

**A SYSTEMATIC STUDY ON BENZIMIDAZOLE DERIVATIVES:
INVESTIGATION OF HYDROGEN BOND, PACKING STRUCTURE, AND
MOLECULAR MOBILITY RELATED TO PROTON TRANSFER IN
ANHYDROUS SYSTEM OF POLYMER ELECTROLYTE MEMBRANE
FUEL CELL**

Autchara Pangon

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

2011

Thesis Title: A Systematic Study on Benzimidazole Derivatives: Investigation of Hydrogen Bond, Packing Structure, and Molecular Mobility Related to Proton Transfer in Anhydrous System of Polymer Electrolyte Membrane Fuel Cell

By: Autchara Pangon

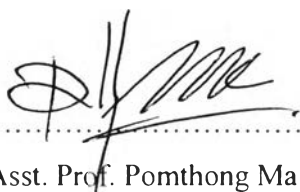
Program: Polymer Science

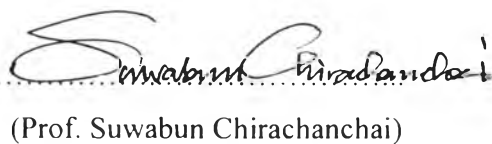
Thesis Advisors: Prof. Suwabun Chirachanchai
Prof. Kohji Tashiro

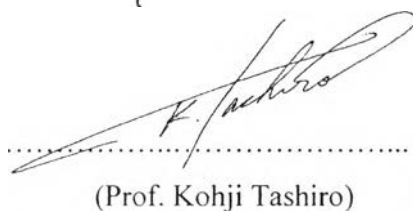
Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

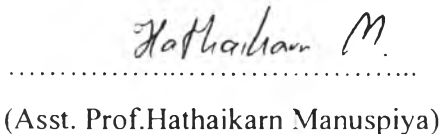

..... Dean
(Asst. Prof. Pomthong Malakul)

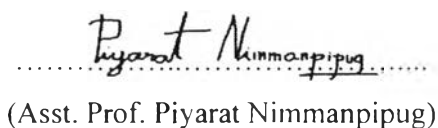
Thesis Committee:


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


.....
(Prof. Suwabun Chirachanchai)


.....
(Prof. Kohji Tashiro)


.....
(Asst. Prof. Hathaikarn Manuspiya)


.....
(Asst. Prof. Piyarat Nimmanpipug)

ABSTRACT

5192003063: Polymer Science Program
Autchara Pangon: A Systematic Study on Benzimidazole
Derivatives: Investigation of Hydrogen Bond, Packing Structure,
and Molecular Mobility Related to Proton Transfer in Anhydrous
System of Polymer Electrolyte Membrane Fuel Cell
Thesis Advisors: Prof. Suwabun Chirachanchai and Prof. Kohji
Tashiro. 91 pp.

Keywords: Proton conductivity / Hydrogen bond network / Polymer electrolyte
membrane / Packing structure / Proton transfer / Molecular mobility
Benzimidazole / Branching polyethylenimine

The present work aims to clarify how proton can be transferred in heterocycle molecules under anhydrous system based on benzimidazole model compounds and model polymer via a simple molecular design and synthesis approach. In the case of benzimidazole model compounds, the number of benzimidazole groups under monofunctional, difunctional, and trifunctional leads us to an understanding that the hydrogen bond network among benzimidazole as well as the packing structure is the key factor for enhancing proton transfer efficiency. The most favorable structure is trifunctional benzimidazoles which gives a helical hydrogen bond network under columnar packing structure of which the conductivity is as high as 10^{-2} S/cm² at 170 °C. In the case of model polymer containing multifunctional benzimidazole, a branching benzimidazole polymer can be easily obtained by simply conjugating benzimidazoles onto branching polyethylenimine. This model polymer suggests that although benzimidazoles form the hydrogen bond network, the tight and strong network obstructs the chain mobility. The favorable condition for polymer containing benzimidazoles is the one with only a few percent of benzimidazole group (~20%) and at that time the conductivity is 10^{-4} S/cm² at 190 °C. The work also extends to show an approach to obtain branching benzimidazole pendant group which will be useful for the conjugation onto polymer backbone in the

next step. The pendant group of aminotris[2-(benzimidazol-2-yl)ethyl]methane is successfully prepared by the reaction between triacid chloride of nitromethanetripropionic acid chloride and diamine of phenylenediamine followed by the reduction of nitro group via Pd/C catalyst.

บทคัดย่อ

อัจฉรา แป้งอ่อน : การพิสูจน์ทราบของพันธะไฮโดรเจน โครงสร้างการจัดเรียงตัว และการเคลื่อนที่เชิงโมเลกุล ที่เกี่ยวกับการส่งผ่านโปรตอนในระบบที่ไม่ใช้น้ำของเซลล์เชื้อเพลิงแบบพอลิเมอร์อิเล็กโตรไลต์เมมเบรน (Investigation of Hydrogen Bond, Packing Structure, and Molecular Mobility related to Proton Transfer in Anhydrous System of Polymer Electrolyte Membrane Fuel Cell) อ. ที่ปรึกษา : ศาสตราจารย์ ดร. สุวบุญ จิราญชัย และ ศาสตราจารย์ ดร. โคจิ ทาชิโระ, 91 หน้า

งานวิจัยนี้มุ่งเน้นให้เห็นชัดเจนถึงการส่งผ่านโปรตอนใน โมเลกุลเฮเทอโรไซเคิลภายใต้ระบบที่ไม่ใช้น้ำของสารต้นแบบและพอลิเมอร์ต้นแบบของเบนซิมิดาโซล โดยวิธีออกแบบและสังเคราะห์โมเลกุลอย่างง่าย จำนวนหมู่เบนซิมิดาโซลภายใต้ หมู่ฟังก์ชันเดี่ยว หมู่ฟังก์ชันคู่ และหมู่ฟังก์ชันสาม นำมาสู่ความเข้าใจที่ว่า ร่างแหของพันธะไฮโดรเจนในหมู่เบนซิมิดาโซลรวมถึงโครงสร้างการจัดเรียงตัวเป็นปัจจัยสำคัญในการเพิ่มประสิทธิภาพการส่งผ่านโปรตอน โครงสร้างที่เอื้อต่อการส่งผ่านโปรตอนมากที่สุดคือ เบนซิมิดาโซลหมู่ฟังก์ชันสาม ซึ่งให้ร่างแหของพันธะไฮโดรเจนแบบเกลียวภายใต้โครงสร้างการจัดเรียงตัวแบบแนวตรง ที่ซึ่งค่าการนำโปรตอนเท่ากับ 10^2 S/cm ที่อุณหภูมิ 170 องศาเซลเซียส ในกรณีของพอลิเมอร์ต้นแบบที่ประกอบด้วยเบนซิมิดาโซลจำนวนมาก นั่นคือเบนซิมิดาโซลที่มีลักษณะเป็นกึ่ง สามารถเตรียมได้อย่างง่ายโดยการติดเบนซิมิดาโซลบนพอลิเอททิลีนอิมินที่เป็นกึ่ง พอลิเมอร์ต้นแบบนี้ชี้ให้เห็นว่า แม้ว่าเบนซิมิดาโซลจะทำให้เกิดร่างแหของพันธะไฮโดรเจน ร่างแหที่แข็งแรงและอยู่กันอย่างแน่นจะขัดขวางการเคลื่อนที่ของสายโซ่ เงื่อนไขที่เหมาะสมสำหรับพอลิเมอร์ที่ประกอบด้วยเบนซิมิดาโซลคือพอลิเมอร์ที่มีเบนซิมิดาโซลจำนวนหนึ่ง (~20%) และในขณะนั้นให้ค่าการนำโปรตอนเท่ากับ 10^4 S/cm ที่อุณหภูมิ 190 องศาเซลเซียส งานนี้ขยายไปสู่การแสดงวิธีได้มาซึ่งหมู่แวนเบนซิมิดาโซลที่มีลักษณะเป็นกึ่ง ซึ่งจะมีประโยชน์สำหรับการเชื่อมติดบนสายโซ่หลักของพอลิเมอร์ในขั้นตอนต่อไป หมู่แวนของ ทริส[2-(เบนซิมิดาโซล-2-อิว)เอทิล]ไนโตรมีเทน ถูกเตรียมได้สำเร็จจากปฏิกิริยาระหว่าง ไตรแอซิดคลอไรด์ของไนโตรมีเทน ไตรโพรไพโอนิก แอซิด คลอไรด์ และไดเอมีนของฟีนิลลีนไดเอมีน ตามด้วยการรีดักชันของหมู่ไนโตรด้วยตัวเร่งปฏิกิริยา แพดลาเดียม/คาร์บอน

ACKNOWLEDGEMENTS

The author would like to express her sincere thanks to her advisor, Professor Suwabun chirachanchai, for giving her knowledge, continuous support, guidance, patience, inspiration, encouragement and for providing her with an excellent research atmosphere. Especially thanks for being her role model.

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

She would also like to express her appreciation to Prof. Ono Masatomi (Toyota Technological Institute, Japan) for his valuable suggestion about the synthesis method.

She wishes to thank her thesis committee, Asst. Prof. Pomthong Malakul, Asst. Prof. Hathaikarn Manuspiya, and Asst. Prof. Piyarat Nimmanpipug for their suggestions and invaluable guidance. A deep gratitude is expressed to all professors at PPC who have given her valuable knowledge.

She would like to acknowledge the scholarships from the Development and Promotion of Science and Technology Talents Project (DPST) for the Ph.D program and Japan Student Services Organization (JASSO) for the short-term research in Japan.

This thesis work is funded by the Petroleum and Petrochemical College, and the National Center of Excellence for Petroleum, Petrochemical, and Advanced Materials, Thailand. The author also acknowledges the National Research Council of Thailand and the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission (EN276B) for research financial supports.

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

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

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	v
Acknowledgements	vi
Table of Contents	viii
List of Schemes	xi
List of Figures	xii
List of Table	xvi
 CHAPTER	
I INTRODUCTION	1
II LITERATURE REVIEW	3
2.1 Fuel Cell	3
2.2 Polymer Electrolyte Membrane Fuel Cell (PEMFC)	5
2.3 High temperature PEMFC	7
2.4 Polymer Electrolyte Membrane	8
2.5 Points of Study	17
III SYSTEMATIC STUDIES ON BENZIMIDAZOLE DERIVATIVES: MOLECULAR STRUCTURS AND THEIR HYDROGEN BOND NETWORK FORMATION TOWARD PROTON TRANSFER EFFICIENCY UNDER POLYPHOSPHORIC ACID MATRICES	18
3.1 Abstract	18
3.2 Introduction	19
3.3 Experimental	20

CHAPTER	PAGE
3.4 Results and discussion	23
3.5 Conclusions	38
3.6 Acknowledgements	39
3.7 References	39
IV POLYETHYLENIMINE CONTAINING BENZIMIDAZOLE BRANCHING: A MODEL SYSTEM TO STUDY PROTON TRANSFER PERFORMANCE THROUGH A BALANCE OF HYDROGEN BOND AND CHAIN MOBILITY	42
4.1 Abstract	42
4.2 Introduction	42
4.3 Experimental	44
4.4 Results and discussion	47
4.5 Conclusions	67
4.6 Acknowledgements	68
4.7 References	69
V SYNTHESIS AND STRUCTURAL CHARACTERIZATIONS OF AMINOTRIS[2-(BENZIMIDAZOL-2-YL)ETHYL]METHANE: MULTI-BENZIMIDAZOLE MOIETY AS PROTON CONDUCTIVE SPECIES IN ANHYDROUS POLYMER ELECTROLYTE MEMBRANE	72
5.1 Abstract	72
5.2 Introduction	72
5.3 Experimental	74
5.4 Results and discussion	76
5.5 Conclusions	82
5.6 Acknowledgements	82
5.7 References	82

CHAPTER	PAGE
VI CONCLUSIONS	84
REFERENCES	86
CURRICULUM VITAE	90

LIST OF SCHEMES

SCHEME	PAGE
CHAPTER III	
3.1 Chemical structures of model compounds: benzimidazole (B-1), ethylene-1,2-di-2-benzimidazole (B-2), 1,4-bis(2-benzimidazolyl)benzene (B-3) and 1,3,5-tri(2-benzimidazolyl)benzene (B-4)	20
CHAPTER IV	
4.1 Synthesis of MPEI	45
CHAPTER V	
5.1 Synthesis of 1 , 2 and 3	75

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 (Carrette <i>et al.</i> , 2001)	3
2.2	Typical fuel cell polarization curves (voltage vs. current density) and power density curves (Haile, S.M., 2003)	6
2.3	CO coverage on a platinum surface as a function of temperature and CO concentration. H ₂ partial pressure is 0.5 bar (Yang <i>et al.</i> , 2001)	8
2.4	Chemical structure of Nafion [®] : m=1; n=2; x=5–13.5; y=1	9
2.5	Cluster-network model of Nafion [®] membranes proposed by Hsu <i>et al.</i> , (1983)	9
2.6	Proton conductivity of Nafion [®] (●), 1.5wt.%Krytox-Si-Nafion [®] (○), 2.5wt.% Krytox-Si-Nafion [®] (▼), and 5.0 wt.%Krytox-Si-Nafion [®] (▽) hybrid membranes (Gosalawit <i>et al.</i> , 2006)	10
2.7	Chemical structures of PEMs based on aliphatic hydrocarbon Polymers	11
2.8	Chemical structures of PEMs based on aromatic hydrocarbon polymers	12
2.9	Proton transfer mechanism of imidazole	13
2.10	Chemical structures of PEMs based on heterocycle main chains	14
2.11	Chemical structures of self conductive polymers based on heterocycle pendent group	15
2.12	Examples of acid-based blended membrane	16

FIGURE	PAGE
CHAPTER III	
3.1 X-ray crystal packing structure diagrams of (a) B-1 ; (b) B-2 ; and (c) B-3 with hydrogen bond interaction. The figures were built with the software Materials Studio (Accelrys, Inc.)	26
3.2 Schematic draws of hydrogen bond chains formed in lamellar structure of (a) B-1 ; (b) B-2 ; (c) B-3 and in columnar structure of (d) B-4 . Some hydrogen atoms were excluded to clarify of viewing	27
3.3 T_1 relaxation times of B-1 , B-2 , B-3 , and B-4	28
3.4 Degradation temperatures of B-1 , B-2 , B-3 and B-4 .	29
3.5 Arrhenius plot comparing the experimental data of PPA (\square); B-1 /PPA (\bullet); B-2 /PPA (\triangle); B-3 /PPA (\blacktriangle); B-4 /PPA (\circ) with the value obtained from VTF equation fitting (broken lines)	30
3.6 (a) Temperature dependence FTIR spectra of (i) B-1 ; (ii) B-2 ; (iii) B-3 ; and (iv) B-4 at room temperature (—), 60 °C (---), 100 °C (·····), 140 °C (-·-·-·) and 200 °C (-·-·-·); (b) possible hydrogen bond changing from strong H-bond to weak H-bond during heating; and (c) isobestic positions of B-1 , B-2 , B-3 and, B-4	34
3.7 WAXD patterns of (a) B-1 ; (b) B-2 ; (c) B-3 ; (d) B-4 during heating and cooling at 3 °C/min under N ₂ atmosphere	36
CHAPTER IV	
4.1 (a) ¹ H NMR and (b) ¹³ C NMR spectra of MPEI 1:0.6 (labeled numbers on MPEI structure identifying the positions of hydrogen and carbon in the NMR spectra)	49

FIGURE	PAGE
4.2 ^1H - ^{13}C DEPT-135 edited-HSQC spectrum (solid line = negative phase peak and dash line = positive phase peak)	50
4.3 Inverse gated ^{13}C NMR spectrum of <i>b</i> PEI	51
4.4 Temperature dependence FTIR spectra of MPEI 1:0.2 during (a) 1 st heating, (b) cooling, and (c) 2 nd heating	54
4.5 Temperature dependence FTIR spectra of (a) MPEI 1:0.2, (b) MPEI 1:0.4, (c) MPEI 1:0.6, (d) MPEI 1:0.8, and (e) MPEI 1:1.0 during the second heating process	55
4.6 FTIR curve fitting of MPEI 1:0.2	56
4.7 Semi-quantitative analysis of hydrogen bond network based on FTIR spectra of MPEI 1:0.2 (●), MPEI 1:0.4 (▲), MPEI 1:0.6 (□), MPEI 1:0.8 (○), and MPEI 1:1.0 (△) (Calculated from those of Figure 4.5)	57
4.8 WAXD profiles under temperature variation of (a) MPEI 1:0.2, (b) MPEI 1:0.4, (c) MPEI 1:0.6, (d) MPEI 1:0.8, and (e) MPEI 1:1.0	58
4.9 Radial distribution functions of (a) MPEI 1:0.2, (b) MPEI 1:0.4, (c) MPEI 1:0.6, (d) MPEI 1:0.8, and (e) MPEI 1:1.0 at approximate temperature 30 °C (—), 50 °C (·····), 75 °C (-----), 100 °C (- - - -), 125 °C (·-·-·-), 150 °C (- - -), 175 °C (-·-·-), and 200 °C (-·-·-)	60
4.10 Proton conductivity of Nafion [®] (◇), MPEI 1:0.2 (●), and MPEI 1:0.4 (▲) as a function of temperature	61
4.11 DSC thermograms of (a) MPEI 1:0.2/PVA, (b) MPEI 1:0.4/PVA, (c) MPEI 1:0.6/PVA, (d) MPEI 1:0.8/PVA, and (e) MPEI 1:1.0/PVA during the second heat treatment at heating rate 10 °C min ⁻¹ under N ₂ atmosphere	62

FIGURE	PAGE
4.12 FTIR spectra of (a) PVA, (b) MPEI 1:0.2/PVA, (c) MPEI 1:0.4/PVA, (d) MPEI 1:0.6/PVA, (e) MPEI 1:0.8/PVA, and (f) MPEI 1:1.0/PVA membranes measured at room temperature (c) MPEI-3/PVA, (d) MPEI-4/PVA, and (e) MPEI-5/PVA during the second heat treatment at heating rate $10\text{ }^{\circ}\text{C min}^{-1}$	63
4.13 Possible hydrogen bond formation of (a) PVA, (b) MPEI, and (c) MPEI/PVA membranes	63
4.14 Arrhenius plot of proton conductivity comparing the experimental data of PVA (\diamond), and PVA blended with MPEI 1:0.2 (\bullet), MPEI 1:0.4 (\blacktriangle), MPEI 1:0.6	64
4.15 Overlaid re-plots of proton conductivity, glass transition temperature, and relative amount of H-bond as a function of DS	67
 CHAPTER V 	
5.1 FTIR spectra of (a) nitromethanetripropionic acid, and the reaction between nitromethanetripropionic acid and SOCl_2 at (b) room temperature for 3 days, and (c) reflux temperature for a day	77
5.2 FTIR spectrum of 2	78
5.3 ^1H NMR spectrum of 2	79
5.4 ESI-MS spectrum of 2	79
5.5 FTIR spectrum of 3	80
5.6 ^1H NMR spectrum of 3	81
5.7 ESI-MS spectrum of 3	81

LIST OF TABLES

TABLE		PAGE
CHAPTER II		
2.1	Characteristics of different types of fuel cell (Boudghene <i>et. al.</i> , 2002 and Carrette <i>et. al.</i> , 2001)	4
CHAPTER III		
3.1	Crystal data and structure refinement parameters for B-1 to B-3	25
3.2	VFT parameters obtained from fitting the proton conductivity data to Eq. (3)	32
CHAPTER IV		
4.1	Effect of <i>b</i> PEI:MBz feeding ratios to % yield of the products, percent contents of hydrogen, carbon and nitrogen and calculated degree of substitution	48
4.2	T_d , percent residue, and T_g of the MPEIs compared with <i>b</i> PEI	53
4.3	Parameters obtained from curve fitting of temperature dependence proton conductivity with VTF equation	65