

รายงานวิจัยฉบับสมบูรณ์

โครงการ การสังเคราะห์โครงสร้างแบบวงของพอลิเอสเทอร์ที่ย่อยสลายได้ในธรรมชาติโดยใช้สารประกอบของโลหะกับลิแกนด์

โดย

ผศ. ดร. คัมภีร์ พรหมพราย
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มหาวิทยาลัยมหิดล

พฤษภาคม 2556

สัญญาเลขที่ RMU5380030

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

สำนักงานคณะกรรมการการอุดมศึกษา และมหาวิทยาลัยมหิดล

กิตติกรรมประกาศ

ผู้วิจัยขอขอบคุณสำนักงานกองทุนสนับสนุนการวิจัย สำนักงานคณะกรรมการการอุดมศึกษา และมหาวิทยาลัยมหิดลสำหรับเงินทุนเพิ่มขีดความสามารถด้านการวิจัยของอาจารย์รุ่นกลางในสถาบันอุดมศึกษา 2553 ที่ทำให้เกิดงานวิจัยชิ้นนี้และทำให้งานวิจัยสำเร็จลุล่วงไปได้ด้วยดี นอกจากนี้ผู้วิจัยขอขอบคุณศูนย์ความเป็นเลิศด้านนวัตกรรมทางเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล สำหรับเงินทุนนักศึกษาและทุนวิจัยส่วนหนึ่ง ขอบคุณบุคลากร ภาควิชาเคมี และ คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล สำหรับความอนุเคราะห์เรื่องวัสดุ อุปกรณ์ และเครื่องมือต่างๆที่ใช้ในงานวิจัย

บทคัดย่อ

รหัสโครงการ: RMU5380030

ชื่อโครงการ: การสังเคราะห์โครงสร้างแบบวงของพอลิเอสเทอร์ที่ย่อยสลายได้ในธรรมชาติโดยใช้สารประกอบของโลหะกับลิแกนด์

ชื่อนักวิจัย: ผู้ช่วยศาสตราจารย์ ดร. คัมภีร์ พรหมพราย
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งานวิจัยชิ้นนี้เป็นการออกแบบตัวเร่งปฏิกิริยาที่มีโลหะหมู่ 14 ได้แก่ เจอมาเนียม ดีบุก และตะกั่วเป็นส่วนประกอบเพื่อใช้เป็นตัวเร่งปฏิกิริยาในปฏิกิริยาพอลิเมอร์ไรเซชันในการสังเคราะห์พอลิเอสเทอร์แบบวงที่ย่อยสลายได้ในธรรมชาติ ได้แก่ พอลิแลกไทด์และพอลิแอบสิลอนคาโปรแลกโทน โดยใช้หลักการของ single-site catalysis ตัวเร่งปฏิกิริยาที่ออกแบบมีโครงสร้างอยู่ในรูป L_2M โดยที่ L คือลิแกนด์กลุ่ม amidine และ salicylaldimine และ M คือโลหะ Ge(II), Sn(II) และ Pb(II) จากการทดลองเบื้องต้นพบว่าสารประกอบโลหะดีบุกมีประสิทธิภาพดีที่สุด ดังนั้นจึงได้ทำการสังเคราะห์สารประกอบโลหะดีบุกมากกว่า 10 ชนิดจากปฏิกิริยาระหว่างลิแกนด์ที่ต้องการกับ $Sn[N(SiMe_3)_2]_2$ ลิแกนด์ได้ถูกออกแบบให้มีความเกะกะ (เช่น R = H, Me, Et, ^{i}Pr) และคุณสมบัติการให้หรือรับอิเล็กตรอนแตกต่างกัน (เช่น R' = OMe, CF_3) พบว่าลิแกนด์ที่มีหมู่แทนที่ที่ให้อิเล็กตรอนจะเป็นตัวเร่งปฏิกิริยาที่ดีในปฏิกิริยาพอลิเมอไรเซชันของ ในขณะที่หมู่แทนที่ที่เกะกะจะยับยั้งปฏิกิริยาในปฏิกิริยาพอลิเมอไรเซชันของแลกไทด์แต่จะเร่งปฏิกิริยาได้ดีในปฏิกิริยาพอลิเมอไรเซชันของแอบสิลอนคาโปรแลกโทน ทั้งนี้พอลิเมอร์ที่สังเคราะห์ได้มีโครงสร้างเป็นแบบวงจริงโดยการยืนยันด้วยเทคนิค gel-permeation chromatography (GPC) coupled with light-scattering detector and viscometer อย่างไรก็ตามการทำโคพอลิเมอร์ระหว่างมอนอเมอร์ต่างชนิดยังพบปัญหาในการยืนยันโครงสร้างแบบเส้นตรงหรือแบบวงที่แน่นอนถึงแม้ว่าจะได้พอลิเมอร์ที่ต้องการโดยใช้ตัวเร่งปฏิกิริยาที่สังเคราะห์ได้

คำหลัก: ε-caprolactone, catalysis, polymerization, aluminium catalysts

Abstract

Project Code: RMU5380030

Project Title: Synthesis of Novel Cyclic Structure of Biodegradable Polyesters using Ligated Metal Complexes

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Project Period: June 2010 – May 2013

Group 14 (Ge, Sn, Pb) metal complexes have been synthesized and used as active catalysts for the polymerization of cyclic esters leading to cyclic polyesters using the concept of single-site catalysis. The catalysts are in the form L_2M where L are amidine and salicylaldimine ligands and M are Ge(II), Sn(II) and Pb(II). Preliminary results have shown that Sn(II) complexes were the most active. Thus, more than 10 tin(II) complexes were synthesized from reactions of the corresponding ligands with $Sn[N(SiMe_3)_2]_2$. The ligands were modified to have different steric (e.g. R= H, Me, Et, ^{i}Pr) and electronic contributions (e.g. R' = OMe, CF_3) to tailor the relationship between catalyst structure and activity. In general, electron donating groups were found to accelerate the polymerization rate. However, higher steric hindrance suppressed the polymerization rate in the polymerization of lactide while rate enhancement was found in the polymerization of ε-caprolactone. Both polylactide and poly(ε-caprolactone) were found to have cyclic structure using gel-permeation chromatography (GPC) coupled with light-scattering detector and viscometer. Copolymerizations between different monomers were successful but proved to be problematic in term of linear/cyclic characterizations.

Keywords: ε-caprolactone, lactide, catalysis, polymerization, cyclic polyester

สารบัญ

1. บทนำ

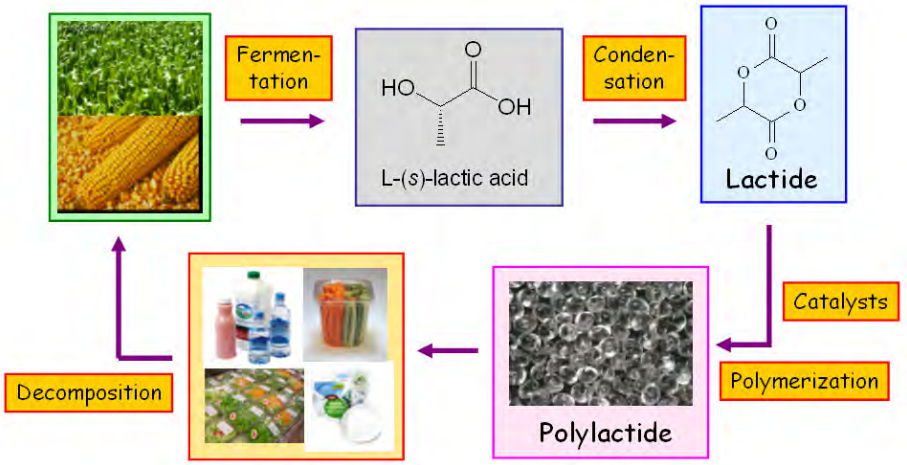
พอลิเมอร์ หรือ พลาสติก จัดว่าเป็นสิ่งที่มีความสำคัญต่อการดำรงชีวิตของคนเราอย่างมากทั้งทางตรงและทางอ้อม เนื่องจากพอลิเมอร์สามารถถูกนำมาประยุกต์ใช้งานได้ในหลายๆด้าน ทำให้อุตสาหกรรมพอลิเมอร์เติบโตอย่างรวดเร็ว จึงเกิดปัญหาที่ตามมาอย่างหลีกเลี่ยงไม่ได้คือปัญหาเรื่องขยะมูลฝอยของผลิตภัณฑ์ต่างๆที่ทำมาจากพลาสติก หากทิ้งขยะเหล่านี้ลงสู่ธรรมชาติแล้วจะไม่ย่อยสลายและกลายเป็นปัญหาสิ่งแวดล้อมไปอีกนับร้อยๆปี การแก้ปัญหาที่ตรงจุดวิธีหนึ่งคือการเปลี่ยนมาใช้พอลิเมอร์ที่ย่อยสลายได้ในธรรมชาติอย่างปลอดภัย ดังนั้นการศึกษาพอลิเมอร์ที่มีคุณสมบัติย่อยสลายได้ในธรรมชาติที่สามารถนำมาใช้แทนที่พอลิเมอร์ที่ใช้กันอยู่ในปัจจุบันจึงเป็นความจำเป็นเร่งด่วน

พอลิเมอร์ที่ย่อยสลายได้นั้นมีอยู่ด้วยกันหลายชนิด เช่น polylactide, poly(Ɛ-caprolactone), polyhydroxyalkanoates, polyglycolide เป็นต้น โดยพอลิแลคไทด์ (polylactide) ได้รับการกล่าวถึงอย่างมากเนื่องจาก

1.พอลิแลคไทด์เป็นพอลิเอสเทอร์ (polyester) ที่มีองค์ประกอบย่อยคือ lactic acid ($HOC(CH_3)HCOOH$) ซึ่งได้มาจากการหมักแป้ง เช่น ข้าวโพด มันสำปะหลังและวัตถุดิบทางการเกษตรซึ่งประเทศไทยมีมาก จึงสังเคราะห์พอลิแลคไทด์ได้เรื่อยๆไม่มีวันหมดซึ่งแตกต่างจากพอลิเมอร์บางตัว เช่น polyethylene, polypropylene ที่ต้องพึ่งพาอุตสาหกรรมปิโตรเคมีที่อาจจะหมดไปได้ในอนาคตอันใกล้

2.จากการศึกษาความแข็งแรงของพอลิแลคไทด์พบว่าเมื่อผ่านกระบวนการผลิตที่ดีแล้วจะมีคุณสมบัติในด้านความแข็งแรงและความทนทานเทียบเท่ากับ polyethylene หรือ polypropylene ที่ใช้ในถุงพลาสติกและวัสดุบรรจุผลิตภัณฑ์ ดังนั้นการใช้พอลิแลคไทด์แทนพอลิเมอร์เหล่านี้จึงกระทำได้

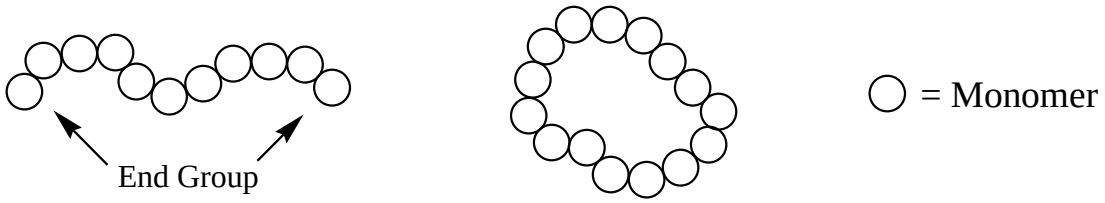
3.การย่อยสลายได้ในธรรมชาติของพอลิแลคไทด์นับว่าเป็นส่วนที่สำคัญที่สุด เมื่อย่อยสลายในธรรมชาติจะได้ lactic acid ซึ่งเป็นสารที่ปลอดภัยไม่เป็นอันตรายต่อมนุษย์และสิ่งแวดล้อม จะเห็นได้จากการที่ร่างกายคนผลิต lactic acid ขึ้นเวลาออกกำลังกายซึ่งทำให้เกิดการเมื่อยล้า แต่จะไม่เป็นอันตรายเพราะร่างกายสามารถกำจัดกรดนี้ได้เอง ทำให้สามารถนำเอาพอลิแลคไทด์มาใช้ในร่างกายคนได้อย่างปลอดภัย จึงมีการนำเอาพอลิแลคไทด์มาใช้ในทางการแพทย์อย่างแพร่หลาย เช่น ใช้เป็นวัสดุดามกระดูก ใช้เป็นด้ายเย็บแผลในร่างกายที่จะค่อยๆสลายไปตามกาลเวลาโดยไม่จำเป็นต้องเอาด้ายเย็บแผลออก หรือ ใช้เป็นตัวนำส่งยาในร่างกายเป็นต้น การย่อยสลาย lactic acid โดยแบคทีเรียท้ายที่สุดแล้วจะได้ CO_2 ซึ่งจะกลายเป็นสารตั้งต้นในการบวนการ photosynthesis ของพืชต่อไป วงจรชีวิตของพอลิแลคไทด์จึงเป็นมิตรต่อสิ่งแวดล้อมอย่างมาก วงจรชีวิตของพอลิแลคไทด์ได้ถูกแสดงไว้ในรูปที่ 1



รูปที่ 1 วงจรชีวิตของพอลิแลคไทด์

อย่างไรก็ตามนักวิทยาศาสตร์เพิ่งจะเริ่มทำงานวิจัยทางด้านการผลิตพอลิแลคไทด์อย่างจริงจังเมื่อประมาณ 15 ปีที่ผ่านมา ทำให้องค์ความรู้ในการผลิตพอลิแลคไทด์นั้นยังจำกัดและยังไม่มีพัฒนาการมากนักหากเทียบกับพอลิเมอร์ตัวอื่นๆ การผลิตพอลิแลคไทด์จะต้องมีการเติมตัวเร่งปฏิกิริยา (catalyst) เพื่อเปลี่ยนแลคไทด์ (lactide, a dimer of 2 lactic acid molecules) ให้กลายเป็นพอลิแลคไทด์ ปฏิกิริยาจะเร็วหรือช้า หรือว่าพอลิแลคไทด์จะออกมามีคุณสมบัติเช่นใดนั้นจะขึ้นอยู่กับชนิดและปริมาณของตัวเร่งปฏิกิริยาทั้งสิ้น ดังนั้นการพัฒนาตัวเร่งปฏิกิริยาให้มีประสิทธิภาพสูงสุดจึงถือว่าเป็นส่วนที่สำคัญที่สุดในการผลิตพอลิเมอร์ทุกชนิด

จากงานวิจัยที่ผ่านมาพบว่าพอลิเมอร์ส่วนใหญ่มีโครงสร้างพื้นฐานเป็นแบบเส้นตรง (linear) ดังแสดงในรูปที่ 2ก เมื่อนำเอาโครงสร้างแบบเส้นตรงมาต่อกันในแบบต่างๆก็จะได้โครงสร้างอื่นๆอีกได้แก่ branched, comb-like, star-like, dendritic, cross-linked และ hyperbranched นอกจากโครงสร้างที่ได้กล่าวไปแล้วยังมีพอลิเมอร์อีกโครงสร้างหนึ่งที่เพิ่งถูกสังเคราะห์ขึ้นเมื่อไม่นานมานี้ คือ โครงสร้างแบบวง ดังแสดงในรูปที่ 2ข โครงสร้างแบบวงจะแตกต่างจากโครงสร้างแบบเส้นตรงคือสายพอลิเมอร์จะม้วนเป็นวงและไม่มีหมู่ปลายสาย (end group) เหมือนในแบบเส้นตรงทั่วไป



ก) โครงสร้างแบบเส้นตรง ข) โครงสร้างแบบวง

รูปที่ 2 โครงสร้างของพอลิเมอร์ ก)แบบเส้นตรง และ ข) แบบวง

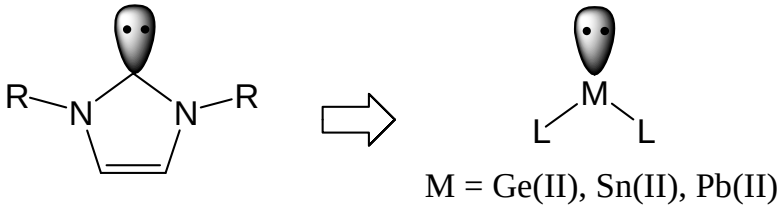
โครงสร้างแบบวงของพอลิเมอร์มีคุณสมบัติพิเศษหลายด้านที่แตกต่างจากโครงสร้างแบบเส้นตรง เช่น การไม่มี end group จึงทำให้พอลิเมอร์แบบวงไม่มี functional group ที่ปลายสายซึ่งอาจไปทำปฏิกิริยาที่ไม่ต้องการกับ substrate ได้ โครงสร้างแบบวงนั้นมีการจัดเรียงตัวในผลึกที่แตกต่างจากแบบเส้นตรงส่งผลให้ viscosity, viscoelasticity รวมไปถึงการย่อยสลายของพอลิเมอร์แตกต่างไปจากแบบเส้นตรง มีการรายงานว่าโครงสร้างแบบวงทนความร้อนได้ดีกว่าแบบเส้นตรงเนื่องจากโครงสร้างแบบวงมี entropy ที่ต่ำกว่าส่งผลให้ melting temperature (T_m) ของโครงสร้างแบบวงสูงกว่าแบบเส้นตรง (จาก $\Delta S = \Delta H/T$ เมื่อ $\Delta H_{melting}$ จากการทดลองของแบบวงและเส้นตรงมีค่าใกล้เคียงกัน) มีผู้ศึกษาพบว่าหากนำเอาพอลิเมอร์แบบวงไปทำเป็นตัวนำส่งยาจะทำให้ตัวยาอยู่ในกระแสเลือดได้นานขึ้นกว่าการใช้พอลิเมอร์แบบเส้น เป็นต้น

ถึงแม้ว่าพอลิเมอร์แบบวงจะมีคุณสมบัติหลายอย่างที่ดีกว่าแบบเส้นตรง การศึกษาคุณสมบัติและการนำไปใช้ประโยชน์ของพอลิเมอร์แบบวงยังอยู่ในวงจำกัดเท่านั้น ปัญหาที่สำคัญที่สุดคือนักวิทยาศาสตร์ยังไม่มีวิธีการสังเคราะห์พอลิเมอร์แบบวงที่มีประสิทธิภาพและปริมาณมากพอ การสังเคราะห์พอลิเมอร์ให้มีโครงสร้างแบบวงมีความยากอยู่ที่การออกแบบตัวเร่งปฏิกิริยาให้สามารถผูกสายพอลิเมอร์ติดกันเป็นวงและได้ร้อยละของผลิตภัณฑ์สูง มิฉะนั้นผลิตภัณฑ์ที่ได้ก็จะเป็นเพียง by-product หรือเป็นเพียงพอลิเมอร์แบบเส้นตรงธรรมดาๆเท่านั้น จากงานวิจัยที่ผ่านมามีการตีพิมพ์วิธีการสังเคราะห์พอลิเมอร์แบบวงที่มีประสิทธิภาพเพียง 2-3 ฉบับเท่านั้น ได้แก่การสังเคราะห์ cyclic polyethylene และ cyclic polylactide เพราะฉะนั้นการศึกษาหาวิธีการสังเคราะห์พอลิเมอร์แบบวงที่มีประสิทธิภาพจึงมีความจำเป็นอย่างมากต่อการพัฒนาและการนำพอลิเมอร์แบบวงไปใช้ประโยชน์

ข้อเสนอโครงการวิจัยที่เสนอมาจะเป็นการพัฒนาตัวเร่งปฏิกิริยาให้มีประสิทธิภาพสูง โดยมีโลหะหมู่ 14 เป็นองค์ประกอบที่สำคัญเพื่อใช้ในการผลิตพอลิเอสเทอร์ ซึ่งจะเน้นที่ พอลิแลคไทด์และพอลิคาโปรแลคโทน ให้มีโครงสร้างเป็นแบบวง โดยจะนำเอาความคิดทางด้าน single-site catalysis (อธิบายเพิ่มเติมในหัวข้อต่อไป) ซึ่งผู้ทำวิจัยมีประสบการณ์มากว่า 10 ปี มาประยุกต์ใช้ ผู้วิจัยจะทำการเปลี่ยนแปลงโครงสร้างของตัวเร่งปฏิกิริยาอย่างมีหลักเกณฑ์และศึกษาถึงผลกระทบต่ออัตราการเกิดปฏิกิริยา งานวิจัยนี้จะทำให้เข้าใจถึงความสัมพันธ์ระหว่างโครงสร้างของตัวเร่งปฏิกิริยากับอัตราการเกิดปฏิกิริยาและโครงสร้างของพอลิเอสเทอร์ในด้าน steric และ electronic effects ซึ่งเป็นพื้นฐานที่สำคัญในการพัฒนาตัวเร่งปฏิกิริยา นอกจากนี้ความรู้ที่ได้ยังสามารถนำมาประยุกต์ใช้กับการพัฒนาตัวเร่งปฏิกิริยาสำหรับปฏิกิริยาทางเคมี หรือพอลิเมอร์ชนิดอื่นที่มีคุณค่าในทางอุตสาหกรรมและการแพทย์ เช่น polyhydroxyalkanoate, polystyrene, polycarbonate ให้มีโครงสร้างเป็นแบบวงได้

2. วิธีการทดลอง

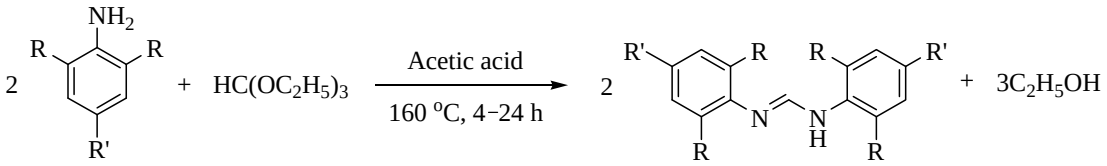
เพื่อให้ได้พอลิเมอร์แบบวง ตัวเร่งปฏิกิริยาจะต้องมี lone-pair functionality คล้ายๆกับใน carbene ซึ่งพิจารณาจากตารางธาตุแล้ว โลหะที่ควรจะมีคุณสมบัติคล้ายกับ carbene ได้แก่โลหะหมู่ 14 กลุ่ม Ge(II), Sn(II) และ Pb(II) โดยโลหะเหล่านี้อยู่ทางด้านล่างของตารางธาตุจึงเกิด Inert Pair Effect ทำให้ oxidation state ที่เป็น +2 เสถียร กล่าวคือโลหะจะเหลือ 2 electron จึงสามารถทำหน้าที่คล้ายกับ carbene ในการเกิดปฏิกิริยา polymerization ดังแสดงในรูปที่ 3 และผลิตพอลิเมอร์แบบวงได้เช่นเดียวกัน และเนื่องจากสารประกอบของโลหะกลุ่มนี้โดยเฉพาะ tin(II) octanoate ($Sn(Oct)_2$) ทนความร้อนได้สูงมากกว่า 150 องศาเซลเซียส จึงเป็นข้อดีที่จะใช้ตัวเร่งปฏิกิริยากลุ่มนี้ที่อุณหภูมิสูงได้ เนื่องจาก L-lactide มีจุดหลอมเหลวประมาณ 100 องศาเซลเซียส แสดงว่าถ้าทำปฏิกิริยา polymerization ของแลคไทด์ที่อุณหภูมิ 120 องศาเซลเซียสแล้วแลคไทด์ก็จะกลายเป็นของเหลวและทำปฏิกิริยากับตัวเร่งปฏิกิริยาโดยที่ไม่ต้องใช้ตัวทำละลาย วิธีนี้เรียกว่า melt polymerization หลังจากปฏิกิริยา melt polymerization สิ้นสุดลงจะได้พอลิเมอร์ที่พร้อมนำไปใช้งานหรือศึกษาต่อได้โดยไม่จำเป็นต้องกำจัดเอาตัวทำละลายออกก่อนเหมือนในกรณีของการใช้ NHCs เป็นตัวเร่งปฏิกิริยา



รูปที่ 3 การเปลี่ยน active atom จาก C เป็น Ge(II), Sn(II) และ Pb(II)

วิธีทำการทดลองได้ถูกแบ่งออกเป็นขั้นตอนโดยย่อได้ดังต่อไปนี้

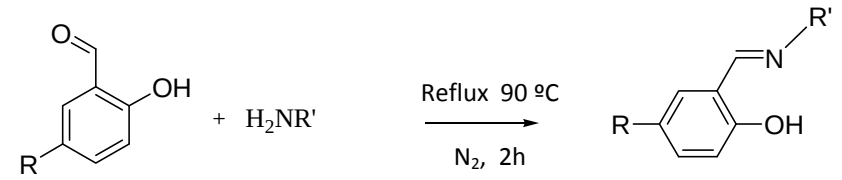
2.1 การสังเคราะห์ ligand ตัวอย่าง ligand ที่จะนำมาสร้างสารประกอบกับโลหะแสดงไว้ในรูปที่ 4 ในงานวิจัยนี้ได้เน้นไปที่ลิแกนด์กลุ่ม amidine และ salicylaldimine เนื่องจากเป็นสารอินทรีย์ที่สังเคราะห์ได้ง่ายและสะดวกรวดเร็วจากปฏิกิริยาเคมีอินทรีย์ทั่วไป นอกจากนี้การออกแบบลิแกนด์ให้มีคุณสมบัติความเกะกะและการให้และรับอิเล็กตรอนที่แตกต่างกันนั้นทำได้ง่าย ทำให้ผู้วิจัยสามารถศึกษาผลกระทบของหมู่แทนที่เหล่านี้ที่มีต่ออัตราเร็วของปฏิกิริยาได้โดยง่ายและเป็นระบบ ลิแกนด์ที่ศึกษาในงานวิจัยได้ถูกแสดงในรูปที่ 4 และ 5



Amidine ligands (**1a**–**e**)

1a; R = H, R' = H
1b; R = CH_3, R' = H
1c; R = ^{i}Pr, R' = H
1d; R = H, R' = OCH_3
1e; R = H, R' = CF_3

รูปที่ 4 การสังเคราะห์ลิแกนด์กลุ่ม amidine



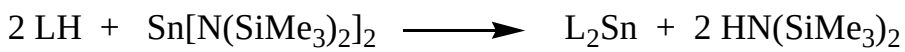
Salicylaldehyde

Salicylaldimine ligand

3a; R = H , R' = Ph
3b; R = H , R' = *o*-2,6-$(CH_3)_2C_6H_3$
3c; R = H , R' = *o*-2,6-$(iPr)_2C_6H_3$
3d; R = H , R' = *p*-$OCH_3C_6H_4$
3e; R = H , R' = *p*-$CF_3C_6H_4$
3f; R = Br , R' = *o*-2,6-$(iPr)_2C_6H_3$
3g; R = H , R' = CH_3
3h; R = H , R' = *t*-Bu

รูปที่ 5 การสังเคราะห์ลิแกนด์กลุ่ม salicylaldimine

2.2 การเตรียมตัวเร่งปฏิกิริยา จากการทดลองเบื้องต้นพบว่าตัวเร่งปฏิกิริยาที่มีโลหะเป็น Sn(II) จะมีประสิทธิภาพในการเป็นตัวเร่งปฏิกิริยาดีที่สุด การทดลองจึงจำเพาะไปที่การใช้งานโลหะ Sn(II) เป็นหลัก การสังเคราะห์ตัวเร่งปฏิกิริยาทำได้โดยการนำ ligand (เขียนอย่างย่อว่า LH) ที่สังเคราะห์ได้ในข้อ 2 มาทำปฏิกิริยากับสารประกอบ $Sn[N(SiMe_3)_2]_2$ จะได้ตัวเร่งปฏิกิริยาตามต้องการในรูป L_2Sn ดังแสดงในสมการ



จากนั้นได้ทำการวิเคราะห์โครงสร้างของตัวเร่งปฏิกิริยาด้วย Nuclear Magnetic Resonance (NMR), Elemental Analysis และ X-ray Crystallography และเนื่องจากสารประกอบเหล่านี้ทำปฏิกิริยาอย่างรวดเร็วกับน้ำและอากาศ การทำงานจึงต้องทำภายใต้บรรยากาศก๊าซเฉื่อย เช่น Ar หรือ N_2 ภายใน glove box ที่มีอยู่ในห้องทดลองของผู้วิจัย

2.3 การศึกษาผลกระทบของหมู่แทนที่ต่ออัตราเร็วของปฏิกิริยา polymerization

เมื่อพิจารณา ligand ในรูปที่ 4 และ 5 จะเห็นได้ว่านอกจากการสังเคราะห์ ligand จะทำได้ง่ายแล้ว ยังสามารถทำการเปลี่ยนแปลงหมู่แทนที่ที่ตำแหน่งต่างๆได้ง่ายอีกด้วย โดยเริ่มต้นจากสารตั้งต้นที่เหมาะสม ทั้งนี้การเปลี่ยนแปลงหมู่แทนที่ต่างๆจึงถูกปรับเปลี่ยนอย่างมีระบบเพื่อศึกษาผลกระทบต่ออัตราเร็วของการเกิดปฏิกิริยา polymerization โดยมีทั้งหมู่แทนที่ที่เกะกะ เช่น H, Me, Et, ^{i}Pr, และ ^{t}Bu เพื่อศึกษาถึงผลของ steric effect และหมู่แทนที่ที่สามารภให้หรือรับอิเล็กตรอนได้แก่ H, OMe และ CF_3 เพื่อศึกษาถึงผลของ electronic effect โดยที่ไม่มีผลกระทบต่อ steric ของตัวเร่งปฏิกิริยาเนื่องจากอยู่ในตำแหน่งที่ไกลออกไป การปรับปรุงตัวเร่งปฏิกิริยาให้มีประสิทธิภาพสูงสุดสามารถทำได้ในลักษณะนี้โดยการเปลี่ยนหมู่แทนที่อย่างมีระบบ ผลของ steric และ electronic effect ของ ligand ทำให้ตัวเร่งปฏิกิริยาที่ได้มีอัตราเร็วที่แตกต่างกันออกไป จากข้อมูลนี้ทำให้เราทราบถึงปัจจัยที่จะทำให้ตัวเร่งปฏิกิริยามีประสิทธิภาพสูงขึ้นจึงเป็นประโยชน์อย่างมากในการออกแบบตัวเร่งปฏิกิริยาในรุ่นต่อๆไป

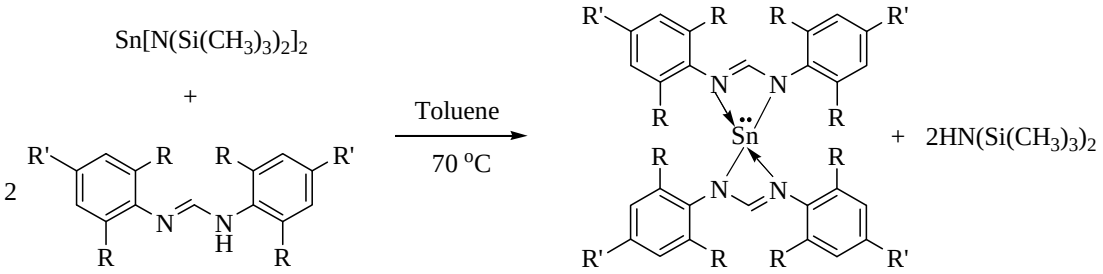
2.4 การศึกษาการสังเคราะห์พอลิเมอร์แบบวง หลังจากที่สังเคราะห์ตัวเร่งปฏิกิริยาได้แล้ว ผู้วิจัยได้ทำการศึกษาถึงความเร็วในการเป็นตัวเร่งปฏิกิริยา polymerization และ copolymerization ของ lactide และ ε-caprolactone โดยใช้อัตราส่วน monomer ต่อตัวเร่งปฏิกิริยาค่าต่างๆ เช่น 100:1 500:1 1000:1 เป็นต้น แล้วให้ความร้อนที่อุณหภูมิ 120°C เมื่อปฏิกิริยา polymerization สิ้นสุดลงจะได้พอลิเมอร์ตามต้องการ แล้วนำมาเปรียบเทียบกับตัวเร่งปฏิกิริยาตัวอื่นๆที่มีการรายงานไว้ เนื่องจากการเปลี่ยนแปลงโครงสร้างของตัวเร่งปฏิกิริยาทำอย่างเป็นระบบ การติดตามผลของการเปลี่ยนแปลงจึงเป็นไปได้ง่าย พอลิเมอร์ที่สังเคราะห์ได้ได้รับการยืนยันโครงสร้างด้วยเทคนิค NMR, Differential Scanning Calorimetry (DSC), Mass Spectrometry และ Gel Permeation Chromatography (GPC) และได้ทำการพิสูจน์โครงสร้างของพอลิเมอร์ว่าเป็นแบบวงจริง

3. ผลการทดลอง

The result section is divided into two parts depending on the ligand systems as 1) amidine ligands and 2) salicylaldimine ligands.

3.1) Amidine ligand system

All amidine ligands, *(E)-N,N′*-diphenylformamidine (**1a**), *(E)-N,N′-bis*(2,6-dimethylphenyl)formamidine (**1b**), *(E)-N,N′-bis*(2,6-diisopropylphenyl) formamidine (**1c**), *(E)-N,N′-bis*(4-methoxyphenyl)formamidine (**1d**), and *(E)-N,N′-bis*(4-(trifluoromethyl)phenyl)formamidine (**1e**) were synthesized according to literature procedures starting from triethylorthoformate and the corresponding anilines as shown in Figure 4.[1] The catalysts were synthesized from the reaction of the corresponding ligands with $Sn[N(SiMe_3)_2]_2$ according to Figure 6.



Amidine ligands (**1a**–**e**) Amidinate tin(II) complexes (**2a**–**e**)

1a; R = H, R' = H
1b; R = CH_3, R' = H
1c; R = ^{i}Pr, R' = H
1d; R = H, R' = OCH_3
1e; R = H, R' = CF_3

2a; R = H, R' = H
2b; R = CH_3, R' = H
2c; R = ^{i}Pr, R' = H
2d; R = H, R' = OCH_3
2e; R = H, R' = CF_3

Figure 6 Synthesis of catalysts **2a**-**e** based on amidine ligand system.

$Sn[N(Si(CH_3)_3)_2]_2$ was synthesized according to literature procedure[2] and used to synthesize amidinate tin(II) complexes. The following representative procedure was for complex **2a**. Other tin(II) complexes were synthesized similarly.

To a mixture of ligand **1a** (0.66 g, 3.36 mmol) and $Sn[N(Si(CH_3)_3)_2]_2$ (0.74 g, 1.68 mmol) was added toluene (20 mL) and allowed to stir at 70 °C overnight. After solvent removal, the product was obtained as a pale yellow microcrystalline (0.86 g, 1.68 mmol, >99%).

$[(C_6H_5)N)_2CH]_2Sn$ (2a) A pale yellow microcrystalline (>99%). ^{1}H NMR (300 MHz, C_6D_6): δ 8.69 (*s*, 2H, N=C*H*), 7.06 (*t*, $^3J_{HH}$ = 7.8 Hz, 8H, C_6H_5), 6.88 (*t*, $^3J_{HH}$ = 7.3 Hz, 4H, C_6H_5), 6.80 (*d*, $^3J_{HH}$ = 7.6 Hz, 8H, C_6H_5). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 157.0 (s, H$\underline{C}$(N(C_6H_3))$_2$), 146.2 (s, *i-C*), 129.2 (s, *m-C*), 123.1 (s, *p-C*) , 120.6 (s, *o-C*). Anal. Calcd for $C_{26}H_{22}N_4Sn$: C, 61.33; H, 4.35; N, 11.00. Found: C, 61.50; H, 4.63; N, 10.99.

$[((2,6\text{-}Me_2C_6H_3)\ N)_2CH]_2Sn$ (2b) A colorless microcrystalline (99%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (*s*, 2H, N=C*H*), 6.92 (*d*, $^3J_{HH}$ =7.4 Hz, 8H, C_6H_3), 6.84 (*t*, 4H, C_6H_3), 2.11 (*s*, 24H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 162.3 (s, H$\underline{C}$(N(C_6H_3))$_2$), 144.6 (s, *i-C*), 132.2 (s, *o-C*), 128.1 (s, *m-C*), 123.4 (s, *p-C*), 19.3 (s, $C_6H_3(\underline{C}H_3)_2$). Anal. Calcd for $C_{34}H_{38}N_4Sn$: C, 65.72; H, 6.16; N, 9.02. Found: C, 66.87; H, 5.94; N, 9.14.

$[((2,6\text{-}^iPr_2C_6H_3)N)_2CH]_2Sn$ (2c) A colorless microcrystalline (90%). ^{1}H NMR (300 MHz, C_6D_6,): δ 8.06 (*s*, 2H, N=C*H*), 7.06 (*m*, 12H, C_6H_3), 3.50 (*sep*, $^3J_{HH}$ = 6.7 Hz, 8H, C*H*(CH_3)$_2$), 1.12 (*m*, 48H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 163.0 (s, H$\underline{C}$(N(C_6H_3))$_2$), 143.8 (s, *o-C*), 142.2 (s, *i-C*), 125.3 (s, *p-C*), 123.6 (s, *m-C*), 28.9 (s, $\underline{C}$H(CH_3)$_2$), 23.9 (s, CH($\underline{C}$H$_3$)$_2$). Anal. Calcd for $C_{50}H_{70}N_4Sn$: C, 71.00; H, 8.34; N, 6.62. Found: C, 71.27; H, 8.06; N, 6.54.

$[(((4\text{-}CH_3O)C_6H_4)N)_2CH]_2Sn$ (2d) A dark-green microcrystalline (81%). ^{1}H NMR (300 MHz, C_6D_6): δ 8.77 (*s*, 2H, N=C*H*), 6.83 (*d*, $^3J_{HH}$ = 8.7 Hz, 8H, C_6H_4), 6.74 (*d*, $^3J_{HH}$ = 8.8 Hz, 8H, C_6H_4), 3.32 (*s*, 12H, OCH_3) $^{13}C\{^1H\}$ NMR(75 MHz, $CDCl_3$): δ 157.3 (s,H*C*(N(C_6H_4)OCH_3)$_2$), 156.3 (s, *i-C*OCH_3), 140.0 (s, *i-C*N), 121.6 (s, *o-C*), 114.7 (s, *m-C*), 55.0 (s, OCH_3). Anal. Calcd for $C_{30}H_{30}N_4O_4Sn$: C, 57.26; H, 4.81; N, 8.90. Found: C, 57.20; H, 4.60; N, 7.90.

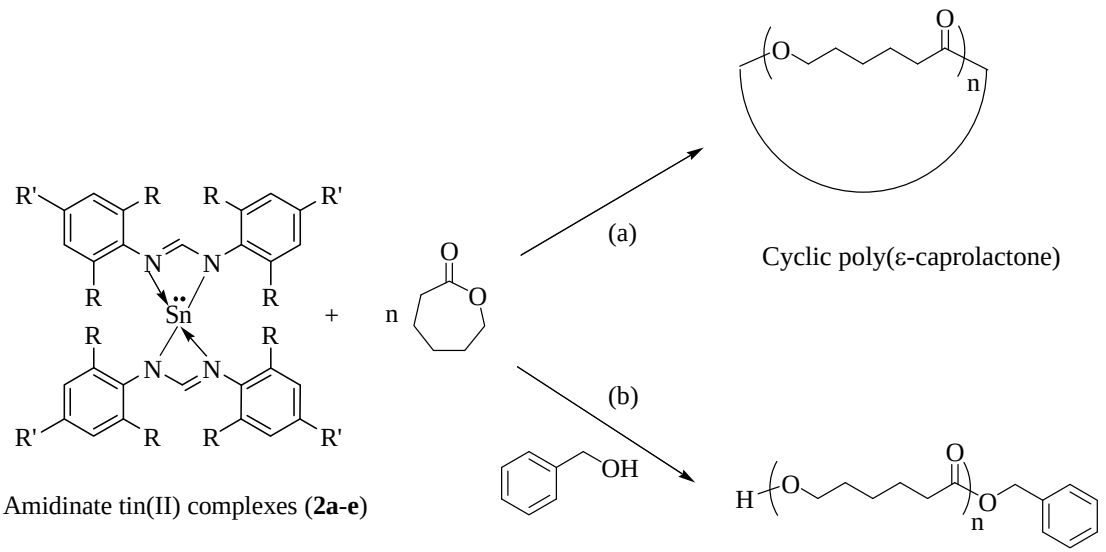
$[((4\text{-}CF_3C_6H_4)N)_2CH]_2Sn$ (2e) A pale yellow microcrystalline (83%). ^{1}H NMR (300 MHz, C_6D_6): δ 8.31 (*s*, 2H, N=C*H*), 7.28 (*d*, $^3J_{HH}$ = 8.4 Hz, 8H, C_6H_4), 6.45 (*d*, $^3J_{HH}$ = 8.0 Hz, 8H, C_6H_3). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 148.2 (s, H*C*(N(C_6H_4)CF_3)$_2$), 129.3 (s, *i-C*), 126.6 (s, *o-*

C), 125.7 (s, *C*CF_3).123.2 (s, *C*F_3), 120.2 (s, *m*-*C*). Anal. Calcd for $C_{30}H_{18}F_{12}N_4Sn$: C, 46.13; H, 2.32; N, 7.17. Found: C, 46.23; H, 2.45; N, 7.14.

3.1.1) Ring-opening polymerization of Ɛ-caprolactone by complexes 2a-e Cyclic and linear poly(Ɛ-caprolactone) were synthesized as shown in Scheme 7. The representative procedure was described below.

Cyclic poly(Ɛ-caprolactone): the catalyst and Ɛ-caprolactone monomer were added to a Schlenk flask with different monomer:catalyst ratio. The reaction was then submerged into a preheated oil bath at the desired temperature. At desired time, a small amount of sample was taken out for NMR analysis. The rest of the polymer was then dissolved in CH_2Cl_2 (20 mL) and precipitated with excess methanol. The solid polymer was dried under vacuum.

Linear poly(Ɛ-caprolactone): the preparation of linear polymer followed the above procedure by adding 1 equiv benzyl alcohol along with the catalyst and Ɛ-caprolactone.



Amidinate tin(II) complexes (**2a**-**e**)

2a; R = H, R' = H
2b; R = CH_3, R' = H
2c; R = ^{i}Pr, R' = H
2d; R = H, R' = OCH_3
2e; R = H, R' = CF_3

Figure 7 Synthetic pathways for a) cyclic and b) linear poly(Ɛ-caprolactone).

Activity of amidinate tin(II) complexes The catalytic activity of tin(II) complexes (**2a—e**) were studied according to the above method. The mole ratio of ε-caprolactone monomer and catalyst was 500:1, 1000:1, 5000:1 and 10000:1. The polymerization temperature was 110 °C.

3.1.2) Ring-opening polymerization of L-lactide

Cyclic poly(L-lactide) was synthesized as shown in Figure 8. Catalyst and L-lactide monomer were weighed out in a dried small reaction flask. The reaction flask was sealed and reacted at 120 °C. The ratio of monomer: catalyst was 300:1. The reaction was stopped once the high viscosity of the reaction mixture was observed. After that, the polymer was dissolved in CH_2Cl_2 (20 mL) followed by the precipitation with excess methanol. The solution was removed and the solid polymer was dried under vacuum. Linear poly(L-lactide) was synthesized similary but with addition of 1 equiv benzyl alcohol.

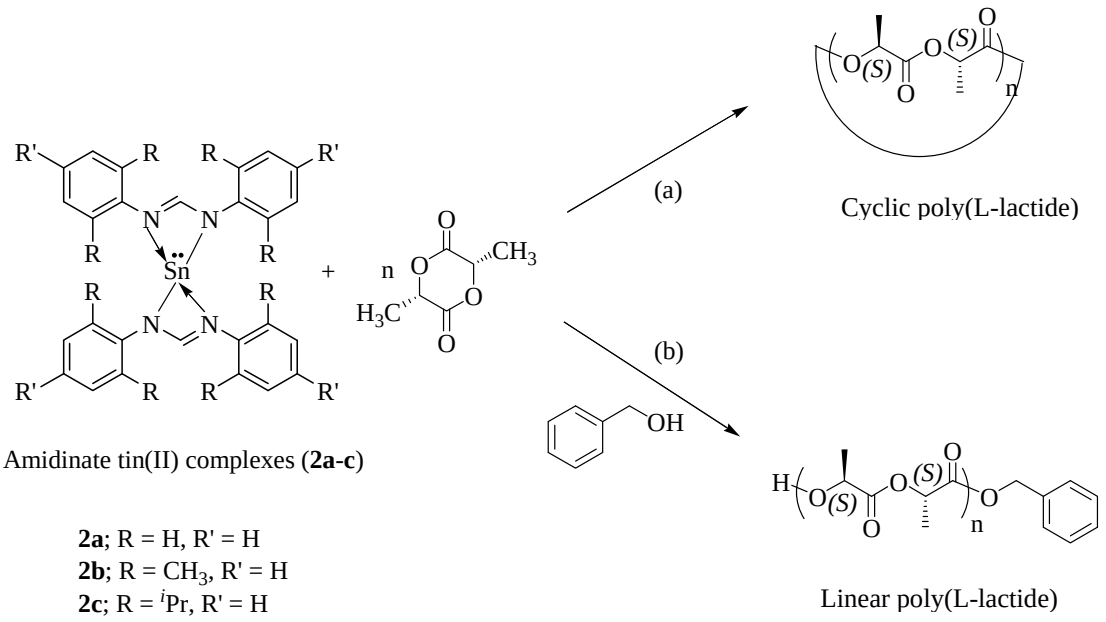


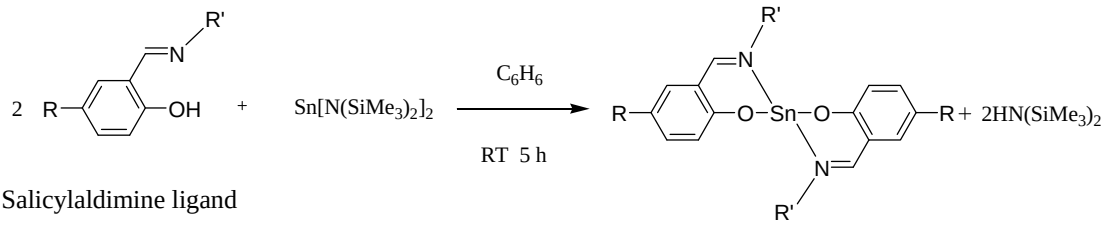
Figure 8 Synthetic pathways for a) cyclic and b) linear poly(L-lactide).

Activity Study of amidinate tin(II) complexes The catalytic activity of tin(II) complexes **2a—c** were studied using the above method to synthesize cyclic polymer. The ratio of L-lactide

and catalyst was 100:1, 200:1, 300:1, and 500:1. The polymerization time and temperature were 25 min and 120 °C, respectively. For stereoselectivity study, *rac*-lactide was polymerized using complex **2c**. The procedure was carried out similarly without addition of benzyl alcohol. The tacticity of the obtained polymer was analyzed using homonuclear decouple ^{1}H NMR of the methine proton in the polymer chains.

3.2) Salicylaldimine ligand system

General syntheses of the tin complexes of salicyladimine ligands were described as shown in Figure 9 starting from the corresponding salicylaldimine ligands and $Sn[N(SiMe_3)_2]_2$.



Salicylaldimine ligand

3a; R = H , R' = Ph
3b; R = H , R' = *o*-2,6-$(CH_3)_2C_6H_3$
3c; R = H , R' = *o*-2,6-$(iPr)_2C_6H_3$
3d; R = H , R' = *p*-$OCH_3C_6H_4$
3e; R = H , R' = *p*-$CF_3C_6H_4$
3f; R = Br , R' = *o*-2,6-$(iPr)_2C_6H_3$
3g; R = H , R' = CH_3
3h; R = H , R' = *t*-Bu

4a; R = H , R' = Ph
4b; R = H , R' = *o*-2,6-$(CH_3)_2C_6H_3$
4c; R = H , R' = *o*-2,6-$(iPr)_2C_6H_3$
4d; R = H , R' = *p*-$OCH_3C_6H_4$
4e; R = H , R' = *p*-$CF_3C_6H_4$
4f; R = Br , R' = *o*-2,6-$(iPr)_2C_6H_3$
4g; R = H , R' = CH_3
4h; R = H , R' = *t*-Bu

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Bis[*N*-(Salicylidene)anilinato]tin(II) complex (4a) This complex was reported earlier using a different preparation.[66] A mixture of ligand **3a** (0.37 g, 1.89 mmol), $Sn[N(SiMe_3)_2]_2$[67] (0.42 g, 0.94 mmol) and dry benzene (20 mL) was stirred at room temperature for 5 h. The volatiles were removed under vacuum and then washed with *n*-hexane giving a yellow powder product (0.24 g, 51%). ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC): δ 8.55 (s, 2H, ArC*H*=N-), 7.43 – 6.89 (m, 14H, Ar*H*), 6.58 – 6.53 (m, 4H, Ar*H*).

Bis[*N*-(salicylidene)-2,6-dimethylanilinato]tin(II) (4b) A light green powder (0.49 g, 72%). ^{1}H-NMR (300 MHz, C_6D_6, 50 ºC): δ 7.71 (s, 2H, ArC*H*=N-), 7.14 – 7.12 (m, 6H, Ar*H*), 7.08 (t, 2H, *p*-C_6H_4), 6.94 (d, 2H, J_{HH} = 6 Hz, *o*-C_6H_4), 6.88 (d, 2H, J_{HH} = 8 Hz, *o*-C_6H_4), 6.61 (t, 2H, *m*-C_6H_4), 2.43 (s, 12H, N- $C_6H_3(CH_3)_2$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 50 ºC): δ ^{13}C 167.35 (Ar-*C*H=N), 165.54 (*C*-O-Sn), 148.83 (*ipso*-C) 135.08 (*o*-C_6H_4-O-Sn), 134.79 (*p*-C_6H_4-O-Sn), 128.80 ($C_6H_3(CH_3)_2$), 125.86 ($C_6H_3(CH_3)_2$), 123.28 (*m*-C_6H_4-O-Sn), 121.42 (*ipso*-$C_6H_3(CH_3)_2$), 116.37 (*m*-C_6H_4-O-Sn), 19.07 (N-$C_6H_3(CH_3)_2$. Elemental Analysis: Calculated for $C_{30}H_{28}N_2O_2Sn$: C, 63.52; H, 4.98; N, 4.94. Found : C, 64.54; H, 4.62; N, 5.10.

Bis[*N*-(salicylidene)-2,6-diisopropylanilinato]tin(II) (4c) A light green powder (0.41 g, 67%). Crystals were grown in a dry box from concentrated benzene solution. The single crystals were characterized by X-ray crystallography. ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC): δ 8.00 (s, 2H, ArC*H*=N), 7.23 – 6.51 (m, 14H, Ar*H*), 4.27 (broad s, 2H, ArC*H*CH_3), 3.18 (broad s, 2H, ArC*H*CH_3), 1.51 – 0.96 (m, 24H, ArCHC*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 ºC): δ 167.18 (Ar-*C*H=N), 165.28 (*C*-O-Sn), 146.12 (*ipso*- C=N- $C_6H_3CH(CH_3)_2$), 141.34 (*ipso*-$C_6H_3CH(CH_3)_2$), 134.94 (*m*-C_6H_4-O-Sn), 134.89 (*m*-C_6H_4-O-Sn), 128.32 (*p*-$C_6H_3CH(CH_3)_2$), 126.85 (*m*-$C_6H_3CH(CH_3)_2$), 123.15 (*p*-C_6H_4-O-Sn), 121.64 (*ipso*-C_6H_4-C=N), 116.64 (*o*-C_6H_4-O-Sn), 24.68 ($C_6H_3CH(CH_3)_2$). Elemental Analysis: Calculated for $C_{38}H_{44}N_2O_2Sn$: C, 67.17; H, 6.53; N, 4.12. Found: C, 66.89; H, 6.40; N, 3.84.

Bis[(*N*-salicylidene)-4-methoxyanilinato]tin(II) (4d) A dark green powder (0.84 g, 84%). ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC): δ 7.98 (s, 2H, ArC*H*=N), 7.52 – 6.63 (m, 16H, Ar*H*), 3.41 (s, 6H, ArOC*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 ºC): δ 164.62 (*ipso*-*C*-O-Sn), 163.43 (Ar-*C*H=N), 158.45 (*ipso*-*C*-OCH_3), 143.26 (*ipso*-C_6H_4-N=C), 134.96 (Sn-O-CCH_2*C*H_2), 134.37 (Sn-O-CC*C*H_2), 123.15 (N-C-*C*H_2), 122.88 (*p*-C_6H_4-O-Sn), 121.19 (*ipso*-C_6H_4-CH=N), 116.37 (*o*-C_6H_4-O-Sn), 114.73 (*C*H_2C-OCH_3) 55.55 (O-*C*H_3). Elemental Analysis: Calculated for $C_{38}H_{44}N_2O_2Sn$: C, 58.87; H, 4.23; N, 4.90. Found: C, 59.53; H, 4.18; N, 4.92.

Bis[(*N*-salicylidene)-4-trifluoromethylanilinato] tin(II) (4e) A yellow powder (0.36 g, 37%). ^{1}H-NMR (300 MHz, C_6D_6, 25 ºC): δ 7.71 (s, 2H, ArC*H*=N), 7.50 (d, 4H, J_{HH} = 8 Hz, CH_2CCF$_3$), 7.26 – 6.95 (m, 10H, Ar*H*), 6.64 (*o*-C$_6H_4$-O-Sn). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 ºC): δ 165.83 (Ar-*C*H=N), 165.64 (*ipso*-*C*-O-Sn), 153.18 (*ipso*-C=N-*C*), 135.98 (Sn-O-CCH$_2$*C*H$_2$), 135.80 (Sn-O-CC*C*H$_2$), 126.86 (*C*H$_2$CCF$_3$), 123.34 (C-*C*F$_3$) 122.89 (N-C-*C*H$_2$), 121.04 (*ipso*-*C*-CH=N), 116.89 (*o*-*C*$_6$H$_4$-O-Sn). Elemental Analysis: Calculated for $C_{38}H_{44}N_2O_2Sn$: C, 51.97; H, 2.80; N, 4.33. Found: C, 51.71; H, 2.70; N, 4.36.

Bis[(*N*-(5-bromosalicylidene))-2,6-diisopropylanilinato]tin(II) (4f) A yellow powder product (0.50 g, 86%) was purifiled by vacuum sublimation. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC): δ 7.69 (s, 2H, ArC*H*=N), 7.27 – 6.55 (m, 14H, Ar*H*), 4.03 (broad s, 2H, ArC*H*CH$_3$), 3.05 (broad s, 2H, ArC*H*CH$_3$), 1.45 – 1.00 (m, 24H, ArCHC*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 50 ºC): δ 165.49 (Ar-*C*H=N), 163.54 (*C*-O-Sn), 145.44 (*ipso*- C=N-*C*$_6$H$_3$CH(CH$_3$)$_2$), 140.90 (*ipso*-*C*$_6$H$_3$CH(CH$_3$)$_2$), 137.10 (Sn-O-CCH$_2$*C*H$_2$), 135.91 (Sn-O-CC*C*H$_2$), 126.65 (*p*-*C*$_6$H$_3$CH(CH$_3$)$_2$), 124.77 (*m*-*C*$_6$H$_3$CH(CH$_3$)$_2$), 123.93 (*o*-*C*$_6$H$_4$-O-Sn), 122.56 (N=*C*$_6$H$_3$Br), 107.53 (*C*-Br), 24.52 (C$_6$H$_3$CH(*C*H$_3$)$_2$). Elemental Analysis: Calculated for $C_{38}H_{44}N_2O_2Sn$: C, 54.51; H, 5.06; N, 3.35. Found: C, 5476; H, 4.38; N, 3.19.

Bis[(*N*-salicylidene)methyliminato]tin(II) (4g) A yellow powder product was purifiled by vacuum sublimation (0.82 g, 94%). ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC): δ 8.26 (s, 2H, ArC*H*=N), 7.13 (t, 2H, J_{HH} = 7 Hz, *m*-Ar*H*), 6.99 (d, 2H, 7 Hz, *m*-Ar*H*), 6.64 (d, 2H, 7 Hz, *o*-Ar*H*), 6.53 (t, 2H, J_{HH} = 7 Hz, *p*-Ar*H*), (s, 6H, C=NC*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 50 ºC): δ 165.30 (Ar-*C*H=N), 164.56 (*C*-O-Sn), 133.84 (Sn-O-CCH$_2$*C*H$_2$), 133.56 (Sn-O-CC*C*H$_2$), 122.45 (*p*-Ar), 120.73 (*ipso*-N=CH*C*$_6$H$_4$), 116.00 (*o*-*C*$_6$H$_4$-O-Sn). Elemental Analysis: Calculated for $C_{38}H_{44}N_2O_2Sn$: C, 49.56; H, 4.17; N, 7.24. Found: C, 50.56; H, 3.80; N, 7.27.

Bis[(*N*-salicylidene)-*t*-butyliminato]tin(II) (4h) A yellow oil (0.31 g, 68%) was purified by distillation under vacuum. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ºC): δ 8.05 (s, 2H, ArC*H*=N), 6.96 – 6.39 (m, 8H, Ar*H*), 4.03, 1.49 (s, 18H, N-C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 50 ºC): δ 162.98 (*C*-O-Sn), 159.94 (Ar-*C*H=N), 134.31 (Sn-O-CCH$_2$*C*H$_2$), 132.89 (Sn-O-CC*C*H$_2$), 122.38 (*p*-Ar), 121.61 (*ipso*-N=CH*C*$_6$H$_4$), 116.13 (*o*-*C*$_6$H$_4$-O-Sn), 59.77 (*ipso*-N-*C*(CH$_3$)$_3$), 30.37 (N-

C(CH_3)$_3$). Elemental Analysis: Calculated for $C_{38}H_{44}N_2O_2Sn$: C, 56.08; H, 5.99; N, 5.95. Found: C, 55.52; H, 5.22; N,5.89.

Polymerization of lactide and ε-caprolactone using catalyst 4a-h L-lactide (0.30 g, 0.20 mmol) and catalyst **4a**-**h** (2.0 mmol) were weighted into a reaction flask inside a glove box. The reaction flask was vacuum sealed and then completely immersed into 115 ºC preheated oil bath for 10 minutes. Subsequently, the melted reaction mixture was cooled by immersing the sealed reaction flask in *n*-hexane. The conversion was determined by ^{1}H NMR in chloroform-d. The crude product was dissolved with dichloromethane. The polymer was precipitated using excess methanol, collected and dried under vacuum. The molecular weight and dispersity (PDI) were determined by gel permeation chromatography. The cyclic structure of products was determined by a combination of techniques, including ^{1}H NMR and mass spectrometry by comparison to the linear polylactide.

4. บทวิจารณ์

4.1) Synthesis of catalyst system containing amidine ligands

All amidine ligands were designed to investigate in electronic and steric effects. The synthesis of all ligands was simple giving high purity. The reactions were carried out by mixing triethylorthoformate with 2 equivalents of the aniline derivatives at high temperature. After work up, the pure ligands were obtained in moderate yields of 32-46%. For the synthesis of tin(II) complexes **2a-2e**, two equivalents of the corresponding ligands were mixed with $Sn[N(SiMe_3)_2]_2$ in toluene at 110 ^{o}C. After the removal of the volatile components, the tin(II) complexes were obtained in high yields of 81-99%. The complexes were air and moisture sensitive. Thus, the reactions were carried out under an argon atmosphere. All tin(II) complexes reported here were novel. They were characterized by spectroscopic techniques (^{1}H NMR, ^{13}C{^{1}H}NMR), X-ray crystallography, and elemental analyses. From ^{1}H NMR spectra of all five catalysts, a chemical shift around 8-9 ppm was distinctive to confirm the coordination between amidine ligands and tin(II) metal.

A single-crystal X-ray crystallography also confirmed the structure of complex **2c** as shown in Figure 10. The complex has C_2 symmetry with four-coordinate tin center. The selected bond distances and bond angles of complex **2c** were shown in Table 1. The geometry of **2c** was distorted square pyramidal where tin was the top of the pyramid and the four nitrogen atoms are the base. A summary of crystallographic and data collection parameters was given in Table 2. Moreover, the crystal structure clearly revealed the position of the active lone pair electrons on the tin atom which was at the top of pyramid. The structure of complexes **2c** was similar to the closely-related bis(amidinate)tin(II) complex reported earlier.[3] Although, the X-ray structures of complexes **2a**, **b**, **d**, **e** have not been carried out, they were believed to have similar structures to that of complex **2c**.

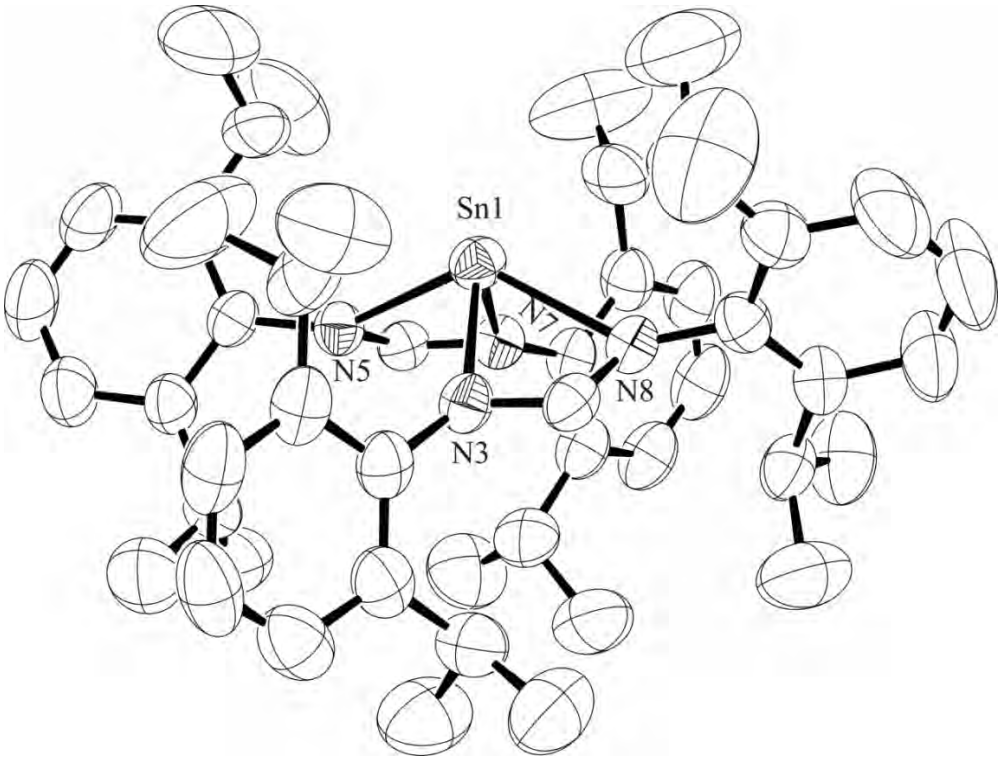


Figure 10 The ORTEP drawing of complex **2c**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids were drawn at 50% probability level.

Table 1 Selected bond distances (Å) and angles (deg) for complex **2c**.

Bond distance (Å)	Sn(1)-N(7)	2.221(3)	Sn(1)-N(3)	2.241(3)
	Sn(1)-N(8)	2.371(3)	Sn(1)-N(5)	2.379(3)
Bond angle (deg)	N(7)-Sn(1)-N(3)	102.4(1)	N(3)-Sn(1)-N(8)	57.8(1)
	N(7)-Sn(1)-N(8)	92.7(1)	N(3)-Sn(1)-N(5)	91.2(1)
	N(3)-Sn(1)-N(5)	57.9(1)	N(8)-Sn(1)-N(5)	133.2(1)

Table 2 Summary of crystallographic and data collection parameters for **2c**.

complex	**2c**
Empirical formula	$C_{50}H_{70}N_4Sn$
M_r	845.828
Crystal system	Monoclinic
Space group	P 2_1/c
a(Å)	14.9195 (4)
b(Å)	16.3981 (5)
c(Å)	21.0942 (6)
α (°)	90.00
β (°)	110.127 (2)
γ (°)	90.00
V (Å^3)	4845.6 (2)
Z	4
λ (Å)	0.71073
μ (mm^{-1})	5.54
T (K)	298
R-factor (%)	5.54

4.1.1 Ring-opening polymerization of ε-caprolactone

The results from all polymerization reactions of ε-caprolactone were summarized in Table 3. The polymerization activities of catalysts **2a-e** were tested. The polymerizations were carried out at 110 ^{o}C for 2 min using the monomer:catalyst ratio of 500:1. The results were shown in Table 3, entries 1-5. Clearly, these complexes were active for the neat polymerization of ε-caprolactone. Complex **2c** had the highest catalytic activity. The polymerization approached 97% conversion in just 2 min. Other complexes were inferior compared to complex

2c. The polymerization using complexes **2a-e** can be classified into two groups based on different steric and electronic contributions.

4.**1.1.1 Electronic contribution**

Complexes **2a**, **2d** and **2e** were designed to monitor the electronic effect of the ligands. The polymerization results were shown in Table 3 (entry1, 4 and 5). The order of activities of the three catalysts was in the order **2d** > **2a** > **2e**. The R' substituent of complex **2d** (OCH_3) was the electron donating group while complex **2e** (CF_3) was the electron withdrawing group compared to complex **2a** (H). Hence, the order of electron donating ability of the ligands would be **2d** > **2a** > **2e**. This order agreed very well with the order of polymerization activities where **2d** > **2a** > **2e**. Because of the CF_3 was the electron withdrawing group, tin should be the most electron deficient compared to the other two complexes. This led to a lower activity of the lone pair electrons. In the case of electron donating group (R' = OCH_3), the lone pair electrons on tin would be more nucleophilic. Thus, complex **2d** was the most active. The M_n value of complex **2e** was higher than those of complexes **2a** and **2d**. The M_n of the polymer obtained from complex **2e** was very high possibly due to the higher rate constant of the propagation step compared to the initiation step ($k_p >> k_i$). In bulk polymerization, the reactions were also affected by the viscosity of the polymer mixture including the solubility of the catalyst in the monomer. There was a chance that all of the catalyst was not active at the same time. So the actual monomer:catalyst ratio was higher than what it should be leading to high molecular weight of the polymers. High PDI usually accompanied. For example, entry 5 (catalyst **2e**), the M_n was 145,802 and PDI was 1.6. Other catalysts could be explained using the same reasons.

4.1.1.2 Steric hindrance

Complexes **2a-c** were designed to investigate the steric effect. The order of steric hindrance was **2c** (R' = ^{i}Pr) > **2b** (R' = CH_3) > **2**a (R' = H). Thus, the order of reactivity should be **2c < 2b < 2a** in agreement with decreasing steric hindrance. However, the results of percent conversion in Table 3**,** entry 1-3 revealed the order of reactivity as **2c > 2b > 2a**. This was very puzzling at first because the results suggested that steric hindrance had little effect to

Table 3 Polymerization of Ɛ-caprolactone at 110 °C.

Entry	Catalyst	M/Cat.	Time(min)	%conversion[a]	Mn[b]	Mw/Mn[b]
1	**2a**	500	2	47	97,500	1.55
2	**2b**	500	2	80	68,600	1.85
3	**2c**	500	2	97	102,600	1.85
4	**2d**	500	2	75	71,400	1.85
5	**2e**	500	2	30	145,800	1.69
6	**2c**	1,000	5	>99	103,100	1.80
7	**2c**	5,000	20	82	202,000	1.94
8	**2c**	10,000	60	94	236,200	2.07
9	$Sn(Oct)_2$ [c]	500	50	58	45,100	1.32
10	**2a** [c]	500	3	>99	101,600	1.70
11	**2b** [c]	500	3	>99	62,000	1.84
12	**2c** [c]	500	3	>99	103,600	1.65
13	**2d** [c]	500	3	>99	60,200	1.78
14	**2e** [c]	500	3	>99	157,900	1.90

[a] Determined by ^{1}H NMR spectroscopy.

[b] Determined by GPC, calibrated using polystyrene standards.

[c] Added benzyl alcohol as initiator in ratio of monomer: catalyst: benzyl alcohol = 500:1:1

the polymerization activities. However, a consideration based on electronic effect would be more probable. The larger the size of the alkyl groups, the more electrons donating the ligands would be. Thus, the order of electron donating abilities was **2a** > **2b** > **2c**. This order agreed very well with the order of reactivities where **2c** > **2b** > **2a**. Thus the electronic effect was more pronounced than the steric effect in this ligand system.

4.1.1.3 Effect of temperature

The effect of temperature was studied in the neat polymerization of ε-caprolactone using **2c** and the monomer:catalyst ratio of 500:1 at various temperatures (room temperature, 75 ^{o}C and 110 ^{o}C). The polymers obtained at high temperature (75 and 110 ^{o}C) were over 90% conversion (shown in Table 4 entry 2 and 3) in 25 and 2 min, respectively. On the other hand, the polymerization at room temperature did not produce any appreciable amount of polymer.

Table 4 Polymerization of ε-caprolactone at different temperature using catalyst **2c**.

Entry	M/Cat.	Temperature (^{o}C)	Time (min)	%conversion[a]
1	500	30	1440	0
2	500	70	25	8
3	500	110	2	97

[a] Determined by ^{1}H NMR spectroscopy.

4.1.1.4 Chain end of poly (Ɛ-caprolactone)

As characterization data has shown, the novel amidinate tin(II) catalysts have one active lone pair of electrons similar to the NHCs used in the polymerization of cyclic polyester.[4,5] Thus, the amidinate tin(II) catalysts should produce the cyclic poly(Ɛ-caprolactone) as in the case of NHCs. To study the chain end of the polymer, the polymerization was carried out with and without the addition of benzyl alcohol in a low monomer:catalyst ratio of 10:1 at 110 ^{O}C for 20 min. In the case of added benzyl alcohol, 1 eq of benzyl alcohol to the catalyst was used. The ^{1}H NMR spectra of the obtained polymer are shown in Figure 11(a). The peaks corresponding to the methylene end group —CH_2—OH (t, δ 3.56) and Ph—CH_2O— (s, δ 5.02) were observed. On the other hand, these peaks were absent when benzyl alcohol was not added as shown in the Figure 11(b). Thus, the polymer obtained without added benzyl alcohol did not have chain ends.

This results were also confirmed using MALDI-TOF mass spectrometry. Figure 12(a) showed the MALDI-TOF mass spectrum of the obtained poly(Ɛ-caprolactone) in the present of benzyl alcohol. The repeating masses of 114n+108+23 D were detected, corresponding to $H[CL]_nOBn + Na^+$ consistent with the presence of the chain end of the polymer. In contrast, the repeating masses of 114n+23 D were assigned to $[CL]_n + Na^+$ as shown in Figure 12(b). The masses of the chain end were not observed in the MALDI-TOF spectrum, which was in good agreement with results from the ^{1}H NMR spectrum. Thus, the polymerization of Ɛ-caprolactone using the tin catalysts gave linear polymer when benzyl alcohol was added. On the other hand, cyclic polymer was obtained if the polymerization was carried out in the absence of alcohol.

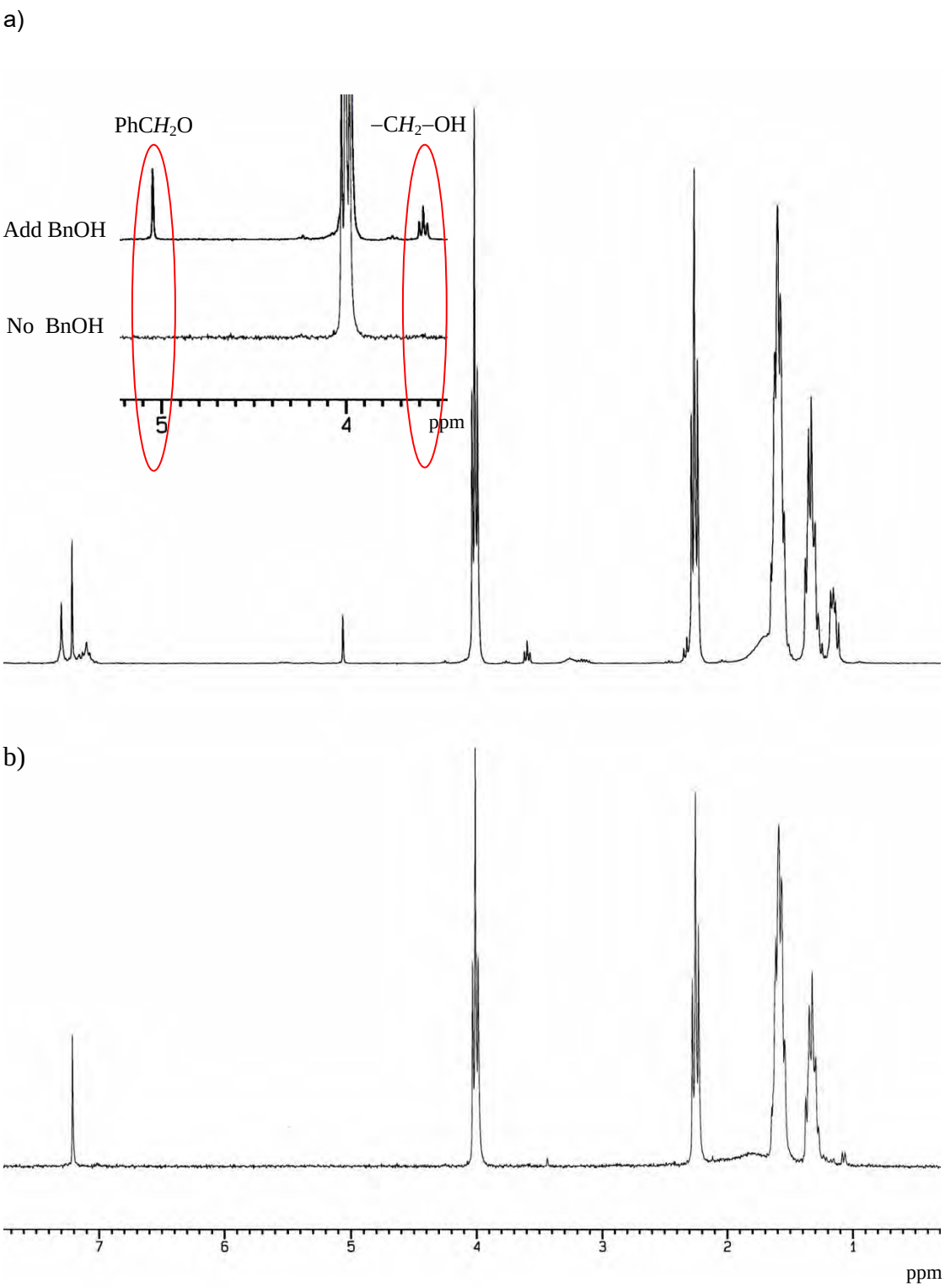


Figure 11 ^{1}H NMR of PCL catalyzed by catalyst **2c** using monomer:catalyst ratio of 10:1 (a) with added benzyl alcohol and (b) without benzyl alcohol.

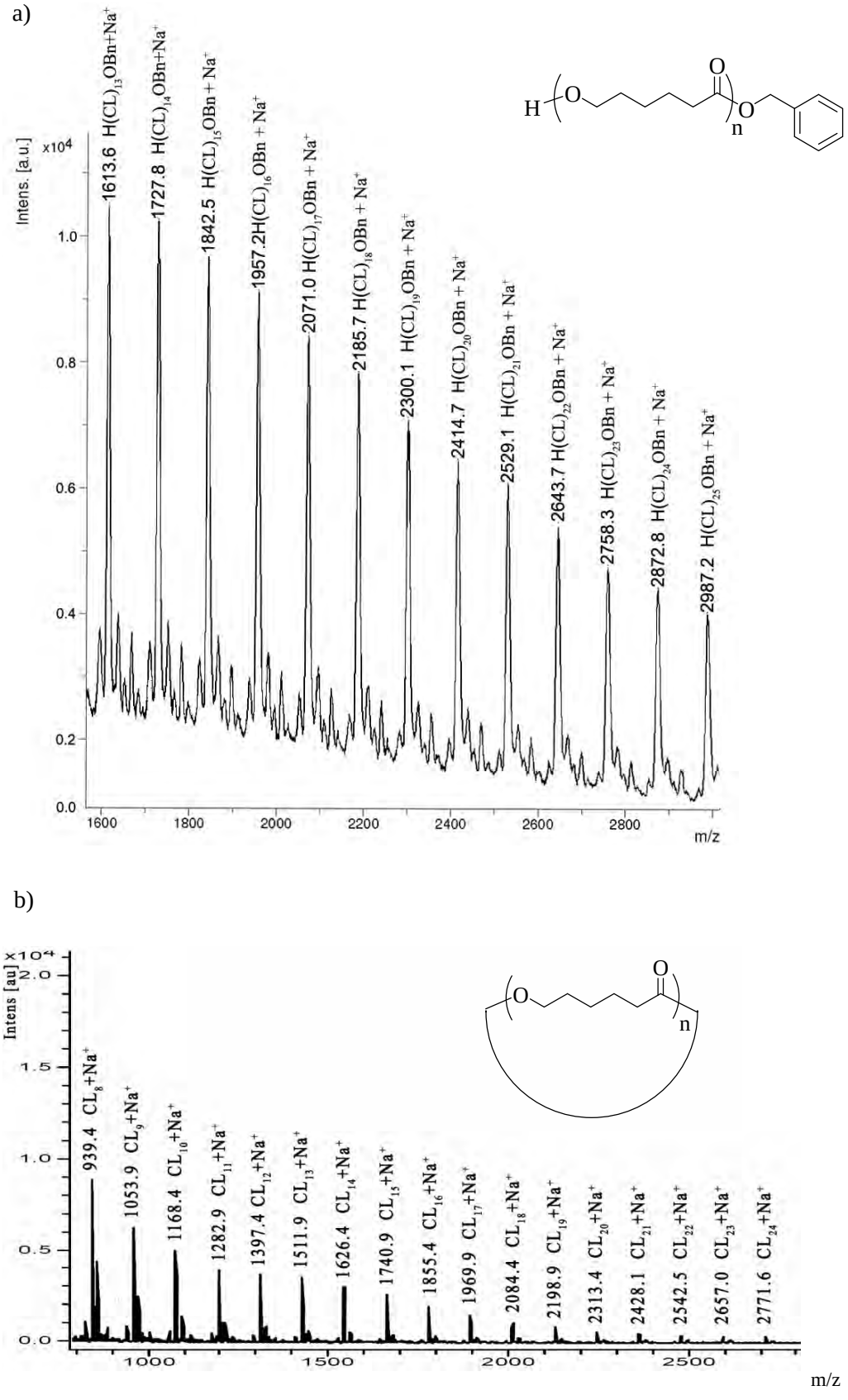


Figure 12 MALDI-TOF mass spectrum of a) linear and b) cyclic poly(Ɛ-caprolactone).

4.1.1.5 Surface analysis of linear and cyclic poly(Ɛ-caprolactone)

The water contact angle was used for confirm the difference between the linear and cyclic poly(Ɛ-caprolactone). The linear polymer contained the chain end which was the hydroxyl group (—OH). Thus, linear polymer should be more hydrophilic compared to the cyclic polymer. The contact angles in the case of the linear polymer should be smaller than the cyclic polymer. From the result in Figure 13, the average contact angle of the cyclic polymer (Figure 13a) was 107.4 ± 2.5^{O} and that of the linear polymer (see in Figure 13b) was 92.8±0.6^{O}. This results agreed very well with the hypothesis described above.

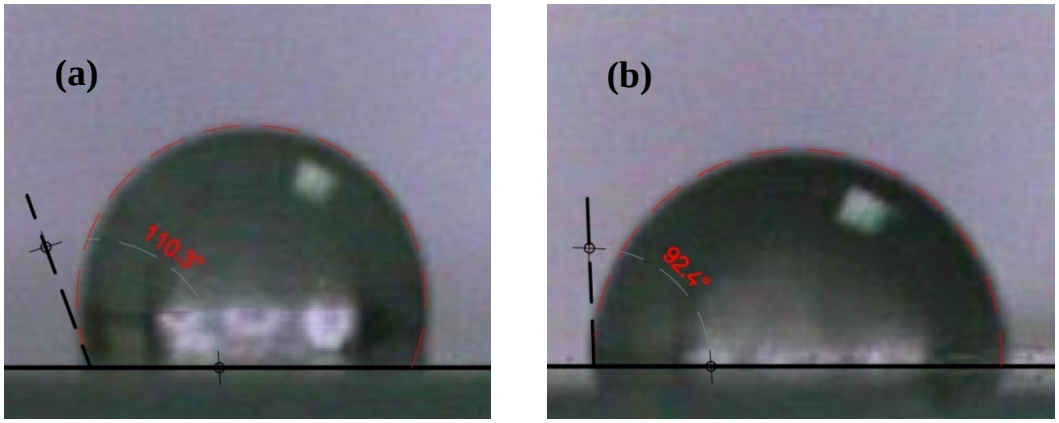


Figure 13 Water contact angle of poly(Ɛ-caprolactone) using catalyst **2c** in ratio of monomer:catalyst as 500:1 (a) without BnOH and (b) with added BnOH.

4.1.2 Ring-opening polymerization of L-lactide

4.1.2.1 Activity of amidinate tin(II) complexes In this section, the catalytic activities of the catalysts for the polymerization of L-lactide using complexes **2a-c** were studied in the melt polymerization at 120 ^{O}C. The ratio of monomer:catalyst was 300:1 and the reaction time was 25 min. The results were shown in Table 4, entries 1-3. From percent conversions, the order of activity was **2a > 2b > 2c** in agreement with the increasing steric hindrance of the substituents

on the phenyl ring. The steric contribution was more pronounced in the polymerization of lactide possibly because lactide was bulkier than ε-caprolactone.

Table 4 Polymerization of L-lactide at 120 ^{O}C.

Entry	Catalyst	M/Cat.	Time (min)	%conversion[a]
1	**2a**	300	25	97
2	**2b**	300	25	92
3	**2c**	300	25	90
4	**2c**	100	15	93
5	**2c**	200	20	96
6	**2c**	500	60	87

[a] Determined by ^{1}H NMR spectroscopy.

4.1.2.2 Stereoselectivity of *rac*-lactide polymerization

The selectivity of the bis(amidinate)tin(II) complexes was studied for the neat polymerization of lactide using complex **2c** as a catalyst and *rac*-lactide as monomer. The ratio of monomer:catalyst was 300:1 and the reaction temperature was 120 ^{O}C. The polymerization times were varied at 30 and 120 min giving the polymer in 85% and 100% conversion, respectively. The selectivity of the polymer can be analyzed using homonuclear decouple ^{1}H NMR technique. The results were shown in Figure 14. The spectra were identical. Thus, only one spectrum was shown in the spectra, the tacticity of the polymer was atactic PLA with slightly enhanced heterotactic bias. The spectrum predicted from a Bernouillian analysis of a totally random poly(*rac*-lactide) was reported earlier.[6] Hence, the catalyst did not show stereoselectivity for the polymerization of *rac*-lactide.

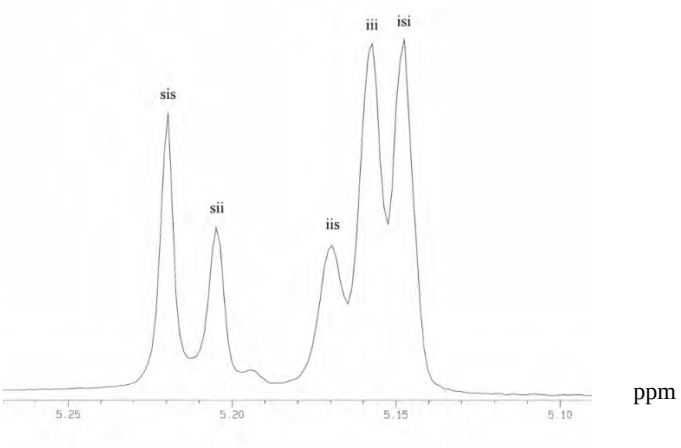


Figure 14 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of poly(*rac*-lactide) prepared using complex **2c**.

4.1.2.3 Chain end analysis of poly (L-lactide)

The study of chain end was also performed similar to poly (ε-caprolactone). The polymerizations were compared with and without the addition of benzyl alcohol using a low monomer:catalyst (**2c**) ratio as 10:1 at 120 ^{o}C and 20 min. In the case of benzyl alcohol addition, 1 eq benzyl alcohol was used. The ^{1}H NMR spectrum is shown in Figure 15(a). The peak corresponding to the quartet of the end group —C*H*(CH_3)—OH was observed at δ 4.30. On the other hand, this peak was absent in the case of the polymerization without benzyl alcohol (Figure 15(b)). Thus, the chain end was not observed.

Figure 16 showed a mass spectrum for poly(L-lactide) obtained in the presence of benzyl alcohol. The repeating mass of 72n +108+23 Da was detected assignable to $H[LA/2]_nOBn + Na^+$ confirming the presence of the chain end of the polymer. In contrast, the repeating mass of 72n +23 Da and 72n +39 Da were observed for the polymerization without alcohol addition assignable to $[LA/2]_n + Na^+$ and $[LA/2]_n + K^+$, respectively, as shown in Figure 17. The mass of the chain end was not observed on the spectrum in good agreement with the result from the ^{1}H NMR. Thus, poly(L-lactide) produced in presence of benzyl alcohol was linear while poly(L-lactide) produced in the absence of benzyl alcohol was cyclic.

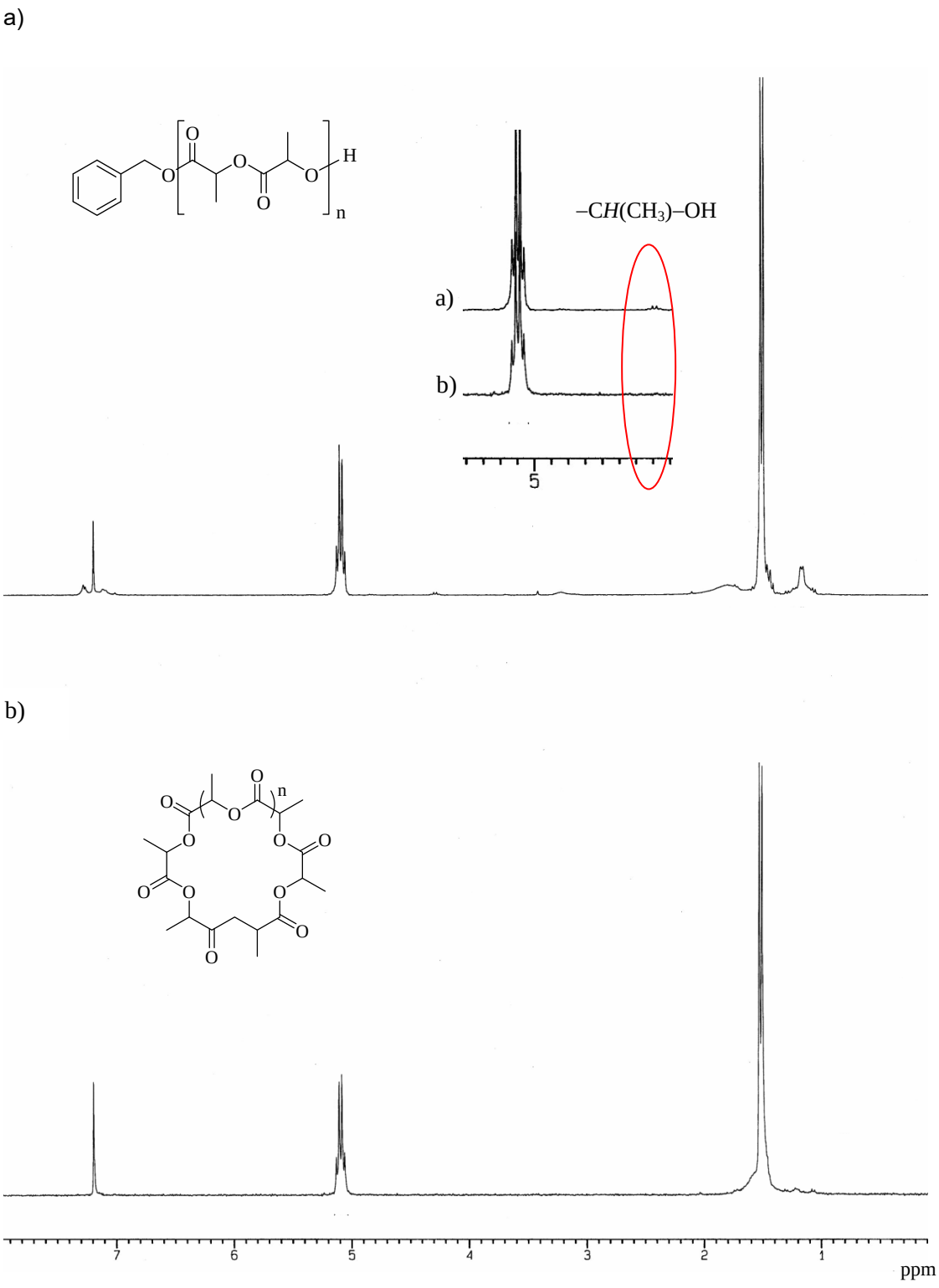


Figure 15 ^{1}H NMR of poly(L-lactide) using catalyst **2c** in monomer:catalyst ratio of 10:1 a) with benzyl alcohol addition and b) without benzyl alcohol addition.

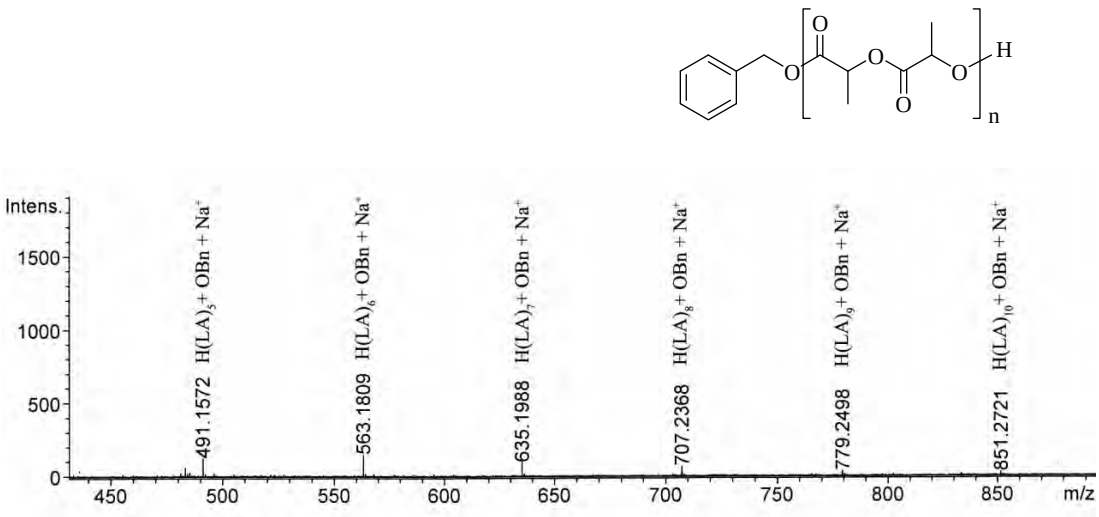


Figure 16 ESI mass spectrum of linear poly(L-lactide).

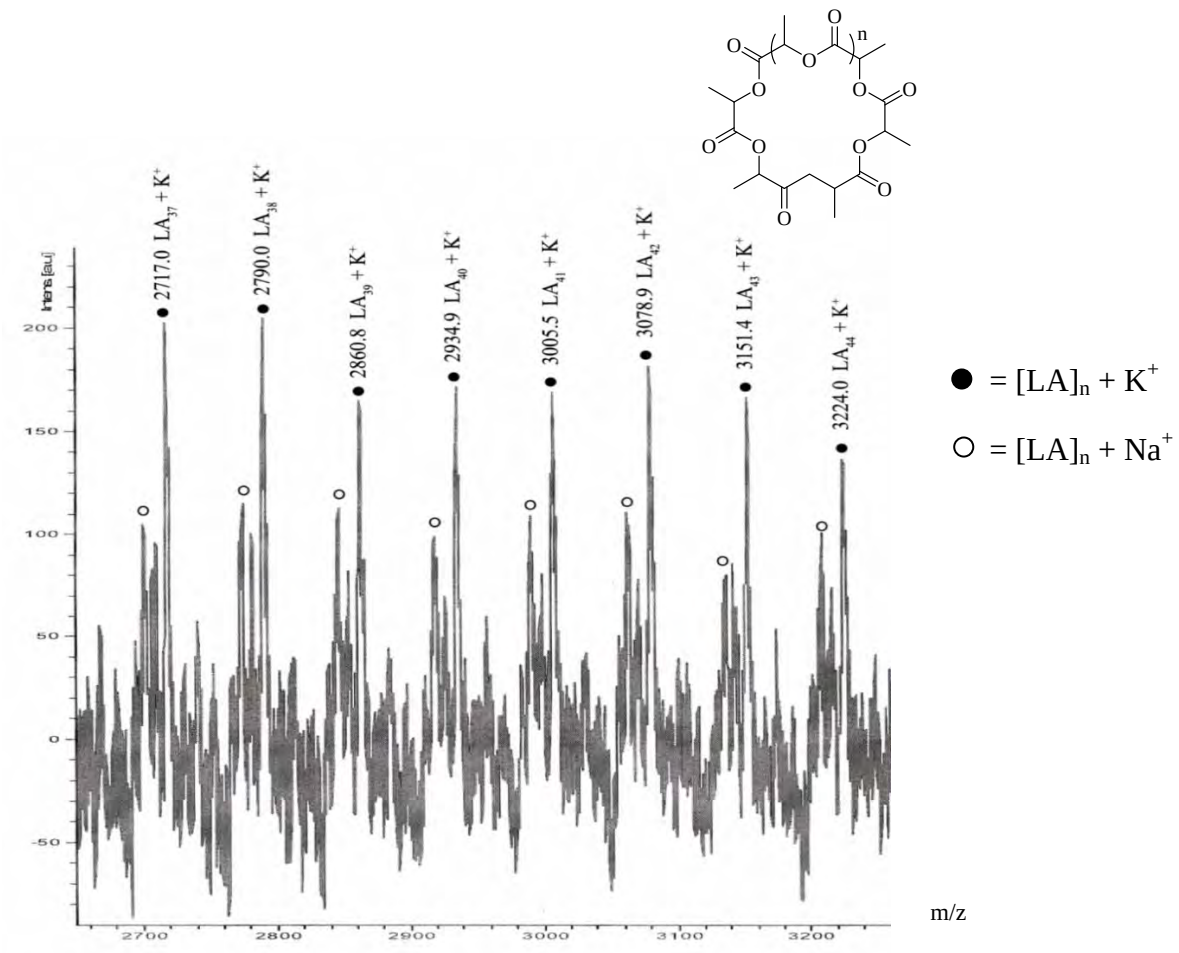


Figure 17 MALDI-TOF mass spectrum of cyclic poly(L-lactide).

4.2) Synthesis of catalyst system containing salicylaldimine ligands

Bis(salicylaldiminato)tin(II) complexes have a lone pair electrons on tin similar to the stanylene complex. Moreover, The investigation of steric and electronic influences of the tin(II) complexes can be done easily by changing the substituents on salicylaldimine ligands. The reaction between 2 eq of the corresponding salicylaldimine ligands with $Sn[N(SiMe_3)_2]_2$ gave the products as shown in Figure 9. In the ^1H NMR spectrum, chemical shift at 13 - 14 ppm of the hydroxy proton disappeared. This was indicative of the complexation of tin(II) and penoxy-imine ligands. Complexes **4b**–**h** are all new compounds.

4.2.1 Structural Studies of Complex 4c

Light green crystals of complex **4c** were grown from benzene. The molecular structure was confirmed by X-ray crystallography. The selected bond distances and angles of **4c** were summarized in Table 5. Complex **4c** contained a four-coordinate tin center having two six-membered amine-phenolate metalla-rings (Figure 18). The geometry can be described as a saw-horse. A summary of crystallographic data for complex **4c** was given in Table 6.

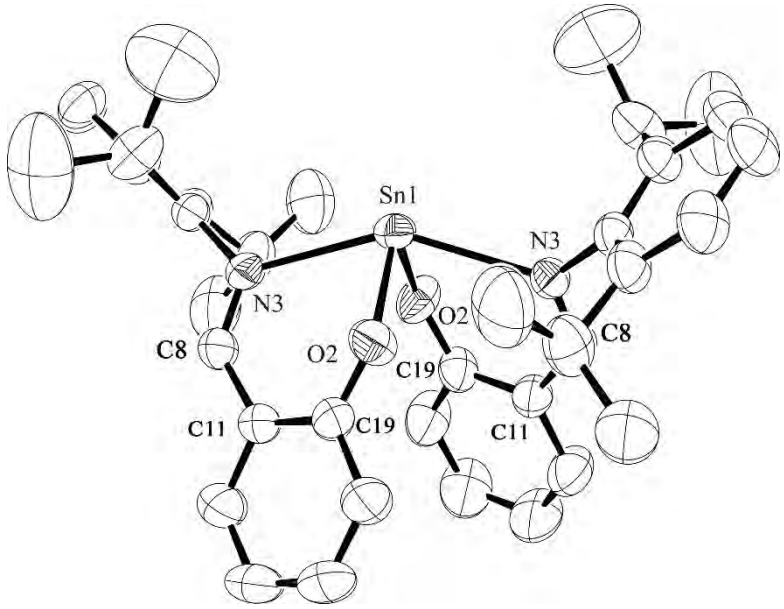


Figure 18 ORTEP drawing of **4c**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids were drawn at the 50% probability level.

Table 5 Selected bond distances (Å) and angles (deg) for **4c**

Sn1 – N3	2.473(3)	N3 – C8	1.274(4)
Sn1 – O2	2.053(2)	C19 – C11	1.408(5)
O2 – C19	1.320(4)	C8 – C11	1.448(5)
O2–Sn1–N3	78.34(9)	O2–Sn1–N3	80.94(9)
O2–Sn1–O2	95.0(1)	N3–Sn1–O2	80.94(9)

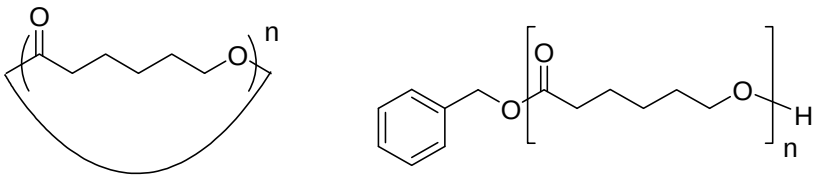
Table 6 Summary of crystallographic data for complex **4c**

complex	**4c**
Empirical formula	$C_{38}H_{44}N_2O_2$
Crystal system	Orthorhombic
Space group	C 2/c
a (Å)	8.8207(4)
b(Å)	17.2625(5)
c(Å)	23.1793(10)
α (°)	90.00
β (°)	90.977(2)
γ (°)	90.00
V (Å^3)	3528.94
Z	6
λ	0.71073
μ	1.087 mm^{-1}

T	298 K
R-Factor(%)	4.14

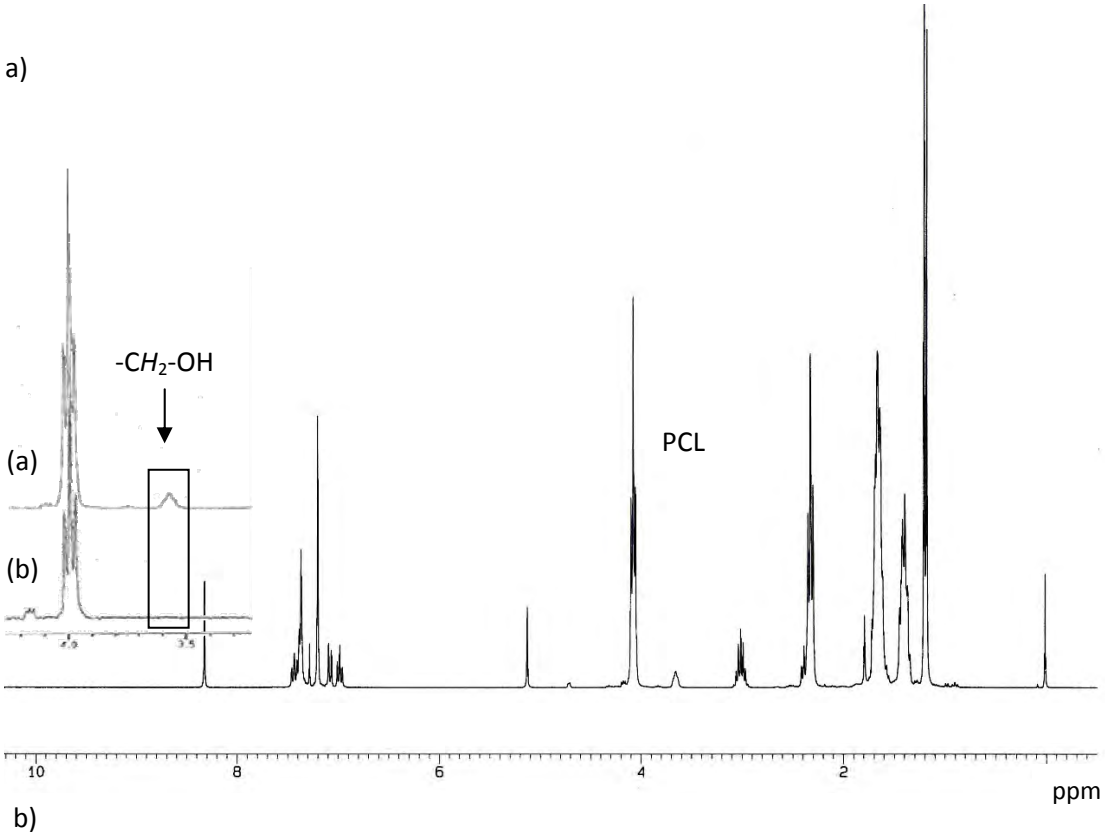
4.2.2 Polymerization of Ɛ-caprolactone to linear and cyclic poly(Ɛ-caprolactone) using bis(salicylaldimine) tin(II) complexes

The phenoxy-imine ligands were chosen in this work because the phenoxide is not very nucleophilic. Moreover, bis(salicylaldiminato)tin(II) complexes has lone-pair electrons similar to carbene. This complex was expected to polymerize cyclic esters giving cyclic polymer as shown in Figure 19. The polymerization of Ɛ-CL using [CL]: [Sn]: [BnOH] was performed at 115 ºC for 10 min. The ^{1}H NMR spectrum showed a characteristic peak of the –CH_2-OH end group at 3.6 ppm as shown in Figure 20a suggesting linear poly(Ɛ-caprolactone). The polymerization was also carried out under same condition without the addition of alcohol. The proton NMR spectrum was shown in Figure 20b. The end group was not observed suggesting a cyclic polymer. In mass spectrometry, both linear and cyclic poly(Ɛ-caprolactone) showed the peak pattern separated by 114 mass unit (mass of caprolactone monomer). The mass spectra of linear and cyclic poly(Ɛ-caprolactone) were different in the remaining mass after substracting the PLA units. The mass spectrum of PCL obtained with the addition of benzyl alcohol was shown in the Figure 21. The mass pattern was 114n + 108 + 23 Da corresponding to the mass of CL_n + BnOH + Na^+. This result confirmed the linear nature of the polymer. The mass spectrum of PCL obtained without adding of alcohol was shown in Figure 22. The mass pattern was 114n + 23 Da corresponding to the mass of CL_n + Na^+. The result of mass spectrum and NMR confirmed the cyclic nature of the polymer.



Cyclic PCL Linear PCL

Figure 19 Structures of cyclic and linear poly(Ɛ-carprolactone) having benzyl alcohol as an end group.



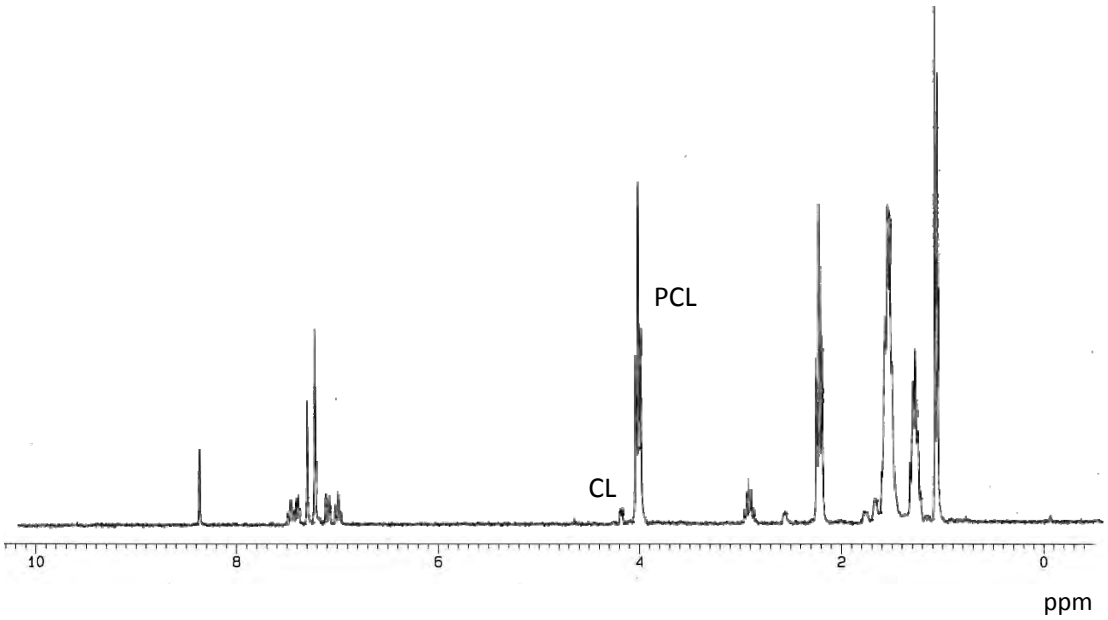


Figure 20 ^{1}H NMR spectra of PCL catalyzed by **4c** a) with addition of benzyl alcohol and b) without addition of benzyl alcohol.

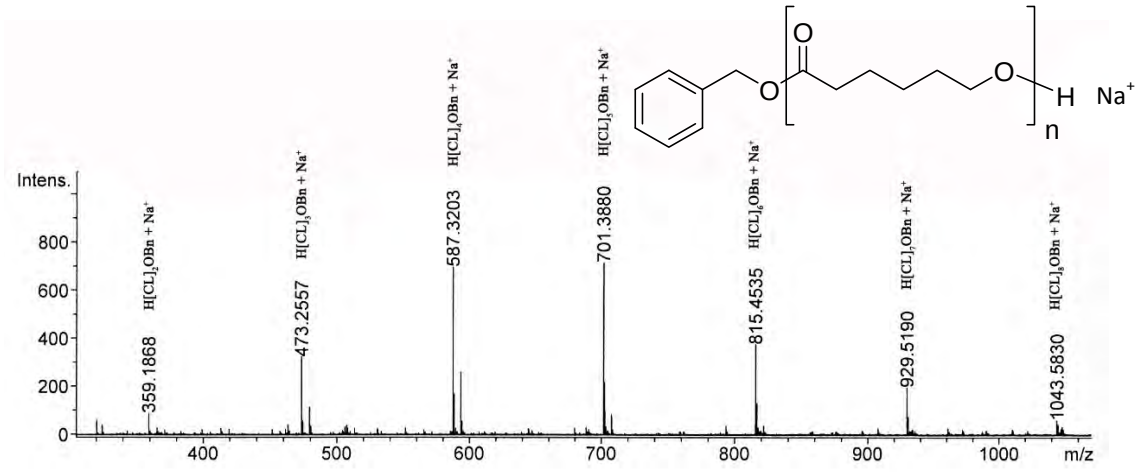


Figure 21 Mass spectrometry of linear poly(Ɛ-caprolactone) obtained from complex **4c**.

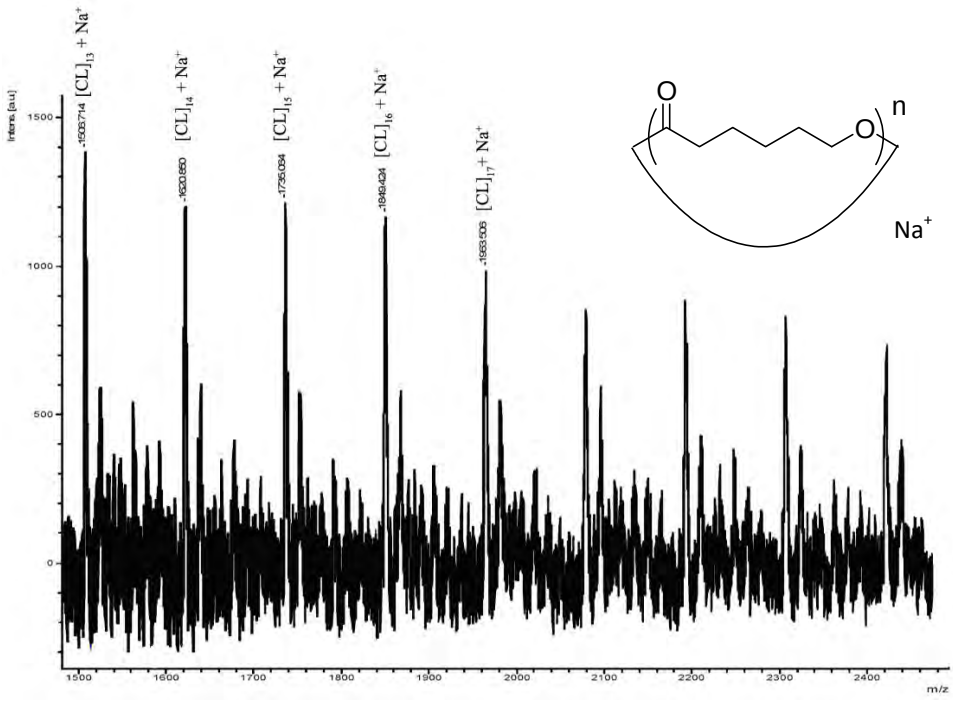


Figure 22 Mass spectrometry (MALDI-TOF) of cyclic poly(ε-caprolactone) obtain from complex **4c**

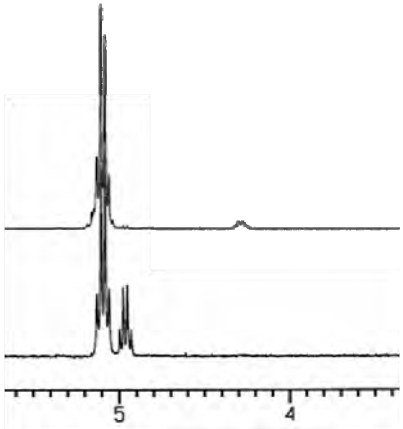
Although, the results confirmed that cyclic poly(ε-caprolactone) was successfully synthesized using bis(salicylaldiminato)tin(II) complexes, catalytic activity was low when mole ratio of [CL]:[Sn] = 200:1 was used. The observed percent conversion at 112 ºC and 25 min was only 17%. The low percent conversion was possibly caused by ε-caprolactone being vaporized to the side of the flask during the reaction. This prevented the reaction from going to completion.

4.2.3 Polymerization of lactide to linear and cyclic polylactide using bis(salicylaldiminato) tin(II) complexes

Similar results were expected when the monomer was changed from ε-CL to lactide. The polymerizations were carried out with and without the addition of benzyl alohol to produce linear and cyclic polylactides, respectively. In the polymerization with benzyl alcohol addition, bis(salicylaldiminato)tin(II) complexes generated the linear polylactide via ring-opening polymerization. The ^{1}H NMR peak at 4.2 ppm was a characteristic of the –C*H*Me-OH end group

in linear polylactide as shown in Figure 23a. The peak disappeared in ^{1}H NMR spectra of cyclic polylactide (Figure 23b) obtained when alcohol was not added. In addition, mass spectrometry, gel permeation chromatography and contact angle measurement were used for compare between cyclic and linear polylactide. For mass spectrometry, both linear and cyclic polylactide showed the peak pattern separate by 72 mass units (half lactide unit) as $(LA/2)_n$ + BnOH + Na^+ for linear PLA (Figure 24) and $(LA/2)_n$ + Na^+ for cyclic PLA (Figure 25). For contact angle measurement shown in Figure 26, a contact angle of water on the cyclic polylactide surface was higher than that of linear polylactide. The result suggested that linear polylactide was more hydrophilic than cyclic polylactide. Since linear polylactide has polar hydroxyl end group, the hydrophilicity on polylactide surface should be higher than the cyclic PLA.

a)



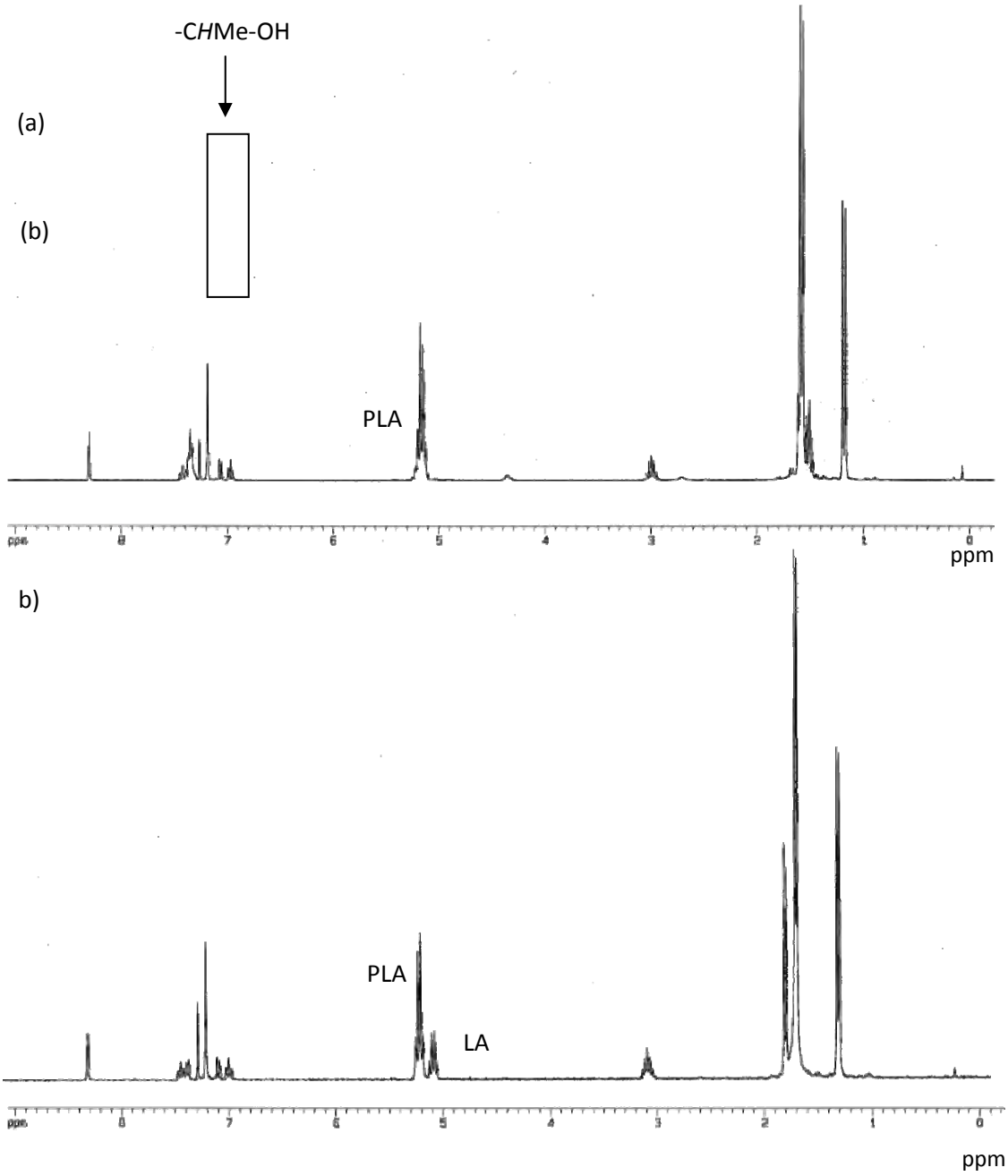


Figure 23 ^{1}H NMR spectrum of a) linear and b) cyclic polylactide catalyzed by **4c**.

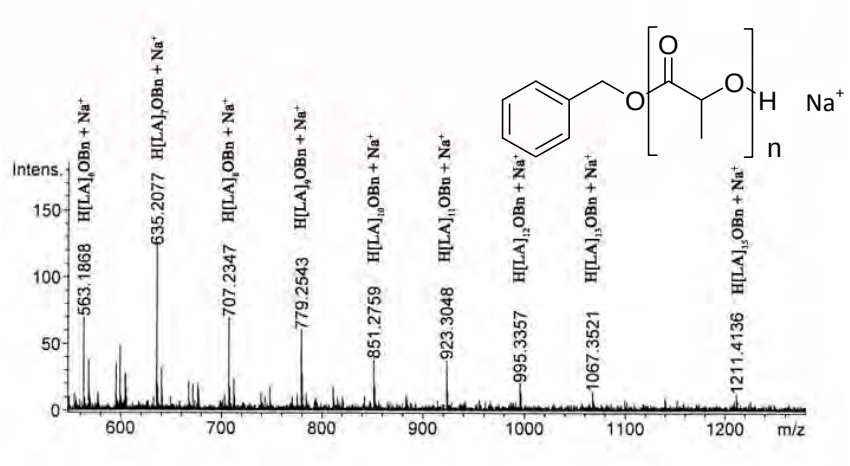


Figure 24 Mass spectrometry of linear polylactide obtained from complex **4c**.

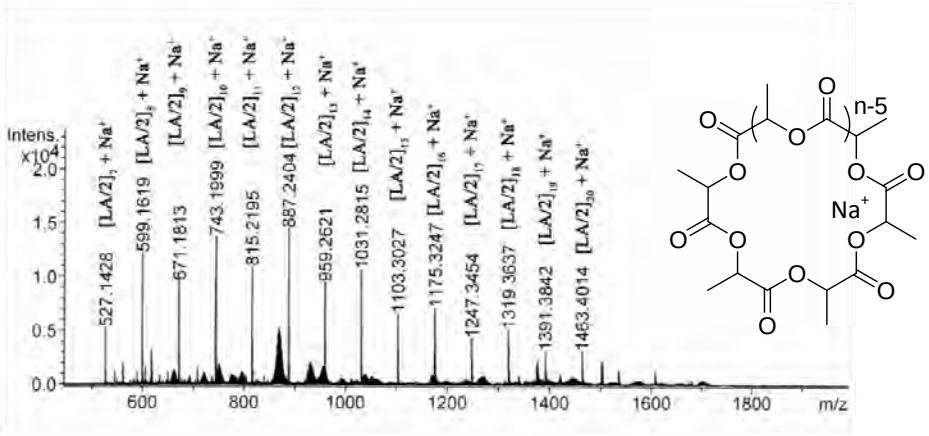


Figure 25 Mass spectrometry of cyclic polylactide obtained using **4c**.

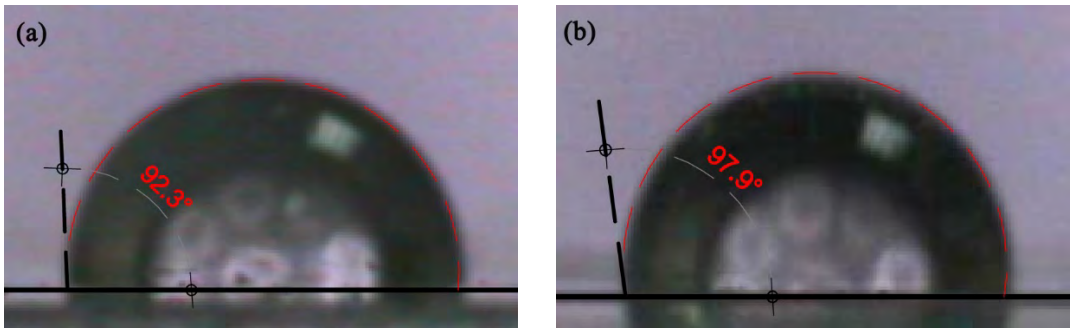


Figure 26 Contact angle of water a) on linear polylactide surface (92.3º, synthesized with benzyl alcohol addition) and b) on cyclic polylactide surface (97.9º, synthesized without benzyl alcohol addition).

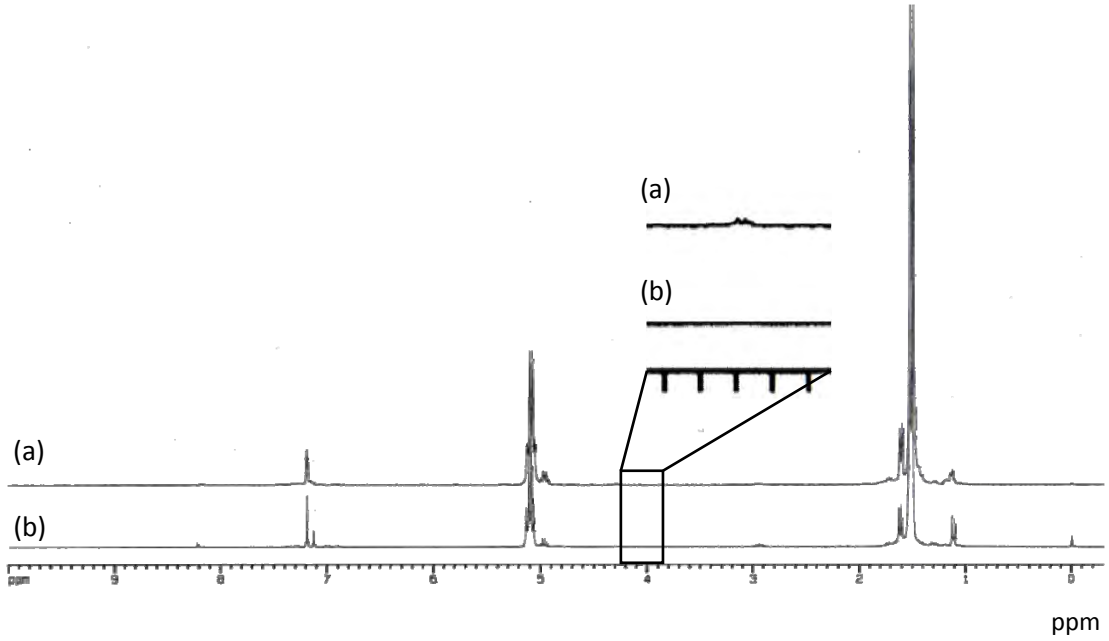


Figure 27 ^{1}H NMR spectrum of a) linear and b) cyclic polylactide catalyzed by **4c** [LA]:[Sn] = 100:1 at 112ºC.

At high [LA]: [Sn] mole ratio of 100: 1, the cyclic nature was still preserved as shown in Figure 27. From ^{1}H NMR spectra, the peak at 4.2 ppm (characteristic of the –C*H*Me-OH end group) appeared in linear polylactide but disappeared in cyclic polylactide. These results indicated that bis(salicylaldiminato)tin(II) complex can produce high molecular weight cyclic PLA.

4.2.4 Lactide polymerization activity

The polymerization activities using different catalyst were summarized in Table 7. All bis(salicylaldiminato)tin(II) complexes were active for lactide polymerization giving cyclic polylactide. However, some catalysts had lower catalytic activity than the commercial tin octanoate. Steric and electronic effects were investigated by changing the substituent on the ligands.

Table 7 Polymerization of lactide using bis(salicylaldiminato)tin(II) complexes at 112 °C

Entry	Catalyst	$[LLA]_0:[Sn]_0$	Time (min)	Conv.[a] (%)	M_n[b]	PDI[c]
1	**4a**	200:1	25	>99	109700	1.90
2	**4b**	200:1	25	85	96800	1.96
3	**4c**	200:1	25	77	113500	1.72
4	**4d**	200:1	25	>99	88500	1.59
5	**4e**	200:1	25	89	132200	1.85
6	**4f**	200:1	25	63	71400	1.60
7	**4g**	200:1	25	>99	92000	1.90
8	**4h**	200:1	25	54	13600	1.39
9	**4c**[d]	100:1	30	90	14400	1.22
10	**4c**	100:1	25	91	50000	1.76
11	**4c**	200:1	30	92	55000	1.96
12	**4c**	300:1	40	93	52900	1.79
13	$Sn(Oct)_2$[*]	200:1	25	85	203100	1.42
					6845	1.43

[a] Determined by ^1H NMR spectroscopy. [b] Number-average molecular weight determined by GPC, calibrated using polystyrene standards. [c] Polydispersity index determined by GPC. [d] Benzyl alcohol added as an initiator. [*] Bimodal distribution was observed in GPC.

4.2.5 Steric effect of catalysts 4a-c and 4g-h for L-lactide polymerization

Complexes **4a, 4b, 4c, 4g** and **4h** were investigated for steric effect. All complexes were tested for the melt polymerization of lactide under the same condition at 112 ºC and 25 min. The ratio of [LLA]:[Sn] = 200:1 was used. The polymerization using complex **4a** and **4g** approached over 99% conversion (Table 7, entry 1 and 7). Polymerization using complexes **4b** and **4c** were 85 and 77% conversion, respectively (Table 7, entry 2 and 3). The preliminary result of catalyst activity was in the order **4a ≈ 4g > 4b > 4c**. The polymerization time was reduced to 5 min to differentiate the catalytic activity between **4a** and **4g**. The results shown in Table 8 clearly indicated that **4g** was more active than **4a**. Thus, the catalyst activity was in the following order **4g > 4a > 4b > 4c** in agreement with the increasing steric hindrance of the ligands. Complexes **4a**, **4b** and **4c** were different in steric hindrance of the substituents at the *othro* position. The steric hindrance of the substituent followed the order: iPr (**4c**) > Me (**4b**) > H (**4a**). Complex **4g** gave the highest activity because of the least steric hindrance. From Table 8, the catalyst activity of **4a**, **4d** and **4g** were in the order of **4g > 4a > 4b**. Thus, the least bulky complex **4g** showed the highest catalytic activity. This result implied that the steric effect was significant.

Compared with complex **4g**, complex **4h** had more bulky N-moiety of salicylaldimine ligand. Then complex **4h** showed much lower catalytic activity than **4g.** These results indicated that the steric effect of the ligand significantly influenced the polymerization activities of the bis(salicylaldiminato) tin(II) complexes. The M_n and polydispersity index (in parenthesis) of polylactide were 109,749 (1.90), 96,801 (1.96), 113,508 (1.72), 91,978 (1.90) and 13,600 (1.39) for complexes **4a**, **4b**, **4c**, **4g** and **4h**, respectively.

Table 8 Polymerization of L-lactide at 120 °C for 5 min.

Entry	Catalyst	Conversion (%)
1	**4a**	15
2	**4d**	42
3	**4g**	78

4.2.6 Electronic effect of catalyst 4a, 4c, 4d, 4e, and 4f for L-lactide polymerization

Complexes **4a**, **4c**, **4d**, **4e**, and **4f** were investigated for electronic effect. All complexes were tested for the melt polymerization of lactide under the same condition at 112 ºC for 25 min (Table 7). The ratio of [LLA]:[Sn] = 200:1 was used. Compared with complex **4a**, complex **4d** had OMe-substituent on the N-moiety of the salicylaldimine ligand. Complex **4d** exhibited higher catalytic activities, indicating that electron-donating group improved catalytic performance of the bis(salicylaldiminato) tin(II) complexes. In the case of complex **4e** (CF_3) lower catalytic activity than **4a** was observed. The result indicated that electron-withdrawing group decreased catalytic performance of the bis(salicylaldiminato) tin(II) complexes. Complexes **4a**, **4d** and **4e** were different by the substituents at the *para* position. Thus, the polymerization activities were in the order **4e < 4a < 4d** in agreement with increasing electron donating ability.

Compared with complex **4c**, complex **4f** had Br-substituent on the *p*-phenoxy moiety of the salicylaldimine ligand. It exhibited lower catalytic activities in agreement with the electron – withdrawing Br substituent.

4.2.7 Investigation of mole ratio by using complex 4c

Ring-opening polymerizations of L-lactide using complex **4c** in different molar ratios of [LA]:[Sn] were carried out at 112 °C. The percent conversion was monitored to over 90% as shown in Table 7, entries 10 - 12. The number average molecular weight (M_n) of all [LA]:[Sn] ratio were around 50,000. The polydispersity index were high ranging from 1.76 – 1.96. This observation suggested that the initiation or the first insertion of LA monomer to complex **4c** was much slower than the subsequent propagation ($k_{initiation} < k_{propagation}$).

4.2.8 Investigation of stereoselective polymerization of *rac*-lactide

All bis(salicylaldiminato)tin(II) complexes (**4a-h**) were tested in the melt polymerization of *rac*-lactide at 112 °C. The ratio of [*rac*-LA]:[Sn] was 200:1. Homonuclear decoupled ^{1}H NMR of the methine proton of PLA obtained from all catalysts showed the same pattern as seen in Figure 28. Thus, only one spectrum was shown. These results indicated that the polymer atactic with slight heterotactic enhancement.[68]

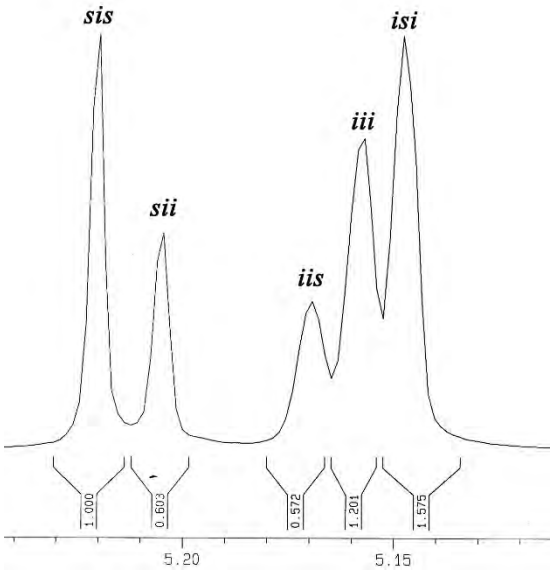


Figure 28 Homonuclear decoupled ^{1}H NMR spectrum of the methine proton of PLA prepared using complex **4c**.

5. บทสรุปงานวิจัย

The novel monomeric amidinate tin(II) complexes (**2a-e**) have been synthesized. The X-ray structure of the tin complex **2c** shows a distorted square pyramidal geometry. Moreover, the structure reveals lone pair electrons on the tin atom that is the active site of the catalysts. These complexes are active catalysts for the ring-opening polymerization of both Ɛ-caprolactone and lactide under solvent-free and high temperature conditions. All displays very high catalytic activity for the polymerization of Ɛ-caprolactone. The complexes **2a-e** can be classified into two groups having different steric (**2a-c**) and electronic contributions (**2a** and **2d-e**). The steric contribution is less pronounced than the electronic contribution for Ɛ-caprolactone polymerization. Complex **2c** was the most active to rapidly polymerize Ɛ-caprolactone at high monomer:catalyst molar ratios. For the polymerization of lactide, complexes **2a-c** exhibit high catalytic activities. The order of activity is **2a** > **2b** > **2c**. However, these complexes are not stereoselective for the polymerization of *rac*-lactide. The tacticity of the polymer is atactic with enhanced heterotactic bias.

For catalysts containing salicylaldimine ligand system, novel bis(salicylaldiminato)tin(II) complexes were successfully synthesized. The X-ray crystallography of complex **4c** revealed a saw horse structure (distorted square pyramidol) suggesting one pair electrons on tin atom. Bis(salicylaldiminato) tin(II) complexes were used in both Ɛ-carprolactone and L-lactide polymerization. In the case of Ɛ-carprolactone, complex **4c** slowly polymerized Ɛ-carprolactone to poly(Ɛ-carprolactone) with the conversion around 17% in 25 min. For the lactide polymerization, the reaction in the presence of alcohol yielded linear polylactide. In the absence of alcohol, the cyclic polylactide was obtained. The ^{1}H NMR, mass spectrometry and gel permeation chromatography (GPC) were used to characterized and compare the linear and cyclic polymer. The complexes having higher steric hindrance showed lower catalytic activities. The complexes having electron donating group revealed better catalytic activities. Higher polymerization temperatures increased the catalytic activity indicating that the catalysts were stable even at high temperature. The polymerization of *rac*-lactide using all catalysts gave atactic PLA with enhanced heterotactic bias. This result indicated that the catalysts had a low stereoselectivity.

In this research, we have discovered a selective polymerization of cyclic esters to either linear or cyclic polymers. We have shown that the catalyst systems produced both cyclic and linear of poly(Ɛ-caprolactone) and poly(lactide) similar to the N-heterocyclic carbene system. The polymers obtained in the present of benzyl alcohol are linear while the polymers obtained in the absence of benzyl alcohol are cyclic.

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Output จากโครงการวิจัยที่ได้รับทุนจาก สกว.

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2 การนำผลงานวิจัยไปใช้ประโยชน์

- เชิงพานิชย์ ในปัจจุบันยังไม่มีการนำไปใช้เชิงพานิชย์ แต่เนื่องจากพลาสติกชีวภาพแบบบวงมีจุดเด่นหลายด้าน คาดว่าจะนำไปสู่การใช้งานเชิงพานิชย์ได้ในอนาคต

- เชิงนโยบาย งานวิจัยนี้เป็นการสนับสนุนการพัฒนาพลาสติกชีวภาพที่จะช่วยผลักดันนโยบายการลดการใช้พลาสติกที่ไม่ย่อยสลายเพื่อรักษาธรรมชาติและสิ่งแวดล้อมที่ดีในประเทศไทย

- เชิงสาธารณะ งานวิจัยชิ้นนี้ชี้ให้เห็นถึงความสำคัญและความต้องการโพลิเมอร์ที่ย่อยสลายได้ในธรรมชาติ มีการนำเสนอผลงานวิจัยในเวทีชุมชนเช่นงาน open house ของมหาวิทยาลัยมหิดล เพื่อกระตุ้นให้เกิดจิตสำนึกในการรักษาธรรมชาติและสิ่งแวดล้อม

- เชิงวิชาการ การศึกษานี้ก่อให้เกิดความรู้ในการออกแบบตัวเร่งปฏิกิริยาที่ดีมีประสิทธิภาพสูง ซึ่งจะเป็นประโยชน์ต่อการออกแบบตัวเร่งปฏิกิริยารุ่นต่อๆไป ผลงานวิจัยนี้ทำให้มีนักศึกษาปริญญาเอก 1 คนและโท 2 คนสำเร็จการศึกษา และนักศึกษาปริญญาโทอีก 1 คนกำลังศึกษาอยู่ซึ่งจะเป็นการ

เพิ่มจำนวนนักวิจัยรุ่นใหม่ในอนาคต นอกจากนี้ทุนวิจัยนี้ได้ช่วยให้คณะผู้วิจัยมีเครือข่ายความร่วมมืองานวิจัยในด้านพลาสติกชีวภาพกับ Prof. Tae-Lim Choi จาก Seoul National University ประเทศเกาหลีอีกด้วยซึ่งจะเป็นการพัฒนาพลาสติกชีวภาพไปสู่การใช้งานทางการแพทย์ อีกทั้งหลังจากที่ได้มีการตีพิมพ์ผลงานวิจัยข้างต้นออกไปแล้ว ได้มีนักวิจัยชาวอังกฤษชื่อ Prof. Geoffrey R. Mitchell จาก University of Reading, UK ได้สนใจในงานวิจัยและขอทำวิจัยร่วมกัน โดยทาง Prof. Mitchell ต้องการใช้ตัวเร่งปฏิกิริยาของเราไปสังเคราะห์พอลิเมอร์เพื่อศึกษาการจัดเรียงตัวของ PCL ด้วยวิธี Neutron Diffraction ผู้วิจัยจึงได้เชิญมาพูดสัมมนาที่ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล นับว่าเป็นจุดเริ่มต้นของความร่วมมือทางการวิจัยที่เป็นผลพวงมาจากงานวิจัยที่ได้รับการสนับสนุนจาก สกว. สกอ. และ มหาวิทยาลัยมหิดล

3 อื่น ๆ

กลุ่มผู้วิจัยได้นำเสนอผลงานวิจัยแบบโปสเตอร์ในที่ประชุมวิชาการนานาชาติดังแสดง และได้รับรางวัลการนำเสนอผลงานวิจัยดีเยี่ยมแบบโปสเตอร์จากทั้งสามงานดังนี้

1) Phonpimon Wongmahasirikun, Khamphee Phomphrai,* “Synthesis and Characterization of Tin(II) Complex Containing Schiff’s Base Ligand for the Polymerization of L-Lactide and ε-Caprolactone” *Poster presentation*, PERCH-CIC International Congress VIII: Chemistry for Creative Economy on May 5th - 8th, 2013, Jomtien Palm Beach Hotel & Resort, Pattaya, Chonburi, Thailand

2) Khamphee Phomphrai,* Chatyapha Pongchan-o, Wipavee Thumrongpatanaraks, “Polymerization of ε-Caprolactone Catalyzed by Bis(amidinate) Tin(II) Complexes” *Poster presentation*, Pure and Applied Chemistry International Conference: Challenges in Chemistry for Sustainable Development on January 5th -7th, 2011, Miracle Grand Hotel, Bangkok, Thailand

3) Khamphee Phomphrai,* Chatyapha Pongchan-o, Wipavee Thumrongpatanaraks, “Synthesis and Characterization of Bis(amidinate) Tin(II) Complexes for Ring-Opening Polymerization of ε-Caprolactones” *Poster presentation*, PERCH-CIC International Congress VII: Towards a

Sustainable Future on May 4th - 7th, 2011, Jomtien Palm Beach Hotel & Resort, Pattaya, Chonburi, Thailand

นอกจากนี้กลุ่มผู้วิจัยได้นำเสนอผลงานวิจัยแบบโปสเตอร์และแบบบรรยายในที่ประชุมวิชาการนานาชาติทั้งในและต่างประเทศดังแสดง

1. Khamphee Phomphrai “Synthesis of Cyclic Polyesters Catalyzed by Ligated Tin(II) Complexes.” Oral Presentation, The 2nd Taiwan-Thailand Bilateral Mini-Symposium: Chemistry for Creative Economy, Bangkok, Thailand, January 17, 2013.

2. Khamphee Phomphrai “Cyclic Polyesters: Synthesis Made Easy.” Oral Presentation, The 38th Congress on Science and Technology of Thailand (STT38), The Empress Convention Centre, Chiangmai, Thailand, October 17-19, 2012.

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4. Khamphee Phomphrai “Synthesis of ligated tin(II) complexes for the polymerization of lactide and ε-caprolactone.” Oral Presentation, International Symposium on Nano Science and Functional Materials: Post-symposium of International Symposium on Catalysis and Fine Chemicals 2011, Nara, Japan, December 10, 2011.

5. Khamphee Phomphrai, Passachon Ratanapanee “Polymerization of Cyclic Esters Catalyzed by Tin(II) Complexes.” Poster Presentation, International Symposium on Catalysis and Fine Chemicals 2011, Nara, Japan, December 4-8, 2011.

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7. Sadanan Kerdpocha, Khamphee Phomphrai “Syntheses and characterizions of tin(II) complexes containing 2-imminopyrrolyl ligands.” Poster Presentation, Pure and Applied

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9. Khamphee Phomphrai “Synthesis of Biodegradable Polymers using Ligated Metal Complexes.” Oral Presentation, 14th Asian Chemical Congress (14ACC): Contemporary Chemistry for Sustainability and Economic Sufficiency, Bangkok, Thailand, September 5-8, 2011.

ภาคผนวก

This article is published as part of the *Dalton Transactions* themed issue entitled:

New Talent Asia

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Guest Editor Masahiro Yamashita
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Published in issue 10, 2011 of *Dalton Transactions*

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Synthesis of high-molecular-weight poly(ε-caprolactone) catalyzed by highly active bis(amidinate) tin(II) complexes†

Khamphee Phomphrai,* Chatyapha Pongchan-o, Wipavee Thumrongpatanaraks, Preeyanuch Sangtrirutnugul, Palangpon Kongsaeree and Manat Pohmakotr

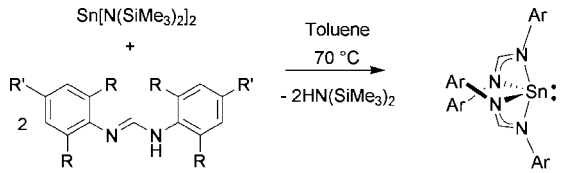
Received 18th August 2010, Accepted 10th November 2010
DOI: 10.1039/c0dt01050b

A series of bis(amidinate) tin(II) complexes is synthesized and shown to rapidly polymerize ε-caprolactone (ε-CL) in the presence and absence of benzyl alcohol giving high-molecular-weight poly(ε-CL) (M_n up to 160,600 Da). Ligands having electron donating groups were found to accelerate the polymerization by making the complex more nucleophilic.

There has been increasing attention towards biodegradable and biocompatible polymers during the past decade. Polyesters such as polyglycolide, polylactide (PLA), poly(ε-caprolactone) (PCL) and their copolymers have received significant attention.[1] Their properties such as tensile strength, degradation rate, and compatibility in the body are undoubtedly determined by the stereochemistry, composition, molecular weight, and dispersity of the polymers. Such polyesters have been successfully synthesized using various metal alkoxide complexes.[2] While electropositive metal complexes such as Zn, Mg, and Ca have been found to be highly active, the less active tin(II) complex specifically tin(II) bis(2-ethylhexanoate), $Sn(Oct)_2$, has been used industrially.[2,3] This is due to its high solubility and thermal stability in the molten monomers, thus allowing the melt polymerization in the absence of solvents. In addition, several well-defined tin(II) complexes have been shown to be active for the polymerization of cyclic esters giving high-molecular-weight polymers with narrow polydispersity index.[2,4] For organocatalysts, N-heterocyclic carbenes (NHCs) were reported to be efficient catalysts for high molecular weight linear PLA,[5] and recently, for linear PCL.[6] However, in the absence of suitable initiators, Culkin *et al.* later reported the NHC catalysts to generate cyclic PLA in THF.[7]

Following the success of carbene initiators, we hypothesized that, being three rows below carbon in the periodic table, the stannylene[8] could be an efficient initiator for the polymerization of cyclic esters as well. Herein, we reported the synthesis of highly active bis(amidinate) tin(II) complexes and their application in the solvent-free polymerization of ε-caprolactone (ε-CL) leading to high-molecular-weight PCL.

Amidine ligands were chosen in this work due to the ease of ligand preparation and modification. The substituents on the aryl groups can be modified systematically to maximize the catalyst activity. Ligands **1a–1e** were prepared from the reaction of triethyl orthoformate with the corresponding anilines. Reactions of 2 equiv of ligands **1a–1e** with $Sn[N(SiMe_3)_2]_2$ gave the bis(amidinate) tin(II) complexes **2a–2e**, respectively (Scheme 1). All complexes were isolated in moderate to high yields. Although related bis(amidinate) tin(II) complexes have been reported,[9] they have never been used as a catalyst for the polymerization of ε-CL.



1a; R = H, R' = H
1b; R = H, R' = OCH_3
1c; R = H, R' = CF_3
1d; R = CH_3, R' = H
1e; R = ^{i}Pr, R' = H

2a; R = H, R' = H
2b; R = H, R' = OCH_3
2c; R = H, R' = CF_3
2d; R = CH_3, R' = H
2e; R = ^{i}Pr, R' = H

Scheme 1 Synthesis of bis(amidinate) tin(II) complexes.

Complex **2e** was characterized crystallographically (see ESI†) indicating a four-coordinate tin complex having a distorted square pyramidal geometry where Sn is at the top of the pyramid and the four nitrogen atoms are at the base similar to the related bis(amidinate) tin(II) complexes reported earlier.[9] The position of the lone-pair electrons above Sn atom is clearly evidenced.

Complex **2e** was tested for the solvent-free polymerization of ε-CL using a low ε-CL:**2e** molar ratio of 10 : 1 at 110 °C for 1 min (>99% conversion by ^{1}H NMR) in order to study the polymer structure by mass spectrometry and NMR. MALDI-TOF spectrum of the resulting polymer is shown in Fig. 1 (top). Interestingly, the repeating mass is assigned to $[\varepsilon\text{-CL}]_n + Na^+$. The mass of the end group is clearly missing. This is in agreement

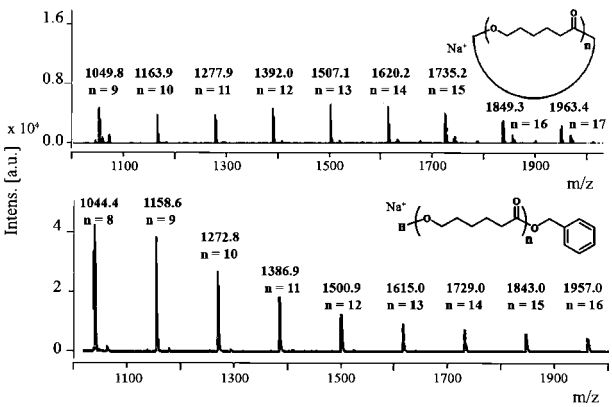


Fig. 1 MALDI-TOF spectra of PCL synthesized without addition of BnOH (top) and with addition of 1 equiv of BnOH (bottom).

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† Electronic supplementary information (ESI) available: Synthesis and characterization of **2a–e**, polymerization procedure, ORTEP drawing of **2e**, water contact angles of PCL, and GPC traces. CCDC reference number 795658. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01050b

with the ^{1}H NMR spectrum of the resulting polymer as shown in Fig. 2(a) where a triplet peak of the HOCH_2- end group at 3.6 ppm is not observed. These results suggest that the majority, if not entirety, of the low-molecular-weight polymer is cyclic PCL.[10] The peaks with much lower intensities observed at 1600-2200 Da (*e.g.* 1753.3, 1867.2, 1981.4, 2098.5) are assigned to linear H[CL]$_n$OH+Na$^+$. This minor linear polymer having H_2O end group may arise during polymer precipitation and purification. For comparison, a polymerization using ε-CL:**2e** molar ratio of 10 : 1 was performed under the same condition but with the addition of 1 equiv of benzyl alcohol (>99% conversion by ^{1}H NMR). MALDI-TOF spectrum of the resulting polymer is shown in Fig. 1 (bottom). The repeating mass is assigned to H[ε-CL]$_n$OBn + Na$^+$. The ^{1}H NMR spectra of the resulting polymer shown in Fig. 2(b) clearly reveals a triplet peak of the HOCH_2- end group at 3.6 ppm confirming the linear structure of the polymer. At higher ε-CL:**2e** molar ratio, the NMR signal of the end group is too small to be observed. The polymerization mechanism accounted for the observed linear and cyclic PCL is still under investigation. A similar mechanism to the NHC catalyst system is possible by using the lone-pair electrons to attack the ester group of monomer.[7] However, a polymerization initiated by anionic ligand followed by intramolecular transesterification leading to cyclic PCL cannot be ruled out at this point.

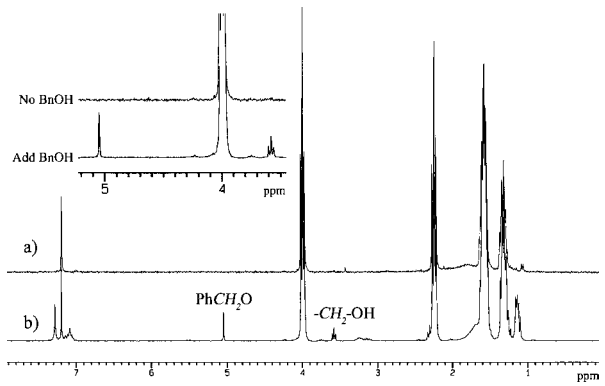

Fig. 2 ^{1}H NMR spectra of PCL synthesized from ε-CL:**2e** ratio = 10 : 1 (a) without addition of BnOH and (b) with addition of 1 equiv of BnOH.

Complexes **2a–e** were used to polymerize ε-CL under solvent-free condition at 110 °C using ε-CL:Sn:BnOH molar ratio of 500 : 1 : 1 and a fixed time at 3 min. The polymerization results were summarized in Table 1, entries 1–5. All catalysts were highly active for the polymerization of ε-CL giving complete conversion in only 3 min. The polymers have high M_n (42,200–107,400 Da) and broad PDI of 1.65–1.90. The unusually high M_n and broad PDI are indicative of slow initiation compared to the propagation. This is also supported by the observation that the complexes **2a–e** are soluble in ε- CL only at elevated temperature but not at room temperature. In addition, the broad PDI could be a result of the mass transportation problems due to high viscosity. For comparison, a commercial Sn(Oct)$_2$ was used as catalyst under identical condition as shown in entry 14. The polymerization was much slower compared to our catalysts giving only 58% conversion in 50 min.

For polymerizations without the addition of alcohol, complexes **2a–e** were used to polymerize ε-CL under solvent-free condition at 110 °C using ε-CL:Sn molar ratio of 500 : 1 and a fixed time at 2 min. The polymerization results were summarized in Table 1, entries 6–10. All catalysts were also active for the polymerizations of ε-CL. The order of activity based on conversion is **2e** > **2d** > **2b** > **2a** > **2c**. The polymerization using **2e** is the fastest giving 97% conversion in only 2 min. The polymer has high M_n of 69,800 Da and a PDI of 1.85. Other catalysts were less active producing PCL with M_n (46,600–99,100 Da) and PDI of 1.55–1.85. For complex **2e**, a plot of M_n and PDI *versus* % conversion is shown in Fig. 3. The polymer has low PDI at low conversion and higher PDI at later stage. The M_n of the polymer also increases with increasing conversion. Interestingly, polymerization in toluene at 70 °C for 25 h using ε-CL:**2e** = 500 : 1 with and without alcohol addition gave no polymer. Blank polymerizations (no catalyst) with and without alcohol addition at 110 °C were also carried out for 2 days giving no polymer.

Table 1 Solvent-free polymerizations of ε-CL at 110 °C

Entry	Catalyst	[CL]/[Sn]	Time/min	Conv.[a] (%)	M_n[b] (Dalton)	PDI[b]
1	**2a**[c]	500	3	>99	69,100	1.70
2	**2b**[c]	500	3	>99	40,900	1.78
3	**2c**[c]	500	3	>99	107,400	1.90
4	**2d**[c]	500	3	>99	42,200	1.84
5	**2e**[c]	500	3	>99	70,400	1.65
6	**2a**	500	2	47	66,300	1.55
7	**2b**	500	2	75	48,600	1.85
8	**2c**	500	2	30	99,100	1.69
9	**2d**	500	2	80	46,600	1.85
10	**2e**	500	2	97	69,800	1.85
11	**2e**	1,000	5	>99	70,100	1.80
12	**2e**	5,000	20	82	137,400	1.94
13	**2e**	10,000	60	94	160,600	2.07
14	Sn(Oct)$_2$[c]	500	50	58	30,700	1.32

[a] Conversions determined by ^{1}H NMR spectroscopy. [b] Determined by GPC, calibrated using polystyrene standards. Correction factor of 0.68 was also applied.[11] [c] Polymerization with addition of 1 equiv of BnOH.

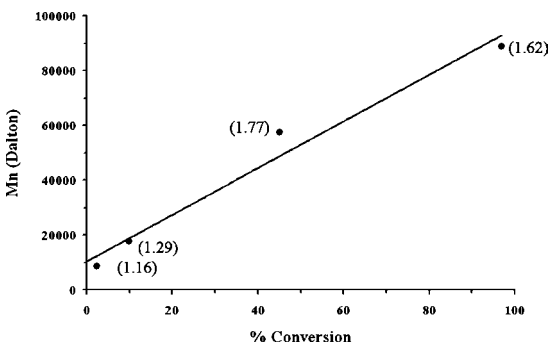

Fig. 3 Molecular weight data (PDI in parenthesis) of PCL obtained at different conversion using ε-CL:**2e** molar ratio of 500 : 1 at 110 °C.

Complexes **2a–e** can be classified into two groups having different electronic (**2a–c**) and steric (**2a**, **2d**, **2e**) contributions. In term of electronic contribution, the order of reactivity is **2c** (R′ = CF_3) < **2a** (R′ = H) < **2b** (R′ = OMe) in agreement with the increasing electron donation of the aryl groups. Based on the polymerization mechanism for NHC catalyst system,[7] the metal in complex **2b** is electron-rich and more nucleophilic and hence more susceptible to attack ε-CL. In term of steric hindrance, the order of reactivity is **2a** (R = H) < **2d** (R = Me) < **2e** (R = ^{i}Pr) in

agreement with the increasing steric hindrance of the *ortho*-alkyl groups. This was surprising at first since more hindered complex gave higher activity. However, these results are not unprecedented because there are reports that sterically demanding substituents enhanced the catalytic activity of the catalysts.[12] In addition, the ^{i}Pr groups in **2e** are more electron donating making the complex more nucleophilic.

For complex **2e**, the polymerizations using higher ε-CL:Sn molar ratios of 1000, 5000, and 10000 were performed at 110 °C (Table 1, entries 11–13). Great care was taken to exclude moisture or impurities from the reaction. In entry 13, PCL with M_n = 160,600 Da was obtained in 1 h. For 1000 : 1 and 5000 : 1 molar ratios, the polymerizations finished in 5 and 20 min having the M_n′s of 70,100 and 137,400 Da, respectively.

The difference between surfaces of PCL synthesized with and without addition of BnOH was also observed by water contact angle analysis.[13] Polymers having similar molecular weights based on GPC were chosen. The average water contact angle of PCL (Table 1, entry 10, synthesized without addition of alcohol) is 107.4 ± 2.5° while that of entry 5 (with addition of BnOH) is 92.8 ± 0.6°.

In conclusion, a series of bis(amidinate) tin(II) complexes were successfully synthesized and characterized. The major advantage is the simplicity of complex preparation and a large number of possible ligand library to fine tune both reactivity and selectivity of the catalysts. The bis(amidinate) tin(II) complexes are active for the polymerization of ε-CL in the presence and absence of alcohol giving high-molecular-weight PCL. Although the low-molecular-weight PCL synthesized using a low ε-CL:Sn molar ratio of 10 : 1 in the absence of alcohol was shown to be cyclic based on mass spectrometry and NMR, the exact topology (linear or cyclic) of high-molecular-weight PCL synthesized using higher ε-CL:Sn molar ratio is still uncertain due to the lack of access to required instruments (*e.g.* viscometer, light scattering detector) used to prove the cyclic structure.[7,14] Nonetheless, the bis(amidinate) tin(II) complexes are highly active for the solvent-free polymerization of ε-CL in the presence and absence of BnOH giving high-molecular-weight PCL. This catalyst system is much more active than the commercial $Sn(Oct)_2$ catalyst. Amidinate ligands having electron-donating group were found to accelerate the polymerization by making the complex more nucleophilic. Further attempts to characterize the polymers and to understand the insight mechanism of the polymerization are in progress.

We acknowledge financial support from Commission on Higher Education, The Thailand Research Fund, and Mahidol University. Financial support from the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education is gratefully acknowledged. This work is also supported by Center for Catalysis and Faculty of Science, Mahidol University. We thank Pailin Srisuratsiri for help with X-ray crystallography.

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Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 12704

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PAPER

Synthesis of cyclic polylactide catalysed by bis(salicylaldiminato)tin(II) complexes†

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Received 25th July 2012, Accepted 24th August 2012
DOI: 10.1039/c2dt31678a

Eight bis(salicylaldiminato)tin(II) complexes have been synthesized from the reaction of $Sn[N(SiMe_3)_2]_2$ and 2 equiv of the corresponding ligands at room temperature. The ligands, synthesized from salicylaldehyde and amines, were designed to have different electronic and steric properties using different amines to synthesize the tin(II) complexes as aniline (**2a**), 2,6-dimethylaniline (**2b**), 2,6-diisopropylaniline (**2c**), 4-methoxyaniline (**2d**), 4-trifluoromethylaniline (**2e**), methylamine (**2g**), and *tert*-butylamine (**2h**). Ligand variation at the salicyl group synthesized from 4-bromosalicylaldehyde and 2,6-diisopropylaniline was used to form complex **2f**. Complex **2c** was characterized crystallographically. All catalysts were active for the neat polymerization of L-lactide at 115 °C. At a lactide : Sn molar ratio of 10 : 1, cyclic polylactide (PLA) was obtained as demonstrated by ^{1}H NMR and mass spectrometry. Addition of 1 equiv of benzyl alcohol in the polymerization produced linear PLA. At a higher lactide : Sn molar ratio of 200 : 1, high molecular weight PLAs with M_n up to 132 200 Daltons were obtained. Results from GPC coupled with light scattering detector and viscometer suggested that they are cyclic PLA. The order of reactivity based on conversion was determined to be **2c** < **2b** < **2a** in accordance with lower steric hindrance. For electronic contribution, the order of **2e** < **2a** < **2d** was observed in agreement with the increasing electron donation of the ligands. Complex **2g** having the smallest substituents was found to be the most active catalyst.

Introduction

Biodegradable polyesters such as polylactide (PLA) and polylactones have been extensively explored in both academic and industrial research due to several appealing properties such as biodegradability and biocompatibility.[1–3] The polymers have found numerous applications for instance in drug delivery,[4] scaffolds,[5,6] and food packaging.[7] The physical properties of the polymers can be fine-tuned by copolymerization with other monomers giving polymers with different regio- and stereochemistry resulting in specific properties or functions.[8–11] In addition to copolymerization, the physical properties of the polymers can be adjusted by changing the topologies of the polymers such as star, graft, cross-linked, and hyperbranched structures.[12–15] Among these elaborate polymer topologies, cyclic polymers have received significant attention.[16–18] Cyclic structures have several physical properties such as glass transition temperatures (T_g), melting temperatures (T_m), morphologies, melt viscosities, thermostabilities, compatibilities, hydrodynamic volume, and intrinsic viscosity different from their linear counterparts of the same molecular weight.[17] There are two general methods to synthesize cyclic polymers: ring-closure and ring-expansion techniques.[19] The ring-closure techniques usually suffer from highly diluted conditions and the need to purify cyclic structures from the linear impurities. However, high dilution is not required for the ring-expansion techniques making large-scale synthesis of cyclic polymers possible.

Although several metal alkoxide complexes have been reported in the polymerizations of lactide or lactones, they only produced linear polymers or cyclic impurities.[20] One of the most successful syntheses[16,17] of cyclic polylactide or polylactones using a ring-expansion technique was reported by Waymouth and co-workers.[21–23] Zwitterionic polymerization of lactides by *N*-heterocyclic carbenes (NHCs) has led to cyclic polylactides in high yield. Interestingly, polymerization of lactides using NHCs in the presence of alcohol initiators gave linear polylactide.[24] Furthermore, NHCs can be used in the synthesis of linear[25] and cyclic[26] poly(ε-caprolactone) (PCL) in a similar concept. Following the success of carbene initiators, we hypothesize that stannylenes,[27] being three rows below carbon in the periodic table, could be active catalysts for the polymerization of cyclic esters leading to cyclic polymers similar to carbenes. We recently reported that bis(amidinate)tin(II) complexes were active for the

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† Electronic supplementary information (ESI) available: ^{1}H and $^{13}C\{^1H\}$ NMR spectra of complexes **2b–h**. CCDC 893746. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31678a

polymerization of ε-caprolactone.[28] At a low monomer : catalyst ratio, cyclic PCL was obtained as confirmed by NMR and mass spectrometry. Thus, tin(II) complexes under selected ligand sets can function similarly to carbenes in the polymerization. This work was the only example that attempted to use the lone-pair electrons on tin atom as initiator in the polymerization as opposed to using tin alkoxides as an initiator.[20] Herein, we demonstrate another example using this concept in the polymerization of lactide by bis(salicylaldiminato)tin(II) complexes.

Results and discussion

Syntheses and characterizations of tin(II) complexes

Salicylaldimine ligands were chosen in this study due to the simplicity of ligand preparation and modification. Both steric and electronic contributions of the ligands can be tailored systematically and independently. This ligand set was extensively used in catalyst development such as in olefin polymerization[29] and in the polymerization of cyclic esters.[30] Ligands **1a–h** were prepared by simple condensation reaction between salicylaldehyde and the corresponding amines. Reactions between 2 equiv of ligands **1a–h** with $Sn[N(SiMe_3)_2]_2$ gave the corresponding bis(salicylaldiminato)tin(II) complexes **2a–h** as shown in Scheme 1. Complex **2c** was characterized crystallographically and shown in Fig. 1 indicating a four-coordinate tin center having distorted seesaw geometry. The crystal structure clearly reveals the position of the lone-pair electrons on tin atom often seen in tin(II) complexes.[28,30g,h,31,32] The NMR spectrum (see ESI†) of complexes **2b**, **2c**, and **2f** at room temperature revealed several broad peaks as a result of a fluxional process. These peaks become sharper and coalescent at 50 °C. This result indicated a slow rotation of $N–C_{Ar}$ bonds (*e.g.* N1–C8 bond in Fig. 1) compared to NMR time-scale.

Polymerizations of lactide

The catalysts were designed to have different steric contributions experienced by the metal center where the order of increasing steric hindrance of the substituents at the *ortho* positions is **2a** (H) < **2b** (Me) < **2c** (^{i}Pr). The catalysts were also designed to have different electronic contributions experienced by the metal center where the order of increasing electron donation of the substituents at the *para* positions is **2e** (CF_3) < **2a** (H) < **2d** (OMe). In addition, catalysts containing smaller salicylaldiminato ligands that do not contain *N*-phenyl rings were also investigated as in complexes **2g** (Me) and **2h** (^{t}Bu). The electronic effect of bromine at the *para* position of the salicyl group was also investigated as in complex **2f** compared to **2c**.

As demonstrated in bis(amidinate)tin(II) complexes,[28] we believe that the lone-pair electrons of tin behave similarly to the NHCs in the polymerization of LA giving cyclic PLA. To test this hypothesis, complex **2c** was reacted with 10 equiv of L-LA at 115 °C for 10 min in the absence of solvent (melt polymerization). For comparison, the polymerization was conducted with and without the addition of benzyl alcohol in order to observe the chain end for linear/cyclic analysis. Great care was taken to exclude moisture or impurities from the reaction. ^{1}H NMR spectra of the crude polymers are shown in Fig. 2. Clearly, in addition to the signals of the ligand at 1.2, 3, 7–7.5 ppm, the linear polymer synthesized with addition of 1 equiv of benzyl alcohol reveals the chemical shift of the HOC*H*Me– end group at 4.3 ppm (Fig. 2a). This is in agreement with the result from ESI mass spectrometry as shown in Fig. 3 (bottom) where the repeating mass of 72.02*n* + 108.1 + 23 was assigned to

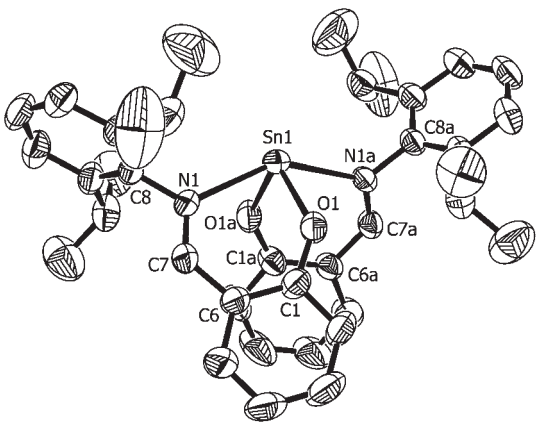
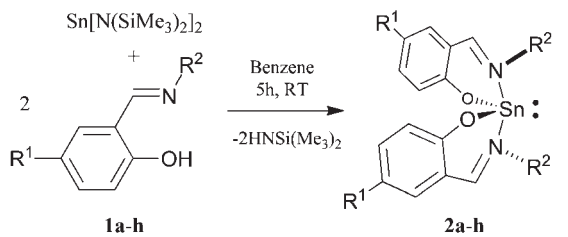


Fig. 1 ORTEP drawing of complex **2c** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Sn1–N1 2.477(2), Sn1–O1 2.052(2), O1–C1 1.323(3), N1–C7 1.276(3), N1–C8 1.438(3); O1–Sn1–O1a 95.0(1), O1–Sn1–N1 78.35(8), N1–Sn1–N1a 148.5(1).



a; R^1 = H, R^2 = Ph
b; R^1 = H, R^2 = 2,6-$Me_2C_6H_3$
c; R^1 = H, R^2 = 2,6-$^i Pr_2C_6H_3$
d; R^1 = H, R^2 = 4-(OMe)C_6H_4
e; R^1 = H, R^2 = 4-$(CF_3)C_6H_4$
f; R^1 = Br, R^2 = 2,6-$^i Pr_2C_6H_3$
g; R^1 = H, R^2 = Me
h; R^1 = H, R^2 = ^{t}Bu

Scheme 1 Synthesis of bis(salicylaldiminato)tin(II) complexes.

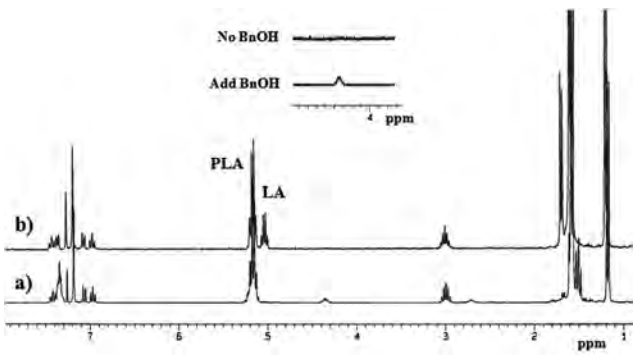


Fig. 2 ^{1}H NMR spectra of PLA synthesized from LA : **2c** molar ratio = 10 : 1 (a) with and (b) without addition of 1 equiv of BnOH.

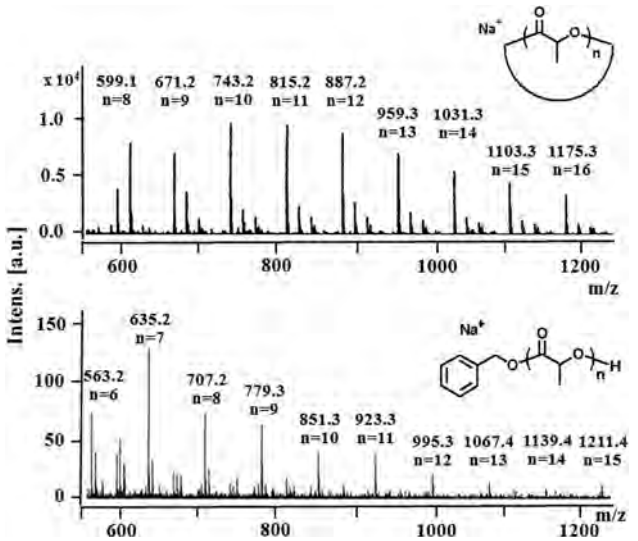


Fig. 3 ESI mass spectra of PLA synthesized from LA : **2c** molar ratio = 10 : 1 with (bottom) and without (top) addition of 1 equiv of BnOH.

H[LA/2]$_n$OBn + Na^+ indicating linear PLA with *H*OCHMe– and –C(O)*OBn* end groups. For the polymerization without the addition of benzyl alcohol, the chemical shift of the HOC*H*Me– end group at 4.3 ppm is not observed as shown in Fig. 2b. This result indicates the cyclic structure of PLA. The cyclic structure is also confirmed by ESI mass spectrometry as shown in Fig. 3 (top). The repeating mass (72.02*n* + 23) was assigned to cyclic [LA/2]$_n$ + Na^+ where the mass of the end group was not detected. Two minor repeating masses were also observed in Fig. 3 (top). The taller series are 72.02*n* + 39 assignable to cyclic [LA/2]$_n$ + K^+ and the shorter series are 72.02*n* + 32 + 23 assignable to linear H[LA/2]$_n$OCH$_3$ + Na^+. The shorter series having methoxy end group were possibly generated during the polymer precipitation where methanol was used. Interestingly, the repeating mass having ligand **1c** as an end group was not observed indicating that the ligand did not participate in the ring-opening/closing steps. We also found that the cyclic and linear structures of PLA were retained at a higher LA : **2c** molar ratio of 100 : 1 under the same polymerization condition where, from ^{1}H NMR spectra, the chemical shift of the HOC*H*Me– end group at 4.3 ppm appeared in linear PLA but disappeared in cyclic PLA.

To confirm the cyclic structure of PLA at higher molecular weight, gel permeation chromatography (GPC) coupled with a light-scattering detector and viscometer was used. In order to compare between linear and cyclic structures, both polymers must have enough molecular weight overlap in GPC. We found that, in melt polymerization, the molecular weight of PLA cannot be correctly predicted by the monomer : catalyst molar ratio as in the NHC system. Thus, several batches of L-lactide polymerization using complex **2c** with (LA : **2c** : BnOH = 500 : 1 : 1) and without (LA : **2c** = 200 : 1) addition of BnOH were carried out at 115 °C and quenched at different times. Linear PLA having M_n = 43 000 Daltons (PDI = 1.66) and cyclic PLA having M_n = 71 200 Daltons (PDI = 1.74) were selected and the GPC results are shown in Fig. 4. For polymers having the same molecular weight, cyclic PLA prepared by

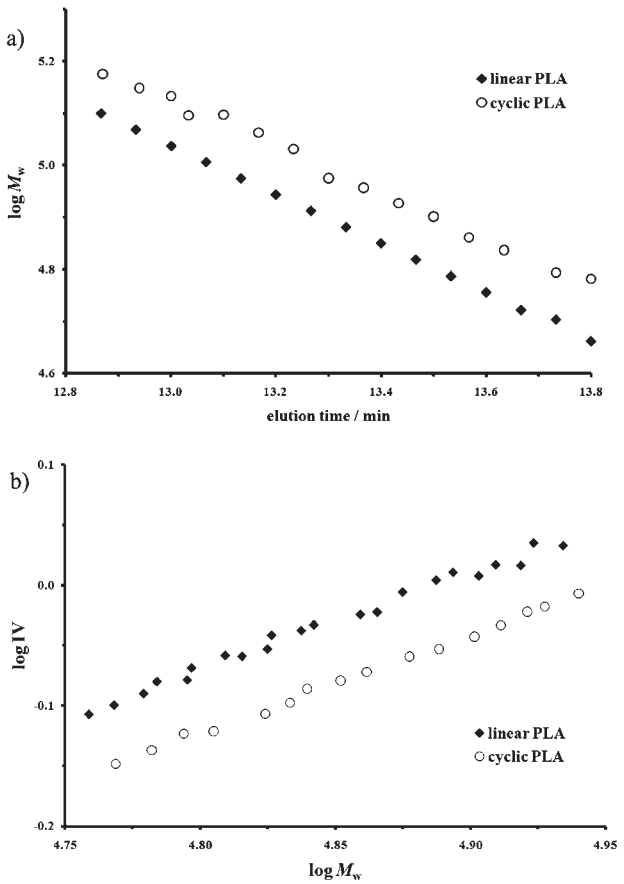


Fig. 4 (a) Plot of logarithm of molecular weight *vs.* elution time and (b) double logarithmic plots of intrinsic viscosity (IV) *vs.* molecular weight.

complex **2c** in the absence of BnOH eluted slower than linear PLA prepared in the presence of BnOH as demonstrated in Fig. 4a. This is a result of smaller hydrodynamic volume of the cyclic structure compared to the linear structure. Results from the viscometer also confirmed the cyclic structure of PLA synthesized in the absence of alcohol. A plot of log IV *vs.* log M_w is shown in Fig. 4b. The cyclic structure has less intrinsic viscosity compared to the linear structure of the same molecular weight.[21,33,34]

Melt polymerizations of L-LA were performed at 115 °C using complexes **2a–h** as catalyst. The melt polymerization results using a LA : Sn molar ratio of 200 : 1 and a fixed time of 25 min are summarized in Table 1, entries 1–8. All catalysts were active for the melt polymerization of L-LA. In general, the molecular weights of PLA are much higher than the expected values and the PDIs are rather broad. This is indicative of a slow initiation step compared to the propagation step. In addition, the broad PDI could be a result of mass transportation problems due to high viscosity. We have designed the substituents of the ligands in order to tailor the effect of the electronic and steric influences. Based on these considerations, it is more informative to split the catalysts into 3 groups having different steric (**2a–c**) and electronic (**2a**, **2d–f**) contributions of the ligands derived from substituted anilines. The third group contains ligands derived from alkyl amines (**2g**, **2h**).

Table 1 Melt polymerization of L-LA using complexes **2a–h** at 115 °C

Entry	Catalyst	[LA] : [Sn]	Time/min	Con.[a] (%)	M_n[b]	PDI[b]
1	**2a**	200	25	>99	109 700	1.90
2	**2b**	200	25	85	96 800	1.96
3	**2c**	200	25	77	113 500	1.72
4	**2d**	200	25	>99	88 500	1.59
5	**2e**	200	25	89	132 200	1.85
6	**2f**	200	25	63	71 400	1.60
7	**2g**	200	25	>99	92 000	1.90
8	**2h**	200	25	54	13 600	1.39

[a] Conversion determined by ^{1}H NMR spectroscopy. [b] Determined by GPC, calibrated using polystyrene standards.

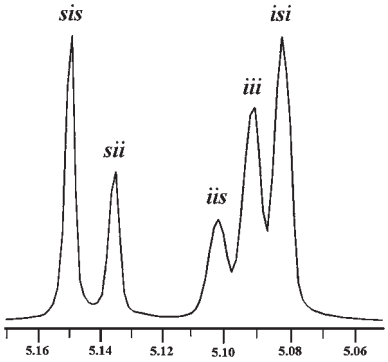


Fig. 5 Homonuclear decoupled ^{1}H NMR spectrum of the methine proton of poly(*rac*-lactide) prepared using complex **2c**.

According to the percent conversions (Table 1, entries 1–3), the order of reactivity of the first group having different steric hindrance is **2c** (^{i}Pr, 77%) < **2b** (Me, 85%) < **2a** (H, >99%). This order is in agreement with decreasing steric hindrance of the *ortho*-alkyl groups (^{i}Pr, Me, and H) where the crowded ligands should suppress the polymerization rates. The order of reactivity of the second group (Table 1, entries 1, 4–5) having different electronic contribution is **2e** (CF_3, 89%) < **2a** (H, >99%), **2d** (OMe, >99%). Because the polymerizations using complexes **2a** and **2d** were greater than 99% in 25 min, another set of polymerizations having shorter polymerization time was used for complexes **2a** and **2d**. The conversions of L-LA polymerization at 115 °C and 5 min were 15 and 42% for complexes **2a** and **2d**, respectively. Thus, the order of reactivity for the second group is **2e** (CF_3) < **2a** (H) < **2d** (OMe) in agreement with the increasing electron donation of the ligands where OMe group is more electron-donating than the CF_3 group. The electron donation from the ligand makes the tin complex more nucleophilic[28] and susceptible to attack the ester group of LA in agreement with the polymerization mechanism using NHCs proposed by Waymouth.[21] This explanation is also in agreement with the result in entry 6 when complex **2c** is compared with complex **2f** where the Br atom pulls electrons from the metal making complex **2f** less active. For the third group (Table 1, entries 7–8), the order of reactivity is **2h** (^{t}Bu, 54%) < **2g** (Me, >99%) in agreement with decreasing steric hindrance (^{t}Bu > Me) of the ligands. When complex **2g** was used to polymerize L-LA at 115 °C and 5 min, the conversion was 78%. Thus, the reactivity of complex **2g** derived from methyl amine is higher than those of complexes **2a** and **2d** derived from substituted anilines possibly because of the much less crowded environment around the metal center in **2g**. Note that racemization of the stereocenter of poly(L-lactide) was not observed for all catalysts. All complexes were active in the melt polymerization of *rac*-lactide under the same conditions. Homonuclear decoupled ^{1}H NMR of the methine proton of poly(*rac*-lactide) obtained from all catalysts showed the same pattern as seen in Fig. 5 indicating atactic PLA with slight heterotactic enhancement.[35]

At this point we believe that the mechanism of LA polymerization using bis(salicylaldiminato)tin(II) complexes is similar to that using NHCs.[21] Thus, the polymerization is believed to occur using the lone-pair electrons on tin(II) to attack the ester group of lactide. Cyclic PLA is formed after the intramolecular ring-closing step. This is different from the synthesis of cyclic poly(ε-caprolactone) by Okuda,[36] Duchateau and Mountford,[37] and Trifonov and Kerton[38] where the multidentate di-anionic ligands participated in the ring-opening polymerization. In our case, if the mono-anionic salicylaldiminato ligand participated in the ring-opening polymerization, the ligand should come off the metal and become the chain end because there is nothing else to hold the ligand firmly to the metal as in the di-anionic ligands giving linear PLA as a product. Because linear PLA was not observed in our system, ligand participation can be excluded. This is because the negative charge on oxygen atom delocalized into the π-system reducing its nucleophilicity to attack the monomer. It is interesting to note that both odd and even numbers of *n* are observed in the ESI mass spectrum (Fig. 3). This information implies that, during the ring-closing step, the alkoxy group of the growing polymer chain can attack any ester group along the macrocycles.

Conclusions

We have demonstrated a simple and convenient preparation of bis(salicylaldiminato)tin(II) complexes that are active catalysts for the polymerization of L-LA leading to cyclic PLA. The catalyst activities are greatly affected by steric and electronic contributions of the ligands where steric hindrance suppresses the polymerization rates and electron-donating groups enhances the polymerization rates. The electronic effect in this catalyst system is in agreement with our recent findings in the polymerization of ε-caprolactone leading to PCL using bis(amidinate)tin(II) complexes.[28] In addition, the melt polymerization does not need solvent, thus, making the process more environmentally friendly and suitable for large-scale synthesis. Since the ligand libraries for tin(II) are endless, the improved catalysts can be easily and systematically fine-tuned in both electronic and steric contributions.

Experimental

General details

All operations were carried out under dry argon atmosphere using standard Schlenk techniques. Benzene, hexanes, and toluene were dried using a PURE SOLV MD-5 solvent purification system from Innovative Technology Inc. Ligands **1a–h**

were synthesized according to the literature with minor modification.[39–42] The syntheses of complex **2a**[43] and $Sn[N(SiMe_3)_2]_2$[44] were reported in the literature. Lactides were purchased from Aldrich and sublimed three times before use. All compounds used in the synthesis of ligands were purchased from Aldrich or Acros and used as received.

Measurements

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 or AVANCE 500 spectrometer and referenced to protio impurities of commercial chloroform-d ($CDCl_3$, δ 7.26 ppm) or benzene-d_6 (C_6D_6, δ 7.16 ppm) as internal standards. The X-ray crystallography data were collected at 293 K on a Bruker SMART CCD area-detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Mass spectrometry was obtained by micro-TOF-LC Bruker mass spectrometer. Mass spectrometry was carried out using a Bruker Data Analysis Esquire-LC mass spectrometer, ESI mode. Gel permeation chromatography (GPC) analyses were carried out on a Waters e2695 instrument equipped with Model 3580 refractive index detectors (Viscotek), Model 270 Differential Viscometer/Light Scattering Dual Detector and two 10 μm PL Gel columns. The GPC columns were eluted using tetrahydrofuran with a flow rate of 1.0 mL min^{-1} at 35 °C. Molecular weights and molecular weight distributions were calibrated with polystyrene standards ranging from 500 to 10 000 000 amu. Elemental analyses were performed on a Perkin-Elmer series II CHNS/O Analyzer 2400.

The synthesis of some bis(salicylaldiminato)tin(II) complexes was reported earlier starting from $SnCl_2$ and sodium salt of the corresponding ligands.[43] However, a preparation using 2 equiv of ligands and $Sn[N(SiMe_3)_2]_2$ is preferred.

General synthesis for complexes 2b–h

Benzene (20 mL) was added to a mixture of $Sn[N(SiMe_3)_2]_2$ (0.420 g, 0.956 mmol) and the corresponding salicylaldimine ligand (1.91 mmol) in a Schlenk flask. The mixture was stirred at room temperature for 5 h. The volatile components were subsequently removed under vacuum. The crude product was washed with hexanes giving a yellow or light green powder in moderate to high yield.

Bis[*N*-(salicylidene)-2,6-dimethylanilinato]tin(II), 2b. Light green powder (0.39 g, 72%). ^1H NMR (300 MHz, C_6D_6, 50 °C): δ 7.59 (s, 2H, C*H*═N–), 7.03–6.94 (m, 8H, Ar*H*), 6.82 (d, 2H, J_{HH} = 6.0 Hz, Ar*H*), 6.77 (d, 2H, J_{HH} = 8.3 Hz, Ar*H*), 6.49 (t, 2H, Ar*H*), 2.31 (s, 12H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 50 °C): δ 167.74 (*C*H═N), 165.94 (*C*–O–Sn), 149.22 (C_{Ar}–N–Sn), 135.47, 135.18, 130.82, 129.20, 128.68, 126.26, 123.67, 121.81, 116.76 (C_{Ar}), 19.46 (*C*H_3). Anal. Calcd for $C_{30}H_{28}N_2O_2Sn$: C, 63.52; H, 4.98; N, 4.94. Found: C, 63.84; H, 4.62; N, 5.10.

Bis[*N*-(salicylidene)-2,6-diisopropylanilinato]tin(II), 2c. Light green powder (0.43 g, 67%). X-ray suitable crystals were grown from concentrated benzene solution. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 7.91 (s, 2H, C*H*═N), 7.10 (m, 6H, Ar*H*), 7.01 (t, 2H, Ar*H*), 6.88 (d, 2H, Ar*H*), 6.76 (d, 2H, Ar*H*), 6.47 (t, 2H, Ar*H*), 4.22, 3.13 (broad s, 4H, C*H*(CH_3)$_2$), 1.60–0.80 (broad m, 24H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ 167.57 (*C*H═N), 165.67 (*C*–O–Sn), 146.81 (C_{Ar}–N–Sn), 141.73, 135.34, 135.29, 128.71, 127.21, 123.54, 121.85, 117.03 (C_{Ar}), 28.89 (*C*HMe$_2$) 25.07 (CH*Me*$_2$). Anal. Calcd for $C_{38}H_{44}N_2O_2Sn$: C, 67.17; H, 6.53; N, 4.12. Found: C, 66.89; H, 6.40; N, 3.84.

Crystal data for complex 2c. $C_{38}H_{44}N_2O_2Sn$, M = 679.47, monoclinic, space group $C2/c$, a = 8.8207(4) Å, b = 17.2625(5) Å, c = 23.179(1) Å, α = 90°, β = 90.977(2)°, γ = 90°, V = 3528.9(2) Å^3, Z = 4, λ = 0.71073 Å, μ = 0.757 mm^{-1}, T = 150 K, 7069 reflections measured, 4373 unique, R_{int} = 0.0610, R = 0.0405 (obs. data), wR = 0.0842 (obs. data), GOF = 1.029.

Bis[(*N*-salicylidene)-4-methoxyanilinato]tin(II), 2d. Green powder (0.46 g, 84%). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 8.21 (s, 2H, C*H*═N), 7.41 (d, 4H, Ar*H*), 7.23–7.17 (m, 4H, Ar*H*), 7.00 (d, 4H, Ar*H*), 6.64 (m, 4H, Ar*H*), 3.85 (s, 6H, OCH_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ 164.85 (*C*–O–Sn), 163.66 (*C*H═N), 158.68 (*C*–OMe), 143.50 (C_{Ar}–N–Sn), 135.19, 134.61, 123.39, 123.11, 121.43, 116.60, 114.96 (C_{Ar}), 55.78 (O*C*H_3). Anal. Calcd for $C_{28}H_{24}N_2O_2Sn$: C, 58.87; H, 4.23; N, 4.90. Found: C, 59.25; H, 4.16; N, 4.94.

Bis[(*N*-salicylidene)-4-trifluoromethylanilinato]tin(II), 2e. Yellow powder (0.44 g, 37%). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 7.62 (s, 2H, C*H*═N), 7.40 (d, 4H, Ar*H*), 7.17–7.10 (m, 6H, Ar*H*), 6.97 (d, 4H, Ar*H*), 6.55 (t, 2H, Ar*H*). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C): δ 166.22 (*C*H═N), 166.03 (*C*–O–Sn), 153.58 (C_{Ar}–N–Sn), 136.38, 136.20, 129.03, 127.25 (C_{Ar}), 125.38 (*C*F_3), 123.74, 123.28, 121.44, 117.29 (C_{Ar}). Anal. Calcd for $C_{28}H_{18}F_6N_2O_2Sn$: C, 51.97; H, 2.80; N, 4.33. Found: C, 51.71; H, 2.70; N, 4.36.

Bis[(*N*-(4-bromosalicylidene))-2,6-diisopropylanilinato] tin(II), 2f. Yellow powder (0.68 g, 86%). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.82 (s, 2H, C*H*═N), 7.18–7.07 (m, 10H, Ar*H*), 6.23 (d, 2H, Ar*H*), 3.64, 2.85 (br, 4H, C*H*Me$_2$), 1.50–0.80 (br m, 24 H, CH*Me*$_2$). ^1H NMR (500 MHz, $CDCl_3$, 50 °C): δ 7.82 (s, 2H, C*H*═N), 7.16–7.09 (m, 10H, Ar*H*), 6.24 (d, 2H, Ar*H*), 3.26 (br, 4H, C*H*Me$_2$), 1.16 (br, 24 H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 50 °C): δ 165.72 (*C*H═N), 163.78 (*C*–O–Sn), 145.68 (C_{Ar}–N–Sn), 141.13 (C_{Ar}–^{i}Pr), 137.33, 136.15, 128.58, 126.89, 125.00, 124.16, 122.79 (C_{Ar}), 107.76 (C_{Ar}–Br), 28.40 (*C*HMe$_2$), 24.75 (CH*Me*$_2$). Anal. Calcd for $C_{38}H_{42}Br_2N_2O_2Sn$: C, 54.51; H, 5.06; N, 3.35. Found: C, 54.74; H, 5.38; N, 3.18.

Bis[(*N*-salicylidene)methyliminato]tin(II), 2g. Yellow powder (0.35 g, 94%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.96 (s, 2H, C*H*═N), 7.13 (t, 2H, J_{HH} = 7 Hz, Ar*H*), 6.99 (d, 2H, J_{HH} = 7 Hz, Ar*H*), 6.64 (d, 2H, J_{HH} = 7 Hz, Ar*H*), 6.53 (t, 2H, J_{HH} = 7 Hz, Ar*H*), 3.49 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 165.53 (*C*H═N), 164.79 (*C*–O–Sn), 134.07, 133.79, 122.69, 120.97, 116.24 (C_{Ar}), 45.62 (*C*H_3). Anal. Calcd for $C_{16}H_{16}N_2O_2Sn$: C, 49.65; H, 4.17; N, 7.24. Found: C, 49.76; H, 3.92; N, 7.17.

Bis[(*N*-salicylidene)-*tert*-butyliminato]tin(II), 2h. Yellow oil purified by vacuum distillation (0.31 g, 68%). ^1H NMR

(300 MHz, C_6D_6, 25 °C): δ 8.05 (s, 2H, C*H*═N), 7.17 (t, 2H, ArH), 7.00 (d, 2H, ArH), 6.92 (d, 2H, ArH), 6.65 (t, 2H, ArH), 1.46 (s, 18H, C*Me*$_3$). ^{13}C{1H} NMR (75 MHz, $CDCl_3$, 25 °C): δ 163.21 (*C*–O–Sn), 160.18 (*C*H═N), 134.55, 133.13, 122.62, 121.85, 116.37 (C_{Ar}), 60.00 (*C*Me$_3$), 30.61 (C*Me*$_3$). Anal. Calcd for $C_{22}H_{28}N_2O_2Sn$: C, 56.08; H, 5.99; N, 5.95. Found: C, 55.85; H, 5.79; N, 5.88.

Polymerization of L-lactide

The following representative polymerization is for a lactide : **2c** molar ratio of 200 : 1. The amount of other tin(II) complexes can be adjusted accordingly.

Polymerization without the addition of benzyl alcohol. Complex **2c** (11.8 mg, 17.4 μmol, 1 equiv) and L-lactide (0.500 g, 3.47 mmol, 200 equiv) were added to a small reaction flask. The flask was flame sealed and completely submerged in a preheated oil bath at 115 °C with stirring. At the required time, the flask was taken out of the oil bath and then submerged into a cold water bath. A small amount of sample was taken for NMR analysis. The rest of the polymer was dissolved in CH_2Cl_2 (10 mL) and precipitated with excess methanol. The solid polymer was collected and dried under vacuum.

Polymerization with addition of benzyl alcohol. The polymerization was carried out similarly as described above except that 1 equiv of benzyl alcohol was added to the reaction along with the tin complex and L-lactide.

X-ray crystallography

The single crystal X-ray analysis was carried out at the Mahidol crystallographic facility. Diffraction measurements were made on a 4 K Bruker SMART[45] CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were mounted in paratone oil and held in a low-temperature N_2 stream during data collection. Cell constants and an orientation matrix for data collection were obtained from a least-square refinement using the measured positions of reflections in the range $3.52° < 2\theta < 57.4°$ for complex **2c**. The frame data were integrated by the program SAINT[46] and corrected for Lorentz and polarization effects. The structure was solved by the maXus crystallographic software package,[47] using direct methods (SIR97)[48] and refined by full-matrix least-squares method on $(F_{obs})^2$ using the SHELXTL-PC V 6.12 software package.[49] ORTEP drawing was generated using Ortep-3 for Windows.[50]

Acknowledgements

We acknowledge financial supports from National Innovation Agency (NIA) and from Office of the Higher Education Commission. We gratefully acknowledge financial support from the Royal Golden Jubilee Ph.D. Program (PHD/0039/2553), The Thailand Research Fund, and Mahidol University. Financial and instrumental supports from the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education is gratefully acknowledged. Office of the Higher Education Commission and Mahidol University under the National Research University Initiative are acknowledged. This work is also supported by Center for Catalysis, Faculty of Science, Mahidol University. We thank Prof. Tae-Lim Choi for help with linear/cyclic structural determination of PLA and Pailin Srisuratsiri for the help with X-ray crystallography.

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Syntheses of bis(pyrrolylaldiminato)aluminum Complexes for the Polymerisation of Lactide

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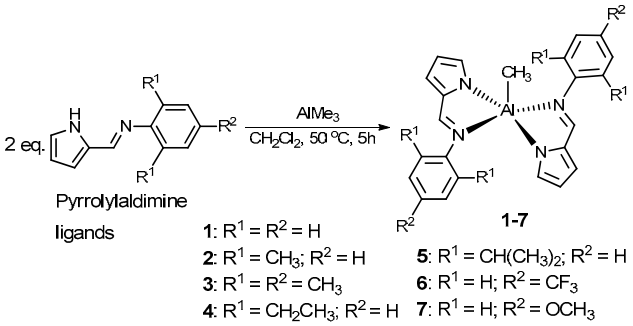
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Seven bis(pyrrolylaldiminato)aluminum methyl complexes were synthesized from the reactions of $AlMe_3$ and two equiv. of the corresponding pyrrolylaldimine ligands. The ligands were modified to have different steric hindrance (C_6H_5 (**1**), 2,6-$Me_2C_6H_3$ (**2**), 2,4,6-$Me_3C_6H_2$ (**3**), 2,6-$Et_2C_6H_3$ (**4**) and 2,6-$^iPr_2C_6H_3$ (**5**)) and electronic contribution (4-$CF_3C_6H_4$ (**6**) and 4-$OMeC_6H_4$ (**7**)). Crystal structures of complexes **3**-**7** were determined and shown to have distorted trigonal bipyramidal geometry (**4**, **6**, **7**) and intermediates between trigonal bipyramidal and square pyramidal geometries (**3** and **5**). The rotation around the N-C_{aryl} bond was fast for ligands having small *ortho* substituents and became slower as the size of the substituents increased. Polymerisations of L-lactide using complexes **1**-**7** and benzyl alcohol as initiator were carried out giving the rate dependent on steric hindrance (**5** < **4** < **3** < **2** < **1**) and electronic contribution (**6** < **7** < **1**). Larger substituents and electron withdrawing groups were found to suppress the polymerisation rates. Despite having C_2 symmetry in the crystal structures of compounds **3**-**7**, only slight enhancement for isotactic enchainment was found in the polymerisation of *rac*-lactide.

Introduction

Polylactide (PLA) is one of the most recognized biodegradable polyesters extensively explored due to their appealing properties such as biocompatibility and biodegradability.[1] PLA has found numerous applications especially in pharmaceutical industries as in drug delivery systems,[2, 3] scaffolds[4] and dissolvable sutures.[5] The ring-opening polymerisation (ROP) of lactide by several ligated monomeric metal complexes was proven the most effective for the syntheses of PLA.[6] However, bimetallic complexes for the polymerisation of cyclic esters have attracted recent attention.[7] The two metal centers were designed to cooperate giving higher catalytic activity.[8, 9] In conjunction with biocompatible polymers, biocompatible metals such as calcium, magnesium, zinc, and aluminum have received significant remarks due to the low toxicity.[10, 11] Particularly, ligated aluminum complexes have gained special interests due to the well-controlled behavior in ROP of cyclic esters.[6, 12-14] Thus, systematic modifications of the ligands have led to a better understanding of electronic and steric influences of the ligands in the ring-opening polymerisations. Although aluminum complexes are relatively slow catalysts compared to other metal complexes, the low activities have allowed detailed kinetic and mechanistic studies of the initiation and propagation of the polymerisations. Several chiral salicylaldiminato aluminum complexes have expressed stereoselectivity[15, 16] in the ROP of lactides leading to unique tacticities such as heterotactic, syndiotactic and isotactic stereoblock PLA.[17] Despite numerous reports on aluminum complexes bearing salicylaldimine ligands, the study of the closely-related pyrrolylaldiminato aluminum complexes[18] for the polymerisation of cyclic esters has been rather limited. Only one report by Wang has been found on the polymerisation of ε-caprolactone.[19] In an extension of this research, we describe herein the preparation of bis(pyrrolylaldiminato)aluminum complexes and their applications in lactide polymerisations.



Scheme 1 Syntheses of *bis*(pyrrolylaldiminato)aluminum complexes **1**-**7**.

Results and discussion

Syntheses and characterisations of Al complexes

Pyrrolylaldimine ligands were selected in this study due to the flexibility and simple ligand modification of electronic and steric contributions. Thus, electronic and steric factors can be tailored separately and systematically. Aluminum was also the metal of choice because of low toxicity and generally well-controlled

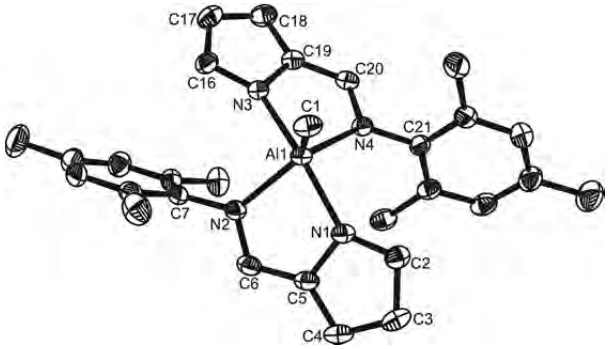


Fig. 1 X-ray crystal structure of **3** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

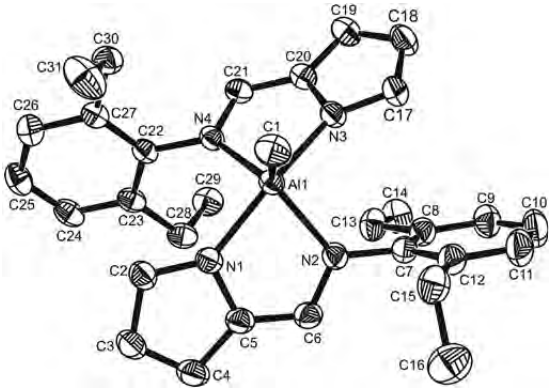


Fig. 2 X-ray crystal structure of **4** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

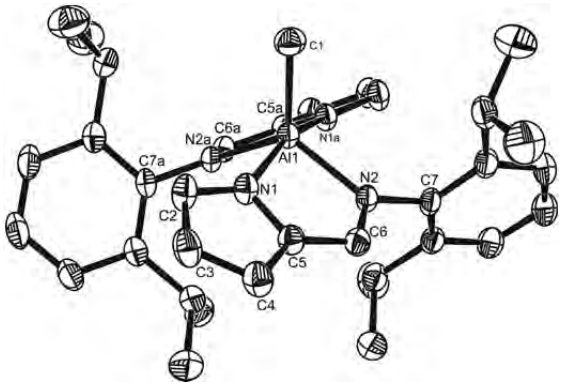


Fig. 3 X-ray crystal structure of **5** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

behavior in ROP of cyclic esters. Pyrrolylaldimine ligands were synthesized by a condensation reaction in acidic condition between pyrrole-2-carboxaldehyde and the corresponding anilines with minor modification.[20] The ligands were purified by recrystallization in cold methanol giving the products in moderate yields (47-62%). Two equivalents of the ligands were then reacted with $AlMe_3$ in CH_2Cl_2 at 50 °C for 5 h giving the *bis*(pyrrolylaldiminato)aluminum complexes **1**-**7** in 63-91 % yields (Scheme 1). Steric contributions of the ligands were investigated by changing the substituents at the *ortho* positions from H to ^{i}Pr groups as in complexes **1**-**5**. Electronic contributions were modified from electron withdrawing CF_3 group (**6**) to electron donating OCH_3 group (**7**) at the *para* position. Complexes **3**-**7** were characterized crystallographically and shown in Figures 1-5, respectively, with selected bond distances and angles in Table 1.

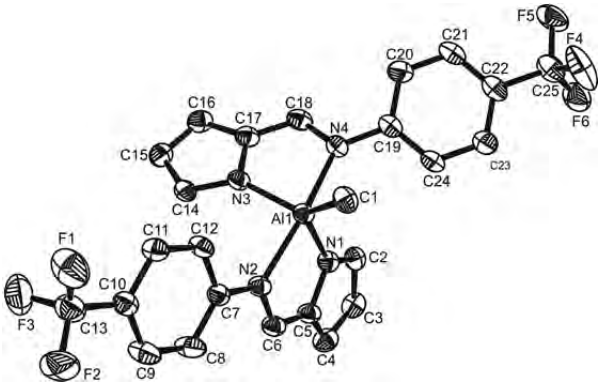


Fig. 4 X-ray crystal structure of **6** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

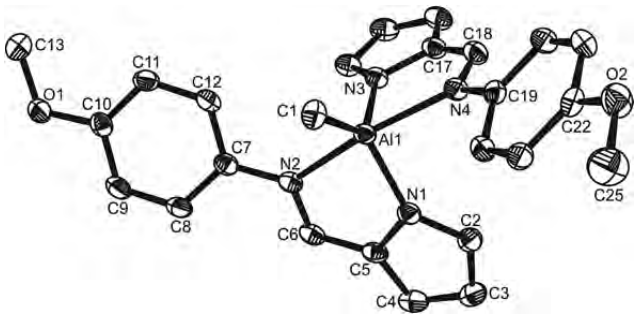


Fig. 5 X-ray crystal structure of **7** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1 Selected bond distances (Å) and angles (°) for complexes **3**-**7**.

	3	**4**	**5**[a]	**6**	**7**
			Bond Distances (Å)		
Al1-C1	1.968(2)	1.965(2)	1.968(3)	1.957(3)	1.962(2)
Al1-N1	1.993(2)	1.991(2)	1.994(1)	1.899(2)	1.916(1)
Al1-N2	2.014(2)	2.016(2)	2.022(1)	2.129(3)	2.123(1)
Al1-N3	2.008(2)	2.001(2)	1.994(1)	1.909(2)	1.914(1)
Al1-N4	2.009(2)	2.020(2)	2.022(1)	2.127(3)	2.119(1)
			Bond Angles (°)		
C1-Al1-N1	99.82(8)	101.57(8)	99.94(5)	122.4(1)	125.16(7)
C1-Al1-N2	118.24(8)	116.00(8)	117.71(4)	98.1(1)	97.46(7)
C1-Al1-N3	99.70(8)	97.97(8)	99.94(5)	128.1(1)	126.95(7)
C1-Al1-N4	113.95(8)	119.27(8)	117.71(4)	93.9(1)	96.79(7)
N1-Al1-N2	80.59(7)	80.30(6)	80.51(5)	81.0(1)	80.88(6)
N1-Al1-N3	160.48(7)	160.45(7)	160.13(9)	109.4(1)	107.88(6)
N1-Al1-N4	91.15(7)	89.94(6)	90.26(5)	92.8(1)	90.37(6)
N2-Al1-N3	90.17(7)	91.43(6)	90.26(5)	91.6(1)	90.93(6)
N2-Al1-N4	127.82(7)	124.72(6)	124.58(8)	168.1(1)	165.74(6)
N3-Al1-N4	80.94(7)	80.21(6)	80.51(5)	80.8(1)	81.01(6)
τ	0.54	0.60	0.59	0.67	0.65

[a] For complex **5**, the atoms N3 and N4 in the first column are N1a and N2a, respectively.

All complexes are monomeric having a five-coordinate aluminum center. The structural geometry of complexes **4**, **6** and **7** is distorted trigonal bipyramid as indicated by the τ values[21] of 0.60, 0.67 and 0.65, respectively. For complexes **3** and **5**, intermediates between trigonal bipyramid and square pyramid are found with τ values[21] of 0.54 and 0.59, respectively. The orientations of the phenyl rings in all complexes are pointing away from each other generating a C_2 symmetry. This orientation of the phenyl rings creates a chiral center at the metal center

Table 2 Polymerisations of lactides using complexes **1-7**.[a]

Entry	Catalysts	Monomer	Time (h)	% Conversion[b]	k_{obs} (h^{-1})	M_n[c]	$Đ$[c]	% *iii* [d]
1	**1**	L-LA	6	97	0.533	2,600	1.14	-
2	**2**	L-LA	6	90	0.390	5,100	1.14	-
3	**3**	L-LA	6	86	0.357	6,800	1.20	-
4	**4**	L-LA	6	86	0.321	3,900	1.15	-
5	**5**	L-LA	13	92	0.181	6,700	1.15	-
6	**6**	L-LA	6	94	0.341	4,100	1.16	-
7	**7**	L-LA	10	86	0.383	6,700	1.23	-
8	**1**	*rac*-LA	7	95	-	7,100	1.14	33
9	**2**	*rac*-LA	7	92	-	6,800	1.11	45
10	**3**	*rac*-LA	7	94	-	6,900	1.12	47
11	**4**	*rac*-LA	7	92	-	7,000	1.13	44
12	**5**	*rac*-LA	14	98	-	3,800	1.18	35
13	**6**	*rac*-LA	7	99	-	9,200	1.27	34
14	**7**	*rac*-LA	11	96	-	6,700	1.35	34

[a] *Polymerisation condition:* 5.00 mmol LA, 0.100 mmol Al complexes, 0.100 mmol BnOH, 6.00 mL toluene, [LA]:[Al]:[BnOH] = 50:1:1, reaction temperature at 70 °C. [b] Obtained from ^{1}H NMR analysis. [c] Obtained from GPC analysis in THF using polystyrene standard, multiplied by 0.58.[22] [d] Determined from the integration in ^{1}H NMR spectra defined by 100% × (*iii*)/(*sis*+*sii*+*iis*+*iii*+*isi*).

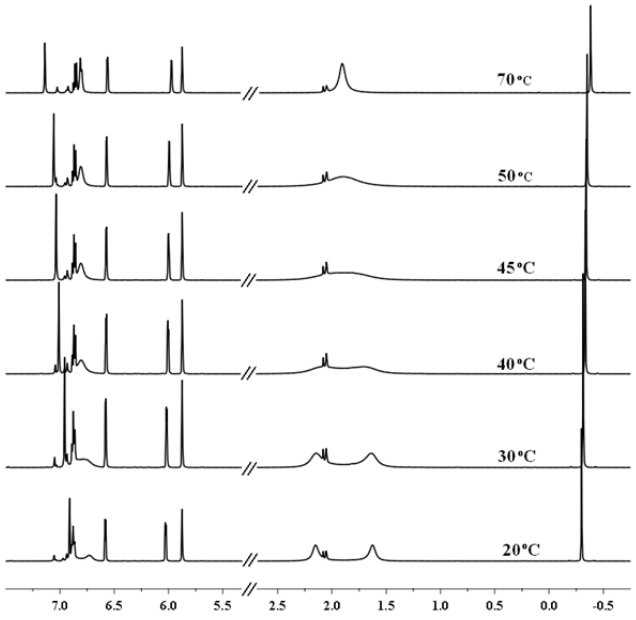


Fig. 6 Variable temperature NMR spectra of complex **2** in toluene-d_8.

suitable for the study of stereoselectivity of the catalysts. The Al-N_{pyrr} bond distances are slightly shorter than those of Al-N_{aryl} bonds in complexes **3-5**. However, the Al-N_{pyrr} bond distances are significantly shorter (~0.2 Å) than those of Al-N_{aryl} bonds in complexes **6** and **7**. Inspection of the torsional angles between C=N and the phenyl ring (C=N–C_{ipso}–C_{ortho}) reveals interesting information. The C=N–C_{ipso}–C_{ortho} torsional angles of the complexes **3-5** having *ortho* substituents varies from 83.1 to 87.3° while those of complexes **6** and **7** having no *ortho* substituents varies from 19.9 to 27.0°. The low C=N–C_{ipso}–C_{ortho} torsional angles of complexes **6** and **7** allow electron delocalization from N_{aryl} into the aryl π system. This observation suggests that the N-C_{aryl} bonds can be controlled as free rotation or restriction depending on the substituents at the *ortho* positions. ^{1}H NMR of complexes **1**, **6**, and **7** (see ESI) reveals only one set of the aromatic protons indicating a fast rotation around the N-C_{aryl} bonds on NMR time-scale. This is in agreement with the low C=N–C_{ipso}–C_{ortho} torsional angles in the crystal structures. However, the restricted rotation on NMR time-scale was found in complex **5** where 4 doublets and 2 septets, corresponding to CH*Me*$_2$ and C*H*Me$_2$ protons respectively, were found in ^{1}H NMR recorded at room temperature. Heating complex **5** to 90 °C in toluene-d_8 did not broaden the NMR signals. For complexes **2-4**, a fluxional process at room temperature was observed as indicated by broad NMR signals of the *ortho* substituents attributed to a slow rotation around N-C_{aryl} bond. Variable-temperature (VT) ^{1}H NMR experiment was carried out for complex **2** in toluene-d_8 as shown in Fig. 6. Broad singlets were found at 20 °C at 2.17 and 1.65 ppm corresponding to the *ortho*-methyl protons. The two broad singlets coalesced at 45 °C and became a sharp singlet at higher temperature. Free energy of activation at coalescence temperature[23] of 14.6 kcal/mol was estimated from the VT experiment.

Polymerisation of lactide

Complexes **1-7** were tested for the polymerisation of L-lactide. Benzyl alcohol (1 equiv) was added as an initiator. The polymerisations were carried out in toluene at 70 °C using [LA]:[Al]:[BnOH] = 50:1:1. The polymerisation results are summarized in Table 2, entries 1-7. The GPC trances of the polymers obtained from all catalysts are monomodal and have narrow molecular weight distributions ($Đ$ = 1.14-1.23) indicative of a well-controlled polymerisation. This behaviour is common in the polymerisations using aluminum catalysts. Complex **1** (entry 1) having no substituents on the phenyl rings displayed the highest activity while complex **5** (entry 5) having bulky ^{i}Pr groups was the slowest catalyst. Polymerisations were rather slow requiring 6-13 h to completion. However, the slow rates of polymerisations allow a detailed analysis of kinetic information.

Kinetic studies of all catalysts were conducted at least three times for each catalysts and plotted as $\ln([A]_t/[A]_0)$ versus time in Fig. 7a for the investigation of steric hindrance (complexes **1-5**) and Fig. 7b for electronic contributions (complexes **1**, **6** and **7**). All polymerisations are pseudo first order in the concentration of L-lactide. The observed rate constants k_{obs} (from $\ln([A]_t/[A]_0) = -k_{obs}t$), having the values from 0.181 to 0.533 h^{-1}, are summarized in Table 2. For the effects of steric hindrance of the ligands, the order of **5** < **4** < **3** < **2** < **1** was observed in agreement with the

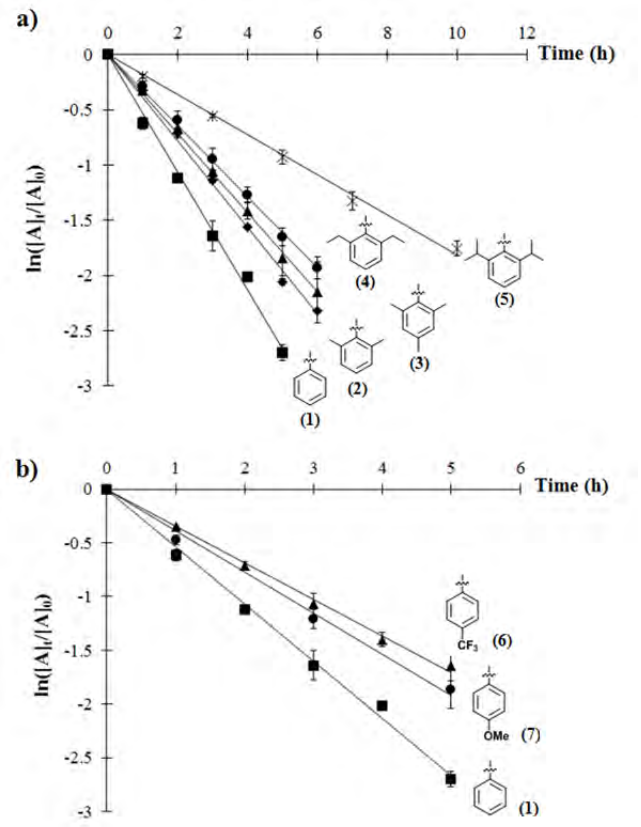


Fig. 7 Plots of $\ln([A]_t/[A]_0)$ *vs* time in the polymerisation of L-lactide using a) complexes **1**-**5** and b) complexes **1**, **6** and **7**.

decreasing steric hindrance. Ligands having larger substituents suppress the polymerisation rates. The presence of the methyl substituent at the *para* position as in **3** (k_{obs} = 0.357 h^{-1}) does not significantly affect the polymerisation rate compared to compound **2** (k_{obs} = 0.390 h^{-1}). For electronic contributions, the order of **6** < **7** < **1** was determined with k_{obs} of 0.341, 0.383 and 0.533, respectively. The observed rates were puzzling at first because complexes having ligands with electron withdrawing and electron donating groups decreased the polymerisation rates. We suggest that, in this catalyst system, one of these ligands may not be innocent as it may seem. The CF_3 groups in complex **7** certainly withdraw electron density from the metal through σ bonds. However, in the case of methoxy group in **6**, the oxygen atom may also behave as electron withdrawing group through σ bonds in addition to the anticipated electron donation through the π system. This is possible since oxygen is more electronegative than carbon and this effect could be more pronounced in this catalyst system. Thus, the electron withdrawing group and steric hindrance decrease the rates of lactide polymerisation in the bis(pyrrolylaldiminato) aluminum catalyst system.

Because complexes **1**-**7** has a C_2 axis through Al-Me bond, stereoselectivity for isotactic enhancement is anticipated from the chiral complexes. Thus, complexes **1**-**7** were tested for the polymerisation of *rac*-lactide under identical conditions. Polymerisation results are summarized in Table 2, entries 8-14. The percentage of *iii* tetrads was determined from the integration of the peaks in ^{1}H NMR spectra ($CDCl_3$, 500 MHz) of the homonuclear decoupled CH resonance of poly(*rac*-lactide). The

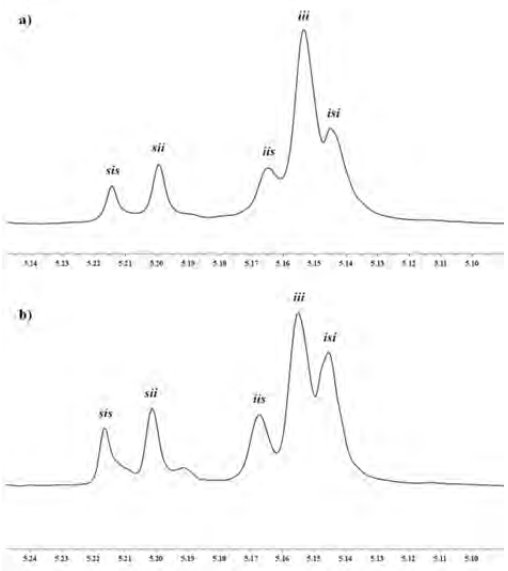


Fig. 8 ^{1}H NMR spectra ($CDCl_3$, 500 MHz) of the homonuclear decoupled CH resonance of poly(*rac*-lactide) prepared using a) complex **4** and b) complex **7**.

enhancement for *iii* tetrads was observed from 33 (atactic polylactide) to 45, 47 and 44% for compounds **1**, **2**, **3** and **4**,respectively (Fig. 8a). Larger substituents were found to promote isotactic enchainment. However, this effect dissipates in compound **5**. The substituents at the *para* position have no effect in the stereoselectivity. Thus, compounds **6** and **7** gave atactic polylactide having *iii* tetrads of 34% (Fig. 8b).

Conclusions

We have demonstrated that steric and electronic contributions of the ligands have played an important role in the ring-opening polymerisation of lactide. A new bis(pyrrolylaldiminato) aluminum catalyst system having different steric and electronic contributions on the ligands has been developed. Five new crystal structures were reported. Fast rotation of the N-C_{aryl} bond was observed for ligands having small substituents on the phenyl rings. The rotation diminished in complexes with larger substituents. The catalysts were active for the polymerisation of L-lactide giving polylactide with low molecular weight distributions indicating that the polymerisations are well-controlled. Pseudo first order was determined in the polymerisation of L-lactide along with the observed rate constants. Ligands having larger substituents or electron withdrawing groups were found to suppress the polymerisation rates. In addition, polymerisation of *rac*-lactide gave atactic polymer for compounds **1**, **5**-**7**. However, a slight enhancement for isotactic enchainment was found for compounds **2**-**4**. It is clear that ligand design is vital to the development of new catalysts. Even slight changes of the ligand structures could influence the polymerisation rates and stereoselectivities.

Experimental

General details

All experiments were carried out under dry argon atmosphere using double manifold Schlenk line and Schlenk-type glassware.

All solvents used under inert atmosphere were dried using PURE SOLV MD-5 solvent purification system from Innovative Technology Inc. All reagents were purchased from commercial suppliers (Acros, Aldrich, Fluka). Deuterated solvents were dried over 4 Å molecular sieve (benzene-d_6, toluene-d_8) and 3 Å molecular sieve (chloroform-*d*). L-lactide and *rac*-lactide were purchased from Aldrich and sublimed three times under vacuum before use. Pyrrolylaldimine ligands were synthesized by a condensation reaction in acidic condition between pyrrole-2-carboxaldehyde and the corresponding anilines with minor modification.[20]

Measurements

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DPX-300 or AVANCE 500 spectrometer and referenced to protio impurity of commercial chloroform-*d* ($CDCl_3$, δ 7.26 ppm) or benzene-d_6 (C_6D_6, δ 7.16 ppm) as internal standards. ^{19}F NMR spectra were recorded on AVANCE 500 spectrometer and referenced to external CF_3COOH. Gel permeation chromatography (GPC) analyses were carried out on a Waters e2695 instrument equipped with Model 3580 refractive index detectors (Viscotek) and two 10 μm PL Gel columns. The GPC columns were eluted using tetrahydrofuran with flow rate of 1.0 mL/min at 35 °C. Molecular weights and molecular weight distributions were calibrated with polystyrene standards ranging from 500 to 10,000,000 amu. X-ray crystallography data was collected on a Bruker SMART CCD area-detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Elemental analyses were obtained using Perkin Elmer series II CHNS/O Analyzer 2400.

General preparation for complexes 1-7. A solution of the corresponding ligand (5.80 mmol) in CH_2Cl_2 (30 mL) was added dropwise to a solution of $AlMe_3$ (1.45 mL, 2.0 M solution in toluene, 2.90 mmol) in CH_2Cl_2 (30 mL). The reaction was then heated at 50 °C for 5 h followed by solvent removal under vacuum. The complex was washed with n-hexane and subsequently dried under vacuum giving the product in moderate to high yield.

[2-(C_6H_5N=CH)C_4H_3N]$_2$AlCH$_3$, 1. A pale yellow solid (0.95 g, 86 %). ^{1}H NMR (500 MHz, C_6D_6): δ 7.85 (s, 2H, N=C*H*), 7.28 (d, *J* = 5.0 Hz, 4H, Ar), 7.06 (m, 6H, Ar),6.96 (t, 2H, *J* = 12.0 Hz, py), 6.78 (d, 2H, *J* = 5.0 Hz, py), 6.32 (d, 2H, *J* = 5.0 Hz, py),-0.03 (s, 3H, Al-C*H*$_3$).^{13}C{^{1}H} NMR (C_6D_6, 125 MHz,): δ 153.0 (N=*C*H), 146.6 (*ipso*-C), 137.51 (Ar), 137.2 (*ipso*-C), 129.6 (Ar), 126.3 (py), 121.9 (Ar), 120.4, 115.1 (py), -5.5 (Al-*C*H$_3$). Anal. Calcd. for $C_{23}H_{21}AlN_4$: C, 72.62; H, 5.56; N, 14.73. Found: C, 72.29; H, 5.32; N, 14.72.

[2-(2,6-(CH_3)$_2$$C_6H_3$N=CH)$C_4H_3$N]$_2$AlCH$_3$, 2. A white solid (0.80 g, 63%). ^{1}H NMR (500 MHz, C_6D_6): δ 7.37 (s, 2H,N=C*H*), 7.16-7.02 (m, 6H, Ar), 6.86 (d, 2H, *J* = 5.0 Hz, py), 6.35 (d, 2H, *J* = 5.0 Hz, py), 6.21 (s, 2H, py),2.39 (br s, 6H, Ar-C*H*$_3$), 1.91 (br s, 6H, Ar-C*H*$_3$),0.07 (s, 3H, Al-C*H*$_3$).^{13}C{^{1}H} NMR (C_6D_6, 125 MHz,): δ 161.4 (N=*C*H), 146.92 (*ipso*-C), 138.1, 135.2, 134.0, 132.6 (Ar), 126.1, 119.9, 114.9 (py), 18.6 (Ar-*C*H$_3$), -3.4 (Al-*C*H$_3$). Anal. Calcd. for $C_{27}H_{29}AlN_4$: C, 74.29; H, 6.70; N, 12.83. Found: C, 74.29; H, 6.69; N, 12.91.

[2-(2,4,6-(CH_3)$_3$$C_6H_2$N=CH)$C_4H_3$N]$_2$AlCH$_3$, 3. A white solid (1.08 g, 79%). Crystals suitable for X-ray crystallography were grown by placing a concentrated hexane solution in a freezer. ^{1}H NMR (500 MHz, C_6D_6): δ7.07 (s, 2H,N=C*H*), 6.75-6.66 (m, 6H, py), 6.16 (d, 2H, *J* = 5.0 Hz, Ar), 6.09 (s, 2H, Ar),2.22-2.14 (m, 12H, Ar-C*H*$_3$), 1.72 (s, 6H, Ar-C*H*$_3$), -0.10 (s, 3H, Al-C*H*$_3$).^{13}C{^{1}H} NMR (C_6D_6, 125 MHz,): δ 161.7 (N=*C*H), 152.1(*ipso*-C), 143.9 (Ar), 138.0 (*ipso*-C), 128.7, 119.4, 114.8 (py), 20.7, 18.3 (Ar-*C*H$_3$), -3.4 (Al-*C*H$_3$). Anal. Calcd. for $C_{29}H_{33}AlN_4$: C, 74.97; H, 7.16; N, 12.06. Found: C, 74.59; H, 7.45; N, 11.96.

Crystal data for 3. $C_{29}H_{33}AlN_4$, M = 464.57, monoclinic, space group $P2_1/c$, a = 8.7290(2) Å, b = 21.8650(9) Å, c = 13.8320(6) Å, α = 90°, β = 91.841(3)°, γ = 90°, V = 2638.61(17)Å^3, Z = 4, λ = 0.71073 Å, μ = 0.100 mm^{-1}, T = 150 K, 17018 reflections measured, 4629 unique, R_{int} = 0.0699, R = 0.0462 (obs. data), wR = 0.1168 (obs. data), GOF = 1.034.

[2-(2,6-(C_2H_5)$_2$$C_6H_3$N=CH)$C_4H_3$N]$_2$AlCH$_3$, 4. A white solid (1.32 g, 91%). Crystals suitable for X-ray crystallography were grown by placing a concentrated toluene solution in a freezer. ^{1}H NMR (500 MHz, C_6D_6): δ7.79 (s, 2H, N=C*H*), 7.42 (d, 2H, *J* = 1.0 Hz, Ar), 7.19 (t, 4H, *J* = 7.7 Hz, Ar), 6.75 (q, 2H, *J* = 1.8 Hz, py), 6.18 (q, 2H, *J* = 1.9 Hz, py), 6.13 (d, 2H, *J*= 1.0 Hz, py), 2.64 (q, 8H, *J* = 7.5 Hz, C*H*$_2$CH$_3$), 1.23 (t, 12H, *J*= 7.5 Hz, CH$_2$C*H*$_3$), -0.08 (s, 3H, Al-C*H*$_3$).^{13}C{^{1}H} NMR (C_6D_6, 125 MHz,): δ161.6 (N=*C*H), 145.1 138.0, 134.6 (*ipso*-C), 126.5, 126.2, 126.1 (py),119.4, 114.8 (Ar), 20.7 (ArC*H*$_2$CH$_3$), 18.3 (ArCH$_2$C*H*$_3$), -3.45 (Al-*C*H$_3$). Anal. Calcd. for $C_{31}H_{37}AlN_4$: C, 75.58; H, 7.57; N, 11.37. Found: C, 75.74; H, 7.62; N, 10.91.

Crystal data for 4. $C_{31}H_{37}AlN_4$, M = 492.63, Triclinic, space group $P\bar{1}$, a = 8.86600(10) Å, b = 20.2470(4) Å, c = 24.0550(5) Å, α = 102.0720(8)°, β = 90.2860(15)°, γ = 96.0910(15)°, V = 4197.14(13)Å^3, Z = 6, λ = 0.71073 Å, μ = 0.098 mm^{-1}, T = 153(2) K, 30818 reflections measured, 16089 unique, R_{int} = 0.0218, R = 0.0509 (obs. data), wR = 0.1281 (obs. data), GOF = 1.043.

[2-(2,6-(^{i}Pr)$_2$$C_6H_3$N=CH)$C_4H_3$N]$_2$AlCH$_3$, 5. A white solid (0.97 g, 63%). Crystals suitable for X-ray crystallography were grown by placing a concentrated toluene solution in a freezer. ^{1}H NMR (300 MHz, C_6D_6): δ7.61 (s, 2H, N=C*H*), 7.14 (m, 4H, Ar), 6.98 (d, 2H, *J* = 9.0 Hz, Ar), 6.66 (d, 2H, *J* = 3.0 Hz, py), 6.11 (s, 2H, py), 6.05 (s, 2H, py), 3.46 (t, 2H, *J* = 5.0 Hz, C*H*(CH$_3$)$_2$), 2.96 (t, 2H, *J* = 5.0 Hz, C*H*(CH$_3$)$_2$),1.33 (d, 6H, *J* = 6 Hz, CH(C*H*$_3$)$_2$), 1.06 (d, 6H, *J* = 6.0 Hz, CH(C*H*$_3$)$_2$), 1.00 (d, 6H, *J* = 6.0 Hz, CH(C*H*$_3$)$_2$), 0.74 (d, 6H, *J* = 9.0 Hz, CH(C*H*$_3$)$_2$), -0.15 (s, 3H, Al-C*H*$_3$).^{13}C{^{1}H} NMR (C_6D_6, 125 MHz,): δ160.9 (N=*C*H), 144.2, 143.4 (*ipso*-C),138.5 (Ar), 134.6 (*ipso*-C), 127.1, 124.9 (Ar), 123.0, 119.6, 114.6 (py), 29.7, 28.0 (*C*H(CH$_3$)$_2$), 25.8, 25.5 (CH(*C*H$_3$)$_2$), 24.9, 21.0 (CH(*C*H$_3$)$_2$), -5.7 (Al-*C*H$_3$). Anal. Calcd. for $C_{35}H_{45}AlN_4$: C, 76.61; H, 8.27; N, 10.21. Found: C, 76.61; H, 8.53; N, 10.24.

Crystal data for 5. $C_{35}H_{45}AlN_4$, M = 548.73, monoclinic, space group *C2/c*, a = 20.2580(11) Å, b = 9.8370(8) Å, c = 16.2040(12) Å, α = 90°, β = 99.646(5)°, γ = 90°, V = 3183.4(4)Å^3, Z = 4, λ = 0.71073 Å, μ = 0.093 mm^{-1}, T = 293(2) K, 8318 reflections measured, 3655 unique, R_{int} = 0.0790, R = 0.0525 (obs. data), wR = 0.1291 (obs. data), GOF = 1.074.

[2-(4-(CF_3)C_6H_4N=CH)C_4H_3N]$_2$AlCH$_3$, 6. A white solid (1.24 g, 83%). Crystals suitable for X-ray crystallography were grown by placing a concentrated CH_2Cl_2 solution in a freezer. ^{1}H NMR (500 MHz, C_6D_6): δ 7.69 (s, 2H, N=C*H*), 7.27 (d, 4H, *J* =

10.0 Hz, Ar), 7.26 (d, 4H, *J*= 10.0 Hz, Ar), 6.93 (s, 2H, py), 6.82 (d, 2H, *J* = 5.0 Hz, py), 6.34 (d, 2H, py), -0.15 (s, 3H, Al-CH_3).^{13}C{^{1}H} NMR (C_6D_6, 125 MHz,): δ153.4 (N=*C*H), 149.0 (*ipso*-C), 138.5 (Ar), 137.2 (*ipso*-C), 126.9 (py), 126.0(*ipso*-C), 122.2 (py), 121.8 (Ar), 116.0 (py), -6.0 (Al-*C*H_3).^{19}F NMR (C_6D_6): δ -62.7 (CF_3). Anal. Calcd. for $C_{25}H_{29}AlF_6N_4$: C, 58.14; H, 3.71; N, 10.85. Found: C, 58.24; H, 3.71; N, 10.73.

Crystal data for 6. $C_{25}H_{19}AlF_6N_4$, M = 516.42, monoclinic, space group *P2$_1$/c*, a = 9.8580(2) Å, b = 56.7400(13) Å, c = 9.3090(2) Å, α = 90^O, β = 116.1470(10)^O, γ = 90^O, V = 4674.08(17)Å^3, Z = 8, λ = 0.71073 Å, μ = 0.157 mm^{-1}, T = 150(2) K, 13571 reflections measured, 8223 unique, R_{int} = 0.0378, R = 0.0570 (obs. data), wR = 0.1493 (obs. data), GOF = 1.058.

[**2-(4-(OCH$_3$)C$_6$H$_4$N=CH)C$_4$H$_3$N]$_2$AlCH$_3$, 7**. A light brown solid (1.28 g, 65%). Crystals suitable for X-ray crystallography were grown by placing a concentrated CH_2Cl_2 solution in a freezer. ^{1}H NMR (500 MHz, C_6D_6): δ7.89 (s, 2H, N=C*H*), 7.28 (d, 4H, *J* = 9.0 Hz, Ar), 7.16 (s, 2H, py), 6.82 (s, 2H, py), 6.67 (d, 4H, *J* = 9.0 Hz, Ar), 6.40 (q, 2H, *J* = 3.0 Hz, py), 3.28 (s, 6H, O-CH_3), 0.03 (s, 3H, Al-CH_3).^{13}C{^{1}H} NMR (C_6D_6, 125 MHz,): δ 158.5 (*ipso*-C), 151.6 (N=*C*H), 139.6, 137.2 (*ipso*-C), 136.7, 122.9 (Ar), 119.4, 114.8, 114.6 (py), 55.0 ((O-*C*H$_3$), -5.5 (Al-*C*H$_3$). Anal. Calcd. for $C_{35}H_{45}AlN_4$: C, 68.70; H, 5.72; N, 12.72. Found: C, 68.77; H, 5.67; N, 12.64.

Crystal data for 7. $C_{25}H_{25}AlN_4O_2$, M = 440.47, monoclinic, space group *P2$_1$/c*, a = 14.8420(6) Å, b = 9.1460(2) Å, c = 16.6480(6) Å, α = 90^O, β = 97.0740(13)°, γ = 90^O, V = 2242.68(13)Å^3, Z = 4, λ = 0.71073 Å, μ = 0.120 mm^{-1}, T = 150(2) K, 7379 reflections measured, 3924 unique, R_{int} = 0.0239, R = 0.0381 (obs. data), wR = 0.0958 (obs. data), GOF = 1.048.

Polymerisation of lactide

L- and *rac*-lactide polymerisations were conducted in toluene in a 25 mL Schlenk flask as followed. The aluminum complex (**1-7**, 0.100 mmol) and lactide (720 mg, 5.00 mmol) was added into a Schlenk flask in a drybox. Toluene (6.00 mL) was added and the reaction was heated to 70 °C. The polymerisation was started by the addition of benzyl alcohol (0.100 mmol). A small aliquot was collected at desired time and quenched with a drop of acetic acid. The polymer conversion was determined by ^{1}H NMR in $CDCl_3$ after the solvent was removed. At the end of the polymerisation, a few drops of acetic acid were added and solvent was removed under vacuum. The mixture was dissolved in the least amount of dichloromethane followed by the precipitation of the polymer in cold methanol. The polymer was isolated and dried to constant weight under vacuum.

X-ray crystallography

The single crystal X-ray analysis was carried out at the Mahidol crystallographic facility. Diffraction measurements were made on a 4 K Bruker SMART[24] CCD area detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å). The crystals were mounted in paratone oil and held in a low-temperature N_2 stream during data collection. Cell constants and an orientation matrix for data collection were obtained from a least-square refinement. The frame data were integrated by the program SAINT[25] and corrected for Lorentz and polarization effects. The structure was solved by the maXus crystallographic software package,[26] using direct methods (SIR97)[27] and refined by full-matrix least-squares method on $(F_{obs})^2$ using the SHELXTL-PC V 6.12 software package.[28] X-ray crystal structures were generated using Ortep-3 for Windows.[29]

Acknowledgements

We acknowledge financial support from Commission on Higher Education, The Thailand Research Fund, and Mahidol University (RMU5380030). We gratefully acknowledge financial support from the Royal Golden Jubilee Ph.D. Program (PHD/0136/2553), The Thailand Research Fund. Financial supports from the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education and Siam Cement Group (SCG-Chemical) are gratefully acknowledged. This work is also supported by Center for Catalysis, Faculty of Science, Mahidol University. We thank Prof. Kotohiro Nomura for help with CHN analysis. We also thank Mr Samran Prabpai for help with X-ray data collection.

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† Electronic Supplementary Information (ESI) available: NMR spectra for **1-7**, CCDC reference numbers 918076-80. For crystallographic data in CIF see DOI: 10.1039/b000000x/

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