not result in a clear difference in the spectrum of ^1H NMR, the signal of the proton, which is assigned by c1, has a small difference. It could become more distinguished when a different type of deuterated NMR solvent or other conditions is applied. This is because of the changes in the molecular level interactions and proton coupling constant of c-assigned proton with neighborhood protons (this is planned for our future study). Specific optical rotation of R,S-MPDD and S,S-MPDD was examined, and it was found that R,S-MPDD for $[\alpha]_{20}^D = +123.8^\circ$ and S,S-MPDD for $[\alpha]_{20}^D = +109.8^\circ$, respectively. The stereo structures of alkaline hydrolysis products of S,S-MPDD and R,S-MPDD were also examined by HPLC. The hydrolysis products from S,S-MPDD comprise L-ma and L-la, which are detected at 6 and 13 min. Conversely, the hydrolysis products from R,S-MPDD comprise L-man and D-la, which are detected at 6 and 16 min. The peak of L-ma is shown as a negative peak because of its decreased low refractive index. This data strongly supports the two different stereo-configuration of MPDD. Because of the differences in stereo-configuration, S,S-MPDD showed a T_m at 172°C , while its diastereomer R,S-MPDD with a trans-configuration showed a lower T_m , which is detected at 147°C . As it is also reported, differences in stereo-configuration of mandelide results in differences in T_m ,

for example, rMN shows T_m at 248°C and 137°C for mMN, respectively.^[20] Therefore, the differences in T_m of S,S- and R,S-MPDD are also recognized as a strong support for the different stereo-configurations.

As the practical yield of MPDD is currently still not adequately high for industrial production processes, we will work on improved processes in the future.

2.2. Polymerization of MPDD

2.2.1. Polymerization of R,S-MPDD and S,S-MPDD

The step of ROP of MPDD is displayed in Scheme 1b. The ROP was catalyzed by tin octoate, and the catalyst concentration was fixed to 1/500 mol% in relation to MPDD. Aluminum isopropoxide, diethylzinc/ H_2O , and azobicyclodecene were also used as catalyst for ROP of MPDD, but these were not active for MPDD. **Table 1** is the summary of ROP of MPDD in bulk or the solution state. In the bulk polymerization, the amount of moisture was not precisely controlled, and it was true we might have had a risk that the content of moisture was not appropriate. However, we previously reported that this polymerization approach is effective for such small scale polymerizations of lactones.^[28] The conversion of polymers from S,S-MPDD and R,S-MPDD, which is displayed in **Table 1** are adequately high, while the final molecular weight of PML1 from each run is not constant. The difference is derived from the stability of S,S-MPDD and R,S-MPDD, which can be explained by the difference in T_m of each monomer. As the T_m of S,S-MPDD is 25°C higher than that of R,S-MPDD, the reactivity of S,S-MPDD at the same polymerization condition is lower than that of R,S-MPDD. It was found that the molecular weight of the resultant polymers from solution polymerization was higher than those from bulk polymerization. This could have been caused by less side reactions, such as chain transfer and depolymerization, which occurred at the high polymerization temperature of the bulk polymerization were applied without any initiators, and a tiny amount of moisture. **Table 2** shows the result of the solution polymerization in toluene with controlled initiator content. It is shown that the polymerization of R,S-MPDD (run 6, 7) shows higher conversion with shorter reaction time, when it is compared with those from S,S-MPDD (run 8, 9). It indicates that the polymerizability of R,S-MPDD is higher than that of S,S-MPDD. The chemical structures of PML1 from run 1 are analyzed by ^1H NMR (**Figure 2**) and ^{13}C NMR (**Figure 3**). (The peak assignment of these are listed in Section 4).

Table 1. ROP of S,S- and R,S-MPDD in bulk and solution condition.

Run	Monomer	Solvent	Reaction temperature [$^\circ\text{C}$]	Time [h]	Conversion [%]	M_n [kDa]	M_w [kDa]	$\bar{\rho}$
1	S,S-MPDD	n.a.	185.0	6	95.8	5.8	6.8	1.2
2	R,S-MPDD	n.a.	175.0	6	92.0	10.7	16.2	1.5
3	S,S-MPDD	Toluene	120.0	20	96.2	45.1	68.6	1.5
4	S,S-MPDD	Chlorobenzene	120.0	80	90.3	7.9	8.8	1.1
5	R,S-MPDD	Toluene	120.0	24	86.7	19.2	28.0	1.3

Table 2. ROP of S,S- and R,S-MPDD in toluene.

Run	Monomer	Reaction temperature [°C]	Reaction time [h]	Initiator	Conversion [%]	M_n [kDa]	M_w [kDa]	$\bar{\rho}$
6	R,S-MPDD	120.0	20	S-PEA	89.8	7.5	9.4	1.3
7	R,S-MPDD	120.0	25	R-PEA	79.1	8.2	10.5	1.3
8	S,S-MPDD	120.0	65	S-PEA	86.7	6.0	6.3	1.1
9	S,S-MPDD	120.0	75	R-PEA	52.1	—	—	—

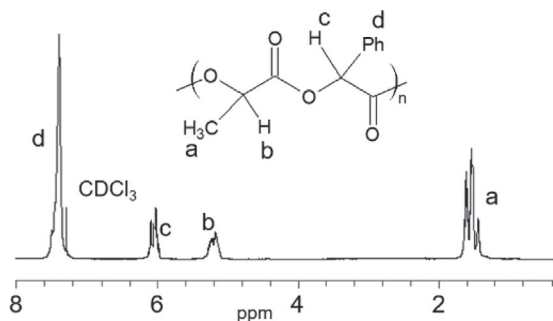


Figure 2. 500 MHz ^1H NMR spectrum of PML1 (run 1) in CDCl_3 .

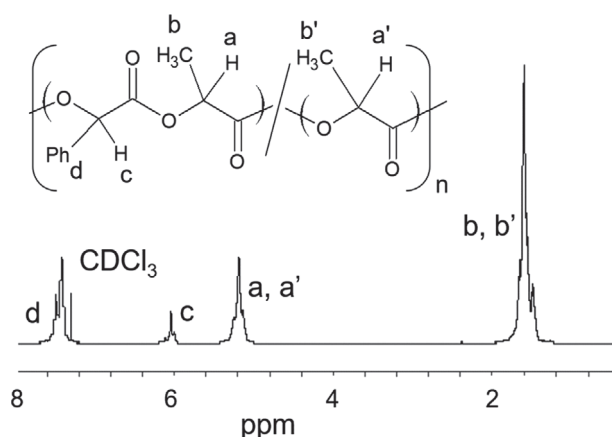


Figure 4. 500 MHz ^1H NMR spectrum of PML2 in CDCl_3 .

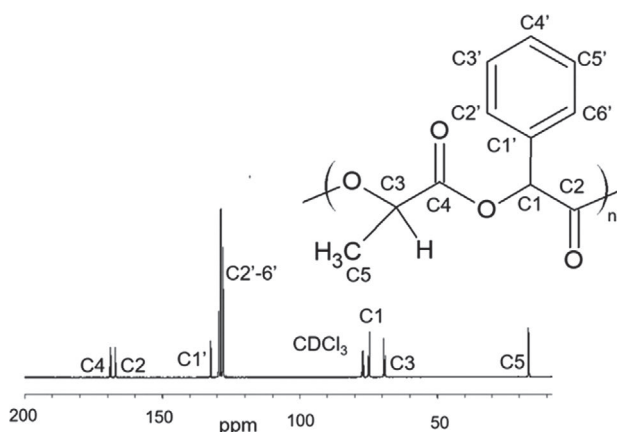


Figure 3. 125 MHz ^{13}C NMR spectrum of PML1 (run 1) in CDCl_3 .

2.2.2. Copolymerization of MPDD and L-LAC

PML2, which is a copolymer of MPDD and L-LAC, was prepared by solution polymerization in toluene with tin octoate as catalyst (Scheme 1c). The feed ratio of MPDD/L-LAC was fixed on 3/7 (mol/mol) in this study. Both S,S- and R,S-MPDD were active to react with L-LAC during the polymerization to attain sufficiently high molecular weight and conversion (shown in Table 3). The M_n and M_w of S,S-MPDD-derived PML2 are higher than those of the R,S-MPDD-derived one. Interestingly, it does not correspond to the stability trend of MPDD in its

homo-polymerization (vide supra). This can be explained by different affinities of different configurations of MPDD and L-LAC, such as steric hindrance of MPDD to L-LAC. (detailed studies about polymerization mechanisms and stabilities of MPDD will be carried out in our future research.) Figure 4 shows the ^1H NMR spectrum of the resulting PML2 (run 1). Thus, both, the original chemical structure of PML1 and PLA are formed in the macromolecular chain of PML2. From the integral ratio of the strength of signals of PML2, it was found that the mandelate composition in PML2 corresponds to the feed ratio. As the original feed ratio is kept in the resultant polymers, we suppose that MPDD and L-LAC have similar polymerizability under the same conditions.

2.2.3. Unit Sequences of PML1 and PML2

Dedicated ^{13}C NMR studies on carbonyl signals of PML1 (run 1) and PML2 (run 11) were performed to study their unit sequence structures (Figure 5). The signals of PML1 and PML2 are reasonably assigned to the tetrads, as noted in similar figures from previous reports.^[31,32] The tetrad formation in PML1 which are detected as relatively strong signals, such as LLML, LLMM, MLML, MLLM, LMLM, LMML, MMLM, and MMLL, represent a repeating combination of

Table 3. Copolymerization of MPDD with L-LAC.

Run	Monomer	Solvent	Time [h]	Conversion [%]	M_n [kDa]	M_w [kDa]	$\bar{\rho}$
10	S,S-MPDD	Toluene	25	91.9	45.4	77.9	1.7
11	R,S-MPDD	Toluene	20	91.3	23.9	58.8	1.6

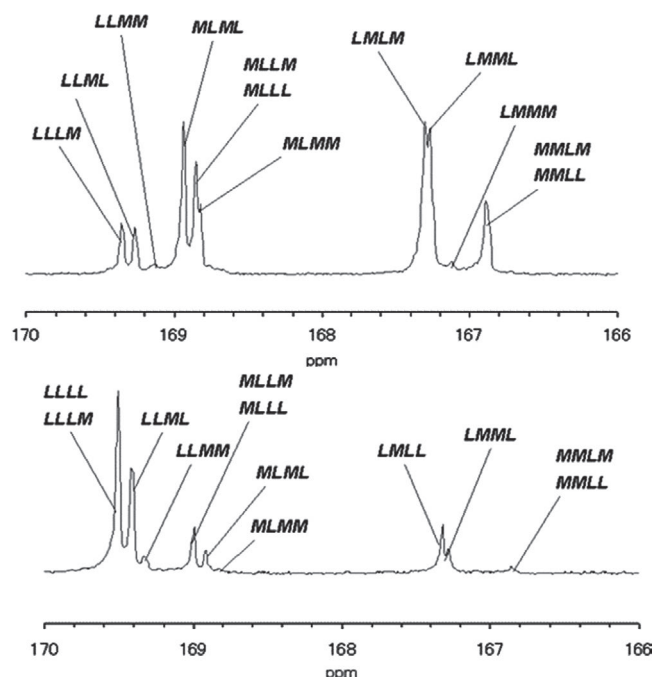


Figure 5. Enlarged carbonyl regions from the ^{13}C NMR spectra of a) PML1 and b) PML2. The mandelate and lactate units are indicated by M and L, respectively.

sequences which consists of a single MPDD monomer unit. Conversely, there are triad forms of LLL and MMM shown in PML1, which are not able to be formed through a simple ring opening of MPDD. These triad forms are derived from side reactions which occurred during the polymerization. Most likely, chain transfers and ester exchanges are the major side reaction for the triad forms. In PML2, similar signal patterns from PML1 are shown, although the signal at δ 169.5 ppm is strengthened because the signal of LLLL and LLLM are the majority sequence of PML2. Accordingly, the copolymer has scrambled sequence structures. This fact supports a mechanism in which the ring-opening of MPDD monomers occurs at both M and L ester units, and these units are scrambled during the polymerization.

2.3. Thermal Properties of Polymers

2.3.1. PML1 and PML2

Solvent cast films of PML1 and PML2 were separately prepared, and their T_g was analyzed by DSC. In advance to the DSC, a visual inspection of the appearance of the films was performed. As shown in **Figure 6**, transparency of the films is excellent, although they have a slightly rough and bumpy surface which is induced by rapid evaporation of solvent during the preparation steps. The DSC thermogram of PML1 (run 2) and PML2 (run 11) of the 2nd heating run are shown in **Figure 7**. The T_g of PML1 appears around 80 °C, which is already adequately high. The high T_g is obtained by an introduction of bulky phenyl groups of mandelate into a macromolecular chain. Two T_g s, the lower one around 56 °C and the higher one around 70 °C

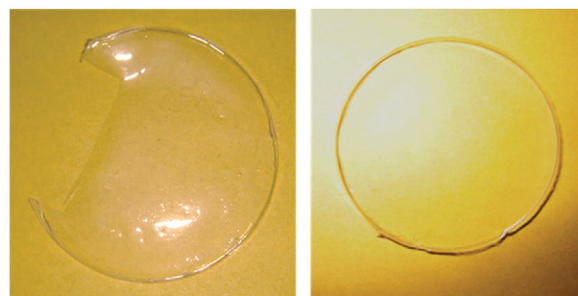


Figure 6. A solvent cast film of a) PML1 (run 2) and b) PML2 (run 11).

are found in the DSC thermogram of PML2. This indicates the existence of two separated phases, which consist of lactate-rich domains and mandelate-rich domains. The lower T_g at 56 °C is close to the generally known T_g of PLA, thus an original semi-crystalline form of lactate units is formed in PML2. The higher T_g of PML2 is close to the one observed in PML1. However, due to the lower content of mandelate units in PML2 than that of PML1, the T_g of PML2 is slightly lower than that of PML1 because of the differences in chain mobility. Both PML1 and PML2 were annealed at 120 °C for 1 h. This annealing program is designed to cause a chain relaxation of the amorphous domain of PML more effectively to form a mixed state of the mandelate unit and the lactate unit. As the separated phase of the lactate unit domain is incorporated into the mandelate unit domain, the original T_g of PLA in PML2 disappears after the annealing. As a result, the chain mobility of the lactate units is reduced by an interaction from mandelate units. This thermal treatment may be able to cause a slight crystallization of the lactate-rich segments. Thus, the chain mobility of PML is further

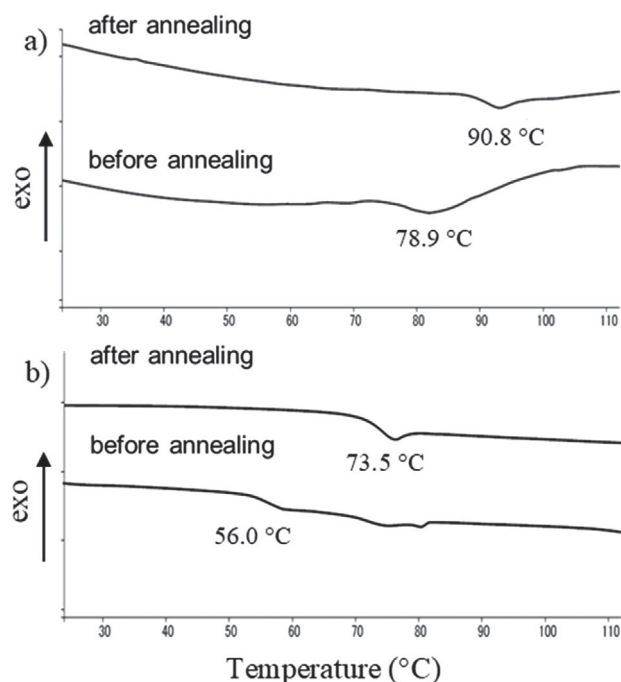


Figure 7. DSC 2nd heating curves of a) PML1 (run 2) and b) PML2 (run 11) before and after annealing.

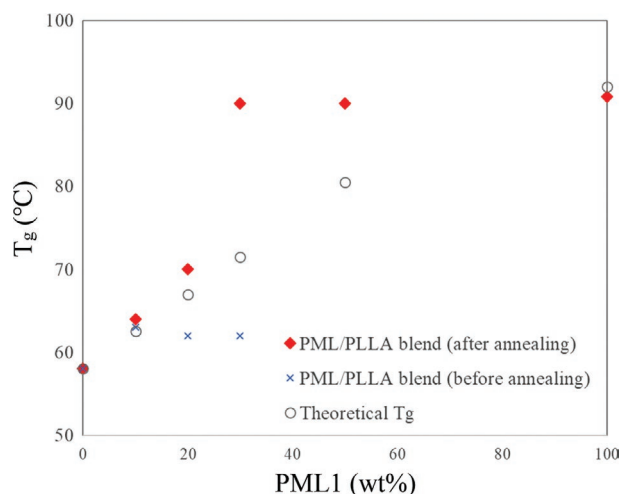


Figure 8. T_g of the PML1/PLLA blend as a function of the blending ratio of PML1.

restricted. Because of these two consequences, the T_g of PML1 and PML2 were effectively enhanced.

2.3.2. Polymer Blending of PML1 and PLLA

PML1 (Run 2) and PLLA were blended by solvent casting, and it is annealed at 120 °C for 1 h, and their thermal properties were compared with ones from without annealing. **Figure 8** shows the T_g from DSC 1st heating of the PML1/PLLA blend as a function of the blending ratio of PML1 content in the blend. PLLA became completely amorphous by the blending, no T_m -derived peaks was observed in the 1st heating DSC run of all the samples.

The high miscibility of PML1 and PLLA is confirmed by the fact that no melting behavior of PLA can be observed in the DSC curves and it is therefore reasonable to consider the material a polymer blend. In our future studies a different temperature set, which is close to an intrinsic crystallization temperature of PLLA, will be applied to study the effect on the crystallization behavior of PLLA.

Before the annealing, small enhancement in T_g is already found, when the PML1 content reached 10 wt%. However, there was no further enhancement by increasing the ratio of PML2. It means the miscibility of mandelate and lactate is not sufficient, if we do not apply any physical treatment such as annealing or mechanical shear force. In fact, by adding the annealing process, there are dramatical enhancement in T_g . The enhancement rate is proportional until the PML1 content reached 20 wt%, and it is almost corresponding to ones from theoretical values from Fox equation.^[33] Once the PML1 content reaches 30 wt% (15 mol% mandelate content in the blend), the T_g of the blend reached 90 °C, and interestingly, there was no further enhancement in T_g by adding more content of mandelate, as it is indicated that 15 mol% content of mandelate unit is sufficient to minimize the chain mobility of lactate.

A scaling-up of the polymerization will be performed in our future studies and key mechanical tests such as stress-strain tests will be conducted.

3. Conclusions

Stereo-configuration controlled R,S- and S,S-MPDD, consisting of mandelate and lactate, were successfully synthesized, and both R,S- and S,S-MPDD were polymerized to high molecular weight polymers. The obtained polymers have excellent amorphous properties, such as high T_g and high transparency, and these are comparable to those of petroleum-derived PS. Because of trans-esterification and chain-transfer reactions during the polymerization, the original stereo-configuration of MPDD was lost in the resultant polymers. The copolymerization of MPDD and L-LAC with fixed molar ratio was also performed, and a high mandelate content PLA was successfully prepared with improved physical properties from conventional lactate homopolymers. A miscibility of PML1 and PLLA in a polymer blend was confirmed, and the miscibility was improved by adding annealing process. As the annealing effectively works to attain excellent miscibility of mandelate and lactate, there was great enhancement of T_g which is much higher than that of induced by theoretical calculation. By applying the method proposed in this study, a significant improvement in T_g of PLA can be attained by an addition of relatively low amount of mandelate unit consisting polymers. It should be practically applied for industrial production of high- T_g PLA for engineering applications.

4. Experimental Section

Materials: (R)- and (S)-2-bromopropionic acid (2-(R)-BPA and 2-(S)-BPA, respectively), thionyl chloride, and L-ma were purchased from Merck (Germany) and used as received. L-lactic acid (L-la), D-lactic acid (D-la), and L-lactide (L-LAC) were supplied by Musashino Chemical Laboratory, Ltd (Japan). Diethyl ether, toluene, and triethylamine were purchased from Nacalai Tesque Co. (Kyoto), and these were distilled before use. The other solvents, including deuterated solvents for NMR, were also purchased from Nacalai Tesque Co, and these were used without purification. Tin octoate was purchased from Nacalai Tesque Co., and it was distilled under high vacuum before use. The obtained Tin octoate was dissolved in a distilled toluene in a concentration of 0.02 g mL⁻¹ for use as the catalyst for ROP.

Measurement: The molecular weight of polymers was determined by gel permeation chromatography (GPC), which was performed with a Shimadzu analyzer system, composed of a LC-10A pump, a refractive-index detector, and a C-R7A plus Chromatopac data processor. A set of two identical columns of a fixed pore size (50 nm; 10 × 250 mm²; Jordi Associates, Bellingham, MA) was used. The mobile phase was tetrahydrofuran (THF) flowing at a rate of 1.0 mL min⁻¹. The molecular weight was calibrated with PS standards from 500 to 100000 Da. 500 MHz ¹H and 125 MHz ¹³C NMR spectra were measured on a Bruker ARX 500 spectrometer. 200 MHz ¹H NMR spectra were measured on a Varian Gemini spectrometer. Deuterated chloroform containing 0.03 vol% tetramethylsilane (TMS) as the internal reference was used as the solvent. Differential scanning calorimetry (DSC) was performed on a Shimadzu DSC-50 thermal analyzer under a nitrogen flow of 20 mL min⁻¹ at a heating rate of 10 °C min⁻¹ for about 2.0 mg of samples. The samples were heated to 250 °C at the first scan. They were then quenched in a liquid nitrogen, and these were used for the second scan. The DSC system was also used to measure the T_g change by annealing at a predetermined temperature. IR spectra were recorded on a Shimadzu FT-IR 8200 PC infrared spectrometer using KBr plate. The specific optical rotation, $[\alpha]_{25}^D$, of the monomers was measured in acetone at a concentration of 4 g L⁻¹ at 25 °C using a Union Giken PM-101 polarimeter at a wavelength of 589 nm. The stereo structures



of MPDD were confirmed by high performance liquid chromatography (HPLC) of their hydrolysis products. The analyzer was composed of a Shimadzu HPLC system comprising an LC-10ADvp pump, SPD-10Avp UV-VIS detector (254 nm), CTO-10Avp column oven, DGU-12AM degasser, SCL-10Avp system controller, and CLASS-VP system. A silica gel column of SUMICHIRAL OA-5000 (4.6 mm I.D. × 150 mm) was used with 1.0 mm aq-CuSO₄ as the eluent at 40 °C. Elemental analysis was done in the Kyoto University, Center for Organic Elemental Microanalysis.

Synthesis of 2-Bromopropionyl Chlorides: 2-(R)-BPA (47.0 g, 0.31 mol) was added to thionyl chloride drop-wisely (54.2 g, 0.46 mol) in an ice bath. The reaction mixture was refluxed at 60 °C in an oil bath for 160 h. Then, the unreacted thionyl chloride evaporated from the reaction mixture under reduced pressure. The residue consisted preferentially of (R)-2-bromopropionyl chloride (2-(R)-BPC) and was directly used in the following step. 2-(R)-BPC: Yield 93.4%, ¹H NMR (200 MHz, CDCl₃): 1.95(d,3H,CH₃), 4.68(q,1H,CH) ppm. 2-(S)-BPC was also synthesized by the same process using 2-(S)-BPA as the starting material. 2-(S)-BPC: Yield; 93.5%, ¹H NMR (200 MHz, CDCl₃): 1.95(d,3H,CH₃), 4.67(q,1H,CH) ppm.

Synthesis of 2-(2-Bromopropionyloxy)-2-Phenylethanoic Acids: In a 300 mL dried three-neck round-bottom flask with a dropping funnel, L-ma (L-ma: 5.28 g 34.7 mmol) was placed and dried under a vacuum. Diethyl ether (136 mL) was charged in it under a nitrogen atmosphere to dissolve L-ma and stirred in an ice bath for 1 h. 2-(S)-BPC (5.83 g 34.7 mmol) and triethylamine in diethyl ether were added to this solution (5.63 g per 34.0 mL; 1.64 mmol L⁻¹) was added dropwise with the temperature kept below 5 °C. After the addition, the solution was stirred at room temperature for 15 h. The resulting reaction mixture was then washed with water with 0.1 N HCl in a separated funnel. The remaining HCl was completely washed by ion exchanged water. The organic layer was separated and dried on magnesium sulfate (MgSO₄). Evaporation of diethyl ether gave pale-yellow solid products of L-BPP. D-BPP was also synthesized by the same way using 2-(R)-BPC. Both products were directly subjected to the ring-closure reaction without purification. L-BPP: Yield; 52.3%, ¹H NMR (200 MHz, CDCl₃): 1.85(d,3H, CH₃), 4.50(q,1H, CH), 5.98(d,1H, CH), 6.15(s,1H, OH), 7.45 (m,5H, C₆H₅) ppm. D-BPP: Yield; 49.5%, ¹H NMR (200 MHz, CDCl₃): 1.85(d,3H, CH₃), 4.52(q,1H, CH), 5.98(d,1H, CH), 6.17(s,1H, OH), 7.46 (m,5H, C₆H₅) ppm.

Synthesis of 3-Methyl-6-Phenyl-1,4-Dioxane-2,5-Dione: In a 1 L two-necked Kjeldahl flask fitted with a dropping funnel and a reflux condenser, sodium carbonate (Na₂CO₃ 0.262 g, 25.0 mmol) was suspended with acetone (300 mL) using mechanical stirrer at 60 °C. To this suspension, L-BPP (1.36 g) dissolved in acetone (200 mL, 25.0 mmol L⁻¹) and was added dropwise in a period of 6 h. After the addition had been completed, the reaction mixture was stirred for 30 min at 60 °C. Then, the reaction mixture was filtered to remove insoluble salts, and the filtrate was evaporated to produce white powdery products. They were dissolved in dichloromethane (CH₂Cl₂) and washed with 0.1 N HCl three times. The organic layer was dried on magnesium sulfate (MgSO₄) and evaporated to obtain pale yellow products which was purified by recrystallization from ethyl acetate. S,S-MPDD was also synthesized from D-BPP by the same way. R,S-MPDD: ¹H NMR (200 MHz, CDCl₃): 1.65(d,3H,CH₃), 5.18(q,1H,CH), 5.95(s,1H,CH), 7.45(m,5H,C₆H₅) ppm. ¹³C NMR (125 MHz, CDCl₃): 16.39, 72.78, 77.64, 127.33, 128.84, 129.83, 131.46, 165.39, 166.75 ppm. IR (KBr) ν 1245.9 (C—O); 1463.9 (Ph); 1745.4 (C=O); 1782.1 (C=O); 2947.0 (C—H); 3014.5 cm⁻¹ (C—H). Anal. Calcd for C₁₁H₁₀O₄: C, 64.08; H, 4.85. Found: C, 64.04; H, 4.92. T_m = 147 °C. [α]₂₀^D = +109.8 °, c = 0.048 g L⁻¹ in acetone. Crude yield; 94.3%. S,S-MPDD: ¹H NMR (200 MHz, CDCl₃): 1.68(d,3H,CH₃), 5.21(q,1H,CH), 5.96(s,1H,CH), 7.48(m,5H,C₆H₅) ppm. ¹³C NMR (125 MHz, CDCl₃): 16.47, 72.85, 77.77, 127.18, 128.89, 129.77, 131.25, 165.24, 166.72 ppm. IR (KBr) ν. Anal. Calcd for C₁₁H₁₀O₄: C, 64.08; H, 4.85. Found: C, 64.06; H, 5.00. T_m = 172 °C. [α]₂₀^D = +123.8 °, c = 0.412 g L⁻¹ in acetone. Crude yield; 98.5%.

Bulk Polymerization of R,S-MPDD and S,S-MPDD: In a dried NMR sample tube, R,S-MPDD (or S,S-MPDD) (30.0 mg; 0.15 mmol) was mixed with a predetermined amount of tin octoate toluene solution. The mixture was dried under a vacuum for 3 h before polymerization. Then, the tube was sealed and heated at a predetermined temperature

in an oil bath for 6 h. The resultant brown solid product was dissolved in chloroform and poured into an excess amount of methanol for reprecipitation. The precipitates were collected by centrifugation at 2000 rpm for 1 h, and the solid products from the precipitate were isolated by decantation and dried in vacuum at 40 °C for 10 h. PML1: ¹H NMR (500 MHz, CDCl₃): 1.13–1.80 (b, 3H, CH₃), 5.01–5.37 (b, 1H, CH), 5.89–6.19 (b, 1H, CH), 7.15–7.60 (b, 5H, C₆H₅) ppm. ¹³C NMR (125 MHz, CDCl₃): 16.72, 69.26, 74.48, 127.89, 128.77, 129.34, 132.24, 167.37, and 168.82 ppm.

Solution Polymerization of R,S-MPDD and S,S-MPDD: In a dried NMR sample tube, MPDD (30.0 mg; 0.15 mmol) and a predetermined amount of tin octoate toluene solution was dried under a vacuum for 3 h. Then, toluene-d₈ (0.4 mL) was added to it, and the tube was sealed and heated at 120 °C in an oil bath for a predetermined time.

It was found that the resultant product after the reaction is insoluble in toluene, so toluene-d₈ was selected as the reaction solvent to allow NMR studies which were originally planned at the beginning stage of this study.

The resultant solution was extracted with chloroform and poured into excess methanol for reprecipitation. The precipitates were collected by centrifugation at 2000 rpm for 1 h. The products isolated by decantation were dried in a vacuum at 40 °C for 10 h. PML1: ¹H NMR (500 MHz, CDCl₃): 1.26–1.83 (b, 3H, CH₃), 5.03–5.34 (b, 1H, CH), 5.94–6.22 (b, 1H, CH), 7.20–7.66 (b, 5H, C₆H₅) ppm. ¹³C NMR: (125 MHz, CDCl₃): 16.69, 69.82, 75.25, 127.77, 128.66, 129.34, 132.35, 167.33, and 168.95 ppm.

Copolymerization of R,S- and S,S-MPDD and L-LAC: In a dried NMR tube, R,S-MPDD (or S,S-MPDD) (11.4 mg; 0.06 mmol), L-LAC (18.6 mg; 0.13 mmol), and tin octoate toluene solution were mixed and dried under vacuum for 3 h. Then a toluene-d₈ (0.4 mL) was added to it, and the tube was sealed and heated at 120 °C in an oil bath for predetermined time. The resultant solution was extracted with chloroform and poured into an excess methanol for reprecipitation. The precipitates were collected by centrifugation at 2000 rpm for 1 h. Then, the products were isolated by decantation and dried at 40 °C for 10 h under vacuum. PML2: ¹H NMR (500 MHz, CDCl₃): 1.37–1.97 (b, 3H, CH₃), 5.03–5.45 (b, 1H, CH), 5.94–6.21 (b, 1H, CH), 7.23–7.68 (b, 5H, C₆H₅) ppm. ¹³C NMR: (125 MHz, CDCl₃): 16.19, 68.78, 74.59, 128.05, 128.64, 129.51, 167.29, and 169.61 ppm.

Fabrication of Cast Films: Chloroform was used as the solvent. 1.7 wt% of polymer solution of PML1 or PML2 was prepared, and a complete dissolved state was confirmed after continuous stirring at room temperature for overnight. The polymer solution was placed in a Petri dish, and the solvent was evaporated at a fume hood for overnight. It was found that the dried film was solidified after overnight drying. The solidified film was peeled and dried in a vacuum at 50 °C for 10 h. In the preparation process of PML1 and PLLA blended cast film, 1.7 wt% of polymer solution of each polymer was prepared separately. These separately prepared solution was then mixed, and another several hours of stirring was added to attain a completely mixed state of each polymer. The mixed polymer solution was poured into Petri dish, and the same drying process was applied.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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