

การสังเคราะห์ไฟลิ (ເອັນທີນິລມາ ເລື່ອມືດ-ໄຄ-ພາຣາອີພອກຊື່ສາຕູວິນ-ໄຄ-ສາຕູວິນ)



นายบัญชา พูลโภค

# ศูนย์วิทยทรัพยากร จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชารเคมี

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

พ.ศ. 2536

ISBN 974-582-429-1

ลิขสิทธิ์ของบัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

019648 i 17155936

SYNTHESIS OF POLY(N-PHENYLMALEIMIDE-CO-*p*-EPOXYSTYRENE  
-CO-STYRENE)



Mister Buncha Pulpoka

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science

Program of Petrochemistry

Graduate School

Chulalongkorn University

1993

ISBN 974-582-427-1

Thesis Title      Synthesis of poly(N-phenylmaleimide-co-*p*-epoxy-styrene-co-styrene)



By                    Mr. Buncha Pulpoka

Department        Multidisciplinary Program of Petrochemistry and Polymer

Thesis Advisor    Associate Professor Supawan Tantayanon, Ph.D.

Accepted by the Graduate School, Chulalongkorn University.

Partial Fulfillment of the Requirements for a Master's Degree.

*Thavorn Vajrabhaya*

..... Dean of Graduate School

(Professor Thavorn Vajrabhaya, Ph.D.)

Thesis Committee

*Pirawan Bhanthumnavin* ..... Chairman

(Associate Professor Pirawan Bhanthumnavin, Ph.D.)

*Supawan Tantayanon* ..... Thesis Advisor

(Associate Professor Supawan Tantayanon, Ph.D.)

*Amorn Petsom* ..... Member

(Assistant Professor Amorn Petsom, Ph.D.)

*Somchai Pengprecha* ..... Member

(Assistant Professor Somchai Pengprecha, Ph.D.)

พิมพ์ด้วยน้ำเงินที่ดื่มน้ำไวท์ทินนิลกันน้ำกรอบสีเขียวที่พิมพ์แบบเดิมๆ

บัญชา พูลโนค้า : การสังเคราะห์โพลี(เอ็น-พินิลมาเลอีเมด-โค-พารา-อีพอกซีสไตรีน-โค-สไตรีน)  
SYNTHESIS OF POLY (N-PHENYLMALEIMIDE-CO-P-EPOXYSTYRENE-CO-STYRENE). อ.ท.ปรีกษา : รศ.ดร. ศุภวรรณ ตันตยานันท์,  
150 หน้า. ISBN 974-582-427-1.

งานวิจัยนี้ ได้ทำการสังเคราะห์โพลี(เอ็น-พินิลมาเลอีเมด-โค-พารา-อีพอกซีสไตรีน-โค-สไตรีน) โดยเริ่มด้วยการสังเคราะห์มอนомер 2 ชนิด คือ เอ็น-พินิลมาเลอีเมด และ พารา-คลอรโรมีทิลสไตรีน ซึ่ง เอ็น-พินิลมาเลอีเมดสามารถสังเคราะห์ได้ โดยการนำเจ้าแอนลีนมาทำปฏิกิริยา กับมาเลิกแอนไไฮด์ริก ได้กรรมมาเลแอนลิก แล้วนำมาทำปฏิกิริยาต่อ กับอะซิติกแอนไไฮด์ริก ส่วนพารา-คลอรโรมีทิลสไตรีนนั้น สามารถสังเคราะห์ได้จากการทำปฏิกิริยา คลอรโรมีทิล เช่นของ 2-พินิลเอทิลไบรามีด แล้วนำมาทำปฏิกิริยาด้วยไครobiromine จากนั้นจึงทำการโดยพลิเมอไรเซชันระหว่างพารา-คลอรโรมีทิลสไตรีน สไตรีนและเอ็น-พินิลมาเลอีเมด ขั้นตอนมาจึงทำการเปลี่ยนหมู่คลอรโรมีทิลไปเป็นหมู่คาร์บอชีลิกด้วย แล้วนำไปทำปฏิกิริยาอีพอกซิเดชันจะได้หมู่อีพอกไซด์ในที่สุด จากผลการทดลองพบว่า เมื่อเปอร์เซนต์ ของเอ็น-พินิลมาเลอีเมดเพิ่มมากขึ้น จะทำให้  $T_g$  ของโคโพลีเมอร์สูงขึ้น การพิสูจน์โครงสร้างของสารที่สังเคราะห์ได้ ในแต่ละขั้นตอนทำได้โดยใช้เทคนิคทางスペกต์โรสโคปี



# ศูนย์วิทยทรัพยากร บุคลากรณ์มหาวิทยาลัย

ภาควิชา สภาพัฒนาฯ สถาบันฯ ฯ ฯ  
สาขาวิชา สถาบันฯ ฯ ฯ  
ปีการศึกษา 2535

ลายมือชื่อนิสิต ..... น.บ.ช. พ.ศ.๒๕๓๕  
ลายมือชื่ออาจารย์ที่ปรึกษา ..... พ.ศ.๒๕๓๕  
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม .....

## C485032: MAJOR PETROCHEMISTRY

KEY WORD: SYNTHESIS PHOTORESIST/ POLY (PARA-EPOXYSTYRENE)

BUNCHA POLPOKA : SYNTHESIS OF POLY (N-PHENYLMALEIMIDE-CO-P-EPOXYSTYRENE-CO-STYRENE).

THESIS ADVISOR : ASSOC. PROF. SUPAWAN TANTAYANON, PH.D.,  
150 PP. ISBN 974-582-427-1

The synthesis of poly (N-phenylmaleimide-co-p-epoxy-styrene-co-styrene was started with the synthesis of two monomers, N-phenylmaleimide and p-chloromethylstyrene. The reaction of aniline and maleic anhydride afforded maleanilic acid and then was converted to N-phenylmaleimide by acetic anhydride. p-Chloromethylstyrene was obtained from chloromethylation of 2-phenylethyl bromide and subsequent dehydrobromination. Then, copolymerization of p-chloromethylstyrene, styrene and N-phenylmaleimide was carried out. The percentage of N-phenylmaleimide was varied as 0, 5, 10, 25 and 50% by mole. Consequently, the chloromethyl group was converted to carboxaldehyde group and, finally, underwent epoxidation to form the epoxide group. The results showed that the more percentage of N-phenylmaleimide in the copolymers, the higher glass transition temperature ( $T_g$ ) was. All the synthesized compounds were characterized by the spectroscopic technique.



# ศูนย์วิทยาทรัพยากร จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา สาขาวิชา ปัจจุบัน ภาคเรียนที่ ภาคเรียนที่ ๒  
สาขาวิชา ปัจจุบัน อาจารย์ที่ปรึกษา ผู้ร่วม  
ปีการศึกษา 2535 อาจารย์ที่ปรึกษาร่วม

### Acknowledgements

Firstly, I'd like to express my sincere appreciation to Assoc. Prof. Dr. Supawan Tantayanon, my thesis advisor who gave me a good opportunity for working this research. I'm also deeply grateful for all of her kindness, valuable advice, and proof of my thesis.

I'm very grateful to Assist.Prof.Ratana Seangprasertkij for verification my thesis and all of her kindness. The special thanks are also extended to the thesis committee for their valuable comments.

Finally, I wish to thank for the kindness of laboratory of Louis Pasteur at Strasbourg, FRANCE, for the contribution of some spectroscopic data. Thanks are due to my parent for encouragement and to everyone who has contributed suggestions and supports for my successful thesis.

The financial support of this research attributed by The National Metals and Materials Technology Center, National Science and Technology Development Agency is acknowledged.

## CONTENT



	Page
ABSTRACT (in Thai) .....	I
ABSTRACT (in English) .....	II
ACKNOWLEDGEMENTS .....	III
CONTENT .....	IV
LIST OF FIGURES .....	IX
LIST OF TABLES .....	XII
ABBREVIATION .....	XV

## CHAPTER

## I. Introduction and Theory

1.1 General .....	1
1.2 Microlithography .....	5
1.2.1 Passivation .....	5
1.2.2 Coating .....	6
1.2.3 Irradiation .....	6
1.2.4 Development .....	6
1.2.5 Removal of SiO <sub>2</sub> .....	7
1.2.6 Removal of Resist .....	7
1.3 Types of Microlithography .....	7
1.3.1 Short-wavelength Photolithography ....	7
1.3.2 X-ray Lithography .....	8
1.3.3 Electron Beam Lithography .....	9
1.3.4 Scanning Ion Beam Lithography .....	10
1.4 Resists .....	11

**CONTENT (continued)**

	Page
1.5 Chemistry of Resists .....	11
1.5.1 Single-Level Resist Chemistry .....	11
1.5.1.1 Negative Resist .....	11
1.5.1.2 Positive Resist .....	17
1.5.2 Non-Conventional Resist Chemistry ....	21
1.5.3 Multilevel Resist Chemistry .....	23
1.5.3.1 Multilevel Resist Processes Employing Reactive Ion Etching Pattern-Transfer Technique ...	26
1.5.4 Gas-Phase Functionalization .....	29
1.5.5 Design and Selection of Resist .....	29
<b>II. Literature Review</b>	
2.1 Literature Review of Negative Resists .....	32
2.1.1 Electron-beam Sensitive Negative Resist .....	32
2.1.2 X-ray Sensitive Negative Resist .....	38
2.1.3 Photosensitive Negative Resist .....	39
2.2 Literature Review of N-substituted Maleimide Copolymer .....	47
2.3 Objective for This Study .....	52
<b>III. Experiments</b>	
3.1 General Information .....	55
3.1.1 Instruments .....	55
3.1.2 Chemicals and Solvents .....	56

## CONTENT (continued)

	Page
3.2 Purification of Solvents and Chemicals .....	58
3.3 Synthesis .....	60
3.3.1 Synthesis of N-phenylmaleimide .....	60
3.3.1.1 Synthesis of Maleanilic acid..	60
3.3.1.2 Conversion of Maleanilic acid to N-phenylmaleimide .....	60
3.3.2 Synthesis of p-Chloromethylstyrene ...	61
3.3.2.1 Chloromethylation of 2-Phenyl- ethyl bromide .....	61
3.3.2.2 Dehydrobromination of p-(2- bromoethyl)benzyl chloride to p-Chloromethylstyrene .....	64
3.3.3 Synthesis of Poly(p-Chloromethylstyrene -co-styrene) and Poly(p-Chloromethyl- styrene-co-styrene-co-N-phenylmalei- mide) .....	65
3.3.3.1 Copolymerization of p-Chloro- methylstyrene and styrene ....	65
3.3.3.2 Copolymerization of p-Chloro- methylstyrene, styrene and N-phenylmaleimide .....	66
3.3.4 Carboxylation of Poly(p-Chloromethyl- styrene-co-styrene) and Poly(p-Chloro- methylstyrene-co-styrene-co-N-phenyl- maleimide) .....	68

## CONTENT (continued)

	Page
3.3.4.1 Carboxylation of poly(p-Chloro-methylstyrene-co-styrene).....	68
3.3.4.2 Carboxylation of poly(p-Chloro-methylstyrene-co-styrene-co-N-phenylmaleimide).....	68
3.3.5 Oxidation of Poly(p-Chloromethylstyrene-co-styrene) and Poly(p-Chloro-methylstyrene-co-styrene-co-N-phenylmaleimide) .....	68
3.3.5.1 Epoxidation of poly(p-Carboxaldehydestyrene-co-styrene)..	70
3.3.5.2 Epoxidation of poly(p-Carboxaldehydestyrene-co-styrene-co-N-phenylmaleimide).....	71
3.4 Characterization of Monomers and Polymers ..	72
3.5 Analysis of Polymer composition .....	74
3.6 Preparation of Trimethylsulfonium Chloride .....	75
 IV. Results and Discussion	
4.1 Synthesis of N-phenylmaleimide .....	77
4.1.1 Synthesis of Maleanic acid.....	77
4.1.2 Conversion of Maleanic acid to N-phenylmaleimide .....	80
4.2 Synthesis of p-Chloromethylstyrene .....	85

## CONTENT (continued)

	Page
4.2.1 Chloromethylation of 2-Phenyl- ethyl bromide .....	85
4.2.2 Dehydrobromination of p-(2-bromo- ethyl)benzyl chloride to p-Chloro- methylstyrene .....	95
4.3 Copolymerization.....	101
4.3.1 Copolymerization of p-Chloromethyl- styrene and styrene.....	101
4.3.2 Copolymerization of p-Chloromethyl- styrene, styrene and N-phenylmalei- mide.....	105
4.4 Carboxylation of Poly(p-Chloromethylstyrene -co-styrene) and Poly(p-Chloromethyl- styrene-co-styrene-co-N-phenylmaleimide) ...	115
4.5 Epoxidation of Poly(p-Chloromethylstyrene -co-styrene) and Poly(p-Chloromethylstyrene- co-styrene-co-N-phenylmaleimide) .....	123
V. Conclusion .....	134
References .....	136
Appendix .....	146
VITA .....	150

## LIST OF FIGURES

Figure	Page
1.1 Scheme of the lithographic process.....	4
1.2 Photolithography using negative resist .....	5
1.3 Chemical reaction occurring during irradiation of negative resist .....	12
1.4 Radiation-sensitive groups use in negative, cross-linking systems .....	13
1.5 Effect of polymer molecular weight on resist sensitivity .....	14
1.6 Effect of polymer molecular weight on resist contrast .....	15
1.7 Chemical reaction occurring during irradiation of positive resist .....	17
1.8 Mechanism of PMMA degradation .....	18
1.9 Structure of the poly(olefin sulfone) resist ...	19
1.10 Photochemical induced radiation of a typical substituted diazonaphthoquinone dissolution inhibitor .....	20
1.11 Image reversal process and related chemistry based on a conventional positive photoresist and monoazoline .....	21
1.12 Process sequence for several multilevel resist scheme .....	24
1.13 Representative contrast curves for (a.) positive resist (b.) negative resist .....	31

**LIST OF FIGURES(continued)**

Figure	Page
3.1 The apparatus for chloromethylation of 2-bromo-phenylethyl bromide. ....	62
4.1 IR (KBr) spectrum of maleanilic acid. ....	79
4.2 IR (KBr) spectrum of N-phenylmaleimide.....	83
4.3 The $^1\text{H}$ NMR spectrum of N-phenylmaleimide in $\text{CDCl}_3$ .....	83
4.4 The mass spectrum of N-phenylmaleimide. ....	84
4.5 IR (KBr) spectrum of <i>p</i> -(2-bromoethyl)benzyl chloride.....	89
4.6 IR (NaCl) spectrum of 2-phenylethyl bromide....	89
4.7 The $^1\text{H}$ NMR spectrum of <i>p</i> -(2-bromoethyl)benzyl chloride in $\text{CDCl}_3$ .....	92
4.8 The $^{13}\text{C}$ NMR spectrum of <i>p</i> -(2-bromoethyl)benzyl chloride in $\text{CDCl}_3$ . ....	92
4.9 The mass spectrum of <i>p</i> -(2-bromoethyl)benzyl chloride.....	94
4.10 IR (NaCl) spectrum of <i>p</i> -chloromethylstyrene....	98
4.11 The $^1\text{H}$ NMR spectrum of <i>p</i> -chloromethylstyrene in $\text{CDCl}_3$ .....	98
4.12 The $^1\text{H}$ NMR spectrum of poly( <i>p</i> -chloromethyl- styrene-co-styrene) in $\text{CDCl}_3$ .....	104
4.13 IR (KBr) spectrum of poly( <i>p</i> -chloromethylstyrene -co-styrene-co-N-phenylmaleimide).....	107

## LIST OF FIGURES(continued)

Figure	Page
4.14 The $^1\text{H}$ NMR spectrum of poly( <i>p</i> -chloromethylstyrene-co-styrene-co-N-phenylmaleimide) in $\text{CDCl}_3$ .....	108
4.15 IR (KBr) spectrum of (a.) poly( <i>p</i> -chloromethylstyrene-co-styrene) (b.) poly( <i>p</i> -carboxaldehydestyrene-co-styrene)...	118
4.16 IR (KBr) spectrum of (a.) poly( <i>p</i> -chloromethylstyrene-co-styrene -co-N-phenylmaleimide) (b.) poly( <i>p</i> -carboxaldehydestyrene-co- styrene-co-N-phenylmaleimide).....	120
4.17 IR (KBr) spectrum of poly( <i>p</i> -epoxystyrene-co-styrene).....	127
4.18 IR (KBr) spectrum of (a.) poly( <i>p</i> -carboxaldehydestyrene-co- styrene-co-N-phenylmaleimide) (b.) poly( <i>p</i> -epoxystyrene-co-styrene-co- N-phenylmaleimide).....	129

## LIST OF TABLES

Table	Page
2.1 Negative X-ray resist .....	39
2.2 Radical polymerization of N-substituted maleimides in benzene at 50 °C for 5 hrs.....	49
3.1 Polymerization data for <i>p</i> -chloromethylstyrene, styrene and N-phenylmaleimide.....	66
3.2 Some physical properties and elemental analysis of poly( <i>p</i> -chloromethylstyrene-co- styrene-co-N-phenylmaleimide).....	67
3.3 Experimental data for carboxylation of poly ( <i>p</i> -chloromethylstyrene-co-styrene-co- N-phenylmaleimide).....	69
3.4 Experimental data for epoxidation of poly ( <i>p</i> -carboxaldehydestyrene-co-styrene-co- N-phenylmaleimide).....	71
3.5 Some resulting T <sub>g</sub> and epoxide contents of poly( <i>p</i> -chloromethylstyrene-co-styrene-co- N-phenylmaleimide) .....	72
4.1 The assignment for the IR spectrum of maleanilic acid .....	78
4.2 The assignment for the IR spectrum of N-phenylmaleimide .....	82
4.3 The assignment for the IR spectrum of <i>p</i> -(2-bromoethyl)benzyl chloride .....	88
4.4 The assignment for the <sup>1</sup> H NMR spectrum of <i>p</i> -(2-bromoethyl)benzyl chloride .....	90

## LIST OF TABLES(continued)

Table	Page
4.5 The assignment for the $^{13}\text{C}$ NMR spectrum of <i>p</i> -(2-bromoethyl)benzyl chloride .....	91
4.6 The assignment for the IR spectrum of <i>p</i> -chloromethylstyrene .....	97
4.7 The assignment for the $^1\text{H}$ NMR spectrum of <i>p</i> -chloromethylstyrene .....	100
4.8 The assignment for the IR spectrum of poly( <i>p</i> -chloromethylstyrene-co-styrene).....	102
4.9 The assignment for the $^1\text{H}$ NMR spectrum of poly( <i>p</i> -chloromethylstyrene-co-styrene).....	103
4.10 The assignment for the IR spectrum of poly( <i>p</i> -chloromethylstyrene-co-styrene-co- N-phenylmaleimide).....	106
4.11 Polymerization data of poly( <i>p</i> -chloromethyl- styrene-co-styrene) and poly( <i>p</i> -chloromethyl- styrene-co-styrene-co-N-phenylmaleimide) ....	111
4.12 The elemental analysis of poly( <i>p</i> -chloromethyl- styrene-co-styrene) and poly( <i>p</i> -chloromethyl- styrene-co-styrene-co-N-phenylmaleimide) ....	112
4.13 The analysis of molecular weight and glass transition temperature of poly( <i>p</i> -chloromethyl- styrene-co-styrene) and poly( <i>p</i> -chloromethyl- styrene-co-styrene-co-N-phenylmaleimide) ....	113
4.14 Determination of chlorine in polymers by modified Volhard method .....	114

## LIST OF TABLES(continued)

Table	Page
4.15 The assignment for the IR spectrum of poly( <i>p</i> -carboxaldehydestyrene-co-styrene).....	117
4.16 The assignment for the IR spectrum of poly( <i>p</i> -carboxaldehydestyrene-co-styrene-co- N-phenylmaleimide).....	119
4.17 The determination of chloride content in poly ( <i>p</i> -chloromethylstyrene-co-styrene) and poly ( <i>p</i> -chloromethylstyrene-co-styrene-co- N-phenylmaleimide) .....	122
4.18 The assignment for the IR spectrum of poly( <i>p</i> -epoxystyrene-co-styrene).....	126
4.19 The assignment for the IR spectrum of poly( <i>p</i> -carboxaldehydestyrene-co-styrene-co- N-phenylmaleimide).....	128
4.20 The analysis data for determination of epoxide content .....	131
4.21 The analysis data for determination of functional groups contents in poly ( <i>p</i> -chloromethylstyrene-co-styrene) and poly( <i>p</i> -chloromethylstyrene-co-styrene-co- N-phenylmaleimide) .....	132
4.22 The glass transition temperature of poly ( <i>p</i> -chloromethylstyrene-co-styrene) and poly( <i>p</i> -chloromethylstyrene-co-styrene-co- N-phenylmaleimide) .....	133

**ABBREVIATION**

AIBN	azobis(isobutyronitrile)
$\text{\AA}$	angstrom
C	coulomb
$\text{cm}^2$	square centimeter
CEL	Contrast enhancement level
CMS	p-chloromethylstyrene
CVD	Coating vapor deposition
EA	ethylacrylate
d	doublet
dd	doublet of doublet
DMSO	dimethylsulfoxide
GA	glycidylacrylate
GC	gas chromatography
GMA	glycidylmethacrylate
GPC	gel permeation chromatography
hrs.	hours
IR	infrared
J	joule
L	liter
min.	minute
ml	millilitre
Mn	number average molecular weight
Mw	weight average molecular weight
MWD	molecular weight distribution
NMR	nuclear magnetic resonance
NPhMI	N-phenylmaleimide

**ABBREVIATION(continued)**

PCMS	chloromethylated polystyrene
PDOP	poly(diallylorthophthalate)
PMMA	poly(methyl methacrylate)
ppm	part per million
psi.	pound per square inch
PVA	polyvinyl alcohol
PVK	poly(vinyl-carbazole)
RIE	Reactive ion etching
rpm	round per minute
s	singlet
sec.	second
ST	styrene
t	triplet
%T	% transmittance
T <sub>g</sub>	glass transition temperature
UV	ultraviolet
χ	contrast
μm	micrometer
ν	wavenumber
δ	chemical shift