The Modification of Lactic Acid Based Poly(ester-urethane) by Copolymerization

JANNE KYLMÄ, MIKA HÄRKÖNEN, JUKKA V. SEPPÄLÄ

Helsinki University of Technology, Department of Chemical Technology, Kemistintie 1, FIN-02150 Espoo, Finland

ABSTRACT: Copolymers of L-lactic acid (LLA) with DL-mandelic acid (DLMA), 4-hydroxybenzoic acid, 4-acetoxybenzoic acid, DL-malic acid, or anhydrous citric acid were synthesized via direct copolycondensation in the presence of 1,4-butanediol, using stannous octoate as catalyst. The effect of the comonomer and the comonomer ratio on polycondensation and the glass transition temperature were investigated. The glass transition temperature of amorphous poly(L-lactic acid-*co*-DL-mandelic acid) increased linearly from 33° to 56°C as the mandelic acid composition was increased from 0 to 45 mol %. For urethane synthesis, prepolymers of LLA and DLMA were condensation polymerized with compositions of 100/0, 90/10, and 80/20 (mol % in feed). The preparation of poly(ester-urethane)(PEU) was carried out in a stirred glass reactor, using 1,6-hexamethylene diisocyanate and isophorone diisocyanate in melt. The glass transition temperature of poly(L-lactic acid-*co*-DL-mandelic acid-urethanes) showed a marked increase with increased mandelic acid composition. The molecular weights of these urethanes were lower than for PEU based on poly(L-lactic acid). Such a depression in the degree of polymerization is attributed to the steric hindrance of the bulky phenyl group as a side chain of mandelic acid. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1865–1872, 1997

Key words: copolyesters; lactic acid; polycondensation; poly(ester-urethane)

INTRODUCTION

Among the synthetic biodegradable polyesters, poly(glycolic acid), poly(L-lactide), poly(DL-lactide), and poly(ε-caprolactone) obtained by ring-opening polymerization have been suggested as the most promising polymers from the point of view of potential commercial applications. Since the properties of homopolymers can only be slightly modified by varying the molecular weight or crystallinity, copolymers are required to provide materials with a wider range of properties.[1,2] Lactic acid based polyesters are especially well-known biodegradable polymers which have seen increasing use, not only for biomedical applications, but also in packaging and consumer goods.[3] However, large-scale lactide production is relatively complicated and expensive; thus, alternative polymerization routes for lactic acid are of interest.

Polyurethanes are an industrially useful and unique class of polymers with a broad range of applications. Their properties can be tailored by varying the type and amount of their components: the chain extender, polyol, polyisocyanates, and catalyst.[4] By copolymerization, there are many possible combinations of biodegradable monomers that can lead to prepolymers with the required properties. Quite recently, biodegradable poly(ester-urethane) networks have been prepared from degradable polyesters of δ-valerolactone, ε-caprolactone, DL-lactide, and L-lactide.[5–7]

In previous papers,[8–11] we have reported the synthesis of thermoplastic poly(ester-urethane) by a two-step process: a condensation polymerization of
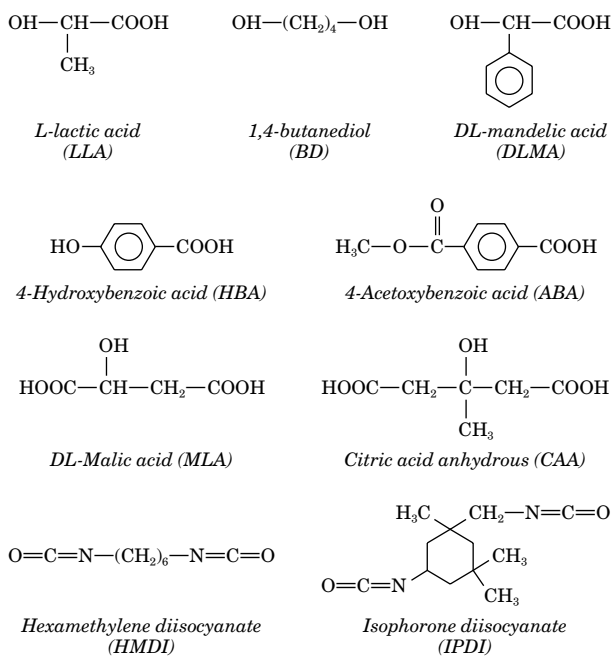
lactic acid to hydroxyl terminated telechelic prepolymer, followed by an increase in molecular weight with 1,6-hexamethylene diisocyanate. This method, and the presence of functional groups in the lactic acid based prepolymer, offers the opportunity to modify the mechanical and thermal properties of the resulting urethane. The object of this study is to investigate the polycondensability of L-lactic acid with different comonomers and the effect of the comonomers on the glass transition temperature. The unmodified poly(ester-urethane) loses its stiffness at 50°C, which can be too low in certain applications. Thus, particular attention was focused on improving heat resistance by the incorporation of rigid groups in the polymer chain.

EXPERIMENTAL

Materials

L-Lactic acid (85–90% L-lactic acid in water; Fluka Chemie AG, Buchs, Switzerland) was purified by distillation under vacuum. DL-Mandelic acid (Fluka), 4-hydroxybenzoic acid (Fluka), 4-acetoxybenzoic acid, DL-malic acid (Fluka), citric acid anhydrous (Fluka), 1,4-butanediol (Fluka), and Sn(II)octoate (Sigma Chemical Co., St. Louis, MO, USA) were used as received. 1,6-Hexamethylene diisocyanate (Fluka) and isophorone diisocyanate (3-isocyanatemethyl-3,5,5-trimethyl-cyclohexyl-isocyanate; Hüls AG, Marl, Germany) were used as the linking agents. The structures and designating codes of materials used are shown below.

OH—CH—COOH
|
CH₃

L-lactic acid
(LLA)

OH—(CH₂)₄—OH

1,4-butanediol
(BD)

OH—CH—COOH
|
(ring)

DL-mandelic acid
(DLMA)

HO—(ring)—COOH

4-Hydroxybenzoic acid (HBA)

H₃C—O—C(=O)—(ring)—COOH

4-Acetoxybenzoic acid (ABA)

HOOC—CH(OH)—CH₂—COOH

DL-Malic acid (MLA)

HOOC—CH₂—C(OH)(CH₃)—CH₂—COOH

Citric acid anhydrous (CAA)

O=C=N—(CH₂)₆—N=C=O

Hexamethylene diisocyanate
(HMDI)

Isophorone diisocyanate
(IPDI)

Measurements

All the materials obtained were characterized by Size Exclusion Chromatography (SEC) and Differential Scanning Calorimetry (DSC). The molecular weights were determined by size exclusion chromatography (Waters System Interface module, Waters 510 HPLC Pump, Waters 410 Differential Refractometer, Waters 700 Satellite Wisp) using monodisperse polystyrene standards for calibration. Measurements were made at room temperature with four linear Polymer Laboratories (PL) gel columns (10^4, 10^5, 10^3, and 100 Å). Chloroform was used as solvent, with a flow rate of 1 ml/min. The thermal properties were determined using a Polymer Laboratories differential scanning calorimeter, at a temperature range of $-20°$ to 180°C and a heating and cooling rate of 10°C/min. Glass transition temperatures were recorded at the second heating scan in order to give the same thermal history.

The poly(L-lactic acid-*co*-DL-mandelic acid) oligomers were characterized with a ^{13}C NMR Varian Unity 400 spectrometer working at 100.557 MHz. Sample concentrations in 5 mm tubes were 10% by weight in CDCl₃, with tetramethylsilane (TMS) as the internal reference.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet Magna-FTIR 750 spectrometer, using film samples cast on a potassium bromide plate from chloroform solutions. Dynamic mechanical thermal analysis (DMTA) was performed on a Perkin Elmer 7 Series Thermal Analysis System instrument. The measurements were made using the three-point bending method at a temperature range of $-20°$ to 70°C at a rate of 3°C/min. All measurements were performed at 1 MHz.

The tensile tests of the compression-molded polymers (2 mm × 10 mm × 50 mm) were performed on an Instron 4204 tensile testing machine equipped with a computer adopting the standard ISO/R 527-1966(E). The mechanical properties of the homopolymers and copolymers were measured using a tensile tester at a crosshead speed of 5 mm/min. The mechanical values for the polymers were measured for five parallel air-conditioned specimens, which were allowed to rest for 72 h at 23°C and 50% relative humidity.

Polymerization Procedures

Test Tube Polymerizations

In the test tube polymerizations, L-lactic acid and different comonomers with 1,4-butanediol and Sn(II)octoate were polymerized under a nitrogen

hydroxyl terminated
poly(L-lactic acid-co-DL-mandelic acid) oligomer
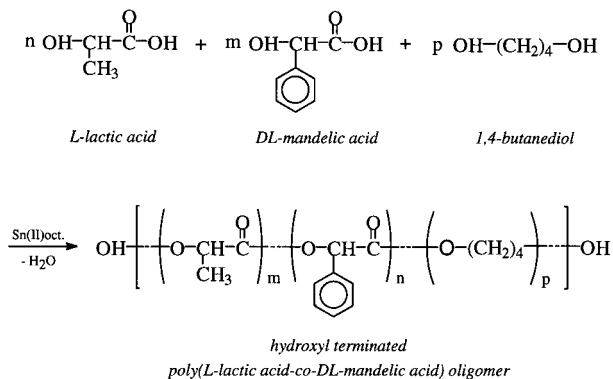
Scheme 1 Condensation copolymerization of L-lactic acid and DL-mandelic acid.

stream in an oil bath. A typical experimental procedure was as follows. The test tube contained 5.90 g purified L-lactic acid (87 mol %), 1.11 g DL-mandelic acid (10 mol %), 0.20 g 1,4-butanediol (3 mol %), and 4 mg of Sn(II)octoate (0.05 wt %) as a catalyst. The test tube reactor was sealed with Glisseal laboratory grease and, after purging with nitrogen, immersed in an oil bath at 160°C. The polymerization temperature was raised to 200° or 210°C for 3 h. During the polymerization, the reaction mixture was stirred by bubbling nitrogen gas through the mixture.

Prepolymer Synthesis

The prepolymers for urethane synthesis were condensation polymerized in a rotation evaporator (Scheme 1). Thus, to a 2000 ml evaporating flask were added 450 g purified L-lactic acid (89.1 mol %) and 76.1 g DL-mandelic acid (8.9 mol %) as a comonomer. 1,4-Butanediol (9.9 g, 2.0 mol %) was used to produce hydroxyl terminated oligomers, and 0.289 g Sn(II)octoate (0.05 wt %) was used as a catalyst. The flask was purged with nitrogen and placed in an oil bath. The rotation speed was

approximately 100 r/min. The reaction mixture was polymerized at 210°C, with a continuous nitrogen stream under the surface of the melt and at a reduced pressure of 50 mbar.
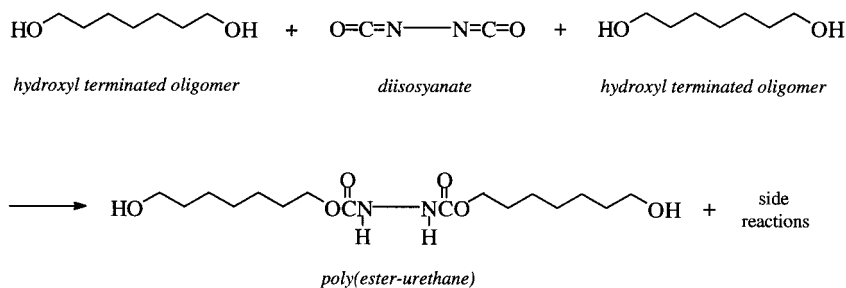
Polyurethane Synthesis

The poly(ester-urethane) was prepared in a melt using 1,6-hexamethylene diisocyanate or isophorone diisocyanate as a chain extender (Scheme 2). The polymers were synthesized in a 300 ml, three-necked, round-bottomed flask equipped with a mechanical stirrer incorporating a nitrogen inlet valve. Typically, 40 g prepolymer was introduced into the flask and melted in an oil bath at 150°C, after which the flask was purged with nitrogen at room temperature to remove residual air. 1,6-Hexamethylene diisocyanate (3.4 g) was added to the stirred liquid oligomer, and the temperature was then raised to the polymerization temperature of 180°C. The polymerization was followed by taking samples every 10 min, which were then analyzed by SEC and FTIR. All the products were used without further purification.

RESULTS AND DISCUSSION

Test-Tube-Scale Copolymerizations

The results of the test-tube-scale copolymerizations of LLA and different comonomers are shown in Table I. Since the DSC analysis did not show any signs of crystallinity, all copolymers were completely amorphous and only a single glass transition was found.

The copolymerization of L-lactic acid and DL-mandelic acid was investigated over a wide range of compositions. Copolymers were hard and brittle, like homopoly(LLA). The phenyl groups of DL-mandelic acid cause steric hindrance, depressing the

hydroxyl terminated oligomer   *diisosyanate*   *hydroxyl terminated oligomer*

poly(ester-urethane)

Scheme 2 Polymerization of poly(ester-urethane).

Table I   Results of the Test-Tube-Scale Copolymerizations of L-Lactic Acid and Different Comonomers

	Monomer Composition in Feed	Polymerization Conditions		GPC			DSC	
	(mol %)	Time (h)	Temperature (°C)	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	MWD	T_g (°C)	T_m (°C)
LLA/—/BD	97/—/3	10	210	4400	7300	1.7	33	—
LLA/DLMA/BD	92/5/3	10	210	6100	12300	2.0	38	—
LLA/DLMA/BD	87/10/3	10	210	3900	7900	2.0	44	—
LLA/DLMA/BD	82/15/3	10	210	4600	9700	2.1	47	—
LLA/DLMA/BD	78/19/3	10	210	3900	7600	2.0	47	—
LLA/DLMA/BD	72/25/3	10	210	3000	5800	1.9	52	—
LLA/DLMA/BD	67/30/3	10	210	4100	8300	2.0	55	—
LLA/DLMA/BD	62/35/3	10	210	2800	5500	2.0	51	—
LLA/DLMA/BD	57/40/3	10	210	3400	6900	2.0	54	—
LLA/DLMA/BD	52/45/3	10	210	3200	6400	2.0	56	—
LLA/HBA/BD	92/5/3	10	210	2700	4400	1.7	35	—
LLA/HBA/BD	87/10/3	10	210	2000	3200	1.6	33	—
LLA/HBA/BD	82/15/3	10	210	1600	2400	1.5	32	—
LLA/HBA/BD	77/20/3	10	210	1200	1600	1.4	34	—
LLA/ABA/—	95/5/—	12	210	2000	4100	2.1	42	—
LLA/ABA/—	90/10/—	12	210	1400	2600	1.8	37	—
LLA/ABA/—	85/15/—	12	210	1100	1900	1.8	40	—
LLA/ABA/—	80/20/—	12	210	750	1200	1.6	36	—
LLA/ABA/—	75/25/—	12	210	700	1100	1.7	36	—
LLA/MLA/BD	92/5/3	10	200	3200	12500	3.9	44	—
LLA/MLA/BD	87/10/3	10	200	1400	4200	3.1	37	—
LLA/MLA/BD	82/15/3	10	200	1000	2000	1.9	33	—
LLA/MLA/BD	77/20/3	10	200	800	1300	1.5	24	—
LLA/CAA/BD	94/3/3	10	200	5200	20800	4.0	41	—
LLA/CAA/BD	92/5/3	10	200	3000	8400	2.8	42	—
LLA/CAA/BD	90/7/3	10	200	2300	6500	2.8	36	—
LLA/CAA/BD	87/10/3	10	200	2100	5600	2.6	40	—

rate of copolymerization. With an increase in mandelic acid feed from 0 to 45 mol %, an increase in T_g from 33° to 56°C was observed, although the molecular weights of (LLA/DLMA)-copolymers decreased. Large and bulky side chains restrict rotation of the polymer chain and cause an increase in T_g.

Copolymers of LLA and p-hydroxybentzoic acid had significantly lower molecular weights than (LLA/DLMA)-copolymers. The copolymers were, however, hard and brittle. Due to relatively low molecular weights, the glass transition temperatures of (LLA/HBA)-copolymers did not increase as expected. Although the number average molecular weight dropped from 4400 to 1200 g/mol, T_g was practically constant around 33° to 35°C when the HBA composition was 0 to 20 mol %. Copolyesters with a similar structure were aimed for with 4-acetoxybenzoic acid. The molecular weights of

(LLA/ABA)-copolymers were even lower, from 2000 to 700 g/mol. The copolymers were, however, especially hard, unlike the hydroxyl terminated homopoly(LLA)s with an equivalent molecular mass ($\bar{M}_n \sim$ 1200 g/mol). These were soft and sticky, having a T_g of about 15°C. The T_g of (LLA/ABA)-copolymers varied from 42° to 36°C when the 4-acetoxybenzoic acid composition was increased from 5 to 25 mol %. The presence of a p-phenylene ring in p-hydroxybenzoic acid and in 4-acetoxybenzoic acid impeded rotation about the main chain bonds, stiffening the chain and causing a clear increase in T_g. At the same time, the bulky ring in the main chain affects the polycondensability, even more than the side chain phenyl of mandelic acid, and the molar masses were lower. The influence of the molecular weight on the transition temperatures is found to be signifi-

Table II Monomer Compositions, Polymerization Conditions, Molecular Weights, and Glass Transition Temperatures of Poly(L-lactic acid-*co*-DL-mandelic acid) Oligomers

	Monomer Composition			Polymerization Conditions		GPC			DSC	Acid number
Prepolymer	L LA	DL MA (mol % in feed)	1,4-BD	Time (h)	Temp. (°C)	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	MWD	T_g (°C)	(mg KOH/g)
1	98.0	—	2.0	8	210	4900	8300	1.7	38	10
2	89.1	8.9	2.0	8	210	3700	7600	2.1	44	29
3	78.9	19.1	2.0	10	210	4200	9300	2.2	52	37
4	86.0	10.0	4.0	10	210	5100	10300	2.0	43	7
5	76.0	20.0	4.0	14	210	4900	11400	2.3	51	19

cant for polymers with relatively low molecular mass. When the molecular mass of the polymer is lower, the concentration of chain ends increases, increasing the free volume and chain flexibility; consequently, the glass transition temperature decreases.

The copolyesters from LLA and trifunctional DL-malic acid, and from LLA and four-functional anhydrous citric acid were bright and especially hard. Even a small quantity (<5 mol %) of MLA or CAA increases the glass transition temperature by 9° to 11°C. A high density of branching, or long chain branching will have the same effect as side groups in restricting chain mobility, hence raising T_g. The drop in T_g values in (LLA/MLA)- and (LLA/CAA)-copolyesters with higher MLA and CAA concentrations was probably due to the formation of low-molecular-weight cyclic structures, and self-condensation reactions of multifunctional comonomers.

Prepolymer Synthesis

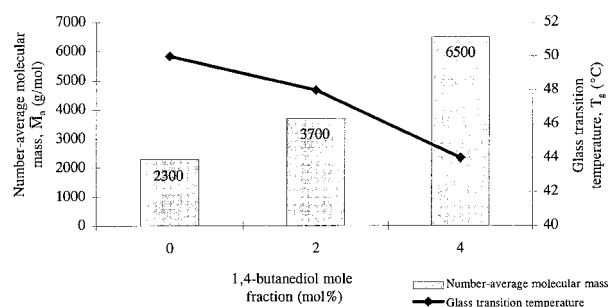The prepolymers for urethane synthesis from L-lactic acid and DL-mandelic acid with 1,4-bu-

Figure 1 Effect of 1,4-butanediol on T_g and $\bar{M}_n$ of poly(L-lactic acid-*co*-DL-mandelic acid) oligomer containing 10 mol % mandelic acid.

tanediol were condensation polymerized in a rotation evaporator. The prepolymer synthesis results are presented in Table II. The increase in the glass transition temperature with growing DLMA content corresponds with the results of test-tube-scale copolymerizations.

The effect of 1,4-butanediol on copolymerization and on the hydroxyl termination was studied in a test tube, since it was noticed that the formation of urethane bonds became complicated when DL-mandelic acid was introduced into prepolymer structure. The amount of butanediol in the oligomers had an effect on the rate of copolycondensation, as seen in Figure 1. Larger amounts of butanediol in the copolymer result in considerably higher molecular weights. As expected, the introduction of the flexible aliphatic groups of 1,4-butanediol increases main chain flexibility, and decreases the glass transition temperature.

The peak integrals of ^{13}C NMR spectra were used to compare the quantity of hydroxyl end groups of (LLA/DLMA) prepolymers with different amounts of 1,4-butanediol. The hydroxyl end group peaks in the methine area were identified through the method presented by Hiltunen et al.[8] The values were calculated from the peak integral ratio to the chain unit. Analysis showed that poly(LLA/DLMA) containing 10 mol % mandelic acid and 4 mol % butanediol had the same number of hydroxyl end groups as poly(L-lactic acid) containing 2 mol % butanediol. This can also be seen in the acid numbers (Table II), which are a measure of the residual amount of carboxyl end groups. These carboxyl end groups react with isocyanate groups to form acidamides; the acidamide groups can then react with additional isocyanate, leading to the formation of acylurea groups which cause branching and undesirable crosslinking.

Table III   Molecular Weights, DSC, and DMTA Results of Poly(L-lactic acid-*co*-DL-mandelic acid-urethanes)

| Prepolymer | GPC | | | DSC | DMTA | | |
	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	MWD	T_g (°C)	tan δ (°C)	Loss Modulus Peak (°C)	Storage Modulus (MPa)
1,6-Hexamethylene diisocyanate							
1	41000	187000	4.6	53	55	51	1.65
2	16000	116000	8.0[1]	58	61	55	1.20
3	23000	120000	6.7[1]	60	64	57	1.40
4	27000	124000	4.5	52	57	51	1.40
5	17600	42000	2.4	54	—	—	—
Isophorone diisocyanate							
1	29000	74000	2.6	61	—	—	—
2	14000	25000	1.9	63	—	—	—
3	7300	18000	2.4	60	—	—	—

[1] End product partially insoluble in trichloromethane.

Moreover, the residual acid content of the polyester negatively affects the catalysis of the polyurethane reaction.[12]

Preparation of Poly(ester-urethane)

Poly(ester-urethanes) were synthesized by reacting (LLA/DLMA) prepolymers and aliphatic 1,6-hexamethylene diisocyanate or cycloaliphatic isophorone diisocyanate with the NCO/OH ratio at 1.0. The resulting polymers did not contain isocyanate groups, as indicated by the total disappearance of the —NCO peak at 2270 cm^{-1} in the FTIR spectra. The results of the urethane synthesis are shown in Table III.

The development of number and weight average molecular weights during polymerization is shown in Figure 2. Adding mandelic acid into the
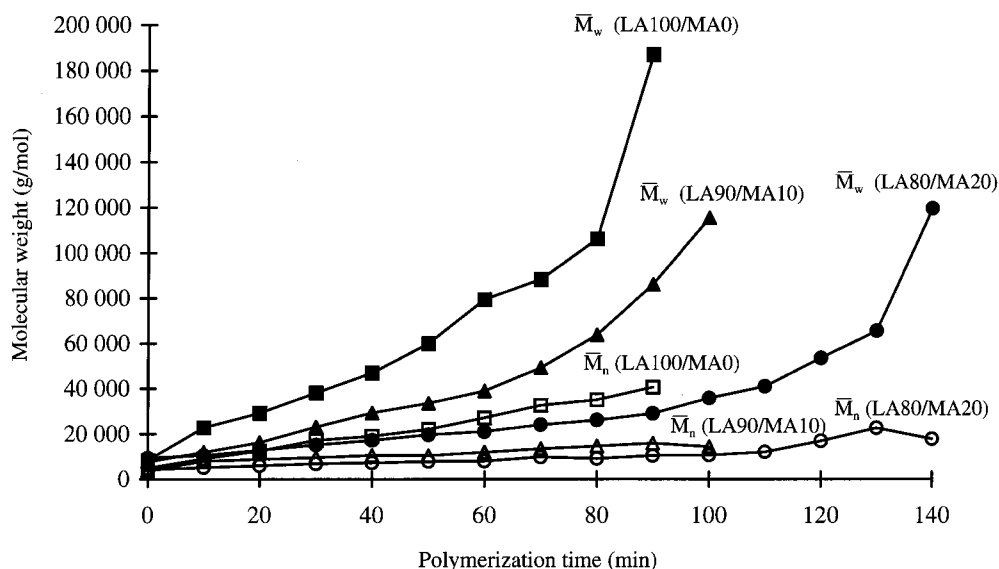

Figure 2   The development of number and weight average molecular weights of poly(ester-urethanes) during polymerization.
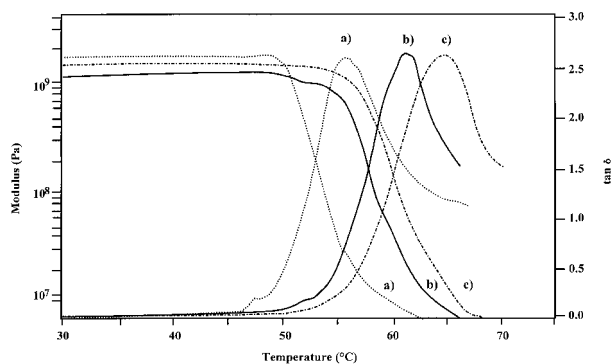
Figure 3 DMTA storage modulus and tan δ curves of poly(L-lactic acid-*co*-DL-mandelic acid-urethanes) LLA/DLMA compositions of (a) 100/0, (b) 90/10, and (c) 80/20 (mol % in feed).

polymer chains and residual monomers made the reaction of polyester prepolymers and difunctional isocyanates more difficult, as discussed earlier. Thus, the molecular weights of the (LLA/DLMA) copolymers increased much more slowly than for the LLA prepolymers, and molecular weights also stayed at a lower level in the resulting polymers. The steric hindrance of the bulky phenyl group causes a decrease in the reactivity of —NCO and —OH, which could make side reactions more favorable. This was seen when HMDI was used, where molecular weight distributions were very wide and some samples were partially insoluble, suggesting the formation of long chain branches and crosslinks. The reaction between —OH and —NCO groups was even more restricted when isophorone diisocyanate was used; consequently, the molecular weights were low and molecular weight distributions were narrow. IPDI with (LLA/DLMA) prepolymer produces very stiff chains which cannot react with each other, since they cannot move freely in the polymerization mixture, and the probability of end group reactivity becomes very low. Similar results have been also obtained in our earlier work.[13]

The DSC results show that the glass transition temperature of prepolymer containing 20 mol % mandelic acid increases by 14°C, and in poly(ester-urethane) the corresponding increase is only 7°C. As mentioned above, the molecular weights of the (LLA/DLMA) urethanes were considerably lower, thus the amount of chain ends increases, increasing the free volume; consequently, the glass transition temperature decreases. Furthermore, there are two competing factors: the introduction of stiff side groups which will sterically hinder the chain rotation, thereby increasing the T_g, and the introduction of large bulky groups, presumably increasing the amount of free volume available and causing a lowering of the T_g. In particular, when isophorone diisocyanate was used, the increase was only a few degrees. It is also noteworthy that steric phenyl groups affect hydrogen bonding negatively, causing a lowering in T_g.[14]

Three-point bending DMTA analysis gave similar results to DSC: the T_g measured from the peak value of tan δ increased in proportion and the storage modulus decreased at a temperature shown in Table III and Figure 3, indicating the loss in stiffness of the poly(ester-urethane).

Tensile properties of poly(ester-urethanes) are presented in Table IV. All PEUs made with 1,6-hexamethylene diisocyanate were hard and brittle, having tensile modulus 2.0 GPa, tensile strength 47 MPa, and maximum strain 3.5%. Considering that the molecular weights of the (LLA/DLMA)-copolymers were clearly lower than those of lactic-acid-based PEU, it is worth noting that the mechanical properties were at the same level. Poly(ester-urethanes) made with isophorone diisocyanate were even more brittle, and the difference between LLA and (LLA/DLMA)-based PEU was significant.

CONCLUSIONS

We have shown that this method is a highly efficient route for converting lactic acid to high molec-

Table IV Tensile Properties of Poly(L-lactic acid-*co*-DL-mandelic acid-urethanes)

Urethane	Tensile Modulus (MPa)	Tensile Strength (MPa)	Maximum Strain (%)
1,6-hexamethylene diisocyanate			
1	1930 ± 60	46.8 ± 1.8	3.7 ± 0.3
2	2010 ± 60	34.4 ± 7.6	1.8 ± 0.4
3	2010 ± 20	49.3 ± 0.3	3.1 ± 0.1
4	1970 ± 50	47.4 ± 1.3	3.4 ± 0.2
Isophorone diisocyanate			
1	1740 ± 130	21.6 ± 1.7	1.3 ± 0.1
2	1310 ± 50	4.5 ± 0.3	0.4 ± 0.2

ular weight polymer, and it also offers excellent possibilities for structural modification. In this study, the copolymers of L-lactic acid and different comonomers were investigated as to their suitability for the urethane synthesis. Polymerization of thermoplastic poly(ester-urethane) was performed by a two-step process: a condensation polymerization of lactic acid and mandelic acid to hydroxyl terminated telechelic prepolymer, followed by an increase in molecular weight with diisocyanate. The incorporation of comonomers which impede rotation and stiffen the chain clearly causes a large increase in T_g, while the same comonomers depress the rate of polycondensation. Mandelic acid increased the glass transition temperature of amorphous PEU, but it made the urethane reaction more difficult, and side reactions produced long chain branches and crosslinks. In conclusion, the heat resistance of a biodegradable thermoplastic poly(ester-urethane) based on lactic acid can be improved with DL-mandelic acid. By introducing stiff side groups into the polymer chain, the glass transition temperature is increased. The mechanical properties of poly(L-lactic acid-*co*-DL-mandelic acid-urethanes) are comparable with PEU based on lactic acid.

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