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

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งานวิจัยนี้ได้สังเคราะห์และศึกษาสมบัติของโพลิเมอร์สหพันธ์ของสไตรีนและเมทิลเมทา-
ครีเลตที่มีขนาดอนุภาคเล็กพิเศษ ด้วยวิธีดีสเปอร์ชันโคโพลิเมโรเซชัน โดยมีโพลิเมทิลไวนิล
อีเทอร์ เป็นโพลิเมอร์เมทริกซ์ซึ่งละลายในสารละลายผสมของเอทานอลและนอร์มัลเฮกเซน ได้
ตรวจสอบโพลิเมอร์สหพันธ์ที่ได้ด้วย NMR และ EA ศึกษาขนาดอนุภาคด้วย SEM น้ำหนักโมเล
กุลเฉลี่ยต่าง ๆ ด้วย GPC และได้ศึกษาสมบัติทางความร้อนด้วย DSC, TG/DTA นอกจากนี้ ยัง
พิสูจน์การตกค้างของโพลิเมอร์เมทริกซ์ในโพลิเมอร์สหพันธ์ โดยการศึกษาสมบัติพื้นผิว โดยใช้
XPS ในงานวิจัยนี้ ได้สังเคราะห์โพลิเมอร์สหพันธ์ด้วยวิธีบัลค์ และโซลูชันโคโพลิเมโรเซชัน
โดยทำการทดลองเช่นเดียวกับดีสเปอร์ชันโคโพลิเมโรเซชัน แต่ปราศจากโพลิเมอร์เมทริกซ์ เพื่อ
ศึกษาอิทธิพลของโพลิเมอร์เมทริกซ์

โพลิเมอร์สหพันธ์แบบดีสเปอร์ชันที่ได้มีลักษณะทรงกลม มีขนาดอยู่ในช่วง 1 ถึง 5 ไม
ครเมตร พบค่าน้ำหนักโมเลกุลเฉลี่ยสูงในอนุภาคขนาดเล็ก โพลิเมอร์สหพันธ์ที่สังเคราะห์ได้
จากระบบโซลูชันและบัลค์โคโพลิเมโรเซชันซึ่งไม่มีโพลิเมอร์เมทริกซ์ อนุภาคจับตัวเป็นกลุ่มก้อน
หรือเป็นแผ่น ไม่สามารถหาขนาดอนุภาคได้ ขนาดอนุภาคที่ใหญ่ที่สุดและเล็กที่สุดของโพลิเมอร์
สหพันธ์แบบดีสเปอร์ชัน คือ โพลิเมทิลเมทาครีเลต และโพลีสไตรีน ตามลำดับ ขนาดของ
อนุภาคลดลงและมีการกระจายตัวของอนุภาคแคบลง เมื่อมีการป้อนสไตรีนมากขึ้น นอกจากนี้
ขนาดของอนุภาคยังถูกควบคุมโดยการเปลี่ยนอัตราส่วนสารละลายผสม กล่าวคือ เมื่อเพิ่มปริมาณ
เอทานอลในสารละลายผสม ขนาดของอนุภาคลดลง ค่าการละลายของโพลิเมอร์เมทริกซ์ในตัวทำ
ละลาย อาจเป็นองค์ประกอบสำคัญในการควบคุมการจัดตัวของโพลิเมอร์เมทริกซ์ เป็นผลให้เกิด
ความแตกต่างของปริมาตรอิสระในระบบโพลิเมโรเซชัน นำไปสู่ความแตกต่างของอนุภาคที่เกิด
ขึ้นในที่สุด อย่างไรก็ตามไม่พบอนุภาคขนาดใหญ่ในระบบที่ไม่มีเอทานอลและ 20% เอทานอล
แต่พบขนาดอนุภาคเล็กมาก ซึ่งไม่เป็นไปตามแนวโน้มที่กล่าวข้างต้น อุณหภูมิของปฏิกิริยาที่สา
มารถสังเคราะห์โพลิเมอร์สหพันธ์แบบดีสเปอร์ชัน อยู่ในช่วง 50 ถึง 64 °C ที่อุณหภูมิ 40 °C
ปฏิกิริยาไม่สามารถเกิดได้ และที่ 73 °C อนุภาคเกาะรวมกันเป็นก้อน เมื่ออุณหภูมิปฏิกิริยา
โคโพลิเมโรเซชันเพิ่มขึ้น ขนาดอนุภาคใหญ่ขึ้นและการกระจายตัวของอนุภาคกว้างขึ้น งานวิจัยนี้
ได้อธิบายผลของตัวแปรต่าง ๆ ด้วย

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KEY WORDS: DISPERSION POLYMERIZATION/ POLY(STYRENE-CO-METHYL METHACRYLATE)MICROSPHERE

SAOWALUK APIWATTANANON: SYNTHESIS AND CHARACTERIZATION OF NOVEL SUPER-FINE PARTICLE-SIZE POLYMERS

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

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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.

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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