# A study of the ring-opening polymerization (ROP) of L-lactide by Ph₂SnX₂ precursors (X = NMe₂, OPrⁱ): the notable influence of initiator group

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Studies of the ring-opening polymerization (ROP) of L-lactide by Ph₂SnX₂ reveal that X (X = NMe₂ or OPrⁱ) influences not only the rate of polymerization but also the nature of the polymer formed. Gel permeation chromatography (GPC), mass spectral analysis and ¹H NMR spectroscopy of the polymers from these reactions revealed that for X = NMe₂, a bimodal molecular weight distribution of polylactide (PLA) is obtained. This is indicative of both cycles and long chains (24 kDa) being formed by both intra- and interchain transesterification. This extensive transesterification results in regeneration of the Ph₂Sn[OCHMeC(O)NMe₂]₂ species as the resting state of the tin(IV) species. Conversely, for X = OPrⁱ only a unimodal molecular weight distribution is observed in addition to Ph₂Sn[OCHMeC(O)OPrⁱ]₂, which is indicative of only interchain transesterification. Similar observations were seen in studies of ROP of L-lactide by Ph₃SnX precursors.

## Introduction

The current interest in polymers derived from lactides (L, D, *rac* and *meso*) and related cyclic esters has been well-described in the recent literature.[1] An excellent review has appeared dealing with their preparation *via* well-defined metal alkoxides and their related coordination to metals.[2] The potential advantages of well-defined coordination catalysts lies in their ability to facilitate ring-opening polymerization with control of both molecular weight and polymer microstructure. For a given $L_nM$–OR initiator, the relative rate of ROP roughly correlates with M–O bond polarity such that, for example, for a given ligand environment $Ca^{2+} > Mg^{2+} > Zn^{2+}$.[3] However, much still needs to be learned concerning the intimate mechanism of ring-opening polymerization and slower systems may offer greater insight into the details of the various reactions, including competing side reactions such as transesterification and chain transfer (Scheme 1). In this regard, we initiated a study of ROP of lactides by Ar₃SnX compounds where X = NMe₂ and OR (R = Me, Prⁱ and Buᵗ).[4] In some instances we were able to study the initail ring-opening event in isolation from subsequent ROP and this formed part of the study reported in our previous papers.[4,5] The study of ROP by Ar₃SnX initiators was, as we show here for Ar = Ph, hindered by aryl group transfer reactions. This led us to examine Ph₂SnX₂ systems, which appear inert with respect to this deleterious group scrambling reaction. We describe these results and show that the initiating group X has a remarkable and quite unexpected influence on the nature of the polymer due to the relative stabilities of the SnOCHMeC(O)X moieties.

## Results and discussion

### (a) ROP with Ph₃SnNMe₂ and Ph₂SnX₂ where X = NMe₂, OPrⁱ

The polymerization of L-lactide by Ph₂SnX₂ and Ph₃SnNMe₂ was performed under the same reaction conditions, that is

the same ratio of L-lactide to X groups (50:1, 80 °C). It was found that Ph₂Sn(OPrⁱ)₂ polymerizes L-lactide more rapidly than either Ph₂Sn(NMe₂)₂ or Ph₃SnNMe₂ under these conditions (see below). The rate of ROP is faster than that observed for the Ph₃SnX systems, presumably because the Sn center is more electrophilic in Ph₂Sn(OP)₂ relative to Ph₃Sn(OP) (where OP is the propagating polymer chain). This is supported by the recent electronic structure calculations involving the ring-opening of lactide and glycolide by Me₃SnOMe *vs.* Me₂Sn(OMe)₂.[6] However, it is not apparent why there should be such a discrepancy between the Ph₂Sn(OPrⁱ)₂ and Ph₂Sn(NMe₂)₂ systems. This is unusual since ROP would be expected to be independent of initiating group once the initial ring-opening event has occured. Insight into this difference in rates of ROP has been gained by analyzing polymer samples by GPC, mass spectrometry and ¹H NMR studies and is discussed in detail below.
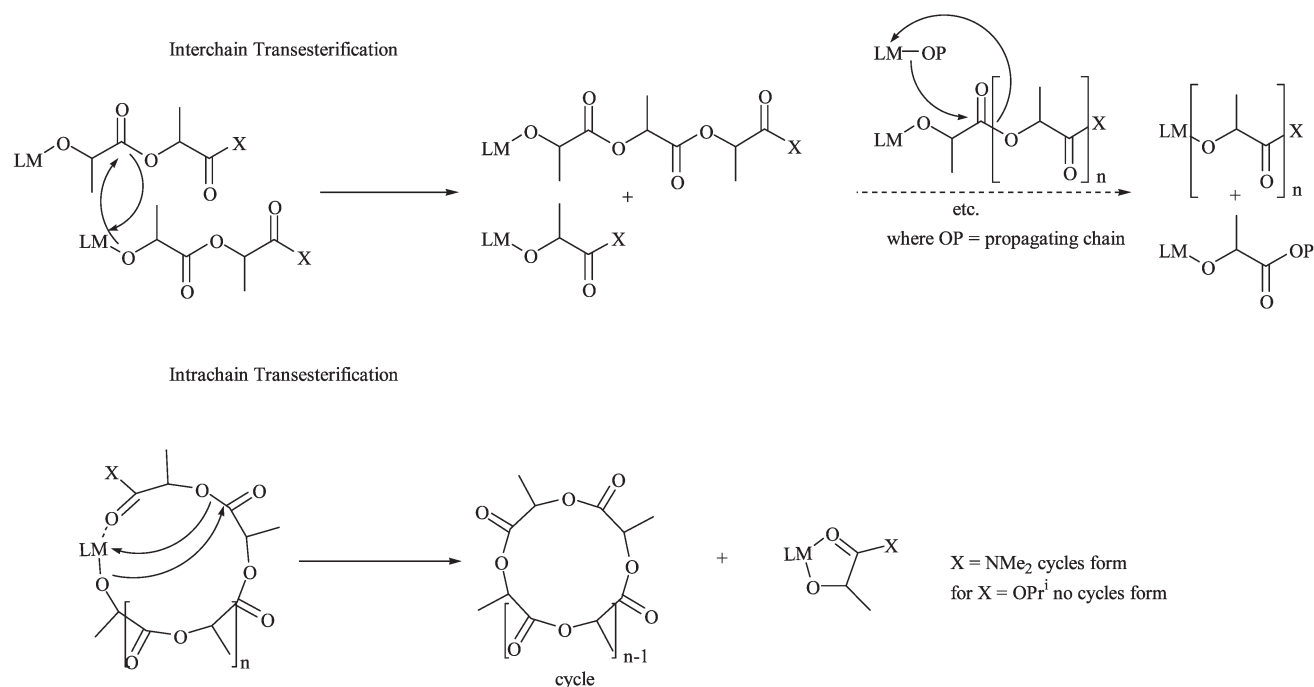
### (b) Kinetics

It is obviously important to quantify the conclusions drawn above and to do this we have studied in detail the kinetics of the reactions between Ph₂SnX₂ (X = NMe₂ and OPrⁱ) and L-lactide at various temperatures. We also attempted to do likewise for Ph₃SnX but found that these systems were complicated by the formation of Ph₂Sn(OP)₂ (where OP is the propagating polymer) and Ph₄Sn. Ph₄Sn is inactive in ROP while Ph₂Sn(OP)₂ is somewhat more active than Ph₃SnOP. However, this complication is not present in the Ph₂SnX₂ system.

Studies at higher temperatures were thus needed, which required knowledge of the equilibrium monomer concentration of lactide with respect to its polymer, as in eqn. (1):

$$\frac{1}{n}(PLA) \underset{\text{cat.}}{\overset{\text{cat.}}{\rightleftharpoons}} n(LA) \quad K_{eq} \qquad (1)$$

This phenomenon has been discussed in detail by Duda and Penczek[7] for Sn(II) octanoate in 1,4-dioxane. We determined

Interchain Transesterification

Intrachain Transesterification

where OP = propagating chain

etc.

X = NMe$_2$ cycles form

for X = OPr$^i$ no cycles form

cycle

**Scheme 1** Inter- and intrachain transesterification pathways that lead to the formation of chains and cycles, respectively, as well as LM[OCH-MeC(O)X] moieties. Notice that cycle formation is end-group dependent such that only X = NMe$_2$ cycles form.

$K_{eq}$ at various temperatures for eqn. (1) in benzene-$d_6$ since all our polymerization studies were done in this solvent. A plot of $-\ln(LA_{eq})$ vs. $1/T$ is shown in Fig. 1. The Ph$_2$Sn(OPr$^i$)$_2$ catalyst precursor was used in the determination (see Experimental for details). The straight line obtained was used to predict the equilibrium monomer concentration for a given temperature. From the graph in Fig. 1 we have determined $\Delta H^{\circ} = -5.1(3)$ kcal mol$^{-1}$ and $\Delta S^{\circ} = -6.9(3)$ eu, which compare favorably with the thermodynamic parameters determined in dioxane by Duda and Penczek[7]: $\Delta H^{\circ} = -5.4(3)$ kcal mol$^{-1}$ and $\Delta S^{\circ} = -9.8(3)$ eu.

The equilibrium monomer concentrations of LA were then used to calculate $k_{prop}$ for both the Ph$_2$Sn(NMe$_2$)$_2$ and Ph$_2$Sn(OPr$^i$)$_2$ systems at various temperatures (Fig. 2). Note that Fig. 2 illustrates that only when the equilibrium concentration of LA is taken into consideration is the plot linear.

In both systems a plot of $-\ln[(A - A_{eq})/(A_o - A_{eq})]$ {where $A = $ [LA], $A_{eq} = $ the equilibrium [LA] for a given temperature and $A_o = $ [LA] at $t = 0$} was plotted vs. time. The gradients of these lines were found to be straight, suggesting psuedo-first-order kinetics and the results are given in Table 1.

The values obtained and calculated in Table 1 (entries 1, 10 and 11) indicate that both Ph$_2$SnX$_2$ systems polymerize LA more rapidly than Ph$_3$SnNMe$_2$, which is as expected[6] since the tin(IV) center is more electrophilic, thus facilitating lactide coordination and ring-opening (see above).

A plot of $\ln(k_{prop}/T)$ vs. $1/T$ (Fig. 3) allowed for the determination of the following activation parameters: for Ph$_2$Sn(O-Pr$^i$)$_2$ $\Delta H^{\neq} = 11(1)$ kcal mol$^{-1}$ and $\Delta S^{\neq} = -48(3)$ eu and for Ph$_2$Sn(NMe$_2$)$_2$ $\Delta H^{\neq} = 12(1)$ kcal mol$^{-1}$ and $\Delta S^{\neq} = -45(3)$
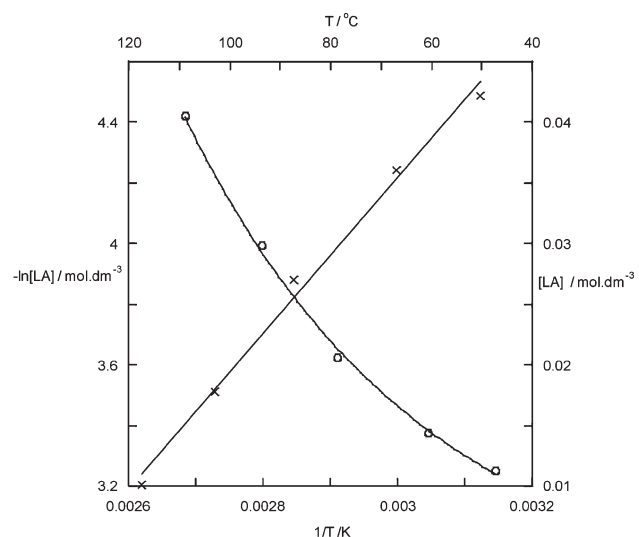
**Fig. 1** Plots of $-\ln(LA)$ vs. $1/T$, giving a straight line, and [LA] vs. $T$, giving a curved line. The straight line allows for the determination of the equilibrium monomer concentration of LA at various temperatures.
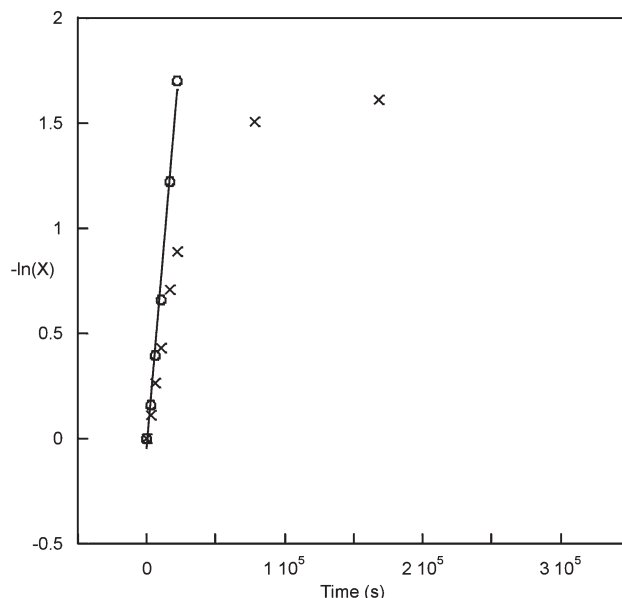
**Fig. 2** Typical plot of $-\ln(X)$ vs. time (s) in the ROP of L-lactide by Ph$_2$Sn(OPr$^i$)$_2$ at 82 °C, where $X = A/A_o$ for crosses and $(A - A_{eq})/(A_o - A_{eq})$ for circles. ($A = $ [LA], $A_{eq} = $ the equilibrium [LA] for a given temperature and $A_o = $ [LA] at $t = 0$).

**Table 1** Rates constants, $k_{prop}$, determined for the ROP of L-lactide by $Ph_2SnX_2$ and $Ph_3SnNMe_2$ where X = $NMe_2$ and $OPr^i$. All polymerization reactions were performed at the same X:LA ratio of 1:50

| Entry | Catalyst | $k_{prop}/s^{-1}$ | $T/^\circ C$ |
|---|---|---|---|
| $1^a$ | $Ph_3SnNMe_2$ | $2.8(4) \times 10^{-6}$ | 80 |
| 2 | $Ph_2Sn(NMe_2)_2$ | $3.8(2) \times 10^{-5}$ | 81 |
| 3 | $Ph_2Sn(NMe_2)_2$ | $1.9(2) \times 10^{-5}$ | 68 |
| 4 | $Ph_2Sn(NMe_2)_2$ | $9.4(2) \times 10^{-6}$ | 54 |
| 5 | $Ph_2Sn(NMe_2)_2$ | $4.4(2) \times 10^{-6}$ | 44 |
| 6 | $Ph_2Sn(OPr^i)_2$ | $7.6(2) \times 10^{-5}$ | 82 |
| 7 | $Ph_2Sn(OPr^i)_2$ | $3.8(2) \times 10^{-5}$ | 67 |
| 8 | $Ph_2Sn(OPr^i)_2$ | $2.6(2) \times 10^{-5}$ | 61 |
| 9 | $Ph_2Sn(OPr^i)_2$ | $9.1(2) \times 10^{-6}$ | 41 |
| $10^b$ | $Ph_2Sn(NMe_2)_2$ | $3.7(2) \times 10^{-5}$ | 80 |
| $11^b$ | $Ph_2Sn(OPr^i)_2$ | $6.8(2) \times 10^{-5}$ | 80 |

[a] The determination of this value was complicated by aryl group scrambling reactions (see text). [b] These values are calculated from $\ln(k_{prop})$ vs. $1/T$ plots (see below) to compare with Entry 1.

eu. These activation parameters can be compared with $\Delta H^{\neq} = 13(1)$ kcal $mol^{-1}$ and $\Delta S^{\neq} = -37(3)$ eu, which were determined for the initial ring-opening event in the reaction between $Ph_3SnOPr^i$ and L-lactide.[5]

**(c)   The effect of initiating groups: polymer structure and MW distribution with $Ph_3SnNMe_2$ and $Ph_2SnX_2$ where X = $NMe_2$, $OPr^i$**

The molecular weight of the PLA was monitored as a function of time and percent conversion ($^1H$ NMR spectroscopy) in tandem with ESI and MALDI mass spectrometry. These studies have been carried out for $Ph_3SnNMe_2$, $Ph_2Sn(NMe_2)_2$ and $Ph_2Sn(OPr^i)_2$ as catalyst precursors.

**(i)   $Ph_3SnNMe_2$.** As the polymerization of L-lactide by $Ph_3SnNMe_2$ progresses the GPC data reveal that the increase in molecular weight is not uniform; at high percent PLA conversion the MW distribution is bimodal (Fig. 4). Significantly, a high molecular weight fraction is formed, which is consistent with the formation of chains, and a lower molecular weight fraction that we attribute to cycles formed by intrachain

transesterification (Scheme 1). As indicated in Fig. 4 the peak molecular weight for the chain portion of the distribution is around 5.8 kDa at 50% conversion, which is reasonably consistent with one active site per $Ph_3Sn(OP)$ group based on a 50:1 $LA:NMe_2$ ratio and the fact that the GPC is calibrated to polystyrene standards. At low percent conversion (ca. 15%) the growing polymer chain conforms almost exclusively to H–$(LA)_n$–$NMe_2$ as detected by ESI MS [where LA = –OCHMe-C(O)OCHMeC(O)– and $LA/2$ = –OCHMeC(O)–] (Fig. 5). Just detectable in the MALDI spectra are chains H–$(LA)_n$–OH, which presumably arise from trace hydrolysis of $Ph_3SnNMe_2$, in addition to a minor series of H–$(LA)_n$–$NMe_2$ offset by 72 Da. In both cases the repeat unit is clearly 144 Da, indicating transesterification is not yet significant (Fig. 5).

At ca. 40% conversion, we observe the same two series of polymer chains, except that the minor series (offset by 72 Da) is now more significant in intensity when compared with the major series. For each series the repeat is again 144 Da. The growth of the minor series is indicative of (intermolecular) transesterification. Note that each event of transesterification can produce an even- or odd-number of half-lactide units (72 Da). Thus, the initial growth rate of the odd series represents half the rate of (intermolecular) transesterification. Careful inspection of the spectra reveal the formation of a polymer series based on $(LA/2)_n$, that is a polymer with no detectable end-groups and a separation of 72 Da. The appearance of these cycles, which can only arise from intramolecular intrachain transesterification, is more obvious by ESI MS relative to MALDI MS since the former emphasizes the lower molecular weight fraction.

At ca. 75% conversion the polymer sequences are all represented by repeat units of 72 Da, which indicates extensive inter- and intrachain transesterification; the former process produces chains and the latter produces cycles (Fig. 5). Indeed, it is the cycles that predominate in the ESI mass spectra as most chains are too large to be detected by either the MALDI or ESI mass spectral analysis.

**(ii)   $Ph_2Sn(NMe_2)_2$.** As with the $Ph_3SnNMe_2$ system, the polymerization of L-lactide by $Ph_2Sn(NMe_2)_2$ again indicates a non-uniform MW distribution by GPC, which is bimodal at high percent PLA conversion (Fig. 4). The major difference between this system and the $Ph_3SnNMe_2$ system is the peak
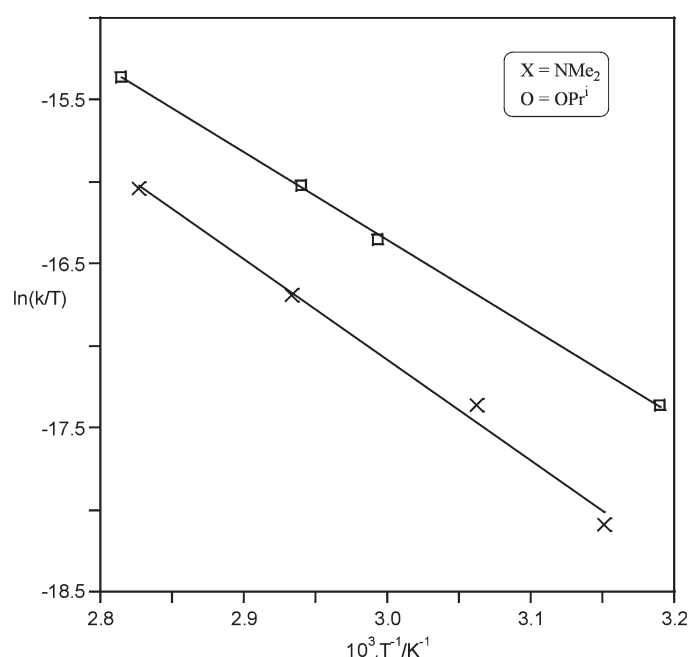


**Fig. 3**  Plot of $\ln(k_{prop}/T)$ vs. $1/T$ for the reaction between $Ph_2SnX_2$ and L-lactide (1:50) where X = $NMe_2$ and $OPr^i$.

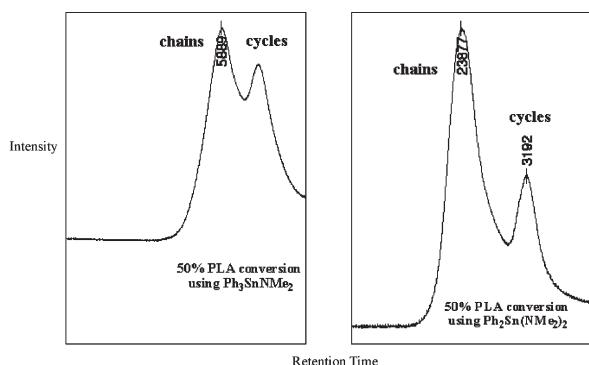**Fig. 4** Bimodal distributions of PLA observed by GPC for both $Ph_3SnNMe_2$ and $Ph_2Sn(NMe_2)_2$ catalyst precursors at about 50% PLA conversion, indicating peak molecular weights.

molecular weight of the chains, which at about 50% conversion is *ca.* 24 kDa. Based on the ratio of $NMe_2$:LA (1:50) a molecular weight of 7.2 kDa could be expected for two active sites per Sn center. However, a much larger peak molecular weight is observed, indicating fewer active propagating sites present.

A plausible explanation for this lies in the formation of the thermodynamically stable $Ph_2Sn[OCHMeC(O)NMe_2]_2$ compound, which is initially formed upon reaction with lactide (1 equiv.) and can be reformed by both inter- and intrachain transesterification (Scheme 1). In order to test this hypothesis,

we studied the reactions of $Ph_2Sn(NMe_2)_2$ with $n$(LA) ($2 < n < 5$) in benzene-$d_6$ at room temperature. Within minutes of initiating the reaction, two species were dominant in the $^1H$ NMR spectrum: $Ph_2Sn[OCHMeC(O)NMe_2]_2$ and $Ph_2Sn[OCHMeC(O)OCHMeC(O)NMe_2]_2$ in addition to free L-lactide (Fig. 6). With time the free L-lactide was consumed and the resonances of $Ph_2Sn[OCHMeC(O)NMe_2]_2$ increased while that of $Ph_2Sn[OCHMeC(O)OCHMeC(O)NMe_2]_2$ decreased. By $^1H$ NMR spectroscopy the other resonances appeared as PLA (Fig. 6). This indicates that transesterification occurs preferentially at the α-ketonic ester carbon, leading to formation of $SnOCHMeC(O)NMe_2$ groups.

At low percentage polymer conversion (~15%) mass spectrometry revealed a similar molecular weight behavior as observed for $Ph_3SnNMe_2$ where chains represented by H–$(LA)_n$–$NMe_2$ with $n$ being even predominate (Fig. 5). In addition to this major series, a minor series of polymer chains represented by H–$(LA/2)_n$–$NMe_2$ where $n$ is odd is also observed. This series is offset by 72 Da from the major series.

Given that the initial ring-opening event is followed by a rapid intramolecular amidation to give $Ph_2Sn[OCHMeC(O)NMe_2]_2$,[5] this observation is at first surprising. Seemingly, the only explanation for this is that the ring-opening of the next equivalent of lactide produces a kinetically labile species, $Ph_2Sn[OCHMeC(O)NMe_2][OCHMeC(O)OCHMeC(O)OCHMeC(O)NMe_2]$, which reacts rapidly by transesterification to give $Ph_2Sn[OCHMeC(O)OCHMeC(O)NMe_2]_2$.



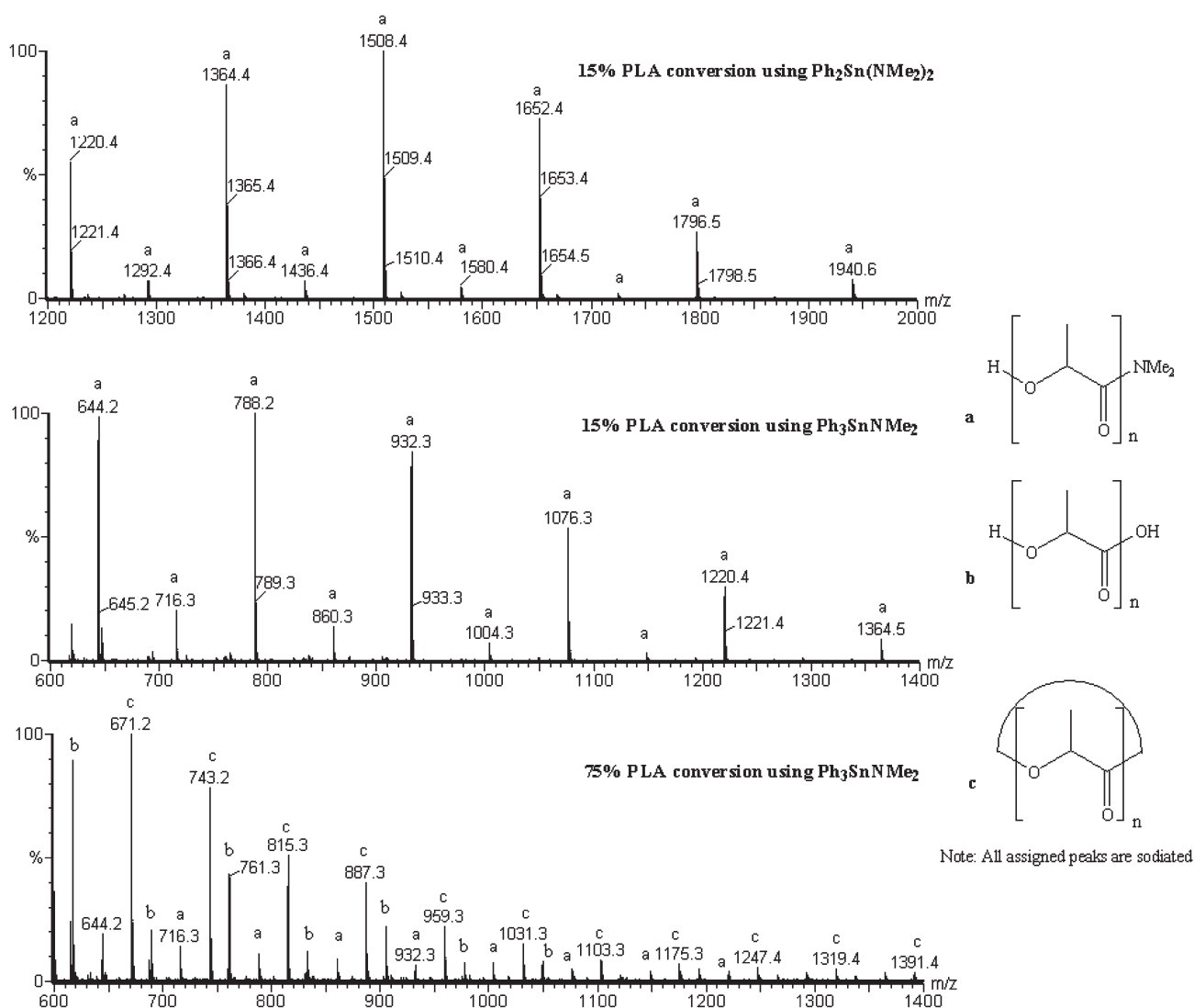**Fig. 5** ESI mass spectra of PLA samples at various conversions using either $Ph_3SnNMe_2$ or $Ph_2Sn(NMe_2)_2$ catalyst precursors. End-group and cycle assignments are indicated.

Further ring-opening events occur without transesterification during the early stages of the polymerization (Fig. 5).

At *ca.* 50% conversion, MALDI mass spectrometry reveals predominantly $(LA/_2)_n$ cycles with $n = 15 \pm 6$. These cycles must arise from intramolecular intrachain transesterification where one growing polymer chain reacts with its head group. The progression in 72 Da does not distinguish between even and odd values of $n$.

By 75% conversion the high molecular weight chains extend to greater than 30 kDa (Fig. 5), resulting in only the lower mass cycles $[-OCHMeC(O)-]_n$ being visible in the mass spectrum.

Examination of the nature of the Sn residue by $^{119}$Sn NMR does not allow the detection of $Ph_4Sn$ or $Ph_3SnOP$. The predominant tin-containing compound at $t_\infty$ is $Ph_2Sn[OCHMeC-(O)NMe_2]_2$.[4,5] The catalytically active system behaves similarly to the sample of $Ph_3Sn[OCHMeC(O)NMe_2]$ that undergoes disproportonation to $Ph_3Sn[OCHMeC(O)NMe_2]$ and $Ph_3Sn[OCHMeC(O)]_{n+1}NMe_2$ at room temperature. In this manner the high molecular weight chains of $H-(LA/_2)_n-NMe_2$ arise as the thermodynamic product $Ph_2Sn[OCHMeC-(O)NMe_2]_2$ is formed by transesterification. This also parallels the behavior seen in the reactions between $Ph_2Sn(NMe_2)_2$ and $n(LA)$ with $2 < n < 5$ in benzene-$d_6$ (Fig. 6).

**(iii) $Ph_2Sn(OPr^i)_2$.** The PLA that is formed from the $Ph_2Sn(OPr^i)_2$ catalyst precursor is markedly different from that seen for $Ph_2Sn(NMe_2)_2$ and $Ph_3SnNMe_2$. From GPC studies (Fig. 7) it is apparent that a single molecular weight distribution is observed, which is primarily comprised of chains. This distribution migrates to larger molecular weight and higher polydispersity with time ($Mn = 3970$ Da and PDI $= 1.57$ at 78% PLA conversion), indicative of only intermolecular and/or interchain transesterification (Fig. 7). The ESI mass spectra revealed mostly chains separated by 72 Da where $H-(LA/_2)_n-OPr^i$ predominates with a trace amount of $H-(LA/_2)_n-OH$,



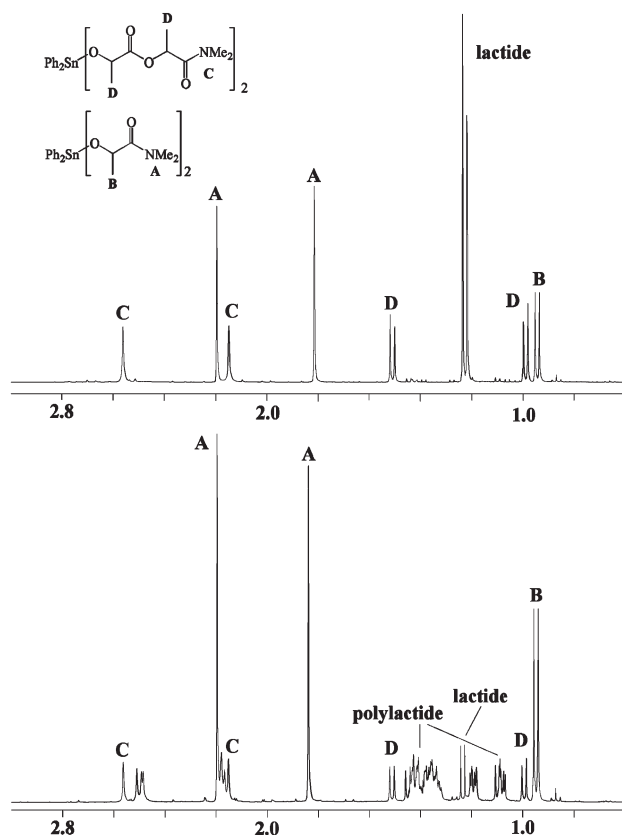**Fig. 6** $^1$H NMR spectra of the room temperature reaction between $Ph_2Sn(NMe_2)_2$ and $n(LA)$ with $2 < n < 5$. The top spectrum is at $t = 0$ and the lower one is at $t = 24$ h.



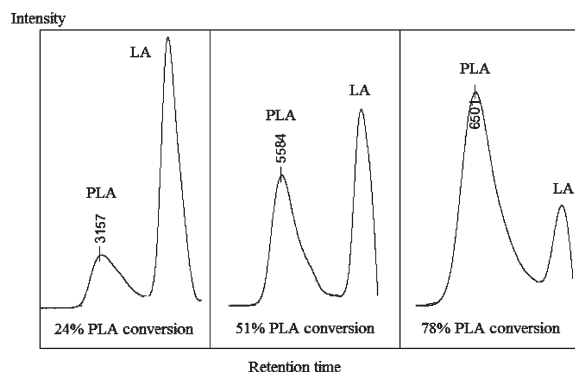**Fig. 7** Unimodal distributions of PLA chains observed by GPC for the $Ph_2Sn(OPr^i)_2$ catalyst precursor at various PLA conversions, indicating peak molecular weights. Notice the migration to higher molecular weight with increasing PLA conversion.

which becomes more significant at higher PLA conversions (Fig. 8). There are, however, some cycles that are apparent but these are far less abundant than found for the $NMe_2$ catalyst systems as indicated by the GPC data. The relatively low abundance of any cycles may reflect the poorer stability of $Ph_2Sn[OCHMeC(O)OPr^i]_2$ *vs.* $Ph_2Sn[OCHMeC(O)N-Me_2]_2$.[8] This lower stability of $Ph_2Sn[OCHMeC(O)OPr^i]_2$ presumably also accounts for the formation of lower molecular weight polymer chains (6.0 kDa at 70% PLA conversion) than observed for $Ph_2Sn[OCHMeC(O)NMe_2]_2$.

## Concluding remarks

The $Sn-OCHMeC(O)NMe_2$ group has been shown to have a high stability and a pronounced influence on the nature of the polymer formed, as seen in the molecular weight distribution and in the relative abundance of chains *vs.* cycles. Undoubtedly, the stability of the $Sn-OCHMeC(O)NMe_2$ moiety results from chelation, which is assisted by the amido group $\pi$-donation. Thus, in the reactions involving $Ph_2SnX_2$ we observed that extensive cyclic PLA is formed when $X = NMe_2$ but not for $X = OPr^i$.

The many subtleties revealed in these studies are made possible by the relative kinetic labilities of the $Sn-O$ bonds. In relation to other metallic systems such as those involving Mg and Zn, the $Sn-O$ bonds are relatively inert and this probably reflects the M–OR bond polarity, which follows the order $M = Mg^{II} > Zn^{II} > Sn^{II} > Al^{III} > Sn^{IV}$.[2,3] This experimental observation supports the recent theoretical investigation of the ring-opening of lactide wherein the reactivity order was found to be $Me_2AlOMe > Me_2Sn(OMe)_2 > Me_3SnOMe$.[6]

Finally, it is worthy of note that this seemingly simple, if not seemingly trivial study, proved so complex. However, it is within the complexities of these systems that we have learned the most and seen the effects of the kinetic and thermodynamic factors of $Sn-X$ bonds. Indeed, it may prove possible now to devise a system for the production of cycles $(LA/_2)_n$ at the expense of chains. These could have significant applications as a new class of PLAs.

## Experimental

### General

**Caution: Organotin(IV) compounds are highly toxic and require appropriate handling!**

The manipulation of air-sensitive compounds involved standard Schlenk line and dry box techniques. All solvents were distilled under nitrogen from alkali metals (sodium or sodium/potassium alloy) and stored over 4 Å molecular
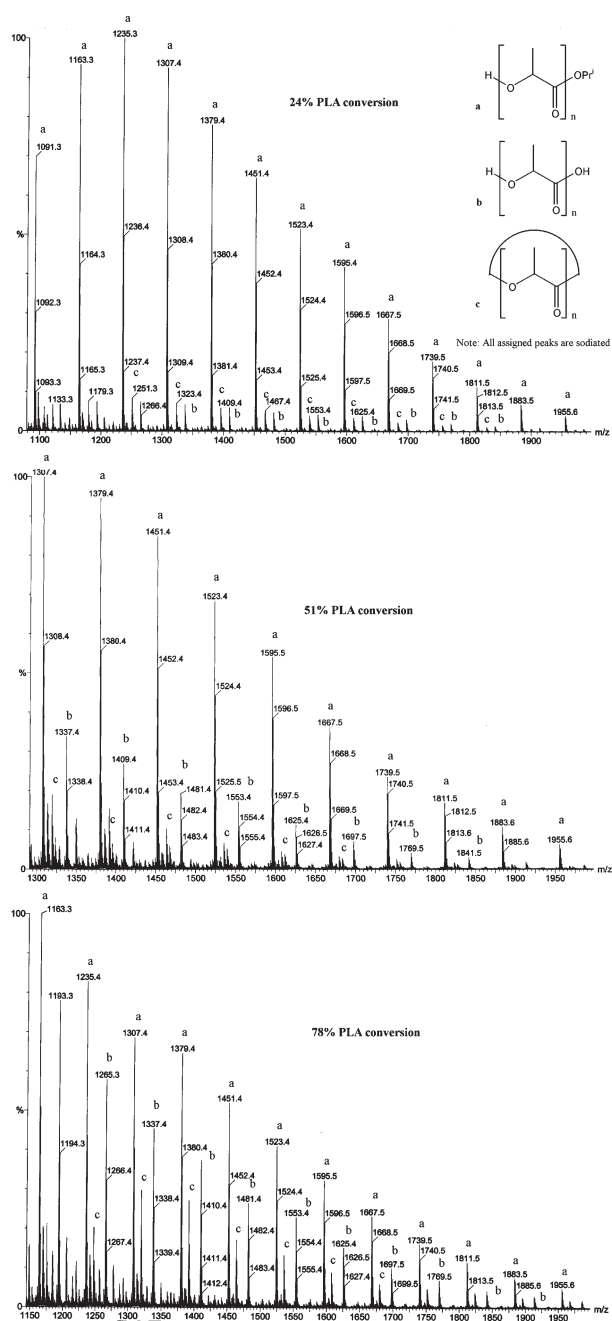
**Fig. 8** ESI mass spectra of PLA samples at various conversions using the Ph$_2$Sn(OPr$^i$)$_2$ catalyst precursor. End-group and cycle assignments are indicated. Notice the increase in **b** and **c** with increasing PLA conversion.

sieves. L-Lactide was purchased from Aldrich and sublimed prior to use. Benzene-$d_6$ and anhydrous *iso*-propanol were purchased from Acros Scientific whilst diphenyltin(IV) dichloride and triphenyltin(IV) chloride was purchased from Alfa Aesar. Benzene-$d_6$ was dried over sodium and vacuum transferred to a Schlenk flask containing activated molecular sieves.

The synthesis of Ph$_3$SnNMe$_2$ and Ph$_2$SnX$_2$ (X = NMe$_2$, OPr$^i$) have been described previously[4,5,9] where Ph$_3$SnCl or Ph$_2$SnCl$_2$ were treated with 1 or 2 equiv. of LiNMe$_2$, respectively. Ph$_2$Sn(OPr$^i$)$_2$ was generated by treating Ph$_2$Sn(NMe$_2$)$_2$ with excess *iso*-propanol.[5]

## Measurements and analyses

$^1$H NMR spectra were obtained on either Bruker DPX-400 or DRX-500 spectrometers using benzene-$d_6$. Spectra were

referenced internally to the residual protio impurities for $^1$H (benzene-$d_6$: $\delta$ 7.15 $^1$H). Mass spectra were obtained from either Mircomass QTOF or MALDI QTOF mass spectrometers. GPC analysis of polymers was performed using a Waters 1525 Binary HPLC pump coupled to two $7/8 \times 300$ mm Styragel® HR4 columns and a Waters 40 differential refractometer. The eluent was HPLC grade THF running at 1 mL min$^{-1}$ (sample concentration 0.1% w/v THF). Polystyrene standards were used for calibration of the instrument. Breeze® software was used in peak analysis and calibration procedures.

## Polymerization reactions

In all cases the reaction temperatures were regulated *via* a thermostatically controlled oil bath.

**NMR reactions.** All kinetic data were obtained from NMR scale reactions. Standard solutions of the appropriate Ph$_3$SnNMe$_2$ or Ph$_2$SnX$_2$ (X = NMe$_2$, OPr$^i$) complexes (0.027 M) and L-lactide (0.338 M) were made in benzene-$d_6$ and stored in the dry box. Appropriate aliquots of R$_3$SnX solutions were transferred along with an aliquot (200 μL) of L-lactide to a J. Young® NMR tube. The total volume was made up to 800 μL with benzene-$d_6$ to ensure a constant initial lactide concentration (0.084 M).

**Large scale reactions.** For GPC and mass spectral analysis large scale reactions were performed in benzene. At given intervals an aliquot was syringed (0.5 ml) from the reaction mixture and the benzene was evaporated at room temperature to yield LA and PLA. This was then dissolved in THF (GPC and mass spectrometry) or benzene-$d_6$ (NMR spectroscopy). $^1$H NMR spectroscopy was used to determine the extent of polymerization (see below).

## Kinetics analysis

For lactide polymerization reactions rates of polymerization were determined from $^1$H NMR data where the sum of the area of monomer and polymer peaks (CH and Me) was assumed to be 100% and rates of disappearance of monomer were calculated by the subtraction of the polymer peaks from the monomer peaks and dividing by the concentration of monomer at $t = 0$ to give a ratio.

Equilibrium monomer concentrations were determined by polymerizing L-lactide using the Ph$_2$Sn(OPr$^i$)$_2$ catalyst precursor in benzene-$d_6$ (1:25 OPr$^i$:L-lactide; [LA]$_{init}$ = 0.084 M) at various temperatures. Initially, the tube was heated to a high temperature (*ca.* 95 °C) and the tube was periodically monitored by $^1$H NMR spectroscopy. Once the concentration of L-lactide had stabilized the temperature was lowered and the procedure was repeated for a series of different temperatures The lower the temperature the slower the rate of ROP and the lower the equilibrium monomer concentration. Finally, the reversibility of this reaction was assessed by increasing the temperature from the lowest temperature back up to the highest. The natural log of the equilibrium monomer concentration was then plotted against $1/T$ to give a straight line. This data was used in the various polymerization reactions as indicated in Fig. 2.

The value of $k_{prop}$ was determined from the gradient a plot of $-\ln[(A - A_{eq})/(A_o - A_{eq})]$ *vs.* time (Fig. 2) where $A = $ [LA], $A_{eq} = $ the equilibrium [LA] for a given temperature and $A_o = $ [LA] at $t = 0$.

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