Synthesis and Characterization of Lactic Acid Based Telechelic Prepolymers

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ABSTRACT: The synthesis of low molecular weight (M_n (NMR) < 7000 g/mol) lactic acid prepolymers by condensation polymerization of L-lactic acid was investigated. Besides the L-lactic acid polymer, hydroxyl- and carboxyl-terminated telechelic prepolymers were also prepared by the addition of small amounts of 1,4-butanediol and adipic acid, respectively. All polymerizations were carried out in a melt with tin octoate as the catalyst. The products were characterized by differential scanning calorimetry, gel permeation chromatography (GPC), IR, ^{1}H-NMR, and ^{13}C-NMR. According to NMR, the resulting prepolymers contained less than 1 mol % of lactic acid monomer and less than 4.1 mol % of lactide. End group analysis of the polymers was carried out by comparing the NMR spectra of different polymers. According to NMR, the lactic acid can be copolymerized so that the resulting prepolymer chains have only one kind of end group, hydroxyl or carbonyl. The integrated area of the identified end group peak (hydroxyl or acid) was then used in molecular weight calculations. In ^{13}C-NMR studies, the molecular weights were calculated by using the peaks in the methine area. The molecular weights were also calculated by using the peak integrals of ^{1}H-NMR spectra of different polymers. The calculated molecular weights were systematically smaller than the molecular weights determined by GPC, and on about the same order as the molecular weights determined by titrimetric methods. The number-average molecular weights of prepared prepolymers determined by GPC varied from 2800 to 18 000 g/mol, depending on the amount of difunctional substance added. The glass transition temperatures varied from 16.7 to 46 °C.

Introduction

Until now, all NMR studies on the structure of poly(lactic acid) polymers have been carried out with the high molecular weight polymers manufactured through the lactide route. Lillie and Schulz[1] analyzed $SnCl_4$-catalyzed polymers manufactured from L-lactide and different amounts of racemic lactide. They noticed that all the main peaks observed in the ^{13}C-NMR spectra of racemic poly(lactides) show fine structure, except in the case of pure poly(L-lactide). Apart from the mole ratio of L-lactide/racemic lactide, the ester interchange and racemization reactions that occur during the polymerization also influenced the fine structure of the poly(lactic acid) polymers. Bero *et al.*[2] studied the influence of the type of coordination initiator (containing Zn and Al) on the microstructure of the poly(lactic acid) chain. They discovered that the initiators can be divided into three groups according to their influence on the chain structure. Chabot *et al.*[3] analyzed the configurational structures of lactic acid stereopolymers. They studied the ^{13}C-NMR carboxyl area peaks of lactic acid polymers and discovered that the more *rac*-lactide mixed with L-lactide, the more complicated the fine structure of the polymer was. Kricheldorf *et al.*[4−10] have studied the polymerization and copolymerization of lactide in several publications. One of their conclusions[7] was that, in principle, ^{13}C-NMR spectroscopy is best suited for sequence analysis, because the ^{1}H-NMR signals of copolylactones are not sensitive to sequence effects. They also concluded that ^{1}H-NMR spectroscopy is better suited for comonomer ratio and end group determination than ^{13}C-NMR. In the polymerization mechanism study,[5] they examined the effect of various metal alkoxides as initiators of different lactone polymerizations. The special purpose of that study was to use ^{1}H- and ^{13}C-NMR spectroscopy for the end group analysis of polylactide. The quantitative end group analysis was carried out with ^{1}H-NMR, while the ^{13}C-NMR spectra were only used in qualitative end group analysis. The identification of the end group peaks was based on the use of suitable model compounds. The conclusion was that the ^{1}H- and ^{13}C-NMR data agree with the theoretical structures and that the quantitative values of ^{1}H-NMR were reasonable. Barakat *et al.*[6] studied the selective end-functionalization of poly(D,L-lactide). They used functional aluminum alkoxides as initiators in the lactide polymerization. The end group analysis of these telechelics was carried out with ^{1}H-NMR, and the results were in good agreement with the theoretical, VPO (vapor pressure osmometry), and gel permeation chromatography (GPC) results.

In this work we have studied the polycondensation of relatively low molecular weight ($\bar{M}_n$ (NMR) < 7000 g/mol) lactic acid polymers and characterized the products by ^{1}H-NMR, ^{13}C-NMR, differential scanning calorimetry (DSC), GPC, titrimetric methods, and IR. The purpose of this study was to prepare low molecular weight telechelic lactic acid polymers which can be used as prepolymers. These telechelic prepolymer molecules can be linked together using chain extenders such as diisocyanates. In this kind of process, it is essential that the structure and end groups of prepolymers can be qualitatively and quantitatively analyzed. It shoul be noted that these prepolymers must be considered as new starting material in addition type chemistry and not as high molecular weight poly(lactic acid). The use of these prepolymers are presented in our other publications.[7−9]

Experimental Section

Materials. L-Lactic acid (LA) from Fluka was a 90% aqueous solution of the monomer, 99% optically pure according

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Table 1. Raw Materials and Some Characterization Results of Prepared Polymers[a]

polymer	lactic acid, mol	butanediol, mol	adipic acid, mol	$\bar{M}_n$ (GPC), g/mol	$\bar{M}_w$ (GPC), g/mol	T_g, °C	hydroxyl number	acid number	$\bar{M}_n$ (titr), g/mol	$\bar{M}_n$ (calc), g/mol
1	5			15500	24000	44.5	12	12	4700	
2	5	0.05		18000	26000	46.0	15.6	1.4	6600	7200
3	5	0.1		7900	11900	40.8	33.4	1.6	3200	3600
4	5	0.2		3800	5500	27.9	69.0	1.0	1600	1800
5	5	0.3		2300	3400	16.7	91.8	1.5	1200	1200
6	5		0.05	12000	16000	45.4	0.2	21	5300	7200
7	5		0.1	6600	9000	41.1	0.4	36	3100	3600
8	5		0.2	2700	4200	34.8	0.4	64	1700	1800
9	5		0.3	1800	2800	27.7	0.3	85	1300	1200
PLLA				88000	171000	55.0	2.0	1.0	37000	

[a] The calculated number average molecular weight is based on the presumption that all lactic acid monomers and lactic acid oligomers are joined to the polymer chain which contains only one kind of end group.

to the manufacturer. The excess water was removed before use by distillation under reduced pressure at 100 °C. The following products were used without further treatment: 1,4 butanediol (+98%) from Fluka; adipic acid (pure) from Merck; tin(II) octoate from Sigma Chemical Co.; tetrahydrofuran (HPLC grade) from Rathburn Chemicals Limited; chloroform-d_1 with TMS (1%), deuteration degree not less than 99.5% from Merck; and potassium bromide (spectroscopy grade) from Riedel-de Haen Ag.

Characterizations. IR spectra were measured on a Nicolet Magna Spectrometer 750 with 4 cm^{-1} resolution from KBr disks. The sample concentration in the discs 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 PL gel columns (10^4, 10^5, 10^3, and 100 Å) connected in series, and a Waters 410 differential refractometer. All samples were analyzed at room temperature. Tetrahydrofuran (THF) was used as eluent and was delivered at a flow rate of 1.0 mL/min. The samples were dissolved in THF 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 NOE were recorded on a Varian Unity 400 NMR spectrometer, working at 100.577 MHz for ^{13}C-NMR and at 399.958 MHz for ^{1}H-NMR. 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 hydroxyl and acid numbers were determined by standard titrimetric methods (DIN 53 240 and DIN 53 402). The molecular weights based on hydroxyl and acid numbers were calculated using the formula

$$\bar{M}_n\,(\text{titr}) = \frac{56.1 \times 2 \times 1000}{(\text{hydroxyl number} + \text{acid number})}$$

Every titration was repeated four times, and the reported result is an arithmetic average of these titers.

Synthesis of Lactic Acid Polymers. Besides the poly(L-lactic acid) polymer, the synthesis of telechelic poly(L-lactic acids) with two different types of functionalized end groups was attempted. In preparing of telechelic polymers with hydroxyl or carbonyl end groups, L-lactic acid was condensation polymerized with 1,4-butanediol or adipic acid, with 0.05% tin(II) octoate as the catalyst. All polymerizations were carried out in melt and under vacuum, using a Büchi Rotavapor equipped with an oil bath. A continuous nitrogen gas 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. Table 1 lists the polymerizations and the materials used.

After 8 hours of 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. The synthesis of the L-lactic acid polymers is outlined in Figure 1. The polymerizations are presented as they were expected to proceed.

The main presumption was that there is only one butanediol or adipic acid unit in every telechelic polymer chain. The use of a difunctional substance allows changes in the balance between the hydroxyl and acid groups, so instead of having equal numbers of functional groups, the added difunctional compound moves the balance toward the desired composition. At some point in the polymerization process the lactic acid monomers or lactic acid oligomers are joined to the telechelic polymer chains by the reaction of the hydroxyl and acid groups. If this presumption is correct, the resulting telechelic polymer chains should contain mainly one kind of end group and the molecular weight of these polymers could be controlled by the amount of difunctional substance.

Results and Discussion

Polymers **1**−**9** were produced by using the polycondensation process, where the lactic acid was polymerized to a low molecular weight polymer or telechelic polymers with two different kinds of functionalized end groups. The telechelic polymers were prepared using a small amount of difunctional compounds, 1,4-butanediol or adipic acid. In principle, the difunctional compound reacts with the lactic acid molecule or the lactic acid oligomer, and the product of this reaction is telechelic oligomer chains which have only one kind of end group. With further polymerization, the lactic acid monomers or lactic acid oligomers are joined to these telechelic polymer chains by the reaction of the hydroxyl and acid groups. As a result, at the end of the polymerization there are polymer chains which contain mainly one kind of end group.

The yields were high in every polymerization (>95%). Only a small amount of lactide (<1%) was sublimed and less than 3% of the lactic acid was distilled off with the condensating water. The amounts of lactide and distilled lactic acid were determined by weight and compared with the total amount of polymer produced.

Molecular Weight Determination by GPC and Titrimetric Methods. Molecular weights were first determined by GPC. All polymers were soluble in tetrahydrofuran (THF). The GPC was calibrated with narrow polystyrene standards, and therefore the GPC results were used only as a qualitative tool to check the peak shape and size distribution of the different polymers. The molecular weights ($\bar{M}_n$ and $\bar{M}_w$) of prepared polymers are shown in Table 1. According to GPC, the molecular weights of the hydroxyl- and acid-terminated polymers followed the following rule: the greater the amount of difunctional substance used in the polymerization reaction, the lower the molecular weight. The resulting polymers have quite narrow molecular weight distributions.

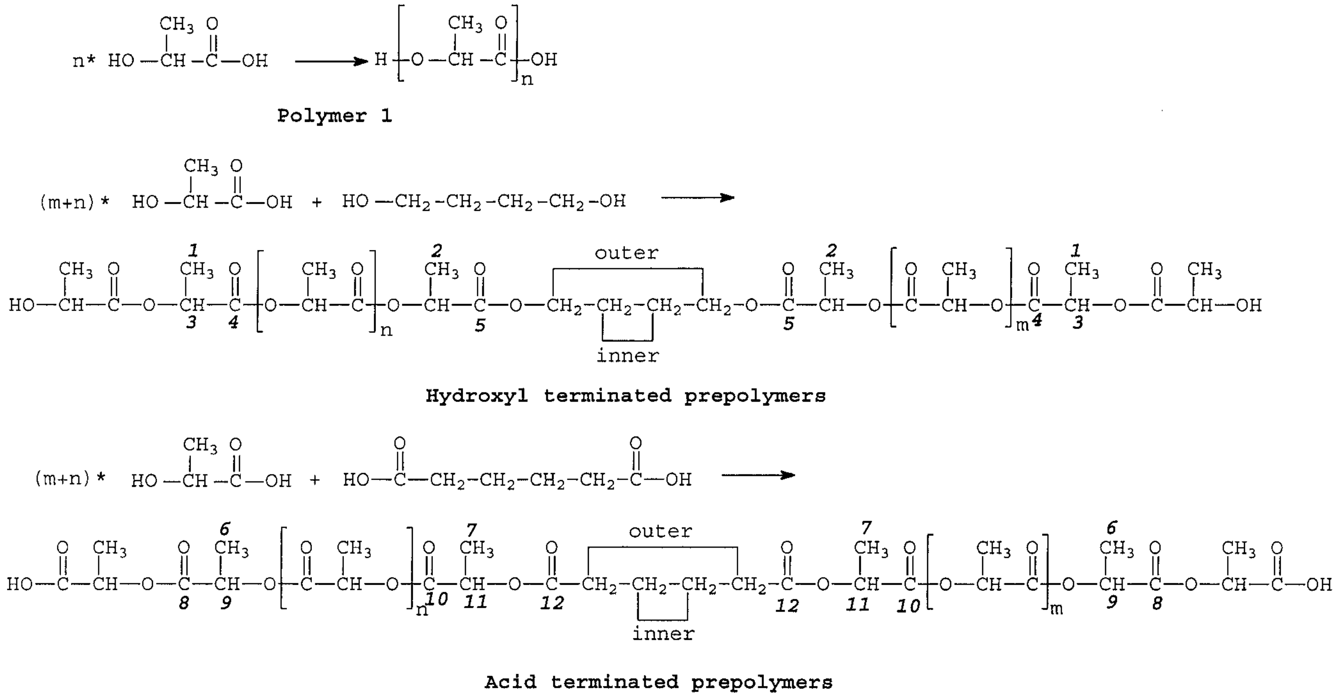

Figure 1. The synthesis of lactic acid based polymers. For the telechelic modifications, the basic polymer structure is the same, only the molecular weight varies. The numbers indicate the fine structure peaks which can be identified from Figures 2 and 3.

In addition, number-average molecular weights were determined by titrimetric methods, which involved the titration of hydroxyl and acid groups of the prepared polymers. The titrimetric results are shown in Table 1. The titrimetric results indicate that the prepared lactic acid telechelic prepolymers have mainly one kind of end group and that the molecular weights of these polymers can be controlled by the amount of difunctional substance added. The hydroxyl-terminated polymers **2**−**5** have acid numbers of less than 2, which indicates that acid-containing groups such as lactic acid monomers and lactic acid oligomers have reacted almost completely with the hydroxyl-terminated chains. The low hydroxyl values of polymers **6**−**9** indicate that the polymers were almost completely acid terminated.

Thermoanalyses. Thermoanalytical measurements were made with DSC equipment. The glass transition temperatures of the polymers obtained are shown in Table 1. According to DSC, all of the polymers prepared were amorphous except the PLLA sample, which showed the melting peak of the crystals. In polycondensation of L-lactic acid, substantial racemization was observed when tin(II) octoate was used as the polycondensation catalyst. According to our studies, which will be reported later, this racemization can be controlled by the use of different catalysts.

The glass transition temperatures of the telechelic prepolymers prepared were strongly dependent on the molecular weights. The higher the molecular weights, the higher the glass transition temperatures of these polymers. This conclusion closely fits the theory[10] which says that end groups increase free volume and decrease the glass transition temperature of polymers. According to our studies, the glass transition temperatures of the hydroxyl-terminated polymers vary from 16.7 to 46.0 °C and those for the acid-terminated polymers vary from 27.7 to 45.4 °C. The high molecular weight PLLA has a glass transition temperature of 55.0 °C, which is only 9 °C higher than the glass transition temperature for the highest molecular weight telechelic polymer. If the GPC molecular weights are compared, the PLLA has a molecular weight over 4 times higher than polymer **2**. This result indicates that lactic acid polymers reach their highest glass transition temperature at quite a low molecular weight. The differences in T_g's of the hydroxyl- and acid-terminated telechelic polymers are quite small at higher molecular weights, but the lower the molecular weight, the bigger the difference in T_g's. The difference between the glass transition temperatures of hydroxyl-terminated polymer **5** and acid-terminated polymer **9** (lowest molecular weights) is 11 °C, even though there is no significant difference between the molecular weights of these polymers. The reason for this could be that the hydroxyl group creates a bigger free volume than the acid group, and therefore, the hydroxyl terminated chains have more room to rotate. The reason could also be that the carboxyl group is ideally structured for forming two hydrogen bonds between a pair of molecules. A pair of hydrogen-bonded carboxylic acid molecules is often referred to as a carboxylic acid dimer. The differences between the T_g's of these polymers were significant when the number-average molecular weights determined by titrimetric methods were less than 1800 g/mol. Above this molecular weight, there is only a slight difference between the T_g's.

IR Analysis. IR analysis was used only as a qualitative tool to check if the differences in end groups could be seen in the spectra of the polymers prepared. All IR spectra exhibited characteristic absorption peaks of ester (at 1760 and 1090 cm^{-1} for −COO− and −O−) and $-CH_2-$, CH_3 groups (at 2850−3050 cm^{-1}). Polymer **1** had one broad acid absorption peak at 3000−3750 cm^{-1}, with an equally deep hydroxyl shoulder.

Hydroxyl-terminated polymers **2**−**5** gave a broad hydroxyl absorption peak at 3100−3700 cm^{-1}. The acid absorption peak was not detected. As expected, the hydroxyl absorption became stronger when the molecular weight of the polymer decreased. The spectra of

Table 2. ^{13}C-NMR Spectral Data (ppm) for Groups within the Prepared Polymers

group	in lactic acid	the polymer chain units	near OH end group	near COOH end group	in lactide	1,4-butanediol in chain (inner)	1,4-butanediol in chain (outer)	adipic acid in chain (inner)	adipic acid in chain (outer)
CH_3	20.17	16.70	20.58	18.11	15.89				
CH_2CH_2						25.09	64.87	24.15	33.49
CH	66.65	69.05	66.76	68.79	72.54				
COO		169.69	175.15		167.45		170.09		170.43
COOH	179.76								

carboxyl acid terminated polymers **6**−**9** exhibited a broad acid absorption peak at 3750−3000 cm^{-1} and as expected no hydroxyl shoulder. The acid absorption also became stronger when the molecular weight of these polymers decreased. According to FTIR, the expected structures and molecular weights of these polymers seem to be qualitatively correct.

^{13}C-NMR Analysis. The structures of the prepared polymers **1**−**9** and PLLA were qualitatively and quantitatively studied using ^{13}C-NMR spectroscopy. Besides determining the structure of the polymers, the aim was to assign the end group signals. The main components of the polymers can be recognized in the main ^{13}C-NMR spectra. Lines due to lactic acid (monomer), end groups of the polymer, lactide, and poly(lactic acid) were observed for all samples. Solvent and TMS lines were also present. The carbons were identified through a comparison of the different polymer spectra. The groups and their place in the scale which can be identified from the main spectra of polymers are shown in Table 2.

The data presented in Table 2 were correct for all polymers prepared. The end group peaks for the PLLA sample were very small, and identification without the aid of small molecular weight samples would have been impossible. The reason why the PLLA end group peaks were so difficult to identify was that the molecular weight of the PLLA was high, and therefore the number of end groups was very small.

The fine structure of polymers was investigated from expansions around the main peaks. The first expansion was taken around the methyl (CH_3) area, the second around the methine (CH) area, and the third around the carbonyl (COO) area. The expansions of the telechelic prepolymers are shown in Figures 2 and 3.

Figure 1 shows the probable structures of polymers which were identified from the expansion spectra presented in Figures 2 and 3. The expansion spectra of polymers which contain only lactic acid units (polymer 1 and PLLA) are shown in Figure 4.

The spectra of polymers which contain only lactic acid units in their chain was used to confirm that the identification of the carbons near the end groups would be correct. The telechelic polymers should have only lactic acid units near the chain ends, so both the telechelic and pure lactic acid polymers have the same kind of structure at the chain ends. And on the other hand, pure lactic acid polymers did not have the peaks which were caused by the 1,4-butanediol or adipic acid. When the spectra of polymers were compared, the conclusion was that the identification of the end group peaks and find structure peaks was correct.

The presence of hydroxyl end groups, and the identification of the hydroxyl end group carbon in polymer **3**, was confirmed by putting a few drops of acetic acid into a test tube containing polymer **3** solution and after 24 hours recording the spectrum. The expansions before and after the acetic acid addition are shown in Figure 5.

The peaks, which were assigned to be near end groups in the main spectra of polymer **3**, disappeared. The fine structure spectra presented in Figure 5 show that the peak (69.2 ppm) assigned to the methine group in the next lactic acid chain unit from the hydroxyl end group (carbon 9 in Figure 1) disappeared. Only the peaks assigned to be close to the end group disappeared, while all other peaks remained the same.

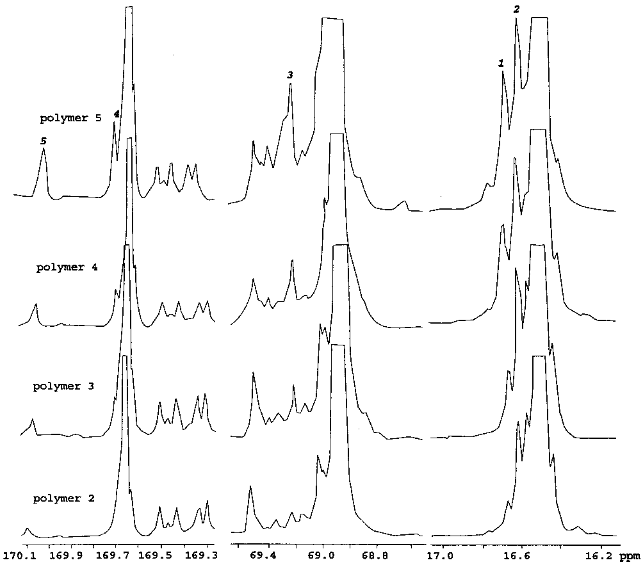

Figure 2. The ^{13}C-NMR expansion spectra of hydroxyl-terminated telechelic prepolymers. The expansions were taken around the methylene (CH_3), methine (CH), and carbonyl (COO) areas. The results of the fine structure identification are shown in Figure 1.

The presence of transesterification and different configurational structures in the polymer chains can be seen in all the expansions in Figures 2−4. Every polymer prepared had four peaks in the carbonyl area (169.2−169.5 ppm), at least three peaks in the methine area (69.15−69.5 ppm) and one very small peak in the methylene area. The peaks were shown to be due to different optical isomers in the polymer chain by preparing a polymer from D,L-lactic acid in the same way as polymer **3**. The main spectrum of prepared hydroxyl-terminated D,L-lactic acid polymer looks like the main spectrum of polymer **3**, but the expansion spectra of these polymers are different. The expansion spectra of prepared D,L-lactic acid prepolymer are shown in Figure 5. If the expansion spectra of D,L- and L-lactic acid prepolymers are compared, the conclusion is that D-units in the polymer chain have different peaks from the L-units in ^{13}C-NMR spectra. The spectra of prepolymers presented in Figure 5 prove that the peaks which were thought to be due to different optical isomers really are caused by them. The DSC data presented in Table 1 shows that the polymers prepared were amorphous. One possible reason for this could be that these polymers have D-lactic acid units in their chains, and therefore the long homogeneous blocks which can form crystalline domains are absent. In this study, we did not try to identify these different D-lactic acid structures and peaks, but the identification of these peaks will be reported.

Table 3. Calculated Values based on the Integrated Area of the Identified Peaks in the ^{1}H- and ^{13}C-NMR Spectra

	^{13}C-NMR			^{1}H-NMR			^{13}C- and ^{1}H-NMR			
polymer	hydroxyl end groups, mol %	acid end groups, mol %	$\bar{M}_n$, g/mol	hydroxyl end groups, mol %	acid end groups, mol %	$\bar{M}_n$, g/mol	butanediol, mol %	adipic acid, mol %	^{13}C-NMR: other isomers, mol %	^{13}C- and ^{1}H-NMR: lactide, mol %
1	0.7	0.6	5600	0.9	0.9	4100			23.1	4.1
2	1.1		6600	1.1		6600	0.95		29.0	2.8
3	2.4		3000	2.3		3300	1.9		29.5	2.4
4	5.2		1500	4.0		1900	4.0		27.4	2.1
5	7.8		1000	6.0		1300	5.6		21.4	2.0
6		1.5	5000		1.4	5200		0.95	24.7	1.1
7		2.4	3000		2.2	3400		1.7	24.7	2.7
8		5.4	1400		4.8	1600		3.2	17.2	2.9
9		6.9	1100		5.9	1300		4.8	14.8	2.4
PLLA	0.1	0.1	36000	0.1	0.2	24000			1.30	1.3

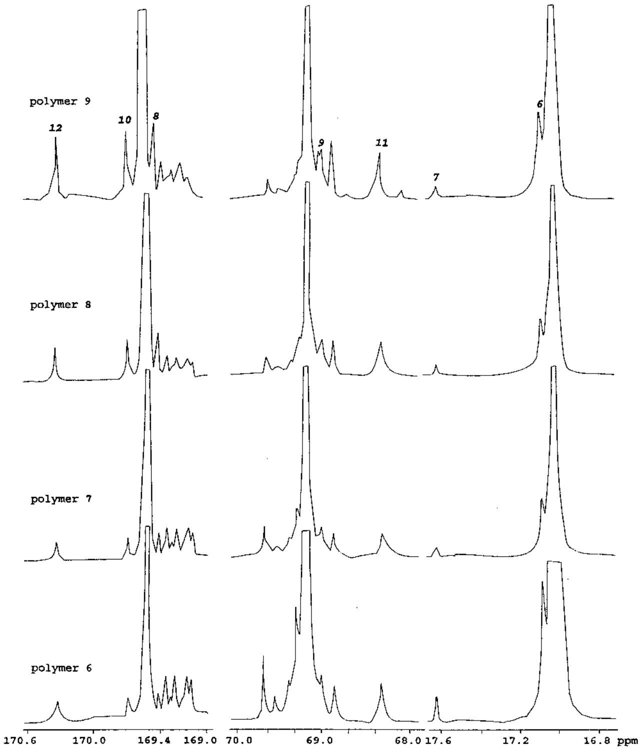

Figure 3. The ^{13}C-NMR expansion spectra of acid-terminated telechelic prepolymers. The expansions were taken around the methylene (CH_3), methine (CH), and carbonyl (COO) areas. The results of the fine structure identification are shown in Figure 1.

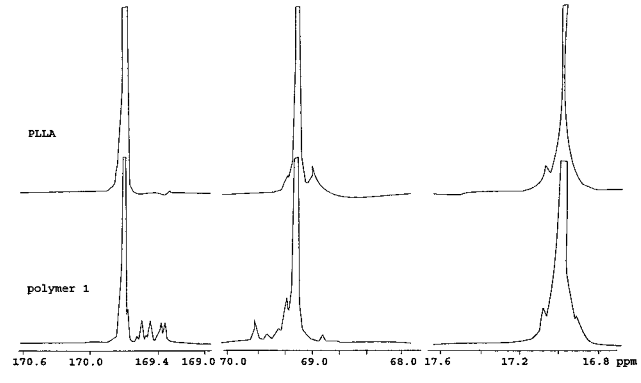

Figure 4. The ^{13}C-NMR expansion spectra of lactic acid polymer **1** and PLLA.

Quantitations. The peak integrals of the ^{13}C-NMR spectra were used for calculating quantitative values. The amounts of lactic acid, end groups, and lactide were calculated from the peak data of the methine area. All values were calculated from the identified peak integral ratio to the chain units. The amounts of lactic acid were very small for every polymer prepared (<1 mol %), and for PLLA, the lactic acid peaks were so small that the results were not reliable. The amounts of different optical isomers were calculated from the recognized peak integrals in the carbonyl area. Table 3 shows the calculated values for the polymers.

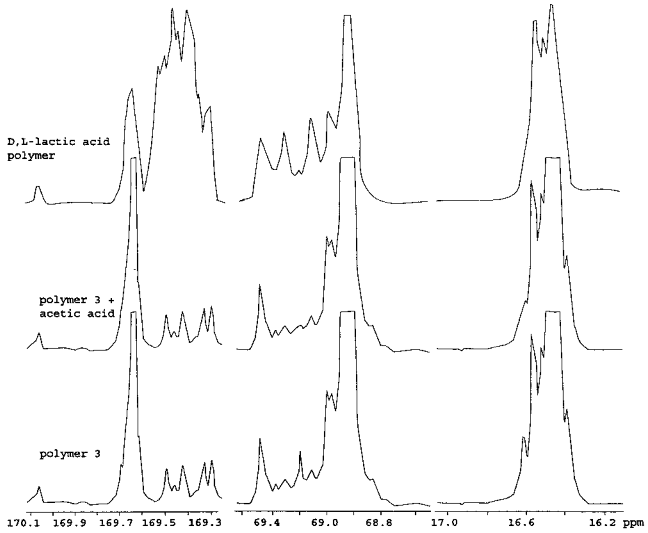

Figure 5. The ^{13}C-NMR expansion spectra of polymer **3** before and after the addition of acetic acid. The ^{13}C-NMR expansion spectra of D,L-lactic acid polymer, which was polymerized like polymer **3**, except that D,L-lactic acid was used as a raw material.

The molecular weights were calculated using the ratio of end group carbons to the chain carbons. The calculated molecular weights were systematically smaller than those determined by GPC, but the order was the same. The molecular weights determined by titrimetric methods were very similar. This is again strong evidence that the peaks were correctly identified. The amounts of 1,4-butanediol or adipic acid in the chain are very close to the fed amounts. These values prove that the polymerization process worked as expected The amounts of different optical isomers were fairly large in every polymer (>14 mol %), and this could be the reason why the polymers were amorphous.

Besides ^{13}C-NMR, the polymers were also analyzed with ^{1}H-NMR. The identification of end groups, lactic acid, lactide, 1,4-butanediol in the chain, and adipic acid in the chain was carried out using the same methods as in ^{13}C-NMR. The results are shown in Table 3. All results are very close to those determined with ^{13}C-NMR. The different optical isomers did not have peaks in the ^{1}H-NMR spectra.

Conclusions

Lactic acid can be condensation polymerized directly to low molecular weight telechelic poly(L-lactic acid) polymer. In the polymerization of telechelic polymers, the molecular weight of the resulting polymer depends on the amount of difunctional compound added, and the end groups depend on the nature of the compound. We have shown that lactic acid can be polymerized with diols or diacids in such a way that the resulting polymer has only hydroxyl or acid end groups and a particular molecular weight. The carefully characterized low molecular weight telechelic prepolymers are valuable raw materials in addition type chemistry. Analysis of the normal and telechelic polymers showed that the structures and molecular weights are predictable. The end groups of the polymers can be identified by ^{1}H- and ^{13}C-NMR, and their amounts can be calculated by peak integration. The calculated molecular weights were reasonable according to theoretical, titrimetric, and GPC methods. Detailed studies of the microstructure of these polymers and the factors affecting the microstructure (for example, initiator and polymerization conditions) will be published later.

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