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PREPARATION AND DOPING OF POLY(3-HEXYLTHIOPHENE) FILMS

Miss Ketthip Anuwareephong

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for the Degree of Master of Science Program in Petrochemistry and Polymer Science

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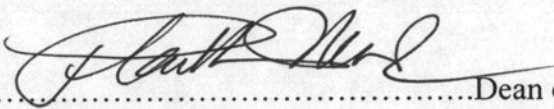
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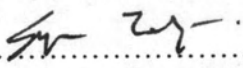
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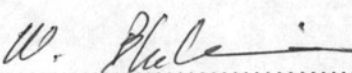
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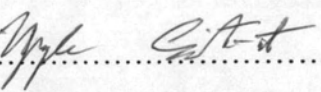

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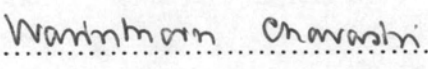
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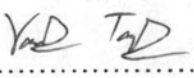
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เกศทิพย์ อนุวาริพงษ์ : การเตรียมและการโด๊ปฟิล์มพอลิ(3-เฮกซิลไทโอฟิน)
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งานวิจัยนี้เป็นการศึกษาการสังเคราะห์พอลิ(3-เฮกซิลไทโอฟิน) ด้วยวิธีออกซิเดทีฟพอลิ
เมอไรเซชันของไทโอฟินมอนอเมอร์ด้วยแอนไฮดรัสเฟอร์ริกคลอไรด์ ในตัวทำละลายอินทรีย์ โดย
มีปัจจัยต่างๆทางการทดลองที่ใช้ในปฏิกิริยา ได้แก่ อัตราส่วนของ 3-เฮกซิลไทโอฟินมอนอเมอร์ต่อ
เฟอร์ริกคลอไรด์ อุณหภูมิที่ใช้ทำปฏิกิริยา ชนิดของตัวทำละลาย และสารเติมแต่ง โดยมีเป้าหมาย
เพื่อให้ได้เปอร์เซ็นต์ผลิตภัณฑ์ และสัดส่วนของ Head-to-Tail (%HT) ที่สูงขึ้น จากการทดลอง
พบว่า เมื่อใช้ไดคลอโรมีเทนเป็นตัวทำละลาย ทำปฏิกิริยาที่อุณหภูมิห้อง อัตราส่วนของ 3-เฮกซิล
ไทโอฟินต่อเฟอร์ริกคลอไรด์ เท่ากับ 1:3 เหมาะสมต่อการสังเคราะห์ที่สุด คือจะมีเปอร์เซ็นต์
ผลิตภัณฑ์เท่ากับ 94 และ %HT เท่ากับ 78 ส่วนการศึกษาการโด๊ปพอลิ(3-เฮกซิลไทโอฟิน)ด้วย
วิธีการต่างๆพบว่า สามารถใช้กรดไตรคลอโรอะซิติกและกรดไตรฟลูออโรอะซิติกโด๊ป
พอลิ(3-เฮกซิลไทโอฟิน)ได้โดยตรงโดยไม่เกิดปัญหาการตกตะกอนของพอลิเมอร์ที่ถูกโด๊ป
ในขณะที่กรดลิวอิสพบปัญหาการตกตะกอนของพอลิเมอร์ที่ถูกโด๊ปทำให้ไม่สามารถขึ้นฟิล์มได้
และการโด๊ปแบบโซลวาโต-คอนโทรล ที่ใช้ส่วนผสมของกรดมัทเทนซัลโฟนิค-ไทโอฟิน,
เฟอร์ริกคลอไรด์ -ไพรีดีน หรืออะลูมิเนียมคลอไรด์ -ไพรีดีนจะสามารถขึ้นฟิล์มได้โดยไม่เกิด
ปัญหาการตกตะกอน

สาขาวิชา... ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... ลายมือชื่อนิสิต... เกศทิพย์ อนุวาริพงษ์
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KETTHIP ANUWAREEPHONG: PREPARATION AND DOPING OF
 POLY(3-HEXYLTHIOPHENE) FILMS. THESIS ADVISOR: ASST. PROF.
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The synthesis of poly(3-hexylthiophene) by the oxidative coupling of thiophene monomer with anhydrous ferric chloride in organic solvent was investigated. Various experimental factors in the polymerization reactions to yield poly(3-hexylthiophene) including reaction temperatures, the mole ratios of 3-hexylthiophene and ferric chloride, types of solvent and additives, with the goal of obtaining higher %yield and Head-to-Tail ratio (%HT). The best synthesis condition of poly(3-hexylthiophene) was obtained when running the reaction at room temperature in dichloromethane and at the mole ratio of 3-hexylthiophene monomer : ferric chloride = 1:3. Under this condition, the polymer was obtained in 94%yield with 78%HT. Various doping methods of poly(3-hexylthiophene) were investigated. For protonic acid doping, trichloroacetic acid and trifluoroacetic acid were found to successfully give the doped products without precipitation while all Lewis acid dopings resulted in precipitation of the doped products. Solvato-controlled doping with the combinations of either methanesulfonic acid -thiophene, ferric chloride -pyridine, or aluminium chloride -pyridine gave the doped polymer films without pre-precipitation problem.

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

°C	: degree celsius
μL	: microliter
μmol	: micromole
AC-index	: absorption-conjugation index
cm	: centimeter
CDCl ₃	: deuterated chloroform
DMF	: dimethylformamide
EDOT	: 3,4-ethylenedioxythiophene
eV	: electron volt
g	: gram
GPC	: gel permeation chromatography
h	: hour
HH	: head to head
HOMO	: highest occupied molecular orbital
HT	: head to tail
LED	: light emitting diode
LDA	: lithium diisopropylamide
LUMO	: lowest unoccupied molecular orbital
M_n	: number average molecular weight
MeOH	: methanol
mg	: milligram
min	: minute
mL	: milliliter
mmol	: millimole
MSA	: methanesulfonic acid
nir	: near infrared
nm	: nanometer
NMR	: nuclear magnetic resonance spectroscopy
PEDOT	: poly(3,4-ethylenedioxythiophene)
P3AT	: poly(3-alkylthiophene)
P3HT	: poly(3-hexylthiophene)

ppm	: part per million
PT	: polythiophene
S	: Siemens
TCA	: trichloroacetic acid
TEA	: triethylamine
TFA	: trifluoroacetic acid
TT	: tail to tail
UV	: ultra-violet
vis	: visible
wt	: weight