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Synthesis of polylactides in the presence of co-initiators with different numbers of hydroxyl groups

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Abstract

Linear and star-shaped polylactides were prepared by using alcohols with different numbers of hydroxyl groups as co-initiators. ^{1}H-NMR analysis of low molecular weight polymers showed that the number of hydroxyl groups initiating polymerisation was near theoretical for 1,4-butanediol (2 OH groups) and pentaerythritol (4 OH groups). The numbers for polyglycerines were somewhat lower than theoretical (8 or 12 OH groups), but they clearly suggested the star-shaped structure, with more arms than in polymers initiated with pentaerythritol. The preparation of high molecular weight polymers showed that the polymerisation rate increases with the number of hydroxyl groups in the co-initiator. Along with the faster polymerisation, higher molecular weight polymers were obtained. High hydroxyl group content in the polymer did not cause a drop in the conversion level or enhanced backbiting during extended polymerisation. Furthermore, the co-initiator did not affect the thermal properties of the polymers except that slightly lower melting temperatures were measured for star-shaped than linear polylactides. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polylactide; Star-shaped; Polymerisation

1. Introduction

Polylactide is known for the applications in the biomedical field, and recently advances in industrial processes have created interest in their use as environmentally friendly polymers [1]. Most applications require high molecular weight polymers, and the preferred route for the synthesis of such polylactides is bulk ring-opening polymerisation of lactide in the presence of Sn(II)2-ethylhexanoate (Sn(Oct)$_2$). This catalyst is preferred because of the high reaction rate of the polymerisation, the low degree of racemisation even at high temperatures, and its acceptance by the FDA [1–3]. In addition, Sn(Oct)$_2$ is commercially available, easy to handle, and soluble in common organic solvents and cyclic ester monomers [4].

Several mechanisms have been proposed for the Sn(Oct)$_2$ induced polymerisation [1,5–12]. According to the most recent results [9–12], Sn(Oct)$_2$ first reacts with compounds containing hydroxyl groups to form a tin alkoxide that acts as an actual initiator in the polymerisation. Hence, the use of alcohols as co-initiator increases the reaction rate of polymerisation. The propagation is stopped via a chain transfer with another alcohol molecule, which causes the polymerisation to yield hydroxyl-terminated polymers with molecular weight depending on the ratio of monomer to co-initiator.

The structure of the polymer depends on the alcohols used as co-initiators. Mono- and difunctional alcohols yield linear polymers, while alcohols with hydroxyl functionality higher than 2 give star-shaped polymers. For example, pentaerythritol has been used in the preparation of 4-arm polymers, dipentaerythritol or sorbitol for 6-arm polymers, and multifunctional poly(ethylene oxide) for 9-arm polymers [13–18]. With synthesis under the same reaction conditions, higher molecular weights have been achieved for star-shaped polylactides with pentaerythritol as co-initiator than for linear ones without co-initiator [15]. In addition, star-shaped polymers have been reported to have interesting rheological properties [18].

As presented in the literature for the polymerisation of star-shaped poly[(trimethylene carbonate)-*co*-(ϵ-caprolactone)], high hydroxyl content of the co-initiator should accelerate polymerisation by increasing the number of growing chain ends [19]. Fast polymerisation is desired in the preparation of polylactides by reactive extrusion where activators such as triphenylphosphine have been used to increase the polymerisation rate [20–22]. We wished to know whether high molecular weight polylactides could be prepared in short polymerisation time through the use

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of polyglycerine as co-initiator. Polyglycerine is a compound with higher hydroxyl group content than dipentaerythritol or sorbitol, and thus a star-shaped polylactides with large number of arms can be achieved. In this study, we report the effect of alcohols with different numbers of hydroxyl groups on the preparation of high molecular weight polylactides. To confirm the effect of co-initiator on the polymer structure, we also prepared low molecular weight polylactides and characterised them by ^{1}H-NMR.

2. Experimental

2.1. Materials

D,L-Lactide and L-lactide (Purac) were recrystallised twice from toluene before use. Benzyl alcohol (Fluka Chemica), 1,4-butanediol (BD) (Fluka Chemica), pentaerythritol (PERYT) (Acros Organics), and polyglycerine-06 and polyglycerine-10 (PGl-06 and PGL-10, both from Daicel Chemical Industries) were used as co-initiators without further treatment. Sn(II)2-ethylhexanoate (Sigma) was used as a catalyst in the ring-opening polymerisation.

2.2. Synthesis

Poly(D,L-lactide) oligomers. Polylactide oligomers were polymerised from D,L-lactide in a 2.5-l batch reactor designed for agitation of viscous materials. Monomer was fed to the reactor with appropriate amount of co-initiator and 0.02 mol% of $Sn(Oct)_2$. The reaction was carried out at 160°C for 3 h under nitrogen atmosphere. The co-initiator/monomer molar ratio was varied between 1:100 and 12.5:100 as presented in Table 1. The samples are referred to with the amount of co-initiator used in the preparation. For example, poly(D,L-lactide) oligomers polymerised with 3:100 ratio of butanediol to lactide is designated PDLA (3% BD).

High molecular weight poly(L-lactides). The reactor was heated to the polymerisation temperature of 200°C, the mixture of co-initiator, $Sn(Oct)_2$ (0.03 mol%), and L-lactide was fed to the reactor, and polymerisations were carried out for 60–75 min under nitrogen atmosphere. The extent of the reaction during the polymerisations was followed by taking the samples from the reactor. An overview of he polymerisations is presented in Table 3.

2.3. Characterisations

Molecular weights (M_n and M_w) and molecular weight distributions (MWD) were determined with respect to polystyrene standards by gel permeation chromatography (GPC). The Waters Associates system 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 analysed at room temperature. Chloroform (Riedel-de Haen Ag, stabilised with 1% ethanol) was used as eluent, delivered at a flow rate of 1.0 ml/min. The samples were dissolved in chloroform at a concentration of 1.0% (w/v). The injection volume was 200 ml.

For ^{1}H-NMR measurements, the samples were dissolved in chloroform-d_1 (Fluka Chemica, deuteration degree not less than 99.8%) in 5-mm NMR tubes at room temperature. The sample concentration was about 1.0% by weight. NMR spectra were recorded on a Varian XL-300 NMR spectrometer working at 300.032 MHz for protons.

Differential scanning calorimetric (DSC) measurements were made on a Mettler Toledo Star^e DSC 821^e. The measurements were run from −40 to 180°C for oligomers and from 0 to 200°C for high molecular weight polymers, at a heating rate of

Table 1
Initiation activity of hydroxyl groups in co-initiators

Co-initiator	BD			PERYT			PGL-06			PGL-10
Co-initiator/lactide	3/100	5/100	10/100	5/100	8/100	12.5/100	1/100	3/100	5/100	5/100
Average chain lengths										
Theoretical	16.7	10.0	5.0	5.0	3.1	2.0	12.5	4.2	2.5	1.7
^{1}H-NMR										
Chain length based on $-\mathrm{O}\bar{\mathrm{H}}$	18.1	10.3	5.2	5.8	3.5	2.3	16.0	5.7	5.0	2.4
Chain length based on $-\mathrm{C}\bar{\mathrm{H}}-\mathrm{OH}$	16.2	10.0	5.0	5.9	3.2	2.1	10.1	3.5	2.5	1.8
Numbers of initiating OH groups										
Theoretical	2	2	2	4	4	4	8	8	8	12
Calculation via the ratio of measured to theoretical chain lengths										
$-\mathrm{O}\bar{\mathrm{H}}$	1.8	1.9	1.9	3.4	3.5	3.5	6.2	5.9	4	8.3
$-\mathrm{C}\bar{\mathrm{H}}-\mathrm{OH}$	2.0	2.0	2.0	3.4	3.9	3.8	9.9	9.5	8.0	11.1
Calculation via the characteristic peaks of reacted and unreacted OH groups in co-initiator										
$-\mathrm{C}\bar{\mathrm{H}}_2-\mathrm{OH}/-\mathrm{C}\bar{\mathrm{H}}_2-\mathrm{O}-$polymer	2.0	2.0	2.0	3.8	3.7	3.7	–	–	–	–

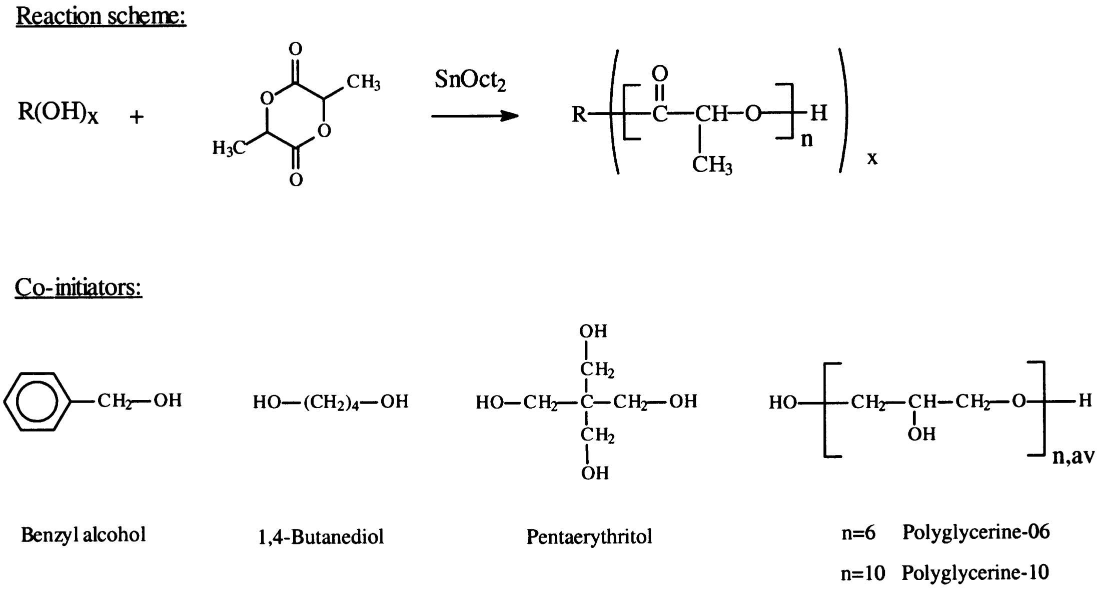


Fig. 1. Reaction scheme of the polymerisations.

10°C/min and a cooling rate of 10°C/min. The glass transition temperatures, melting temperatures, and crystallinity were measured during the second heating period.

3. Results and discussion

Linear and star-shaped polylactides were prepared by using alcohols with different numbers of hydroxyl groups as co-initiators. The assumed reaction scheme of the polymerisations is shown in Fig. 1 together with the co-initiators employed.

3.1. Polylactide oligomers

Poly(D,L,-lactide) oligomers were characterised by ^{1}H-NMR to determine the effect of the type and amount of co-initiator on the oligomer structure. D,L-Lactide was

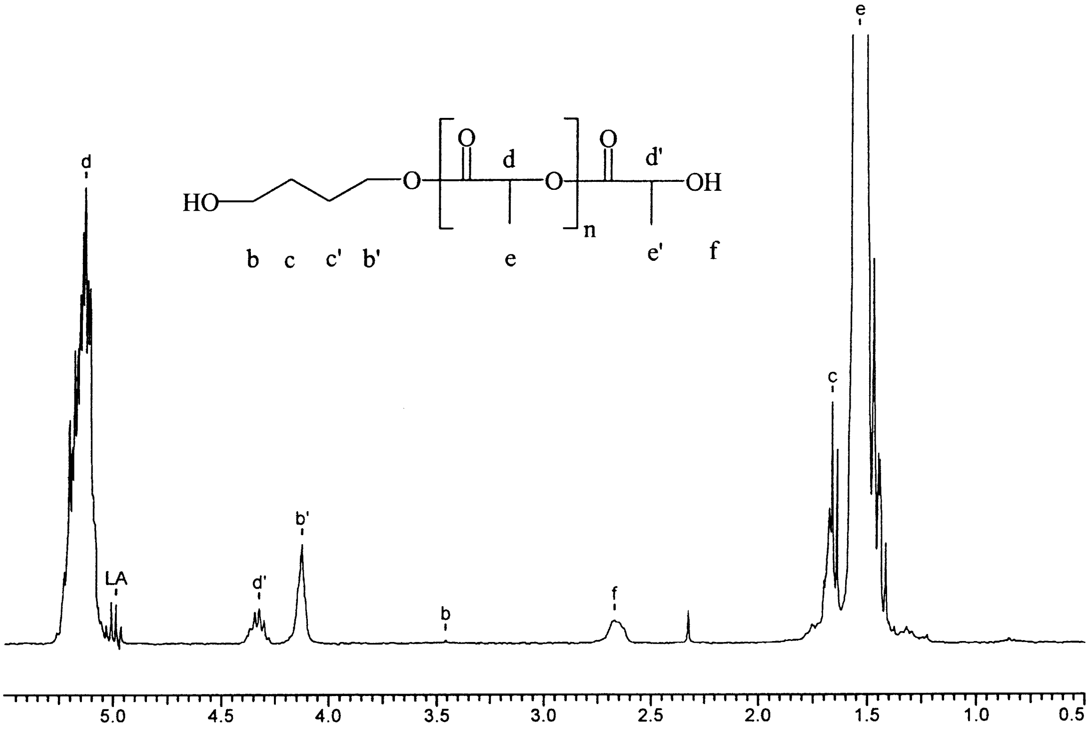


Fig. 2. ^{1}H-NMR spectrum of PDLA(5% BD).

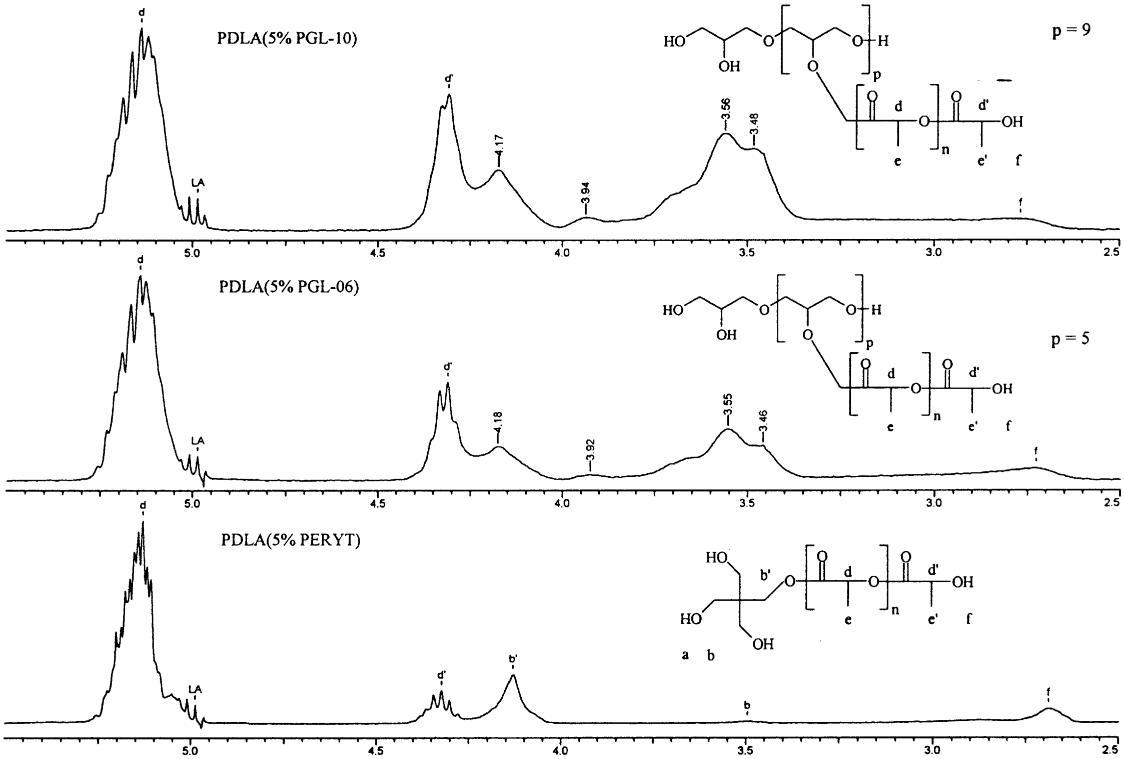


Fig. 3. ^{1}H-NMR spectra of PDLA(5% PERYT), PDLA(5% PGL-06), and PDLA(5% PGL-10).

used in the synthesis of the oligomers, since the oligomers were to be used in the production of amorphous crosslinked matrices [23]. ^{1}H-NMR spectra of the oligomers synthesised with 5 mol% of co-initiator are shown in Figs. 2 and 3 with their structure and characteristic peaks. Further characterisation was done by GPC and thermal analysis.

^{1}H-NMR was used to calculate the average number of OH groups in the co-initiator that participate in the initiation. Calculations were performed by two methods. The first method was to compare characteristic peaks of the unreacted and reacted OH groups of the co-initiator. However, this method could not be applied for oligomers initiated with polyglycerines owing to overlapping of the peaks. In this case, initiation activity was estimated indirectly by comparing theoretical chain lengths with chain lengths determined by NMR. Oligomers initiated by 1,4-butanediol and pentaerythritol were analysed by both methods and the results compared.

Average polylactides chain lengths were calculated by comparing the peak integrals of chain methine protons (*d* in Fig. 2, 5.10 ppm) with those of methine protons next to the terminal hydroxyl group ($-\mathrm{C\bar{H}{-}OH}$) (d', 4.32 ppm). This gives the chain length in lactic acid units and, as presented in Eq. (1), it must be divided by two to obtain the chain length in lactide units. Since the peak integrals of the terminal hydroxyl groups ($-\mathrm{CH{-}O\bar{H}}$) (f, 2.67 ppm) should be equal to the peak integral of $-\mathrm{C\bar{H}{-}OH}$ (d'), the chain length was also calculated as in Eq. (2).

Both ways to calculate the average chain lengths have their benefits and drawbacks. The peak of the terminal hydroxyl group in a polylactides chain is broad and it may drift in the spectrum. Moreover, polyglycerines have peaks that overlap with the $-\mathrm{C\bar{H}{-}OH}$ peak (d') preventing quantitative analysis based on methine peaks. The peaks are presented in Fig. 1.

$$\text{chain length based on } -\mathrm{C\bar{H}{-}OH} = \frac{d+d'}{2\times d'} \qquad (1)$$

$$\text{chain length based on } -\mathrm{O\bar{H}} = \frac{d+f}{2\times f} \qquad (2)$$

The average number of hydroxyl groups in the co-initiator that take part in the polymerisation process was determined by comparing the theoretical chain length with the chain length determined by NMR as in Eq. (3).

$$\text{initiating OH} = \frac{\text{theoretical chain length}}{\text{chain length determined by NMR}} \times \text{functionality} \qquad (3)$$

Linear oligomers were produced with 1,4-butanediol as a co-initiator. As we assumed, butanediol initiates the growth of lactide chains from both ends. For example, PDLA(5% BD) had a theoretical chain length of 10.0 lactide units, whereas the chain lengths determined by NMR were 10.0 ($-\mathrm{C\bar{H}{-}OH}$) and 10.3 ($-\mathrm{O\bar{H}}$). The results correspond to values of 2.0 and 1.9 as the average number of hydroxyl groups initiating polymerisation. Similar results were achieved when the amount of BD was varied, as can be seen in Table 1 where ^{1}H-NMR results are presented. Direct method to calculate the initiation activity of hydroxyl groups in butanediol is to compare the peak integrals for butanediol (Eq. (4)). The peak at 3.46 ppm (b, Fig. 1) is due to the free methylene proton in BD next to hydroxyl group and it is shifted to 4.13 ppm (b') when lactide is connected to it. The initiation activity calculated in this way was found to be 98%, which is equivalent to 1.96 growing lactide arms.

$$\text{initiating OH} = \frac{b'}{b + b'} \tag{4}$$

Pentaerythritol is a symmetrical star-shaped molecule with four hydroxyl groups in equivalent positions. For PDLA(5% PERYT) we achieved average chain lengths of 5.9 ($-\mathrm{C}\bar{\mathrm{H}}-\mathrm{OH}$) and 5.8 ($-\mathrm{O}\bar{\mathrm{H}}$). The theoretical chain length was 5.0, which means that 3.4 hydroxyl groups initiated the polymerisation. With the direct method, based on the ratio of the peaks of the methine protons (b, 3.50 ppm and b', 4.13 ppm, Fig. 2) corresponding to unreacted and reacted hydroxyl groups, we obtained 3.8 as the number of initiating hydroxyl groups. For similar molar ratios Kim et al. [14] evaluated the conversion of the hydroxyl groups of pentaerythritol to be about 95%. This corresponds to 3.8 initiating hydroxyl groups on average, and is in excellent agreement with our results. Comparison of the results obtained by different methods shows that the average chain length method estimates the number of hydroxyl groups initiating polymerisation in pentaerythritol reasonably well.

The co-initiators of main interest to us were polyglycerine-06 (PGL-06) and polyglycerine-10 (PGL-10). According to the producer, PGL-06 consists of six glycerol units connected with ether bonds, so it possesses a linear structure with 8 hydroxyl groups on average, as shown in Fig. 3. Correspondingly, the number of hydroxyl groups in PGL-10 is 12 on average. The purpose of including polyglycerines as co-initiators was to achieve an even more branched structure than with pentaerythritol. According to the ^{1}H-NMR results, the chain lengths were greater than expected from the theoretical values. With 5% of PGL-06 the chains contained 10.0 lactide units on average when calculated from the ratio of the hydroxyl proton (f) to methine protons in the lactic acid chain (d). This is twice the theoretical value and corresponds to 4.0 initiating hydroxyl groups. With smaller amounts of co-initiator, the average length of the chains was closer to the theoretical value and more hydroxyl groups seemed to initiate the polymerisation, i.e. 5.9 initiating hydroxyl groups with 3% of polyglycerine-06 and 6.2 with 1%. With PGL-10 (5%) the number of initiating hydroxyl groups was estimated with a similar calculation to be 8.3. Probably, the difference between the calculated and theoretical values is due to the lower initiation activity of the secondary hydroxyl groups. However, the calculated values were considerably greater than 2, which would correspond to the primary OH groups, which means that a substantial proportion of secondary hydroxyl groups take part in the initiation, and that their participation increases as the co-initiator content decreases. For polyglycerines we were forced to evaluate the chain length with hydroxyl groups only. Broad peaks of the co-initiator at 4.18, 3.92, and 3.55 ppm overlapped the signal from methine proton next to the hydroxyl group (d', $-\mathrm{C}\bar{\mathrm{H}}-\mathrm{OH}$) and the amount of initiating hydroxyl groups could not be estimated accurately in that way, i.e. values were considerably higher than expected.

GPC showed that the molecular weight distribution of the oligomers was narrow, as presented in Table 2. In every polymerisation, the number average molecular weight decreased with increasing co-initiator content. The values given by GPC are affected not only by the size of the molecule but also the structure of the molecule. For oligomers initiated with butanediol, M_n's values closely corresponded to the theoretical values. For star-shaped polylactides oligomers initiated with pentaerythritol and the polyglycerines the differences were much smaller.

Thermal properties of the oligomers determined by

Table 2
Properties of low molecular weight polylactides

Co-initiator	BD			PERYT			PGL-06			PGL-10
Co-initiator/lactide	3/100	5/100	10/100	5/100	8/100	12.5/100	1/100	3/100	5/100	5/100
Functionality	2	2	2	4	4	4	8	8	8	12
Theoretical										
M_n (g/mol)	4890	2970	1530	3020	1940	1290	14,860	5260	3340	3640
GPC										
M_n (GPC) (g/mol)	8200	5100	2600	4000	2800	1700	15,700	5400	3500	3000
M_w (GPC) (g/mol)	10,600	6300	3200	5400	3300	2200	19,800	6600	4300	3700
MWD	1.3	1.2	1.2	1.4	1.2	1.3	1.3	1.2	1.2	1.2
^{1}H-NMR										
Lactide-% (%)	2.4	2.5	2.6	2.1	2.2	1.9	2.7	2.6	1.6	2.9
DSC										
T_g (°C)	38	30	17	34	27	15	42	30	23	18

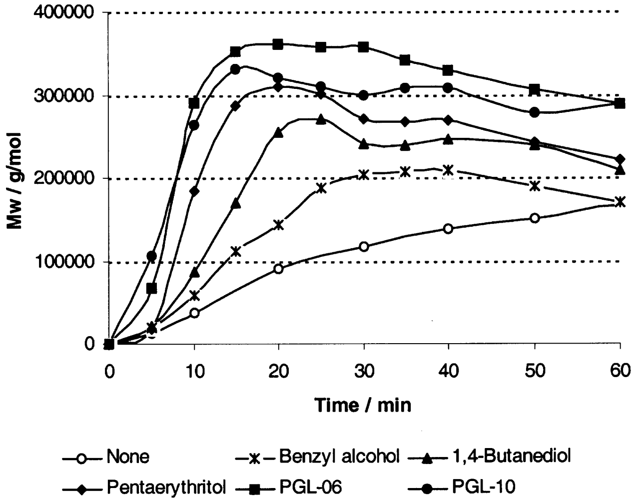


Fig. 4. Effect of co-initiator on the weight average molecular weights of polylactides.

differential scanning calorimetry showed higher glass transition temperature with longer polylactides chains. Surprisingly, T_g was increased from 30°C for BD initiated oligomer to 34°C with an equal amount of PERYT despite the shorter chain lengths of the PERYT initiated oligomer. Further branching, however, decreased the T_g significantly as the lactide chains were shortened.

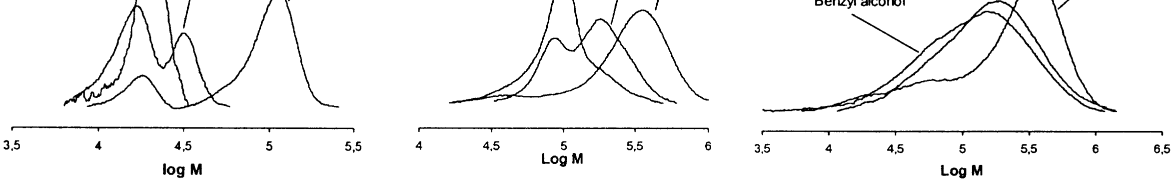
3.2. High molecular weight polymers

Since the ratio of co-initiator to lactide controls the molecular weight of the polymer, the amount of co-initiator must be low when high molecular weight polymers are prepared. However, the total concentration of hydroxyl groups in polymerisation can be increased by increasing the number of hydroxyl groups in the co-initiator. To investigate the relationship between the number of hydroxyl groups in the co-initiator and the polymerisation rate, we polymerised high molecular weight polylactides at 200°C in the presence of $Sn(Oct)_2$ and co-initiators containing different numbers of hydroxyl groups. Polymerisations were carried out for one hour, even though in most cases shorter times would have been sufficient to reach the maximum molecular weight. The longer times allowed us to determine whether higher hydroxyl content in the polymer has an effect on degradation of the polymer.

The dependence of molecular weight on polymerisation time for different co-initiators is shown in Fig. 4. Compared with polymerisation by $SnOct_2$ alone, initiation and propagation were considerably enhanced by all the co-initiators. Polymerisation was fastest with the co-initiator having highest hydroxyl group content (PGL-10). This can be explained by the larger number of growing chains. In addition to faster polymerisation, increasing hydroxyl group content in the co-initiator yielded polymer with higher molecular weight. Because the polymerisation is faster, there is less time for the polymer to degrade during the molecular weight buildup and we suggest that this is the reason for the higher molecular weights. Similarly to us, Kim et al. [15] report that star-shaped polylactides exhibits higher molecular weight than linear polylactide when polymerised under the same conditions. Faster polymerisation for star-shaped than for linear poly[(trimethylene carbonate)-*co*-(ϵ-caprolactone)] has been reported by Joziasse et al. [19].

All the polymers showed some decrease in molecular weights after passing the molecular weight maximum. There was little difference in the decrease of weight average molecular weights, but the decrease in number average molecular weights was higher for star-shaped than for linear polymers. This caused broadening of the molecular weight distribution of the star-shaped polymers resulting in MWDs from 2.4 (pentaerythritol) to 3.0 (PGL-10) at the end of the polymerisation. In contrast, MWD of 1,4-butanediol initiated linear polymer remained at 2.0 throughout the polymerisation.

All the co-initiators except monofunctional benzyl alcohol yielded a bimodal molecular weight distribution at the beginning of the polymerisation (Fig. 5). Bimodality was clearly seen before the molecular weight maximum. As the polymerisation proceeded, the shoulder in the MWD curve became smaller, resulting in a unimodal curve for linear polymer and a curve with a tail of low molecular weights for star-shaped polymers. The disappearance of the bimodality is probably due to intermolecular transesterification,



5 min 15 min 60 min

Fig. 5. Molecular weight distribution curves for benzyl alcohol, 1,4-butanediol, and polyglycerine-10 initiated polylactides.

which gradually randomises chain lengths during the polymerisation. Bimodality disappeared faster with co-initiators having higher hydroxyl content, suggesting that transesterification via hydroxyl groups is faster than ester–ester interchange.

The reason for the bimodality is less obvious. $Sn(Oct)_2$ contains small amounts of water that could act as co-initiator in parallel to separately added co-initiator. However, in that case benzyl alcohol should have generated a bimodal GPC curve. Furthermore, 1,4-butanediol yielded a bimodal distribution even though the hydroxyl groups are identically located at either end of an aliphatic chain of four methylene groups. However, it seems that, when propagation begins, not all 1,4-butanediol molecules initiate chain growth from both hydroxyl groups; some of them initiate growth from only one hydroxyl group. A possible explanation for this is that propagation is considerably faster than chain transfer between active species and hydroxyl groups. Similarly, Penczek et al. [24] have found that tin(II) butoxide initiated polymerisation of lactide yielded a bimodal distribution. They explained that bimodality appears when there are two species, propagating with different rate constants and that do no exchange fast enough. In our polymerisations, bimodality may also be due to differences in the reactivities of hydroxyl groups of the co-initiator in the case of polyglycerine and partly reacted pentaerythritol.

Besides intermolecular transesterification, hydroxyl end groups have been reported to cause backbiting via intramolecular transesterification [25,26]. To determine whether backbiting reactions are enhanced by larger numbers of hydroxyl groups, we analysed the conversions of lactide by GPC by comparing the peak areas of monomer and polymer. Similarly to molecular weights, conversions showed that the fastest polymerisation was achieved with the highest hydroxyl group content in the co-initiator: that is, the time needed to reach equilibrium was shortest with PGL-06 and PGL-10 (Fig. 6). However, with time all the co-initiators yielded conversion of about 95%, and the conversion stayed on the same level to the end of the polymerisation. These results suggest that the hydroxyl content of the co-initiator affects the polymerisation rate but not the monomer/polymer equilibrium.

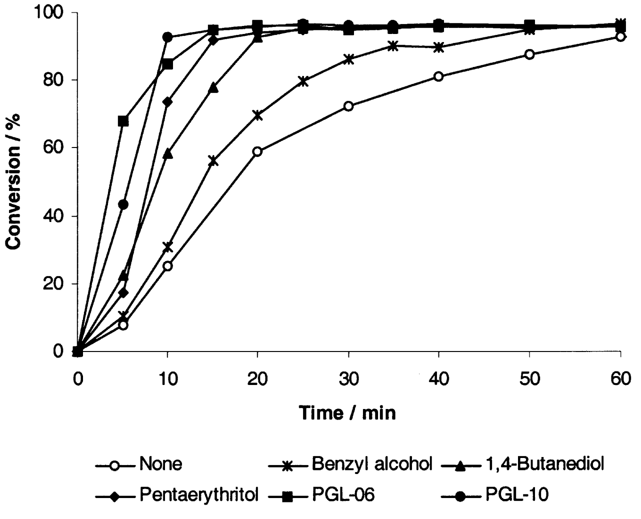


Fig. 6. Dependence of conversions on time for different co-initiators.

The inexact nature of the results obtained by GPC persuaded us to analyse the conversions by ^{1}H-NMR as well. The two methods gave similar results: the conversion measured by GPC were 94–96%, while those obtained by NMR were in the range of 90–94%. Furthermore, the narrowness of the conversion range analysed by ^{1}H-NMR confirms the observation that maximum conversions are not affected by the hydroxyl content of the co-initiator. Similarly to GPC, ^{1}H-NMR showed that the hydroxyl content of the co-initiator does not significantly affect the monomer/polymer equilibrium during extended polymerisation time. The polymerisation initiated by butanediol proceeded to a conversion of 90% in 25 min, and a conversion of 91% was measured after 60 min. Correspondingly, a conversion of 92% was measured for 20 and 60 min samples for PGL-10 initiated polymerisation.

The effect of co-initiator concentration on polymerisation was studied with different concentrations of PGL-10 (Fig. 7). The time required to reach maximum molecular weight decreased from 20 to 15 min when the concentration was doubled from 0.025 to 0.05 mol%. However, further increase in polymerisation rate was not observed when the concentration of PGL-10 was raised from 0.05 to 0.075 mol%. As expected, the highest molecular weight was achieved with the lowest concentrations of co-initiator, which clearly shows that the ratio of monomer to co-initiator controls the molecular weight. Co-initiator concentration also seemed to affect the degradation rate of the polymers, since the decrease in molecular weight was faster with lower concentration. In addition, low co-initiator concentration yielded broader molecular weight distribution. GPC did not reveal differences in the amounts of low molecular weight compounds, suggesting that the decrease in molecular weight is not due to backbiting. We suppose, therefore,

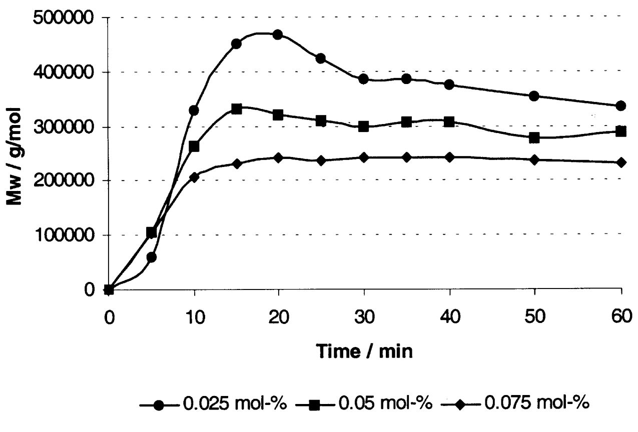


Fig. 7. Effect of polyglycerine-10 concentration on the weight average molecular weight of polylactide.

Table 3
Properties of high molecular weight polylactides at maximum conversion

Co-initiator	Co-initiator (mol%)	Time[a] (min)	X_{GPC} (%)	X_{NMR} (%)	M_w (g/mol)	M_n (g/mol)	MWD	T_g (°C)	T_m (°C)	T_{cr} (°C)	ΔH (J/g)
None	–	75	94	90	1,60,000	82,000	2	53	172	91	43
BD	0.05	25	95	90	2,34,000	1,20,000	2	53	173	93	40
PERYT	0.05	20	94	92	3,09,000	1,65,000	1.9	53	172	93	37
PGL-06	0.05	20	96	94	3,62,000	1,76,000	2.1	53	170	93	38
PGL-10	0.05	15	95	92	3,33,000	1,94,000	1.7	54	168	94	37
PGL-10	0.025	20	96	91	4,68,000	2,01,000	2.3	53	170	93	38
	0.05	15	95	92	3,30,000	1,94,000	1.7	54	168	94	37
	0.075	15	96	94	2,31,000	1,53,000	1.5	52	165	95	38

[a] Time required to reach maximum conversion.

that in spite of recrystallisation of lactide, traces of lactic acid or other impurities were present and this caused random breakages in the polymer chains. The importance of such chain breakages is relatively greater at lower concentration of co-initiator, i.e. the breakage of long chain causes a marked drop in molecular weight.

Thermal data of the polymers is shown in Table 3. Star-shaped polymers are reported to have lower melting temperatures (T_m) and higher cold-crystallisation temperatures (T_{cr}) than linear ones [16]. The melting temperatures of our polymers roughly followed this trend but the differences in the measured values were small. Depending on their molecular weight, the star-shaped polylactides initiated with PGL-10 exhibited T_m of 165–170°C. The linear polymer initiated with 1,4-butanediol exhibited a melting temperature of 173°C. No other differences in thermal properties were observed, but a cold crystallisation temperature of 95°C and glass transition temperature of 53°C were measured for all polymers. In addition, melting enthalpies (ΔH) of the polymers were similar, indicating that crystallinities of the polymers were on the same level.

4. Conclusions

Linear and star-shaped polylactides were prepared by using alcohols with 1–12 hydroxyl groups as co-initiators. Low molecular weight polymers were prepared to investigate the initiation activity of hydroxyl groups by ^{1}H-NMR. High molecular weight polymers were prepared to study whether the hydroxyl group content of the co-initiator affects the polymerisation rate.

^{1}H-NMR analysis of the low molecular weight polymers showed that the numbers of hydroxyl groups that initiate polymerisation were near theoretical for 1,4-butanediol (2 OH groups) and pentaerythritol (4 OH groups). The values measured for polyglycerines (8 or 12 OH groups) were somewhat lower than the theoretical ones, but they clearly suggested star-shaped structure, with larger number of arms than in polymer initiated with pentaerythritol.

In the preparation of high molecular weight polymers, an increasing number of hydroxyl groups in the co-initiator led to faster polymerisation and higher molecular weight. Furthermore, increasing hydroxyl group content did not cause a drop in the maximum conversions or enhanced backbiting during extended polymerisation time.

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