

การสังเคราะห์อนุพันธ์ของ 4-คลอโร-2,5-ไดฟีนิลออกซาโซลและพอลิเมอร์ร่วม



นางสาวณัฐพร พิมพะ

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จุฬาลงกรณ์มหาวิทยาลัย

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SYNTHESIS OF 4-CHLORO-2,5-DIPHENYLOXAZOLE DERIVATIVES AND THEIR COPOLYMERS



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ศูนย์วิทยทรัพยากร

จุฬาลงกรณ์มหาวิทยาลัย

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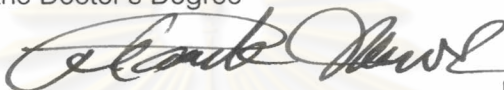
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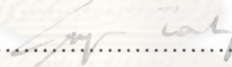
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ณัฐพร พิมพะ : การสังเคราะห์อนุพันธ์ของ 4-คลอโร-2,5-ไดฟีนิลออกซาโซลและพอลิเมอร์ร่วม (SYNTHESIS OF 4-CHLORO-2,5-DIPHENYLOXAZOLE DERIVATIVES AND THEIR COPOLYMERS) อ. ที่ปรึกษา : รศ.ดร.ศุภวรรณ ตันตยานนท์, อ.ที่ปรึกษาร่วม : Prof.Frank W.Harris; 155 หน้า. ISBN 974-17-3928-1.

มอนอเมอร์ 2 ชนิดที่มี 4-คลอโร-2,5- ไดฟีนิลออกซาโซล ได้ถูกออกแบบและสังเคราะห์ขึ้นด้วยผลผลิตสูง เกิดผ่านปฏิกิริยาการปิดวงของเบนโซอิลไฮยาไนด์ และเบนซาลดีไฮด์ที่เหมาะสม ได้เสนอกฎไกการเกิดปฏิกิริยาที่น่าจะเป็นไปได้บนพื้นฐานของผลการทดลองและการสังเคราะห์ พอลิเมอร์ซึ่งประกอบด้วย 4-คลอโร-2,5-ไดฟีนิลออกซาโซลอยู่ในสายโซ่หลักและโซ่กิ่งได้ถูกเตรียมขึ้น ฟรีเรดิคัลพอลิเมอร์สังเคราะห์ขึ้นจากปฏิกิริยาโคพอลิเมอไรเซชันของแอกริเลตมอนอเมอร์ ซึ่งมีหมู่แทนที่หลายหมู่ ดังนี้ ไฮโดรเจน ฟลูออรีน เมทอกซี, ไนโตร และ แอมิโน กับเมทิลเมทาคริเลต พอลิเมอร์เหล่านี้แสดงสมบัติทนความร้อนที่สูงในช่วง 247-280 องศาเซลเซียส อุณหภูมิสถานะการหลอมเหลวคล้ายแก้วมีค่าในช่วง 114-120 องศาเซลเซียส 4-คลอโร-2,5-บิส(4-ฟลูออโรฟีนิล)ออกซาโซลมอนอเมอร์ควบแน่นกับบิสฟีนอล เอ เพื่อเตรียมพอลิ(เอริลอีเทอร์) ซึ่งมี 4-คลอโร -2,5- ไดฟีนิลออกซาโซลเป็นองค์ประกอบเวลาที่เหมาะสมสำหรับการพอลิเมอไรเซชันคือ 9 ชั่วโมง พอลิ(เอริลอีเทอร์)มีสมบัติทนความร้อนดีเยี่ยมในช่วง 334-360 องศาเซลเซียส และมีอุณหภูมิสถานะการหลอมเหลวคล้ายแก้วมีค่าในช่วง 192-205 องศาเซลเซียส ผลจากการตรวจสอบสมบัติทางด้านแสงของอนุพันธ์ของ4-คลอโร -2,5- ไดฟีนิลออกซาโซลและพอลิเมอร์ได้ถูกรวบรวม พอลิเมอร์เหล่านี้ให้แสงฟลูออเรสเซนส์ ในช่วงเดียวกับ 2,5- ไดฟีนิลออกซาโซล และยังสามารถเรืองแสงได้ เมื่อได้รับรังสีบีต้า

ภาควิชา.....เคมี..... ลายมือชื่อนิสิต..... *ณัฐพร พิมพะ*  
 สาขาวิชา.....เคมี..... ลายมือชื่ออาจารย์ที่ปรึกษา..... *Prof. Frank W. Harris*  
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KEY WORD: 4-CHLORO-2,5-DIPHENYLOXAZOLE / POLYMERIZATION / SCINTILLATION EFFICIENCY / OPTICAL PROPERTIES / 2,5-DIPHENYLOXAZOLE

NUTTAPORN PIMPHA : SYNTHESIS OF 4-CHLORO-2,5-DIPHENYLOXAZOLE DERIVATIVES AND THEIR COPOLYMERS. DISSERTATION ADVISOR : ASSOC.PROF. SUPAWAN TANTAYANON,Ph.D.; DISSERTATION COADVISOR : PROF. FRANK W. HARRIS,Ph.D.; 155 pp. ISBN 974-17-3928-1.

Two types of monomers containing 4-chloro-2,5-diphenyloxazole moiety were designed and successfully been synthesized with reasonable yield via a cyclization of the corresponding benzoyl cyanides and benzaldehydes. A plausible mechanism of this reaction is proposed based on an experimental results and observation. Having established an efficient synthetic route to monomers, the construction of polymer containing functionalized 4-chloro-2,5-diphenyloxazole scintillant moiety in both main chain and side chain by condensation and free radical polymerization, respectively, have been proceeded. To obtain free radical polymers, acrylate monomers with various substituents including H, F, OCH<sub>3</sub>, NO<sub>2</sub> and NH<sub>2</sub> were copolymerized with methyl methacrylate in two different feed ratios, 1% and 5%. These polymers showed a high thermal stability in the range of 247-280°C. The glass transition temperature (*T<sub>g</sub>*) valued in the range of 114-128°C. 4-Chloro-2,5-bis-(4-fluorophenyl)oxazole monomer was synthesized and condensed with bisphenol A to construct a poly(aryl ether) containing 4-chloro-2,5-diphenyloxazole. The optimum polymerization time to obtain a high molecular weight was around 9 h. These poly(aryl ether) exhibited an excellent thermal stability ranging from 334-364°C and *T<sub>g</sub>* valued in the range of 192-205°C. All polymers show the distinct and well-defined fluorescence of the characteristic 2,5-diphenyloxazole chromophore. These materials are possess the ability to scintillate efficiently in the presence of  $\beta$ -ionizing radiation.

Department.....Chemistry.....Student's signature.....*Nuttaporn Pimpha*  
 Field of study....Chemistry.....Advisor's signature.....*Supawan Tantayanon*  
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**List of Abbreviation and Signs**

$\text{cm}^{-1}$	Unit of Wavelength
m.p.	Melting Point
b.p.	Boiling Point
$^{\circ}\text{C}$	Degree Celsius
m/z	Mass per Charge
NMR	Nuclear Magnetic Resonance
$J$	Coupling Constant
Hz	Herzt
ppm	Parts Per Millon
$\delta$	Chemical Shift
s	Singlet (NMR)
d	Doublet (NMR)
dd	Doublet of Doublets (NMR)
m	Multiplet (NMR)
$\epsilon$	Molar Absorption Coefficient
M	Molar
mmol	Millimole
mL	Mililiter
THF	Tetrahydrofuran
PPO	2,5-Diphenyloxazole
GPC	Gel Permeation Chromatography
$M_n$	Number Average Molecular Weight
$M_w$	Weight Average Molecular Weight
PDI	Polydispersity Index
DSC	Differential scanning calorimetry
TGA	Thermogravimetric Analysis
$T_g$	Glass Transition Temperature
$T_d$	Decomposition Temperature

### List of Numbered Compounds

- [1a] 4-fluorobenzoyl cyanide
- [1b] 4-methoxybenzoyl cyanide
- [1c] 4-nitrobenzoyl cyanide
- [2] 4-chloro-2-(4'-ethylphenyl)-5-phenyloxazole
- [3] 2-[4'-(1-bromoethyl)phenyl]-4-chloro-5-phenyloxazole
- [4] 4-chloro-5-phenyl-2-(4'-vinylphenyl)oxazole
- [5a] 4-(4'-chloro-5'-phenyloxazol-2'-yl)benzaldehyde
- [5b] 4-[4'-chloro-5'-(4-fluorophenyl)oxazol-2'-yl]benzaldehyde
- [5c] 4-[4'-chloro-5'-(4-methoxyphenyl)oxazol-2'-yl]benzaldehyde
- [5d] 4-[4'-chloro-5'-(4-nitrophenyl)oxazol-2'-yl]benzaldehyde
- [6a] [4-(4'-chloro-5'-phenyloxazol-2'-yl)phenyl]methanol
- [6b] {4-[4'-chloro-5'-(4-fluorophenyl)oxazol-2'-yl]phenyl}methanol
- [6c] {4-[4'-chloro-5'-(4-methoxyphenyl)oxazol-2'-yl]phenyl}methanol
- [6d] {4-[4'-chloro-5'-(4-nitrophenyl)oxazol-2'-yl]phenyl}methanol
- [7a] [4-(4'-chloro-5'-phenyloxazol-2'-yl)phenyl]methyl methacrylate
- [7b] {4-[4'-chloro-5'-(4-fluorophenyl)oxazol-2'-yl]phenyl}methyl methacrylate
- [7c] {4-[4'-chloro-5'-(4-methoxyphenyl)oxazol-2'-yl]phenyl}methyl methacrylate
- [7d] {4-[4'-chloro-5'-(4-nitrophenyl)oxazol-2'-yl]phenyl}methyl methacrylate
- [7e] {4-[4'-chloro-5'-(4-aminophenyl)oxazol-2'-yl]phenyl}methyl methacrylate
- [8] 4-chloro-2,5-bis-(4'-fluorophenyl)oxazole
- [P1] free-radical copolymer of 1% [4-(4'-chloro-5'-phenyloxazol-2'-yl)phenyl]methyl methacrylate and MMA
- [P5] free-radical copolymer of 5% [4-(4'-chloro-5'-phenyloxazol-2'-yl)phenyl]methyl methacrylate and MMA

- [Pf1] free-radical copolymer of 1% {4-[4'-chloro-5'-(4-fluorophenyl)-oxazol-2'-yl]phenyl}methyl methacrylate and MMA
- [Pf5] free-radical copolymer of 5% {4-[4'-chloro-5'-(4-fluorophenyl)-oxazol-2'-yl]phenyl}methyl methacrylate and MMA
- [Pm1] free-radical copolymer of 1% {4-[4'-chloro-5'-(4-methoxyphenyl)-oxazol-2'-yl]phenyl}methyl methacrylate and MMA
- [Pm5] free-radical copolymer of 5% {4-[4'-chloro-5'-(4-methoxyphenyl)-oxazol-2'-yl]phenyl}methyl methacrylate and MMA
- [Pn1] free-radical copolymer of 1% {4-[4'-chloro-5'-(4-nitrophenyl)-oxazol-2'-yl]phenyl}methyl methacrylate and MMA
- [Pn5] free-radical copolymer of 5% {4-[4'-chloro-5'-(4-nitrophenyl)-oxazol-2'-yl]phenyl}methyl methacrylate and MMA
- [Pnh2] free-radical copolymer of 5% {4-[4'-chloro-5'-(4-aminophenyl)-oxazol-2'-yl]phenyl}methyl methacrylate and MMA
- [CP3] copolymer of 4-chloro-2,5-bis-(4'-fluorophenyl)oxazole and bisphenol A at 3 hours of condensation polymerization
- [CP6] copolymer of 4-chloro-2,5-bis-(4'-fluorophenyl)oxazole and bisphenol A at 6 hours condensation polymerization
- [CP9] copolymer of 4-chloro-2,5-bis-(4'-fluorophenyl)oxazole and bisphenol A at 9 hours condensation polymerization
- [CP12] copolymer of 4-chloro-2,5-bis-(4'-fluoro-phenyl)-oxazole and bisphenol A at 12 hours condensation polymerization