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Chain extending of lactic acid oligomers. Effect of 2,2′-bis(2-oxazoline) on 1,6-hexamethylene diisocyanate linking reaction

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Abstract

New L-lactic acid polymers were synthesised with the use of highly effective carboxyl and hydroxyl reactive chain extenders. The chain extending behaviour of 2,2′-bis(2-oxazoline) (BOX) and 1,6-hexamethylene diisocyanate (HMDI) with two different oligomers was followed by means of acid value (AV) and molecular weight increments measured by size exclusion chromatography (SEC). Both chain coupling agents were found to react selectively with end-groups, forming oxamide and urethane groups as characterised by spectroscopy (FTIR and ^{1}H NMR). Reaction between BOX and carboxyl groups of lactic acid oligomer led to hydroxyl terminated prepolymer with low AV, which provided significant increase of molecular weight in the HMDI linking reaction. In addition, an improvement in the thermal stability of the resulting polymers was observed with excess amount of BOX. The material properties of the polymers were characterised by dynamic mechanical thermal analysis (DMTA), dynamic rheometry and tensile testing. Introduction of oxamide groups into the polymer structure increased the chain stiffness, which was detected in mechanical properties and increment in glass transition temperature. © 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, is produced by microbial fermentation of biomass. Lactic acid is a hydroxy acid, which possesses one asymmetric carbon and exists in two stereoisomeric forms, referred to as L- and D-lactic acid. The polymers derived from the optically active D- and L-monomers are semicrystalline materials, but the optically inactive poly(D,L-lactic acid) is always amorphous. The polycondensation of lactic acid requires long reaction times, high polymerisation temperatures and efficient removal of the water. Even where the reaction is driven close to completion, any deviation from the reaction stoichiometry has a detrimental effect on the chain length [1]. Thus, the average molecular weight of the polymers typically ranges from about 10,000–20,000 g/mol. High molecular weight PLA is usually obtained by ring-opening polymerisation of lactide, i.e. cyclic diesters of lactic acid [2–4].

An alternative way to achieve high molecular weight polyester is to treat condensation polymers with chain extenders. Chain extenders are usually bifunctional low molecular weight chemicals that can increase the molecular weight of polymers in a fast reaction without a separate purification step. The chain extending process can be conveniently performed in an extruder if the reaction rate is high enough [5,6]. Previously, we have used 1,6-hexamethylene diisocyanate (HMDI) as the chain linking agent with hydroxyl-telechelic lactic acid prepolymers to obtain high molecular weight poly(ester-urethane) [7–9]. OH-group containing compounds are by far the most important reactants for isocyanates, but they also react at different rates with amines, carboxylic acids, urethanes, ureas and water. Among the quality requirements of polyester prepolymers acid number is of particular importance because the residual acid content of the polyester negatively affects the catalysis of the polyurethane reaction and decreases the hydrolytic stability of the polyurethane [10,11].

Bis(2-oxazolines) are an attractive class of chain extenders for linear carboxyl-terminated polyesters [12–15], polyamides [16,17] and copolyamide-*block*-polyesters [18]. Recently, we applied 2,2′-bis(2-oxazoline) (BOX) as a

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chain extender for carboxyl-terminated lactic acid oligomer to produce poly(ester-amide) [19]. Bifunctional carboxyl-reactive chain extenders have two advantages: the molecular weight is increased by coupling of two chains and the content of carboxyl end-groups decreases, resulting in improved thermal stability [20]. The fact that 2-oxazolines are inert towards aliphatic alcohols enables selective modification of the carboxyl end-group of polyester without significant side reactions [16,21].

On the basis of this background, we became interested in applying carboxyl and hydroxyl reactive chain extenders together in lactic acid polymerisations. The addition of highly reactive coupling agents during the final step of polycondensation leads to polymers with higher molecular weight and lower acid value (AV) in shorter reaction times and at lower polymerisation temperature. This method also limits the influence of the side reactions (i.e. lactide formation, racemisation) which tend to take place during the final steps of polycondensation. In this study, we use BOX as end-group modifier and chain coupling agent of the lactic acid prepolymers before actual chain linking with diisocyanate. The effects of BOX on the carboxyl end-group content of different prepolymers and on the progress of the diisocyanate reactions were investigated.

2. Experimental

2.1. Polymerisation

The prepolymers were condensation polymerised in a rotation evaporator. L-lactic acid (88% L-lactic acid in water, 99% optically pure; ADM) was purified by distillation under vacuum. In condensation polymerisations, 0–2 mol% 1,4-butanediol (used as received, Acros Organics) was added to produce hydroxyl-terminated oligomers and 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 prepolymers obtained were used without further purification.

The linking polymerisation of the prepolymers was done in the Brabender melt mixer with use of BOX (Tokyo Kasei) and HMDI (Fluka) as chain extenders. The polymerisations were carried out at mixing speed of 60 rpm and 150°C for the predetermined time. Typically, for 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, if used, BOX was added, proportioned to the concentration of carboxyl groups determined by titration. After the desired reaction time the chain extender, HMDI, was added. Different OH/NCO ratios were used, where the hydroxyl content of the prepolymer was calculated from the AV and the initial proportions of reactants. The course of the reactions was followed by means of torque–time curves measured during the melt mixer polymerisation. The polymerisation was 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, which means that the Mark–Houwink constants were not used.

AVs, 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 thermal properties of prepolymers 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. Glass transition temperatures, T_g, were recorded during the second heating scan to ensure that thermal histories were the same. Dynamic mechanical thermal analysis (DMTA) was performed on a Perkin–Elmer 7 Series instrument. The measurements were made using the three-point bending method in a temperature range of 0–80°C at a rate of 4°C/min. All measurements were performed at 1 Hz. The glass transition temperature was determined as the peak of loss modulus.

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).

The degree of cross-linking (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.

The mechanical values of the polymers were measured for parallel air-conditioned specimens that had been left for 72 h at 23°C and 50% relative humidity. The specimens were prepared with a mini-injection moulding machine (DSM). The melt temperature in the injection moulding was 160°C and the temperature of the mould, 40°C. Tensile properties were characterised with an Instron 4204 tensile testing machine. Crosshead speed was 10 mm/min and specimen type was 1BA according to ISO/R 527-1993(E) standard.

The dynamic rheological measurements were carried out on a Rheometric Scientific stress-controlled dynamic rheometer SR-500. Specimens were prepared with the mini-injection moulding machine as described above. Before rheological characterisation, the samples were dried in vacuum for 24 h. All measurements were made in the linear viscoelasticity region, which was ensured by a stress sweep. Rheological characterisation was performed under nitrogen at 160°C using 25-mm cone-plate geometry with a sample gap of 0.045 mm. In frequency sweeps the angular frequency range was from 0.02 to 100 rad/s and a stress equivalent to 2% strain was used. The specimens for rheological characterisation were unstabilised.

3. Results and discussion

Two different prepolymers for linking reaction study were prepared by polycondensation of L-lactic acid. The typical diisocyanate linking reaction for formation of polyurethane requires prepolymer with only hydroxyl end-groups. We used 2 mol% 1,4-butanediol (BD) in the synthesis of prepolymer having one butanediol unit in each chain (designated here as prepolymer E2%), so that the lactic acid chains were hydroxyl terminated and the AV was low as required. Without butanediol we obtained PLA chains with both carboxyl and hydroxyl end-groups (designated as prepolymer E0%). By using BD we affect the amount of prepolymer chains and thereby the molecular weight as seen from the SEC results presented in Table 1. In addition to this molecular weight difference, the molecular weight distribution (MWD) curve of E0% shows a low fraction of small oligomers. The number average molecular weights ($\bar{M}_n$) of the prepolymers were also estimated by ^{1}H NMR and ^{13}C NMR end-group analysis [8]. The $\bar{M}_n$ values were fairly comparable, but a little higher than the theoretical molecular weights based on the feed stoichiometry and AV. The difference is partly due to deviation of the amounts of butanediol measured and fed.

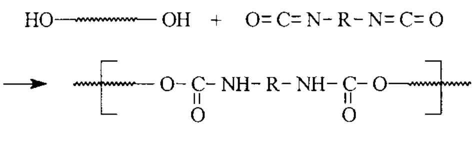
The optical activity of lactic acid units changes during the condensation polymerisation [22]. The amount of racemisation can be estimated by ^{13}C NMR in the carbonyl region. The presence of D-structures (about 20%) affects the stereoregularity of chains and leads to an amorphous prepolymer. Thus, neither lactic acid polyester prepolymers showed evidence of crystallinity in DSC. Furthermore, DSC showed the effect of flexible butanediol units on the glass transition temperature of the prepolymer. It should be noted as well that, due to the thermal depolymerisation of PLA chains, typically 2% lactide monomer is present, as determined by ^{13}C NMR. Table 1 summarises the properties of the lactic acid prepolymers.

Table 1
Properties and characterisation of oligomers

		E0%	E2%
Amount of BD in feed (mol%)		0	2
Acid value		11.3	1.4
Calc.	$\bar{M}_n$ (g/mol)	5000	4000
SEC	$\bar{M}_n$ (g/mol)	8800	8700
	$\bar{M}_w$ (g/mol)	19,600	12,900
	MWD	2.24	1.49
DSC	T_g (°C)	47	40
^{1}H NMR	$\bar{M}_n$ (g/mol)	6300	5300
	Amount of BD (mol%)	0	1.62
^{13}C NMR	$\bar{M}_n$ (g/mol)	7100	5100
	Amount of BD (mol %)	0	1.62
	Amount of lactide (%)	1.68	1.58
	Amount of D- structures (mol %)	21.9	25.7

3.1. Chain extending with HMDI

Chain extending reactions with HMDI take place by addition across the C=N double bond (Scheme 1). With hydroxyl-terminated prepolymer at equimolar amount of diisocyanate relative to –OH groups, the weight average molecular weight ($\bar{M}_w$) increased rapidly within the first few minutes, as seen in Fig. 1. After obtaining the maximum, a decrease occurred due to lack of reactive groups and degradation of thermally unstable lactic acid prepolymer chains. With increase in the NCO/OH ratio, the $\bar{M}_w$ curves gradually became flatter. When the NCO/OH ratio was 1.2:1, the weight average molecular weight increased at the beginning of the reaction to a level 50% lower than with a ratio of unity. The excess of chain extending agent in the reaction mixture caused a rapid decrease in the hydroxyl group concentration as the lactic acid oligomers became terminated with isocyanate groups. Further increase in the molecular weight is prevented by the lack of –OH groups. Isocyanate groups can further react with –OH or –COOH groups formed by thermal and hydrolytical degradation of PLA chain, but the observed gradual increase in $\bar{M}_w$ during the reaction and faster increase at a certain point of the polymerisation is caused by branching and cross-linking reactions. The excess of HMDI also retards these reactions, in such a way that highest molecular weights were achieved at 80 and 100 min for OH/NCO ratios of 1:1.1 and 1:1.2, respectively. Concurrent with the fast increases in $\bar{M}_w$, the



$$\mathrm{HO}\sim\sim\mathrm{OH} + \mathrm{O{=}C{=}N{-}R{-}N{=}C{=}O} \longrightarrow \sim\left[\mathrm{O{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NH{-}R{-}NH{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}O}\right]\sim$$

Scheme 1.

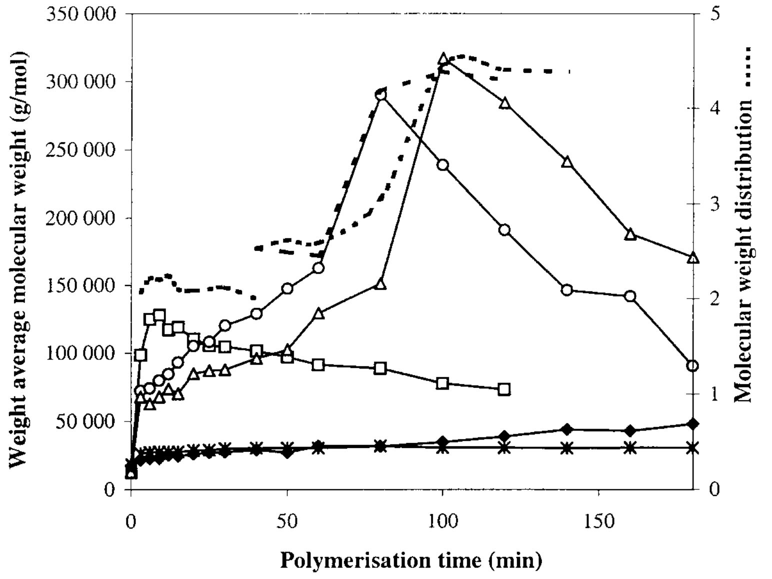


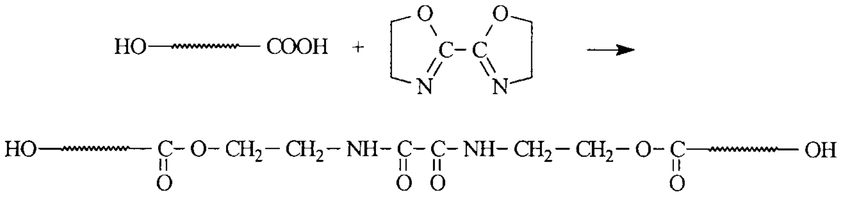
Fig. 1. Development of the weight average molecular weight and molecular weight distribution (dashed line) for prepolymer E2% (open symbols) with OH/NCO ratios of 1:1 (□), 1:1.1 (○) and 1:1.2 (△), and for prepolymer E0% (solid symbols) with OH/NCO ratios of 1:1.1 (*) and 1:2 (◆).

number average molecular weight remains essentially unchanged for the whole period of time. This is observed as an instant broadening of the molecular weight distributions from 2 to 4.5 as seen in Fig. 1 (dashed lines). Samples were soluble, however, and gel fractions were not observed. In contrast, with the OH/NCO ratio of 1:1, the MWD was consistently 2 during the polymerisation.

Chain linking of lactic acid oligomer (prepolymer E0%) with equimolar amounts of –NCO and –OH groups connects two chains together to form a longer acid-terminated chain. Thus, the molecular weight was doubled in the linking reaction, as expected (Fig. 1). Isocyanates can also react with carboxyl end-groups leading to amides, carboxylic anhydrides or ureas. The reactivity in the present system was tested by using an amount of isocyanate corresponding to both –OH and –COOH end-groups. As seen in Fig. 1, the molecular weight increased slowly during the 3 h reaction time and at the same time the AV decreased from 11 to 7. Isocyanate groups thus react with carboxyl groups, but not fast enough to be utilised in the chain linking of lactic acid oligomers. In addition, the relatively broad molecular weight distribution of prepolymer E0% will narrow immediately when the reaction begins as the smaller molecules will first react.

3.2. Effect of bis(2-oxazoline) on carboxyl end-group content

The reaction between carboxylic acid groups and the 2-oxazoline ring proceeds through attack of the carboxyl group on the carbon atom in the 5-position of the oxazoline ring. The product of this reaction is the esteramide structure (Scheme 2). In this study, the function of BOX is to lower the AV and couple two oligomers to hydroxyl-terminated prepolymer, which can further chain extend with diisocyanate. In general, reaction behaviour between BOX and carboxyl terminal groups can be classified into three types: coupling, blocking, where only one of the two rings have reacted, and unreacted [12]. The coupling and blocking efficiency of BOX depends on the structure of the compound and the electron-withdrawing property of the substituent at position 2 in the oxazoline ring. According to Inata and Matsumura [23], once one of the two rings of BOX is involved in the reaction, it affects the reactivity of the other ring and thus accelerates the coupling reaction. In addition, it is supposed that in our system the high reactivity is partly due to the structure of terminal carboxylic acid, which determines the acidity of the end-groups and thus affects the reactivity of carboxyl-terminated prepolymer



Scheme 2.

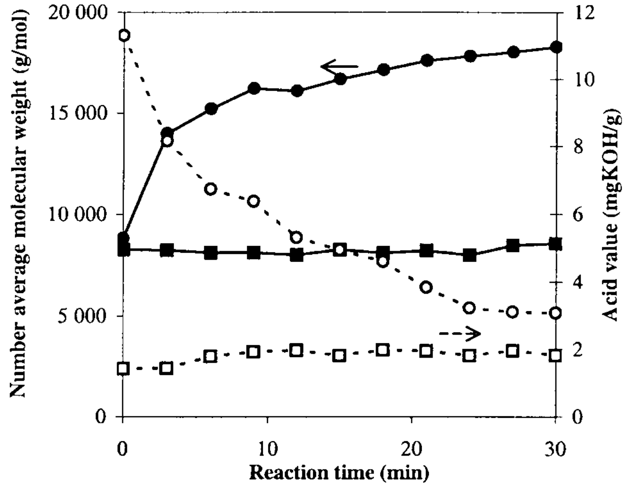


Fig. 2. Effect of 2,2′-bis(2-oxazoline) (BOX) in COOH/BOX ratio 1:1.1 on molecular weight (—) and acid (- - -) value of E0% (○) and E2% (□) prepolymers.

with BOX. Both blocking and coupling reactions decrease the carboxyl content of the prepolymer, which is advantageous for the HMDI linking reaction, but only coupling increases the molecular weight.

Fig. 2 displays the effect of BOX at COOH/BOX ratio of 1:1.1 on the AV and number average molecular weight of the two prepolymers. The increase in molecular weight is twofold when BOX connects two oligomer chains together. As in the HMDI coupling, once the BOX linking begins the small molecules will disappear from the MWD curves. The AV of prepolymer E0% decreased from 11 to 3 mg KOH/g in 30 min reaction time, to the level of typical hydroxyl-terminated lactic acid prepolymer. Nevertheless, this AV level is slightly higher than for the prepolymers generally used in urethane chemistry. This is a consequence of the lactide present in the prepolymer, which hydrolyses during measurement of the AV and increases the amount of carboxyl end-group. It is worth noting that this minor amount of lactide does not take part in the chain extending reaction. In E2% prepolymer, where the initial AV is already low, the addition of BOX did not seem to have an effect on either the AV or the molecular weight.

The effect of the amount of BOX on the AV of prepolymer E0% is seen in Fig. 3. Theoretically, since it is not reactive with hydroxyl groups, BOX should be added in equimolar amount to the carboxyl groups of the oligomer, if totally hydroxyl-terminated prepolymer is to be obtained. In 30 min reaction time, an equimolar amount of BOX decreased AV from 11 to 5, whereas without BOX the AV of the prepolymer increased slightly owing to thermal degradation. When the ratio of COOH/BOX is decreased from 1:1 to 1:2 the AV decreased faster and to a considerably lower level. Since the molecular weight increases in proportion to the BOX content (Fig. 3a), obtaining of prepolymer with doubled molecular weight at large excess of BOX confirms the greater effectiveness of BOX coupling than of blocking reaction.

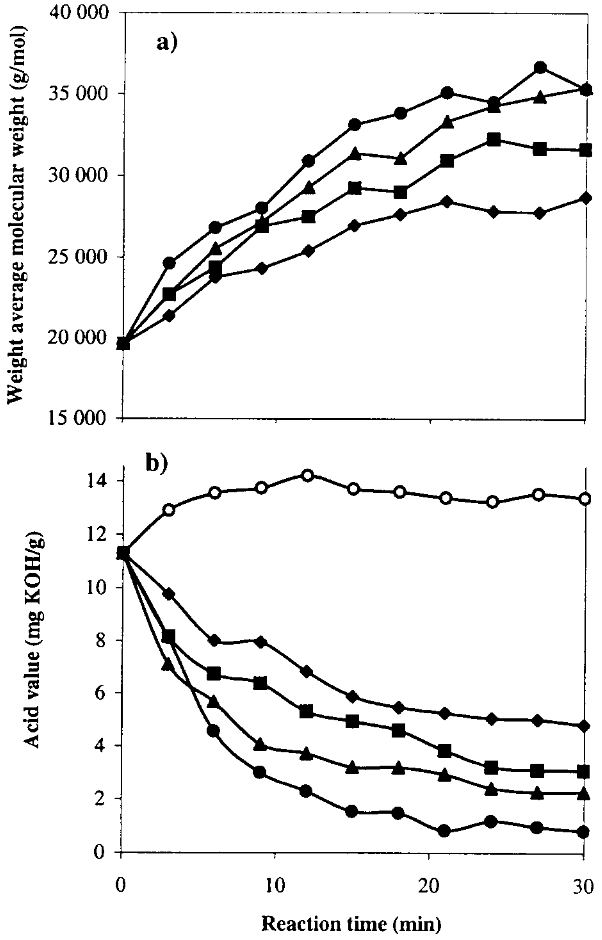


Fig. 3. Effect of COOH/BOX ratio on (a) weight average molecular weight and (b) acid value of prepolymer E0% plain polymer without BOX (○), COOH/BOX ratio of 1:1 (◆), 1:1.1 (■), 1:1.4 (▲) and 1:2 (●).

An inspection of chain coupling reactions was carried out with FTIR in the spectral regions 3600–3150 and 1850–1420 cm^{-1} and with ^1H NMR in the spectral region 5.0–3.3 ppm. The FTIR spectra of prepolymers E0% and E2% and of prepolymer E0% coupled with 1:1 and 1:2 of BOX are given in Fig. 4a–d. BOX reacts with carboxyl groups of the prepolymer (broad band between 3400 and 3150 cm^{-1}) forming oxamide groups shown as NH peak at 3380 cm^{-1} and amide I and amide II bands at 1685 and 1510 cm^{-1}, respectively. When large excess of BOX is used in the chain extending reaction, the unreacted 2-oxazoline groups are detected as an absorption band at 1645 cm^{-1} (spectra 4d and 4f). It is worth noting that the OH peak at 3510 cm^{-1} remains unchanged after BOX treatment, showing that the groups do not react with each other. When reaction between prepolymer E0% and HMDI takes place (spectrum 4e), the hydroxyl peak diminishes to a small peak. Meanwhile, an absorption peak for urethane NH forms at 3410 and 1525 cm^{-1}. In addition to these peaks, during the reaction the NCO stretching band of diisocyanate at 2270 cm^{-1}

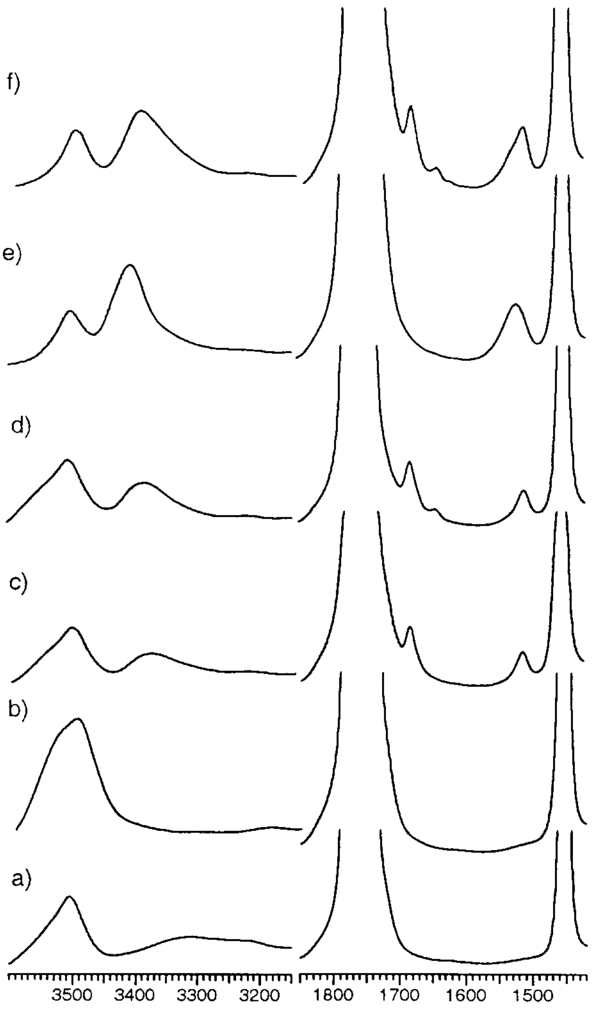


Fig. 4. FTIR spectra of: (a) prepolymer E0%, (b) prepolymer E2%, (c) E0% coupled 1:1 with BOX, (d) E0% coupled 1:2 with BOX, (e) E2% coupled 1:1.1 with HMDI, and (f) E0% coupled 1:2 with BOX and 1:1.1 with HMDI.

decreases and in all polymerisations it disappears upon completion of the reactions.

Confirmation that the coupling reaction between BOX and oligomer E0% has taken place is also provided by ^{1}H NMR spectroscopy. The two methylenes of reacted oxazoline moieties give resonances at 4.20 and 3.55 ppm (Fig. 5a). In Fig. 5b is shown the spectrum of BOX reacted with E0% at 150°C for 3 min with the molar ratio of COOH/BOX 1:2. Besides the reacted oxazoline, the methylenes of unreacted BOX can be seen in the resonances at 4.43 and 4.05 ppm and the methylenes of terminal 2-oxazoline group, whose one ring had reacted with the carboxyl group, at 3.75 and 3.46 ppm. Peaks were identified by using a solvent mixture of trifluoroacetic acid (TFA) and $CDCl_3$ (1:3 vol). TFA reacts with oxazoline groups so that the mentioned peaks of the oxazoline rings disappear.

The reaction of 2-oxazoline and carboxylic acid end-group is fast, since in samples taken after 3 min reaction time the triplets of the methylene groups in the monomeric oxazoline ring have disappeared almost completely. In this situation, where the amount of BOX is twofold to carboxyl groups, it can be estimated from integrals that about 60% of BOX monomers have linked two oligomers, i.e. both of the two rings of BOX have reacted (Fig. 5c). This result suggests that a slight excess of BOX should be used. It is supposed that a small amount of BOX is lost by volatilisation from the reaction system and besides that, some of the monomers are consumed with carboxylic acid groups formed in the thermal decomposition of oligomer. From the rest of the additional BOX only one ring has reacted. Because these reactions do not forbid the increase of the molecular weight of prepolymer as seen in Fig. 3a, it is improbable that blocking reaction with COOH group dominates. The only possible side reaction is the reaction between amide and oxazoline groups [24,25]. Because of the low concentration of the formed bond, this could not be verified by NMR measurements. It is worth noting that in both situations (COOH/BOX 1:1 and 1:2), the peak at 4.32 ppm, corresponding to the terminal *CH*–OH group of the prepolymer, shows the group to be unreacted, as expected. This is essential for further linking reaction with diisocyanate.

3.3. Effect of bis(2-oxazoline) on HMDI chain extending reaction

When the two chain extenders are used together, both types of end-group of the lactic acid oligomer can be utilised to obtain polymer with adequate molecular weight for realising good mechanical properties. In these combination chain linking polymerisations, we allowed BOX to react for a defined time before HMDI was fed to the Brabender apparatus at a time point set as 0 min. Both chain extending reactions took place, as was evident from the FTIR (Fig. 4f) and ^{1}H NMR spectra (not shown) as stated above. In addition, in the case where BOX was used in excess (1:2), the assigned signals at 3.75 and 3.46 ppm for unreacted 2-oxazoline ring disappeared in the course of the reaction when the highest molecular weight had been reached, although we deduced from the measurements that the 2-oxazoline group did not react with an isocyanate group.

Fig. 6 shows the weight average molecular weight of the polymer versus polymerisation time for E0% with COOH/BOX ratio of 1:1.1 and OH/HMDI ratio of 1:1.1. In order to understand the significance of the AV for the polymerisation behaviour, we first reacted BOX with the oligomer for a predetermined time (5, 10 and 25 min) until the AVs achieved levels of 10, 7 and 5, respectively. Then, at time point 0 min, the diisocyanate was added. The result of the HMDI linking is modest if the reaction time of BOX is not long enough to reduce the amount of acid end-groups. Therefore, the weight average molecular weight of the resulting polymer remains at the low level of 75,000 g/mol, as seen in Fig. 6. When the AVs are lower before the

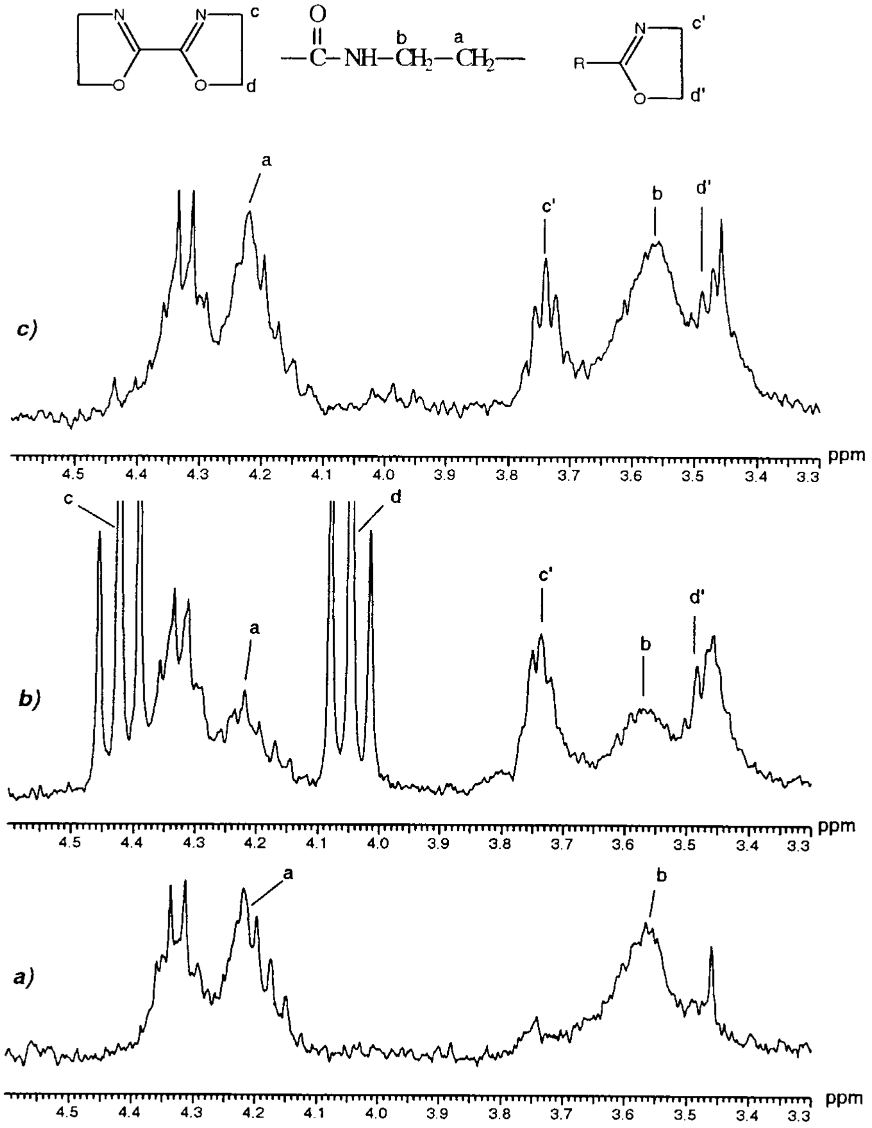


Fig. 5. ^{1}H NMR spectra of E0% coupled with BOX (a) COOH/BOX 1:1 (b) COOH/BOX 1:2 after 3 min reaction time, and (c) COOH/BOX 1:2 after 15 min reaction time.

diisocyanate linking reaction, the molecular weight of the polymer increases manifold, exceeding 170,000–190,000 g/mol, and the polymerisation rate is much faster. The linking behaviour of the other two polymers is basically the same, though the increase in the reaction rate at the beginning of the polymerisation is more dramatic in the case of lower AV. Indeed, the acid content seems to inhibit the reaction between hydroxyl and isocyanate groups. It is worth noting that the AVs 5 and 7 are still fairly high, compared for example with the AV of hydroxyl-terminated prepolymer E2%.

Because lower AVs clearly accelerate the polymerisation rate, we applied large excess of BOX to achieve very low AV. The polyurethane reactions were conducted at OH/NCO ratios of 1:1, 1:1.1 and 1:1.2 for the E0% prepolymer, as plotted in Fig. 7. The BOX ratio of 1:2 with 20 min reaction time before diisocyanate addition decreased the AV from 11.3 to as low as 1.5. The low AV had a marked effect on the polymerisation rate. If we compare the development of the molecular weight of polymer with OH/NCO ratio 1:1.1 with the curves presented in Fig. 6, which are drawn for the same OH/NCO ratio and under the same polymerisation conditions, we see that $\bar{M}_w$ increased distinctly faster, with the low AV achieving 120,000 g/mol within 15 min. Although there were differences in reaction behaviour, the obtained molecular weights were more or less equal. The important observation is that a large excess of BOX prevents the drop in polymer molecular weight at longer reaction times, such as occurred without BOX and with BOX ratio 1:1.1 (see Figs. 1 and 6). It was expected that the BOX or oxazoline end-groups would react with newly formed carboxyl groups, which are formed by thermal degradation of PLA chains and thus improve the thermal stability of the polymer [19]. It was

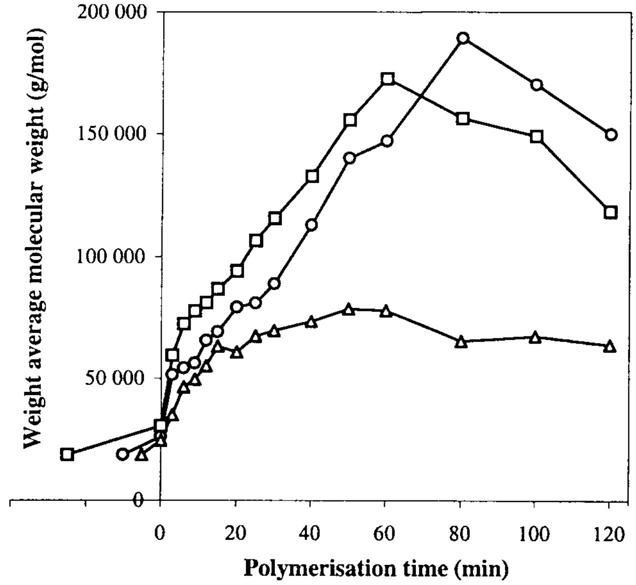


Fig. 6. Molecular weight development of E0% prepolymer with different acid values before chain linking with HMDI (OH/NCO 1:1.1); acid value 10 (△), 7 (○) and 5 (□).

interesting, however, that the molecular weights stayed at the highest level for as long as 40 min, which is important from the practical point of view of further processing, for example.

The development of the molecular weight is also dependent on the amount of HMDI and development was similar to that for E2% (see Fig. 1). Since the $\bar{M}_w$ of prepolymer E0% after BOX linking was threefold that of prepolymer E2%, it was unexpected that the molecular weight obtained was somewhat lower than for E2% in analogous HMDI linking. Similarly, however, a slight excess of diisocyanate (ratio 1:1.2) retarded the development of the molecular weight before $\bar{M}_w$ reached the high level of 200,000 g/mol. The most striking difference was that the rapid leap in weight average molecular weight, which we saw earlier in Fig. 1, especially as broadening of the molecular weight distribution, was absent in these BOX–HMDI combination chain linking polymerisations.

In hydroxyl-terminated prepolymer E2%, the acid groups are almost totally absent, but because of equilibrium reaction there are always some residual carboxyl groups. To examine the effect of BOX on the linking reaction behaviour of E2%, we reproduced the polymerisation experiments for E2% with different ratios of HMDI. These results, obtained by using a COOH/BOX ratio of 1:2, are in line with data set out in Fig. 1. Indeed, the effect of excess hexamethylene diisocyanate that we noted earlier for E2% can be seen in Fig. 8, too. In addition, as discussed above, the excess of BOX impedes the drop in molecular weight and the thermal degradation effect is less pronounced. In this BOX–HMDI combination the clearest difference associated with BOX is seen for OH/NCO ratio 1:1.2. The BOX reacts with the remaining carboxyl groups in the prepolymer and with the carboxyl groups newly formed by thermal degradation, which means that there are slightly more isocyanate groups than basic HMDI chain extending polymerisation. This additional diisocyanate is assumed to lead to branching and cross-linking reactions, which were observed as insolubility in the SEC eluent. The gel fraction measurements, however, demonstrate that the gel content of samples was $\ll 1\%$; that is, polymers were clearly thermoplastic.

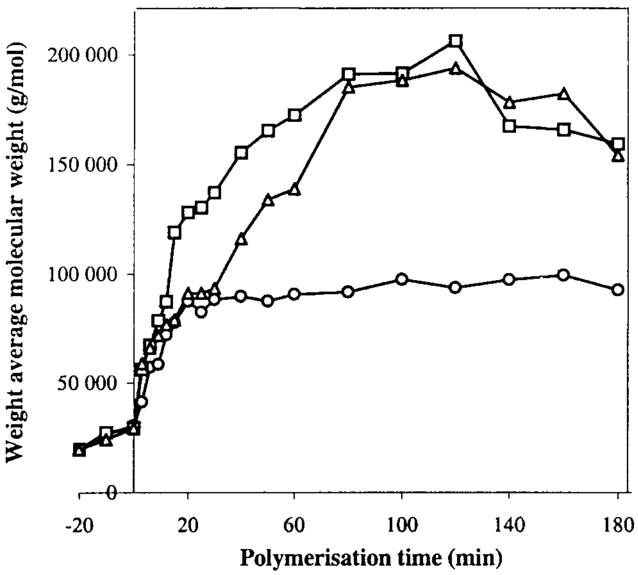


Fig. 7. Molecular weight development versus polymerisation time for prepolymer E0% chain linked with BOX (ratio 1:2) and with different amounts of hexamethylene diisocyanate: OH/NCO ratios of 1:1 (○), 1:1.1 (□) and 1:1.2 (△).

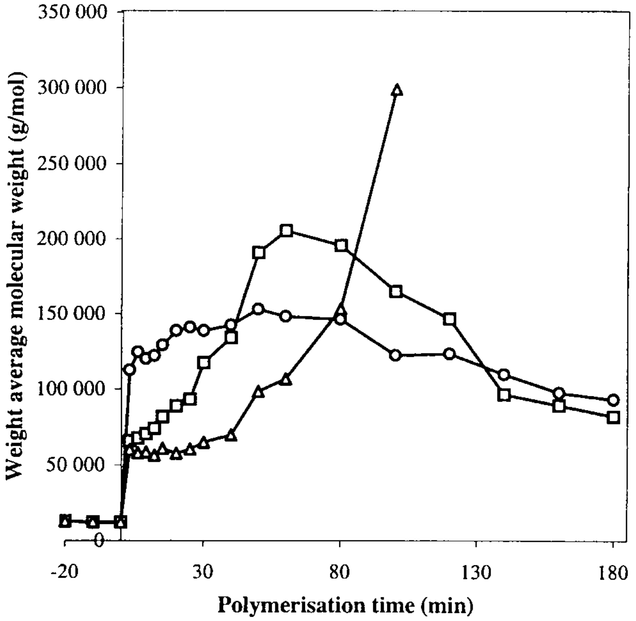


Fig. 8. Development of the weight average molecular weight of E2%, which is first linked with BOX (COOH/BOX ratio 1:2) and then with HMDI, with OH/NCO ratios of 1:1 (○), 1:1.1 (□) and 1:1.2 (△).

Table 2
Mechanical properties of lactic acid polymers

Polymer	COOH/BOX ratio	OH/NCO ratio	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	MWD	Tensile modulus (MPa)	Tensile strength (MPa)	Strain at break (%)
P2%	–	1:1.1	63,000	188,000	3.0	1640 ± 30	55 ± 4	11 ± 2
P0%	1:2	1:1.1	53,000	162,000	3.0	1750 ± 20	57 ± 3	5.8 ± 2.6

Tensile testing, DMTA and rheological measurements were carried out to determine the differences in properties between representative samples of the synthesised polymers: prepolymer E0% chain linked with BOX (COOH/BOX ratio of 1:2) and with HMDI (OH/NCO ratio of 1:1.1) (designated hereafter as P0%) and E2% chain linked with HMDI (OH/NCO ratio of 1:1.1) (designated as P2%). There are thus two main factors differentiating the structures of P0% and P2%. The introduction of stiffer BOX units for half of the HMDI units stiffens the polymer chains of P0% compared to P2%. Also, 2 mol% of 1,4-butanediol increases the chain flexibility and mobility even more in P2%. The mechanical properties of polymers P0% and P2% are compared in Table 2. A slight difference between P0% and P2% was detected in tensile modulus and strength due to the difference in polymer structure. Similarly, the chain flexibility causes a marked difference in strain between the two polymers.

Plots of storage modulus (E'), loss modulus (E'') and tan δ as a function of temperature obtained from dynamic mechanical analysis are shown in Fig. 9 for P0% and for P2%. Molecular weights of these polymers are presented in Table 2. The storage modulus is considerably higher for P0%. The overshoot on the E' for P2% is caused by molecular rearrangements that occur due to the increased free volume at the transition. Storage modulus fell abruptly at T_g, as is typical for completely amorphous polymers. The values of the E'' and tan δ peak temperatures also are higher for P0%. The loss modulus values were 52 and 55°C for P2% and P0%, respectively. These values of glass transition temperature are closely related to the polymer structure. 1,4-Butanediol and a larger amount of HMDI units with six flexible aliphatic methylene groups increase the chain flexibility and mobility and cause a marked decrease in the T_g even in the prepolymers (see Table 1).

In addition to the mechanical and DMTA characterisation, we studied the rheological behaviour of the samples at 160°C. The two polymers, P2% and P0%, showed similar behaviour in the shear rate range of 1–100 rad/s. The values of complex viscosity and both moduli were higher for P2%, but the shapes of the curves were the same, as seen in Fig. 10. Even though the molecular weights and molecular weight distributions are similar in the two samples, differences begin to appear in the terminal region at low shear rates, where the molecular structure affects the behaviour of the polymers most. As stated above, owing to the isocyanate reactions, sample P2% may be slightly branched and signs of the presumed long-chain-branching are evident in Fig. 10.

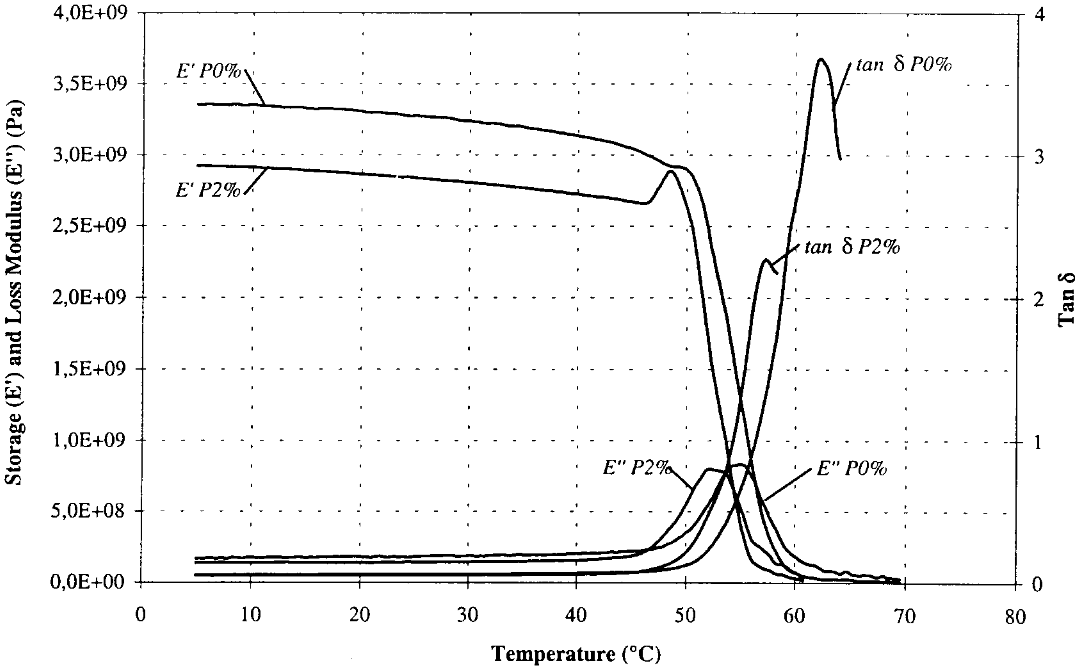


Fig. 9. DMTA plot of polymers P2% and P0%.

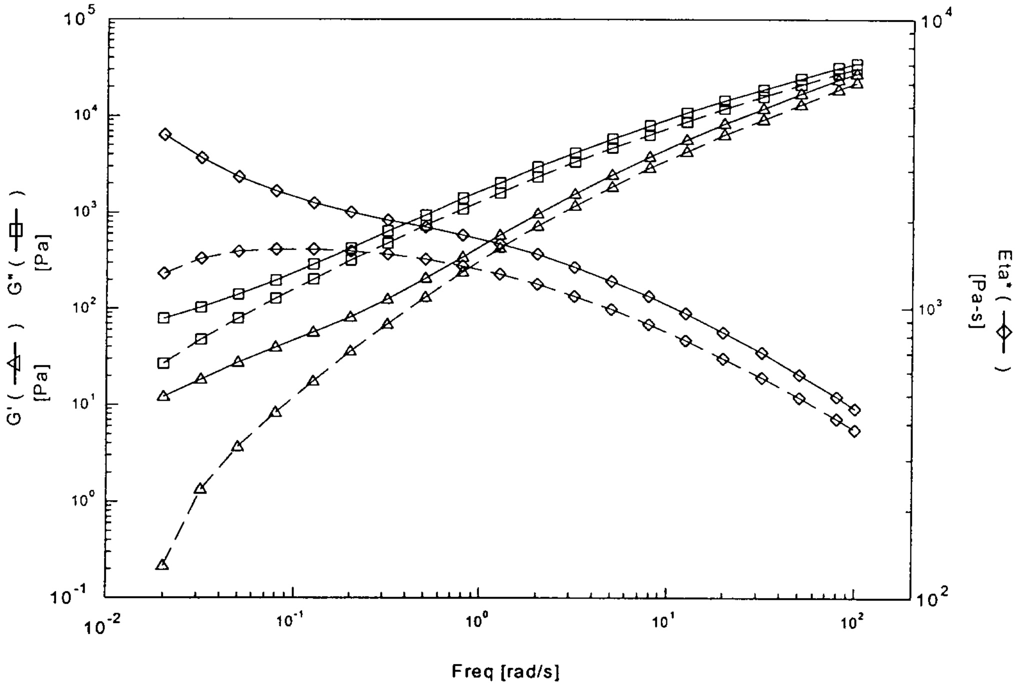


Fig. 10. Storage modulus (△), loss modulus (□), and complex viscosity (◇) for P0% (- - -) and P2% (—) at 160°C.

Complex viscosity at 0.02 rad/s, which nearly correlates with zero-shear viscosity, is significantly higher for P2% than for the more linear P0%, and the storage modulus for P2% does not drop as abruptly as that of P0% at low shear rates.

4. Conclusions

We have described a method that gives us a new way to influence the chain linking of lactic acid polymers. The results show that BOX is simultaneously an effective chain coupling agent and AV reducer. In particular, the combination of BOX and HMDI allowed us to polymerise lactic acid polymers from oligomers having both hydroxyl and carboxyl groups. The $\bar{M}_w$ values of the new polymers surpassed 200,000 g/mol, which is far above the threshold for realising good mechanical properties in PLA derivatives. The system also allows the introduction of different functional groups into polyester chains, which affect the properties of the final polymers. In addition, BOX was found to have a beneficial impact on thermal stability.

We conclude that the addition of highly reactive coupling agents during the final steps of melt polycondensation of polyester allows the production of higher molecular weight prepolymers, with lower AVs. Since effective diisocyanate linking reactions require low AVs, which are reached with very long condensation times at high temperature and low pressure, the main advantages of this kind of process on the polymerisation of low molecular weight oligomers are the shorter condensation time and lower temperature. With lactic acid polymers, in particular, the shorter polymerisation time and lower temperature will prevent thermal degradation and lactide formation. The use of the two coupling reactions simultaneously for the preparation of lactic acid polymer will be described in the next article of this series.

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