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Contributed Paper

Synthesis of Poly(*rac*-lactide) Using Tri-*n*-butyltin(IV) *n*-butoxide as Initiator: The Investigation on Stereochemistry and Polymerization Mechanism

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ABSTRACT

The ring-opening polymerization (ROP) of *racemic*-lactide (*rac*-LA) initiated by the synthesized tri-*n*-butyltin(IV) *n*-butoxide ($n\text{Bu}_3\text{SnO}n\text{Bu}$) was investigated for first time by proton- and carbon-13 nuclear magnetic resonance spectroscopy (^1H - and ^{13}C -NMR). The polymerization of *rac*-LA with $n\text{Bu}_3\text{SnO}n\text{Bu}$ and tin(II) octoate ($\text{Sn}(\text{Oct})_2$) was conducted under bulk condition. The synthesized $n\text{Bu}_3\text{SnO}n\text{Bu}$ showed high moisture-oxygen stability and solubility in the molten *rac*-LA. The ^{13}C -NMR spectra of poly(*rac*-LA) obtained from $n\text{Bu}_3\text{SnO}n\text{Bu}$ and $\text{Sn}(\text{Oct})_2$ were slightly different indicating the different stereochemistry of synthesized polymers. The probabilities in forming of a new isotactic dyad (P_i) and the average block length of L-lactyl units (L_i) in poly(*rac*-LA) obtained from $n\text{Bu}_3\text{SnO}n\text{Bu}$ was higher than $\text{Sn}(\text{Oct})_2$. From the results, the preferentially isotactic and heterotactic poly(*rac*-LA) were obtained from $n\text{Bu}_3\text{SnO}n\text{Bu}$ and $\text{Sn}(\text{Oct})_2$, respectively. The polymerization mechanism of *rac*-LA with the synthesized $n\text{Bu}_3\text{SnO}n\text{Bu}$ and $\text{Sn}(\text{Oct})_2$ initiating systems was proposed through the well-known coordination-insertion mechanism.

Keywords: *Racemic*-lactide, stereoselective, ring-opening polymerization, tributyltin alkoxide, Tin(II) octoate

1. INTRODUCTION

Poly(lactides) such as poly(L-lactide) (PLL), poly(D-lactide) (PDL) and poly(lactides) stereocomplex (Sc-PL) have become the most interested biodegradable polyester in the recent years due to their various applications and the increasing of world's environmental

awareness [1-3]. Poly(lactides) are generally synthesized by ring-opening polymerization (ROP) of lactides catalyzed by organometallic compounds [4] and organic catalysts [5]. The tin-containing compounds such as tin(II) alkoxide ($\text{Sn}(\text{OR})_2$) [6] and tin(II) octoate

(Sn(Oct)₂) [7] act as effective initiating systems for producing the high molecular weight polylactide. Most previous works [6, 7] have mainly focused on the synthesis of polylactides with controllable of molecular weight because it is commonly known that molecular weight plays an important role in various properties of polymer. In addition to molecular weight, stereoregularity or tacticity is also a crucial factor that affects the properties of polymer. In the last five years, many researchers have paid the attention to the stereoselective ROP of *racemic*-lactide (*rac*-LA) using various organometallic initiators which contain different metals center such as Zn [8], Al [9, 10], Ti [11, 12], and In [13]. These initiators produce various stereochemistry of poly(*rac*-LA) via solution polymerization.

Zoltowska *et al.* [8] reported about the ROP of *rac*-LA using diethylzinc (Et₂Zn)/gallic acid (GAc) and Et₂Zn/propylgallate (PGAc) as catalytic systems. These systems produce the predominantly isotactic, disyndiotactic or atactic poly(*rac*-LA) depending on the reaction conditions. The stereosequences of poly(*rac*-LA) was analyzed by carbon-13 nuclear magnetic resonance spectroscopy (¹³C-NMR). These catalytic systems not only control molecular weight of polylactide but also stereochemistry. Bian *et al.* [9] studied the stereoselective ROP of *rac*-LA using aluminum chiral anilido-oxazolinone complexes as initiator in the presence of alcohol co-catalyst. These complexes produce poly(*rac*-LA) with stereochemistry ranging from isotactic to heterotactic. Deivasagayam *et al.* [11] used various titanium(IV) *i*-propoxide complexes based on various aminodiols ligands for controlling the stereochemistry of poly(*rac*-LA). The results showed that the *racemic*-aminodiols ligand gave the partially heterotactic poly(*rac*-LA). Furthermore, all titanium(IV) complexes

produce atactic poly(*rac*-LA) via bulk polymerization. Gao *et al.* [14] used the titanium complexes which contained N, N-bidentate phenanthrene derivatives (R = *i*Pr, C₆H₅ and 2,6-*i*Pr₂C₆H₃) to control the stereochemistry of poly(*rac*-LA). Their results demonstrated that the titanium complexes with 2,6-*i*Pr₂C₆H₃ shows the highest stereoselectivity in the ROP of *rac*-LA. Furthermore, this complex produces the partially heterotactic poly(*rac*-LA). Recently, Wang *et al.* [15] studied the stereoselective ROP of *rac*-LA using zinc complexes with tridentate chiral aminophenol proligands. Most of these complexes produce isotactic enriched poly(*rac*-LA).

Interestingly, there is a report about the stereoselective ROP of cyclic esters initiated by organotin initiators. Kricheldorf *et al.* [16] reported the preparation of syndiotactic poly(β -D,L-hydroxybutyrate) (poly(β -D,L-HBu) by the ROP of β -D, L-butyrolactone (BL) initiated by butyltin trimethoxide (BuSn(OMe)₃), dibutyltin dimethoxide (Bu₂Sn(OMe)₂) and tributyltin methoxide (Bu₃SnOMe). They found that the polymerization temperature affects the stereoselectivity of initiator and the completely atactic poly(β -D,L-HBu) was obtained at 100 °C. Nowadays, it is well-known that Sn(Oct)₂ is the most widely used initiating system in the ROP of cyclic esters [1, 7, 17]. Sn(Oct)₂ reacts with alcohol or hydroxyl impurities and reversibly converts to tin(II) mono-alkoxide (OctSnOR) and di-alkoxides (Sn(OR)₂) before initiates polymerization. This conversion results in the formation of octanoic acid (OctH) which can act as the retarder in the ROP of cyclic esters. Although Sn(Oct)₂ produces high polymerization rate and molecular weight of polyester, its stereoselectivity in the bulk ROP of *rac*-LA is still not clear. The reversible reaction of Sn(Oct)₂, OctSnOR and Sn(OR)₂

may cause the difficulty in the stereocontrolled ROP of *rac*-LA. Recently, we successfully synthesized the tri-*n*-butyltin(IV) *n*-butoxide ($n\text{Bu}_3\text{SnO}n\text{Bu}$) that can be utilized as a true initiator in the ROP of ϵ -caprolactone (ϵ -CL) [18] and L-lactide (LL) [19]. This synthesized $n\text{Bu}_3\text{SnO}n\text{Bu}$ initiator has some advantages such as: (i) easy to handle due to its high oxygen-moisture stability, (ii) synthesized from simple synthesis process and (iii) completely soluble in cyclic ester monomers. However, the stereoselectivity of the synthesized $n\text{Bu}_3\text{SnO}n\text{Bu}$ initiator in ROP of lactides has not been described before. Therefore, it is very important for us to investigate and understand the stereocontrolled ability of this initiator in ROP of *rac*-LA. The obtained information will be useful for designing the biodegradable polymeric materials because their microstructure (isotactic, syndiotactic, heterotactic and atactic) certainly affects the biodegradation process and thermal property of poly(*rac*-LA) [20-22].

To this end, we aim to investigate the stereocontrolled ROP of *rac*-LA using our synthesized $n\text{Bu}_3\text{SnO}n\text{Bu}$ initiator by bulk polymerization. We expect that the synthesized $n\text{Bu}_3\text{SnO}n\text{Bu}$ can be used to control the stereochemistry of poly(*rac*-LA) due to: (i) the presence of three butyl groups reduces the coordination ability of lactide monomers with reactive center (Sn-O) which can increase the stereoregularity of the poly(*rac*-LA) and (ii) $n\text{Bu}_3\text{SnO}n\text{Bu}$ initiator contains only one Sn-O active center (mono-functional) that limits the coordination with monomer. We also expect that the synthesized $n\text{Bu}_3\text{SnO}n\text{Bu}$ should show the higher stereoselectivity than the conventional initiating system of $\text{Sn}(\text{Oct})_2$.

Therefore, this work is the first report on the ROP of *rac*-LA using the high steric hindrance $n\text{Bu}_3\text{SnO}n\text{Bu}$ initiator. The

stereoselectivity of $n\text{Bu}_3\text{SnO}n\text{Bu}$ is firstly benchmarked with the conventional initiating system of $\text{Sn}(\text{Oct})_2$ via bulk polymerization using ^1H - and ^{13}C -NMR techniques. Furthermore, the polymerization mechanism of the ROP of *rac*-LA with both initiating systems is also investigated and discussed.

2. MATERIALS AND METHODS

2.1 Materials Preparation

L- and D-lactide (LL and DL) were synthesized from L- and D-lactic acid (LLA and DLA) (Archer Daniels Midland (ADM), 88.0%) and purified by recrystallized three times in dry ethyl acetate (Sigma-Aldrich, 99.5%). The crystallized LL and DL were filtered by vacuum filtration and dried at 55 °C in vacuum oven until constant weight was reached. The purified lactides were kept in dry round bottom flask under vacuum condition before used. *Racemic*-lactide (*rac*-LA) was accurately prepared by mixing LL and DL in the equimolar ratio of 50:50 mol%. Tin(II) octoate ($\text{Sn}(\text{Oct})_2$, Acros Organics, 98%) was purified by vacuum distillation before use. Tri-*n*-butyltin(IV) *n*-butoxide ($n\text{Bu}_3\text{SnO}n\text{Bu}$) was synthesized according to the method described in our previous study [18].

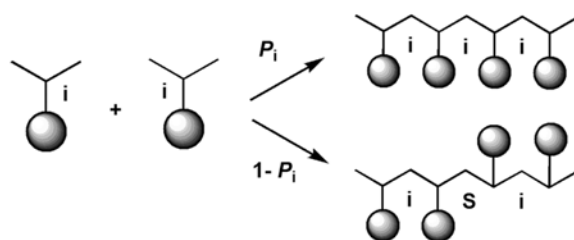
2.2 Synthesis and Characterization of Poly(*rac*-lactide)

Under nitrogen atmosphere in the glove box (LABCONCO), 4 g of *rac*-lactide with 0.1 mol% of $n\text{Bu}_3\text{SnO}n\text{Bu}$ or $\text{Sn}(\text{Oct})_2$ was weighed in dry round bottom flask. The reaction flasks were immersed in pre-heated silicone oil bath at 120 °C for 24 h. The obtained crude poly(*rac*-LA) was purified by dissolving in chloroform and precipitated in cold methanol. The purified poly(*rac*-LA) was dried in vacuum oven at 55 °C until constant weight was reached.

The chemical structure and stereochemistry of poly(*rac*-LA) was analyzed by proton- and carbon-13 nuclear magnetic resonance spectroscopy (400 MHz ¹H- and 100 MHz ¹³C-NMR) using a Bruker Avance 400 NMR spectrophotometer. Chloroform-*d*₁ (CDCl₃, Sigma-Aldrich) with tetramethylsilane (TMS) was used as solvent in NMR analysis.

2.3 Theoretical Consideration

Kasperczyk [22] proposed a method that can be used to identify the stereochemistry of poly(*rac*-LA) based on the probability of generating a new bond by combining isotactic dyads initially preformed *rac*-LA molecules. The chain growing from the ROP of *rac*-LA is illustrated in Scheme 1: *i* and *s* represent as the isotactic and syndiotactic dyads, respectively [23].



Scheme 1. The simple illustration for the growing chain of poly(*rac*-LA) from the ROP of *rac*-LA modified from literature [23].

From Scheme 1, P_i and $1-P_i$ are the probability of forming a new *i*-dyad and *s*-dyad, respectively. This P_i value can be determined from the tetrads and hexads intensities of ¹³C-NMR spectrum as listed in Table 1. When $0 < P_i < 0.5$, the polymerization proceeds through the syndiotactic pair addition. If the P_i is in the range of 0.5-1.0, the polymerization follows isotactic pair

addition. Therefore, the value of P_i can be used to determine the stereochemistry of poly(*rac*-LA) or the stereoselectivity of a given initiating system. From statistical analysis of ¹³C-NMR spectrum, the average length of L-lactyl units (L_i) in poly(*rac*-LA) chain can be determined from Eq. (1) [23].

$$L_i = \frac{2}{1 - P_i} \quad (1)$$

Table 1. The probabilities to form *n*-ades in polymer chain obtained from the ROP of *rac*-LA as a function of P_i [23].

Tetrads	iii	isi	iis	sii	sis	
Ratio	$P_i(P_i+1)/2$	$(1-P_i)/2$	$P_i(1-P_i)/2$	$P_i(1-P_i)/2$	$(1-P_i)^2/2$	
Hexads	iiii	isii, iisii	iiis, iisii, siiii	iiis, siiii, siii	isii	sisis
Ratio	$P_i^2(1+P_i)/2$	$P_i(1-P_i)/2$	$P_i^2(1-P_i)/2$	$P_i(1-P_i)^2/2$	$(1-P_i)^2/2$	$(1-P_i)^3/2$

3. RESULTS AND DISCUSSION

The synthesized tri-*n*-butyltin(IV) *n*-butoxide ($n\text{Bu}_3\text{SnO}n\text{Bu}$) is a colorless liquid and completely soluble in molten *rac*-LA monomer. The identification of $n\text{Bu}_3\text{SnO}n\text{Bu}$ structure has been previously described in our

work [18]. After complete characterization of $n\text{Bu}_3\text{SnO}n\text{Bu}$ structure, it is utilized as initiator for the ROP of *rac*-LA. The ¹H-NMR spectra of the poly(*rac*-LA) synthesized by $n\text{Bu}_3\text{SnO}n\text{Bu}$ and Sn(Oct)₂ systems are illustrated in Figures 1 and 2, respectively.

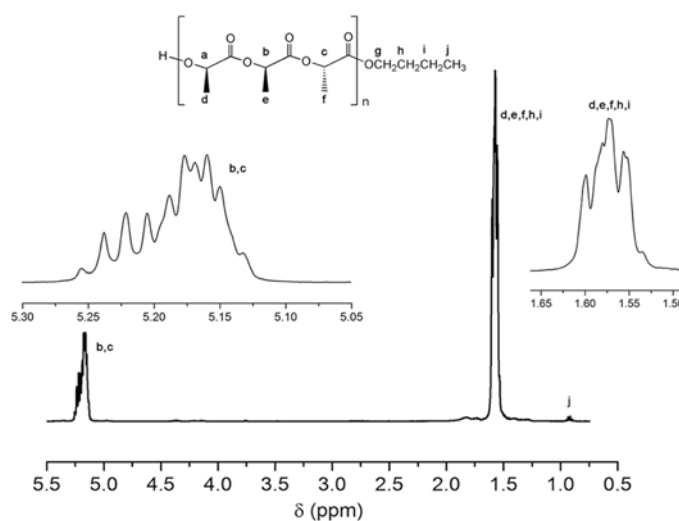


Figure 1. 400 MHz ^1H -NMR spectrum of the poly(*rac*-LA) synthesized from the ROP of *rac*-LA initiated by $n\text{Bu}_3\text{SnOnBu}$.

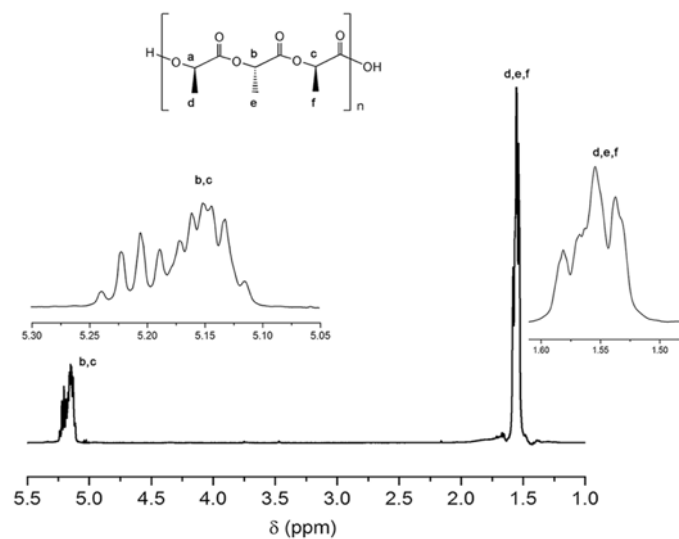


Figure 2. 400 MHz ^1H -NMR spectrum of the poly(*rac*-LA) synthesized from the ROP of *rac*-LA initiated by $\text{Sn}(\text{Oct})_2$.

The spectra of poly(*rac*-LA) obtained from both initiators show the multiplet signal of methine and methyl protons around 5.15 (b, c) and 1.55 ppm (d, e, f, h, i), respectively. Furthermore, the spectrum of poly(*rac*-LA) obtained from $\text{Sn}(\text{Oct})_2$ (Figure 2) shows a higher intensity of the peaks around 5.20 ppm than that of $n\text{Bu}_3\text{SnOnBu}$. This may be contributed from the different stereochemistry of

poly(*rac*-LA) chain. To further investigate the stereochemistry of poly(*rac*-LA), the ^{13}C -NMR is used to support the results obtained from ^1H -NMR. The ^{13}C -NMR spectra of the poly(*rac*-LA) synthesized by $n\text{Bu}_3\text{SnOnBu}$ and $\text{Sn}(\text{Oct})_2$ initiating systems are illustrated in Figures 3 and 4, respectively. Overall, the spectra of both poly(*rac*-LA) show the sharp doublet signal of methyl group (CH_3 -) connected to methine carbon

(-CH-) at 19 ppm (f, g). The sharp doublet signal of methine (-CH-) proton is found at 69 ppm (b,d). Furthermore, the moderate intensity of multiplet signal of carbonyl (-CO-) group is found around 169 ppm (a, c, e). When the spectra were expanded, it is found that they are slightly different. The expanded signal of methine and carbonyl group of the synthesized poly(*rac*-LA) from *n*Bu₃Sn*n*Bu and Sn(Oct)₂ are illustrated in Figures 5 and 6, respectively.

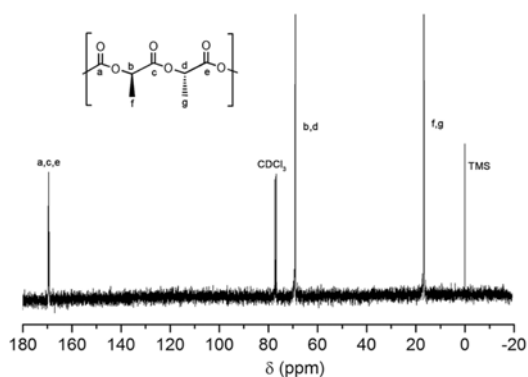


Figure 3. 100 MHz ¹³C-NMR spectrum of the poly(*rac*-LA) synthesized from the ROP of *rac*-LA initiated by *n*Bu₃Sn*n*Bu.

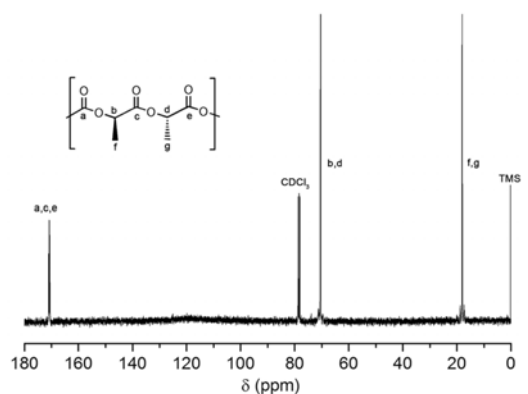


Figure 4. 100 MHz ¹³C-NMR spectrum of the poly(*rac*-LA) synthesized from the ROP of *rac*-LA initiated by Sn(Oct)₂.

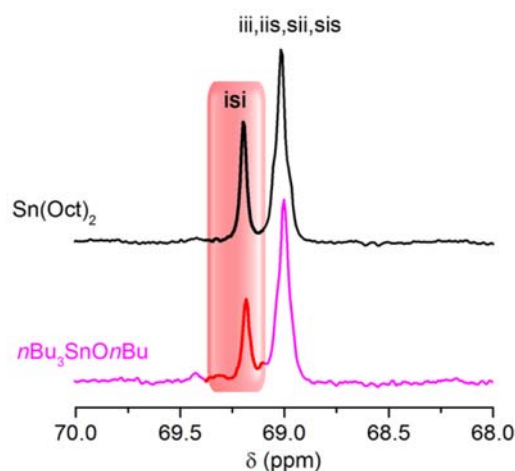


Figure 5. 100 MHz ¹³C-NMR spectra of the expanded methine signal for the poly(*rac*-LA) synthesized from the ROP of *rac*-LA initiated by Sn(Oct)₂ and *n*Bu₃Sn*n*Bu.

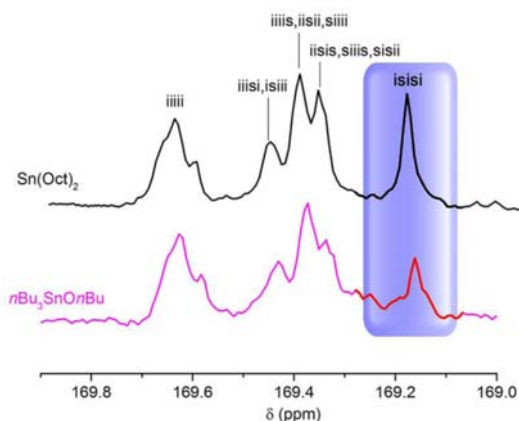


Figure 6. 100 MHz ¹³C-NMR spectra of the expanded carbonyl signal for the poly(*rac*-LA) synthesized from the ROP of *rac*-LA initiated by Sn(Oct)₂ and *n*Bu₃Sn*n*Bu.

The results from Figure 5 show the different relative tetrads intensity of the isi and iii, iis, sii, sis peaks of methine signal of poly(*rac*-LA) obtained from Sn(Oct)₂ and *n*Bu₃Sn*n*Bu initiators. This clearly indicates that the stereoregularity of poly(*rac*-LA)

obtained from both initiating systems is different. The relative intensity of iii, iis, sii, sis to isi peak of poly(*rac*-LA) obtained from $n\text{Bu}_3\text{SnO}n\text{Bu}$ is higher than $\text{Sn}(\text{Oct})_2$.

The tetrads intensities, P_i , L_i and tacticity of the synthesized poly(*rac*-LA) are summarized in Table 2.

Table 2. The tetrads intensities of ^{13}C -NMR spectra of the poly(*rac*-LA) synthesized from the ROP of *rac*-LA initiated by $\text{Sn}(\text{Oct})_2$ and $n\text{Bu}_3\text{SnO}n\text{Bu}$.

Initiators	Tetrads intensities (%)					P_i	L_i	Tacticity
	ssi	sss	isi	iss	sis, iis, sii, iii			
$\text{Sn}(\text{Oct})_2$	-	-	31.2	-	68.8	0.40	3.3	Heterotactic
$n\text{Bu}_3\text{SnO}n\text{Bu}$	-	-	28.6	-	71.4	0.60	5.0	Preferential isotactic

From Table 2, it is found that the $n\text{Bu}_3\text{SnO}n\text{Bu}$ produces the preferentially isotactic poly(*rac*-LA) due to the higher intensity of iii,iis,sii,sis peak than isi peak and the value of $P_i = 0.6$. Furthermore, the $\text{Sn}(\text{Oct})_2$ produces the heterotactic poly(*rac*-LA) because the intensity of the isi and iii,iis,sii,sis peak is not equal. Zoltolska *et al.* [8] reported the expanded methine signal of ^{13}C -NMR spectrum of poly(*rac*-LA) synthesized from diethylzinc (Et_2Zn)/poprylgallate (PGAc) initiating system. They found that this initiating system produces the disyndiotactic poly(*rac*-LA) due to the intensity of the isi and iii,iis,sii,sis peak is very similar which is different from $\text{Sn}(\text{Oct})_2$ found in our work. From tetrads intensity analysis (Table 2), it is found that the values of L_i (determined from Eq. (1)) of poly(*rac*-LA)

obtained from $\text{Sn}(\text{Oct})_2$ and $n\text{Bu}_3\text{SnO}n\text{Bu}$ are 3.3 and 5.0, respectively. This demonstrates that $n\text{Bu}_3\text{SnO}n\text{Bu}$ produces longer isotactic chain length of L-lactyl unit than $\text{Sn}(\text{Oct})_2$.

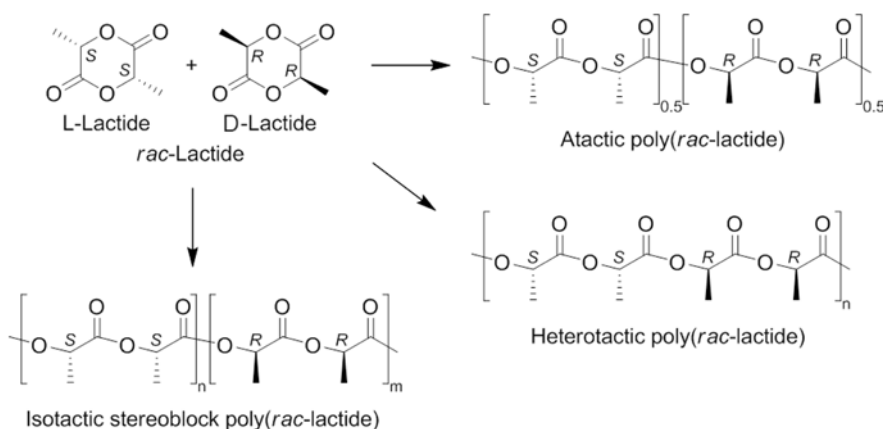
For more detail in the stereochemistry of poly(*rac*-LA), we also analyzed the carbonyl signal of ^{13}C -NMR spectrum in the hexads level. The expanded carbonyl signal of ^{13}C -NMR spectra of the synthesized poly(*rac*-LA) from both initiating systems are displayed in Figure 6. The results show that the relative intensity of iiiii and isisi peak of poly(*rac*-LA) obtained from $\text{Sn}(\text{Oct})_2$ is lower than $n\text{Bu}_3\text{SnO}n\text{Bu}$, suggesting the higher irregularity of L- and D-lactyl unit in poly(*rac*-LA) chain. The hexad intensities, P_i , L_i and tacticity of the synthesized poly(*rac*-LA) are summarized in Table 3.

Table 3. The hexad intensities of ^{13}C -NMR spectra of the poly(*rac*-LA) synthesized from the ROP of *rac*-LA initiated by $\text{Sn}(\text{Oct})_2$ and $n\text{Bu}_3\text{SnO}n\text{Bu}$.

Initiators	Hexads intensities (%)					P_i	L_i	Tacticity
	iiii	isiii, iisii	iiis, iisii, siiii	iiis, siis, sisi	isisi			
$\text{Sn}(\text{Oct})_2$	27.0	13.0	21.0	21.0	18.0	0.40	3.3	Heterotactic
$n\text{Bu}_3\text{SnO}n\text{Bu}$	29.0	15.0	24.0	18.0	14.0	0.49	3.9	Preferential isotactic

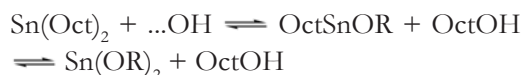
From statistic considerations of both tetrad and hexad intensities of ^{13}C -NMR spectra, it is found that $n\text{Bu}_3\text{SnO}n\text{Bu}$ and $\text{Sn}(\text{Oct})_2$ initiating systems produce the preferential isotactic and heterotactic poly(*rac*-LA), respectively. The results obtained

from Table 3 demonstrate that $n\text{Bu}_3\text{SnO}n\text{Bu}$ produces longer average chain length of L-lactyl units than $\text{Sn}(\text{Oct})_2$ which is similar to that of tetrad intensity analysis (Table 2). The stereochemistry of poly(*rac*-LA) can be simply illustrated in Scheme 2 [24].



Scheme 2. The stereochemistry of poly(*rac*-LA) synthesized from the ROP of *rac*-LA reported in literature [24].

From obtained results, $n\text{Bu}_3\text{SnO}n\text{Bu}$ is found to have higher stereoselectivity than $\text{Sn}(\text{Oct})_2$ that may be related to: (i) the presence of three butyl groups of $n\text{Bu}_3\text{SnO}n\text{Bu}$ reduce the coordination ability of *rac*-LA to reactive Sn-O center resulting in the limitation in the approaching of monomer to active center, (ii) the $\text{Sn}(\text{Oct})_2$ contains more active site than $n\text{Bu}_3\text{SnO}n\text{Bu}$ initiator resulting in the lower selectivity in the ROP of *rac*-LA and (iii) as described in literature [7], $\text{Sn}(\text{Oct})_2$ is not a true initiator because it reacts with hydroxyl-containing impurities to form the tin(II) mono-alkoxide (OctSnOR) or tin(II) di-alkoxide ($\text{Sn}(\text{OR})_2$) active species before initiating polymerization as shown in the following reaction. This reversible reaction causes the difficulty on the control of polymerization, especially stereochemistry of poly(*rac*-LA).



For mechanistic consideration, the ROP mechanism of *rac*-LA with the synthesized $n\text{Bu}_3\text{SnO}n\text{Bu}$ is proposed through the classic coordination-insertion mechanism as depicted in Figure 7. In this mechanism, the polymerization is initiated by the coordination of lactide monomer with reactive center (Sn-O) resulting in the more susceptible of carbonyl carbon of lactide ring. For the next step, the *n*-butoxy group from $n\text{Bu}_3\text{SnO}n\text{Bu}$ attacks the carbonyl carbon of lactide. Then, the opened lactide monomer is inserted into the initiator molecule to form the propagating specie. The new lactide monomers are coordinated and inserted to Sn-O reactive center of propagating specie yielding the poly(*rac*-LA) via the same

mechanism. In the case of $\text{Sn}(\text{Oct})_2$, the water trace and hydroxyl-containing impurities presented in the polymerization mixture can react with $\text{Sn}(\text{Oct})_2$ and converts to OctSnOR

and $\text{Sn}(\text{OR})_2$ before initiates polymerization [4]. After forming of the true active species, the ROP of *rac*-LA is also proceeded through the same mechanism to $n\text{Bu}_3\text{SnO}n\text{Bu}$.

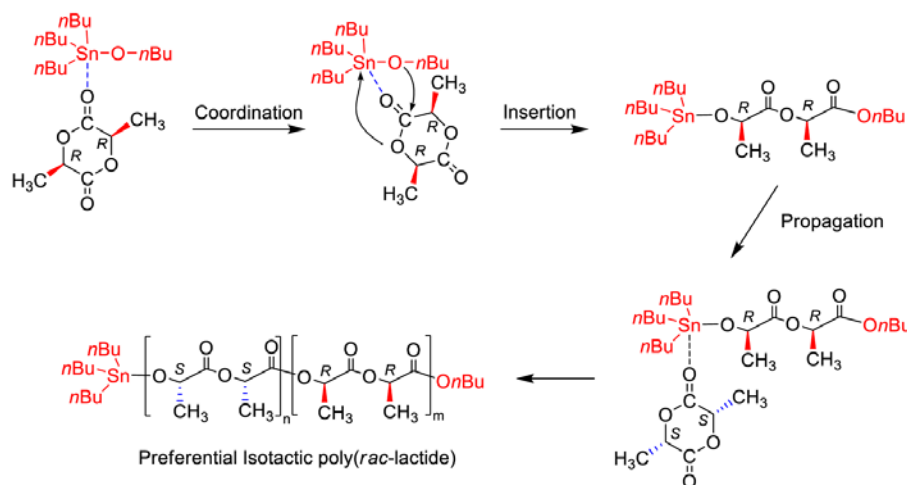


Figure 7. The coordination-insertion mechanism for the ROP of *rac*-LA initiated by $n\text{Bu}_3\text{SnO}n\text{Bu}$.

4. CONCLUSIONS

The stereochemistry of poly(*rac*-LA) obtained from the bulk ROP of *rac*-LA with the synthesized $n\text{Bu}_3\text{SnO}n\text{Bu}$ initiator was successfully investigated by ^1H - and ^{13}C -NMR techniques. The stereoselectivity of $n\text{Bu}_3\text{SnO}n\text{Bu}$ was compared with the $\text{Sn}(\text{Oct})_2$ initiating system. The spectroscopic and statistical analysis on the ^{13}C -NMR spectra demonstrated that the synthesized $n\text{Bu}_3\text{SnO}n\text{Bu}$ initiator produced the preferential isotactic poly(*rac*-LA) with P_i values of 0.60 (methine) and 0.49 (carbonyl) whereas $\text{Sn}(\text{Oct})_2$ produced the heterotactic poly(*rac*-LA) with P_i values of 0.40 (methine) and 0.40 (carbonyl), respectively. Furthermore, the average isotactic block length of L-lactyl units in poly(*rac*-LA) obtained from $n\text{Bu}_3\text{SnO}n\text{Bu}$ initiator was longer than that of $\text{Sn}(\text{Oct})_2$. Therefore, our synthesized $n\text{Bu}_3\text{SnO}n\text{Bu}$ initiator has higher stereoselectivity in the ROP of *rac*-LA than

the conventional $\text{Sn}(\text{Oct})_2$ initiating system. The results obtained from this work can be applied to describe the stereoselectivity of other initiators in the ROP of *rac*-LA or *meso*-lactide (*meso*-LA).

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