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SYNTHESIS AND *IN VITRO* DEGRADATION
OF POLY(L-LACTIDE-*BLOCK*-GLYCIDOL)


Miss Pattarapond Gonil

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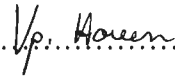

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ภัทรพร โคนิล: การสังเคราะห์และการย่อยสลายอินวิโทรของพอลิ(แอล-แลกไทด์-บล็อก-ไกลซิโดล) (SYNTHESIS AND *IN VITRO* DEGRADATION OF POLY(L-LACTIDE-BLOCK-GLYCIDOL) อาจารย์ที่ปรึกษา: ผู้ช่วยศาสตราจารย์ ดร. วรารุณี ตั้งพสุธาตล; 110 หน้า. ISBN: 974-17-2240-7

บล็อกโคพอลิเมอร์ของแอล-แลกไทด์ (LLA) และ ไกลซิโดล (G) สังเคราะห์โดยปฏิกิริยาพอลิเมอไรเซชันแบบเปิดวงของ LLA โดยใช้ทินออกโทเอต $[Sn(Oct)_2]$ และพอลิไกลซิโดลแบบกึ่งเป็นระบบบริเริ่ม น้ำหนักโมเลกุลของบล็อกโคพอลิเมอร์ขึ้นกับอุณหภูมิ, เวลาในการทำปฏิกิริยา, และอัตราส่วนเริ่มต้นของ LLA ต่อ G ผลจากจีพีซีโครมาโตแกรมบ่งบอกว่ามีชนิดของพอลิเมอร์ที่ต่างๆ กัน รวมทั้งโฮโมพอลิแอล-แลกไทด์ (PLLA) อาจเกิดขึ้นระหว่างการทำปฏิกิริยา เมื่อใช้อัตราส่วนเริ่มต้นของ LLA:G เป็น 10:1 พบว่าเกิดพอลิเมอร์ 2 ชนิดที่มีการละลายในเมทานอลต่างกัน ส่วนที่ไม่ละลายในเมทานอลมีน้ำหนักโมเลกุลสูงกว่าส่วนที่ละลายในเมทานอล ภาวะที่เหมาะสมของปฏิกิริยาการเปิดวงของ LLA ด้วย PG คือการทำปฏิกิริยาโดยปราศจากตัวทำละลายที่ 130 องศาเซลเซียสเป็นเวลา 24 ชั่วโมง ปริมาณ $Sn(Oct)_2$ ที่ใช้คือ 5 เปอร์เซ็นต์โดยโมลของปริมาณหมู่ไฮดรอกซิลในพอลิไกลซิโดล อุณหภูมิเปลี่ยนสถานะคล้ายแก้ว (T_g) ของบล็อกโคพอลิเมอร์มีค่าอยู่ระหว่าง T_g ของ PG และ PLLA และเพิ่มขึ้นตามการเพิ่มขึ้นของน้ำหนักโมเลกุลของโคพอลิเมอร์ บล็อกโคพอลิเมอร์มีความชอบน้ำมากกว่า PLLA และความชอบน้ำมากขึ้นเมื่อมีปริมาณ LLA ในบล็อกโคพอลิเมอร์ลดลงซึ่งเป็นผลจากการวัดค่ามุมสัมผัสของอากาศกับน้ำ อัตราการสลายตัวของบล็อกโคพอลิเมอร์ในฟอสเฟตบัฟเฟอร์ซาลินที่พีเอช 7.4 ช้ากว่าโฮโม PLLA ที่มีน้ำหนักโมเลกุลใกล้เคียงกัน แต่การสูญเสียน้ำหนักของโคพอลิเมอร์มีมากกว่าโฮโม PLLA ซึ่งอาจเป็นเพราะบล็อกของ PG ที่ละลายน้ำได้นั้นสลายตัวละลายออกมา


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PATTARAPOND GONIL: SYNTHESIS AND *IN VITRO* DEGRADATION OF POLY(L-LACTIDE-*BLOCK*-GLYCIDOL). THESIS ADVISOR: ASSISTANT PROFESSOR VARAWUT TANGPASUTHADOL, Ph.D.; 110 pp. ISBN: 974-17-2240-7

Block copolymers of L-lactide (LLA) and glycidol (G) were synthesized by ring-opening polymerization of LLA using tin octoate [Sn(Oct)₂] and branched polyglycidol (PG) as an initiation system. The molecular weight of the block copolymers depend on the reaction temperature, reaction time, and monomer feed ratio (LLA:G). Results from GPC chromatograms suggested that different polymeric species including homo PLLA might occur during the polymerization. At high LLA:G feed ratio (10:1) two types of polymeric products having different solubilities in methanol were obtained. It was found that the methanol-insoluble portion having higher molecular weight than the methanol-soluble portion. The suitable polymerization condition was carried out without solvent at 130°C for 24 hours. The amount of Sn(Oct)₂ was 5%mol of the total hydroxyl group content in PG. The glass transition temperatures (T_g) of the block copolymers were found to be between those of PG and PLLA and increased with increasing the copolymer molecular weight. The block copolymer was more hydrophilic than homo PLLA and increased with decreasing LLA content as examined by air-water contact angle measurement. The obtained block copolymer degraded in phosphate buffer saline at pH 7.4 at a slower rate than the homo PLLA having the same molecular weight. The weight loss of the copolymer was however slightly more than that of homo PLLA, probably due to dissolution of the cleaved water-soluble PG block.

Field of study Petrochemistry and Polymer Science Student's signature Pattarapond Gonil
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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
\overline{M}_n	: Number-average molecular weight
\overline{M}_w	: Weight-average molecular weight
MWD	: Molecular weight distribution
PDI	: Polydispersity index