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SYNTHESIS OF SUPER-FINE PARTICLES OF POLY(STYRENE-CO-METHYL METHACRYLATE) BY SPG EMULSION POLYMERIZATION

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ได้เตรียมพอลิสไตรีนโคพอลิเมทิลเมทาคริเลต ที่มีขนาดอนุภาคเท่า ๆ กัน โดยการใช้เอสพีจีเมมเบรน หยดของมอนอเมอร์ขนาดเท่า ๆ กัน เกิดขึ้นได้เมื่อมอนอเมอร์ได้ขับผ่านรูพรุนของเมมเบรนภายใต้การควบคุมความดันของแก๊สไนโตรเจน หยดมอนอเมอร์ซึ่งประกอบด้วยมอนอเมอร์เป็นส่วนใหญ่ ตัวเติมไม่ชอบน้ำ และตัวเร่งแขวนลอยอยู่ในวัฏภาคของน้ำที่มีสเตบิไลเซอร์และตัวยับยั้งบรรจุอยู่ หลังจากนั้นได้ถ่ายอิมัลชันสู่ถังปฏิกรณ์ และทำปฏิกิริยาซัสเพนชันพอลิเมอไรเซชัน ณ 75 องศาเซลเซียส ภายใต้บรรยากาศไนโตรเจนเป็นเวลา 24 ชั่วโมง อนุภาคขนาดเท่า ๆ กันของพอลิสไตรีนโคเมทิลเมทาคริเลต ที่มีเส้นผ่านศูนย์กลางในช่วง 7 ถึง 14 ไมโครเมตร และมีการกระจายของขนาดอนุภาคแคบ โดยมีค่าสัมประสิทธิ์ของการเปลี่ยนแปลงใกล้เคียงกันร้อยละ 10 เมื่อใช้เมมเบรนที่มีรูพรุน 1.42 ไมโครเมตร ผลของสารเชื่อมขวาง ตัวเติมไม่ชอบน้ำ ชนิดของตัวเร่ง องค์ประกอบของโคพอลิเมอร์ และการเติมมอนอเมอร์แอลคิลเมทาคริเลต ต่อขนาด การกระจายขนาดอนุภาค และสัณฐานวิทยาของอนุภาค พบว่าขนาดของอนุภาคลดลงและมีการกระจายของขนาดอนุภาคแคบเมื่อเปลี่ยนตัวเติมจากแอลเคนโซ่ยาว เป็นแอลกอฮอล์โซ่ยาว และเอสเทอร์โซ่ยาวตามลำดับ การเกิดอนุภาคขนาดเล็กที่มีความหลากหลายทางสัณฐานวิทยาขึ้นอยู่กับองค์ประกอบในวัฏภาคของน้ำมัน และยังพบว่า อนุภาคที่มีรูปทรงกลมของพอลิสไตรีนโคเมทิลเมทาคริเลต สามารถเตรียมได้เมื่อใช้ปริมาณของสารเชื่อมขวางที่พอเหมาะ และใช้เมทิลพาล์มมิเทตเป็นตัวเติม ยิ่งกว่านั้น ค่าอุณหภูมิสภาพแก้วของโคพอลิเมอร์สามารถควบคุมได้โดยการเปลี่ยนแปลงสัดส่วนของมอนอเมอร์แอลคิลเมทาคริเลต

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Relatively uniform microspheres of poly(styrene-co-methyl methacrylate) were prepared employing a microporous glass membrane (Shirasu porous glass; SPG). The uniform monomer droplets were produced when monomer was allowed to permeate through the membrane pores under a controlled nitrogen pressure. The monomer droplets composed mainly of monomers, hydrophobic additives, and oil-soluble initiator, were suspended in the aqueous phase containing stabilizer and inhibitor, then transferred to a reactor, and subsequent suspension polymerization followed. The droplets obtained were polymerized at 75°C under a nitrogen atmosphere for 24 h. The uniform poly(styrene-co-methyl methacrylate) microspheres with diameters ranging from 7-14 μm, and a narrow particle size distribution with a coefficient of variation close to 10% were prepared using membranes pore size 1.42 μm. The effects of crosslinking agent, hydrophobic additives, oil-soluble initiator, the composition of the copolymer, and the addition of alkyl methacrylate monomers on the particles size, particle size distribution, morphologies were investigated. It was found that the particles size decreased with a narrow size distribution when the additives were changed from long-chain alkane to long-chain alcohols and long-chain esters, respectively. Various microspheres with different morphologies were obtained, depending on the composition of the oil phase. The spherical poly(styrene-co-methyl methacrylate) particles without phase separation was obtained when using an adequate amount of crosslinking agent and methyl palmitate as additive. Furthermore, the glass transition temperature (Tg) of copolymer can be controlled by the various fractions of lower Tg monomer of alkyl methacrylate monomers.

ภาควิชา ....-............ ลายมือชื่อนิสิต ......R. Nuisin......
สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา ......Suda Kiatkamjornwong......
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CONTENTS

	PAGE
ABSTRACT (IN THAI)..	
ABSTRACT (IN ENGLISH)..	iv
ACKNOWLEDGEMENTS...	v
CONTENTS...	vi
LIST OF TABLES...	vi
LIST OF FIGURES..	xi
ABBREVIATIONS..	xix
CHAPTER	
1 INTRODUCTION...	1
1.1 The interest of the membrane emulsification..................	1
1.2 Objectives of the research work...............................	2
1.3 Scope of the research work....................................	3
2 RETICAL BACKGROUND...	4
2.1 General features of polymerization process....................	5
2.2 The Theory of SPG Emulsification..............................	5
2.2.1 The formation of droplets...................................	6
2.2.2 Preparation of each emulsion type by SPG emulsification.....	8
2.2.2.1 Preparation of an oil-in-water (O/W) emulsion.............	8
2.2.2.2 Preparation of water-in-oil (W/O) emulsion................	9
2.2.2.3 Preparation of a double emulsion..........................	9
2.3 Literature Review...	10
3 EXPERIMENTAL...	15
3.1 Materials, apparatus, and analytical instruments..............	15
3.1.1 Materials...	15
3.1.1.1 Monomers..	15
3.1.1.2 Initiator...	16
3.1.1.3 Hydrophobic additives/reagents............................	16

CONTENTS (Continued)

3.1.1.4 Stabilizers.................................. 17

3.1.1.5 Solvents.................................. 18

3.1.1.6 Other chemicals.................................. 18

3.1.2 Apparatus.................................. 18

3.1.2.1 SPG emulsification apparatus.................................. 18

3.1.2.2 Polymerization.................................. 19

3.1.3 Analytical instruments.................................. 19

3.2 Procedures.................................. 20

3.2.1 Purification of monomers.................................. 20

3.2.2 Emulsification.................................. 20

3.2.2.1 Preparative condition of copolymer by using theSPG pore size 1.42 μm 22

3.2.2.2 Preparative condition of copolymer by using the SPG pore size 0.90 μm......... 22

3.2.3 Polymerization.................................. 24

3.2.4 Treatment of polymer particles.................................. 24

3.3 Characterization.................................. 24

3.3.1 Percent conversion of monomer.................................. 24

3.3.2 Monomer droplets diameter.................................. 24

3.3.3 Polymer particles diameter.................................. 25

3.3.4 Average molecular weight and molecular weight distribution (GPC).................................. 26

3.3.5 Glass transition of polymer.................................. 26

3.3.6 Functional group of copolymer.................................. 27

3.3.7 Copolymer composition.................................. 27

4 RESULTS AND DISCUSSION.................................. 30

4.1 Effect of crosslinking agent.................................. 30

4.1.1 Non-crosslinked poly(styrene-co-MMA) microspheres.................................. 30

4.1.2 Synthesis of solid uniform crosslinked poly(styrene-co-MMA) microspheres.............. 30

CONTENTS (Continued)

4.1.2.1 Phase separation in lightly crosslinked networks.................................... 31

4.1.2.2 Phase separation in highly crosslinked networks.................................... 35

4.2 Effect of additives.. 36

4.2.1 Effect of additives on particle sizes and particle size distribution of poly(styrene-co-MMA)......... 36

4.2.2 Effect of various additives on morphologies........ 37

4.2.3 Effect of composition of hydrophobic additives.... 41

4.2.3.1 Average diameter of poly(styrene-co-MMA) particles............................ 41

4.2.3.2 Morphologies of poly(styrene-co-MMA) particles.................................... 42

4.2.4 Effect of additive on particle size and size distribution of poly(styrene-co-n-BMA) and poly(styrene-co-2-EHMA) particles 49

4.2.5 Effect of additive on morphologies of poly(styrene-co-n-BMA) and poly(styrene-co-2-EHMA) particles 49

4.3 Effect of initiator type.. 59

4.4 Effect of copolymer composition of poly(styrene-co-MMA) 64

4.4.1 Effect of copolymer composition on particle size and particle size distribution of poly(styrene-co-MMA)... 65

4.4.2 Effect of copolymer composition on morphologies of particles.. 65

4.4.3 Microstructure of poly(styrene-co-MMA) using ^{1}H NMR Spectroscopy................................ 69

4.4.4 Determination of composition of poly(styrene-co-MMA) by FT-IR spectroscopy....................... 73

CONTENTS (Continued)

4.5 Effect of addition monomer........ 77
4.5.1 Effect of various alkyl methacrylate monomer compositions on particle size and size distribution of the terpolymer 77
4.5.2 Effect of various alkyl methacrylate monomer compositions on morphologies 77
4.5.3 Predicted terpolymer composition by ^{1}H NMR..... 85
4.5.4 Effect of various alkyl methacrylate monomer compositions on glass transition temperature...... 87
5 CONCLUSION........ 90
REFERENCES........ 92
APPENDICE........ 96
A Chain copolymeization........ 96
A-1 Type of copolymers........ 96
A-2 Copolymer composition........ 97
A-2 a Copolymer equation........ 97
A-2 b Copolymer equation; statistical derivation......... 98
A-2 c Variation of copolymer composition with conversion 101
A-3 Microstructure of copolymer........ 103
A-4 Multicomponent copolymerization........ 104
B Glass transition temperature of random copolymers........ 107
C Nuclear magnetic resonance spectra........ 108
D Differential scanning calorimeter........ 114
E Fourier-Transform infrared spectra........ 119
VITA........ 121

LIST OF TABLES

TABLE **PAGE**

2.1 Comparison of characteristics of different polymerization processes.. 5

4.1 Polymerization recipe of poly(styrene-co-MMA) and experimental results with and without crosslinking agent using SPG pore size 1.42 μm... 32

4.2 Polymerization recipe and experimental results of poly(styrene-co-MMA) with various hydrophobic additives using SPG pore size 1.42 μm... 44

4.3 Polymerization recipe and experimental results of poly(styrene-co-n-BMA) and poly(styrene-co-2-EHMA) with various hydrophobic additives using SPG pore size 1.42 μm............. 52

4.4 Characterization of poly(styrene-co-n-BMA) and poly(styrene-co-2-EHMA); the feed composing 50:50 weight ratio of St-n-BMA and St-2-EHMA.. 51

4.5 Effect of initiator type on particle size and size distribution, molecular weight and molecular weight distribution of poly(styrene-co-MMA).. 59

4.6 Polymerization recipe and experimental results of poly(styrene-co-MMA) particles with various compositions of monomer...... 64

4.7 Composition of styrene (f_S), copolymer composition (F_S), and triad relative intensities of poly(styrene-co-MMA)................ 69

4.8 Assignment of the FT-IR spectrum of poly(styrene-co-MMA)... 73

4.9 Copolymer composition of styrene in copolymer from FT-IR.... 73

4.10 Copolymerization recipe and experimental results for non-crosslinked terpolymer poly(styrene-co-MMA-co-n-BMA) and poly(styrene-co-MMA-co-2-EHMA)................................ 79

4.11 Copolymerization recipe and experimental results for crosslinked terpolymer poly(styrene-co-MMA-co-n-BMA) and poly(styrene-co-MMA-co-2-EHMA)................................ 84

LIST OF TABLES (Continued)

4.12 Predicted and experimental composition in radical terpolymerization.. 86

LIST OF FIGURES

FIGURE **PAGE**

2.1 Cross section of membrane from SEM image.................. 6

2.2 Applied pressure corresponding to formation of the emulsion droplets.. 7

2.3 Average diameters of emulsion droplets as a function of pore size of SPG membrane 8

3.1 SPG emulsification kit.. 21

3.2 The cross- section model of SPG membrane..................... 22

3.3 Photographs of emulsion droplets taken by an optical microscope: a) Using SPG pore size 1.42 μm, and b) SPG pore size 0.9 μm, respectively..................................... 23

3.4 Suspension polymerization reactor................................ 29

4.1 SEM photographs of non-crosslinked poly(styrene-co-MMA) particles: a) St/MMA 80:20 wt% ratio in the feed, and b) 50:50 wt% ratio in monomer feed................................ 31

4.2 SEM photographs of crosslinked poly(styrene-co-MMA) particles: a) DVB 6.67 wt%, b) EGDMA 10 wt%, c.) EGDMA 20 wt%, and d) EGDMA 42 wt% of monomer in the feed, respectively... 33

4.3 Schematic drawing of crosslinked polymer network synthesized during free-radical polymerization.................. 34

4.4 Histograms of size distribution of poly(styrene-co-MMA); Effect of additives a) Hexadecane, b) 1-Hexadecanol, c) Methyl palmitate, d) Bees wax, respectively................. 37

4.5 Interfacial tension causes the equilibrium in the right drawing, where the circular shape is formed 36

4.6 a) Photographs of poly(styrene-co-MMA) in Run 143 without additive: a) Photograph of the droplets taken by an optical microscope, and b) SEM photograph; CV = 20.15%, and $\overline{D}_p = 8.12$ μm.. 39

LIST OF FIGURES (Continued)

4.7 SEM photographs of poly(styrene-co-MMA) particles by various additives: a) Hexadecane, b) 1-Hexadecanol, c) Methyl palmitate, d) Bees wax, respectively.................... 45

4.8 Average diameter of polymer particles with various compositions of hydrophobic additives......................... 48

4.9 SEM photographs of poly(styrene-co-MMA) particles by various compositions of additives: a) HD/(HD-OH) 50:50 wt% ratio, b) HD/(HD-OH) 25:75 wt% ratio, c) HD/MP 50:50 wt% ratio, and d) HD/MP 25:75 wt% ratio, respectively.. 46

4.10 SEM photographs of poly(styrene-co-MMA) particles by various compositions of additives: a) (HD-OH)/MP 50:50 wt% ratio, b) MP/BW 50:50 wt% ratio, and c) MP/BW 75:25 wt% ratio, respectively... 47

4.11 Schematic diagram for the morphology classification in the preparation of poly(styrene-co-MMA), the wt% ratio of St/MMA in the feed of 50:50..................................... 48

4.12 Histograms of the size distribution; emulsion droplets and polymer particles; Effect of additives on St-n-BMA copolymer: a) Hexadecane, b) 1-Hexadecanol, c) Methyl palmitate, and d) Bees wax, respectively........................ 53

4.13 Histograms of the size distribution; emulsion droplets and polymer particles; Effect of additives on St-2-EHMA copolymer: a) Hexadecane, b) 1-Hexadecanol, c) Methyl palmitate, and d) Bees wax, respectively....................... 54

4.14 SEM photographs of poly(styrene-co-n-BMA) particles by various additives: a) Hexadecane, b) 1-Hexadecanol, c) Methyl palmitate, and d) Bees wax, respectively.............. 55

4.15 SEM photographs of poly(styrene-co-2-EHMA) particles by various additives: a) Hexadecane, b) 1-Hexadecanol, c) Methyl palmitate, and d) Bees wax, respectively.............. 56

LIST OF FIGURES (Continued)

4.16 DSC curves of poly(styrene-co-n-BMA) with a weight ratio of styrene/n-BMA 50:50 in the feed............................ 57

4.17 DSC curves of poly(styrene-co-2-EHMA) with a weight ratio of styrene/2-EHMA 50:50 in the feed.......................... 58

4.18 Histograms of the size distribution, emulsion droplets and polymer particles: a) BPO, b) AIBN, and c) ADVN, respectively.. 62

4.19 GPC chromatogram of poly(styrene-co-MMA); Effect of initiator: a) BPO, b) AIBN, and c) ADVN, respectively........ 61

4.20 SEM photographs of poly(styrene-co-MMA); Effect of initiator: a) BPO, b) AIBN, and c) ADVN, respectively........ 63

4.21 Histograms of the size distribution of homopolymer and St-MMA copolymer; Effect of copolymer composition St/MMA in the feed: a) Polystyrene, b) PMMA, c) 75:25, d) 50:50, e) 25:75, wt% ratio, respectively................................. 67

4.22 SEM photographs of homopolymer and St-MMA copolymer particles; Effect of copolymer composition St-MMA in the feed a) Polystyrene b) PMMA, c) 75:25, d) 50:50, e) 25:75 wt% ratio respectively... 68

4.23 ^{1}H NMR spectrum of poly(styrene-co-MMA) weight ratio of St/MMA in the feed a) 75:25, b) 50:50 70

4.23 (continued) ^{1}H NMR spectrum of poly(styrene-co-MMA) weight ratio of St/MMA in the feed c) 25:75................. 71

4.24 Theoretical triad proportions, calculated from Markov equation for St/MMA copolymer 72

4.25 FT-IR spectrum of a) Polystyrene, b) PMMA homopolymer 74

4.25 (continued) FT-IR spectrum of poly(styrene-co-MMA) weight ratio of St/MMA in the feed c) 75:25, and d) 50:50 ... 75

4.25 (continued) FT-IR spectrum of poly(styrene-co-MMA) weight ratio of St/MMA in the feed e) 25:75 76

LIST OF FIGURES (Continued)

4.26	FT-IR calibration curve...	76
4.27	Histograms of the size distribution; emulsion droplets and polymer particles; weight fraction of St/MMA/n-BMA in the feed: a) 50:40:10, b) 50:30:20, c) 50:20:30, and d) 50:10:40, respectively..	80
4.28	Histograms of the size distribution; emulsion droplets and polymer particles; weight% ratio of St/MMA/2-EHMA in the feed: a) 50:40:10, b) 50:30:20, and c) 50:20:30, respectively..	81
4.29	SEM photographs of poly(styrene-co-MMA co-n-BMA) particles, weight% ratio of St/MMA/n-BMA in the feed: a) 50:40:10, b) 50:30:20, c) 50:20:30, and d) 50:10:40, respectively..	82
4.30	SEM photographs of poly(styrene-co-MMA co-2-EHMA) particles, weight% ratio of St/MMA/2-EHMA in the feed: a) 50:40:10, b) 50:30:20, c) 50:20:30, and d) 50:10:40, respectively..	83
4.31	Relationship between Tg of non-crosslinked terpolymer with various compositions of monomer: a) poly(styrene-co-MMA-co-n-BMA), and b) poly(styrene-co-MMA-co-2-EHMA)...	88
4.32	Relationship between Tg of crosslinked terpolymer with various compositions of monomer: a) poly(styrene-co-MMA -co-n-BMA), and b) poly(styrene-co-MMA-co-2-EHMA)...	89
C-1	^{1}H NMR spectrum of poly(styrene-co-MMA-co-n-BMA) weight% ratio of St/MMA/n-BMA in the feed: a) 50:40:10, b) 50:35:15..	107
C-1	(continued) ^{1}H NMR spectrum of poly(styrene-co-MMA-co-n-BMA) weight% ratio of St/MMA/n-BMA in the feed: c) 50:30:20, d) 50:20:30...	108
C-1	(continued) ^{1}H NMR spectrum of poly(styrene-co-MMA-co-n-BMA) weight% ratio of St/MMA/n-BMA in the feed: e) 50:10:40...	109

LIST OF FIGURES (Continued)

C-2	^{1}H NMR spectrum of poly(styrene-co-MMA-co-2-EHMA) weight% ratio of St/MMA/2-EHMA in the feed: a) 50:40:10, b) 50:35:15	110
C-2	(continued) ^{1}H NMR spectrum of poly(styrene-co-MMA-co-2-EHMA) weight% ratio of St/MMA/2-EHMA in the feed: c) 50:30:20 d) 50:20:30	111
C-2	(continued) ^{1}H NMR spectrum of poly(styrene-co-MMA-co-2-EHMA) weight% ratio of St/MMA/2-EHMA in the feed: e) 50:10:40	112
D-1	DSC curves of polystyrene and PMMA homopolymer	113
D-2	DSC curves of polystyrene and DSC curves of non-crosslinked poly(styrene-co-MMA-co-n-BMA) weight fraction of St/MMA/n-BMA in the feed: a) 50:40:10 (Run 1402), b) 50:30:20 (Run 1403), c) 50:20:30 (Run 1404), and d) 50:10:40 (Run 1405), respectively	114
D-3	DSC curves of non-crosslinked poly(styrene-co-MMA-co-2-EHMA) weight fraction of St/MMA/2-EHMA in the feed a) 50:40:10 (Run 1602), b) 50:30:20 (Run 1603), c) 50:20:30 (Run 1604), and d) 50:10:40 (Run 1605), respectively	115
D-4	DSC curves of crosslinked poly(styrene-co-MMA-co-n-BMA) weight fraction of St/MMA/n-BMA in the feed a) 50:40:10, (Run 1407), b) 50:30:20 (Run 1408), c) 50:20:30 (Run 1409), and d) 50:10:40 (Run 1410), respectively	116
D-5	DSC curves of crosslinked poly(styrene-co-MMA-co-2-EHMA) weight fraction of St/MMA/2-EHMA in the feed: a) 50:40:10 (Run 1607), b) 50:30:20 (Run 1608), c) 50:20:30 (Run 1609), and d) 50:10:40 (Run 1610), respectively	117
E-1	FT-IR spectrum of poly(styrene-co-MMA) weight% ratio of St/MMA in the feed 50:50 with various additives: a) Hexadecane b) 1-Hexadecanol	118

LIST OF FIGURES (Continued)

E-1 (continued) FT-IR spectrum of poly(styrene-co-MMA) weight% ratio of St/MMA in the feed 50:50 with various additives: c.) Methyl palmitate, d.) Bees wax.................. 119

ABBREVIATIONS

SPG	Shirasu porous glass
St	styrene
MMA	methyl methacrylate
n-BMA	n-butyl methacrylate
2-EHMA	2-ethylhexyl methacrylate
EGDMA	ethyleneglycol dimethacrylate
DVB	divinylbenzene
BPO	benzoyl peroxide
AIBN	2,2′-azo-bis-isobutyronitrile
ADVN	2,2′-azo-bis-2,4-dimethylvaleronitrile
HD	hexadecane
HD-OH	1-hexadecanol
MP	methyl palmitate
BW	bees wax
μm	micrometer
nm	nanometer
wt	weight
$\overline{D}_m$	membrane pore diameter
P_c	critical pressure
γ	interfacial tension
$\overline{D}_e$	average diameter of emulsion droplets
$\overline{D}_p$	average diameter of polymer particles
σ	standard deviation
CV	coefficient of variation
$\overline{M}_n$	number-average molecular weight
$\overline{M}_w$	weight-average molecular weight
k_d	decomposition rate constant of initiator
f	feed composition
F	copolymer composition

ABBREVIATIONS (Continued)

Tg	glass transition temperature
δ	chemical shift
OM	optical microscopy
SEM	scanning electron microscopy
GPC	gel permeation chromatography
NMR	nuclear magnetic resonance spectroscopy
DSC	differential scanning calorimetry
FT-IR	Fourier-transform infrared spectroscopy