

**ENHANCEMENT OF ANHYDROUS PROTON CONDUCTIVE
SULFONATED POLY (ETHER ETHER KETONE) (SPEEK) BASED ON
IMIDAZOLE MOLECULAR MOBILITY AND SPEEK THERMOCHROMIC
PHENOMENON**

Chatchai Jarumaneroj

A Dissertation Submitted in Partial Fulfilment of the Requirements
For the Degree of Doctor of Philosophy
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
and Case Western Reserve University

2014

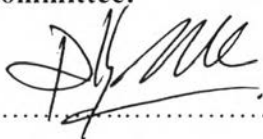
Thesis Title: Enhancement of Anhydrous Proton Conductive Sulfonated Poly (Ether Ether Ketone) (SPEEK) Membrane Based on Imidazole Molecular Mobility and SPEEK Thermochromic Phenomenon
By: Chatchai Jarumaneeroj
Program: Polymer Science
Thesis Advisor: Prof. Suwabun Chirachanchai

Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.



..... College Dean
(Asst. Prof. Pomthong Malakul)

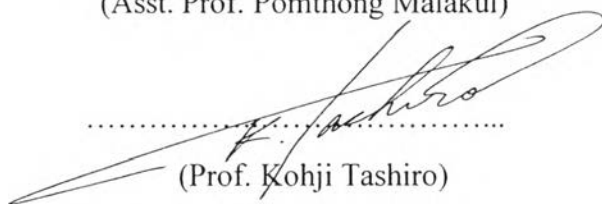
Thesis Committee:



.....
(Asst. Prof. Pomthong Malakul)



.....
(Prof. Suwabun Chirachanchai)



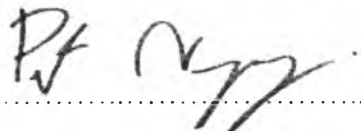
.....
(Prof. Kohji Tashiro)



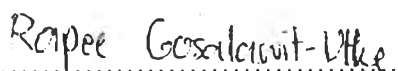
.....
(Assoc. Prof. Hathaikarn Manuspiya)



.....
(Asst. Prof. Thanyalak Chaisuwan)



.....
(Asst. Prof. Piyarat Nimmanpipuk)



.....
(Asst. Prof. Rapee Gosalawit-Utke)

ABSTRACT

5182004063: Polymer Science Program

Chatchai Jarumaneeroj: Enhancement of Anhydrous Proton
Conductive Sulfonated Poly (Ether Ether Ketone) (SPEEK)
Membrane Based on Imidazole Molecular Mobility and SPEEK
Thermochromic Phenomenon.

Thesis Advisor: Prof. Suwabun Chirachanchai, 131 pages.

Keywords: Proton conductivity / Hydrogen bond network / Polymer electrolyte
membrane / Packing structure / Proton transfer / Molecular mobility/
Imidazole / Thermochromic property

The present work focuses on a systematic study of imidazole derivatives by varying the methylene units in urocanic acid system from mono to heptyl groups as an efficiency proton transfer channel. Methylene units introducing in urocanic acid system can provide various kinds of packing structures, and the chain mobility with developed melting temperature lower than 100 °C. With this thermal property, alkyl urocanates can form in molten state which are highly molecular mobility under high temperature. Proton conductivity of pure compounds exhibits the significant increase closed to melting temperature as high as 10^{-4} S cm⁻¹ which performs as good proton conductive species. Sulfonated poly(ether ether ketone), SPEEK, blended with alkyl urocanates are prepared as model membranes. Proton conductivity of blended membranes performs synchronized effect between water and imidazole molecules as high as 10^{-4} S cm⁻¹ under high temperature compared to neat SPEEK membrane (10^{-7} S cm⁻¹). It is worth noticing that SPEEK can perform another phenomenon as an reversible thermochromic property. This phenomenon can occur by shifting interaction of hydrogen bond network to π - π stacking of polymer backbone under high temperature. Based on structure of heterocycles, a balance of hydrogen bond network and molecular mobility provide enhancement of proton conductivity and induction of π - π stacking in SPEEK polymer at high temperature generates reversible thermochromic property through sulfonic acid groups and aromatic rings.

บทคัดย่อ

ฉัตรชัย จารุมณีโรจน์: การพัฒนาพอลิเมอร์เหนียวนำโปรตอน sulfonated poly (ether ether ketone) (SPEEK) แบบไม่ใช้น้ำโดยอาศัยการเคลื่อนไหวยของโมเลกุลอิมิดาโซล และปรากฏการณ์ตอบสนองการเปลี่ยนสีเมื่อถูกความร้อน (Enhancement of Anhydrous Proton Conductive Sulfonated Poly (Ether Ether Ketone) (SPEEK) Membrane Based on Imidazole Molecular Mobility and SPEEK Thermochromic Phenomenon) อ. ที่ปรึกษา: ศาสตราจารย์ ดร. สุวบุญ จิรชาณชัย, 131 หน้า

งานวิจัยนี้มุ่งเน้นการศึกษาโมเลกุลอิมิดาโซลที่เป็นระบบ โดยการเพิ่มหมู่เมทิลีนลงบนกรดยูโรคานิก ตั้งแต่หนึ่งหมู่ถึงเจ็ดหมู่ เพื่อใช้เป็นช่องทางในการถ่ายโอนโปรตอนที่มีประสิทธิภาพ หมู่เมทิลีนที่เติมแต่งลงบนกรดยูโรคานิกสามารถปรับแต่งการจัดเรียงตัวของโมเลกุลที่หลากหลาย และการเคลื่อนไหวยของโมเลกุล พร้อมทั้งลดอุณหภูมิการหลอมเหลวให้ต่ำกว่า 100 องศาเซลเซียส ด้วยลักษณะการหลอมเหลวแบบนี้ อนุพันธ์ของอัลคิลยูโรคานเทสามารถแสดงการเคลื่อนไหวยของโมเลกุลที่ดีที่อุณหภูมิสูงได้ โดยค่าการนำโปรตอนของสารอนุพันธ์เพิ่มขึ้นอย่างเด่นชัดเมื่อเข้าใกล้จุดหลอมเหลวของสารอนุพันธ์อยู่ที่ประมาณ $10^{-4} \text{ S cm}^{-1}$ ซึ่งแสดงให้เห็นว่าสารอนุพันธ์สามารถเป็นช่องทางถ่ายโอนโปรตอนที่มีประสิทธิภาพได้ ซัลโฟเนต-พอลิ อีเทอร์ อีเทอร์ คีโตน (SPEEK) ผสมกับอนุพันธ์ของแอลคิลยูโรคานเทถูกเตรียมขึ้นเพื่อใช้เป็นพอลิเมอร์คั่นแบบ ค่าการนำโปรตอนของพอลิเมอร์ผสม แสดงให้เห็นถึงปัจจัยส่งเสริมร่วมกันระหว่างโมเลกุลน้ำ และอิมิดาโซล ที่มีค่าการนำโปรตอนสูงถึง $10^{-4} \text{ S cm}^{-1}$ ที่อุณหภูมิสูง เมื่อเปรียบเทียบกับ SPEEK ที่ไม่ได้ผสมสารอนุพันธ์ ($10^{-7} \text{ S cm}^{-1}$) เป็นที่น่าสังเกตว่า SPEEK สามารถแสดงอีกคุณสมบัติหนึ่งได้ คือ การเปลี่ยนสีเมื่อถูกความร้อน (Thermochromic property) ปรากฏการณ์นี้สามารถเกิดขึ้นได้จากการควบคุมการเปลี่ยนอันตรกิริยาระหว่างโครงสร้างร่างแหไฮโดรเจนบอนด์ไปสู่อันตรกิริยาชนิด π อิเล็กตรอนของหมู่กรดซัลโฟนิค และวงแอมดิคบนสายโซ่หลักของพอลิเมอร์ที่อุณหภูมิสูง ดังนั้น ด้วยการศึกษาในระดับโครงสร้าง ความสมดุลระหว่างพันธะไฮโดรเจน การเคลื่อนไหวยของโมเลกุล และอันตรกิริยาชนิด π อิเล็กตรอน นำไปสู่การพัฒนาของค่าการนำโปรตอน และการเกิดปรากฏการณ์ตอบสนองการเปลี่ยนสีเมื่อถูกความร้อนได้

ACKNOWLEDGEMENTS

The author would like to sincerely thank his advisor, Professor Suwabun Chirachanchai, for giving him continuous support, guidance, patience, inspiration and encouragement especially for providing him with an excellent research atmosphere. Thanks for being his role model.

He would like to extend his thanks to Professor Kohji Tashiro (Department of Future Industry-oriented Basic Science and Materials, Toyota Technological Institute, Japan) not only for giving him the chance to experience doing the research in his laboratory but also for giving him strong support, worth advices, and concerns during his stays in Japan. He also wishes to thank to all Tashiro laboratory's members for their many helps and good taking care during his stay in Japan.

He wishes to thank his thesis committee, Asst. Prof. Pomthong Malakul, Asst. Prof. Hathaikarn Manuspiya, Asst. Prof. Thanyalak Chaisuwan, Asst. Prof. Piyarat Nimmanpipug, and Asst. Prof. Rapee Gosalawit-Utke for their suggestions and great guidance. A deep gratitude is expressed to all professors at PPC who have given her valuable knowledge.

He would like to acknowledge the scholarships from The Thailand Research Fund, Royal Golden Jubilee (Grant no. PHD/006/2551) for the Ph. D. program and the short-term research in Japan.

He acknowledges the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission (EN276B) and The Ratchadaphiseksomphot Endowment Fund of Chulalongkorn University (RES560530272-EN) for research fund.

This thesis work is funded by The Petroleum and Petrochemical College, and The Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand.

His thanks are also to all Suwabun's group members for their helps, good suggestions, encouragement, friendship and all the good memories.

Last, but not least, he thanks his family for giving his life, encouragement, and unconditional support to pursue his interests and especially for their love and understanding.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Table	x
List of Figures	xi
List of Schemes	xv
 CHAPTER	
I INTRODUCTION	1
II LITERATURE REVIEW	3
2.1 Fuel Cell	3
2.2 Polymer Electrolyte Membrane Fuel Cell (PEMFC)	5
2.2.1 Hydrous-based Membrane System	6
2.2.2 Anhydrous-based Membrane System	10
2.3 Fundamental Study of Model Compounds Based on Heterocycles Related to Proton Conductivity	18
2.4 Thermochromic Polymer	19
2.5 Points of Study	23
III MOLECULAR MOBILITY OF IMIDAZOLE IN MOLTEN STATE AS A KEY FACTOR TO ENHANCE PROTON CONDUCTIVITY	24
3.1 Abstract	24
3.2 Introduction	25

CHAPTER	PAGE
3.3 Experimental	29
3.4 Results and Discussion	31
3.5 Conclusions	45
3.6 Acknowledgements	46
3.7 References	46
IV ALKYL UROCANATES AS PROTON TRANSFER SPECIES IN MOLTEN STATE: AN ACCESS TO PROTON CONDUCTIVITY IN THE LONG RANGE OF OPERATING TEMPERATURE	48
4.1 Abstract	48
4.2 Introduction	49
4.3 Experimental	52
4.4 Results and Discussion	54
4.5 Conclusions	65
4.6 Acknowledgements	66
4.7 References	66
V SHIFTING FROM HYDROGEN BOND NETWORK TO π-π STACKING: A KEY MECHANISM FOR REVERSIBLE THERMOCHROMIC SULFONATED POLY (ETHER ETHER KETONE)	70
5.1 Abstract	70
5.2 Introduction	71
5.3 Experimental	72
5.4 Results and Discussion	73
5.5 Conclusions	78
5.6 Acknowledgements	79
5.7 References	79

CHAPTER	PAGE
VI CONCLUSIONS	81
REFERENCES	82
APPENDICES	91
Appendix A Structural Characterization of Alkyl Urocanates	91
Appendix B Proton Conductivity of C1U, C2U, C3U, C5U, and C7U by VTF Equation	94
Appendix C Glass Transition Temperature of Alkyl urocanates	97
Appendix D Determination of Ion Exchange Capacity (IEC) and Degree of Sulfonation (DS)	98
Appendix E Characterization of SPEEK-CxU by FTIR	100
Appendix F Degradation Temperatures of SPEEK-CxU	106
Appendix G Proton Conductivity of SPEEK-CxU by VTF Equation	110
Appendix H Isosbestic Point of SPEEK-CxU	112
Appendix I Full Width Haft Maximum of Symmetric Sulfonic Acid Peak of SPEEK-CxU as a Function of Temperatures	115
Appendix J Temperature Dependence FTIR of Inter- and Intra- Hydrogen Bond Networks	117
Appendix K Comparison of Proton Conductivity between SPEEK-C4U and SPEEK-C6U	121
Appendix L Solubility of SPEEK	122
Appendix M Calculation of Energy Band Gap (E_g) and Aromatic Carbon in Cluster (N)	123
Appendix N Thermochromic Property of PEEK Thin Film	126
Appendix O Temperature Dependence FTIR of PEEK Thin Film	127
Appendix P SPEEK Thin Film in Dry System	128

CHAPTER

PAGE

CURRICULUM VITAE

130

LIST OF TABLES

TABLE		PAGE
	CHAPTER II	
2.1	Characteristics of different types of fuel cell	4
	CHAPTER III	
3.1	Single crystal parameter of C0-C7	37

LIST OF FIGURES

Figure	PAGE
CHAPTER II	
2.1 Schematic draw of a single fuel cell components and operations based on hydrogen/oxygen fuel cell	1
2.2 Structure of commercial PFSA polymers, Nafion [®] : m=1; n=2; x=5–13.5; y=1, Flemion [®] : m=0,1; n=1–5; x=5–13.5; y=1, Aciplex [®] : m=0; n=2–5; x=1.5–14; y=1, Dow [®] : m=0; n=2; x=3.6–10, y=1	6
2.3 Aromatic polymer	9
2.4 Imidazole-based compounds for PEMFC: type I-mixing imidazole derivatives with other species	11
2.5 Imidazole-based compounds for PEMFC: type II-incorporating into polymer matrices	13
2.6 Imidazole-based compounds for PEMFC: type III-ionic liquids	14
2.7 Imidazole-based compounds for PEMFC: type III-side chain structures	16
2.8 Imidazole-based compounds for PEMFC: type IV-main chain structures	17
2.9 Series of benzimidazole model compounds with varied numbers of benzimidazole units	18
2.10 Structure of multi-benzimidazole functionalized branched polyethyleneimine (MPEI)	19
2.11 Ligand exchange thermochromic system mechanism	20
2.12 Leuco dye compounds	20
2.13 Thermochromic responsive polymer based on aromatic and conjugated polymer	21

Figure	PAGE
CHAPTER III	
3.1 T_m (●), and T_d (○) of alkyl urocanates	32
3.2 Unit cells and packing structure of C0-C7 including possible hydrogen bond network	33
3.3 Hydrogen bond distances of imidazole ring (○: NH--O bond distance, ●: NH--N bond distance) interpreted from single crystal analyses	35
3.4 T_1 -relaxation time belonging to the methylene protons (-O-CH ₂ -) of the alkyl chain.	36
3.5 Proton conductivity of C1U (-●-), C2U (-○-), C3U (-▼-), C4U (-Δ-), C5U (-□-), C6U (-■-), and C7U (-◆-) as a function of temperature	38
3.6 Plausible proton transfer mechanism (a) Grotthuss mechanism ($<T_m$) and (b) vehicle mechanism ($>T_m$)	40
3.7 Proton conductivity of C4U (a) evaluated by Arrhenius equation and (b) evaluated by VTF equation, and C6U (c) evaluated by Arrhenius equation and (d) evaluated by VTF equation with a dot line referring to T_m	41
3.8 E_a of C1U – C7U for (a) solid form, and (b) molten form	42
3.9 Plots of (a) proton conductivity at 130 °C, (b) $1/E_a$ (melt), and (c) $1/T_m$.	43
3.10 Proton conductivity of neat SPEEK (●) and SPEEK containing C4U (2 % (wt/v)) (○) under variation of temperatures	45
CHAPTER IV	
4.1 Degradation temperatures of (a) SPEEK, (b) SPEEK-C4U and (c) SPEEK-C6U	56

Figure	PAGE
4.2 Proton conductivity of SPEEK blended with C1U (-●-), C2U (-○-), C3U (-▼-), C4U (-△-), C5U (-□-), C6U (-■-), and C7U (-◆-)	57
4.3 Proton conductivity of (a) SPEEK, (b) SPEEK-C4U , and (c) SPEEK-C6U by VTF equation	58
4.4 Activation energy of SPEEK-CxU	60
4.5 Temperature dependence FTIR spectra of SPEEK-C4U ; (a) in range of wavenumber 1000 cm ⁻¹ – 1400 cm ⁻¹ , and (b) in range of wavenumber 1200 cm ⁻¹ .– 1240 cm ⁻¹	61
4.6 FWHM of sulfonic acid group as a function of temperatures of (a) SPEEK-C4U , and (b) SPEEK-C6U	62
4.7 Proton conductivity of (a) SPEEK, (b) SPEEK-C4U as a function of temperatures based on VTF equation, and schematic proton transfer mechanism of (c) SPEEK, and (d) SPEEK-CxU with synchronized effect of water and imidazole molecules related to different temperatures	64
4.8 Schematic of SPEEK-CxU at different operating temperatures	66

CHAPTER V

5.1 Chemical structure of (a) SPEEK, and (b) PEEK, (c) SPEEK thin film at room temperature, (d) at high temperature (above 190°C), (e) after leaving at room temperature, and (f) after putting into water or hot water (80 °C)	72
5.2 (a) Temperature dependence UV-Vis spectra of SPEEK thin film at various temperatures, (b) optical energy band gap, and (c) number of aromatic carbon in cluster as a function of temperatures	75

Figure**PAGE**

- 5.3 (a) Temperature dependence FTIR spectra of SPEEK thin film, (b) symmetric peak position of O=S=O, and (c) FWHM of O=S=O as a function of temperatures, and (d) thermochromic recovery time under variation of humidity

77

LIST OF SCHEMES

SCHEME	PAGE
CHAPTER III	
3.1 Alkyl urocanates	30
CHAPTER IV	
4.1 Sulfonated poly (ether ether ketone), SPEEK, - and alkyl urocanates, CxU	51
4.2 Preparation of SPEEK	53
CHAPTER V	
5.1 Possible reversible thermochromic SPEEK thin film at molecular level	78