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**Synthesis and Characterization of Novel
Super-fine Particle-sized Polymers**

Miss Saowaluk Apiwattananon

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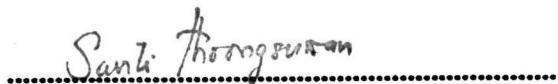
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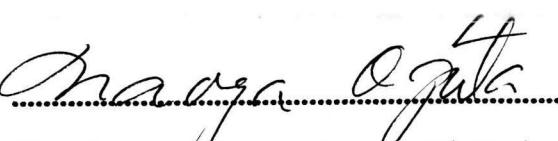
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งานวิจัยนี้ได้สังเคราะห์และศึกษาสมบัติของโพลิเมอร์สหพันธุ์ของสไตรินและเมทิลเมทา-
คริเลตที่มีขนาดอนุภาคเล็กพิเศษ ด้วยวิธีสเปอร์ชันโคโพลิเมอไรเซชัน โดยมีโพลิเมทิลไวนิล
อีเทอร์ เป็นโพลิเมอร์เมทริกซ์ชั่งละลายในสารละลายผิวเผือนอกจากน้ำ และน้ำมัน เช่น ได้
ตรวจสอบโพลิเมอร์สหพันธุ์ที่ได้ด้วย NMR และ EA ศึกษาขนาดอนุภาคด้วย SEM น้ำหนักโมเล
กุลเฉลี่ยต่าง ๆ ด้วย GPC และได้ศึกษาสมบัติทางความร้อนด้วย DSC, TG/DTA นอกจากนี้ ยัง
พิสูจน์การตกค้างของโพลิเมอร์เมทริกซ์ในโพลิเมอร์สหพันธุ์ โดยการศึกษาสมบัติพื้นผิว โดยใช้
XPS ในงานวิจัยนี้ ได้สังเคราะห์โพลิเมอร์สหพันธุ์ด้วยวิธีบัลล์ และโซลูชันโคโพลิเมอไรเซชัน
โดยทำการทดลองเช่นเดียวกับสเปอร์ชันโคโพลิเมอไรเซชัน แต่ปราศจากโพลิเมอร์เมทริกซ์ เพื่อ
ศึกษาอิทธิพลของโพลิเมอร์เมทริกซ์

โพลิเมอร์สหพันธุ์แบบดิสเปอร์ชันที่ได้มีลักษณะทรงกลม มีขนาดอยู่ในช่วง 1 ถึง 5 ไม
โครเมตร พบร้าน้ำหนักโมเลกุลเฉลี่ยสูงในอนุภาคขนาดเล็ก โพลิเมอร์สหพันธุ์ที่สังเคราะห์ได้
จากระบบโซลูชันและบัลล์โคโพลิเมอไรเซชันชั่งไม่มีโพลิเมอร์เมทริกซ์ อนุภาคจับตัวเป็นกลุ่มก้อน
หรือเป็นแผ่น ไม่สามารถพาณิชย์ได้ ขนาดอนุภาคที่ใหญ่ที่สุดและเล็กที่สุดของโพลิเมอร์
สหพันธุ์แบบดิสเปอร์ชัน คือ โพลิเมทิลเมทาคริเลต และโพลิสไตริน ตามลำดับ ขนาดของ
อนุภาคลดลงและมีการกระจายตัวของอนุภาคแคบลง เมื่อมีการป้อนสไตรินมากขึ้น นอกจากนี้
ขนาดของอนุภาคยังถูกควบคุมโดยการเปลี่ยนอัตราส่วนสารละลายผิวเผือนอกจากนี้
การทำงานอยู่ในสารละลายผิวเผือน ขนาดของอนุภาคลดลง ค่าการละลายของโพลิเมอร์เมทริกซ์ในตัวทำ
ละลาย อาจเป็นองค์ประกอบสำคัญในการควบคุมการจัดตัวของโพลิเมอร์เมทริกซ์ เป็นผลให้เกิด
ความแตกต่างของปริมาตรอิสระในระบบโพลิเมอไรเซชัน นำไปสู่ความแตกต่างของอนุภาคที่เกิด
ขึ้นในที่สุด อย่างไรก็ตามไม่พบอนุภาคขนาดใหญ่ในระบบที่ไม่มีการทำanol และ 20% เอทานอล
แต่พบขนาดอนุภาคเล็กมาก ซึ่งไม่เป็นไปตามแนวโน้มที่กล่าวข้างต้น อุณหภูมิของปฏิกริยาที่สา
มารถสังเคราะห์โพลิเมอร์สหพันธุ์แบบดิสเปอร์ชัน อยู่ในช่วง 50 ถึง 64 °C. ที่อุณหภูมิ 40 °C.
ปฏิกริยาไม่สามารถเกิดได้ และที่ 73 °C. อนุภาคเกะรูมกันเป็นก้อน เมื่ออุณหภูมิปฏิกริยา
โคโพลิเมอไรเซชันเพิ่มขึ้น ขนาดอนุภาคใหญ่ขึ้นและการกระจายตัวของอนุภาคกว้างขึ้น งานวิจัยนี้
ได้อธิบายผลของตัวแปรต่าง ๆ ด้วย

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ปีการศึกษา ๒๕๓๗

ดำเนินชื่อผู้เขียน Saowaluk Apwattanawon
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**KEY WORDS: DISPERSION POLYMERIZATION/ POLY(STYRENE-CO-METHYL
METHACRYLATE)MICROSPHERE**

**SAOWALUK APIWATTANANON: SYNTHESIS AND CHARAC-
TERIZATION OF NOVEL SUPER-FINE PARTICLE-SIZE POLYMERS**

THESIS ADVISOR: ASSOC. PROF.SUDA KIATKAMJORNWONG, Ph.D.,

THESIS CO-ADVISOR: PROF. NAOYA OGATA, Ph.D., 167 pp

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The objectives of this research work are the synthesis and characterization of the super-fine particles of poly(styrene-co-methyl methacrylate) by a dispersion copolymerization technique. Dispersion copolymerization of styrene and methyl methacrylate was carried out in the mixed solvent of ethanol and n-hexane where poly(methyl vinyl ether) was used as a matrix polymer. The copolymer compositions were identified by NMR and EA, the particle sizes were characterized by SEM, the average-molecular weights by GPC, FT-IR was used to characterize the functional groups, XPS was used for the surface analysis and DSC,TG/DTA were for the thermal analysis. The effects of matrix polymer, feed ratios, solvent mixing ratios and reaction temperatures were also investigated. To study the effect of the matrix polymer, solution and bulk copolymerizations were also carried out under the same set of conditions in the absence of PMVE.

The results indicated that all the dispersion copolymer particles were obtained in a spherical shape with the size range of 1-5 μm . The average-molecular weights became larger in the smaller particles. In contrast, when the systems were polymerized without the PMVE matrix polymer, the copolymers in solution and bulk copolymerizations were aggregated and formed in random shapes. It was found that the biggest and smallest particles were obtained in the homopolymers of PMMA and PS, respectively. When increasing the styrene feed, the particle sizes decreased with a narrower size distribution. The particle sizes of the dispersion copolymers were found to be controlled by changing the solvent mixing ratios. The increase in ethanol content resulted in smaller particle sizes. Solubility of the matrix polymer containing a good solvent is probably the main factor controlling the morphology of the matrix polymer and providing different free volumes of the polymerizing system that leads to different particle sizes. However, the bigger particles were not found in the 0 and 20% ethanol contents; surprisingly, the particle size and size distribution of the copolymers were very small with narrow distributions. The appropriate temperature range for this dispersion copolymerization was 50 to 64°C. The reaction did not occur at 40°C and it gave the agglomerated particles at 73°C. The particle size and size distribution were increased and became broader with increasing the reaction temperatures. The effects of each parameter were discussed.

ภาควิชา วิศวกรรมเคมี - ไมโครไบโอด์

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ABBREVIATIONS

| | |
|----------------|--|
| St | styrene |
| MMA | methyl methacrylate |
| PS | polystyrene |
| PMMA | poly(methyl methacrylate) |
| PMVE | poly(methyl vinyl ether) |
| AIBN | α,α' -Azobis-iso-butyronitrile |
| EtOH | ethanol |
| g | gram |
| ml | milliliter |
| μm | micrometre |
| S.D. | standard deviation |
| f | feed composition |
| F | copolymer composition |
| wt | weight |
| δ | solubility parameter |
| M_n | number-average molecular weight |
| M_w | weight-average molecular weight |
| cps | count per second |
| T _g | glass transition temperature |
| T _d | decomposition temperature |
| kV | kilovolt |
| mA | milliampere |
| GPC | gel permeation chromatography |
| SEM | scanning electron microscopy |
| EA | elemental analysis |
| XPS | X-ray photoelectron spectroscopy |
| DSC | differential scanning calorimeter |
| TG/DTA | thermal gravimetry/differential thermal analysis |
| NMR | nuclear magnetic resonance spectroscopy |
| FT-IR | Fouier-transform infrared spectroscopy |