

論文の内容の要旨

生物材料科学専攻
平成 27 年度博士課程進学

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Synthesis and characterization of polyamides and polyesters from D-glucaric acid (グルカル酸を原料としたポリアミドとポリエステル合成および物性評価)

To reduce the use of petroleum-based polymers, the research of bio-based polymer has been greatly developed in the past few decades. Among these renewable bio-based resources, carbohydrates and their derivatives are very important sustainable building blocks because of their large supply, rich stereochemistry and environmentally friendly. Aldaric acids are one kind of these noticeable carbohydrates derivatives that have been studied these years. However, the molecular weights of the aldaric acid-based polymers were as low as several thousand, and the properties of these polymers are not sufficiently studied.

D-Glucaric acid (GA) is an aldaric acid based on an acyclic sugar main-chain with a carboxyl group at either end of its structure (Figure 1). GA occurs naturally in low concentrations in various vegetables and fruit. GA can be obtained by the oxidation of D-glucose with nitric acid, nitroxide derivatives, or microorganisms. Because of the low yield of GA production by chemical oxidation from D-glucose or D-gluconic acid, its complex stereochemical structure and easy lactones formation, the application of GA had been limited. Recently, the mass production of GA using bioengineering method have been developed rapidly. GA has become a sustainable resource and can be used in industry in large quantities. However, GA could form lactones easily. In order to synthesize GA-based polymers with linear structures, four hydroxyl groups need to be protected to prevent undesired side reactions and to allow polymerization with counter monomers through carboxyl groups.

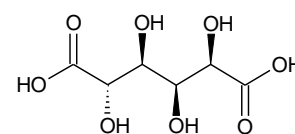
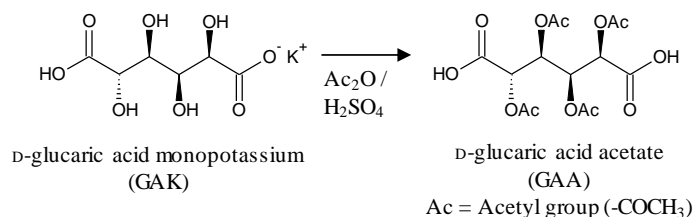


Figure 1. D-Glucaric acid

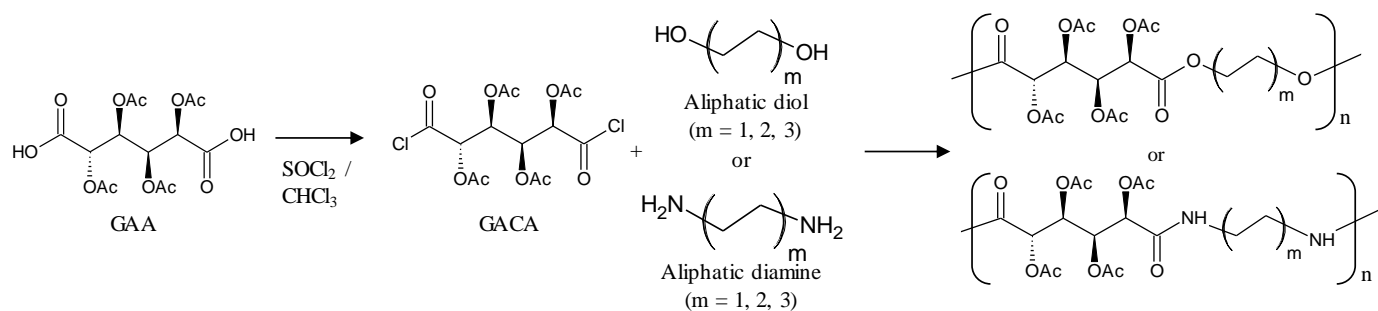
In chapter 2, all hydroxyl groups of GA were protected with acetyl groups using acetic anhydride and sulfuric acid (Scheme 1). The chemical structure of GAA was confirmed by one-dimension (1D) and two-dimension (2D) NMR techniques. The ^1H and ^{13}C NMR peaks for GAA were assigned based on COSY, HSQC, and HMBC. The results showed that D-

glucaric acid acetate (GAA) with an acyclic structure was synthesized successfully. The thermal stability of GAA was so low that it is difficult to use GAA in bulk polymerization.



Scheme 1. Acetylation of D-glucaric acid

In chapter 3, as shown in Scheme 2, GAA was converted to D-glucaric acid chloride acetate (GACA) for further application as a monomer. Polymerization of GACA was performed with aliphatic diols (EO, BO, and HO) and diamines (EA, BA, and HA) via solution or interfacial polymerization.



Scheme 2. Polymerization of GACA and aliphatic diols or diamines

The GAA-based aliphatic polyesters and aliphatic polyamides were dissolved in water, alcohol, and other common organic solvents. The weight-average molecular weights of the polyesters were 400 – 700; those of the polyamides obtained by solution and interfacial polymerizations were 5,900 – 8,000 and 14,500 – 20,800, respectively. The polyamides synthesized via interfacial polymerization are potential polymer materials because of their high molecular weight. DSC thermograms (Figure 2.) showed that the polyamides were thermoplastic and melted at ca. 140 °C that confirmed by POM (Figure 3.), indicating crystallinity. The melting points increased with increasing number of diamine alkyl carbons, which probably because of steric hindrance by acetyl groups in amide bond formation. However, these aliphatic polyamides were soluble in water and common organic solvent, which make it very difficult to purify them.

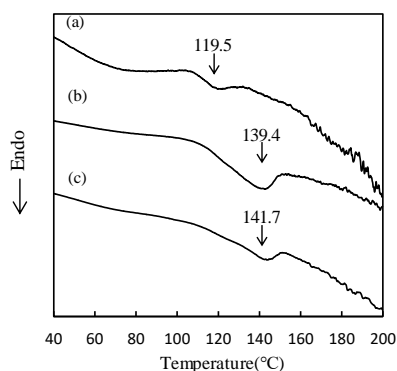


Figure 2. DSC thermograms of the polyamides consisting of GAA and (a) EA, (b) BA, and (c) HA, obtained by interfacial polymerization.

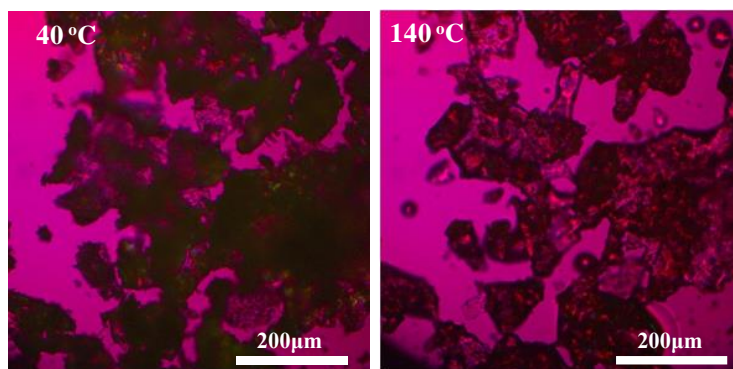
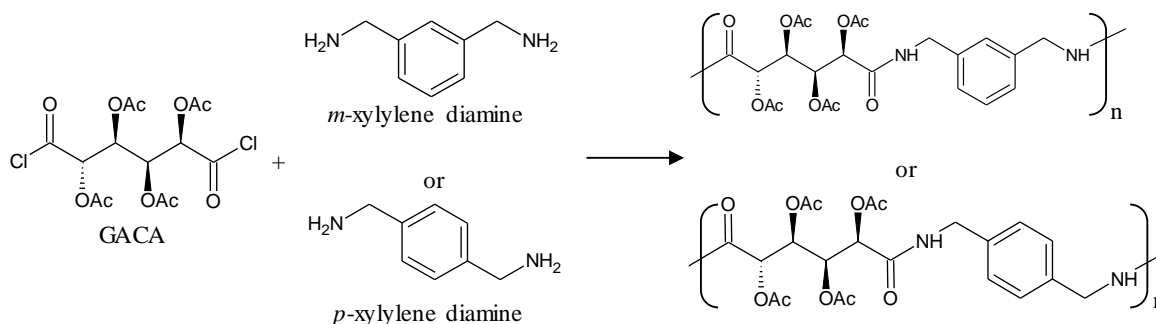


Figure 3. POM images of the polyamides consisting of GAA and (a) EA, (b) BA, and (c) HA obtained by interfacial polymerization.

In chapter 4, in order to improve the physical properties of GA-based polyamides and make the polyamides can be easily purified, aromatic rings structure was introduced into the polymer chain. Aromatic polyamides were synthesized from GAA and two types of aromatic diamines, *m*-xylylene diamine (*m*XDA) or *p*-xylylene diamine (*p*XDA).



Scheme 3. Synthesis of polyamides from GACA acid and aromatic diamines

The obtained polyamides were soluble in DMSO and DMAc, and insoluble in chloroform, acetone, methanol and water. The NMR measurements confirmed the successful polymerization and no formation of lactones derived from GAA monomer. The M_w s of the polyamides varied from 3,300 to 11,500 with polydispersity of ca. 1.6 - 1.9, depending on monomer ratio or monomer concentration in solution. The molecular weights were lower than the polyamides obtained from GAA and aliphatic diamines, but these aromatic polyamides could be purified easier. The TGA curves (Figure 4.) show that these polyamides have good thermal stability. The polyamides exhibited a small endothermic peak at ca. 147 °C in their DSC thermograms (Figure 5.), accompanied by melting-like behavior which was observed by POM. As shown in Figure 6, the XRD measurement revealed that the polyamides were mostly amorphous, but they exhibited a broad diffraction at small angle region, which could be attributed to an ordered structure in larger scale. It was proposed that the polyamides had some interactions, such as π - π stacking between aromatic rings. The endothermic melting-like behavior could be attributed to the deformation of these interactions.

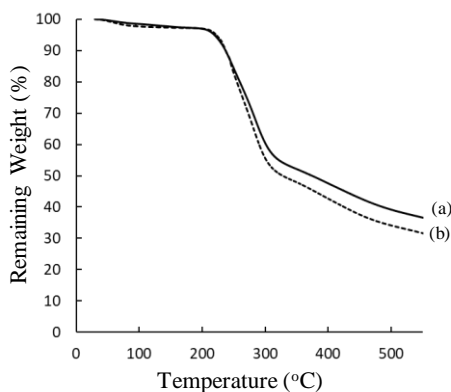


Figure 4. TGA curves of (a) poly(GAA-*m*XDA) and (b) poly(GAA-*p*XDA)

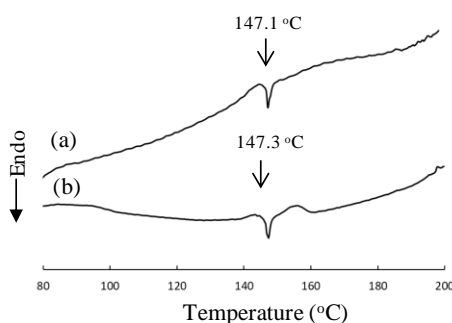


Figure 5. DSC thermograms of (a) poly(GAA-*m*XDA) and (b) poly(GAA-*p*XDA)

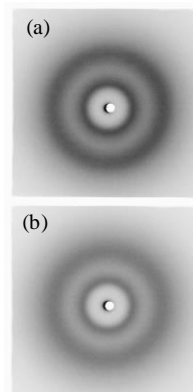
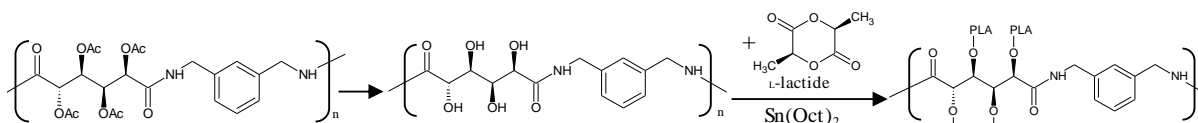


Figure 6. X-ray diagrams of (a) poly(GAA-*m*XDA) and (b) poly(GAA-*p*XDA)

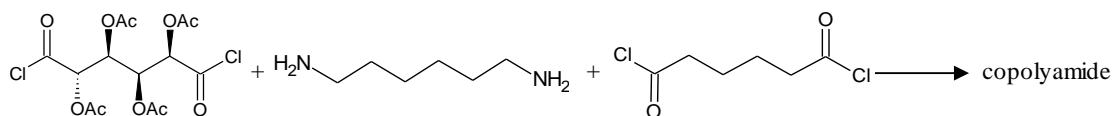
In chapter 5, as shown in Scheme 4, the acetyl groups of poly(GAA-*m*XDA) could be removed using 28% ammonia solution which was confirmed by NMR measurement. The obtained poly(GA-*m*XDA) was used to polymerize with *L*-lactide.

The molecular weight of the obtained poly(GA-*m*XDA)-*g*-PLA decreased with the increase in poly(GA-*m*XDA) content. The thermal stability of poly(GA-*m*XDA)-*g*-PLA was lower than PLA.



Scheme 4. Deprotection of GAA-based polyamide and synthesis with *L*-lactide

Furthermore, a series of copolyamides were synthesized from GACA, HA and AA with different monomer feeding ratios as shown in Scheme 5. These new class of polymers contained GA contents that was confirmed by NMR measurement. These three-component copolymers were expected to be more biocompatibility and possible to expand function because of the multi-functional of GA unit.



Scheme 5. Synthesis of copolyamide via interfacial polymerization

The above results show that it is important to improve the purification methods, yields, and molecular weights of GAA-based polymers for future applications of GA. However, these results show that GAA-based polymers have a potential to be used as novel bio-based polymer materials.