Chain-Linked Lactic Acid Polymers by Benzene Diisocyanate

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ABSTRACT: Chain-linked lactic acid polymers with high molecular weight were synthesized by two-step polymerization method, including polycondensation and chain extending reactions. The effects of chain extender toluene diisocyanate (TDI) on the chain-linked lactic acid polymers were studied. The polymers obtained were characterized by gel permeation chromatography, fourier transform infrared spectroscopy, ^{1}H NMR, and differential scanning calorimeter. Reactions between 1,4-butanediol and lactic acid oligomers led to hydroxyl-terminated prepolymer, which provided significant increase of molecular weight in the chain extending reaction. In addition, the glass transition temperature (T_g) and the melting temperature (T_m) were increased. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1045–1049, 2006

Key words: poly(lactic acid); polycondensation; chain extending

INTRODUCTION

Biodegradable plastics refer to the plastics that can degrade environmentally after having served their purposes to be eventually recycled to nature in the form of low-molecular-weight compounds. Poly(lactic acid) (PLA) is the most typical of the biodegradable plastics based on aliphatic polyesters, since they are not only high in degradability and transparency but also so highly compatible with other polymers that can be easily modified in characteristics. Additionally, PLA, generated from annually renewable resources such as corn, can reduce the consumption of nonrenewable petrochemicals.

PLA is currently produced by two methods: in one method, lactide, which is a cyclic dimer of lactic acid,[1,2] is used as a starting material and subjected to ring-opening polymerization; the other method comprises subjecting lactic acid to dehydrative polycondensation. The first approach from which the PLA obtained is limited to the use in high-value regions, such as medical area, for its higher cost, compared with other polymers. The second means can significantly reduce the spending of PLA. However, it is difficult to obtain PLA with high molecular weight in a solvent-free system.[3,4]

Because of the relatively complicated and expensive ring-opening polymerization of lactide, and the need for the modification of the polymer properties of PLA for many different type of applications, alternative polymerization routes for lactic acid are of considerable interest. An alternative way to achieve high-molecular-weight PLA is to treat condensation polymers with chain extenders.[5–7] Inata and Matsumura studied extensively carboxyl [8–10] and hydroxyl-reactive [11,12] addition-type chain extenders for polyesters. Suitable chain extenders for polyesters are bis(2-oxazolines), diisocyanates, bisepoxides, bis(ketene acetals), dianhydrides, bis[5(4H)-oxazolones], and bis(5,6-dihydro-4H-1,3-oxazines).[13–16] The very high reactivity of the isocyanates has enlarged their use for coupling and chain extension of oligomers.[17–20]

On the basis of the background, we became interested in applying isocyanates as chain extenders. Hydroxyl-terminated prepolymers, prepared by using 0–4 mol % of 1,4-butanediol (BD), were linked with toluene diisocyanate (TDI). Prepolymer E1% denotes that prepolymer reacts with 1 mol % of BD.

EXPERIMENTAL

Materials

L-Lactic acid, 90% L-lactic acid in water, was provided by PURAC, Holland. Sn(II) chloride (99%), BD (99%),
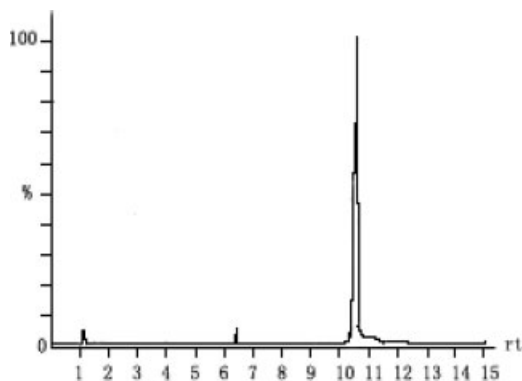
Figure 1 Chromatogram of ʟ-lactic acid.

chloroform (99%), TDI (99%), and Sn(II) octoate (99.5%) were provided by Shanghai Chemical, China.

The properties of lactic acid, such as purity, are vital to the outcome of the polymerization. In our research, ʟ-lactic acid solution was dehydrated first, and the properties of ʟ-lactic acid were determined with a chromatogram–mass apparatus. There are two major impurities existing in the ʟ-lactic acid (Fig. 1), and mass spectra confirm that the impurities are acetaldehyde and ethylic acid. Table I displays the contents of impurities in the ʟ-lactic acid without water.

Polymerization

ʟ-Lactic acid was dehydrated for 2 h at 120°C in the presence of 0.1 mol % Sn(II) chloride. After removing water, 0–4 mol % BD was added to produce hydroxyl-terminated oligomers, and 0.1 mol % Sn(II) octoate was used as a catalyst. The flask, purged with nitrogen, was placed in an oil bath. The ʟ-lactic acid was polymerized at 150°C for 20 h at a mixing speed of 200 rpm and under a reduced pressure of 50 mbar. The prepolymer obtained by polycondensation was used without further purification.

The chain extending of the prepolymer was carried out with TDI as chain extender at a mixing speed of 100 rpm and 180°C for the desired reaction time.

Characterization

Chromatogram spectrum and mass spectra were recorded to determine the properties of lactic acid on a Voyager chromatogram–mass apparatus.

Molecular weight was determined with a Waters 150C-GPC gel permeation chromatography, using chloroform as the solvent. The degree of viscidity ($[\eta]$) was tested using capillary with a diameter of 0.4–0.5 mm and chloroform as the solvent.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on an EQUINOX 55 spectrometer using compression molded film samples at a range of 400–4000 cm^{-1}. ^{1}H NMR spectra were obtained at room temperature with a Bruker 500 MHz spectrometer in $CDCl_3$.

Thermal properties of polymers were determined with a Setaram DSC92 differential scanning calorimeter (DSC) between 0 and 200°C with a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Schemes of reactions

High-molecular-weight chain-linked LA polymers are prepared by applying the two-step polymerization method, including polycondensation and chain extending. The self condensation polymerization of LA results in low-molecular-weight oligomers (Scheme 1(1)), which have an equimolar concentration of carboxyl and hydroxyl end-groups.

Regarding the TDI chain extending reactions, the diisocyanate linking reaction for the formation of polyurethane requires prepolymer with only hydroxyl end-groups; therefore, the low-molecular-weight PLA is modified by reacting with BD for hydroxyl-terminated prepolymer (Scheme 1(2)). However, when the diisocyanate is used in excess, the side reactions cause branches of the polymer (Scheme 2).

Chain extending with tdi

As seen in Figure 2, the weight-average molecular weight increases within the first 2 h. After reaching the maximum, a decrease occurs owing to the thermal degradation and the decrease of reactive groups. With decrease in the OH/NCO ratio, the weight-average molecular weight curves gradually become flatter. However, highest molecular weight is achieved at 120 min for OH/NCO ratio of 1:1.2.

With the polymerization time, the trend of $[\eta]$ is similar to that of the weight-average molecular weight

TABLE I
Compositions of ʟ-Lactic Acid

Entry	Name	Chromatogram	RT	Area	Area%
1	Acetaldehyde	TIC	1.219	261096	0.06
2	Ethylic acid	TIC	468	263211	0.06
3	ʟ-(+)-Lactic acid	TIC	10.689	455291968	99.88

Scheme 1 Reactions of lactic acid polycondensation, hydroxyl termination, and chain extending.

of chain-linked LA polymers (Fig. 3). However, it is abnormal with the increase of TDI. For example, although the weight-average molecular weight of polymer for OH/NCO ratio of 1:1 is comparative with that of polymer for OH/NCO ratio of 1:2 at 120 min, the $[\eta]$ of polymer for OH/NCO ratio of 1:2 is higher than that of polymer for OH/NCO ratio of 1:1. Possibly, it is because that the degree of branching augments with the increase of TDI.

The analysis of chain extending reactions was carried out with FTIR and ^{1}H NMR.

The FTIR spectra of prepolymers and prepolymers coupled with TDI are given in Figure 4. In the spectrum of prepolymer E1%, the OH peak at 3520 cm^{-1} enlarges when compared with prepolymer E0%. When the reaction between prepolymer E1% and TDI takes place, the OH peak decreases with the increase of TDI. Meanwhile, TDI reacts with hydroxyl group of prepolymer forming an absorption peak for urethane NH at 3370 and 1540 cm^{-1}, and amide band at 1600 cm^{-1}. Besides these peaks, the NCO stretching band of TDI at 2361 cm^{-1} increases with the augment of TDI.

Representative samples of the chain extending with TDI at OH/NCO ratio of 1:1.2 were analyzed by ^{1}H NMR spectroscopy, compared with prepolymer E0% and prepolymer E1%, as seen in Figure 5. The solvent peak appears at 7.27 ppm. The formation of urethane

bond can be seen at 3.2 ppm (Fig. 5(a)). In accordance with the conclusion of FTIR, it can be found that amide bonds exist in the sample at 6.2 ppm, which result from the reaction of remaining carboxyl group with TDI. The peaks at 0.8, 2.5, and 7.1 ppm come from the hydrogen of benzene.

Thermal properties of the prepolymers and of the chain-linked polymers (samples at $[\eta]$ maximum) were determined by DSC. The glass transition temperature (T_g) of the prepolymer E0% is 45°C, and the melting temperature (T_m) is 121°C. The T_g of prepolymer E1% is 31°C and T_m is 144°C. Additionally, the T_g of prepolymer E1% coupled with TDI with OH/NCO ratio of 1:1.2 is 53°C and T_m is 181°C (Fig. 6). Owing to the soft segment of BD and ester transform reactions, the stereoregularity of PLA chains was destroyed, and the crystallisability of the chains decreased, which led to the lower T_g and T_m values of the prepolymer E1%. As for the higher T_g and T_m values of the chain-linked polymers, on the one hand, the molecular weight of chain-linked polymer is significantly higher than the

Figure 2 Development of the weight-average molecular weight for prepolymer E1% with OH/NCO ratios of 1:1, 1:1.1, 1:1.5, 1:2, and for prepolymer E0% with OH/NCO ratio of 1:1.2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scheme 2 Reactions of isocyanate with alcohol, carboxyl acid, urethane, and amide.

Figure 3 Development of the [η] for prepolymer E1% with OH/NCO ratios of 1:1, 1:1.1, 1:1.5, 1:2, and for prepolymer E0% with OH/NCO ratio of 1:1.2. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

prepolymers and branching exists in the chains for the high reactivity of NCO group, which increases the T_g and T_m values of polymer by introducing restrictions in chain mobility. On the other hand, the hard groups of benzene existing in the chains of polymer result in
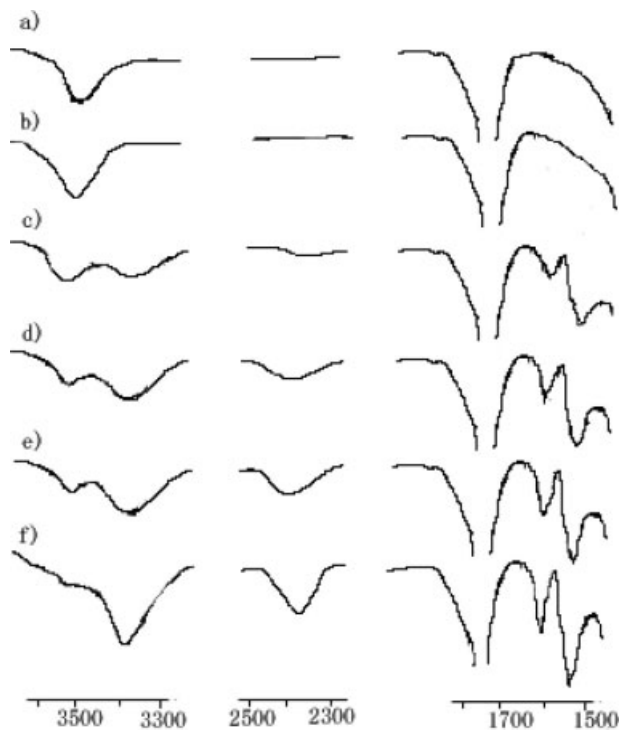
Figure 4 FTIR spectra of (a) prepolymer E0%, (b) prepolymer E1%, (c) polymer of E1% coupled 1:1 with TDI, (d) polymer of E1% coupled 1:1.2 with TDI, (e) polymer of E1% coupled 1:1.5 with TDI, and (f) polymer of E1% coupled 1:2 with TDI.


Figure 5 ¹H NMR spectra of (c) prepolymer E0%, (b) prepolymer E1%, and (a) prepolymer E1% coupled with TDI with OH/NCO ratio of 1:1.2.

the increase of the chain stiffness, which led to the increment of T_g and T_m values.

CONCLUSIONS

The molecular weight of chain-linked lactic acid polymers can be significantly enhanced by the reaction between hydroxyl-terminated lactic acid prepolymers and the chain extender TDI.

The main benefits of the chain extending polymerization are the high molecular weight of lactic acid polymers, the shorter polymerization time, and lower polymerization temperature. Shorter reaction time and lower temperature will prevent thermal degradation and side reactions. In addition, the chain extending polymerization can be conveniently and economically carried out using the extruder, a polymerization reactor. Finally, chain extender TDI has a beneficial impact on thermal stability.
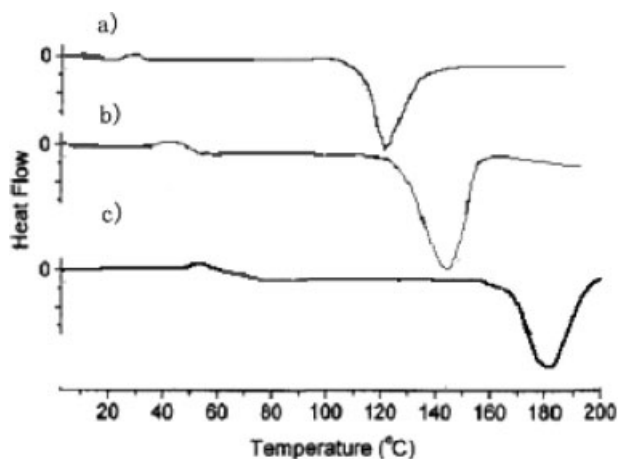
Figure 6 DSC spectra of (a) prepolymer E1%, (b) prepolymer E0%, and (c) prepolymer E1% coupled with TDI with OH/NCO ratio of 1:1.

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