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ประวัติผู้วิจัย

1. หัวหน้าโครงการ

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2. ผู้ร่วมวิจัย 1

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3. ผู้ร่วมวิจัย 2

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เอกสารการตีพิมพ์ผลงานวิจัย

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The Preparation of Poly(lactic acid) via Chain Linked Hydroxy-terminated Lactic Acid Prepolymer

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Abstract. In this work, hydroxyl-terminated lactic acid prepolymer was firstly prepared by adding diethylene glycol in the condensation of lactic acid. Molecular weight, acid value and structure of prepolymer were characterized. The results showed that the prepolymer was hydroxyl-terminated with weight average molecular weight (M_W) of 10,000 g/mol. After that, the chain linking polymerization of the prepolymer was carried out in a glass tube at 160 °C for 1 h employing 1,6-hexamethylene diisocyanate (HMDI) as a chain extender. By varying the hydroxyl/isocyanate ratio, it was found that the OH/NCO ratio of 1:2 seemed to be the most suitable ratio which gave PLA with the maximum M_W of 93,000 g/mol.

Introduction

Poly(lactic acid), PLA, is an attractive biodegradable polyester in respect that it is synthesized from raw materials derived from renewable resources such as corn, sugarcane and cassava. The main polymerization processes of producing PLA are ring-opening polymerization and direct condensation polymerization. Ring-opening polymerization is normally used to produce high molecular weight PLA [1,2]. By this process, PLA is made by the polymerization of lactide which is prepared from oligocondensate of lactic acid. The crude lactide contains impurities like water, lactic acid and oligomers. These impurities can interfere with the polymerization reaction. Therefore, crude lactide need to be purified. The purification process makes PLA high-priced. Condensation polymerization is the least expensive route but it is difficult to obtain high molecular weight PLA except the use of organic solvent [3].

An alternative way to achieve high molecular weight PLA is to prepare low molecular weight lactic acid prepolymer via condensation polymerization and link the prepolymer with chain extenders. Chain extenders are usually bifunctional low molecular weight chemicals that can increase molecular weight of polymers in a fast reaction without a separate purification step. Examples of chain extenders that can be used to link lactic acid prepolymer are bis-oxazolines [4] and diisocyanates [5]. Bis-oxazolines are reactive with carboxyl group whereas diisocyanates are react faster with hydroxyl group than carboxyl group [6]. Isocyanates are more often used because they are highly reactive [5, 7, 8].

In this work, hexamethylene diisocyanate was used to link hydroxyl-terminated lactic acid prepolymers. Hydroxyl-terminated lactic acid prepolymers were prepared by using 1.5 mol% of diethylene glycol.

Experimental

Materials. L-Lactic acid, LA, 80% LA in water was purchased from Aldrich. Titanium (IV) butoxide, TNBT (99%), 1,6-hexamethylene diisocyanate, HMDI (99%) and diethylene glycol, DEG (99%) were obtained from Acros.

Synthesis of prepolymers. Lactic acid prepolymer and hydroxyl-terminated lactic acid prepolymer were synthesized as follows: pure LA or LA with 1.5 mol% DEG was dehydrated for 2 h at 130 °C in an oil bath. After removing of water, the temperature was raised to 170 °C and 0.2 vol% TNBT catalyst was added. The condensation polymerization was carried on for 24 h at a mixing speed of 100 rpm and under a reduced pressure of 800 mbar. After 24 h, another 0.1 vol% catalyst was added and condensation reaction was continued for another 18 h. The polymer was precipitated by pouring the polymer solution into an excess of methanol, filtered and dried in a vacuum oven at 60 °C to a constant weight.

Chain linking polymerization with HMDI. A simple small scale chain linking polymerization of the hydroxyl-terminated lactic acid prepolymer was carried out as follows: 10 g of the prepolymer was weighed into a glass tube. The glass tube was heated in an oil bath at a temperature of 160 °C under a mechanical stirring (100 rpm). After the melting of the prepolymer, HMDI with a desired hydroxyl/isocyanate ratio was added. After 1 h polymerization, the molten polymer was poured into petri dish and placed in a desiccator to cool.

Characterization. Weight average molecular weight (M_w), number average molecular weight (M_n) and molecular weight distribution (MWD) of the prepolymers and HMDI linked polymers was determined using gel permeable chromatography (GPC/Agilant series) and HPLC grade chloroform was applied as an eluent. The eluent flow rate was kept constant at 0.5 ml/min. Polystyrene standards (Shodek standard) were used to generate a calibration curve.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Perkin-Elmer SPECTRUM GX spectrometer using KBr pellet method. The spectra were recorded in the 400-4000 cm^{-1} region with 4 cm^{-1} resolution.

Acid value, defined as the weight in milligrams of potassium hydroxide required to neutralize 1 g of the polymer, were determined by titrimetric method. Samples were dissolved in 12.5 ml of mixed solution (chloroform : methanol, 80:20) and titrated against 0.01 N KOH in methanol solution in the presence of phenolphthalein.

Results and Discussion

Characterization of hydroxyl-terminated lactic acid prepolymer. Acid value, molecular weight and MWD of the hydroxyl-terminated lactic acid prepolymer were compared with that of lactic acid prepolymer in Table 1.

Table 1 Acid value, molecular weight and MWD of prepolymers.

Sample	Acid value	Molecular weight (g/mol)		MWD
		M_w	M_n	
Hydroxy-terminated lactic acid prepolymer	5.04	10,524	8,379	1.24
Lactic acid prepolymer	10.72	17,048	12,946	1.32

The results presented in Table 1 showed that the acid value of hydroxyl-terminated lactic acid prepolymer is a half value of that of lactic acid prepolymer. This proved that acid end group of lactic acid prepolymer was replaced by hydroxyl group when DEG was added into the condensation of lactic acid. Molecular weight of hydroxyl-terminated prepolymer was lower than that of lactic acid prepolymer. This is not unusual for esterification reaction because the reaction will end earlier when hydroxyl group and acid group in the system is not in stoichiometric ratio. The resulting prepolymers have quite narrow molecular weight distribution.

FTIR spectra of hydroxyl-terminated prepolymer and lactic acid prepolymer are given in Fig. 1. In the spectrum of hydoxyl-terminated lactic acid prepolymer, the OH peak at 3500 cm^{-1} is relatively large when compared with lactic acid prepolymer.

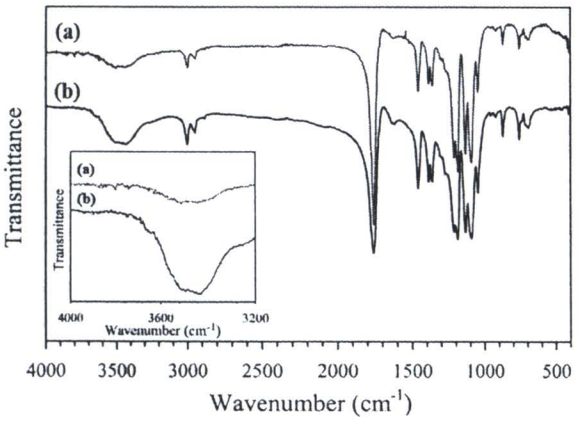

Fig. 1 FTIR spectra of (a) lactic acid prepolymer and (b) hydroxyl-terminated lactic acid prepolymer.

The results from acid value determination and FTIR analysis confirmed the successful preparation of hydroxyl-terminated lactic acid prepolymer.

Characterization of PLA prepared from chain linked hydroxyl-terminated lactic acid prepolymer. GPC chromatograms of the polymer prepared by chain linking polymerization of hydroxyl-terminated lactic acid prepolymer using HMDI with 3 different ratios of OH/NCO are compared in Fig. 2.

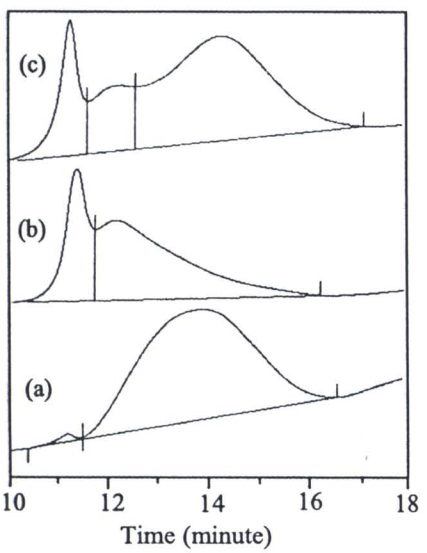

Fig. 2 GPC chromatograms of PLA prepared using OH/NCO ratio of (a) 1:1 (b) 1:2 and (c) 1:2.5.

The results from GPC chromatograms can be interpreted as follow: The first peak of all chromatograms correspond to the highest molecular weight obtained from each condition. when OH/NCO ratio of 1:1 was used, only small amount of the prepolymer (about 1 %) was converted to a high molecular weight PLA (M_w = 120,000 g/mol). When the ratio of OH/NCO was increased to 1:2, 34% of PLA with M_w of 93,000 g/mol were obtained. The GPC peak also rather separated. This means that the PLA with M_w of 93,000 g/mol was not difficult to be separated from the less PLA. For the PLA prepared using OH/NCO ratio of 1:2.5, PLA with M_w of 99,000 g/mol was also produced but only in the proportion of 18%. Therefore, the OH/NCO ratio of 1:2 is the most suitable ratio for producing PLA with high molecular weight using a simple glass tube and 1 h linking reaction.

FTIR spectra of hydroxyl-terminated lactic acid prepolymer and PLA prepared by linking with HMDI are compared in Fig. 3.

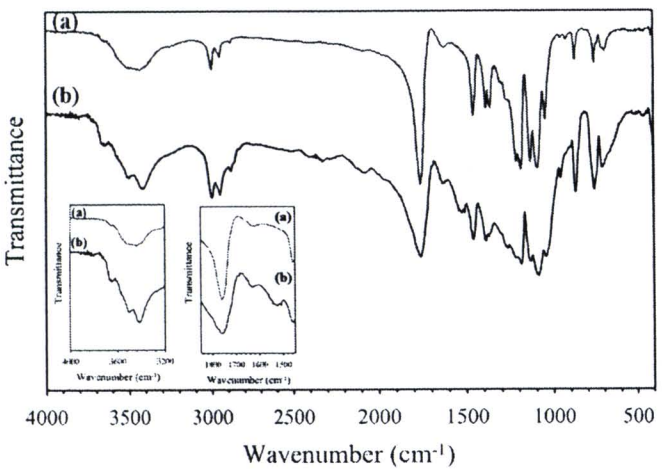

Fig. 3 FTIR spectra of (a) hydroxyl-terminated lactic acid prepolymer and (b) PLA prepared by linking with HMDI (OH/NCO = 1:2).

When reaction between the prepolymer and HMDI occurred the OH peak decreased. The urethane NH at about 3400 and 1540 cm^{-1} also formed from the reaction between OH and HMDI.

Conclusions

The acid value and FTIR analysis confirmed the occurrence of hydroxyl-terminated lactic acid prepolymer with a molecular weight of 10,000 g/mol. Chain linking polymerization of the prepolymer using HMDI with OH/NCO ratio of 1:2 seemed to be the most suitable condition that gave the PLA with the maximum M_w of 93,000 g/mol.

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