

การสังเคราะห์ปีดสไตรีนสำหรับดูดซึมและคายตัวทำลายโดย

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต  
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SYNTHESIS OF SOLVENT ABSORPTION-DESORPTION STYRENIC  
IMBIBER BEADS BY SUSPENSION POLYMERIZATION

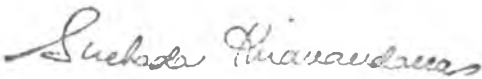
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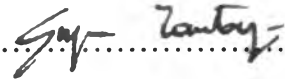
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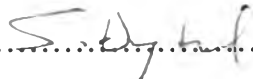
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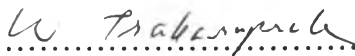
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วิจัย กังวานศุภมมงคล : การสังเคราะห์บีดสไตรีนสำหรับดูดซึมและคายตัวทำละลายโดยการเกิดพอลิเมอร์แบบ  
แขวนลอย (SYNTHESIS OF SOLVENT ABSORPTION-DESORPTION STYRENIC  
IMBIBER BEADS BY SUSPENSION POLYMERIZATION) อ. ที่ปรึกษา : รศ. ดร. สุกดา เกียรติกำจรวงศ์;  
อ. ที่ปรึกษาร่วม : ศ. ดร. สมศักดิ์ ดำรงค์เลิศ; 199 หน้า. ISBN 974-332-795-9.

งานวิจัยนี้ได้สังเคราะห์บีดพอลิเมอร์ร่วมสไตรีน-ไดไวนิลเบนซีนด้วยวิธีการเกิดพอลิเมอร์แบบแขวนลอย โดยมีเบนโซอิล  
เพอร์ออกไซด์และพอลิไวนิลแอลกอฮอล์ทำหน้าที่เป็นตัวริเริ่มปฏิกิริยาและสารแขวนลอย ตามลำดับ ได้ศึกษาตัวแปรต่างๆ อย่างละเอียด ซึ่งมี  
ผลต่อขนาดอนุภาคเฉลี่ย การกระจายขนาดอนุภาค องค์ประกอบของการเชื่อมขวาง และสมบัติการบวมตัวของพอลิเมอร์ที่สังเคราะห์ได้ อันได้แก่  
อัตราส่วนของวัฏภาคมอนอเมอร์โดยน้ำหนัก อัตราการกวน อุณหภูมิในการทำปฏิกิริยา เวลาในการทำปฏิกิริยา ความเข้มข้นของตัวริเริ่ม  
ปฏิกิริยา ความเข้มข้นของสารเชื่อมขวาง ความเข้มข้นของสารแขวนลอย องค์ประกอบของตัวเจือจาง และมอนอเมอร์ร่วมชนิดที่สาม อันได้แก่  
นอร์แมลบิวทิลอะครีเลต หรือ 2-เอทิลเฮกซิลอะครีเลต ตรวจสอบสมบัติต่างๆ ของพอลิเมอร์ที่สังเคราะห์ได้โดยการหาขนาดอนุภาคเฉลี่ยและ  
การกระจายขนาดอนุภาคจากการผ่านตะแกรงร่อน สมบัติการบวมตัวจากการชั่งน้ำหนัก สมบัติทางความร้อนด้วย DSC หมู่ฟังก์ชันด้วย FT-IR  
จลนพลศาสตร์ของการดูดซึมและการคายตัวทำละลายด้วยกล้องจุลทรรศน์ สัณฐานวิทยาของผิวด้วย SEM ความหนาแน่นด้วยเทคนิค  
การแทนที่ของเหลว สมบัติของโพรงด้วยเครื่องวิเคราะห์โพรงด้วยปรอท และค่าพารามิเตอร์แห่งการละลายด้วยวิธีการวัดการบวมตัว อีกทั้ง  
ตรวจสอบการดูดซึมตัวทำละลายผสมบนผิวน้ำ

ภาวะที่เหมาะสมสำหรับการเกิดพอลิเมอร์คือ เบนโซอิลเพอร์ออกไซด์ร้อยละ 0.5 โดยน้ำหนัก พอลิไวนิลแอลกอฮอล์ร้อยละ  
0.1 โดยน้ำหนัก อัตราส่วนของวัฏภาคมอนอเมอร์โดยน้ำหนักคือ 0.1 ปริมาณไดไวนิลเบนซีนร้อยละ 6 โดยน้ำหนัก อัตราส่วนโดยน้ำหนัก  
ระหว่างโทลูอินและเฮพเทนคือ 60/40 อัตราการกวน 270 รอบ/นาที อุณหภูมิและเวลาในการทำปฏิกิริยาคือ 70°C. และ 10 ชม. ตามลำดับ  
หลังจากวิเคราะห์ด้วยวิธีต่างๆ บีดที่สังเคราะห์ได้มีลักษณะเป็นทรงกลม และมีสมบัติดังนี้ ขนาดอนุภาคเฉลี่ยอยู่ระหว่าง 0.82 – 1.49 มม.  
เส้นผ่านศูนย์กลางเฉลี่ยของโพรง  $(1.33 - 2.12) \times 10^{-2}$  ไมโครเมตร พื้นที่ผิวของโพรง 17.466 – 44.057 ตร.ม./ก. ปริมาตรของโพรง  
 $5.8 \times 10^{-2} - 2.34 \times 10^{-1}$  ลบ.ซม./ก. ความหนาแน่นของบีดอยู่ในพิสัย 0.9375 – 1.0581 ก./ลบ.ซม. อัตราส่วนการบวมตัวในโทลูอินอยู่ใน  
พิสัย 4.2 – 12.3 เท่า ค่าพารามิเตอร์แห่งการละลายอยู่ระหว่าง 18.2 – 19.0 (เมกกะพาสคัล)<sup>1/2</sup> อุณหภูมิสภาพแก้วอยู่ในพิสัย 42 – 107°C.  
สัมประสิทธิ์การแพร่อยู่ในพิสัย  $6.40 \times 10^{-6} - 1.52 \times 10^{-5}$  ตร.ซม./วินาที บีดที่สังเคราะห์ได้นี้สามารถดูดซึมและคายตัวทำละลายอุตสาหกรรม  
หลายชนิดที่มีค่าพารามิเตอร์แห่งการละลายอยู่ระหว่าง 18.2 – 19.0 (เมกกะพาสคัล)<sup>1/2</sup> ซึ่งนับว่ามีประโยชน์มากต่อการกำจัดคราบตัวทำละลาย  
และคราบน้ำมันที่อยู่บนผิวน้ำในสิ่งแวดล้อม อายุการใช้งานของบีดมากกว่า 3 ครั้ง โดยที่ยังคงลักษณะทรงกลมไว้

ภาควิชา .....  
สาขาวิชา ปิโตร เคมีและวิทยาศาสตร์พอลิเมอร์ .....  
ปีการศึกษา 2542 .....

ลายมือชื่อนิสิต วิจัย กังวานศุภมมงคล .....  
ลายมือชื่ออาจารย์ที่ปรึกษา .....  
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม .....

# # 3971723423 : MAJOR POLYMER SCIENCE

KEY WORD: STYRENE-DIVINYLBENZENE / SUSPENSION POLYMERIZATION / SOLUBILITY PARAMETER /  
CROSSLINKING DENSITY / ABSORPTION / DESORPTION

WIYONG KANGWANSUPAMONKON : SYNTHESIS OF SOLVENT ABSORPTION-DESORPTION  
STYRENIC IMBIBER BEADS BY SUSPENSION POLYMERIZATION. THESIS ADVISOR :  
ASSOC. PROF. SUDA KIATKAMJORNWONG, Ph.D., THESIS CO-ADVISOR : PROF. SOMSAK  
DAMRONGLERD, Ph.D. 199 pp. ISBN 974-332-795-9.

Syntheses of styrene-divinylbenzene copolymer beads were carried out by suspension copolymerization. The reactions were performed in the presence of benzoyl peroxide and poly(vinyl alcohol) as the initiator and suspending agent, respectively. The effects of reaction parameters, namely, monomer phase weight fraction, agitation rate, reaction temperature, reaction time, initiator concentration, crosslinking agent concentration, concentration of suspending agent, diluent composition, and the third comonomer, *n*-butyl acrylate or 2-ethyl hexyl acrylate, on the average particle size, size distribution, crosslinking density, and swelling properties of the resulting copolymers were thoroughly investigated. The average particle size and size distribution was measured by sieve analysis, the swelling properties by gravimetric measurement, thermal properties by DSC, the functional groups by FT-IR, kinetics of absorption and desorption by optical microscopy, surface morphology by SEM, density by the liquid displacement technique, pore properties by a mercury porosimeter and solubility parameters by swelling experiments. The absorption of the solvent mixture on the water surface was also investigated.

The optimum conditions for the polymerization were found to be as follows: 0.5% w/w BPO; 0.1% w/w PVA; 0.1 of the monomer phase weight fraction; 6% w/w DVB; the Tol/Hep ratio (w/w) was 60/40; the agitation rate was 270 rpm; the reaction temperature and time were 70°C and 10 hrs, respectively. After various characterizations, the resulting synthesized copolymers were spherical beads and had the following properties: average particle sizes were in the range of 0.82 – 1.49 mm; average pore diameter  $(1.33 - 2.12) \times 10^{-2} \mu\text{m}$ ; surface area 17.466 – 44.057 m<sup>2</sup>/g; pore volume  $5.81 \times 10^{-2} - 2.34 \times 10^{-1} \text{ cm}^3/\text{g}$ ; density 0.9375 – 1.0581 g/cm<sup>3</sup>; swelling ratios in the range of 4.2 – 12.3 times in toluene; solubility parameter 18.2 – 19.0 (MPa)<sup>1/2</sup>; the glass transition temperature ( $T_g$ ) in the range of 42 – 107°C; the diffusion coefficient in the range of  $6.40 \times 10^{-6} - 1.52 \times 10^{-5} \text{ cm}^2/\text{sec}$ . The advantage of these synthetic copolymer beads is that they are capable of sorption and desorption of several industrial solvents with solubility parameters in the range of 18.2 – 19.0 (MPa)<sup>1/2</sup> which are beneficial for the removal of spilled solvents and oil on the surface of water in our environment. The lifespan of the beads is longer than 3 repeated uses while still retaining their spherical shape.

ภาควิชา.....

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

ปีการศึกษา 2542

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# CONTENTS

	PAGE
ABSTRACT (IN THAI).....	iv
ABSTRACT (IN ENGLISH).....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LIST OF TABLES.....	xiii
LIST OF FIGURES.....	xviii
ABBREVIATIONS.....	xxv
CHAPTER 1 : INTRODUCTION.....	1
1.1 Scientific Rational.....	1
1.2 Objectives of the Research Work.....	2
1.3 Scopes of the Research Work.....	2
1.4 Contents of the Research Work.....	4
CHAPTER 2 : THEORETICAL BACKGROUND.....	5
2.1 Free-Radical Polymerization.....	5
2.2 Suspension Polymerization.....	7
2.3 Polymer Solubility.....	15
2.3.1 General Rules for Polymer Solubility.....	15
2.3.2 The Thermodynamic Basis of Polymer Solubility.....	17
2.3.3 The Flory-Huggins Theory.....	18
2.3.4 Solubility Parameter.....	20

**CONTENTS (continued)**

	PAGE
2.3.5 Hansen's Three-Dimensional Solubility Parameter.....	23
2.3.9 Properties of Diluent Solutions.....	26
2.4 Crosslinked Polymers.....	27
2.4.1 Chemical Crosslinking.....	28
2.4.2 Physical Crosslinking.....	29
2.4.3 Crosslink Density.....	31
2.5 Absorption-Desorption Kinetics.....	32
2.5.1 Absorption Kinetics.....	32
2.5.2 Desorption Kinetics.....	34
2.6 Literature Review.....	35
CHAPTER 3 : EXPERIMENTAL.....	41
3.1 Chemicals.....	41
3.1.1 Monomers.....	41
3.1.2 Initiator.....	42
3.1.3 Suspending Agent.....	42
3.1.4 Solvents.....	42
3.1.5 Other Chemicals.....	44
3.2 Glassware.....	45
3.3 Equipment.....	45
3.4 Procedures.....	46



## CONTENTS (continued)

	PAGE
3.4.1 Purification of Chemicals.....	46
3.4.1.1 Styrene and Other Monomers.....	46
3.4.1.2 Solvents.....	47
3.4.1.3 Other Chemicals.....	47
3.4.2 Synthesis of Styrene-divinylbenzene Copolymer.....	47
3.4.2.1 Suspension Copolymerization of Styrene and Divinylbenzene with Benzoyl peroxide.....	47
3.4.2.2 The Effect of Monomer Phase Weight Fraction.....	49
3.4.2.3 The Effect of Agitation Rate.....	49
3.4.2.4 The Effect of the Reaction Temperature.....	50
3.4.2.5 The Effect of Reaction Time.....	50
3.4.2.6 The Effect of Initiator Concentration.....	51
3.4.2.7 The Effect of Crosslinking Agent Concentration.	52
3.4.2.8 The Effect of Suspending Agent Concentration...	52
3.4.2.9 The effect of Diluent Composition.....	53
3.4.2.10 The Effect of Monomer Composition.....	54
3.4.3 Copolymer Characterization.....	54

**CONTENTS (continued)**

	PAGE
3.4.3.1 Determination of Particle Size and Size Distribution of Styrene-divinylbenzene Copolymer Beads (Sieve Analysis).....	54
3.4.3.2 Determination of Swelling Properties of Styrene-divinylbenzene Copolymer Beads.....	55
3.4.3.3 Determination of Crosslinking Density of Styrene-divinylbenzene Copolymer Beads.....	55
3.4.3.4 Determination of Surface Morphology of Styrene-divinylbenzene Copolymer Beads (Scanning Electron Microscopy).....	56
3.4.3.5 Determination of Thermal Properties of Styrene-divinylbenzene Copolymer Beads.....	57
3.4.3.6 Determination of Styrene-divinylbenzene Copolymer Beads Density.....	57
3.4.3.7 Determination of Solvent Absorption and Desorption Kinetics of Styrene-divinylbenzene Copolymer Beads.....	57
3.4.3.8 Determination of Pore Properties of Styrene-divinylbenzene Copolymer Beads.....	58

## CONTENTS (continued)

	PAGE
CHAPTER 4 : RESULTS AND DISCUSSION.....	59
4.1 Effect of Monomer Phase Weight Fraction.....	59
4.2 Effect of Agitation Rate.....	63
4.3 Effect of Reaction Temperature.....	68
4.4 Effect of Reaction Time.....	72
4.5 Effect of Initiator Concentration.....	76
4.6 Effect of Crosslinking Agent Concentration.....	81
4.7 Effect of Suspending Agent Concentration.....	89
4.8 Effect of Diluent Composition.....	94
4.9 Effect of the Third Monomer.....	104
4.10 Morphology of the Surface of Sty-DVB Copolymer.....	114
4.10.1 The effect of the crosslinking agent concentration.....	114
4.10.2 The effect of the diluent composition.....	115
4.11 Mechanism of Porous Structure Formation.....	118
4.12 Glass Transition Temperature of Copolymer.....	121
4.13 Absorption-Desorption and Diffusion Coefficient in Toluene- Heptane Solution of the Copolymer Beads [the Toluene Volume Fraction ( $z$ ) = 0.5].....	126
4.13.1 Absorption.....	126
4.13.2 Desorption.....	129

## CONTENTS (continued)

	PAGE
4.14 Absorption of Solvent Mixture Layer on Water Surface of the Copolymer Beads.....	140
4.15 Determination of Copolymer Bead Density.....	142
4.16 Determination of Pore Properties of Copolymer Beads.....	143
CHAPTER 5 : CONCLUSION AND SUGGESTION.....	145
5.1 Conclusion.....	145
5.2 Suggestions for Further Work.....	149
REFERENCES.....	151
APPENDICES.....	156
APPENDIX A.....	157
APPENDIX B.....	158
APPENDIX C.....	160
APPENDIX D.....	163
APPENDIX E.....	166
APPENDIX F.....	173
APPENDIX G.....	178
APPENDIX H.....	193
VITA.....	199

## LIST OF TABLES

TABLE	PAGE
2.1 Materials used in suspension polymerization.....	9
2.2 Polymerization processes in water.....	14
2.3 Classification of solvating power of the diluents according to their solubility parameters.....	23
2.4 Hildebrand solubility parameters, coordinates of three-dimensional solubility parameters $\delta_t$ ( $\delta_d$ , $\delta_p$ , and $\delta_h$ ).....	25
2.5 Classification of the solvating power of the diluents according to diluent-polymer distances ( $R$ ) in a three-dimensional $\delta_d$ , $\delta_p$ , and $\delta_h$ ....	26
3.1 Various monomer phase weight fraction for suspension copolymerization of styrene and divinylbenzene.....	49
3.2 Various agitation rates for suspension copolymerization of styrene and divinylbenzene.....	50
3.3 Various reaction temperatures for suspension copolymerization of styrene and divinylbenzene.....	50
3.4 Various reaction times for suspension copolymerization of styrene and divinylbenzene.....	51
3.5 Various initiator concentrations for suspension copolymerization of styrene and divinylbenzene.....	51
3.6 Various crosslinking agent concentrations for suspension copolymerization of styrene and divinylbenzene.....	52

**LIST OF TABLES (continued)**

TABLE	PAGE
3.7 Various suspending agent concentrations for suspension copolymerization of styrene and divinylbenzene.....	53
3.8 Various diluent compositions for suspension copolymerization of styrene and divinylbenzene.....	53
3.9 Various monomer compositions for suspension copolymerization of copolymerization of styrene and divinylbenzene.....	54
4.1 Effect of monomer phase weight fraction on the particle size and size distribution of styrene-divinylbenzene copolymer beads.....	60
4.2 Effect of monomer phase weight fraction on swelling properties of styrene-divinylbenzene copolymer beads.....	62
4.3 Effect of agitation rate on the particle size and size distribution of styrene-divinylbenzene copolymer beads.....	65
4.4 Effect of agitation rate on swelling properties of styrene-divinylbenzene copolymer beads.....	65
4.5 Effect of reaction temperature on the particle size and size distribution of styrene-divinylbenzene copolymer beads.....	69
4.6 Effect of reaction temperature on swelling properties of styrene-divinylbenzene copolymer beads.....	70
4.7 Effect of reaction time on the particle size and size distribution of styrene-divinylbenzene copolymer beads.....	73

**LIST OF TABLES (continued)**

TABLE	PAGE
4.8 Effect of reaction time on swelling properties of styrene-divinylbenzene copolymer beads.....	75
4.9 Effect of initiator concentration on the particle size and size distribution of styrene-divinylbenzene copolymer beads.....	77
4.10 Effect of initiator concentration on swelling properties of styrene-divinylbenzene copolymer beads.....	79
4.11 Important peak of the styrene-divinylbenzene copolymers beads.....	82
4.12 Effect of crosslinking agent concentration on the particle size and size distribution of styrene-divinylbenzene copolymer beads.....	83
4.13 Effect of crosslinking agent concentration on swelling properties of styrene-divinylbenzene copolymer beads.....	88
4.14 Effect of suspending agent concentration on the particle size and size distribution of styrene-divinylbenzene copolymer beads.....	91
4.15 Effect of suspending agent concentration on swelling properties of styrene-divinylbenzene copolymer beads.....	93
4.16 Effect of diluent composition on the particle size and size distribution of styrene-divinylbenzene copolymer beads.....	96
4.17 Effect of diluent composition on swelling properties of styrene-divinylbenzene copolymer beads.....	101

## LIST OF TABLES (continued)

TABLE	PAGE
4.18 Effect of monomer composition on the particle size and size distribution of styrene-divinylbenzene copolymer beads.....	105
4.19 Swelling ratio of the synthetic copolymer beads in various solvents....	111
4.20 Solubility parameters of used diluents distribution of styrene-divinylbenzene copolymer beads.....	116
4.21 Diffusion coefficient of the copolymer beads in toluene-heptane solution [the toluene volume fraction ( $z$ ) = 0.5].....	128
4.22 Solubility of the synthetic copolymers.....	128
4.23 Swelling ratio of the synthetic copolymer beads in solvent mixtures...	141
4.24 The densities of the copolymers.....	142
4.25 Pore properties of the styrene-divinylbenzene copolymer.....	144
F-1 Swelling Ratio of the Copolymer Beads (Run PS) in Different Solvents.....	173
F-2 Swelling Ratio of the Copolymer Beads (Run B24) in Different Solvents.....	174
F-3 Swelling Ratio of the Copolymer Beads (Run B47) in Different Solvents.....	175
F-4 Swelling Ratio of the Copolymer Beads (Run E24) in Different Solvents.....	176



## LIST OF TABLES (continued)

TABLE	PAGE
F-5 Swelling Ratio of the Copolymer Beads (Run E47) in Different Solvents.....	177
G-1 Absorption and desorption of copolymer bead (Run. PS: 1st).....	178
G-2 Absorption and desorption of copolymer bead (Run. PS: 2nd).....	179
G-3 Absorption and desorption of copolymer bead (Run. PS: 3rd).....	180
G-4 Absorption and desorption of copolymer bead (Run. B24: 1st).....	181
G-5 Absorption and desorption of copolymer bead (Run. B24: 2nd).....	182
G-6 Absorption and desorption of copolymer bead (Run. B24: 3rd).....	183
G-7 Absorption and desorption of copolymer bead (Run. B47: 1st).....	184
G-8 Absorption and desorption of copolymer bead (Run. B47: 2nd).....	185
G-9 Absorption and desorption of copolymer bead (Run. B47: 3rd).....	186
G-10 Absorption and desorption of copolymer bead (Run. E24: 1st).....	187
G-11 Absorption and desorption of copolymer bead (Run. E24: 2nd).....	188
G-12 Absorption and desorption of copolymer bead (Run. E24: 3rd).....	189
G-13 Absorption and desorption of copolymer bead (Run. E47: 1st).....	190
G-14 Absorption and desorption of copolymer bead (Run. E47: 2nd).....	191
G-15 Absorption and desorption of copolymer bead (Run. E47: 3rd).....	192
H-1 Data for the calculation of the diffusion coefficient of the copolymers beads.....	194

## LIST OF FIGURES

FIGURE	PAGE
2.1 Determination of polymer solubility parameter by swelling a lightly crosslinked polymer in a series of solvents.....	22
2.2 The effect of solvent power and temperature on a polymer molecule in solution.....	27
2.3 Schematic representation of a chemically crosslinked polymer network swollen by a low molecular weight solvent.....	28
2.4 Representation of aggregation in an ABA block thermoplastic elastomer.....	30
3.1 Rough diagram of suspension copolymerization of styrene-divinylbenzene copolymer beads.....	48
4.1 Bead size distribution of styrene-divinylbenzene copolymer under the effect of monomer phase weight fractions.....	61
4.2 Effect of monomer phase weight fraction on the crosslinking density...	62
4.3 Effect of monomer phase weight fraction on the swelling ratio.....	63
4.4 Bead size distribution of styrene-divinylbenzene copolymer under the effect of agitation rates.....	66
4.5 Effect of agitation rate on the crosslinking density.....	67
4.6 Effect of agitation rate on the swelling ratio.....	67
4.7 Bead size distribution of styrene-divinylbenzene copolymer under the effect of reaction temperatures.....	70

## LIST OF FIGURES (continued)

FIGURE	PAGE
4.8 Effect of reaction temperature on the crosslinking density.....	71
4.9 Effect of reaction temperature on the swelling ratio.....	71
4.10 Bead size distribution of styrene-divinylbenzene copolymer under the effect of reaction times.....	74
4.11 Effect of reaction time on the crosslinking density.....	75
4.12 Effect of reaction time on the swelling ratio.....	76
4.13 Bead size distribution of styrene-divinylbenzene copolymer under the effect of initiator concentrations.....	78
4.14 Effect of initiator concentration on the crosslinking density.....	80
4.15 Effect of initiator concentration on the swelling ratio.....	80
4.16 Bead size distribution of styrene-divinylbenzene copolymer under the effect of crosslinking agent concentrations.....	84
4.17 SEM photographs of the copolymer prepared at different crosslinking agent concentrations ( $\times 50$ ).....	85
4.18 SEM photographs of the copolymer prepared at different crosslinking agent concentrations ( $\times 100$ ).....	86
4.19 SEM photographs of the copolymer prepared at different crosslinking agent concentrations ( $\times 3000$ ).....	87
4.20 Effect of crosslinking agent concentration on the crosslinking density.	88
4.21 Effect of crosslinking agent concentration on the swelling ratio.....	89

## LIST OF FIGURES (continued)

FIGURE	PAGE
4.22 Mechanism for stabilizing polymer dispersion (polystyrene/styrene monomer by hydrolyzed poly(vinyl alcohol) with residual acetate groups.....	91
4.23 Bead size distribution of styrene-divinylbenzene copolymer under the effect of suspending agent concentrations.....	92
4.24 Effect of suspending agent concentration on the swelling ratio.....	94
4.25 Bead size distribution of styrene-divinylbenzene copolymer under the effect of diluent compositions between toluene and heptane.....	97
4.26 SEM photographs of the copolymer prepared at different toluene/heptane ratios ( $\times 50$ ).....	98
4.27 SEM photographs of the copolymer prepared at different toluene/heptane ratios ( $\times 100$ ).....	99
4.28 SEM photographs of the copolymer prepared at different toluene/heptane ratios ( $\times 3000$ ).....	100
4.29 Effect of diluent composition on the crosslinking density.....	102
4.30 Effect of diluent composition on the swelling ratio.....	103
4.31 Bead size distribution of terpolymer beads under the effect of monomer compositions.....	106
4.32 SEM photographs of the copolymer prepared with different third comonomers ( $\times 50$ ).....	107

## LIST OF FIGURES (continued)

FIGURE	PAGE
4.33 SEM photographs of the copolymer prepared with different third comonomers ( $\times 100$ ).....	108
4.34 SEM photographs of the copolymer prepared with different third comonoers ( $\times 3000$ ).....	109
4.35 Comparative solubility parameter of synthetic copolymer beads by swelling experiments.....	113
4.36 A schematic model for the process of pore formation in the copolymerization stage.....	120
4.37 Schematic model of the internally compact crosslinked particles possessing microgel.....	120
4.38 DSC traces of styrene-divinylbenzene copolymers prepared by varying crosslinking agent concentration.....	122
4.39 DSC traces of styrene-divinylbenzene copolymers prepared by varying diluent composition.....	123
4.40 DSC traces of styrene-divinylbenzene copolymers prepared by varying monomer composition.....	124
4.41 Effect of crosslinking agent concentration on glass transition temperature of the copolymer beads.....	125
4.42 Effect of monomer feed composition on glass transition temperature of the terpolymers.....	126

## LIST OF FIGURES (continued)

FIGURE	PAGE
4.43 Absorption of bead with time: Run PS.....	130
4.44 Desorption of bead with time: Run PS.....	130
4.45 Absorption of bead with time: Run B24.....	131
4.46 Desorption of bead with time: Run B24.....	131
4.47 Absorption of bead with time: Run B47.....	132
4.48 Desorption of bead with time: Run B47.....	132
4.49 Absorption of bead with time: Run E24.....	133
4.50 Desorption of bead with time: Run E24.....	133
4.51 Absorption of bead with time: Run E47.....	134
4.52 Desorption of bead with time: Run E47.....	134
4.53 Absorption and desorption of bead with time: Run PS.....	135
4.54 Absorption and desorption of bead with time: Run B24.....	136
4.55 Absorption and desorption of bead with time: Run B47.....	137
4.56 Absorption and desorption of bead with time: Run E24.....	138
4.57 Absorption and desorption of bead with time: Run E47.....	139
B-1 Conceptual representation of a mercury porosimeter.....	158
E-1 FT-IR spectrum of the polystyrene.....	167
E-2 FT-IR spectrum of styrene-divinylbenzene copolymer of Run H04.....	168
E-3 FT-IR spectrum of styrene-divinylbenzene-24% <i>n</i> -butyl acrylate terpolymer of Run B24.....	169

**LIST OF FIGURES (continued)**

FIGURE	PAGE
E-4 FT-IR spectrum of styrene-divinylbenzene-47% <i>n</i> -butyl acrylate terpolymer of Run B47.....	170
E-5 FT-IR spectrum of styrene-divinylbenzene-24% 2-ethyl hexyl acrylate terpolymer of Run E24.....	171
E-6 FT-IR spectrum of styrene-divinylbenzene-47% 2-ethyl hexyl acrylate terpolymer of Run E47.....	172
G-1 Variation of copolymer bead volume with time (Run. PS: 1st).....	178
G-2 Variation of copolymer bead volume with time (Run. PS: 2nd).....	179
G-3 Variation of copolymer bead volume with time (Run. PS: 3rd).....	180
G-4 Variation of copolymer bead volume with time (Run. B24: 1st).....	181
G-5 Variation of copolymer bead volume with time (Run. B24: 2nd).....	182
G-6 Variation of copolymer bead volume with time (Run. B24: 3rd).....	183
G-7 Variation of copolymer bead volume with time (Run. B47: 3rd).....	184
G-8 Variation of copolymer bead volume with time (Run. B47: 2nd).....	185
G-9 Variation of copolymer bead volume with time (Run. B47: 3rd).....	186
G-10 Variation of copolymer bead volume with time (Run. E24: 1st).....	187
G-11 Variation of copolymer bead volume with time (Run. E24: 2nd).....	188
G-12 Variation of copolymer bead volume with time (Run. E24: 3rd).....	189
G-13 Variation of copolymer bead volume with time (Run. E47: 1st).....	190
G-14 Variation of copolymer bead volume with time (Run. E47: 2nd).....	191

**LIST OF FIGURES (continued)**

FIGURE	PAGE
G-15 Variation of copolymer bead volume with time (Run. E47: 3rd).....	192



## ABBREVIATIONS

PS	: polystyrene
P-BuA	: poly( <i>n</i> -butyl acrylate)
P-2-EHA	: poly(2-ethyl hexyl acrylate)
Sty-DVB	: styrene-divinylbenzene copolymer
Sty/DVB/ <i>n</i> -BA	: styrene-divinylbenzene- <i>n</i> -butyl acrylate terpolymer
Sty/DVB/2-EHA	: styrene-divinylbenzene-2-ethyl hexyl acrylate terpolymer
Sty	: styrene
DVB	: divinylbenzene
<i>n</i> -BA	: <i>n</i> -butyl acrylate
2-EHA	: 2-ethyl hexyl acrylate
Tol	: toluene
Hep	: heptane
BPO	: benzoyl peroxide
PVA	: poly(vinyl alcohol)
EtAc	: ethyl acetate
DIBP	: diisobutyl phthalate
Deacl	: decaline
BuAc	: butyl acetate
MIBK	: methyl-isobutyl ketone
DEP	: diethyl phthalate
<i>i</i> -AmA	: isoamyl alcohol

### ABBREVIATIONS (continued)

DOP	: dioctyl phthalate
<i>i</i> -AmAc	: isoamyl acetate
ACP	: acetophenone
$\delta_i$	: solubility parameters
CED	: cohesive energy density
$R_{ij}$	: diluent-polymer distances
$\overline{M}_c$	: number average molecular weight of polymer between crosslinks
$M_o$	: molecular weight of polymer repeat unit
$\rho_p$	: density of polymer
$\rho_s$	: density of solvent
$q$	: crosslinking density
$\phi_p$	: volume fraction of polymer in the swollen gel
$\chi_{12}$	: Flory-Huggins interaction parameter between polymer and solvent
$D$	: diffusion coefficient
$U$	: shear of polymer network alone
$K$	: bulk modulus of polymer network alone
$f$	: frictional coefficient between the network and fluid medium
$\tau$	: characteristic swelling time
$a$	: the final radius of the fully swollen gel

**ABBREVIATIONS (continued)**

$\Delta a_t$	: the difference between the size at time t and that at saturation swelling
$\Delta a_0$	: the total change in radius throughout the entire swelling process
$I$	: the depth of penetration
$r$	: the radius of the cylindrical capillaries
$t$	: time of penetration
$\eta$	: the viscosity of the liquid
$\gamma$	: the surface tension of the liquid
$\theta$	: the contact angle of the liquid on the capillary walls
HPMC	: hydroxypropyl methyl cellulose
HEC	: hydroxyethyl cellulose
b.p.	: boiling point
f.p.	: freezing point
m.p.	: melting point
ppm	: part per million
M	: molecular weight
mol%	: percent by mole
wt%	: percent by weight
SEM	: Scanning Electron Microscope
DSC	: Differential Scanning Calorimeter
FT-IR	: Fourier Transform Infrared Spectrometer

**ABBREVIATIONS (continued)**

KBr	: potassium bromide
mm	: millimeter
°C	: degree Celsius
rpm	: revolution per minute
cm <sup>3</sup>	: cubic centimeter
mm <sup>3</sup>	: cubic millimeter
hrs	: hours
<i>S</i>	: swelling ratio
<i>W<sub>s</sub></i>	: the weight of the copolymer at equilibrium
<i>W<sub>p</sub></i>	: the weight of the dry copolymer
<i>V<sub>s</sub></i>	: molar volume of solvent
<i>V<sub>p</sub></i>	: molar volume of polymer
T <sub>g</sub>	: glass transition temperature
%conv.	: percent conversion
Std. Dev.	: standard deviation
1st	: the first
2nd	: the second
3rd	: the third
Dia.	: diameter
Vol.	: volume
const.	: constant

**ABBREVIATIONS (continued)**

min	: minute
sec	: second
$R_p$	: the polymerization rate
$R_d$	: the rate constant for the initiator decomposition
$R_p$	: the rate constant for the propagation step
$R_t$	: the rate constant for the termination step
Ave.	: average
ASTM	: American Standard of Testing Material
MPa	: megapascal
pp.	: page