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SYNTHESIS AND CHARACTERIZATION OF
POLY(L-LACTIDE-CO-GLYCIDOL)

Miss Weerawan Sunsaneeyametha



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

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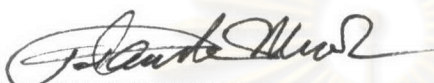
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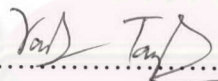
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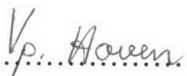
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ได้สังเคราะห์โคพอลิเมอร์ของแอล-แลกไทด์ (LLA) และไกลซิดอล (G) ขึ้น เพื่อต้องการเพิ่มส่วนชอบน้ำให้กับพอลิแอล-แลกไทด์ซึ่งเป็นพอลิเอสเทอร์เชิงพาณิชย์และย่อยสลายได้ทางชีวภาพ แนวทางแรกเป็นการสังเคราะห์โคพอลิเมอร์ที่มีโครงสร้างแบบสุ่มโดยเติมมอนอเมอร์ทั้งสองชนิดดังกล่าวพร้อมกันให้เกิดพอลิเมอร์โซ่แบบเปิดวง และแปรเปลี่ยนชนิดของตัวริเริ่มปฏิกิริยา คือ $Mg(OEt)_2$, $Al(O^iPr)_3$, $SnPh_4$, หรือ $Sn(Oct)_2$ พบว่าโคพอลิเมอร์ที่สังเคราะห์ได้มีมวลโมเลกุลไม่สูงพอที่จะสามารถทำให้บริสุทธิ์ได้ แนวทางที่สองได้ดำเนินการสังเคราะห์โคพอลิเมอร์แบบบล็อกของ LLA และ G ซึ่งมี 2 ขั้นตอนคือ ขั้นที่ 1 เริ่มด้วยการสังเคราะห์พอลิไกลซิดอล (PG) ที่มีโครงสร้างแบบกิ่งโดยใช้ $BF_3 \cdot OEt_2$ เป็นตัวริเริ่มปฏิกิริยา น้ำหนักโมเลกุลของ PG วิเคราะห์โดย MALDI-TOF MS มีค่า 800-1500 Da และค่าการกระจายของน้ำหนักโมเลกุลเป็น 1.0-1.3 ในขั้นที่สอง ใช้หมู่ไฮดรอกซิลของ PG ร่วมกับ $Sn(Oct)_2$ เป็นตัวริเริ่มพอลิเมอร์โซ่แบบเปิดวงของ LLA แล้ววิเคราะห์โครงสร้างของโคพอลิเมอร์โดย proton และ COSY-NMR พบว่าน้ำหนักโมเลกุลของโคพอลิเมอร์ขึ้นกับอัตราส่วนเริ่มต้นระหว่าง LLA และ PG แต่ไม่ขึ้นกับปริมาณ $Sn(Oct)_2$ ที่ใช้ (10 และ 20 %) ทั้งนี้ยังได้สังเคราะห์บล็อกโคพอลิเมอร์แบบสายตรงของ LLA และ G ผ่าน 2 ขั้นตอน ในขั้นแรก ได้สังเคราะห์พอลิเมอร์ของไกลซิดอลที่มีหมู่ปกป้องที่ออกซิเจน (GBn) โดยใช้ $SnCl_4$ เป็นตัวริเริ่มปฏิกิริยา ขั้นที่ 2 ใช้หมู่ไฮดรอกซิลที่ปลายสายโซ่ของ PGn เป็นตัวช่วยริเริ่มการเปิดวงของ LLA โดยมี $Sn(Oct)_2$ อยู่ด้วย

งานวิจัยนี้จึงนำเสนอแนวการสังเคราะห์โคพอลิเมอร์ของแอล-แลกไทด์และไกลซิดอลสองแนวทาง โดยโครงสร้างของโคพอลิเมอร์ที่ได้ขึ้นกับโครงสร้างของบล็อกของโฮโมพอลิเมอร์เริ่มต้น

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KEYWORD: POLYLACTIDE/ GLYCIDOL/ RING-OPENING POLYMERIZATION

WEERAWAN SUNSANEYAMETHA: SYNTHESIS AND CHARACTERIZATION OF POLY(L-LACTIDE-CO-GLYCIDOL). THESIS ADVISOR: ASSISTANT PROFESSOR VARAWUT TANGPASUTHADOL, Ph.D.; 89 pp. ISBN: 974-17-5156-7

In order to add hydrophilic segment to poly(L-lactide) (PLLA), a commercially available biodegradable polyester, copolymers of L-lactide (LLA) and glycidol (G) were synthesized. In the first part, an attempt was made to synthesize random copolymers. Both LLA and G monomers were added simultaneously in the ring-opening polymerization with various initiators: $Mg(OEt)_2$, $Al(O^iPr)_3$, $SnPh_4$, or $Sn(Oct)_2$. It was found that this method could not produce copolymers with molecular weight high enough to be purified. In the second part, block copolymers of LLA and G were prepared in 2 steps. First, branched polyglycidol (PG) was synthesized using BF_3OEt_2 as an initiator. The molecular weight of PG obtained from MALDI-TOF MS analysis was 800-1,500 Da, with polydispersity index of 1.0-1.3. Second, the hydroxyl group of PG together with $Sn(Oct)_2$ was used to initiate the ring-opening polymerization of LLA. Proton and COSY NMR analysis were used to characterize the copolymer structures. The molecular weight of the copolymers depended on LLA:PG feed ratio, but did not depend on mole percent of $Sn(Oct)_2$ (10 and 20 %). Moreover, linear LLA-*b*-G copolymer was synthesized in 2 steps. In the first step, O-protected glycidol (GBn) was polymerized using $SnCl_4$ as an initiator. In the second step, the hydroxyl end group of PGBn was used to initiate the ring-opening of LLA in the presence of $Sn(Oct)_2$.

This work therefore presents two polymerization schemes for the preparation of LLA and glycidol copolymers. The structure of the copolymers depends on the structure of the first homopolymer block.

Field of study Petrochemistry and Polymer Science Student's signature Weerawan Sunsaneyametha
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LIST OF ABBREVIATIONS

ROP	: Ring-opening polymerization
CROP	: Cationic ring-opening polymerization
AROP	: Anionic ring-opening polymerization
ACE	: Active chain end
AM	: Activated monomer
FAD	: American Food and Drug Administration
LLA	: L-lactide, L,L-lactide
DLA	: D-lactide, D,D-lactide
PLLA	: Poly(L-lactide), poly(L-lactic acid)
PGL	: Polyglycolide
ϵ -CL	: ϵ -caprolactam
G	: Glycidol
PG	: Polyglycidol
GL	: Glycerol
SB	: Sorbitol
KO ^t Bu	: Potassium <i>tert</i> -butoxide
Mg(OEt) ₂	: Magnesium diethoxide
Al(O ⁱ Pr) ₃	: Aluminium triisopropoxide

SnPh ₄	: Tetraphenyl tin
Sn(Oct) ₂	: Tin(II) 2-ethylhexanoate, Stannous Octoate
NMR	: Nuclear magnetic resonance
GPC	: Gel permeation chromatography
MALDI-TOF	: Matrix assisted laser desorption ionization time of flight
MS	: Mass spectroscopy
\bar{M}_n	: Number-average molecular weight
\bar{M}_w	: Weight-average molecular weight
MWD	: Molecular weight distribution
PDI	: Polydispersity index

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