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Ring-Opening Polymerization of a New Diester Cyclic Dimer of Mandelic and Glycolic Acid: An Efficient Synthesis Method for Derivatives of Amorphous Polyglycolide with High T_g

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In this study, poly(mandellate-co-glycolate) (PMG), a modified polyglycolide (PGL), is prepared by ring-opening polymerization (ROP) of L-3-phenyl-1,4-dioxane-2,5-dione (PDD); the cyclic dimer of biobased mandelic acid and glycolic acid. The resulting polymer shows an increased glass transition temperature (T_g) due to the incorporation of phenyl groups in the chain. High molecular weight PMG is obtained by bulk ROP at 150 °C, and it exhibits a glassy amorphous state with enhanced thermal properties such as a T_g being 35 °C higher than conventional PGL. PDD is also copolymerized with glycolide (GL) and lactide (LA), resulting in poly(mandellate-co-glycolate/glycolate) ((P(MG/GL)) with GL and poly(mandellate-co-glycolate/lactide) ((P(MG/LA)) with LA. The thermal properties of P(MG/GL) and P(MG/LA) are found to be distinctly different from PMG and conventional PGL and polylactide, and they are tunable with a changing molar ratio of PDD, GL, and LA. Therefore, PDD opens an elegant way to control and tailor the properties of biobased polyesters.

example, due to the simple repeating unit structure of PGL consisting of glycolate unit (G), a linear PGL has excellent crystallization properties, showing a stable crystalline form which contributes to a high melting temperature (T_m) of 230 °C. PGL's high gas barrier property is also a very remarkable functionality for developing packaging applications for food and beverages.^[14–16] Despite these advantages as compared to other biobased polyesters, more specifically to polylactide (PLA), the practical application fields of PGL suffer from limitations due to its insufficient glass transition temperature (T_g) of 35 °C. This relatively low T_g is derived from an insufficient chain rigidity and a restriction of chain mobility in the amorphous domain, even though the simple chain structure contributes to the excellent crystallization properties. As the low T_g is close

1. Introduction

The main application fields of polyglycolide (PGL) and related copolymers have been medical and pharmaceutical, utilizing its biocompatibility, bioabsorbability, and biodegradability.^[1–5] More recently, due to increasingly important needs for a more sustainable industry, PGL has also been featured to explore more general applications for a larger plastic market such as commodities, stationery supplies, containers, etc., as a family member of biobased polymers,^[6–10] with developing production processes of biobased glycolic acid.^[11–13] Not only the sustainable aspect of PGL as a biobased polymer but also the promising functionalities of PGL are important features. For

to an in vivo thermal condition, it causes an unfavorable poor hydrolytic stability of PGL in many general application conditions. The unfavorable hydrolytic stability is also derived from a high hydrophilicity of the main chain of PGL as compared to other slow degrading polyesters such as PLA, polydioxanone, poly(hydroxy alkanate)s, and poly(ϵ -caprolactone).^[17,18] These drawbacks can be sustained by a high crystallinity to reduce the ratio of the amorphous domain, but a high crystallinity always brings a high-haze state, which is also a drawback for exploring general applications of the plastic materials. Therefore, it is promising if a chemical modification on the PGL main chain is achieved, which can increase the rigidity and hydrophobicity of the amorphous domain without deteriorating PGL's safe, biodegradable, and biocompatible aspects.

In this study, the introduction of a phenyl group derived from biobased mandelic acid (maa) into PGL main chain has been attained. Maa is a phenyl group containing α -hydroxyl acid, which is already practically commercialized in cosmetic, pharmaceutical, and food industries, thus, the safe and biocompatible characteristics of maa have already been completely proven.^[19–21] For this reason, maa is a promising building block polymer to design new biobased polyesters showing a high T_g and high hydrolytic stability. In fact, there are several reports about biobased polyesters consisting of maa as their repeating unit component that exhibits a high T_g and hydrolytic stability. For example, an amorphous polymandelate (PMA) prepared by ring-opening polymerization (ROP) of *meso*-mandelide:

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a cyclic dimer of maa is known, showing a T_g of 100 °C and a hydrolysis rate 100 times slower than conventional PLA.^[22] Due to its high T_g , PMA is considered as one of the most promising candidates to replace petroleum-derived polystyrene. To add to this, there is also a reported case of a crystallizable PMA of isotactic tacticity.^[23] It is prepared by ROP of *O*-carboxyanhydride (OCA), exhibiting an outstanding T_m of 316 °C. A crystallizable PMA by ROP of 5-phenyl-1,3-dioxolan-4-one (Ph-DXO)^[24] has also been reported. Although, the ROP of Ph-DXO is managed under milder conditions than the ROP of OCA, it results in occurring racemization to produce atactic tacticity to attain amorphous characteristics. A partial incorporation of a mandelate unit (M) sequence into PLA was attained by ROP of (3S)-6-methyl-3-phenyl-1,4-dioxan-2,5-dione, and the resulting poly(mandelate-*co*-lactate) showed a T_g of 76 °C as compared to the T_g of 55 °C of conventional PLA.^[25] Therefore, the reports mentioned above prove that the incorporation of a M unit into a polylactone can improve thermal properties, specifically T_g . In this study, a new diester cyclic monomer L-3-phenyl-1,4-dioxane-2,5-dione (PDD) consisting of maa and glycolic acid was first synthesized and subjected to ROP for the synthesis of poly(mandelate-*co*-glycolate) (PMG). The ROP in bulk state was successfully managed to obtain a high molecular weight PMG which also showed a greatly improved T_g as compared to conventional PGL. In addition, ROP of PDD and glycolide (GL) for a high glycolate (G) content poly(mandelate-*co*-glycolate/glycolate) ((P(MG/GL))) and ROP of PDD and L-lactide (LA) for a lactate (L) unit containing poly(mandelate-*co*-glycolate/lactide) ((P(MG/LA))) were also performed. In all cases of PMG, P(MG/GL), and P(MG/LA), a successful incorporation of phenyl groups was confirmed, showing an improved T_g , and an improvement of the tunability of T_g was also found.

2. Results and Discussion

2.1. PDD Monomer Synthesis

PDD was synthesized with a 2-step reaction: the first step was the synthesis of L-2-(bromoacetoxy)-2-phenylethanoic acid (BAP) and the second step was the synthesis of PDD by intermolecular cyclization of BAP (Figure 1a). The synthesis of BAP and PDD was confirmed by ¹H NMR (Figure 1b,c), and these were consistent with the designed structure. Figure 1b for ¹H NMR of BAP shows peaks from remaining diethyl ether, but it is completely inert during the following steps for PDD synthesis. The quartet peak of 2H, CH₂ is unique from ¹H NMR of a conventional GL, but the quartet peak is also reported when another counterpart ester of a diester cyclic dimer has an optically active property.^[26] The conversion from BAP to PDD reached above 80% which is adequately high to consider the feasibility of monomer production in a future industrial production. The yield can be even higher, while addition process of L-BAP is optimized in the on-going following studies. In this study, the final yield of purified PDD is 8.2%. It is lower than a theoretical yield, because a certain of oligomers were formed from PDD during the recrystallization processes. Several approaches for improvement in purifications are proposed and tried to avoid these problems in the on-going following studies as well.

2.2. ROP of PDD

The prepared PDD was subjected to a ROP in bulk state (Figure 1a). A PMG from the ROP has a fixed ratio of M and G of 50/50 (in mol/mol), as the PDD consists of an equimolar combination of M and G. Since no initiator such as a hydroxyl compound was added to this ROP, the polymerization must have been initiated by tiny amount of moisture in the reaction mixture as previously reported in the ROP.^[27,28] As a result of characterizing the thermal properties of PDD by differential scanning calorimetry (DSC), it was revealed that the T_m of the prepared PDD was 133.7 °C. Therefore, 150 °C was set as the reaction temperature of the ROP, as it is moderately higher than the T_m of PDD. After 3 h of reaction run, the reaction mixture was completely solidified, as the fed monomers were successfully polymerized. The white solid product was isolated by reprecipitation, and the precipitant was filtered and dried in vacuum with a resulting yield of 59.1%. This low yield is mainly caused by the loss of low molecular weight fraction during the reprecipitation. The number average molecular weight (M_n) of the product was determined by gel permeation chromatography to 43 000 Da with a weight molecular weight (M_w) of 79 900 Da with polydispersity (M_w/M_n) of 1.7. These are comparable to the ones observed in an ordinary bulk ROP of conventional lactones. The ¹H NMR spectrum (Figure 1d) of the product shows M derived phenyl, and methine signals at δ 7.35 and 6.09 ppm, respectively, as well as a G, derived methylene signal at δ 4.72 ppm, supporting the successful incorporation of phenyl groups into the PGL main chain. As shown in the enlarged carbonyl spectrum of Figure 1e, the signal due to the G units is split into two (δ 167.1 and 167.3 ppm) while that (δ 167.1 ppm) of the M units retains a single peak in spite of showing splitting feature. The former two signals at δ 167.1 and 167.3 ppm can be tentatively assigned to the two different diads, G#-M and G#-G, respectively, where G# denotes the ester carbonyl of a glycolate unit to which M and G are connected. Since the ring opening of PDD generates -GM* and -MG* terminals, the next propagation to these terminals takes place at either the G and M sites of PDD to form the following tetrads involving the newly formed diads underlined (Figure 1f). The larger signal of G#-G than that of G#-M indicates that the ring-opening of PDD takes place more readily at the less crowded G site than the M site. Here, the estimated diad ratio of G#-G/G#-M is 58/42. Contrarily, the single M# signal indicates the preferential opening at G site by the action of the bulkier M* terminal. Consequently, the unit sequence of PMG is almost random with the GM and MG diad monomer sequence preserved.

The DSC second heating curve of PMG (Figure 2) shows a T_g of 65.1 °C without showing a T_m and crystallization peak, indicating that the PMG has completely amorphous characteristics. As no melting behavior of homo-PGL or separated T_g of homo-PMA are present in Figure 2, it is also confirmed that there is no presence of homopolymers of PGL and PMA. Due to the non-site specific catalytic activity of tin octoate, only the randomly dispersed M and G were formed to induce atactic tacticity.

2.3. Copolymerization of PDD with GL and LA

To attain a tunable ratio of M and G, a ROP of PDD and GL for P(MG/GL) was performed in bulk state at a PDD/GL feeding

Figure 1. Synthesis scheme and NMR spectra; a) synthesis scheme, b) 200 MHz ^1H NMR of BAP, c) 200 MHz ^1H NMR of PDD, d) 500 MHz ^1H NMR of PMG, e) 125 MHz ^{13}C NMR of PMG, and f) diad formation consisting of G and M units.

ratio of 50/50 and 30/70 (in wt/wt). In these copolymerizations, the initiation was thought to be induced by a tiny amount of moisture remaining in the reactants as in the above homopolymerization. The recoveries of the resultant copolymers of P(MG/GL) were about 40% because of the loss of the oligomeric products during the reprecipitation; a similar result was observed in the homopolymerization of PDD for PMG. Their M_n values were 8900 Da for 50/50 and 8400 Da for 30/70, and

these were lower than expected because of the hygroscopic nature of GL which results in the existence of a larger amount of moisture. The copolymers were dissolved in deuterated trifluoroacetic acid for ^1H NMR measurement, as they were sparingly soluble in chloroform. The spectrum of ^1H -NMR of the P(MG/GL) obtained in the PDD/GL = 30/70 weight ratio is displayed in **Figure 3a**. The methylene signal of the G is shown at δ 5.30 ppm, while the methine and phenyl signals of the

Figure 2. DSC curve of PMG (second heating curve).

M are detected at δ 6.59 ppm and δ 7.69 ppm. The slight differences in chemical shifts result from the different solvent for NMR sample preparation. The spectrum is intrinsically identical to that of the PMG homopolymer which is shown in Figure 1d, except the increased intensity of the G signal as the G content was increased. Therefore, copolymerization of PDD and GL was confirmed. Copolymerization of PDD and LA by ROP was also performed. The yield and M_n of P(MG/LA) were higher than those of P(MG/GL). The reason is the lower hygroscopic property of LA compared to that of GL, and it is also

related to the differences in reactivity of LA and GL. The ROP was done at a fixed PDD/LA feeding ratio of 50/50 (in wt/wt), and it resulted in an M_n of 40.6×10^3 in a yield of 77.8%. Figure 3b shows the 500 MHz ^1H NMR spectrum of P(MG/LA) from 50/50 weight ratio of PDD/LA. The ^1H NMR signal of the methylene of G is detected at δ 4.71 ppm, while the signals of the methine and phenyl from M are seen at δ 6.01 and δ 7.41 ppm. Simultaneously, L derived methine and methyl are detected at δ 5.22 and δ 1.58 ppm, respectively. Additionally, in Figure 3c of ^{13}C NMR of P(MG/LA), the carbon signals of the L derived carbonyl, methyl, and methine appear at δ 169.5 ppm, δ 60.7 ppm, and δ 68.9 ppm, respectively, while the G derived carbonyl and methylene carbon signals appear at δ 167.2 ppm and δ 68.9 ppm. The carbon signals of M derived carbonyl, methine, and phenyl are seen at δ 165.9 ppm, δ 74.6 ppm, and δ 76.9 ppm respectively. As all the chemical shifts for the component units of P(MG/LA) were identical, these data indicate that all the esters from PDD and LA were successfully incorporated into the macromolecular chain of P(MG/LA). On the other hand, the ^{13}C NMR of P(MG/GL) showed no splitting of the carbonyl signals because the spectrum was measured in CF_3COOD (Figure 3d). This polymer was not soluble in the ordinary organic solvent similarly to PGA, it ought to involve sequential G units for which the average length was not estimated yet. In the P(MG/LA), a single carbonyl signal due to the L units is observed (Figure 3c), suggesting the involvement of sequential L units. At the present monomer ratio of PDD/LA = 50/50, the L sequence cannot be long if random polymerization takes place. Therefore, the present observation of relatively

Figure 3. a) 500 MHz ^1H NMR of P(MG/GL); PDD/GL = 30/70 wt/wt, b) 500 MHz ^1H NMR of P(MG/LA); PDD/LA = 50/50 wt/wt, c) 125 MHz ^{13}C NMR of P(MG/LA); PDD/LA = 50/50 wt/wt, and d) 125 MHz ^{13}C NMR of P(MG/GL); PDD/GL = 50/50 wt/wt.

Table 1. Summary of the results of polymerization and thermal characteristics of P(MG/GL), P(MG/LA), and PMG.

P(MG/GL)						
PDD/GL in weight	in feed unit ratio M/G	M/G ratio in P(MG/GL)	Yield [%]	M_n [10 ³ Da]	T_g [°C]	T_m [°C]
50/50	19/81	18/82	40.0	8.9	41	162
30/70	11/89	11/89	40.0	8.4	41	179
P(MG/LA)						
PDD/LA in weight	in feed unit ratio M/G/L	M/G/L ratio in P(MG/LA)	Yield [%]	M_n [10 ³ Da]	T_g [°C]	T_m [°C]
50/50	38/38/100	75/73/100	77.8	40.6	61.2	N.A.
PMG						
PDD in weight	in feed unit ratio M/G	M/G ratio in P(MG/GL)	Yield [%]	M_n (10 ³ Da)	T_g [°C]	T_m [°C]
100	50/50	50/50	59.1	43.0	65.1	N.A.

long L chain may suggest a block copolymerization of the two monomers. This feature is also shown for the above P(MG/GL). Further study will be done for the polymerization kinetics of PDD, LA, and GG monomers.

Table 1 shows a summary of the unit ratios of M, G, and L in the feed and final resultant polymers and their thermal properties. PDD and GL were reacted by ROP in the same reactor, and the M/G ratios in the feed and final resultant polymer in P(MG/GL) are almost identical. The T_g of the P(MG/GL) are not identical with the ones of their homopolymers, but its T_g of 61.2 °C (the value of P(MG/LA)) is higher than that of homo-PGL. Thus the P(MG/GL) contains a random copolymer sequence of PDD and GL, with improving T_g of homo-PGL by incorporation of phenyl units from PDD. It proved a successful incorporation of GL unit into PMG. However, the polymers show T_m which is derived from GL unit consisting of a certain amount of sequence length by showing semicrystalline properties, there is a slight difference in reactivity of PDD and GL. The copolymer composition of M, G, and L in P(MG/LA) was also calculated by the integral ratios of the ¹H NMR signals to be M/G/L = 75/73/100. The thermal characterization on P(MG/LA) only shows glass transition without showing melt of the polymer, therefore, the P(MG/LA) consists of randomly distributed PDD and LA to induce amorphous characteristics. The composition is significantly different from that calculated from the feed ratio, i.e., M/G/L = 38/38/100, suggesting that the PDD has higher polymerizability than LA. The reactivity of PDD, GL, and LA was also practically compared by a control experiment. The PDD, GL, and LA used for this control experiment were subjected to sufficient drying steps to avoid effects from moisture contamination. 1/500 mol of tin octoate as a catalyst and lauryl alcohol as an initiator were used for ROP at 180 °C for 15 min and the conversion of these was monitored by 500 MHz ¹H NMR. The short reaction time was applied to minimize side reactions such as transesterification and back-biting. The conversion of PMG, PGL, and PLA were 95.0%, 84.0%, and 76.0%, respectively. This indicates a higher reactivity of PDD compared to GL and LA. A kinetics study about ROP of GL and LA also reports that GL has a faster reaction

rate than LA when both are catalyzed by the same coordination mechanisms.^[29] Although, fine-tuning of polymerization conditions is required to attain controlled thermal properties, it can be concluded that copolymerization of PDD, GL, and LA is a promising approach.

3. Conclusions

The diester cyclic dimer PDD consisting of GA and MA was successfully synthesized, and its ROP produced PMG with a high molecular weight. The T_g of PMG reached 65.1 °C, which is significantly higher than that of PGL. Its sequence structure was random with respect to the M and G distribution. It was found that PDD is copolymerizable with GL and LA by ordinary ROP. The reaction rate of PDD in a bulk polymerization is higher than that of GL and LA. PDD is a new biobased lactone which is applicable for the introduction of phenyl groups into biobased polyesters to attain a high T_g .

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

biobased polymers, high T_g , modified glycolides, polyglycolides (PGL), polylactides (PLA)

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- [1] K. J. Dickers, H. Huatan, R. E. Cameron, *J. Appl. Polym. Sci.* **2003**, 89, 2937.
- [2] S. Fredenberg, M. Wahlgren, M. Reslow, A. Axelsson, *Int. J. Pharm.* **2011**, 415, 34.
- [3] S. Hurrell, R. E. Cameron, *J. Mater. Sci.: Mater. Med.* **2001**, 12, 817.
- [4] T. A. Hottle, M. M. Bilec, A. E. Landis, *Polym. Degrad. Stab.* **2013**, 98, 1898.
- [5] J. B. Eilert, P. Binder, P. W. McKinney, J. M. Beal, *J. Conn Am. J. Surg.* **1971**, 121, 561.

- [6] Nova institute website, http://bio-based.eu/market_study/media/files/13-06-21MSBiopolymersExcerpt.pdf (accessed: December 2017).
- [7] H. Nakajima, P. Dijkstra, K. Loos, *Polymers* **2017**, 9, 523.
- [8] C. Ding, A. S. Matharu, *ACS Sustainable Chem. Eng.* **2014**, 2, 2217.
- [9] V. Froidevaux, C. Negrell, S. Caillol, J.-P. Pascault, B. Boutevin, *Chem. Rev.* **2016**, 116, 14181.
- [10] D. J. V. van der Pas, K. M. Torr, *Biomacromolecules* **2017**, 18, 2640.
- [11] R. D. Clercq, M. Dusselier, B. F. Sels, *Green Chem.* **2017**, 19, 5012.
- [12] T. Mervi, V. Maija-Leena, K. Outi, M. Dominik, *Appl. Microbiol. Biotechnol.* **2017**, 101, 8151.
- [13] Plastics today website, <https://www.plasticstoday.com/content/finland-research-center-develops-new-technique-bio-based-plastic-packaging/54465275918335> (accessed: February 2018).
- [14] Kureha website, <http://www.kureha.com/pdfs/Kureha-KUREDUX.pdf> (accessed: November 2017).
- [15] K. Yamane, H. Sato, Y. Ichikawa, K. Sunagawa, Y. Shigaki, *Polym. J.* **2014**, 46, 769.
- [16] C. Yu, J. Bao, Q. Xie, G. Shan, Y. Bao, P. Pan, *CrystEngComm* **2016**, 18, 7894.
- [17] DemeTECH Corporation website, <http://www.demetech.us/sutures.php> (accessed: December 2017).
- [18] C. Chu, *J. Appl. Polym. Sci.* **1981**, 26, 1727.
- [19] R. M. Dębowska, A. Kaszuba, I. Michalak, A. Dzwigałowska, C. Cieścińska, E. Jakimiuk, J. Zielińska, A. Kaszuba, *Przegl. Dermatol.* **2015**, 102, 316.
- [20] Y. Bing, W. Victor, G. Jelani, C. Tara, *Biomacromolecules* **2007**, 8, 3308.
- [21] J.-M. Jeon, H.-I. Lee, S. G. Kim, S.-H. Han, J.-S. So, *Food Sci. Biotechnol.* **2010**, 19, 583.
- [22] T. Liu, T. L. Simmons, D. A. Bohnsack, M. E. Mackay, M. R. Smith III, G. L. Baker, *Macromolecules* **2007**, 40, 6040.
- [23] A. Buchard, D. Carbery, M. Davidson, P. Ivanova, B. Jeffery, G. Kociok-Kohn, J. Lowe, *Angew. Chem., Int. Ed.* **2014**, 53, 13858.
- [24] S. A. Cairns, A. Schultheiss, M. P. Shaver, *Polym. Chem.* **2017**, 8, 2990.
- [25] A. Pedna, L. Rosi, M. Frediani, P. Frediani, *J. Appl. Polym. Sci.* **2015**, 132, 42323.
- [26] F. Coumes, V. Darcos, D. Domurado, S. Li, J. Coudane, *Polym. Chem.* **2013**, 4, 3705.
- [27] O.-D. Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* **2004**, 104, 6147.
- [28] A. Dzienia, P. Maksym, M. Tarnacka, I. Grudzka-Flak, S. Golba, A. Zięba, K. Kaminski, M. Paluch, *Green Chem.* **2017**, 19, 3618.
- [29] R. Mazarro, A. De Lucas, I. Gracia, J. F. Rodríguez, *Macromol. Chem. Phys.* **2008**, 209, 818.