

**DEVELOPMENT OF POLYPYRROLE-BASED SENSORS FOR VAPORS
OF FLAMMABLE CHEMICALS**



Ms. Ladawan Ruangchuay Wannatong ,

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By : Ms. Ladawan Ruangchuay Wannatong
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University, in partial fulfillment of the requirements for the Degree of Doctor of
Philosophy.

K. Bunyakiat.
.....
(Assoc. Prof. Kunchana Bunyakiat) College Director

Thesis Committee:

K. Bunyakiat.
.....
(Assoc. Prof. Kunchana Bunyakiat)

Anuvat Sirivat
.....
(Assoc. Prof. Anuvat Sirivat)

Johannes W. Schwank
.....
(Prof. Johannes W. Schwank)

Pitt Supaphol
.....
(Asst. Prof. Pitt Supaphol)

Supa Hannongbua
.....
(Asst. Prof. Supa Hannongbua)

ABSTRACT

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Serial issues concerning development of polypyrrole-based sensors for vapors of flammable chemicals were studied in this dissertation work. Polypyrrole (PPy) was chemically prepared *via* an *in situ* doped polymerization utilizing seven dopant anions (dopant to monomer molar ratio, D/M = 1/12) to stabilize the positive charges on N of pyrrole rings. These dopant anions were found to play important roles on physical, chemical, and electrical properties of PPy as revealed by several techniques, e.g. X-ray photoelectron spectrometer and the custom-made four-point probe conductivity meter. PPys doped with α -naphthalene sulfonate (PPy/A) and β -naphthalene sulfonate (PPy/B) have good pellet appearance, solubility, thermal stability, specific conductivity, and stability in conductivity. PPy/A was chemically synthesized at various D/M ratios. The D/M ratio giving PPy/A with high specific conductivity and stability in conductivity is 1/12.

Upon exposure to acetone vapor at 16.7 vol.% in N₂, negative changes in specific conductivity, $\Delta\sigma$, of PPys were observed. These changes depend critically on the type of the dopants used. For the sulfonate dopants, $\Delta\sigma$ exponentially depended on the doping level (N^+/N) and the initial specific conductivity. It depended linearly on the proportion of the bipolaron species and the ordering and inversely on the proportion of the imine-like nitrogen defect (=N-). PPy/A exhibited the largest specific conductivity decrement: 0.4 S/cm. Various techniques, e.g. an environmental scanning electronmicroscope, were used to investigate the interaction

between PPy and acetone molecules. Swelling, H-bonding, and reduction reaction by acetone are suggested to cause the decrease in specific conductivity of PPy.

In order to improve the selectivity of PPy toward acetone and toluene, which are flammable components in lacquer over the non-flammable components acetic acid and water, PPy/A with D/M ratio of 1/5, PPy/A5 has been blended with several insulating polymers: PEO; PMMA; HDPE; PS; and ABS, by three different methods namely dry mixing, solution mixing, and coating. The electrical conductivity responses towards liquid of water, acetone, acetic acid, or toluene of PPy/A5/PMMA, PPy/A5/PS and PPy/A5/ABS blends from solution mixing towards acetone and toluene were enhanced but those towards water were diminished, relative to that of pure PPy/A5. However, the sensitivity towards acetic acid was not significantly different from that of pure PPy/A5.

The selectivity improvement had been extended focusing on the solution mixing of PPy/A and PMMA. PPy/A with D/M ratio of 1/12 was blended with PMMA by means of solution mixing, with various weight ratios of PMMA. Compared with pure PPy/A, the selectivity ratio of acetone/acetic acid response of PPy/A/PMMA blend with a PMMA/PPy weight ratio of 3.0 was ca. 3.8 times higher. The film was found to be insensitive to moisture unless the relative humidity was lower than 20 %RH in which the selectivity ratio was enhanced. The time required to reach the equilibrium signal at relative humidity of 20 – 30 %RH was 6 – 15 min; it became as high as 20 – 26 min at 50 – 70 %RH.

The surface compositions of non-aging PPy/A were investigated by XPS. Employing liquid nitrogen cooling of the sample holder, the spectra in the regions of C 1s, O 1s, N 1s, and S 2p were found to be reproducible with a gradual change in S 2p spectrum when the accumulated X-ray exposure time was less than 1050 min. Beyond this accumulated X-ray exposure time, dramatic changes were observed in all spectral regions suggesting the deprotonation of the polaron by the dopant and the desulfonation of the protonated dopant. This degradation became more severe when the liquid nitrogen cooling system of the spectrometer was not used. The results indicate that the degradation was mainly induced by heat from the X-ray beam.

บทคัดย่อ

ลดาวัลย์ เรืองช่วย วรรณทอง : การพัฒนาเครื่องตรวจวัดไอระเหยของสารเคมีไวไฟจากพอลิไพร์โรล (Development of Polypyrrole-Based Sensors for Vapors of Flammable Chemicals) อ. ที่ปรึกษา : รศ. ดร. อนุวัฒน์ ศิริวัฒน์ และ ศ. ดร. โจฮานเนส ชววงค์ 222 หน้า ISBN 974-17-1368-1

พอลิไพร์โรล ได้ถูกสังเคราะห์ด้วยวิธีทางเคมีและโคปในขั้นตอนเดียวกัน ด้วยตัวโคป 7 ชนิด ในอัตราส่วนโดยโมล ของตัวโคปต่อไพร์โรล เท่ากัน คือ 1/12 หน้าที่หลักของตัวโคป คือช่วยให้ประจุบวกที่ในโตรเจนเสถียร นอกจากนี้ ยังพบว่า ตัวโคปยังมีผลต่อคุณสมบัติทางกายภาพ ทางเคมี และทางไฟฟ้า ของพอลิไพร์โรล ตามที่ได้วิเคราะห์ด้วยเครื่องมือหลายชนิดเช่น เครื่องเอ็กซ์เรย์โฟโตอิเล็กตรอนสเปกโตรมิเตอร์ และเครื่องวัดค่าการนำไฟฟ้าจำเพาะแบบสี่ขั้วซึ่งสร้างขึ้นเองในห้องปฏิบัติการ พอลิไพร์โรลที่โคปด้วยอัลฟา-แนฟทาลีน ซัลโฟเนต และเบต้า-แนฟทาลีน ซัลโฟเนต มีคุณสมบัติทางกายภาพ การละลาย ความเสถียรต่อความร้อน ค่าการนำไฟฟ้าจำเพาะ และความเสถียรของค่าการนำไฟฟ้าที่ดี จากการสังเคราะห์พอลิไพร์โรลที่โคปด้วยอัลฟา-แนฟทาลีน ซัลโฟเนต ในอัตราส่วนโดยโมลของตัวโคปต่อไพร์โรลต่าง ๆ พบว่า อัตราส่วนโดยโมลของตัวโคปต่อไพร์โรล ที่ให้ค่าการนำไฟฟ้าจำเพาะ และความเสถียรของค่าการนำไฟฟ้าสูง ได้แก่ 1/12

เมื่อให้พอลิไพร์โรลอยู่ในบรรยากาศของไอระเหยของอะซิโตนในโตรเจนที่ความเข้มข้นร้อยละ 16.7 โดยปริมาตร พบว่า ค่าการนำไฟฟ้าจำเพาะลดลง การเปลี่ยนแปลงดังกล่าวขึ้นกับชนิดของตัวโคป อย่างเห็นได้ชัด ค่าการนำไฟฟ้าจำเพาะที่ลดลง ขึ้นกับ ระดับการโคป (N^+/N) และค่าการนำไฟฟ้าจำเพาะเริ่มต้น ตามความสัมพันธ์แบบเอกซ์โปเนนเชียล และขึ้นกับ สัดส่วนของไบโพลารอน และ ความเป็นระเบียบของโมเลกุล ตามความสัมพันธ์แบบเชิงเส้น และแปรผกผันกับ สัดส่วนของส่วนบกพร่อง $=N^-$ พอลิไพร์โรลที่โคปด้วยอัลฟา-แนฟทาลีน ซัลโฟเนต แสดงค่าการนำไฟฟ้าจำเพาะลดลงถึง 0.4 ซีเมนส์ต่อเซนติเมตร จากศึกษาปฏิกิริยาระหว่างพอลิไพร์โรล และอะซิโตน ด้วยเครื่องมือหลายชนิด เช่นเครื่องอิเล็กตรอนไมโครสโคปแบบสูญญากาศต่ำ พบว่า พันธะไฮโดรเจน การบวมตัว และการสูญเสียความเป็นระเบียบระดับ โมเลกุล เป็นสาเหตุของการลดลงของค่าการนำไฟฟ้าจำเพาะของพอลิไพร์โรลภายใต้บรรยากาศของอะซิโตน

เพื่อที่จะปรับปรุงความจำเพาะของพอลิไพร์โรลที่มีต่ออะซิโตน และโทลูอีน ซึ่งเป็นสารไวไฟในน้ำยาเคลือบเงา ให้มากกว่ากรดอะซิติก ซึ่งเป็นส่วนผสมในน้ำยาเคลือบเงาเช่นกัน แต่ไม่ไวไฟมาก และน้ำ ซึ่งมีอยู่ทั่วไปในบรรยากาศ ได้ศึกษาพอลิไพร์โรลที่โคปด้วย อัลฟา-แนฟทาลีน ซัลโฟเนต ที่อัตราส่วน 1/5 โดยผสมกับพอลิเมอร์ที่ไม่นำไฟฟ้า อันได้แก่ PEO PMMA HDPE PS

และ ABS ด้วยวิธีการผสม 3 แบบ คือ แบบแห้ง แบบสารละลาย และ แบบเคลือบ เมื่อให้ของเหลวของน้ำ อะซิโตน กรดอะซิติก หรือโทลูอิน สัมผัสกับตัวอย่าง ผลปรากฏว่า ของผสมระหว่างพอลิไพโรล กับ PMMA PS หรือ ABS จากการผสมแบบสารละลาย มีสภาพไวต่อ อะซิโตน และโทลูอิน มากขึ้น และมีสภาพไวต่อน้ำลดลง เมื่อเทียบกับพอลิไพโรล อย่างไรก็ตาม สภาพไวต่อกรดอะซิติก ยังคงไม่แตกต่างไปจากพอลิไพโรล

เพื่อการปรับปรุงความจำเพาะของพอลิไพโรลให้ดียิ่งขึ้น ได้ศึกษาโดยมุ่งไปที่การผสมแบบสารละลายระหว่าง พอลิไพโรลที่โคปด้วยอัลฟา-แนฟทาลีน ซัลโฟเนต ที่อัตราส่วน 1/12 กับ PMMA โดยปรับเปลี่ยนสัดส่วนโดยน้ำหนักของ PMMA พบว่า เมื่อสัดส่วนโดยน้ำหนักของ PMMA ต่อพอลิไพโรลเป็น 3.0 ค่าสัดส่วนสภาพไวที่มีต่ออะซิโตน ต่อกดอะซิติก สูงกว่าพอลิไพโรลที่ไม่ได้ผสม 3.8 เท่า ฟิล์มดังกล่าวไม่ไวต่อความชื้นสัมพัทธ์ในอากาศ เว้นแต่เมื่อความชื้นสัมพัทธ์ในบรรยากาศต่ำกว่า ร้อยละ 20 ค่าสัดส่วนสภาพไวนี้ จะเพิ่มขึ้น เวลาที่ใช้เพื่อให้ได้สัญญาณคงที่ เมื่อความความชื้นสัมพัทธ์อยู่ระหว่าง ร้อยละ 20 ถึง 30 เป็น 6 ถึง 15 นาที เวลาดังกล่าวจะนานถึง 20 ถึง 26 นาทีเมื่อความชื้นสัมพัทธ์เป็น ร้อยละ 50 ถึง 70

จากการศึกษาองค์ประกอบที่พื้นผิวของพอลิไพโรลที่โคปด้วยอัลฟา-แนฟทาลีน ซัลโฟเนต ที่อัตราส่วน 1/12 และมีคุณสมบัติที่ไม่เปลี่ยนแปลงตามเวลา ด้วยเครื่องเอ็กซ์เรย์โฟโตอิเล็กตรอนสเปกโตรมิเตอร์ โดยมีระบบหล่อเย็นด้วยไนโตรเจนเหลว พบว่า สเปกตรัมในช่วงของ C1s O1s N1s และ S2p สามารถทำซ้ำได้ โดยที่ spectra ของ S 2p มีการเปลี่ยนแปลงเล็กน้อย เมื่อเวลาสะสมของการฉายรังสีเอ็กซ์น้อยกว่า 1050 นาที หลังจากเวลานี้ ได้พบการเปลี่ยนแปลงอย่างเห็นได้ชัดในทุกช่วงของสเปกตรัม ผลเหล่านี้ ซึ่งให้เห็นถึงการสูญเสียโปรตอนทีโพลารอน โดยตัวโคป และการสูญเสียซัลเฟอร์ของตัวโคปที่ดึงโปรตอนมาจากโพลารอน กระบวนการสลายตัวนี้จะเกิดเร็วขึ้น และรุนแรงขึ้น เมื่อไม่ใช้ระบบหล่อเย็นด้วยไนโตรเจนเหลว ซึ่งชี้ให้เห็นว่า การสลายตัวนี้เกิดขึ้นจากความร้อนจากลำแสงของรังสีเอ็กซ์เป็นหลัก

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LIST OF ABBREVIATIONS

ABS	Poly(acrylonitrile-co-butadiene-co-styrene)
APS	Ammonium persulfate
APS/M	Oxidant (ammonium persulfate) to pyrrole monomer molar ratio
BE	Binding energy
D/M	Dopant to pyrrole monomer molar ratio
Deg.	Degree
EA	Elemental analyzer
EDS/SEM	Scanning electron microscope in the energy dispersive mode
EV	Electron volt
FT-IR	Fourier transform infrared spectrometer
FWHM	Full width at half-maximum
HDPE	High density polyethylene
K	Correction factor
MSB	Magnetic susceptibility balance
PEO	Poly(ethylene oxide)
PMA	Poly(methacrylic acid)
PMMA	Poly(methylmethacrylate)
PPy	Polypyrrole
PPy/A	Polypyrrole doped with α -naphthalene sulfonate
PPy/A5	PPy/A with D/M ratio of 1/5
PPy/AB	Polypyrrole doped with p-aminobenzoate
PPy/B	Polypyrrole doped with β -naphthalene sulfonate
PPy/C	Polypyrrole doped with camphor sulfonate
PPy/D	Polypyrrole doped with dodecylbenzene sulfonate
PPy/De	Dedoped polypyrrole
PPy/E	Polypyrrole doped with ethane sulfonate
PPy/P	Polypyrrole doped with perchlorate
PPy/U	Undoped polypyrrole

PPy/ α -NS ⁻	Polypyrrole doped with α -naphthalene sulfonate
PPy/ β -NS ⁻	Polypyrrole doped with β -naphthalene sulfonate
PS	Polystyrene
RH	Relative humidity
SD	Standard deviation
SEM	Scanning electron microscope
TGA	Thermogravimetric analyzer
UV-Vis	Ultraviolet-visible spectrometer
XPS	X-ray photoelectron spectrometer
XRD	X-ray diffractometer

LIST OF SYMBOLS

σ	Specific conductivity (S/cm)
ρ	Specific resistivity (Ω cm)
$\chi_{\text{corr},M}$	Corrected molar magnetic susceptibility (cgs mole^{-1})
λ	Wavelength (nm)
θ	Contact angle (degree)