

# Study on Biodegradable Polymer Materials Based on Poly(lactic acid). I. Chain Extending of Low Molecular Weight Poly(lactic acid) with Methylenediphenyl Diisocyanate

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**ABSTRACT:** Methylenediphenyl diisocyanate (MDI) was used as the chain extender for low molecular weight poly(lactic acid) (PLA) to produce high molecular weight biodegradable polymer material with a better heat resistance. PLA prepolymer with a number-average molecular weight ( $M_n$ ) of 5800 and a weight-average molecular weight ( $M_w$ ) of 9800 was produced by direct polycondensation using stannous octoate as the catalyst. After 40 min of chain extension at 175°C, the resulting polymer had a  $M_n$  of 15,000 and a  $M_w$  of 57,000. The glass transition temperature ( $T_g$ ) of the low molecular weight PLA prepolymer was 48.6°C. After chain extension, the  $T_g$  of the resulting polymer was raised to 67.9°C, as determined by DSC. DMA results also indicate that the heat resistance was improved by the chain extension. The DSC spectrum and X-ray diffraction pattern of annealed samples showed that both the crystallinity and rate of crystallization of PLA were lowered by chain-extension reaction due to the formation of branched molecular structure. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2546–2551, 1999

**Key words:** poly(lactic acid); chain extender; methylenediphenyl diisocyanate

## INTRODUCTION

Waste disposal has become a serious problem world wide. There is a strong need to provide plastic materials suitable for packaging, which at the same time, will also be degradable and result in products that are environmentally safe. Lactic acid-based polyesters are well-known biodegradable polymers that can be used not only for biomedical applications, but also in packaging and consumer goods.<sup>1</sup> However, high molecular weights are needed for poly(lactic acid) (PLA) to have good physical properties.<sup>2</sup> Until now, high

molecular weight PLA was synthesised by ring-opening polymerization of the cyclic dimer of lactic acid–lactide, which is relatively complicated and expensive.<sup>3,4</sup>

Direct polycondensation of lactic acid is a low-cost process to produce PLA; however, it is hard to increase the molecular weight enough because of the difficulty of removing the water from the system.<sup>3,4</sup> Chain extenders such as ethylene carbonate, heterocyclic compounds, and diisocyanate can connect the end groups of PLA so as to produce high molecular weight PLA materials.<sup>2</sup> Hexamethylene diisocyanate (HDI) has been reported to be an effective chain extender not only for direct polycondensed PLA<sup>3</sup> but also for hydroxyl terminated low molecular weight PLA.<sup>4</sup> Nevertheless, the resulting polymer loses its stiffness at temperatures higher than 50°C. So Sepala et al. polymerized lactic acid with aromatic

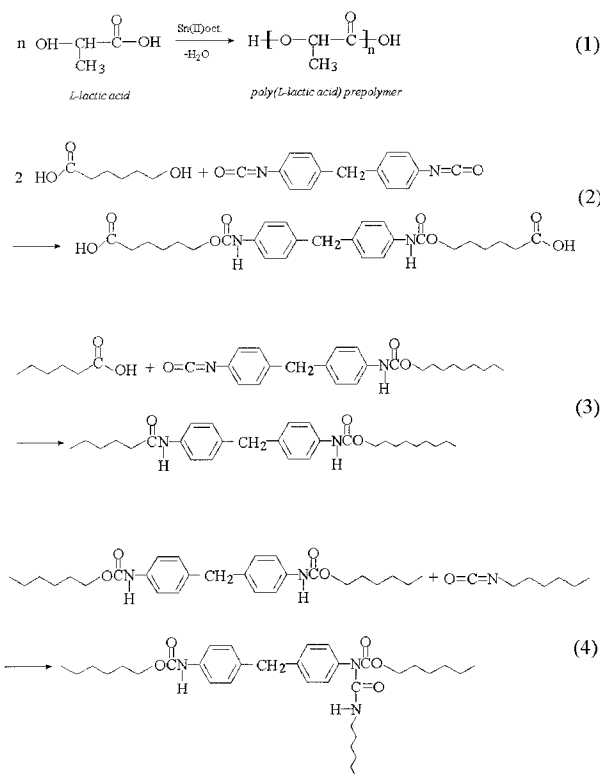
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**Figure 1** The synthesis scheme of the PLA prepolymer and the PLA chain extended with MDI.

comonomers such as DL-mandelic acid before chain extension with HDI to improve the heat resistance of the chain-extended PLA.<sup>5</sup>

In this article, PLA, with higher molecular weight and higher glass transition temperature, was produced by direct polycondensation of lactic acid followed by chain extension. Methylenediphenyl diisocyanate (MDI) was used as the chain extender.

## EXPERIMENTAL

### Materials

L-Lactic acid of 90% aqueous solution was purchased from Fluka, and it was 99% optically pure.

Before using, it was purified by distillation at 100°C under vacuum. The following chemicals were used as received: stannous octoate from Sigma Chemical Co., MDI (+99.5%) was purchased from Wanhua synthesized leather Group, Yantai, China. All other chemicals were reagent grade.

### Synthesis of Polymer

The low molecular weight PLA prepolymer was synthesized through polycondensation. 50 g purified L-lactic acid, and 0.02 g stannous octoate was placed in a 250-mL three-necked flask with a mechanical stirrer and nitrogen inlet; a continuous nitrogen stream was kept under the surface of the liquid. The flask was heated with an oil bath while stirring, and through a period of 8 h the temperature was raised to 200°C while the pressure was reduced to 670 Pa. The total reaction time was 24 h.

After polycondensation, the temperature was lowered to 175°C under atmospheric pressure, and 4 g of MDI was added to the flask while stirring; the reaction was followed by taking samples every 10 min. After the reaction, the resulting polymer was dissolved in 100 mL of chloroform and precipitated in the excess of ethanol. The final product was isolated by filtration and dried in a vacuum at 50°C over night.

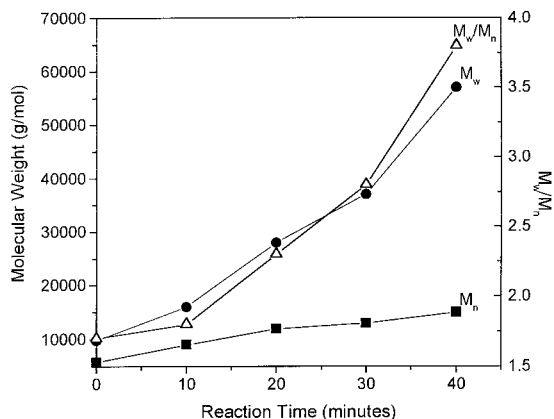
### Characterizations

The molecular weight was determined in chloroform with a Shimadzu LC-3A GPC, using polystyrene standards for calibration. DSC measurements were performed with a Setaram DSC92 at 10°C/min. Dynamic mechanical analysis (DMA) was performed on a Netzsch DMA242 instrument using the three-point bending method at a heating rate of 3°C/min, and a frequency of 1 Hz. A Nicolet IR-550 FTIR was used to scan the IR spectrum, and the X-ray diffraction pattern was recorded with a Rigaku D/MAX-RB X-ray diffractometer.

**Table I** Some of the Analysis Results of Prepared Polymers

Sample	$M_n$	$M_w$	MWD	$T_g$ (°C) (DSC)	$T_g$ (°C) (DMA)	$T_m$ (°C) (DSC)
PLA Prepolymer	5800	9800	1.7	48.6	50.3	151.8
PLA-MDI <sup>a</sup>	15,000	57,000	3.8	67.9	76.1	148.9

<sup>a</sup> Reaction time: 40 min, temperature: 175°C, molar ratio of NCO/OH: 4.



**Figure 2** The increment of the number- and weight-average molecular weight of the PLA with a chain-extending reaction time at 175°C and a molar ratio of NCO/OH = 4. The sample having a reaction time of 40 min is not totally soluble in chloroform; the results listed are the molecular weights of the soluble fraction.

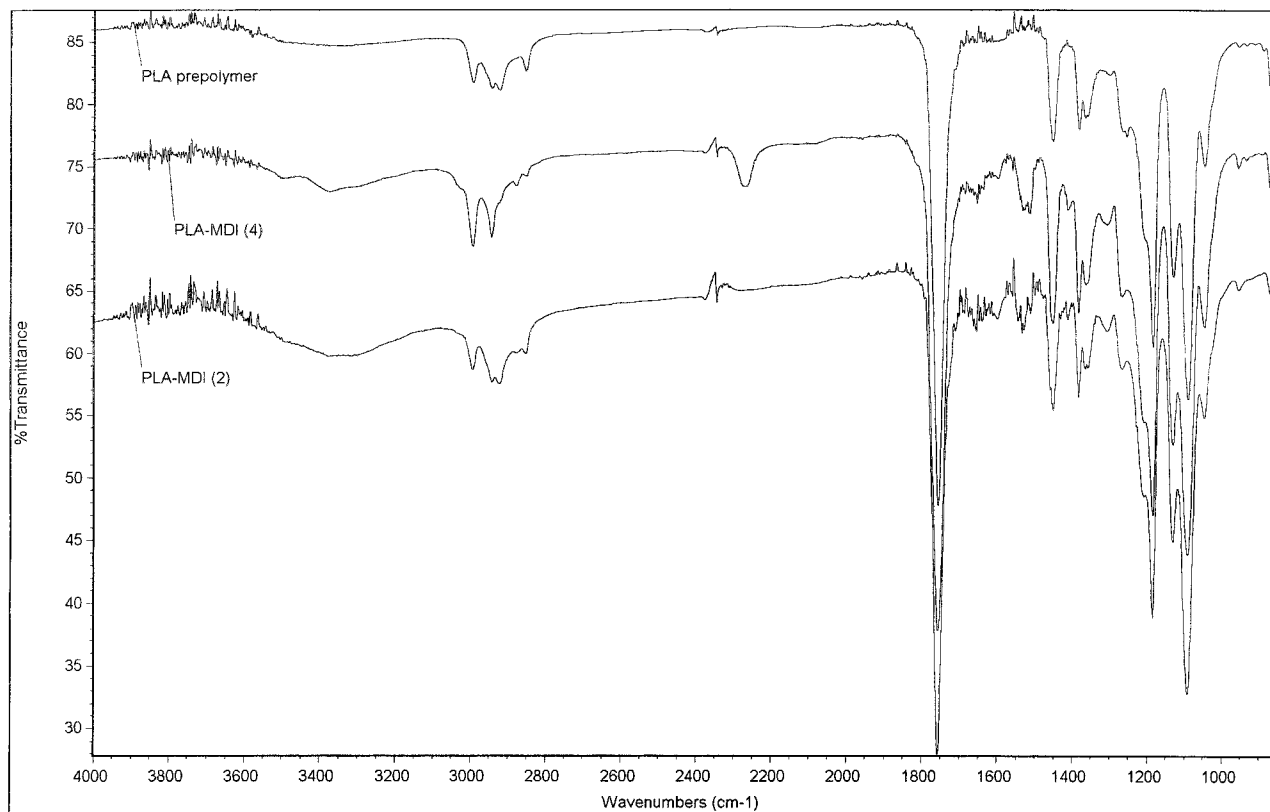
## RESULTS AND DISCUSSION

### Polymerization

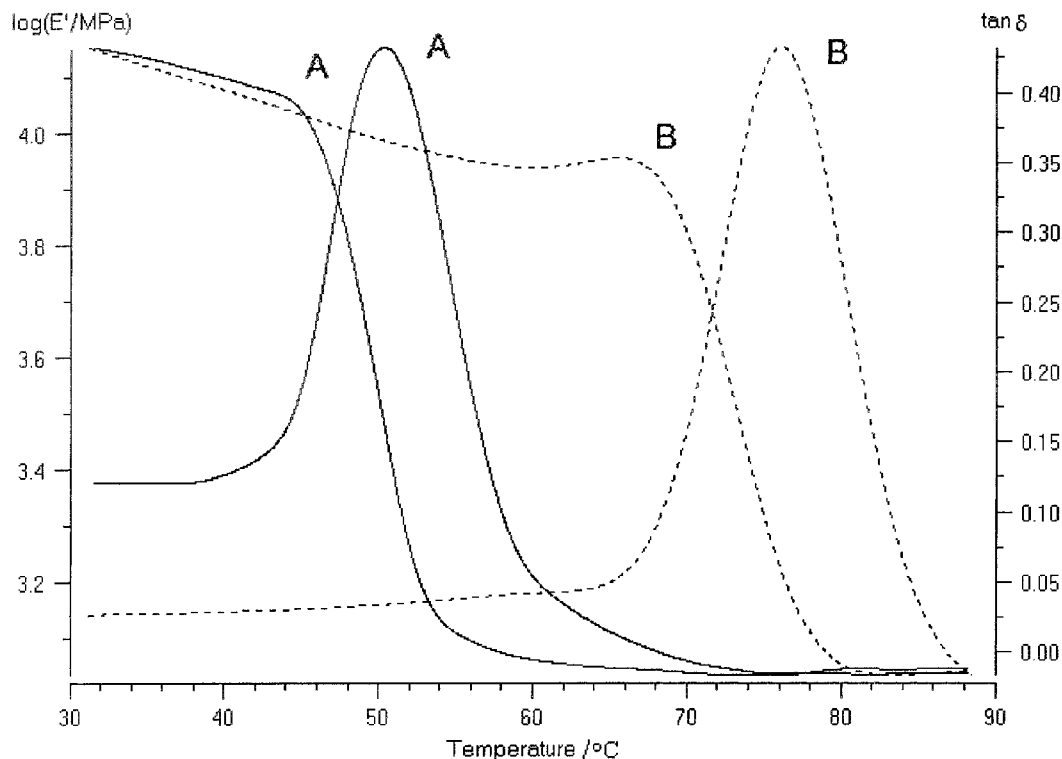
The PLA prepolymer was synthesized using stannous octoate as the catalyst according to reaction

(1) shown in Figure 1. After chain extending at 175°C for 40 min, the reaction product was collected and analyzed. The analysis results were summarized in Table I. The molecular weight was increased remarkably after chain extension. It was suggested that diisocyanate can connect the hydroxyl end groups of PLA molecules through urethane bonds so as to double the molecular weight as shown in reaction (2) of Figure 1. However, the resulting polymer had more than twice the molecular weight of the PLA prepolymer. The excess amount of the isocyanate group may also react with the other end of PLA molecule (—COOH) to form amide linkage according to reaction (3) of Figure 1 or react with the urethane group known as an allophanate reaction<sup>3,6</sup> to cause chain branching or crosslinking [reaction (4)]. The chain branching will widen the molecular weight distribution. That probably is the reason for the greater molecular weight distribution (MWD) of the chain-extended PLA sample than that of the PLA prepolymer listed in Table I.

According to ref. (3), HDI can increase the number-average molecular weight of PLA nearly five times after 20 min reaction at 160°C when



**Figure 3** The IR spectrum of the PLA prepolymer and the PLA chain extended with MDI. The chain-extending reaction time: 40 min; temperature; 175°C, molar ratio of NCO/OH for PLA-MDI (2): 2; PLA-MDI (4): 4.



**Figure 4** DMA storage modulus and  $\tan \delta$  curves of the PLA prepolymer (A) and the PLA chain extended with MDI (B). Test mode: three-point bending; heating rate:  $3^\circ\text{C}/\text{min}$ ; frequency: 1 Hz.

the molar ratio of NCO/OH is around 4. However, the increment effect of MDI on molecular weight of PLA is not so high. This may be because aliphatic isocyanate reacts more easily with the carboxyl group of PLA to form an amide linkage than the aromatic isocyanate.<sup>6</sup>

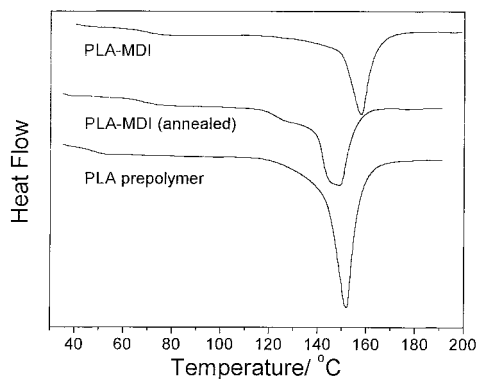
Figure 2 shows the increment of molecular weight with the time of the chain-extending reaction. Both the  $M_w$  and  $M_n$  of PLA increased with increasing the reaction time. At the same time, the molecular weight distribution also increased with the reaction time because of the allophanate reaction. The effect of this side reaction became so remarkable after 40 min that the resulting product was partially insoluble in chloroform due to the crosslinking of the polymer chain.

Figure 3 shows the IR spectra of the PLA prepolymer and two chain-extended products with different molar ratios of NCO/OH after a 40-min reaction. All three IR spectra have characteristic ester absorption bands at  $1760$  and  $1090\text{ cm}^{-1}$ , respectively. The NH absorption peak at  $3400\text{ cm}^{-1}$  appeared after the chain-extending reaction. The isocyanate peak at  $2300\text{ cm}^{-1}$  for PLA-MDI (2) disappeared, which indicates that all free iso-

cyanate groups had been consumed out in the reaction when the molar ratio of NCO/OH is 2, while for PLA-MDI (4) having doubled the NCO/OH, there was still a small peak for free isocyanate groups.

### Thermal Property

The DMA measurement results are shown in Figure 4. The  $T_g$  has been raised to  $76.1^\circ\text{C}$  for chain-extended PLA from  $50.3^\circ\text{C}$  for the PLA prepolymer. Similar conclusions can be drawn from DSC tests according to Table I. There may be two reasons for the elevation of  $T_g$ : first, the increment of the molecular weight reduced the number of free chain ends and thus reduced the free volumes;<sup>4,5</sup> second, the introduction of a rigid aromatic structure into the polymer chain hinders the chain movement sterically. The second reason maybe more important here because the  $T_g$  of the PLA chain extended with HDI was not changed much according to refs. (3) and (4). From the DMA results, it can be concluded that the heat resistance of PLA can be improved by chain extending with MDI.



**Figure 5** DSC thermographs of the PLA prepolymer and the PLA chain extended with MDI. Annealing condition: 100°C, 36 h.

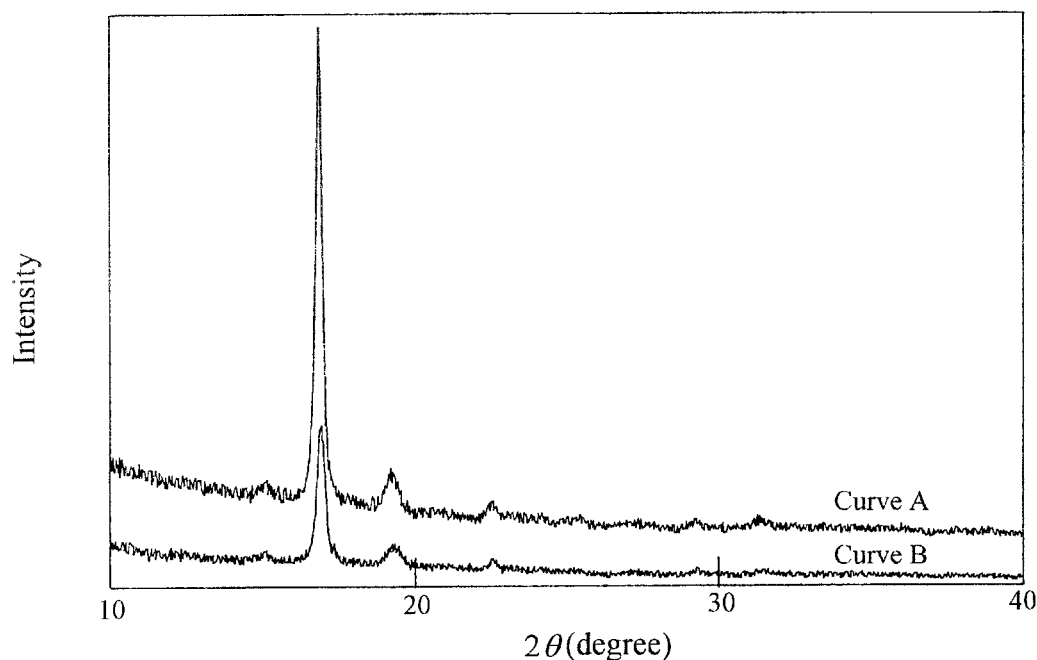
### Crystallinity

Figure 5 shows the DSC thermograms of the PLA prepolymer and chain-extended PLA. Their crystalline enthalpies were  $-38.24$  mJ/mg and  $-23.96$  mJ/mg, respectively. To investigate their crystallization behavior in detail, the samples were annealed at 100°C for 36 h. After annealing, the crystalline enthalpy of the PLA prepolymer and chain-extended PLA were changed to  $-47.05$  mJ/mg and  $-34.25$  mJ/mg, respectively, and the crystalline peak of the PLA-MDI sample became wider and moved toward lower temperatures,

while the peak of the PLA prepolymer remained the same shape and position (data not shown). The crystallization behavior is in close relationship with the tacticity of the polymer chains. After the chain-extending reaction, the chain branching lowered the tacticity of the PLA molecule. Only the chains without branches could crystallize during the short cooling period after the reaction. That is why the crystalline enthalpy of the chain-extended PLA sample was much lower than that of the PLA prepolymer. During the period of annealing, the branched chains could crystallize, although more slowly. However, the crystal perfection was much lower, so the crystalline peak became wider and moved to a lower temperature. The same result can also be obtained from X-ray diffraction tests. From the WAXD pattern of annealed samples (Fig. 6), the PLA prepolymer showed the sharpest peak at  $2\theta$  of about  $16.7^\circ$  (020 reflection). Other peaks were at  $14.8$  (101 reflection) or  $19.1$  (023 reflection),<sup>7</sup> while the peaks of the chain-extended samples were much lower.

### CONCLUSION

Higher molecular weight and higher  $T_g$  PLA material can be prepared through the chain-extend-



**Figure 6** WAXD pattern of the PLA prepolymer (curve A) and the chain-extended PLA (curve B). Both samples were annealed at 100°C for 36 h.

ing reaction of the low molecular weight PLA prepolymer with MDI. The molecular weight of the resulting polymer increases, and the molecular distribution becomes broader with increasing chain-extending time until the product is partially crosslinked. Chain-extended PLA had lower crystallinity and slower crystallization speed determined by DSC and XRD than PLA prepolymer because of the branched structure. The heat resistance of PLA is improved by chain extending according to the results of DMA.

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