

การสังเคราะห์และสมบัติของคาลิกซ์[4]เอรีนชนิดใหม่ที่มีหมู่โคอะเซทิลีน

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SYNTHESIS AND PROPERTIES OF NEW CALIX[4]ARENES CONTAINING
DIACETYLENE PENDANTS

Chantana Sae-Lim

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Chemistry

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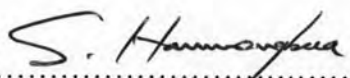
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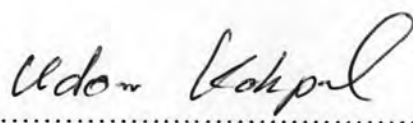
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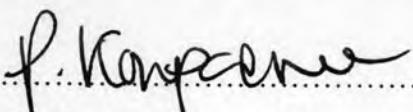
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จันทนา แซ่ลิ้ม : การสังเคราะห์และสมบัติของคาลิกซ์[4]เอรีนชนิดใหม่ที่มีหมู่ไดอะเซทิลีน . (SYNTHESIS AND PROPERTIES OF NEW CALIX[4]ARENES CONTAINING DIACETYLENE PENDANTS) อ. ที่ปรึกษา : รศ.ดร. มงคล สุขวัฒนาสินิทธิ์, 156 หน้า.

การเกิดโทโพโลจิคอลพอลิเมอร์ไรเซชันต้องอาศัยการจัดเรียงตัวระดับซูปราโมเลกุลวาร์ของมอนอเมอร์ที่จำเพาะเจาะจง ซึ่งสามารถทำให้ได้พอลิเมอร์ที่มีโครงสร้างพิเศษที่ไม่สามารถสังเคราะห์ได้จากปฏิกิริยาพอลิเมอร์ไรเซชันทั่วไป การเกิดโทโพโลจิคอลพอลิเมอร์ไรเซชันที่รู้จักกันดีที่สุดเกี่ยวข้องกับไดอะเซทิลีนมอนอเมอร์ที่ทำให้ได้พอลิไดอะเซทิลีนที่มีโครงสร้างเป็นคอนจูเกตของพันธะคู่สลับกับพันธะสาม งานวิจัยนี้ได้ทำการสังเคราะห์อนุพันธ์คาลิกซ์[4]เอรีนกลุ่มใหม่ที่ประกอบด้วยสายไดอะเซทิลีน 2-4 สาย ต่อกับขอบฟีนอกซีของโมเลกุลคาลิกซ์[4]เอรีนเพื่อใช้แสดงเป็นครั้งแรกถึงการเกิดพอลิเมอร์ไรเซชัน โดยเกิดผ่านปฏิกิริยาการเติมของหมู่ไดไฮโดรแบบ 1,4 ภายในโมเลกุล โดยขั้นตอนสำคัญในการสังเคราะห์สายโซ่ไดไฮโดรคือปฏิกิริยาควบรวมระหว่างคาลิกซ์[4]เอรีนที่มีหมู่โพโรโฟนัลกับไอโอดอลโคไนน์โดยมีคอปเปอร์(I) ไอโอดาได์เป็นตัวเร่งปฏิกิริยาในไพโรรีติน การศึกษาพอลิเมอร์ไรเซชันของอนุพันธ์คาลิกซ์[4]เอรีนที่สังเคราะห์ได้ในสถานะของแข็ง พบว่าคาลิกซ์[4]เอรีน ที่มีไดอะเซทิลีนที่มีแอลคิลคาร์บาเมตสี่สายเท่านั้นที่สามารถเกิดพอลิเมอร์ไรเซชันได้เป็นพอลิไดอะเซทิลีนที่มีคาลิกซ์[4]เอรีนเป็นองค์ประกอบ นอกจากนี้ความยาวของสายแอลคิลที่เชื่อมระหว่างไดไฮโดรกับหมู่คาร์บาเมตยังมีอิทธิพลอย่างมากในการเกิดพอลิเมอร์ไรเซชัน พอลิไดอะเซทิลีนที่ได้มีสีแดงการดูดกลืนคลื่นแสงในช่วงวิสิเบิลที่ 350-600 นาโนเมตรและให้สัญญาณรามานที่เลขคลื่น 1500 และ 2100 cm^{-1} ซึ่งสอดคล้องกับโครงสร้างคอนจูเกตของพอลิเมอร์ และพอลิไดอะเซทิลีนที่ได้นี้สามารถจัดเรียงตัวเป็นจานกลมระดับขนาดนาโนเมตรในน้ำและเตตระไฮโดรฟิวเรน และพอลิเมอร์นี้ยังแสดงสมบัติการเปลี่ยนสีจากสีแดงเป็นสีเหลืองแบบผันกลับได้เมื่อได้รับความร้อนที่อุณหภูมิสูงกว่า 120 °C

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CHANTANA SAE-LIM : SYNTHESIS AND PROPERTIES OF NEW
 CALIX[4]ARENES CONTAINING DIACETYLENE PENDANTS THESIS
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Topological polymerization required specific supramolecular assembly of the monomer molecules that can provide unique structures of polymer cannot be attained by conventional polymerization. The best known topological polymerization to date involves diacetylene monomers to produce the corresponding ene-yne conjugated polydiacetylenes. The new series of *tert*-butylcalix[4]arene derivatives containing 2-4 diyne chains on the phenoxy rim were synthesized in this dissertation in the attempt to demonstrate the first polymerization through a topological intramolecular 1,4-addition of diyne. The copper-catalyzed coupling reaction of multipropynyl-*tert*-butylcalix[4]arene with 5-iodo-4-pentynol in pyrrolidine constitutes the key step in the synthesis of the diynes chain. The solid-state photopolymerization study indicates that only the calix[4]arene derivatives containing four diyne units with alkyl urethane groups can be topologically polymerized to afford polydiacetylenes containing calix[4]arene. The length of alkyl linker between the diyne and carbamate group also has a pronounced effect on the polymerizability of the diyne units. The visible absorption band at 350-600 nm and the Raman signals around 1500 and 2100 cm^{-1} signified the ene-yne conjugation of the resulting polymers. The polydiacetylenes obtained displayed the formation of nanodisk in water and tetrahydrofuran probably through a micelle type self-assembly. The polymers also exhibited reversible red to yellow thermochromism near 120 $^{\circ}\text{C}$.

Department.....Chemistry.....Student's signature.....

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List of Abbreviations and Signs

Å	Angstrom
Mp	Melting point
°C	Degree Celsius
¹ H-NMR	Proton nuclear magnetic resonance
¹³ C-NMR	Carbon nuclear magnetic resonance
cm	Centimetre
δ	Chemical shift
<i>J</i>	Coupling constant
g	Gram
Hz	Hertz
kcal	Kilocalorie
mL	Millilitre
mmol	Millimole
M	Molar
nm	Nanometre
ppm	Part per million
cm ⁻¹	Per centimetre
M ⁻¹	Per molar
¹ H-NMR	Proton nuclear magnetic resonance
UV/vis	Ultra violet-visible
λ	Wavelength
Mrad	Megarad
γ	Gamma
kDa	Kilodalton
hr	Hour
min	Minute
M _w	Weight average molecular weight
M _n	Number average molecular weight
kGy	KiloGray
PDI	Polydispersity index

List of Numbered Compounds

BnC2A	25,27-di(octa-4,6-diyn-1-ol)oxy-26,28-dibenzyloxy- <i>tert</i> -butylcalix[4]arene
BnC3A	25,26,27-tri[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-28-benzyloxy- <i>tert</i> -butylcalix[4]arene
PrC2A	25,27-di(octa-4,6-diyn-1-ol)oxy-26,28-dipropyl- <i>tert</i> -butylcalix[4]arene
PrC3A	25,26,27-tri(octa-4,6-diyn-1-ol)oxy-28-propyl- <i>tert</i> -butylcalix[4]arene
C4A'	25,26,27,28-tetra(hexa-2,4-diyn-1-ol)oxy- <i>tert</i> -butylcalix[4]arene
C4A''	25,26,27,28-tetra(hepta-4,6-diyn-1-ol)oxy- <i>tert</i> -butylcalix[4]arene
C4A	25,26,27,28-tetra(octa-4,6-diyn-1-ol)oxy- <i>tert</i> -butylcalix[4]arene
BnC2BU	25,27-di[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-26,28-dibenzyloxy- <i>tert</i> -butylcalix[4]arene
PrC2BU	25,27-di[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-26,28-dipropyl- <i>tert</i> -butylcalix[4]arene
BnC3BU	25,26,27-tri[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-28-benzyloxy- <i>tert</i> -butylcalix[4]arene
PrC3BU	25,26,27-tri[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy-28-propyl- <i>tert</i> -butylcalix[4]arene
C4BU	25,26,27,28-tetra[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy- <i>tert</i> -butylcalix[4]arene
C4BU'	25,26,27,28-tetra[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy- <i>tert</i> -butylcalix[4]arene
C4BU''	25,26,27,28-tetra[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy- <i>tert</i> -butylcalix[4]arene
C4HU	25,26,27,28-tetra[octa-4,6-diyn-1-ol-(carboxy-hexyl-urethane)]oxy- <i>tert</i> -butylcalix[4]arene
C4PU	25,26,27,28-tetra[octa-4,6-diyn-1-ol-(carboxy-phenyl-urethane)]oxy- <i>tert</i> -butylcalix[4]arene
C4PD	25,26,27,28-tetra(pentadeca-2,4-diyne)oxy- <i>tert</i> -butylcalix[4]arene
PC4BU	poly{25,26,27,28-tetra[octa-4,6-diyn-1-ol-(carboxy-butyl-urethane)]oxy- <i>tert</i> -butylcalix[4]arene}

- PC4BU''** poly{25,26,27,28-tetra[octa-4,6-diyne-1-ol-(carboxy-butyl-urethane)]oxy-*tert*-butylcalix[4]arene}
- PC4HU** poly{25,26,27,28-tetra[octa-4,6-diyne-1-ol-(carboxy-hexyl-urethane)]oxy-*tert*-butylcalix[4]arene}