

การสังเคราะห์และวิเคราะห์คณิตกัญญาของ ไฮเปอร์บราวน์ซ์พอลิอีเทอร์บันพอลิอีโน๊



นางสาวบงกช สมบูรณ์ทรัพย์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาชีวกรรมเคมี ภาควิชาชีวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2549
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย



SYNTHESIS AND CHARACTERIZATION OF HYPERBRANCH POLYETHER
ON POLYIMIDE

Miss Bongkoch Somboonsub

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2006
Copyright of Chulalongkorn University

492201

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial
Fulfillment of the Requirements for the Master 's Degree

Direk Lavansiri Dean of the Faculty of Engineering
(Professor Direk Lavansiri, Ph.D.)

THESIS COMMITTEE

EE Smtt. A. J. Chairman

(Associate Professor Suttichai Assabumrungrat, Ph.D.)

 Thesis Advisor

(Associate Professor ML. Supakanok Thongyai, Ph.D.)

..... Member
(Associate Professor Seeroong Prichanont, Ph.D.)

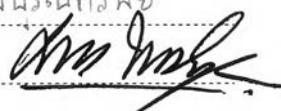
Bunyerd Jongsemijit Member
(Assistant Professor Bunyerd Jongsemijit, Ph.D.)

Sirirat Wacharawichanan Member
(Sirirat Wacharawichanan, Ph.D.)

บงกช สมบูรณ์ทรัพย์: การสังเคราะห์และวิเคราะห์คุณลักษณะของไฮเปอร์บранช์โพลีอีเทอร์บนโพลิอิมิด (SYNTHESIS AND CHARACTERIZATION OF HYPERBRANCH POLYETHER ON POLYIMIDE) อาจารย์ที่ปรึกษา: รศ. ดร. นล. ศุภกนก ทองใหญ่, 90 หน้า

ไฮเปอร์บранช์โพลิอิมิด-โพส (โพลิเมอร์ โอลิโกเมอริก ซินซิสควิอคเซน) คอมโพสิต ถูกสังเคราะห์โดยปฏิกริยาของโนร์ไมด์-ไฮเปอร์บранช์โพลิอีเทอร์-โพส และโพลิอิมิดที่ประกอบด้วยหน่วยครอซิล ไฮเปอร์บранช์โพลิอีเทอร์เตรียมโดยปฏิกริยาของ 3,5 ไดไฮครอซิสเซนติโลโซล แล้วโนนคลอโรไออกบิวทิลโพส (โพส-คลอรีน) โดยชั้นที่ 2 จะเปลี่ยนปลายไฮครอซิลเป็นโนร์ไมด์ด้วยการบอนเตตระโนร์ไมด์ และนำโพลิเมอร์ที่ได้ทำปฏิกริยาเข้าด้วยแอลกอฮอล์โดยวิธีเดิมเพื่อทำเป็นชั้นที่ 3 การวิเคราะห์ทางความร้อนของฟิล์มไฮเปอร์บранช์โพลิอิมิด มีอุณหภูมิของการถ่ายตัวอยู่ระหว่าง 265 ถึง 359 องศาเซลเซียส เช่นเดียวกับค่าอุณหภูมิที่เปลี่ยนสถานะค้ำยแก้วของฟิล์มไฮเปอร์บранช์โพลิอิมิดที่มีค่า 324.64 องศาเซลเซียส ผลการวัดค่าคงที่ไดอิเล็กทริก พบว่า เมื่อใส่พอสในปริมาณแทรกซึบ ในชั้นที่สูงกว่าจะมีค่าคงที่ไดอิเล็กทริกต่ำกว่า ถึงแม้ว่าจะลดปริมาณพอสลง 4 เท่า โพลิอิมิดชั้นที่ 3 ก็ยังคงมีค่าคงที่ไดอิเล็กทริกต่ำที่สุดค่าคงที่ไดอิเล็กทริกต่ำที่สุดมีค่า 2.54 พบในชั้นที่ 3 ของไฮเปอร์บранช์โพลิอิมิด-โพส คอมโพสิตเนื่องจากการมีช่องว่างจำนวนมากภายในโครงสร้างและการยึดเกาะกันหลวมๆ ความหนาแน่นมีผลสอดคล้องกับค่าคงที่ไดอิเล็กทริก คือ ความหนาแน่นที่ต่ำ ช่องว่างภายในโครงสร้างมาก จะมีค่าคงที่ไดอิเล็กทริกต่ำด้วย จากผลการทดลองพบว่าไฮเปอร์บранช์โพลิอิมิด-โพส คอมโพสิตแสดงสภาพการละลายที่เพิ่มขึ้นเมื่อเทียบกับโพลิอิมิดทั่วไป

ภาควิชา วิศวกรรมเคมี
สาขาวิชา วิศวกรรมเคมี
ปีการศึกษา 2549

ลายมือชื่อนิสิต นางสาวมนชนก วงศ์
ลายมือชื่ออาจารย์ที่ปรึกษา 

4870353921: MAJOR CHEMICAL ENGINEERING

KEY WORD: POLYIMIDE, POLYIMIDE/POSS, LOW DIELECTRIC CONSTANT ,
HYPERBRANCH POLYETHER

BONGKOCHE SOMBOONSUB: SYNTHESIS AND CHARACTERIZATION OF
HYPERBRANCH POLYETHER ON POLYIMIDE. THESIS ADVISOR: ASSOC.
PROF. ML. SUPAKANOK THONGYAI, Ph.D.,90 pp.

A hyperbranch polyimide-POSS (Polyhedral Oligomeric SilSesquioxanes) composite was synthesized by a reaction of a bromide-hyperbranch polyether-POSS and a polyimide containing hydroxyl functional group. Hyperbranch polyether was prepared by a reaction of 3,5-dihydroxybenzyl alcohol and MonoChloroIsobutyl-POSS (POSS-Cl) and then convert end chain hydroxyl group to bromide by carbontetrabromide for the formation of the second layer and the obtained polymer was repeated reacted with the alcohol with same procedure for the formation of the third layer. Thermogravimetric analysis indicated that the thermal degradation (T5%) of hyperbranch polyimide films occurs at 265 to 359 °C. The glass transition temperatures of hyperbranch polyimide films are in the range of 324.64°C. Regardless of the fixed amount of POSS, the higher layers yield lower dielectric constant and even reduced four times amount of POSS, the third layer still have the lowest dielectric constants. The lowest dielectric constant value for 2.54 can found in third layer of hyperbranch polyimide-POSS composite due to many free volume and loose polyimide structure. The densities of the hyperbranch polyimide correspond to the dielectric constants. The lower is the density, the higher is the free volume and the lower is the dielectric constant. Experimental results indicated that the hyperbranch polyimide-POSS composite exhibited increase solubility compare with pure polyimide.

Department Chemical Engineering

Student's signature

Field of study Chemical Engineering

Advisor's signature

Academic Year 2006

นางสาว อรุณรัตน์ พานิช

ACKNOWLEDGEMENTS

I would like to express my deeply gratitude to my advisor, Associate Professor Dr. ML. Supakanok Thongyai, Ph.D. to his continuous guidance, enormous number of invaluable discussions, helpful suggestions, warm encouragement and patience to correct my writing. I am grateful to Associate Professor Suttichai Assabumrungrat, Ph.D., Associate Professor Seeroong Prichanont, Ph.D., Assistant Professor Bunjerd Jongsomjit Ph.D. and Sirirat Wacharawichanan, Ph.D. for serving as chairman and thesis committees, respectively, whose comments were constructively and especially helpful.

Sincere thanks are made to Mektec Manufacturing Corporation (Thailand) Ltd. for supporting the materials for synthesis polyimide and the characterize equipments, the financial support from the graduate school at Chulalongkorn University, and Department of Chemical Engineering ,Faculty of Engineering Chulalongkorn University.

Sincere thanks to all my friends and all members of the Center of Excellent on Catalysis & Catalytic Reaction Engineering (Petrochemical Engineering Research Laboratory), Department of Chemical Engineering, Chulalongkorn University for their assistance and friendly encouragement.

Finally, I would like to dedicate this thesis to my parents and my families, who generous supported and encouraged me through the year spent on this study.

CONTENTS

	Page
ABSTRACT (IN THAI)	iv
ABSTRACT (IN ENGLISH)	v
ACKNOWLEDGEMENTS	vi
CONTENTS	vii
LIST OF FIGURES	xii
LIST OF TABLES	xv
CHAPTER I INTRODUCTION	1
1.1 The Objective of This Thesis.....	3
1.2 The Scope of This Thesis	3
CHAPTER II THEORY	4
2.1 Polyimide.....	4
2.1.1 One-step polymerization.....	5
2.1.2 Formation of polyamic acids	6
2.1.3 Reactivity of monomers	7
2.1.4 Thermal imidization of polyamic acid.....	7
2.2 Thermal curing in polyimide films and coatings	8
2.2.1 Substrate preparation	9
2.2.2 Adhesion promoters.....	10
2.2.3 Solution deposition.....	10
2.2.4 Drying	10
2.2.5 Spin Coating and Applicator Blade Coating (Casting).....	11
2.2.6 Curing	12
2.3 Structures of dianhydride.....	13
2.3.1 Pyromellitic dianhydride	13
2.3.2 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride	13
2.3.3 3,3',4,4'-Biphenyltetracarboxylic dianhydride	13
2.4 Structures of diamine	14

	Page
2.4.1 3,4'- Oxydianiline	14
2.5 Structures of polyimide.....	14
2.6 Properties of polyimide.....	15
2.7 Dielectric properties.....	15
2.8 Mechanical properties.....	19
2.8.1 Type of Stress-Strain Curve.....	19
2.8.2 Tensile Tests	20
2.9 Dynamic mechanical analysis.....	21
2.9.1 Introduction to dynamic mechanical analysis.....	21
2.9.2 Basic principles.....	22
2.10 POSS.....	22
2.10.1 Properties and Applications of POSS	23
2.10.2 Properties of POSS nanocomposites	24
2.10.3 Thermal properties.....	25
2.10.4 Dielectric properties.....	25
2.10.5 Applications	25
2.11 Branched systems	26
2.12 Polyurethane	27
2.12.1 Isocyanate	27
2.13 ether	28
2.13.1 Physical properties.....	28
2.13.2 Polyether	29
CHAPTER III LITERATURE REVIEWS	31
3.1 Polyimide synthesis	31
3.2 Polyhedral oligomeric silsesquioxane (POSS).....	34
3.3 Poly (urethane-imide)	36
3.4 Hyperbranched polyether.....	37

	Page
CHAPTER IV EXPERIMENT	40
4.1 Materials and Chemicals.....	40
4.2 Equipments	41
4.2.1 Polyimide synthesis part.....	41
(a) Glove Box	41
(b) Schlenk Line	42
(c) Schlenk Tube	42
(d) The inert gas	43
(e) The vacuum pump	43
(f) Synthesized reactor.....	44
(g) Magnetic Stirrer and Hot Plate	44
(h) Cooling System.....	45
(i) Syringe, Needle.....	45
4.2.2 Film preparation Part	45
(a) Vacuum oven.....	45
(b) Temperature controlled oven	45
4.3 Polyimide polymerization.....	45
4.4 Preparation of 1-3 layers hyperbranch polyether on polyimide	47
4.4.1 Preparation of the first layer	47
4.4.2 Preparation of the second layer.....	47
(a) Synthesis of dendritic Benzyl Alcohols [G-1]OH.....	47
(b) Synthesis of dendritic Benzyl Bromides [G-1]Br	47
(c) Preparation of dendrimer polyimide-ether (layer 2)	48
4.4.3 Preparation of the third layer	48
(a) Synthesis of dendritic Benzyl Alcohols [G-2]OH.....	48
(b) Synthesis of dendritic Benzyl Bromides [G-2]Br	48
(c) Preparation of dendrimer polyimide-ether (layer3)	49
4.5 Preparation of the polyimide films	49
4.6 Characterization Instruments	49

	Page
4.6.1 Infrared Spectroscopy (FTIR).....	49
4.6.2 Thermogravimetric analysis (TGA)	50
4.6.3 Dynamic Mechanical Analysis (DMA)	50
4.6.4 Dielectric properties.....	51
CHAPTER V RESULTS AND DISCUSSION.....	53
5.1 Polyimide synthesis	53
5.1.1 Preparation of polyimide	53
5.1.2 The structure of polyimide.....	54
5.1.3 Preparation of the first layer	55
5.1.4 The structure of POSS-polyimide (First layer).....	57
5.1.5 Preparation of the second layer.....	58
5.1.6 Preparation of the third layer	61
5.1.7 The structure of hyperbranch polyether on polyimide	64
5.2 Thermal properties.....	65
5.2.1 Influence of various layer of polyimide on thermal properties ..	65
5.3 Mechanical properties.....	70
5.3.1 Influence of various layers on Dynamic mechanical properties.	70
5.3.2 Influence of various layers on tensile mechanical properties	73
5.4 Dielectric properties.....	75
5.5 Solubility.....	78
CHAPTER VI CONCLUSIONS AND RECOMMENDATIONS	80
6.1 Conclusions.....	80
6.1.1 Synthesis of polyimide and first layers.....	80
6.1.2 Synthesis of hyperbranch polyimide	80
6.2 Recommendations.....	81
REFERENCES	82
APPENDICES.....	85
APPENDIX A.....	86
APPENDIX B.....	89

	Page
VITA	90

LIST OF FIGURES

	Page
Figure 2.1 Poly (p-phenylene).....	4
Figure 2.2 Two-step condensation polyimide synthesis (PMDA/ODA)	4
Figure 2.3 Avimid N chemistry	5
Figure 2.4 Polyimide film	12
Figure 2.5 PMDA structure.....	13
Figure 2.6 6FDA structure	13
Figure 2.7 BPDA structure.....	13
Figure 2.8 3,4'-ODA structure	14
Figure 2.9 BTDA-ODA	14
Figure 2.10 ODA-PMDA.....	14
Figure 2.11 BTDA-PDA	14
Figure 2.12 A typical stress-strain curve.....	19
Figure 2.13 Types of stress-strain curve	20
Figure 2.14 Diagram illustrating stress-strain curve form which modulus and elongation values are derived	21
Figure 2.15 POSS.....	23
Figure 2.16 Prepolymer reaction.....	27
Figure 2.17 2, 4 -TDI	28
Figure 2.18 2, 5 –TDI.....	28
Figure 2.19 2,6 – TDI.....	28
Figure 4.1 Glove box.....	42
Figure 4.2 Schlenk line	42
Figure 4.3 Schlenk tube.....	43
Figure 4.4 Inert gas supply system.....	43
Figure 4.5 Vacuum pump.....	44
Figure 4.6 Reactor	44
Figure 4.7 Preparation of polyimide capped with non-reactive end groups	46

	Page	
Figure 4.8	Fourier transform infrared spectroscopy (FT-IR) Equipment.....	49
Figure 4.9	Thermogravimetric analysis (TGA) Equipment	50
Figure 4.10	Dynamic Mechanical Analysis (DMA) Equipment	50
Figure 4.11	LCR Meter Equipment	51
Figure 4.12	Flow diagram of research methodology.....	52
Figure 5.1	Structure of polyimide	54
Figure 5.2	FT-IR spectra of hydroxyl polyimide	55
Figure 5.3	Structure of POSS-polyimide (First layer)	56
Figure 5.4	shows a typical FT-IR spectrum of POSS-Cl	57
Figure 5.5	FT-IR spectra of (i) polyimide, (ii) POSS-polyimide (first layer) and (iii) POSS-Cl.....	58
Figure 5.6	Structure of dendritic benzyl alcohols, [G-1] OH (Second layer).....	60
Figure 5.7	Structure of dendritic benzyl, [G-1] Br (Second layer)	60
Figure 5.8	Structure of hyperbranch polyether on polyimide (Second layer).....	61
Figure 5.9	Structure of dendritic benzyl alcohols,[G-2]OH (Third layer).....	62
Figure 5.10	Structure of dendritic benzyl,[G-2]Br (Third layer)	63
Figure 5.11	Structure of hyperbranch polyether on polyimide (Third layer)	64
Figure 5.12	shows a typical FT-IR spectrum of hyperbranch polyimide of (i) hyperbranch polyimide, (ii) polyimide	65
Figure 5.13	TGA curve of pure polyimide, layer1, layer2 and layer3 in O ₂	66
Figure 5.14	TGA curves of pure polyimide in O ₂	67
Figure 5.15	TGA curve of hyperbranch polyimide in O ₂	68
Figure 5.16	TGA curve of pure polyimide in N ₂	69
Figure 5.17	DMA curves (loss modulus (E'')) and temperature) for PI50 and PI50-L3	71
Figure 5.18	DMA curves (storage modulus (E') and temperature) for PI50 and PI50-L3	71
Figure 5.19	DMA curves (tanδ and temperature) for PI50 and PI50-L3.....	72
Figure 5.20	Tensile strength of PI50.....	73

	Page
Figure 5.21	Tensile strength of PI50-L3 73
Figure 5.22	Comparison of Tensile strength of PI50 and PI50-L3 74
Figure 5.23	shows content of mol POSS loading and dielectric constant 76
Figure A-1	Thermogravimetric analysis of polyimide at rate 10°C/min in N ₂ 85
Figure A-2	Thermogravimetric analysis of hyperbranch polyimide (PI-L3) at rate 10°C/min, in N ₂ 85
Figure A-3	Thermogravimetric analysis of polyimide at rate 10°C/min, in O ₂ 86
Figure A-4	Thermogravimetric analysis of POSS-polyimide at rate 10°C/min, in O ₂ 86
Figure A-5	Thermogravimetric analysis of hyperbranch polyimide (PI-L2) at rate 10°C/min, in O ₂ 87
Figure A-6	Thermogravimetric analysis of hyperbranch polyimide (PI-L3) at rate 10°C/min, in O ₂ 87
Figure B-1	DMA diagram of pure polyimide..... 88
Figure B-2	DMA diagram of hyperbranch polyimide (L3)..... 88

LIST OF TABLES

	Page	
Table 2.1	Key requirement for electronics packaging dielectrics	18
Table 2.2	Characteristic features of stress-strain curve as they relate to the polymer properties	20
Table 2.3	Important ethers.....	29
Table 4.1	Conditions and parameter for running DMA	51
Table 5.1	Formulation and definition of polyimide.....	53
Table 5.2	Content of POSS-Cl in first layer.....	56
Table 5.3	Content of POSS-Cl in second layer	59
Table 5.4	Content of POSS-Cl in the third layer	62
Table 5.5	Summary of the degradation temperature of various layers.....	68
Table 5.6	Thermal properties of the polyimide films.....	70
Table 5.7	Tensile properties of PI50 and PI50-L3	74
Table 5.8	Dielectric constant of polyimide films	75
Table 5.9	Density of polyimide films	78
Table 5.10	Solubility of pure polyimide and various layers of polyimide	78