Synthesis and Characterization of Lactic Acid Based Poly(ester−amide)

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ABSTRACT: The effects of polymerization temperature and the amount of chain extender, 2,2′-bis(2-oxazoline), on the synthesis of lactic acid based poly(ester−amide) (PEA) were studied. High molecular weight polymer was produced only within a narrow range of polymerization parameters. The highest molecular weights were achieved with the molar ratio of oxazoline/carboxyl end groups being 1.2/1.0 at 200 °C. Poly(ester−amide) was analyzed (GPC, DSC, IR, NMR), and the mechanical properties were measured and compared with those of some biopolymers and commercial thermoplastics. Measured by GPC, the highest molecular weights were over 300 000. The mechanical properties of PEA were good: tensile strength of the high molecular weight polymer was as much as 67 MPa, and the Charpy impact strength was 34 kJ/m^2.

Introduction

Lactic acid, a nontoxic, naturally occurring, and renewable raw material, is an attractive monomer for biodegradable polymers. Already, lactic acid based polyesters are well-known among biodegradable polymers, finding use not only in biomedical applications but in packaging, consumer goods, and many other articles of short-term use.[1] For many applications, the molecular weight of poly(lactic acid) needs to be relatively high in order for the mechanical properties to be acceptable.[2] Conventional condensation polymerization of lactic acid does not increase the molecular weight sufficiently unless the polymerization time is very long.[3] Another way to achieve high molecular weight poly(lactic acid) is through ring-opening polymerization of lactide.[4,5] However, lactide production is relatively complicated and expensive. Alternative polymerization routes for lactic acid are thus of considerable interest.

The synthesis of lactic acid based biodegradable poly(ester−urethanes), has been reported in a number of papers.[6−9] Seppälä and co-workers[10−12] studied two-step polymerization of lactic acid. They condensation polymerized low molecular weight prepolymer and increased the molecular weight by using 1,6-hexamethylene diisocyanate as chain extender. Experiences with the polymerization, biodegradation, and mechanical properties of lactic acid based poly(ester−urethanes) (PEUs) indicate that lactic acid based low molecular weight telechelic prepolymers could provide the starting materials for other types of high molecular weight biodegradable polymers.[6,13,14]

Bis cyclic imino−ethers are an attractive class of chain extenders for linear polyesters and polyamides, especially for those that are mainly terminated by carboxyl groups. In chain extending reactions by bis cyclic imino−ethers such as bis-2-oxazolines, reaction behavior of carboxyl terminals contained in the initial polymers can be classified in to three groups: coupling, blocking, and unreacted. The reactivity of bis-2-oxazolines as the chain extender is dependent upon the electron-with-drawing property of the substituent at 2-position of the oxazoline ring. There are no significant side reactions during the chain extending reaction when bisoxazolines are used as chain extenders for carboxyl-terminated polyesters and polyamides.[15−19] The ester−amide formed in the reaction between an oxazoline and a carboxylic group is moderately stable.[20] In their studies of addition-type carboxyl-reactive chain extenders for linear PET and PBT, Inata et al.[18,19,21] found that 2,2′-bis(2-oxazoline), 2,2′-bis(5,6-dihydro-4*H*-1,3-oxazine), and *N*,*N*′-hexamethylenebis(2-carbamoyl-2-oxazoline) were very effective chain extenders for linear polyesters. Under melt conditions they reacted with polyesters in just a few minutes. Böhme et al.[22] report that bisoxazolines, 2,2′-bis(2-oxazoline) and phenyl-1,4-bis(2-oxazoline), react very fast with carboxyl-terminated polyester, and phenyl-1,4-bis(2-oxazoline) raises the molecular weight ($\bar{M}_n$) of the polyester from 13 000 to 46 000.

The aim of the present study was to find a new chain extender for lactic acid based biodegradable polyester, to optimize the chain extending reaction conditions for producing high molecular weight polymer, and to achieve good thermal and mechanical properties. The effects of polymerization temperature and the amount of chain extender on the molecular weight were investigated as a function of polymerization time. Poly(ester−amide) was analyzed, and the mechanical properties of the high molecular weight PEA were characterized and compared with those of some biopolymers and commercial thermoplastics.

Experimental Section

Materials. L-Lactic acid (L-LA) based carboxyl-terminated telechelic prepolymer was prepared in a pilot reactor by the method described earlier.[23−25] The following products were used without further treatment: an 88% aqueous solution of L-lactic acid from ADM, succinic anhydride (SAH) from Fluka and Sn(II) octoate from Sigma. 2,2′-Bis(2-oxazoline) was synthesized in a 5-L glass reactor according to the procedure described by Böhme et al.[22] and Wenker.[26] The following materials were used for assessing the mechanical properties of poly(ester−amide) (PEA): polystyrene PS-181 (PS) from Neste Oy, polybutylene terephthalate (PBT) Grilpet XE 3060 from EMS Chemie, polyamide 6 (PA6) Ultramid B 4F from BASF, poly(L-lactide) (PLLA) from Neste Oy, and lactic acid based poly(ester−urethane) (PEU) prepared earlier.[27]

Polymerization Apparatus and Procedure. Polymerizations were carried out in a 150 cm^3 batch reactor equipped with nitrogen inlet and outlet tube for nitrogen atmosphere. Reaction temperature was controlled with a Lauda K 6 KP

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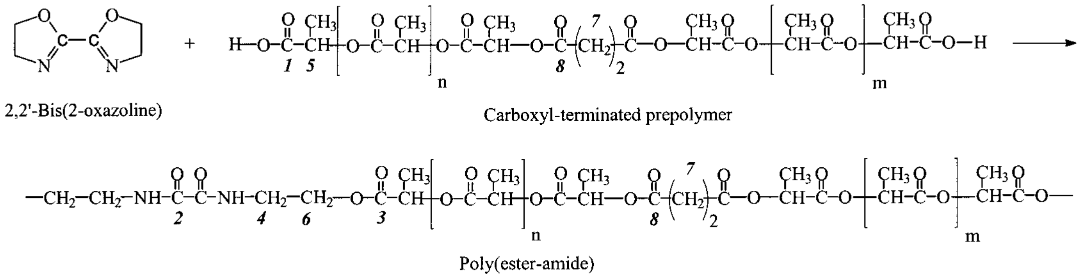

Figure 1. Scheme of the synthesis of lactic acid based poly(ester−amide). Numbers refer to structure peaks which can be identified in Figure 4.

Table 1. Characterization of Prepolymer and Poly(ester−amide) (PEA)

	monomer[a]			GPC			^{13}C NMR						
	L-LA (mol %)	SAH (mol %)	CER[b] Oxa/COOH	$\bar{M}_n$	$\bar{M}_w$	MWD	$\bar{M}_n$	D-structures (mol %)	amount of lactide (mol %)	succinic acid units (mol %)	oxazoline units (mol%)	titrimetry acid no.	DSC T_g (°C)
prep	98	2		6200	10000	1.6	3900	16	1.0	1.8		30.5	49
PEA	98	2	1.2/1.0	74000	390000	5.3		15	1.7	1.4	1.4	1.8	55

[a] In feed. [b] Mole ratio of the end groups at the beginning of chain extending reaction.

thermostat. Carboxyl-terminated lactic acid based prepolymer (60 g) was dry-blended with the chain extender, and the mixture was fed to the heated reactor. The reactor was purged with a continuous flow of nitrogen. The temperature of the reactor and the speed of the mixer (50 min^{-1}) were kept constant. For optimizing the process the polymerization was followed by taking samples every 5 min for 20 min and thereafter every 10 min. The polymerization temperatures were 190, 200, and 210 °C and the molar ratios of end groups (oxazoline/carboxyl) were 1.0/1.0, 1.1/1.0, 1.2/1.0, and 1.3/1.0.

Characterization. Molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and molecular weight distributions (MWD) were determined with respect to polystyrene standards by gel permeation chromatography (GPC), and these results were therefore used only as a qualitative tool to check the peak shape and size distribution of the different polymers. 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. The eluent was chloroform, delivered at a flow rate of 1.0 mL/min. Samples were dissolved in chloroform at a concentration of 1.0% (w/v). The injection volume was 200 μL.

Acid numbers of the prepolymer and poly(ester−amide) were determined by standard titrimetric method (DIN 53402).

Differential scanning calorimetric measurements were made on a Mettler Toledo Star differential scanning calorimeter. The measurements were run from 0 to 200 °C at a heating rate of 10 °C/min. The glass transition temperatures were determined from the second heating period.

Proton-decoupled ^{13}C NMR spectra with NOE were obtained with a Varian Gemini 2000 300 MHz spectrometer working at 75.452 MHz. Sample concentrations in 5 mm tubes were 10 wt % in $CDCl_3$.

FTIR spectra were recorded on a Nicolet Magna-FTIR 750 spectrometer, from film samples of the prepolymer and poly(ester−amide).

Mechanical properties of the poly(ester−amide) were determined with use of an Instron 4204 tensile testing machine adapting the standard ISO 527−1993(E). Crosshead speed was 5 mm/min. The mechanical values for the PEA and other tested materials were measured for five parallel air-conditioned specimens that had been left for 72 h at 23 °C and 50% relative humidity. Modulus, strain, and tensile strength were calculated by Instron Corp. software. Charpy impact strength tests were carried out with a Zwick 5102 pendulum-type testing machine with pendulums of 2 and 5 J adapting the standard ISO 179−1982(E) at 23 °C and 50% relative humidity. Test samples for tensile tests (specimen type 1BA) and Charpy impact strength tests (specimen type 2) were prepared with a co-rotating twin-screw midiextruder (DSM Research; capacity = 16 cm^3; screw length L = 150 mm), equipped with a back-flow channel that allows it to be operated in batch wise. The mixing time, with the screw speed of 50 rpm, was 2 min, after which the polymer was injection molded with a mini-injection molding machine (DSM Research). All polymers were dried for 72 h in a vacuum at 30 °C before injection molding. The mixing and injection molding temperatures were 150 °C for PEA, 140 °C for PEU, 190 °C for PLLA, 200 °C for PS, and 250 °C for PBT and PA. The temperature of the mold was 40 °C for all polymers.

Results and Discussion

Poly(ester−amide) was polymerized from lactic acid based carboxyl-terminated prepolymer and chain extender 2,2′-bis(2-oxazoline). The reaction scheme for the synthesis is shown in Figure 1. Study was made of the effects of polymerization temperature (190 °C, 200 °C, and 210 °C) and the amount of 2,2′-bis(2-oxazoline) on the synthesis, and the best reaction conditions were used for producing poly(ester−amide) for mechanical tests.

The carboxyl-terminated prepolymer for the synthesis was a typical low molecular weight prepolymer, which was condensation polymerized from L-lactic acid and 2 mol % of succinic anhydride with 0.05 wt % tin(II) octoate as catalyst. Determined by GPC, the molecular weights were 6200 ($\bar{M}_n$) and 10 000 ($\bar{M}_w$). According to ^{13}C NMR studies, the prepolymer was mainly carboxyl-terminated (the amount of hydroxyl end groups was less than 1 mol %). The number-average molecular weight was calculated from the ratio of end group peak integrals to chain unit peak integrals and compared with values obtained by GPC and titrimetric methods. Calculated number-average molecular weights, 3900, measured by ^{13}C NMR, and 3700, measured by titration, were lower than those measured by GPC, but the calculated number-average molecular weights were very similar. Titrimetric method was used to calculate the amount of chain extender. The characterization results of the prepolymer is presented in Table 1.

The poly(ester−amide), like the prepolymer, was completely amorphous. The molecular weight of the poly(ester−amide) was strongly dependent on the polymerization temperature and molar ratio of end groups.

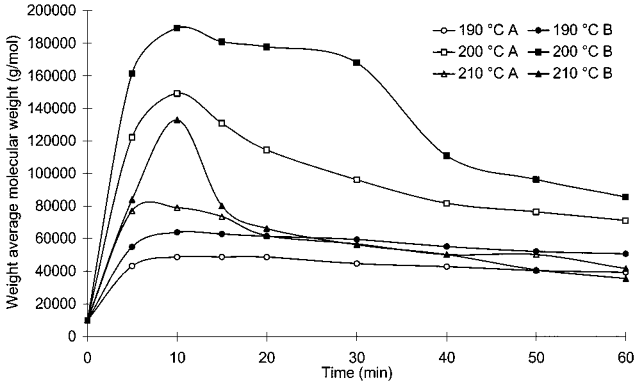

Figure 2. Development of weight-average molecular weights in the chain extending reaction with 1.1/1.0 (A) and 1.2/1.0 (B) molar ratios of end groups at temperatures of 190, 200, and 210 °C.

High molecular weight polymer was produced only within a narrow range of polymerization parameters. The effects of polymerization temperature and molar ratio of the end groups (oxazoline/COOH) on the properties of the poly(ester−amide) are shown in Table 2. A polymerization temperature of 190 °C did not favor high molecular weights at any molar ratio of end groups. Evidently this temperature is too low for chain extending reaction. Highest molecular weights were obtained at 200 °C, which seemed to be the optimal temperature. The best molar ratio of end groups was 1.2/1.0 (excess of oxazoline). A polymerization temperature of 210 °C was too high for producing high molecular weight polymer: thermal degradation of the PEA was marked.

Table 2. Effect of Polymerization Temperature and Amount of 2,2′-Bis(2-oxazoline) on the Properties of Poly(ester−amide)

polymerization temp (°C)	molar ratio of end groups (Oxa/COOH)	GPC $\bar{M}_n$	GPC $\bar{M}_w$	GPC MWD	DSC T_g (°C)
190	1.0/1.0	21 300	47 800	2.2	53
190	1.1/1.0	18 800	48 600	2.6	53
190	1.2/1.0	26 800	62 600	2.3	53
190	1.3/1.0	24 700	50 900	2.1	51
200	1.0/1.0	25 200	72 000	2.9	52
200	1.1/1.0	48 100	149 000	3.1	54
200	1.2/1.0	53 100	189 000	3.6	53
200	1.3/1.0	38 200	114 000	3.0	51
210	1.0/1.0	24 300	56 900	2.3	52
210	1.1/1.0	28 800	78 900	2.7	51
210	1.2/1.0	33 000	133 000	4.0	51
210	1.3/1.0	31 800	78 400	2.5	50

The prepolymer and chain extender reacted very fast. The highest molecular weights were achieved after 10 minutes polymerization. For example, comparison of the molar ratios 1.1/1.0 and 1.2/1.0 at each polymerization temperature (Figure 2) shows that in both cases the highest values were obtained in 10 min. After that, the thermal degradation of the polymer was faster than the polymerization reaction and the molecular weight started to decrease. The same tendency was noticed at all polymerization temperatures and all molar ratios of end groups.

This kind of polymerization behavior, and the requirement of excess 2,2′-bis(2-oxazoline) for producing high molecular weight PEA, can be explained in terms of the thermal instability of the lactic acid based

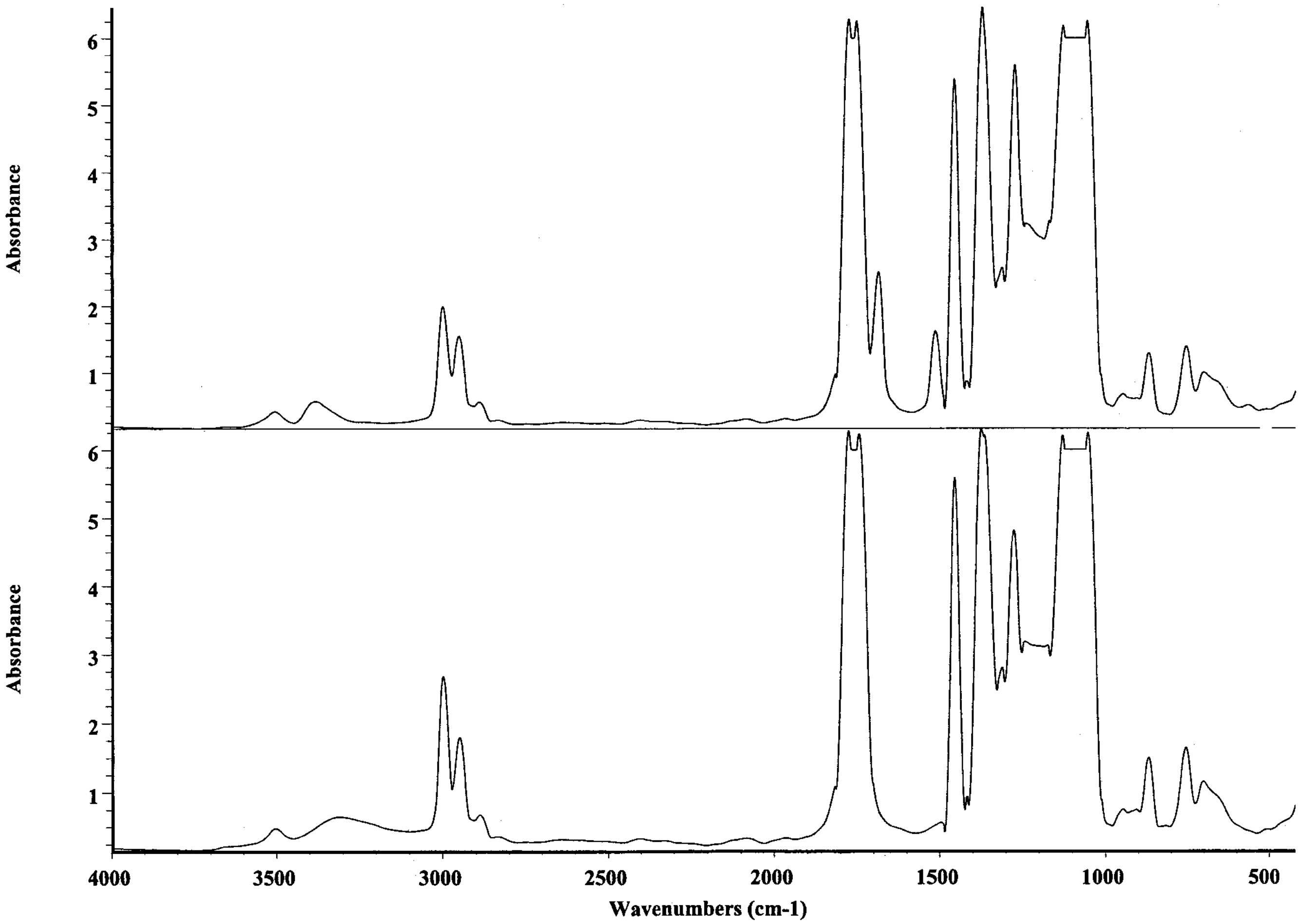

Figure 3. FTIR spectra of prepolymer (lower) and poly(ester−amide) (upper).

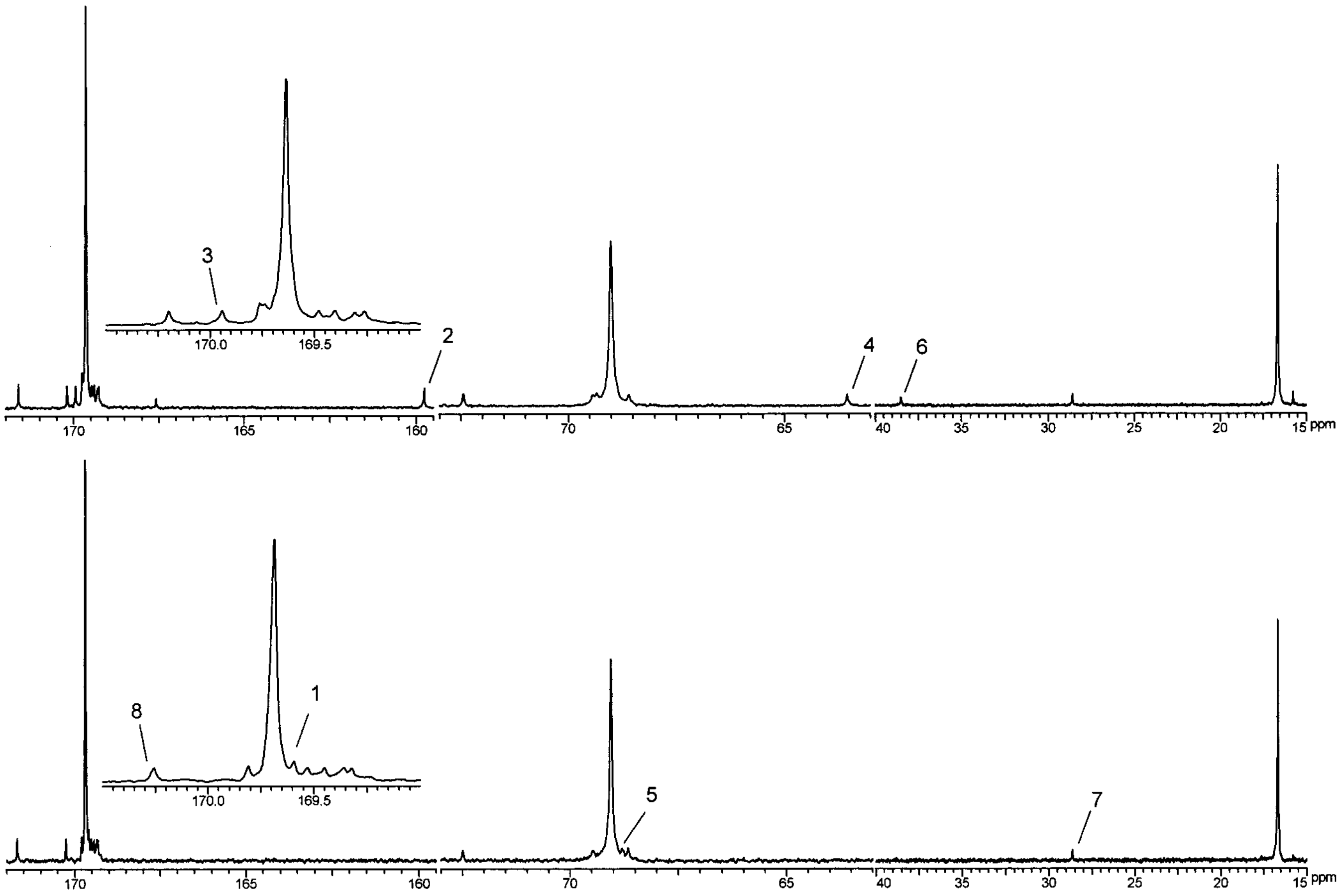

Figure 4. ^{13}C NMR expansion spectra of around the carbonyl, methine, and methylene areas.

Table 3. Identified Groups and ^{13}C NMR Spectral Data (ppm) of Prepolymer and Poly(ester−amide)

group	lactic acid chain units in prepolymer	lactic acid units near COOH end groups	succinic acid chain units	lactic acid units near succinic acid units	oxazoline chain units	lactic acid units near oxazoline units
$\mathit{C}\mathrm{H_3}$	16.63					
$\mathit{C}\mathrm{H_2}$			28.61			
$\mathit{C}\mathrm{H}$	69.01	68.78				
$\mathit{C}\mathrm{OO}$	169.64		170.21	169.77 171.63		169.95
$\mathit{C}\mathrm{OOH}$	169.60					
$\mathit{C}\mathrm{ONH}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2}$					63.56	
$\mathit{C}\mathrm{ONHCH_2}\mathit{C}\mathrm{H_2}$					38.51	
$\mathit{C}\mathrm{ONH}$					159.77	

prepolymer at high temperatures and, reversely, the high temperatures needed for the chain extending reaction. At the beginning of the chain extending reaction, 2,2′-bis(2-oxazoline) reacts quickly with prepolymer chains, forming high molecular weight PEA. Evidently the chain extending reaction is faster than the blocking reaction and high molecular weight polymer is produced fast even when the 2,2′-bis(2-oxazoline) is used in excess. At the same time, however, thermally unstable prepolymer chains start to degrade and the thermal degradation of the prepolymer chain in PEA generates new carboxyl and hydroxyl end groups. The excess of oxazoline groups allows them readily to react with carboxyl group but not with hydroxyl group. The molecular weight of the poly(ester−amide) increases until all oxazoline groups have reacted or the hydroxyl end group concentration becomes too high and degradation occurs faster than polymerization. The amount of oxazoline must be optimized, because with too high excess of oxazoline the blocking reaction becomes dominating and the molecular weight of PEA remains low. The results showed that the optimal polymerization conditions were 200 °C polymerization temperature with 1.2/1.0 molar ratio of end groups for producing high molecular weight PEA.

IR Analysis. IR spectrometry was used for qualitative analysis of the prepolymer and poly(ester−amide) to check for the presence of carboxyl end groups and the formation of the oxamide group. As can be seen in the FTIR spectra in Figure 3, the prepolymer (lower spectrum) exhibits one broad acid absorption peak at 3100−3450 cm^{-1}. In the spectrum of PEA (upper spectrum) this peak has almost disappeared, which indicates that the 2,2′-bis(2-oxazoline) has reacted with carboxyl end groups to form oxamide groups. Only a few carboxyl end groups remain after the chain extending reaction. Titrimetric analysis (Table 1) of high molecular weight PEA gives an acid number of less than two and allows the same conclusion. The spectrum of PEA shows absorption peaks of the oxamide group at 3390 cm^{-1}

Table 4. Mechanical Properties of Poly(ester−amide) Compared with Those of Selected Biopolymers and Commercial Thermoplastics

polymer	tensile modulus (MPa)	tensile stress at max load MPa	max strain (%)	Charpy impact strength (kJ/m^2)
PEA	1720 ± 30	67 ± 4	9 ± 3	34 ± 4
PEU	1670 ± 22	50 ± 2	5 ± 1	20 ± 2
PLLA	1630 ± 60	62 ± 2	7 ± 1	23 ± 3
PS	1510 ± 34	57 ± 4	5 ± 1	21 ± 5
PBT	1100 ± 14	44 ± 1	470 ± 90	NB[a]
PA6	1230 ± 36	59 ± 1[b]	320 ± 45	NB

[a] NB = not broken (pendulum 5 J). [b] Yield stress.

(NH stretching vibration), 1680 cm^{-1} (C=O stretching vibration), and 1520 cm^{-1} (C=O stretching vibration).

^{13}C NMR Analysis. The carbon signals were identified through comparison of the spectra of L-lactic acid, L-lactide, succinic anhydride, 2,2′-bis(2-oxazoline), prepolymer, and poly(ester−amide), and carbons were identified according to Douhi et al.[15] and Hiltunen et al.[25] The identified groups and their location in the ^{13}C NMR spectra are shown in Table 3.

Expanded ^{13}C NMR spectra of the prepolymer and poly(ester−amide) are shown in Figure 4. The lower spectra present the prepolymer and the upper spectra the poly(ester−amide). The expansions were taken around the methylene, methine, and carbonyl areas. As can be seen from the spectra of the poly(ester−amide), chain extending reaction has taken place and the structure of the polymer is as shown in Figure 1. According to the NMR spectra, no significant side reactions occurred during the chain extending reaction. The carboxyl end group peak (1) in the prepolymer spectrum disappeared in the chain extending reaction and two new peaks formed, but all other polymer peaks in the carbonyl area remained the same. The new peaks were due to oxamide carbonyl (2) and to the end group carboxyl of prepolymer (3) which had reacted with 2,2′-bis(2-oxazoline). The three peaks (155.70, 68.37, and 55.10 ppm) due to the 2,2′-bis(2-oxazoline) monomer could not be seen in the poly(ester−amide) spectrum, which confirms that all 2,2′-bis(2-oxazoline) monomer reacted during the chain extending reaction. In the methine area of the poly(ester−amide) there is a new peak (4) due to the 2,2′-bis(2-oxazoline) unit (CH_2) in the polymer chain, and the CH peak (5) near the end group carboxyl peak in the prepolymer spectrum has disappeared. The other CH_2 peak (6) due to the 2,2′-bis(2-oxazoline) unit in the polymer chain can be seen in the methyl area. Carbons of the succinic acid unit can be seen in the methyl (7) and carbonyl (8) areas. Lactide peaks were present in the methylene (15.77 ppm), methine (72.45 ppm), and carbonyl (167.57 ppm) areas.

According to the ^{13}C NMR studies there was less than 1 mol % of free lactic acid and less than 1.7 mol % of lactide in the prepolymer and the poly(ester−amide). The prepolymer was mainly carboxyl-terminated. The prepolymer and poly(ester−amide) contained approximately the fed amount of succinic acid units and the chain extending reaction did not affect the amount of D-structures (169.20−169.50 ppm). Representative results of the ^{13}C NMR analysis are set out in Table 1.

Mechanical Properties of Poly(ester−amide). Poly(ester−amide) was thermoplastic and could be processed by injection molding. Experiments showed the mechanical properties to be substantially better than those of other tested lactic acid based polymers (PEU and PLLA). Table 4 shows a comparison of the mechanical properties with those of some biopolymers and commercial thermoplastics such as PEU, PLLA, PS, PBT, and PA, likewise processed with a mini-injection molding machine. PEA, PEU, and PS were amorphous and PLLA, PBT, and PA were semicrystalline polymers. PEA had higher tensile strength and modulus than the other polymers. The strain of PEA was slightly higher than that of PS, PLLA, and PEU, but considerably lower than that of PBT and PA. Impact strength of PEA was noticeably higher than that of PEU, PLLA, and PS but lower than that of PBT and PA. The explanation of the lower impact value for PEA is that it is an amorphous material and PBT and PA are semicrystalline materials exhibiting high strain.

Conclusions

Study was made of the effects of polymerization temperature and the amount of 2,2′-bis(2-oxazoline) on the synthesis of lactic acid based poly(ester−amide). 2,2′-Bis(2-oxazoline) reacted very fast with the lactic acid based carboxyl-terminated prepolymer. Polymerization conditions were optimized for producing high molecular weight polymer, and the highest molecular weights of the poly(ester−amide) were over 300 000 measured by GPC. These molecular weights were obtained after 10 min polymerization with use of 1.2/1.0 molar ratio of end groups and polymerization temperature of 200 °C. In comparison with those of selected biopolymers and commercial thermoplastics, the mechanical properties of the processed PEA were good: the tensile strength was as much as 67 MPa, and the impact strength was about 34 kJ/m^2. The good results indicate that poly(ester−amide) could provide an alternative to existing biodegradable lactic acid based polymers.

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