

Anhydride 말단 관능기를 갖는 폴리락타이드의 제조

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Preparation of End-functionalized Poly(L-lactide) with Anhydride Moiety Using Ring Opening Polymerization

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1. Introduction

Poly(lactic acid (PLA) is a biodegradable aliphatic polyester and is commonly synthesized by the ring opening polymerization (ROP) of lactide. By the mass production of PLA, its application becomes broaden from conventional biomedical application to commodity plastic field[1]. In order to utilize fully the potential of PLA, sometimes it needs to modify PLA according to the application.

In this article, we prepare end-functionalized PLA with anhydride moiety using a ROP and investigate the possibility as reactive compatibilizers for polymer blends containing nylon.

2. Experimental

2.1. Materials

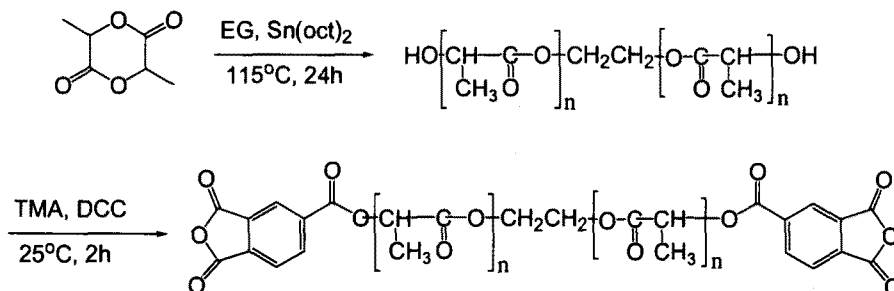
(3S)-cis-3,6-dimethyl-1,4-dioxane-2,5-dione(L-lactide, 98%), ethylene glycol(98% anhydrous, EG), tin(II) ethylhexanoate(95%, Sn(oct)₂), 1,2,4-benzenetricarboxylic anhydride (trimellitic anhydride, 97%, TMA), dicyclohexyl carbodiimide(99%, DCC) were purchased from Aldrich and used as received. Toluene and methylene chloride were stored over molecular sieves.

2.2 Preparation of trimellitic anhydride terminated poly(L-lactide)

First, poly(L-lactide) was prepared in a pre-dried 4-neck round flask equipped with a magnetic stirring bar. L-lactide(5g, 0.0345mol) was added into the flask followed by evacuation and flushing with dried N₂ three times. A mixture of EG and Sn(oct)₂ diluted with toluene was injected into the flask using micro-syringe. After evacuation and flushing with dried N₂, reaction was carried out in an oil bath of 115°C for 24h. The reaction products were diluted with methylene chloride and then precipitated into cold methanol. After filtering, the resultant polymers were dried overnight in a vacuum oven at 45°C prior to characterization.

Trimellitic anhydride terminated PLA (TMA-PLA) was prepared by direct reaction of hydroxyl group attached to the terminal end of PLA and TMA. The reaction was initiated by adding small amount of DCC to the solution of PLA and TMA under dry N₂ atmosphere. The ratio of PLA

and TMA was fixed at 1:10 by mole. The reaction was done at 25°C for 2h and terminated by adding methanol to remove the excess trimellitic anhydride. Scheme 1 shows the procedures for the preparation of trimellitic anhydride terminated PLA.



Scheme 1. procedures for the preparation of trimellitic anhydride terminated PLA.

2.2.3 Characterizations

Molecular weight and its distribution were determined using a GPC (GPCmax, Viscotek, USA) equipped with reactive index detector. THF was used as eluent and before measurement the column was calibrated with PS standards. ¹H-NMR spectrum of TMA-PLA was obtained using an ARX-R300 (Bruker, Germany) spectrometer, in order to assure whether anhydride moiety was introduced to PLA chain. Chloroform-d and tetramethylsilane (TMS) were used as solvent and internal standard, respectively. Thermal properties of PLA and modified PLA were measured using a PerkinElmer DDSC under a nitrogen atmosphere. Samples were heated from room temperature to 200°C (first scan) at the rate of 10°C/min and maintained at the final temperature for 3min to remove prehistory applied to the sample. After quenched to 30°C, the samples were then reheated to 200°C (second run) at the rate of 10°C/min.

3. Results and discussion

Molecular weight (M.W.) of PLA is controlled by changing the feed ratio of L-lactide and Sn(oct)₂. As shown in Fig. 1, M.W. of PLA is inversely proportional to the amount of Sn(oct)₂. When [PLA]/[Sn(oct)₂] > 1,200, the M.W. of PLA reached to 100,000g/mol, sufficiently high M.W. compared to the entanglement M.W. of PLA. The poly dispersity of PLA is in the range of 1.1 ~ 1.5. High M.W. PLA is also obtained when [Sn(oct)₂]/[EG] is about 2.0 (Fig. 1(b)).

Fig. 2 shows ¹H-NMR spectra of PLA and TMA-PLA. The peaks located at δ=1.58 and 5.17 ppm are corresponding to the H atoms of the -CH₃ and -CH, respectively. According to Espartero et al.[2], well-resolved CH contributions from hydroxyl and carboxyl end units appear at 4.2 and 4.99 ppm, respectively, in oligomeric PLA. The hydroxyl end unit of PLA is confirmed from the peak at 4.3 ppm. Contrarily to PLA-OH, several peaks are shown around δ = 7.6 ~ 8.2 ppm for TMA-PLA. These are corresponding to hydrogen atom in aromatic ring of TMA, indicating that TMA units are introduced to PLA chain.

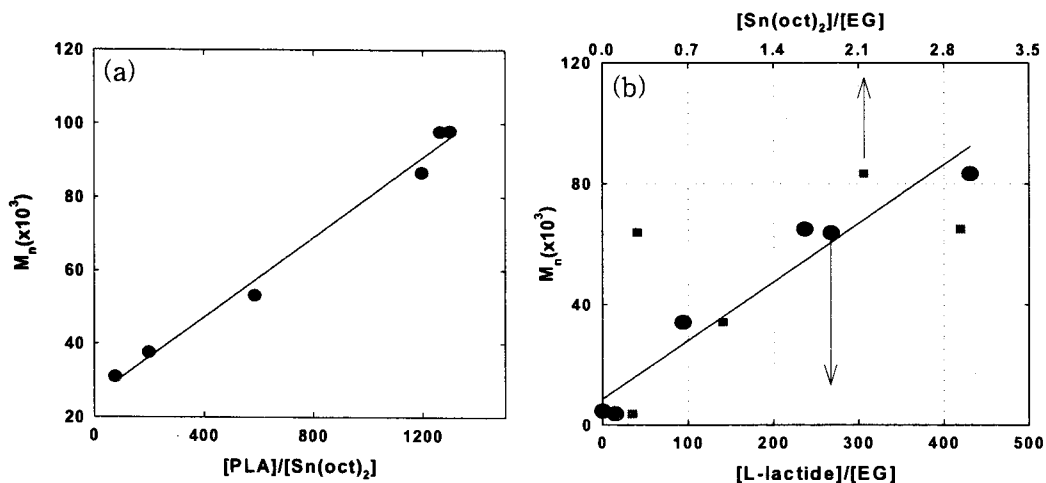


Fig. 1. Changes in the molecular weight of PLA: (a) without ethylene glycol, (b) with ethylene glycol.

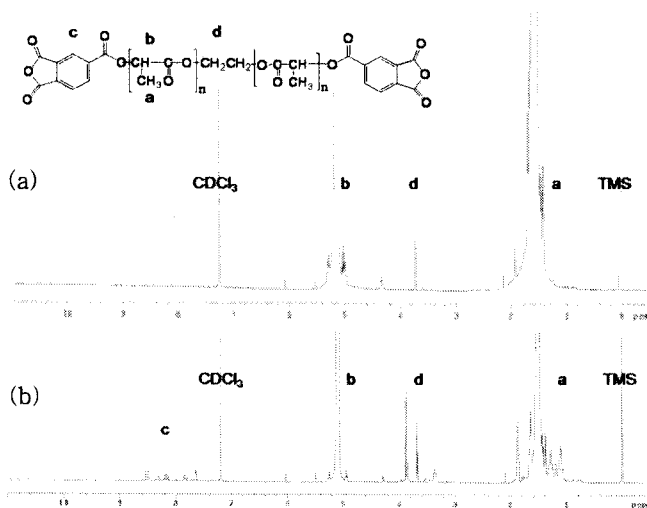


Fig. 2 1H -NMR spectra of (a) poly(L-lactide), (b) trimellitic anhydride terminated PLA

The DSC thermograms of PLA and TMA-PLA, which are obtained during second run, are shown in Fig. 3. Glass transition temperatures appear in the range of 54-62°C and melting peaks are observed in the range of 173-176°C with enthalpy of melting of 38-53J/g. This results are similar to those obtained from the thermal property of stereochemically pure PLA[3]. According to Bachari at al.[4], when PLA is prepared using ethylene glycol (EG) as initiator, T_m is decreased compared to PLA prepared without EG because center ethylene moiety in EG is rejected from the lamella crystals of PLA and tends to limit the crystal thickness and perfection. In Fig. 3, such depression is not found in PLA-OH may be due to the high molecular weight of PLA.

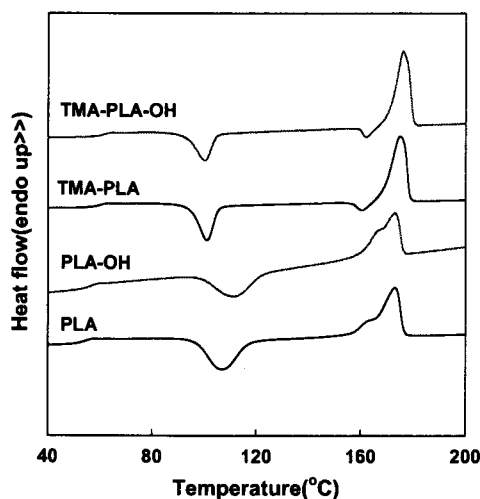


Fig.3 DSC thermograms of PLA and TMA terminated PLA

Nylon6/TMA-PLA blends were prepared using a home made-mini molder at 230°C. As not shown here, the anhydride moiety introduced in PLA contributes to the significant reduction of dispersed phase, indicating that TMA-PLA can be used as reactive compatibilizer for nylon6/PLA blends.

4. Conclusions

Trimellitic anhydride terminated PLA is prepared by ring opening polymerization and then direct coupling with TMA. For preparing PLA with hydroxyl terminal group, EG was used as initiator. The glass transition and melting temperatures do not affected by introducing end-functional group, but thermal stability decreases. TMA-PLA shows the possibility of potential compatibilizer for incompatible nylon6/PLA blends.

Acknowledgment

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References

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