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SYNTHESIS OF COPOLYUREAS AND POLYURETHANE-UREAS CONTAINING
ZINC AND NICKEL DIMETHOXYSALTRIEN COMPLEXES

Miss Khwunta Vanitcho

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for the Degree of Master of Science Program in Chemistry

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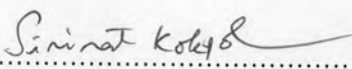
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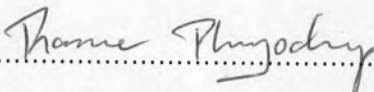
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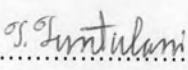
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ขวัญตา วานิชโช : การสังเคราะห์โคพอลิยูเรียและพอลิยูรีเทน-ยูเรียที่มีสารประกอบเชิงซ้อน ไคเมทอกซีซัลไตรเอนของสังกะสีและนิกเกิล. (SYNTHESIS OF COPOLYUREAS AND POLYURETHANE-UREAS CONTAINING ZINC AND NICKEL DIMETHOXYSALTRIEN COMPLEXES)

อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร. นवलพรรณ จันทศิริ, 131 หน้า.

โคพอลิยูเรียและพอลิยูรีเทน-ยูเรียที่มีสารประกอบเชิงซ้อน ไคเมทอกซีซัลไตรเอนของสังกะสีและนิกเกิล ($MSalOMe_2trien$; $M = Zn$ และ Ni) อยู่ในโครงสร้าง สามารถสังเคราะห์ได้จากปฏิกิริยาระหว่างสารประกอบเชิงซ้อน ไคเมทอกซีซัลไตรเอนของสังกะสีและนิกเกิล ไดไอโซไซยานาต และไดเอมีนหรือไดแอลกอฮอล์ตามลำดับ ไดไอโซไซยานาตที่ใช้คือ เฮกซามาทิลีน ไดไอโซไซยานาต (HMDI) และ 4,4'-ไดฟีนิลมีเทน ไดไอโซไซยานาต (MDI) สำหรับไดเอมีนและไดแอลกอฮอล์นั้น ใช้สารประกอบที่มีหมู่อะลิฟาติกและแอโรมาติกที่ต่างกัน เพื่อศึกษาถึงความสัมพันธ์ระหว่างโครงสร้างและสมบัติของพอลิเมอร์ พิสจูจน์เอกลักษณะของพอลิเมอร์ด้วยเทคนิคอินฟราเรดสเปกโทรสโกปี โปรตอนเอ็นเอ็มอาร์สเปกโทรสโกปี และเอกซเรย์ดิฟแฟรกชัน ศึกษาสมบัติการทนต่อความร้อนของพอลิเมอร์ด้วยเทอร์โมกราวิเมตริกอนาลิซิส พอลิเมอร์ละลายได้ดีในไดเมทิลฟอร์มาไมด์และไดเมทิลซัลฟอกไซด์ พอลิเมอร์ที่สังเคราะห์จาก MDI ละลายในตัวทำละลายได้ดีกว่าพอลิเมอร์ที่สังเคราะห์จาก HMDI พอลิยูเรียและพอลิยูรีเทน-ยูเรียมีค่าความหนืดในช่วง 0.0791-0.0947 และ 0.0797-0.1095 dL/g ตามลำดับ อุณหภูมิที่ทำให้น้ำหนักของพอลิเมอร์หายไป 5% จากน้ำหนักเริ่มต้น (T_5) และน้ำหนักที่เหลือจากการเผาไหม้ที่ 600°C มีค่า 253-293°C และ 36-64% ตามลำดับ พอลิยูรีเทน-ยูเรียแสดงสมบัติการทนความร้อนได้ดีกว่าโคพอลิยูเรีย และพอลิเมอร์ที่มีซิงค์อยู่ในโครงสร้างทนความร้อนได้ดีกว่าพอลิเมอร์ที่มีนิกเกิลอยู่ในโครงสร้าง พอลิเมอร์ที่ทนความร้อนได้ดีที่สุด คือ พอลิเมอร์ที่สังเคราะห์จาก $ZnSalOMe_2trien$ MDI และพอลิเอทิลีนไกลคอล โดยมีค่า T_5 เท่ากับ 293°C และน้ำหนักที่เหลือจากการเผาไหม้ที่ 600°C คือ 64%

ภาควิชา.....เคมี.....ลายมือชื่อนิสิต.....
 สาขาวิชา.....เคมี.....ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์หลัก.....
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KHWUNTA VANITCHO : SYNTHESIS OF COPOLYUREAS AND POLYURETHANE-UREAS CONTAINING ZINC AND NICKEL DIMETHOXYALTRIEEN COMPLEXES. THESIS PRINCIPAL ADVISOR : ASSOC. PROF. NUANPHUN CHANTARASIRI, 131 pp.

Copolyureas and polyurethane-ureas containing zinc and nickel dimethoxysaltrien complexes (MSalOMe₂trien; M = Zn and Ni) in the main chain were synthesized by the reaction between MSalOMe₂trien, diisocyanates and diamines or dialcohols, respectively. Diisocyanates employed were hexamethylene diisocyanate (HMDI) and 4,4'-diphenylmethane diisocyanate (MDI). Different aliphatic and aromatic diamines or dialcohols were employed to study the effect of the structure on the polymer properties. The polymers were characterized by IR, ¹H-NMR and XRD. Thermal stability was examined by thermogravimetric analysis. The polymers were soluble in dimethyl formamide and dimethyl sulfoxide. MDI-based polymers showed higher solubility than HMDI-based polymers. Inherent viscosity of metal-containing copolyureas and polyurethane-ureas were found to be in the range 0.0791-0.0947 and 0.0797-0.1095 dL/g, respectively. The temperature at 5% weight loss (T₅) and char yields at 600°C of the polymers were found to be in the range 253-293°C and 36-64%, respectively. Polyurethane-ureas showed higher thermal stability than copolyureas and zinc-containing polymers had higher thermal stability than nickel-containing polymers. The most thermally stable polymer, which was obtained from ZnSalOMe₂trien, MDI and poly(ethylene glycol) showed T₅ equal to initial decomposition temperature at 293°C and char yields at 600°C of 64%.

Department.....Chemistry.....Student's signature.....
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LIST OF SYMBOLS AND ABBREVIATIONS

BPA	Bis(4-Hydroxyphenyl)propane
DAP	4,4'-diaminodiphenylmethane
DBTDL	Dibutyltin dilaurate
DMF	Dimethyl formamide
DMSO	Dimethyl sulphoxide
HMDA	Hexamethylenediamine
HMDI	Hexamethylene diisocyanate
HMDO	1,6-Hexanediol
HMDI-BPA	Polymer synthesized from HMDI and BPA
HMDI-DAP	Polymer synthesized from HMDI and DAP
HMDI-HMDA	Polymer synthesized from HMDI and HMDA
HMDI-HMDO	Polymer synthesized from HMDI and HMDO
HMDI-TDA	Polymer synthesized from HMDI and TDA
HMDI-TEG	Polymer synthesized from HMDI and TEG
HMDI-PEG	Polymer synthesized from HMDI and PEG
HMDI-XDA	Polymer synthesized from HMDI and XDA
LOI	Limiting oxygen index
MDI	4,4'-diphenylmethane diisocyanate
MDI-BPA	Polymer synthesized from MDI and BPA
MDI-DAP	Polymer synthesized from MDI and DAP
MDI-HMDA	Polymer synthesized from MDI and HMDA
MDI-HMDO	Polymer synthesized from MDI and HMDO
MDI-PEG	Polymer synthesized from MDI and PEG
MDI-TDA	Polymer synthesized from MDI and TDA
MDI-TEG	Polymer synthesized from MDI and TEG
MDI-XDA	Polymer synthesized from MDI and XDA
MSalOMe ₂ trien	Dimethoxysaltrien metal complexes
MSalOMe ₂ trien-coPUs	Metal-containing copolyureas
MSalOMe ₂ trien-PUUs	Metal-containing polyurethane-ureas
NiSalOMe ₂ trien	Dimethoxysaltrien nickel complexes

NiSalOMe ₂ trien-HMDI	Polymer synthesized from NiSalOMe ₂ trien and HMDI
NiSalOMe ₂ trien-HMDI-BPA	Polymer synthesized from NiSalOMe ₂ trien, HMDI and BPA
NiSalOMe ₂ trien-HMDI-DAP	Polymer synthesized from NiSalOMe ₂ trien, HMDI and DAP
NiSalOMe ₂ trien-HMDI-HMDA	Polymer synthesized from NiSalOMe ₂ trien, HMDI and HMDA
NiSalOMe ₂ trien-HMDI-HMDO	Polymer synthesized from NiSalOMe ₂ trien, HMDI and HMDO
NiSalOMe ₂ trien-HMDI-TDA	Polymer synthesized from NiSalOMe ₂ trien, HMDI and TDA
NiSalOMe ₂ trien-HMDI-TEG	Polymer synthesized from NiSalOMe ₂ trien, HMDI and TEG
NiSalOMe ₂ trien-HMDI-PEG	Polymer synthesized from NiSalOMe ₂ trien, HMDI and PEG
NiSalOMe ₂ trien-HMDI-XDA	Polymer synthesized from NiSalOMe ₂ trien, HMDI and XDA
NiSalOMe ₂ trien-MDI	Polymer synthesized from NiSalOMe ₂ trien and MDI
NiSalOMe ₂ trien-MDI-BPA	Polymer synthesized from NiSalOMe ₂ trien, MDI and BPA
NiSalOMe ₂ trien -MDI-DAP	Polymer synthesized from NiSalOMe ₂ trien, MDI and DAP
NiSalOMe ₂ trien-MDI-HMDA	Polymer synthesized from NiSalOMe ₂ trien, MDI and HMDA
NiSalOMe ₂ trien-MDI-HMDO	Polymer synthesized from NiSalOMe ₂ trien, MDI and HMDO
NiSalOMe ₂ trien-MDI-TDA	Polymer synthesized from NiSalOMe ₂ trien, MDI and TDA
NiSalOMe ₂ trien-MDI-TEG	Polymer synthesized from NiSalOMe ₂ trien, MDI and TEG
NiSalOMe ₂ trien-MDI-PEG	Polymer synthesized from NiSalOMe ₂ trien, MDI and PEG

NiSalOMe ₂ trien-MDI-XDA	Polymer synthesized from NiSalOMe ₂ trien, MDI and XDA
PEG300	Polyethylene glycol, MW = 300
T ₅	The temperature at 5% weight loss from starting weight
TDA	4,7,10-Trioxa-1,13-tridecanediamine
TDI	Toluene diisocyanate
TEG	Triethylene glycol
TGA	Thermogravimetric analysis
XDA	<i>m</i> -Xylylenediamine
XRD	X-ray diffraction
ZnSalOMe ₂ trien	Dimethoxysaltrien zinc complexes
ZnSalOMe ₂ trien-HMDI	Polymer synthesized from ZnSalOMe ₂ trien and HMDI
ZnSalOMe ₂ trien-HMDI-BPA	Polymer synthesized from ZnSalOMe ₂ trien, HMDI and BPA
ZnSalOMe ₂ trien-HMDI-DAP	Polymer synthesized from ZnSalOMe ₂ trien, HMDI and DAP
ZnSalOMe ₂ trien-HMDI-HMDA	Polymer synthesized from ZnSalOMe ₂ trien, HMDI and HMDA
ZnSalOMe ₂ trien-HMDI-HMDO	Polymer synthesized from ZnSalOMe ₂ trien, HMDI and HMDO
ZnSalOMe ₂ trien-HMDI-TDA	Polymer synthesized from ZnSalOMe ₂ trien, HMDI and TDA
ZnSalOMe ₂ trien-HMDI-TEG	Polymer synthesized from ZnSalOMe ₂ trien, HMDI and TEG
ZnSalOMe ₂ trien-HMDI-PEG	Polymer synthesized from ZnSalOMe ₂ trien, HMDI and PEG
ZnSalOMe ₂ trien-HMDI-XDA	Polymer synthesized from ZnSalOMe ₂ trien, HMDI and XDA
ZnSalOMe ₂ trien-MDI	Polymer synthesized from ZnSalOMe ₂ trien and MDI
ZnSalOMe ₂ trien-MDI-BPA	Polymer synthesized from ZnSalOMe ₂ trien, MDI and BPA

ZnSalOMe ₂ trien-MDI-DAP	Polymer synthesized from ZnSalOMe ₂ trien, MDI and DAP
ZnSalOMe ₂ trien-MDI-HMDA	Polymer synthesized from ZnSalOMe ₂ trien, MDI and HMDA
ZnSalOMe ₂ trien-MDI-HMDO	Polymer synthesized from ZnSalOMe ₂ trien, MDI and HMDO
ZnSalOMe ₂ trien-MDI-TDA	Polymer synthesized from ZnSalOMe ₂ trien, MDI and TDA
ZnSalOMe ₂ trien-MDI-TEG	Polymer synthesized from ZnSalOMe ₂ trien, MDI and TEG
ZnSalOMe ₂ trien-MDI-PEG	Polymer synthesized from ZnSalOMe ₂ trien, MDI and PEG
ZnSalOMe ₂ trien-MDI-XDA	Polymer synthesized from ZnSalOMe ₂ trien, MDI and XDA