ELSEVIER

Polymer 43 (2002) 3–10

polymer

www.elsevier.com/locate/polymer

# Chain extending of lactic acid oligomers. 2. Increase of molecular weight with 1,6-hexamethylene diisocyanate and 2,2′-bis(2-oxazoline)

Jukka Tuominen, Janne Kylmä, Jukka Seppälä*

*Polymer Technology, Department of Chemical Technology, Helsinki University of Technology, P.O. Box 6100, FIN-02150 HUT, Finland*

Received 3 July 2001; received in revised form 24 August 2001; accepted 2 September 2001

**Abstract**

Lactic acid polymers were synthesised from oligomers by the addition of highly reactive 1,6-hexamethylene diisocyanate (HMDI) and 2,2′-bis(2-oxazoline) (BOX) as chain extenders. The effects were studied of adding the extenders simultaneously and sequentially and in different amounts. The reactions were followed and the polymers obtained were structurally characterised by size exclusion chromatography and spectroscopy (NMR and FTIR). High molecular weight poly(lactic acids) were obtained by both simultaneous and sequential addition. The mode of addition and the amounts of extenders had a considerable effect on the branching. The addition of HMDI before BOX in the sequential linking produced more highly branched polymers than did the simultaneous addition. Branching and crosslinking reactions were identified as side reactions of the chain extending reactions. The gel formation was attributed to the reactions of BOX and HMDI with urethane and amide but not with oxamide. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Biodegradable polymers; Chain extenders; Lactic acid

## 1. Introduction

Lactic acid polymers are biodegradable aliphatic polyesters, which are finding increasing use in medical and industrial applications. Poly(lactic acid) (PLA) has the advantage of being not only biodegradable but also renewable since the raw material, lactic acid (LA), is produced by microbial fermentation of biomass. High molecular weight PLA is usually obtained by ring-opening polymerisation of lactide, i.e. cyclic diesters of LA [1–3]. Condensation polymerisation is the least expensive route, but it is difficult to obtain high molecular weights in a solvent free system [4]. The molecular weight typically ranges only from about 10 000 to 20 000 g/mol because the high viscosity of the polyester melt prevents efficient water removal and the equilibrium depolymerisation reaction as side-reaction leads to the formation of lactide. Furthermore, the high polymerisation temperatures that are required increase the thermal degradation, the lactide formation, and the racemization of the polyester chains [2].

An effective way to achieve high molecular weight polyester is to treat condensation polymers with chain extenders. These chain extension reactions are economically advantageous because they can be carried out in the melt, with only low concentrations of chain extending agents, and because separate purification steps are not required. Improved mechanical properties and the flexibility to manufacture copolymers with different functional groups are other benefits of the use of chain extending agents [4]. Typical chain extenders for polyesters, which contain –OH and –COOH groups, are diisocyanates, diepoxides, bisoxazolines, dianhydrides, and bisketeneacetals. The very high reactivity of the isocyanates has encouraged their use for coupling and chain extension of oligomers [5–9]. 2-Oxazolines, which react with carboxylic acids through ring-opening, provide a route to novel families of polyesteramides [10–13]. Moreover, because 2-oxazolines are inert towards aliphatic alcohols, selective modification is possible through the carboxyl end-group of the polyester [14].

The self condensation of LA yields a glassy low molecular weight polymer with an equimolar concentration of hydroxyl and carboxyl end-groups. If maximum increase in molecular weight is to be achieved, both types of end-groups of the polymer need to be utilised. With one type of chain extender, only one of the two functional groups can be utilised, and the effect will be limited [15]. The different kinetic reaction rates of chain linking can be avoided by modifying PLA oligomers by using small amount of di- or multifunctional hydroxyl or carboxyl compounds so that they are solely hydroxyl or carboxyl terminated [16]. The

---

* Corresponding author. Fax: +358-9451-2622.
*E-mail address:* seppala@polte.hut.fi (J. Seppälä).

PII: S0032-3861(01)00606-1

use of two chain extenders has two advantages, however: the molecular weight can be increased through the coupling of two macromolecules and the content of terminal groups can be decreased, which leads to improved thermal stability [17,18].

In the first part of this study [19], we investigated the effects of bis(2-oxazoline) on the carboxyl end-group content of LA prepolymers and on the progress of the diisocyanate reactions. The results showed that, being an effective chain coupling agent, 2,2′-bis(2-oxazoline) (BOX) decreased the acid value of the prepolymers, which is essential for diisocyanate linking reactions. In particular, the combination of BOX and 1,6-hexamethylene diisocyanate (HMDI) allowed us to polymerise high-molecular-weight LA polymers from oligomers having both hydroxyl and carboxyl end-groups. The linking method enables the introduction of different functional groups into polyester chains, which then affect the properties of the final polymer. In this part of the study, we carried out chain linking reactions of LA oligomers employing sequential and simultaneous HMDI and BOX additions and different end-group ratios.

## 2. Experimental section

### 2.1. Polymerisation

The LA prepolymer was condensation polymerised in a rotation evaporator. L-La (88% L-LA in water, 99% optically pure; ADM) was purified by distillation under vacuum. Sn(II) octoate (0.01 mol%, used as received, Aldrich) was used as a catalyst. The flask was purged with nitrogen and placed in an oil bath. The reaction mixture was polymerised at 200°C for 24 h, with a continuous nitrogen stream fed under the surface of the melt at a reduced pressure of 20 mbar. The rotation speed was approximately 100 rpm. The prepolymer obtained was used without further purification.

The linking polymerisation of the prepolymer was carried out in a Brabender melt mixer with use of HMDI (Fluka) and BOX (Tokyo Kasei) as chain extenders. The polymerisations were carried out at 150°C at a mixing speed of 60 rpm and for a predetermined time. Typically, for a linking reaction, 50 g of the dried prepolymer powder was charged into the preheated melt mixer chamber. After 1 min the prepolymer was completely molten, and then HMDI was added. Simultaneously, or after the desired reaction time, the other chain extender, BOX, was added. Different OH/NCO and COOH/OX ratios were used, where the hydroxyl and carboxyl contents of the prepolymer were calculated from the acid values determined by titration. The reactions were followed by means of torque-vs.-time curves recorded during the melt polymerisations. The polymerisations were also followed by taking samples and analysing them by SEC, FTIR, and NMR.

### 2.2. Characterisation

Molecular weights were determined by room temperature size exclusion chromatography, SEC (Waters System Interface module, Waters 510 HPLC Pump, Waters 410 Differential Refractometer, Waters 700 Satellite Wisp, and four PL gel columns: $10^4$, $10^5$, $10^3$, and 100 Å connected in series). Chloroform (Riedel-de Haën) was used as solvent and eluent. The samples were filtered through a 0.5-μm Millex SR filter. The injected volume was 200 μl and the flow rate 1 ml/min. Monodisperse polystyrene standards were used for primary calibration.

FTIR spectra were recorded on a Nicolet Magna-FTIR 750 spectrometer, using compression moulded film samples. Proton decoupled $^{13}$C NMR spectra with NOE and $^1$H NMR spectra were obtained at room temperature with a Varian Gemini 2000 300 MHz spectrometer working at 75.452 MHz for carbons and at 300.032 MHz for protons. Sample concentrations were 10 wt% in 10-mm tubes for $^{13}$C NMR and 1 wt% in 5-mm tubes for $^1$H NMR in $CDCl_3$ (deuteration degree not less than 99.8%, Fluka).

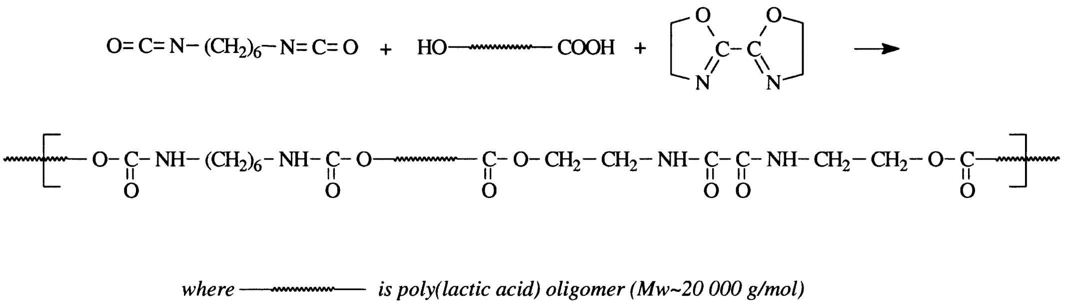
Thermal properties (glass transition temperature, melting temperature, and enthalpy of melting) of polymers were determined with a Mettler Toledo Star DSC821 differential scanning calorimeter (DSC) between 0 and 180°C with a heating and cooling rate of 10°C/min. Thermal properties were recorded during the second heating scan to ensure that thermal histories were the same.

Acid values (AV), defined as the weight in milligrams of potassium hydroxide required to neutralise 1 g of the polymer, were determined by titrimetric methods. Samples were dissolved in chloroform (Riedel–de Haën) and titrated against 0.01 M KOH in ethyl alcohol solution in the presence of α-naphtholphthalein indicator. The number of –COOH end groups present in each polymer sample was calculated.

The degree of crosslinking (i.e. gel content) of the polymers was measured by extracting the soluble phase into acetone in a Soxhlet apparatus for 20 h (ASTM D 2765). The gel content was determined as the portion, in percent, of the non-extractable material divided by the total weight of the original sample.

## 3. Results and discussion

The typical two-step polymerisation method, including polycondensation and polyaddition reactions, was applied to obtain high molecular weight chain linked LA polymers. As mentioned in Section 1, the self condensation polymerisation of LA results in low molecular weight oligomers, which have an equimolar concentration of carboxyl and hydroxyl end-groups. The prepolymer (designated E0% as explained earlier [19]) used displayed SEC molecular weights of 13 000 ($\bar{M}_n$) and 25 000 g/mol ($\bar{M}_w$). The



Scheme 1.

molecular weight distribution curve showed a low fraction of small oligomers (MWD 1.92).

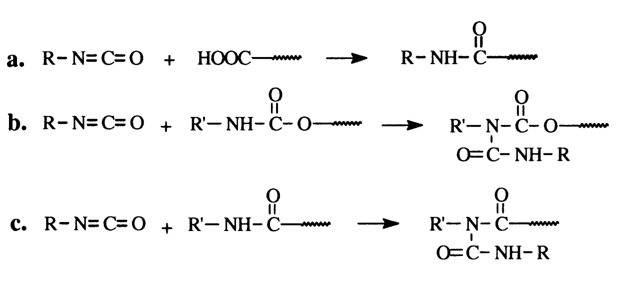
Two series of chain-linked polymers differing in the mode of addition of the chain extending agents were prepared. In the first series, HMDI was allowed to react with the prepolymer for a defined time (10 min) before BOX was fed to the Brabender apparatus at a time point set as 0 min. In the second series, the two chain extending agents were added simultaneously at the beginning of the chain linking polymerisation. In both the sequential and simultaneous additions, two different amounts of BOX were used: a slight excess, where the ratio of carboxyl groups of prepolymer to oxazoline end-groups (OX) was 1:1.1, and a greater excess, where the ratio was 1:2 (designated BOX1:1.1 and BOX1:2). The amount of diisocyanate was varied by changing the OH/NCO ratio from 1:1.0 to 1:1.2. Scheme 1 shows the two different chain extenders that were used and the structural units produced in the chain linking of PLA oligomers.

In our previous study, BOX was applied as a chain coupling agent before the actual chain linking reaction with diisocyanate. It was found to react selectively with the −COOH end-groups of LA oligomers, forming oxamide and ester groups. Furthermore, the greater effectiveness of BOX for coupling, compared with the blocking reaction where only one of the two rings of BOX reacts, was demonstrated. Regarding the HMDI reactions, the typical diisocyanate linking reaction for the formation of polyurethane requires prepolymer with only hydroxyl end-groups, i.e. low acid values. However, it is well known that the −NCO groups of diisocyanate readily react with every active hydrogen in the reaction system. In the case of PLA oligomers, besides engaging in urethane formation, the isocyanate group can also react with the carboxyl group leading to amide bond (Scheme 2a) and the formation of carbon dioxide as by-product. The urethane and amide groups can then further react with additional isocyanate leading to the formation of allophanates (Scheme 2b) and urea groups (Scheme 2c), and thus to the branching of the polymer.

### 3.1. Reaction between HMDI and carboxyl group

To study the reaction between isocyanate and carboxyl group, LA prepolymer (LA oligomer having a hydroxyl group at one end of the polymer chain and a carboxyl group at the other) was allowed to react with HMDI in OH/NCO ratio of 1:2, i.e. in equimolar amount of diisocyanate relative to all end-groups. The molecular weight increased slowly ($\bar{M}_w$ from 13 000 to 48 000 g/mol) during the 180 min reaction time, and at the same time the AV decreased from 11 to 7. As noted earlier, isocyanate groups thus also react with carboxyl groups, but not fast enough to be utilised in the chain linking of LA oligomers [19].

Representative samples of this chain linking with HMDI at OH/NCO ratio of 1:2 were analysed by NMR spectroscopy (Fig. 1). In $^1$H NMR, the formation of amide bonds can be seen as a broad peak at 6.21 ppm. The urethane bonds are partly overlapped by the solvent peak at 7.23 ppm and are not seen well, but the formation of the urethane peak in this region was confirmed with the use of deuterated acetone



Scheme 2.

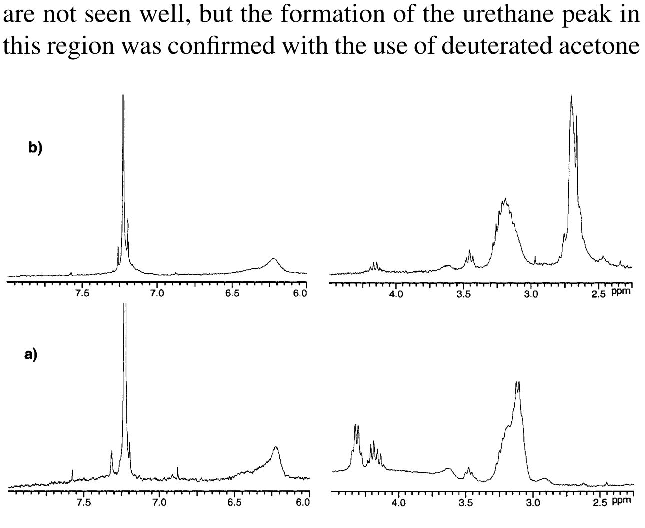


Fig. 1. $^1$H NMR spectra of (a) lactic acid prepolymer chain linked with HMDI and (b) acid-terminated prepolymer chain linked with HMDI.

as solvent. The reactions of HMDI with both the hydroxyl and carboxylic acid end-groups of the prepolymer can be seen more clearly in the region 4.5–2.5 ppm. The formation of urethane bond ($CH_2NHCOO-$) is seen at 3.12 ppm (Fig. 1a). The partly overlapped peak observed as a shoulder at 3.16–3.31 ppm is due to the amide bond. The identification of this resonance was confirmed by reacting an acid-terminated prepolymer with HMDI (Fig. 1b). In addition, some indication of side-reactions, such as formation of allophanates and urea groups (Scheme 2b,c), i.e. branching of the polymer, was observed as a broad shoulder on the NH peak at 6.50–6.26 ppm.

In the $^{13}C$ NMR spectra, the formed urethane and amide groups are seen at 155.5 and 156.3 ppm, respectively. The $^{13}C$ NMR spectra show the resonance at 169.4 ppm (partly overlapping), which is assigned to the carbonyl group of the carboxyl end-groups of the prepolymer, to diminish substantially after just 6 min polymerisation time. This indicates that the reaction between carboxyl groups and isocyanate groups is surprisingly fast; however, the FTIR and AV results indicate that a large number of carboxyl groups are left even after 180 min reaction time. More interesting and unexpected observation, however, is that the resonances assigned to the terminal LA units (i.e. units bonded directly to hydroxyl end-groups with resonances at 175.1 and 66.7 ppm due to the carbonyl groups and methine carbons, respectively) did not disappear during the reaction with isocyanate. This shows clearly, in accordance with our earlier study, that the presence of carboxyl groups retards the rate of reaction between isocyanate and hydroxyl groups. Our results are also in agreement with the deceleration or inhibition of isocyanate–alcohol reactions due to –COOH groups suggested by Draye and Tondeur [20] and favour the use of BOX as coupling agent and acid value reducer together with HMDI.

The HMDI reactions were also studied with FTIR. In the 3600–3100 $cm^{-1}$ range, the characteristic peaks of hydroxyl (3600–3440 $cm^{-1}$) and carboxylic acid (broad band between 3450 and 3150 $cm^{-1}$) end-groups of the oligomer E0% remain substantially unchanged. However, the appearance of the characteristic peak of NH groups (3405 $cm^{-1}$) indicates the formation of urethane and amide groups. Furthermore, the disappearance of the characteristic peaks of –NCO groups (2270 $cm^{-1}$) was evident. In the region between 1800 and 1400 $cm^{-1}$, the urethane bond formed by the reaction between –OH and –NCO groups is coincident with the carbonyl absorption of the LA oligomer, but an amide II band of the urethane bond also appears at 1525 $cm^{-1}$ (Fig. 2a, hydroxyl-terminated LA oligomer linked with HMDI). When the isocyanate group reacts with the carboxyl group, amide I absorption bands of the amide bond appear in the 1595–1700 $cm^{-1}$ region. This was further demonstrated with a model reaction where acid-terminated oligomer was linked with diisocyanate (Fig. 2b, COOH/NCO 1:1). In the case of the amide II peak, a slight shift to higher wavenumber (1537 $cm^{-1}$) relative to urethane is observed. At the beginning of the reaction between LA oligomer E0% and HMDI (after 6 min, Fig. 2c), a clear shoulder indicative of these acid–HMDI reactions is formed beside the urethane amide II peak, but as the reaction time increases the shoulder diminishes (Fig. 2d). Correspondingly, the intensity of the amide I peak at 1640 $cm^{-1}$ decreases.

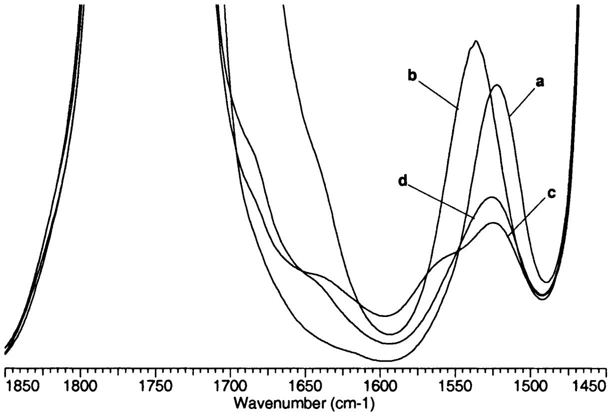


Fig. 2. FTIR spectra of (a) hydroxyl-terminated LA oligomer linked with HMDI, (b) acid-terminated LA oligomer linked with HMDI, (c) E0% reacted with HMDI for 6 min and (d) E0% reacted with HMDI for 160 min.

### 3.2. Sequential addition of HMDI and BOX

The coupling reaction of prepolymer E0% was followed by the change in torque as a measure of increased melt viscosity. The weight average molecular weights measured by SEC for the sequential addition of chain extenders are shown in Fig. 3. The $\bar{M}_w$ increased only slightly, from 25 000 to 30 000 g/mol, during the first 10 min when HMDI was in the reaction system, and only the isocyanate reactions described above took place. At time point 0 min, BOX was added and $\bar{M}_w$ started to increase very fast.

The reaction behaviour with the two amounts of BOX

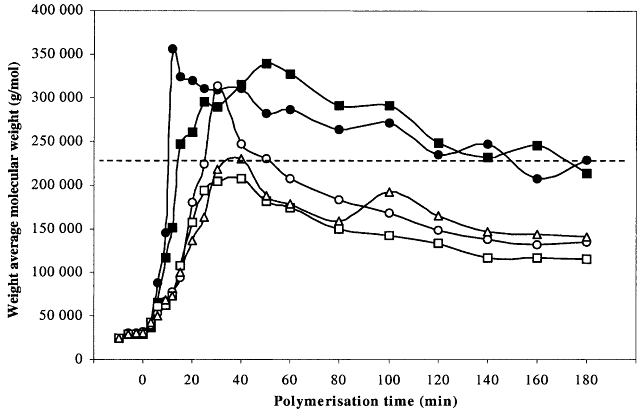
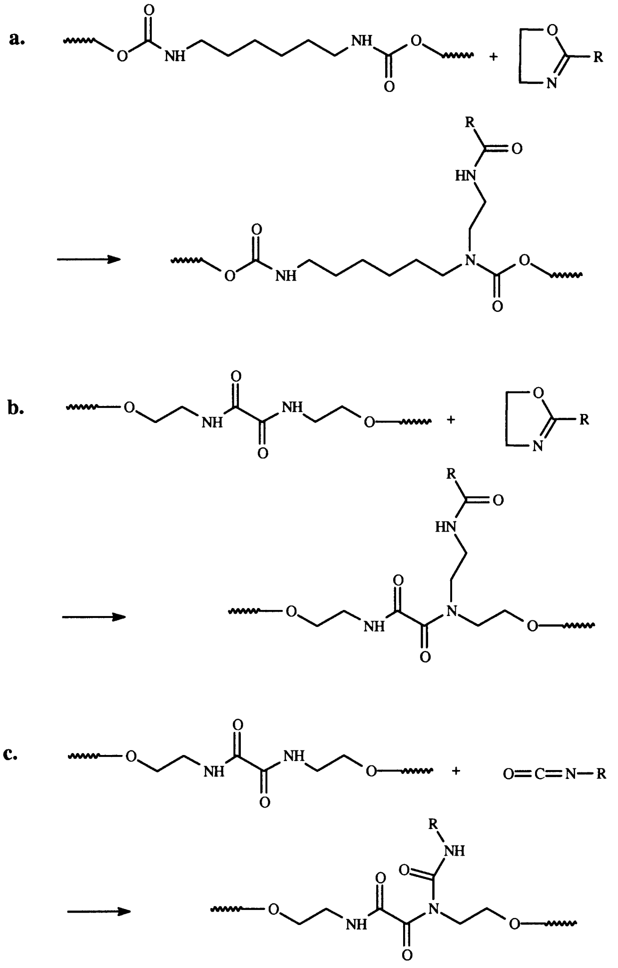


Fig. 3. Development of weight average molecular weight for sequential addition of HMDI with OH/NCO ratios of 1:1 (○), 1:1.1 (□) and 1:1.2 (△), and BOX with COOH/OX ratios of 1:1.1 (open symbols) and 1:2 (solid symbols).



Scheme 3.

was clearly different. The $\bar{M}_w$ increased more rapidly with the larger amount, and similarly AV decreased with BOX1:2 from 8.6 to 0.6 during 20 min reaction time. With the smaller amount of BOX, AV decreased to 3.6 during the same time. Thus, the use of BOX decreases the AV, which also accelerates the reaction between HMDI and –OH and allows the formation of high molecular weight polymer within a short reaction time. The molecular weights obtained likewise were on two different levels, although the molecular weights obtained with the lower ratio of BOX were also far above the threshold for realising good mechanical properties in PLA derivatives. It should be noted that some formation of gel occurred during these chain-linking reactions, and thus the molecular weights above the dashed line in Figs. 3 and 6 are the $\bar{M}_w$ values of the soluble fraction. However, the $\bar{M}_w$ values were proportional to the torque values measured during the chain extending polymerisations. The molecular weights started to decrease after obtaining the maximum values due to lack of reactive groups and degradation of thermally unstable LA prepolymer chains.

The maximum values for gel contents were observed at the highest torque values, i.e. at the highest molecular weights shown in Figs. 3 and 6. These gel contents were 21 and 41 wt% for HMDI1:1.0/BOX1:2 and HMDI1:1.1/BOX1:2, respectively. With the lower amount of BOX (COOH/OX 1:1.1), some network formation was observed (13 wt%) only with the highest amount of HMDI (1:1.2). In the first part of our study [19], we found no sign of gel formation even when BOX was used in high excess (COOH/OX 1:2). In the chain linking polymerisations of LA based poly(ester–urethanes), gradual branching and network formation have always been seen when the amount of diisocyanate was increased over the unity ratio of NCO/OH. Again in these present polymerisations, gel content was increased when the amount of HMDI was increased, but evidently the mode of addition and the amount of BOX had a considerable effect on the branching. Other reactions that may lead to branched and crosslinked structures, besides the HMDI reactions presented in Scheme 2, are reactions between BOX and urethane NH or oxamide NH (Scheme 3a,b). In addition, HMDI can react with oxamide NH (Scheme 3c).

After 10 min reaction time (i.e. at time point 0 min), in the sequential addition of chain extenders at OH/NCO ratio of 1:1.1, the urethane bond was seen at 155.5 ppm in the carbon spectrum and at 3.12 ppm in the proton spectrum (Fig. 4a,b). This result demonstrates the reactivity between the –NCO and –OH groups, though the reaction rate is relatively slow before BOX addition. Moreover the amide peak due to the reaction between the –NCO and –COOH groups is not seen in either the $^{13}$C- or the $^{1}$H NMR spectra (156.3 and 6.21 ppm, respectively) confirming the lower reactivity of –NCO with –COOH than with –OH. The missing amide peak is partly due to the resolution of the spectroscopy; even at the OH/NCO ratio of 1:1.2 it was still missing. Very soon after the addition of BOX, the formation of oxamide group due to the reaction between BOX and –COOH groups is seen at 159.6 ppm ($^{13}$C NMR) and 7.69 ppm ($^{1}$H NMR), (Fig. 4c,d). Some indications of side reactions are evident as small peaks in the NH-region between 155 and160 ppm in $^{13}$C NMR, and as broadening of the NH peak in the $^{1}$H NMR spectra when the amount of BOX was high. The peaks are due to branching and crosslinking reactions, which were also confirmed by gel content measurements. The amount of branching was observed to increase when the amounts of BOX and HMDI were increased.

Fig. 5 shows the FTIR spectra recording the progress of the sequential linking reaction with HMDI1:1.1 and BOX1:2 during the first 30 min. At time point 0 min, when HMDI has reacted for 10 min with both –OH and –COOH groups, the amide II peak of urethane at 1520 cm$^{-1}$ and the broad absorption bands caused by acid–HMDI reactions at 1590–1550 and 1650–1595 cm$^{-1}$ can be seen. Immediately after the addition of BOX (3 min), the top of the peak shifted to 1512 cm$^{-1}$, which absorption we earlier [19] assigned as amide II peak formed by the reaction between BOX and –COOH groups. However, this

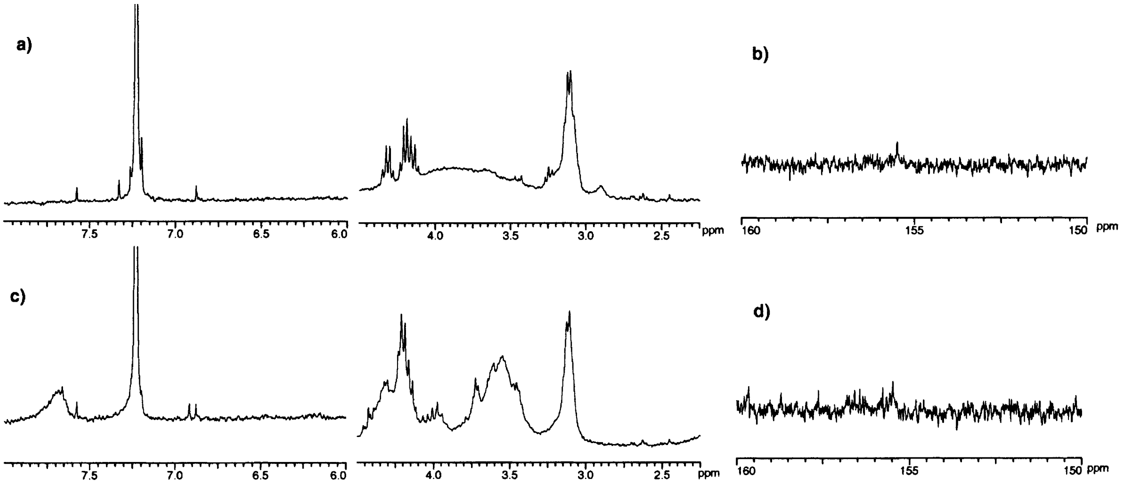


Fig. 4. NMR spectra for sequential addition polymerizations. (a) $^{1}H$ NMR and (b) $^{13}C$ NMR spectra of E0% chain extended with HMDI in OH/NCO ratio of 1:1.1 at time point 0 min, and (c) $^{1}H$ NMR and (d) $^{13}C$ NMR spectra 12 min after BOX addition at COOH/OX ratio of 1:2.

absorption has a very broad shoulder, which also includes all the other amide II peaks mentioned above. The amide I peak of the oxamide group at 1684 cm$^{-1}$ is similarly observed immediately after BOX addition, and gradually increased in intensity with the reaction time. The peak at 1645 cm$^{-1}$, which appeared after 6 min and likewise increased in intensity with reaction time, is associated with the C=O peak of a tertiary amine. In this respect our present data confirm the formation of branched and cross-linked structures.

### *3.3. Simultaneous addition of HMDI and BOX*

In the case of simultaneous addition of chain extenders, i.e. HMDI and BOX fed to the reactor at the same time immediately after the prepolymer has melted, many competing reactions occur simultaneously in the reaction system. When we compare the results of the chain linking polymerisations with simultaneous addition of HMDI and BOX (Fig. 6) and sequential addition (Fig. 3), we can see that the molecular weights start to increase somewhat more slowly in the simultaneous addition. In the simultaneous addition, corresponding acid values at time point 20 min were 1.9 for BOX1:2 and 4.1 for BOX1:1.1. The molecular weights obtained for BOX 1:2 were more or less the same as in the sequential addition polymerisations, but with BOX 1:1.1 they were lower. The maximum values for gel content were, with BOX1:2, 23% for HMDI1:1.0 and 27% for HMDI1:1.1, so that there was no significant difference between the two; with BOX1:1.1, in contrast, no gel formation was observed. The effect of the amount of HMDI on the formation of gel is not as obvious as in the case of the sequential addition of chain extenders, where the amount of gel increased with the amount of HMDI. The molecular weight decrease due to the thermal degradation after the maximum was observed similarly as in the sequential addition.

FTIR signals were in accordance with the above results and with the expected structures. Amide I (at 1684 cm$^{-1}$)

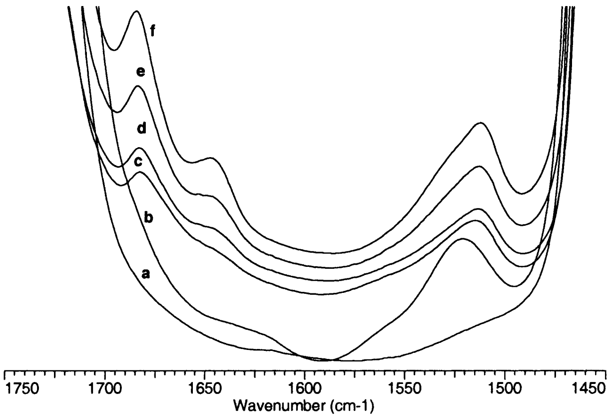


Fig. 5. FTIR spectra of (a) prepolymer E0%, E0% chain linked with sequential addition of HMDI (OH/NCO 1:1.1) and BOX (COOH/OX 1:2) after (b) 0 min, (c) 3 min, (d) 6 min, (e) 9 min, and (f) 30 min polymerisation time.

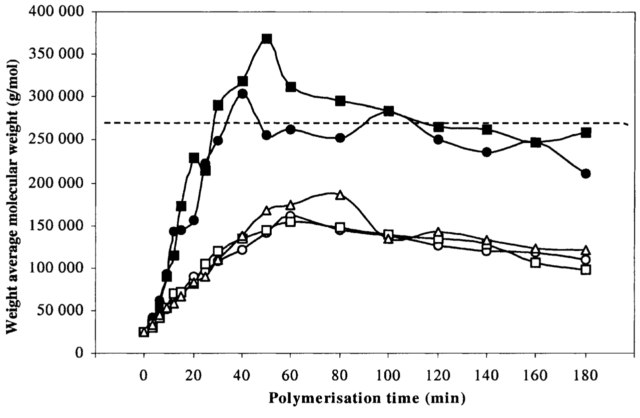


Fig. 6. Development of weight average molecular weight for lactic acid prepolymer chain extended with simultaneous addition of HMDI and BOX: COOH/OX ratios of 1:1.1 (open symbols) and 1:2 (solid symbols) and OH/NCO ratios of 1:1 (○), 1:1.1 (□), and 1:1.2 (△).

and amide II (at 1512 cm$^{-1}$) peaks due to the oxamide group were of the same shape as peaks in the sequential addition and were seen immediately after the addition of the chain extenders. The tertiary amine peak at 1645 cm$^{-1}$ was also detected, after just 6 min. However, it was flatter than in the sequential addition. Interestingly the weak absorption bands at 1590–1550 and 1650–1595 cm$^{-1}$ due to the acid-HMDI reactions are only seen with the COOH/OX ratio of 1:1.1 (after 3 min), as in the sequential addition, and not with the COOH/OX ratio of 1:2, i.e. when there is excess of BOX that can react with the –COOH groups. $^{13}$C- and $^{1}$H NMR studies supported the FTIR results indicating the formation of branched structures, but in lesser amount than in the sequential addition.

In the case of the sequential addition of chain extenders, HMDI accomplishes a wide variation in structures, which further react with excess of HMDI and BOX, increasing the possibilities for side reactions. The probability for crosslinked structures increases when HMDI is added first, and the gel formation is fast after BOX addition. In the case of simultaneous addition, in contrast, the fast reactions of BOX favour normal chain extending reactions over the branching reactions. It was confirmed, therefore, that the branching and crosslinking are highly dependent not only on the amount of chain extenders but on the order of addition.

It can be said that BOX reacts with –COOH groups more selectively than HMDI does with –OH groups. Both chain extending reactions are accompanied by side-reactions, but the chain extending efficiency, or reactivity, of BOX is over the other reactions. BOX reacts very fast with the carboxylic acid end groups, which otherwise retard the reaction between HMDI and hydroxyl groups. Moreover, these acid–BOX reactions reduce the probability of the reaction between HMDI and carboxylic acid end groups. Thus, fewer amide groups, able to participate in further branching reactions, are formed in the simultaneous addition of chain extenders than in the sequential addition. In the sequential addition, HMDI has more time to react with –COOH groups, and through reactions with amide and urethane forms branches before BOX addition. The formation of amide bonds seems to play an important role in the formation of branches and crosslinks.

It can be concluded that the main reactions leading to gel formation are the reaction of BOX with urethane and amide (formed in the reaction between HMDI and –COOH group) and the typical branching reaction, i.e. the reaction of HMDI with urethane. The previous part of this article support this conclusion, because when BOX was allowed to react with all carboxylic acid end groups before the HMDI addition, crosslinking or gelation did not occur, even with large excess of BOX. Thus, it seems probable that the formed amide groups rather than the oxamide or urethane groups preferably react further, forming branches.

### *3.4. Thermal analysis*

Thermal characterization of the prepolymer and of the samples of the chain extending polymerisation (samples at torque maximum) was carried out by DSC. The glass transition temperature of the LA prepolymer was 48°C. As a result of chain extending, the $T_g$ values were 53–54°C for the samples having BOX ratio of 1:2 and for other samples about 52°C. The slightly (1–2°C) higher $T_g$ values are due to the higher molecular weight and the observed crosslinking reactions. Crosslinking increases the $T_g$ of the polymer by introducing restrictions in chain mobility.

Usually, due to racemisation during the condensation polymerisation at 200°C with Sn(II) octoate catalyst, L-LA polyester prepolymers have not shown evidence of crystallinity in DSC measurements. The formation of D-structures (typically more than 20%) affects the stereoregularity of the chains and leads to an amorphous prepolymer. The amount of racemisation of LA oligomer E0%, estimated by $^{13}$C NMR from the carbonyl region, was 21% and thus was in the normal range. However, a clear melting endotherm was detected at 136°C, although the content of the crystalline phase was very low: $\Delta H$ was 1.5 J/g. By comparison, the melting enthalpy for 100% crystalline poly(L-lactide) is reported to be 93.6 J/g [21,22]. The different capability of oligomers to crystallise is attributed to chain length. Typically, in our previous studies, the hydroxyl or carboxyl termination achieved through addition of a small amount of difunctional hydroxyl or carboxyl compound determined the molecular weight by affecting the number of prepolymer chains. Without the use of difunctional compound, the molecular weight of LA oligomers is higher, reflecting the increased crystallisability of the PLA chain.

Melting endotherms were also detected for all the chain linked polymers: the melting temperature ($T_m$, peak) varied in the range 134–138°C, and $T_m$ was higher for the polymers whose molecular weights were lower and whose structures were linear, i.e. polymers with lower amount of BOX. The highest melting endotherm (3.2 J/g) was observed for polymer chain linked through sequential addition of HMDI (1:1.1) and BOX (1:1.1).

## 4. Conclusions

This study investigated the sequential and simultaneous addition of highly reactive chain extenders, HMDI and BOX, for the chain linking of LA oligomers. The development of the polymer structure during the polymerisation and the reaction behaviour of the different functional groups were characterized by NMR and FTIR. The polymerisation results indicate that the branching and crosslinking reactions in the LA polymers very much depend on the order of addition of the chain extenders. The amount of BOX, as well, had a marked effect on the gel formation.

We have now systematically examined the application of our method, which utilizes two chain extenders in LA polymerisation. As a conclusion from the present and our earlier results, we can state that, besides the preparation of high molecular weight LA polymers and the possibilities for variations in the polymer structures (e.g. branching), this method allows the introduction of different groups into PLA chains, which affect the properties of the final polymers. Furthermore, the decrease in the number of terminal groups through the use of chain extenders with different functionality was found to have a beneficial impact on thermal stability.

## Acknowledgements

Financial support was received from the National Technology Agency (Tekes). Thomas Gädda is thanked for technical assistance.

## References

[1] Vert M, Schwarch G, Coudane J. J Macromol Sci, Pure Appl Chem 1995;A32:787–96.

[2] Leenslag JW, Pennings AJ. Macromol Chem 1987;188:1809–14.

[3] Kricheldorf HR, Kreiser-Saunders I, Boettcer C. Polymer 1995;36:1253–9.

[4] Hartmann MH. High molecular weight polylactic acid polymers. In: Kaplan DL, editor. Biopolymers from renewable resources. Berlin: Springer, 1998. p. 367–411.

[5] Pitt D, Gu Z-W, Ingram P. J Polym Sci, Part A: Polym Chem 1987;25:955–66.

[6] Bruin P, Veenstra GJ, Nijenhuis AJ, Pennings AJ. Macromol Chem, Rapid Commun 1988;9:589–94.

[7] Seppälä J, Selin J-F, Tao S. FI Pat 92592, 1994.

[8] Storey RF, Wiggins JS, Puckett AD. J Polym Sci, Part A: Polym Chem 1994;32:2345–63.

[9] Hiltunen K, Seppälä JV, Härkönen M. J Appl Polym Sci 1997;64:865–73.

[10] Inata H, Matsumura S. J Appl Polym Sci 1985;30:3324–37.

[11] Loontjens T, Belt W, Stanssens D, Weerts P. Makromol Chem, Macromol Symp 1993;75:211–6.

[12] Douhi A, Fradet A. J Polym Sci, Part A: Polym Chem 1995;33: 691–9.

[13] Tuominen J, Seppälä J. Macromolecules 2000;33:3530–5.

[14] Po R, Abis L, Fiocca L, Masani R. Macromolecules 1995;28:5699–705.

[15] Loontjens T, Pauwels K, Derks F, Neilen M, Sham CK, Serné M. J Appl Polym Sci 1997;65:1813–9.

[16] Hiltunen K, Härkönen M, Seppälä JV, Väänänen T. Macromolecules 1996;29:8677–82.

[17] Luston J, Böhme F, Komber H, Pompe G. J Appl Polym Sci 1999;72:1047–53.

[18] Böhme F, Leistner D, Baier A. Angew Makromol Chem 1995;224:167–78.

[19] Kylmä J, Tuominen J, Helminen A, Seppälä J. Polymer 2001;42:3333–43.

[20] Draye A-C, Tondeur J-J. J Mol Catal A: Chem 1999;138:135–44.

[21] Fischer EW, Sterzel HJ, Wegner G. Kolloid Z Z Polym 1973;251:980–90.

[22] Fambri L, Pergoretti A, Fenner R, Incardona D, Migliaresi C. Polymer 1997;38:79–85.