Lactic Acid Based Poly(ester-urethanes): Use of Hydroxyl Terminated Prepolymer in Urethane Synthesis

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ABSTRACT: We studied a two step process for lactic acid polymerization: in the first step, the lactic acid is condensation polymerized to a low molecular weight hydroxyl terminated prepolymer and then the molecular weight is raised by joining prepolymer chains together using diisocyanate as the chain extender. The resulting polymer is a thermoplastic poly(ester-urethane). The polymer samples were carefully characterized with ^{13}C-NMR, GPC, DSC, and IR. The results indicate that high conversions of lactic acid can be achieved, as well as independent control of the stereostructure, long chain branches, molecular weight average, and molecular weight distribution. Lactic acid is converted into a poly(ester-urethane) with a weight average molecular weight as high as 390,000 g/mol and a glass transition temperature of 53.7°C. The analyzed content of the monomer in the prepolymer is less than 1 mol % and the lactide content 2.4 mol %, while the final poly(ester-urethane) is essentially monomer and lactide free. The mechanical properties of the poly(ester-urethane) are comparable to those of polylactides. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63**: 1091–1100, 1997

INTRODUCTION

The feasibility of production processes and the possibility of using renewable raw materials have made lactic acid an attractive monomer for biodegradable polymers. However, poly(lactic acid) has to have a relatively high molecular weight in order to have acceptable mechanical properties in many applications.[1] Conventional condensation polymerization of lactic acid does not increase the molecular weight enough, or the polymerization time has to be very long.[2] In condensation polymerization, the yield of cyclic side products, such as lactides, is often too high. Acceptable molecular weights can also be achieved through ring-opening polymerization of the lactides.

Polyurethanes are polymers that are typically synthesized by the addition reaction of an alcohol to an isocyanate group. They contain the urethane group as a characteristic structural element (R—NH—CO—O—R').[3] In the preparation of poly(ester-urethanes), the hydroxyl terminated macroglycols with a low acid number and low water content[4] react with diisocyanate. The polyaddition reaction is influenced by the structure (e.g., steric hindrance) and functionality of the monomers, the nature of the hydroxyl group, polymerization temperature, and —OH/—NCO ratio.

Pitt et al.[5] synthesized oligomeric polyesters by initiating ring-opening copolymerization of δ-valerolactone and ε-caprolactone with glycerol. They converted these prepolymers into crosslinked poly(ester-urethanes) by reacting them with 1,6-hexamethylenediisocyanate (HMDI) in different proportions, and then studied the biodegradation of these poly(ester-urethanes). Their polymers were amorphous and elastomeric, with extensions as great as 2000%. The biodegradation of these

poly(ester-urethanes) was found to be comparable with that observed with other aliphatic polyesters. Storey and colleagues[6] used ethyl 2,6-diisocyanatohexanoate and poly(ester triols) synthesized from D,L-lactide, ε-caprolactone, or comonomer mixtures of them, with glycerol as the initiator. Their networks based on poly(D,L-lactide) triols were rigid and the ε-caprolactone based networks were elastomeric. Copolymer networks were tougher than networks based on the homopolymers. They found that networks based on D,L-lactide were most resistant to degradation.

Gogolewski et al.[7] mixed polylactides with segmented polyurethanes. They showed that porous biomaterials based on physical mixtures of polylactides and segmented polyurethanes are antithrombogenic, show excellent flexibility, and have a satisfactory rate of degradation.

In 1992 Seppälä and cohorts[8] reported one route for converting lactic acid to high molecular weight polymers through condensation oligomerization of pure lactic acid followed by isocyanate linking.[9]

In this article, we report on the linking of lactic acid based hydroxyl terminated prepolymers with HMDI[10] and the investigation of the effects of the isocyanate/hydroxyl ratio on the molecular weights and polymer structure. In addition, the preliminary mechanical characterization was carried out. The synthesis and characterization of the low molecular weight hydroxyl terminated prepolymer was presented in our previous work.[11,12]

EXPERIMENTAL

Materials

L-Lactic acid (LA) from Fluka was a 90% aqueous solution of the monomer that was 99% optically pure (according to the manufacturer). The excess water was distilled off before use under reduced pressure and a temperature of 100°C. The following products were used without further treatment: 1,4 butanediol (+98%) from Fluka Chemika, tin(II) octoate from Sigma Chemical Co., chloroform (stabilized with 1% ethanol) from Riedel−de Haen Ag, chloroform-d_1 with tetramethyl silane (TMS; 1%; deuteration degree not less than 99.5%) from Merck, HMDI from Fluka Chemika, and kalium bromide (spectroscopy grade) from Riedel−de Haen Ag.

Characterizations

IR spectra were measured on a Nicolet Magna Spectrometer 750 with 4 cm^{-1} resolution by using KBr disks. The sample concentration in the disks was 1 wt %.

Molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and polydispersity ($\bar{M}_w/\bar{M}_n$) were determined with respect to polystyrene standards by GPC. The Waters Associates system that was used was equipped with a Waters 700 Satellite wisp injector, a Waters 510 HPLC solvent pump, four linear Polymer Laboratories (PL) gel columns (10^5, 10^4, 10^3, and 100 Å) connected in series, and a Waters 410 differential refractometer. All samples were analyzed at room temperature.

Chloroform was used as the eluent. The eluent was delivered at a flow rate of 1.0 mL/min. The samples were dissolved in chloroform at a concentration of 1.0% (w/v). The injection volume was 200 μL.

For NMR measurements, the samples were dissolved in chloroform-d_1 in 5-mm NMR tubes at room temperature. The sample concentration was about 10% by weight. Proton decoupled ^{13}C-NMR spectra with nuclear Overhauser enhancement were recorded on a Varian Unity 400 NMR spectrometer working at 100.577 MHz for carbon 13.

DSC measurements were made on a PL Thermal Sciences DSC. The measurements were run from −50 to 200°C at a heating rate of 10°C/min. The glass transition temperatures (T_g) were determined from the second heating period.

The mechanical properties were determined from the compression molded specimens with an Instron 4204. The samples were tested using a 5-kN load cell at the speed of 5 mm/min. Modulus, tensile strength, and strain were calculated with Instron Corporation software.

Synthesis of Prepolymer

The LA was condensation polymerized with 2 mol % 1,4-butandiol to produce a hydroxyl terminated telechelic prepolymer.[11] The use of a difunctional alcohol allowed the production of a hydroxyl terminated telechelic prepolymer with quite low molecular weight. The amount of difunctional compound determined the molecular weight of the resulting prepolymer. The more diol used, the smaller the molecular weight of the resulting prepolymer. In the polyurethane literature,[13] the recommended molecular weight of the prepolymer was ca. 2000 g/mol. Using 2 mol % 1,4-butandiol

produced a prepolymer with a number average molecular weight of 3000 g/mol determined by ^{13}C-NMR.[11]

In the polymerization, 0.05 wt % tin(II) octoate was used as the catalyst. The polymerization was carried out in the melt and under vacuum in a Büchi Rotavapor equipped with an oil bath. A continuous nitrogen flow was maintained under the surface of the melt. The rotation speed was approximately 100 rpm. Over a period of 8 h the temperature of the oil bath was raised from 160 to 210°C and the pressure was lowered from 500 to 30 mbar. After an 8 h polymerization, the molten polymer was poured into an aluminum pan and placed in a desiccator to cool down. After cooling, the resulting polymer was pulverized and analyzed.

Synthesis of Poly(ester-urethanes)

The typical polyurethane small-scale synthesis procedure was carried out as follows: 40 g of prepolymer was accurately weighed into a 300-mL glass reactor and the reactor was sealed with Glisseal laboratory grease. The system was purged with a continuous flow of argon. The reactor was placed in an oil bath and the temperature was raised to 150°C. The temperature was kept constant until the prepolymer had melted. The amount of diisocyanate to be added was calculated using the molecular weight of the prepolymer determined by ^{13}C-NMR[11] and the desired isocyanate hydroxyl ratio. The accurate amount of diisocyanate was added, and the temperature was raised to the polymerization temperature of 180°C. The polymerization was followed by taking samples every 15 min. After the polymerization, the molten polymer was poured into an aluminum pan and placed in a desiccator to cool down. After cooling, the resulting polymer was pulverized and analyzed.

RESULTS AND DISCUSSION

The detailed analysis of the prepolymer was described in our previous study.[11] The hydroxyl terminated telechelic poly(L-lactic acid) prepolymer had a number average molecular weight of 7900 g/mol measured by GPC. The GPC was calibrated with narrow polystyrene standards; therefore, GPC results were used only as a qualitative tool to check the peak shape and size distribution of the different polymers. The molecular weights de-

termined by ^{13}C-NMR were then used as quantitative values for the calculation of the amounts of diisocyanate needed. The number average molecular weight calculated from the ratio between main chain carbons and chain end carbons was 3000 g/mol.

Besides the end group analysis, ^{13}C-NMR was a useful tool in the quantitative analysis to determine remaining LA, formatted lactide, and different optical isomers. The amount of LA and lactide was calculated using the methine area peak integrals. The prepolymer had 2.4 mol % lactide and less than 1 mol % LA residues measured by ^{13}C-NMR. The prepolymer contained 29.5 mol % of different optical isomers determined with ^{13}C-NMR. The prepolymer used was amorphous, and its glass transition temperature was 40.8°C.

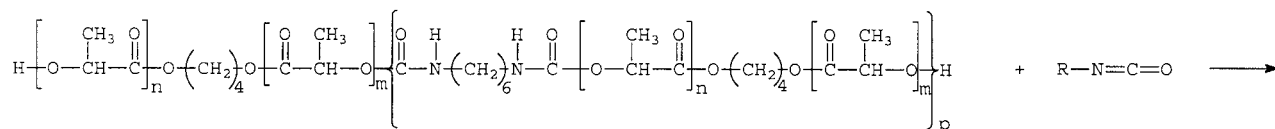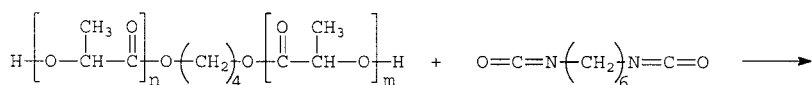### Preparation of Poly(ester-urethane)

The reaction scheme for the synthesis of the LA based poly(ester-urethane) is shown in Figure 1. The resulting poly(ester-urethane) was linear when the ratio of the hydroxyl end groups of the prepolymer and isocyanate groups (OH/NCO) was over unity. When the diisocyanate was used in excess, the rate of the side reactions increased. An important side reaction was the reaction of the urethane group with isocyanate, which led to branching of the polymer. The isocyanate group can also react with other isocyanate groups and form, for example, dimers, trimers, and carbodiimides.[13] Besides the molar ratio of the hydroxyl and isocyanate groups, the polymerization temperature had a strong affect on the structure of the resulting polyurethane. An increase in temperature will also raise the rate of the side reactions. The results of the polymerizations and analysis are listed in Table I.

The solubility of the polymer in chloroform decreased when the OH/NCO ratio was below unity. Polymer 3, which was produced with a ratio of 1 : 1, was totally soluble and had the highest molecular weight. This ratio seems to be the optimum, especially if a linear polymer is required. When the ratio was below unity, a polyurethane network was formed. The higher the diisocyanate excess, the greater the network formation. Ratios over unity produced linear polymers that had quite low molecular weights. The development of weight average molecular weights during the polymerization, determined by GPC, are shown in Figure 2.
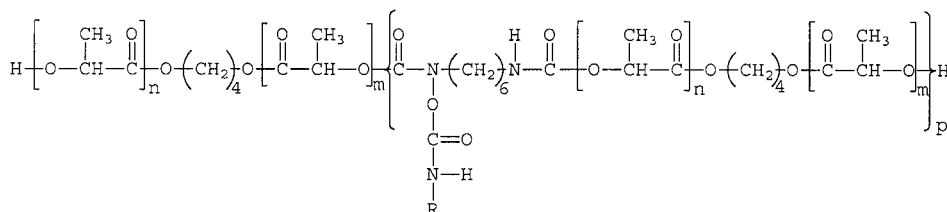
The behavior of the weight average molecular weight curves may be explained by the selectivity
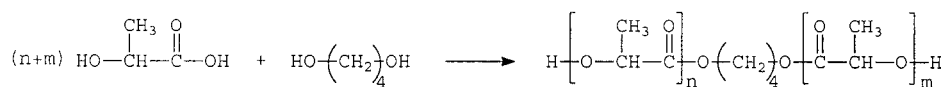
prepolymer synthesis

linear poly(ester-urethane) synthesis

the formation of long chain branches or crosslinking points

Figure 1 The synthesis scheme of lactic acid based poly(ester-urethane).

of various reaction mechanisms. At first, the diisocyanate molecule reacts with the hydroxyl group at the chain end of the prepolymer, and then the prepolymer is isocyanate terminated. Hydroxyl/isocyanate ratios equal or less than unity should produce a polymerization mixture that contains isocyanate and hydroxyl terminated prepolymer chains. If diisocyanate is used in excess, the number of isocyanate terminated prepolymer chains increases and, in the extreme case, all prepolymer chains are isocyanate terminated. The greater the number of the prepolymer chains that are isocyanate terminated, the higher the probability of the reaction of isocyanate with urethane and other isocyanate groups.

This effect can be seen from the weight average molecular weight graph in Figure 2. If the isocyanate was used in excess, the molecular weight of the polymers slowly increased at first and after a short period the network was formed. The mecha-

Table I   Representative Examples of Prepared Polymers and Analysis Results

| Polymer	OH/NCO Ratio	Solubility in CHCl$_3$	M_n (GPC) (g/mol)	M_w (GPC) (g/mol)	T_g (°C)
1	0.67	Insoluble	—	—	52.1
2	0.80	Partially Soluble	24,000[a]	77,000[a]	50.2
3	1.00	Soluble	57,000	390,000	53.7
4	1.33	Soluble	33,200	71,700	53.2
5	1.50	Soluble	10,800	19,500	44.8

(—) The polymer was not totally soluble.
[a] Molecular weight of the soluble fraction.

nism may have been that in the first stage the main reaction products were isocyanate terminated prepolymer chains; therefore, the molecular weight of the polymers increased slowly at first. When the isocyanate groups started to react with themselves or with a urethane group, the polymerization mixture began to crosslink, which was seen especially in a rapid weight average molecular weight increase at the beginning of network formation. The more isocyanate used, the sooner and the greater the network formation. The last points of the weight average molecular weight curves for polymers 1 and 2 represent the last samples that were totally soluble. For polymer 1 the network was formed after 60-min polymerization and for polymer 2 after 75-min polymerization. After these points, the polymers were not totally soluble; and the longer the polymerization was continued, the stronger the network forma-

tion and the smaller the soluble part of the polymer sample.

The weight average molecular weight of the polymers, which were produced with —OH/ —NCO ratios over unity, increased rapidly at first. The reason for this could be that there were plenty of hydroxyl groups where the isocyanate terminated chains could react. After a short period, all the isocyanate groups had reacted, and the molecular weight of these polymers started to decrease due to thermal degradation of the polymer chains. This thermal degradation occurred because all reactions that cause polymer chain growth ceased. For other polymers, there was enough diisocyanate to carry on the polymerization reactions.

In the case where the OH/NCO ratio was unity, the weight average molecular weight increased quite smoothly at first as the hydroxyl terminated
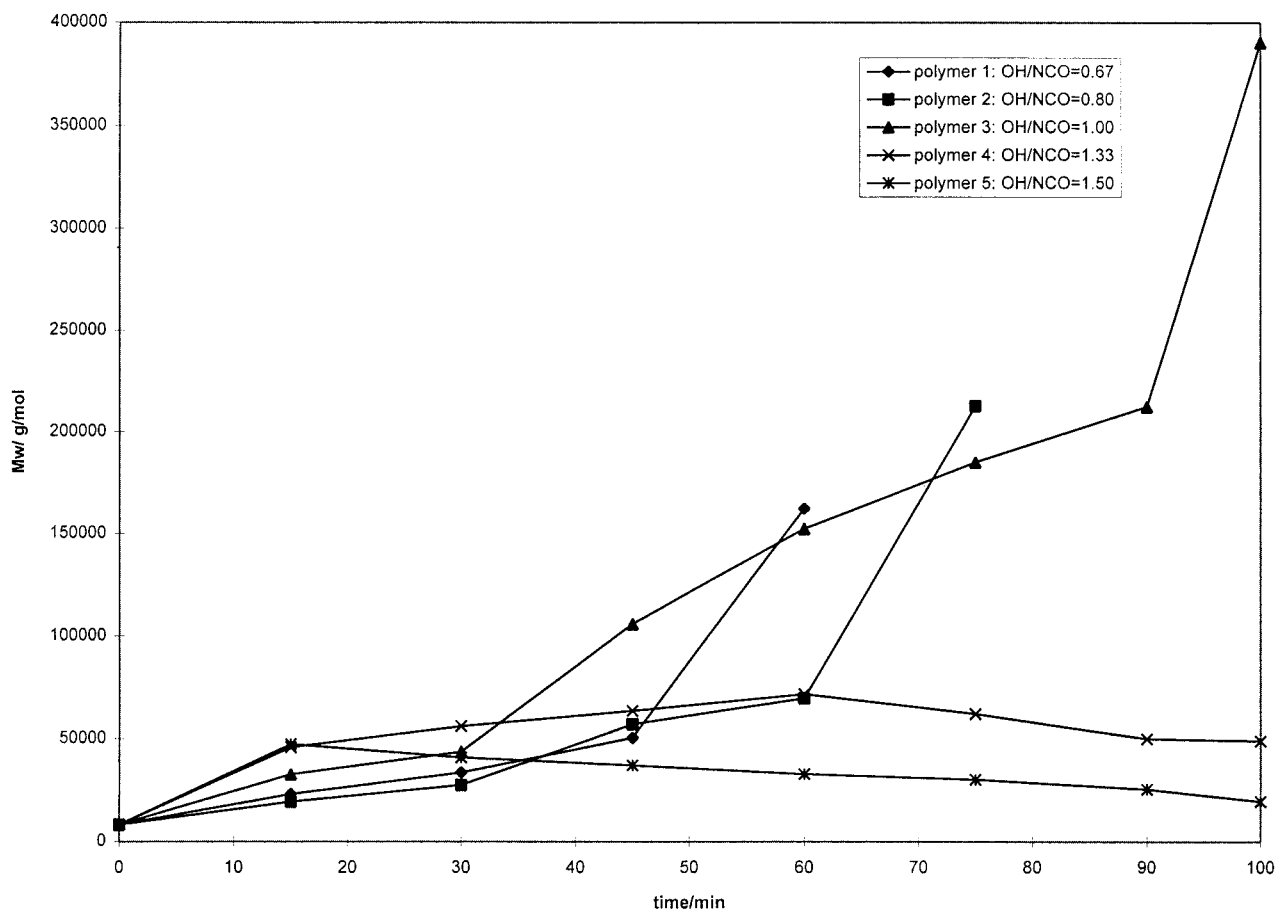
Figure 2 The development of weight average molecular weights. The polymerizations were carried out until the viscosity of the polymerization mixture was raised too high or until the viscosity was near zero. For polymers 1 and 2, the last points represent the weight average molecular weights of the last totally soluble sample.
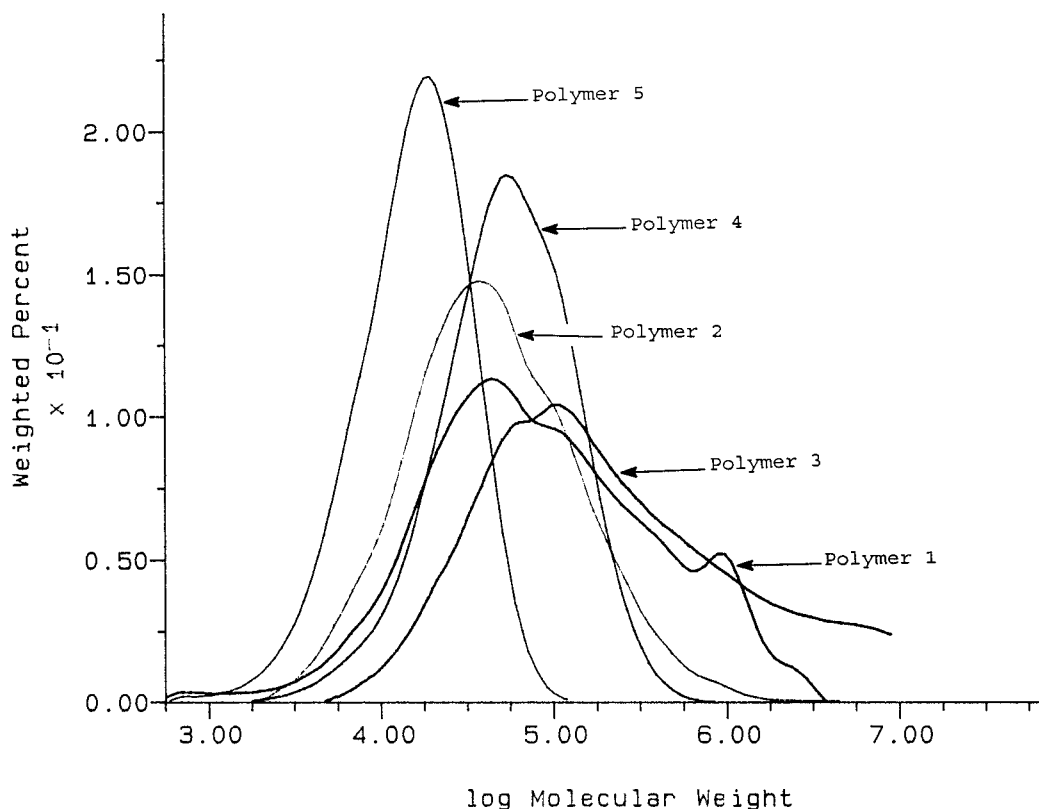
Figure 3 Molecular weight distribution curves of prepared polymers.

prepolymer molecules joined together by the reaction with the isocyanate. When the reaction proceeded long enough, the long polymer chains reacted with each other and, at the end of polymerization, the weight average molecular weight increased dramatically. The three molecular weight development stages for polymer 3 can be seen in Figure 2.

In the first stage (from 0 to 30 min), the weight average molecular weight increased slowly as the small prepolymer chains were joined together. After 30 min the second stage started as the bigger and bigger chains joined together; after 100 min in stage 3, very big chains joined together and the molecular weight increased dramatically. After 100 min the molecular weight of polymer 3 was so high that mixing became impossible due to the high melt viscosity.

The molecular weight distribution curves of the polymers are shown in Figure 3. Polymers 4 and 5, which had been produced with an OH/NCO ratio over unity, had quite narrow molecular weight distribution curves and quite low molecular weights. The molecular weight distribution curves for polymers 1, 2, and 3 all show a

multimodal character, but the molecular weights are not equal. The molecular weight distribution curves for polymers 1 and 2 present the data of the last totally soluble sample. The multimodal character of the molecular weight distribution curves appeared only at the end of the polymerization, and it must have been caused by long chain branching of the polymer chains. This branching was the first stage of crosslinking, and it most probably occurred when the isocyanate terminated chain reacted with the urethane group in a different polymer chain. Observations of the molecular weight distribution curves indicated that the molecular weight, long chain branching, and network formation can be controlled independently by varying the amount of diisocyanate.

Thermal Properties

The glass transition temperatures of the polymers are listed in Table I. Polymer 5 had the lowest glass transition temperature due to the low molecular weight and linear structure of the polymer chains. Polymers 3 and 4 had the highest glass transition temperatures, resulting from the

higher molecular weights and possibly the higher degree of hydrogen bonding caused by a greater number of urethane bonds in the polymer chain and probable branching of the polymer chains. Polymer 1 had a quite high glass transition temperature, probably because of the total crosslinking of the polymer. Polymer 2 was not completely crosslinked, and that must be the reason why it had a lower glass transition temperature than polymer 1. The glass transition temperatures are generally 50–55°C. Because the polymers are amorphous, the glass transition temperature determines the maximum temperature for use of these plastic materials.

IR Analysis

Figure 4 shows the IR spectra of polymer 3 at the beginning and at the end of the linking reaction. Both IR spectra exhibited characteristic ester absorption peaks (at 1760 and 1090 cm^{-1} for —COO— and —O—) and methyl absorption for CH$_2$, CH$_3$ groups (at 2850–3050 cm^{-1}). Also, the NH absorbtion peak (at 3400 cm^{-1}) became wider as the polymerization proceeded. The isocyanate had a very intensive absorption peak at 2300 cm^{-1}, which can be seen from the start curve of polymerization in Figure 4(a). The resulting polymer did not contain free isocyanate, because the isocyanate peak at 2300 cm^{-1} was missing at the end of the linking reaction [Fig. 4(b)].

When the OH/NCO ratio was over unity, all isocyanate was consumed before the end of the polymerization. When the ratio was below unity, there was a slight isocyanate peak in the resulting polymers, indicating unreacted diisocyanates or free isocyanate groups in the chain ends of these polymers.

^{13}C-NMR Analysis

The complete ^{13}C-NMR analysis of the prepolymer was given in our previous study.[11] Although the prepolymer contains less than 1.0 mol % LA and 4.1 mol % lactide analysed by ^{13}C-NMR, the resulting poly(ester-urethanes) did not contain LA monomer or lactide. The diisocyanate reaction probably joined these substances to the main chain of the polymer, because the diisocyanate can also react with acid end groups. The lactide rings were probably opened by tin(II) octoate, and diisocyanate joined these substances to the main polymer chains.

If the linking reaction proceeded as expected, the resulting poly(ester-urethanes) should have some extra peaks in their ^{13}C-NMR spectra that differ from the prepolymer peaks due to the reaction of prepolymer end groups with the diisocyanate. One extra peak should be found in the methylene area, two extra peaks in the methine area, and one extra peak in the carbonyl area, compared to the prepolymer spectrum. The expansions of the prepolymer and polymer 3 ^{13}C-NMR spectra and the carbons identified are shown in Fig. 5. The figure shows that the theoretical expectations were correct and the number of new peaks was as expected. Other polymers had peaks similar to polymer 3, but the peak intensities varied. Polymers prepared with —OH/—NCO ratios over unity had smaller peak intensities than polymer 3. The ^{13}C-NMR spectra of the polymers produced with ratios below unity were unreliable, because the spectra were recorded with swollen polymer samples. The spectra of the swollen polymers were quite good, but their peak integrals were not accurate.

The peaks that were caused by the hydroxyl end group of the prepolymer[11] also became smaller as the reaction with diisocyanate proceeded. This behavior can also be seen in all expansion areas in Figure 5. The peak intensities at 16.74, 69.10, and 169.65 ppm for the poly(ester-urethanes) are smaller than for the prepolymers. In our previous study, it was ascertained that these carbons were caused by the LA unit next to the LA unit at the chain end.

When the peak intensities of the carbons near the end groups were used in molecular weight calculations, polymer 3 had a number average molecular weight of 59,000 g/mol, which was only 2000 g/mol bigger than the number average molecular weight determined by GPC (see Table I). The calculated number average molecular weight of prepolymer determined by ^{13}C-NMR was 3000 g/mol, which suggested that in this polymerization the diisocyanate joined 20 prepolymer molecules together. The calculated molecular weights for polymers with —OH/—NCO ratios of 1.33 and 1.50 were 34,000 and 11,000 g/mol, respectively, and the number of joined prepolymer molecules were 11 and 4, respectively. The calculated molecular weights of polymers 3, 4, and 5 were very close to those determined by GPC (see Table I). It seems that although the GPC was calibrated with narrow polystyrene standards, it gave almost the same results as ^{13}C-NMR.

The diisocyanate methyls had three clear peaks at 41, 29, and 26 ppm. The carbonyl that origi-
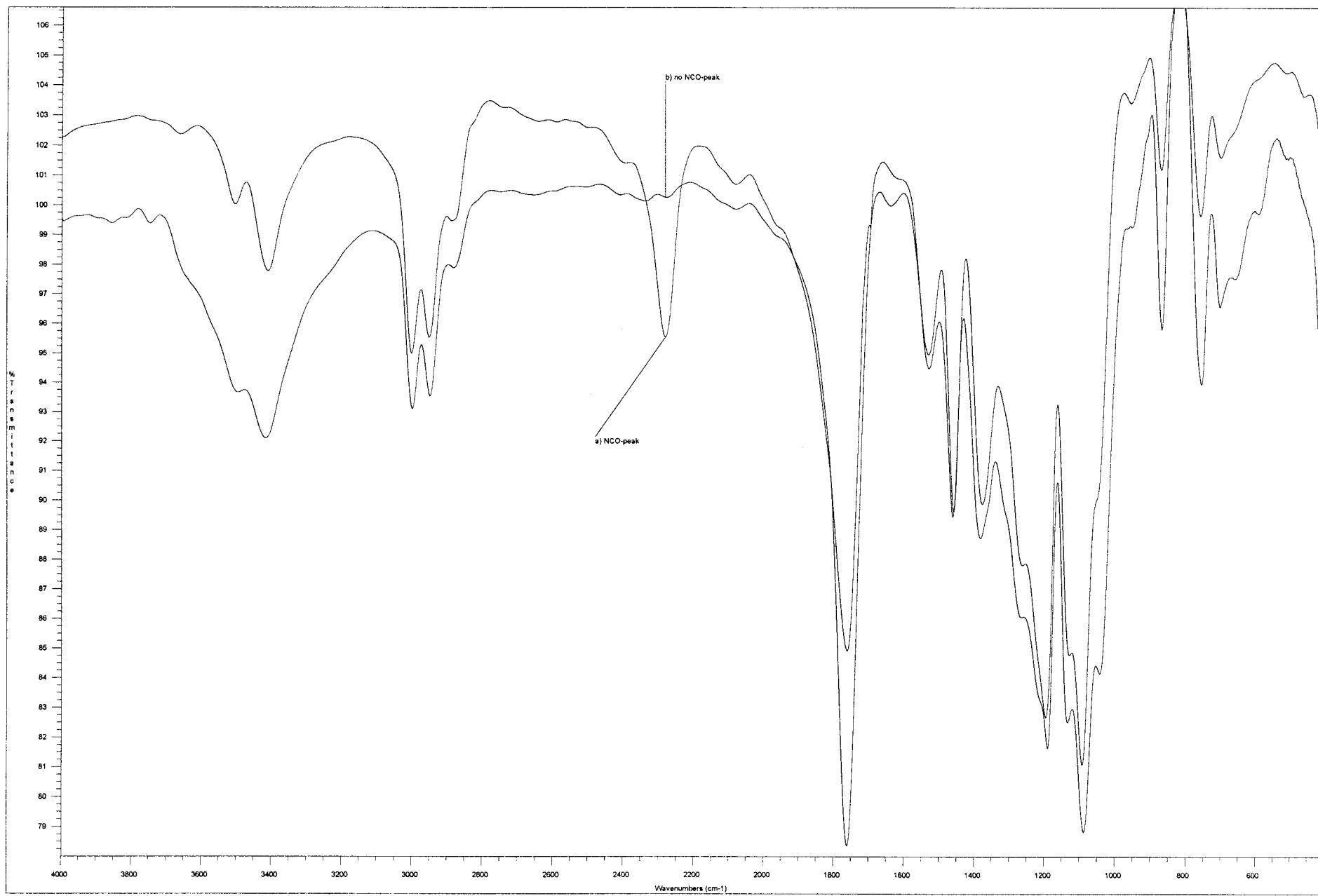
Figure 4 The IR spectra of polymer 3 (a) at the beginning of the linking reaction and (b) after the linking reaction with 1,6-hexamethylene diisocyanate.
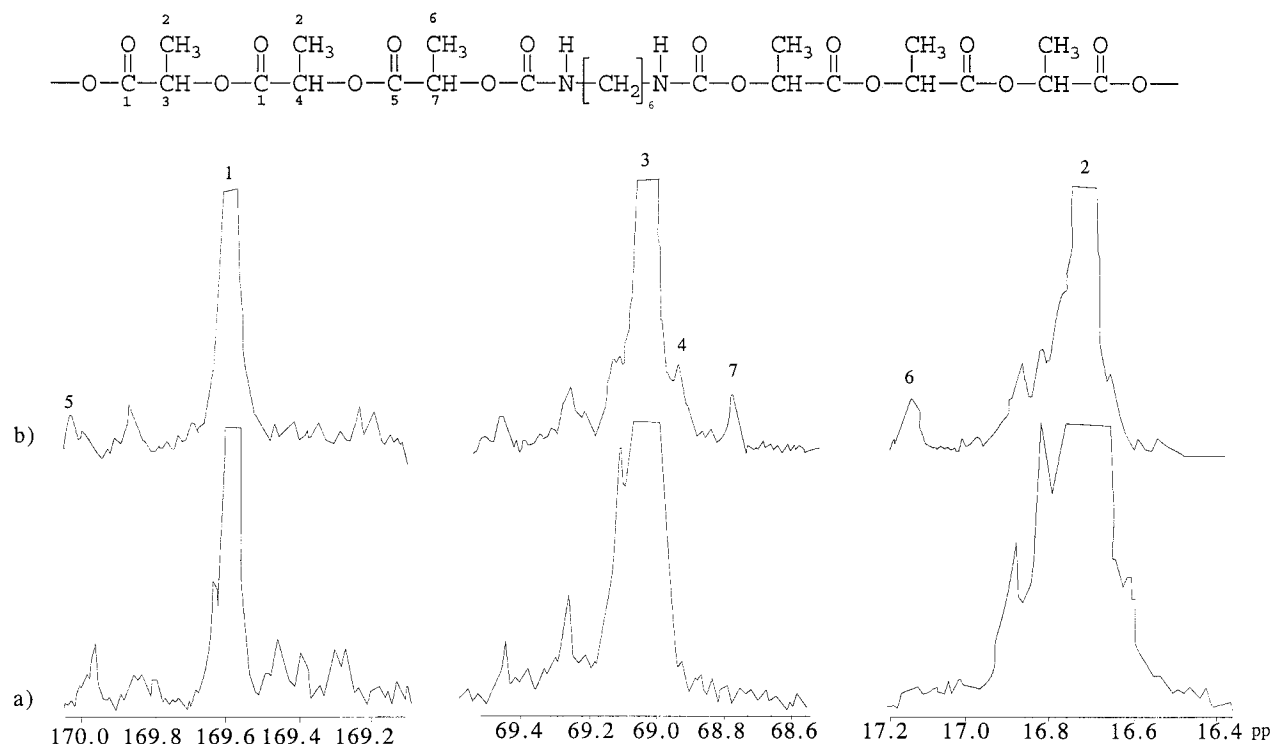
Figure 5 The expansions of polymer 3 ^{13}C-NMR spectra (a) prepolymer spectrum and (b) poly(ester-urethane) spectrum (after the reaction with 1,6-hexamethylene diisocyanate) and the identified carbons.

nated from the isocyanate group (see structure drawing in Fig. 6) had a peak at 175 ppm. Also, the 1,4-butanediol had its previously recognized peaks at 24 and 63.50 ppm, respectively.

The ^{13}C-NMR results were in agreement with the theoretical structures of these poly(ester-urethanes). The structure study of crosslinked poly(ester-urethanes) using ^{13}C-NMR still needs further work. When the NMR spectra of cross-linked and linear poly(ester-urethanes) were compared, only minor differences were detected. This led to the conclusion that reactions between the hydroxyl and isocyanate groups were much more probable than reactions between the isocyanate and amine groups. This means that when the crosslinking happened, long chains were joined together by the reaction of the isocyanate and urethane groups.

Preliminary Mechanical Properties

Polymer 3 was chosen for mechanical tests because it had the highest measurable molecular weight of the polymers prepared. The number average molecular weight of this polymer was 57,000 g/mol and the polydispersity index was 6.8. The tensile strength and modulus of poly(ester-urethane) were very close to the corresponding values for PLLA made via the ring-opening route. The measured tensile results were modulus 2300 MPa, yield stress 18.4 MPa, tensile strength 48.7 MPa, and maximum strain 3.2%. The mechanical properties were similar, although the number average molecular weight of the poly(ester-urethane) was just one-third of the molecular weight of the PLLA. The tested poly(ester-urethane) had a polydispersity index 3.6 times higher than PLLA.

CONCLUSIONS

The results indicated that almost 20 prepolymer molecules can be linked together on a laboratory scale, and the resulting poly(ester-urethane) was mostly linear. The number average molecular weight can be as high as 57,000 g/mol and the polydispersity index 6.8. The results also indicated that the molecular weight, long chain branching, and network formation can be con-

trolled independently by the amount of diisocyanate used and the polymerization conditions. According to ^{13}C-NMR, the structures of linear poly(ester-urethanes) were as expected. The analyzed content of monomer in prepolymer was less than 1 mol %, while the final poly(ester-urethane) was essentially monomer free. The resulting poly-(ester-urethanes) were thermoplastic. The mechanical properties of this poly(ester-urethane) were comparable with those of poly(lactides) made via a ring-opening route. The glass transition temperature of the amorphous material was about 53°C.

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