



รายงานวิจัยฉบับสมบูรณ์

โครงการ อิทธิพลของไวทิลมอนอเมอร์ต่อการเกิดเป็นอนุภาคนาโน แบบ core-shell

ที่มี Polyethyleneimine (PEI) เป็นองค์ประกอบหลัก

โดย อ.ดร. พันธุ์ญา สุนันทบุรณ และคณะ

กันยายน 2550

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Polyethyleneimine (PEI) เป็นองค์ประกอบหลัก

คณะผู้วิจัย

1. ดร.พันธ์ญา สุนันทบุรณ ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล
2. ดร.ประมวล ตั้งบริบูรณ์รัตน์ (นักวิจัยที่ปรึกษา) ภาควิชาเคมี คณะวิทยาศาสตร์

มหาวิทยาลัยมหิดล

สนับสนุนโดยสำนักงานคณะกรรมการการอุดมศึกษา และสำนักงานกองทุนสนับสนุนงานวิจัย

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Abstract

Project code: MRG4880124

Project title: Effects of Vinyl Monomers on the Formation on Polyethyleneimine-based Core-Shell Nanoparticles

Investigator: Panya Sunintaboon, Department of Chemistry, Faculty of Science, Mahidol University

E-mail address: scpsu@mahidol.ac.th

Various core-shell nanoparticle latexes with a PEI shell were prepared from styrene, n-butyl acrylate, ethyl acrylate, methyl methacrylate, and methacrylic acid by the emulsifier-free emulsion polymerization initiated by a PEI/t-butyl hydroperoxide(TBHP) redox pair. pHs of PEI solution, 7 and 11, adjusted by concentrated hydrochloric acid also showed a dramatic effect on the particle formation.

Stable particles of PMMA/PEI and PS/PEI can be prepared from both pHs 7 and 11 of PEI, while those of PnBA/PEI and PEA/PEI were prepared only at PEI pH 7. In contrast, stable particles of PMAA/PEI cannot be obtained, instead, gel products were obtained at both pHs of PEI. The effect of the selected vinyl monomers on the formation of particles were compared from latexes possibly prepared at PEI pH 7, which were PMMA/PEI, PEA/PEI, PnBA/PEI, PS/PEI. It was found that the type of monomers differently affected % monomer conversion, particle size, % grafting, and % grafting efficiency.

The type and strength of particle surface charge were confirmed by a ζ -potential measurement. Degree of protonation of PEI strongly influenced this value. Images from transmission electron microscope (TEM) clearly revealed the morphology of the particles. The resulted grafted copolymers of the corresponding latexes were characterized by an ATR-FTIR technique. In addition, the effect of ethanol as a cosolvent on the formation of PS/PEI at pH 7 was studied as well. It was found that upon increasing the amount of ethanol, % styrene conversion was not significantly altered, however, the particle size was increased.

Key words: core-shell nanoparticle; vinyl monomer; emulsifier-free; PEI.

บทคัดย่อ

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ชื่อโครงการ: อิทธิพลของไวโนลมอนอเมอร์ต่อการเกิดเป็นอนุภาคนาโน แบบ core-shell ที่มี Polyethyleneimine (PEI) เป็นองค์ประกอบหลัก

ชื่อนักวิจัย: นายพันธุ์ญา สุรินทร์บุรณ์ ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล

E-mail address: scpsu@mahidol.ac.th

ในงานวิจัยนี้ได้มีการศึกษาอิทธิพลของไวโนลมอนอเมอร์ชนิดต่างๆคือ styrene (St), n-butyl acrylate (nBA), ethyl acrylate(EA), methyl methacrylate (MMA), และ methacrylic acid (MAA) ในการ สังเคราะห์อนุภาคนาโนแบบ core-shell โดยกระบวนการ emulsion grafted-copolymerization ที่ปราศจากการเติมสาร ลดแรงตึงผิว ในระบบการสังเคราะห์นี้จะใช้ polyethyleneimine (PEI) ซึ่งเป็นพอลิเมอร์ที่มีละลาย น้ำได้ และมีหมู่เอมีนเป็นองค์ประกอบ เป็นพอลิเมอร์หลักสำหรับการกราฟท์พอลิเมอร์ดังกล่าวข้างต้นซึ่งปฏิกิริยาการกราฟท์จะเกิดจากอนุมูลอิสระที่เกิดขึ้นบนโครงสร้างของ PEI ที่ถูกเหนี่ยวนำโดย t-butyl hydroperoxide (TBHP) นอกจากนี้ PEI ที่ pH 7 และ 11 ซึ่งปรับค่าโดยกรดไฮโดรคลอริกเข้มข้น ยังแสดงอิทธิพลต่อการเกิดปฏิกิริยาอีกด้วย

จากการทดลองพบว่าอนุภาคนาโนที่เสถียรของ PMMA/PEI และ PS/PEI สามารถเตรียมได้จาก PEI ทั้ง 2 สภาวะ (pHs 7 และ 11) ในขณะที่อนุภาคนาโนที่เสถียรของ PnBA/PEI และ PEA/PEI เตรียมได้จาก PEI ที่ pH 7 เท่านั้น ในกรณีของ MAA ไม่สามารถเตรียมอนุภาคนาโนที่เสถียรได้ แต่จะได้ผลิตภัณฑ์ที่มีลักษณะ เป็นเจล นอกจากนี้จากการทดลองเปรียบเทียบปฏิกิริยาที่เกิดขึ้นจากมอนอเมอร์ชนิดต่างๆ ที่ PEI pH 7 พบว่าความแตกต่างของมอนอเมอร์มีผลต่อ % conversion, particle size, % grafting, และ % grafting efficiency

ชนิด และค่าความแรงของประจุที่พื้นผิวของอนุภาคสามารถยืนยันได้จากผล ζ -potential และพบว่าสภาวะของ PEI มีผลอย่างมากต่อค่านี้ ภาพจากกล้องจุลทรรศน์อิเล็กตรอนสามารถแสดง morphology ของผลิตภัณฑ์ ลาเท็กซ์ที่สังเคราะห์ได้อย่างชัดเจน ข้อมูลจาก ATR-FTIR สามารถยืนยันว่ากราฟท์โคพอลิเมอร์เกิดขึ้นจริง นอกจากนี้ได้มีการศึกษาอิทธิพลของเอทานอลในบทบาทของ co-solvent ต่อการเกิดอนุภาคนาโนของ PS/PEI ที่ pH 7 และจากผลการทดลองพบว่า การปรับเปลี่ยนปริมาณของเอทานอลไม่มีผลต่อ % conversion ของ styrene มากนัก แต่จะส่งผลอย่างมากต่อขนาดของอนุภาคที่เกิดขึ้น

Executive Summary

1. ความสำคัญและที่มาของปัญหา

อนุภาคนาโน (nanoparticles) เป็นหนึ่งในวัสดุนาโน (nanomaterials) ที่มีการศึกษาอย่างแพร่หลาย อีกทั้งยังเป็น building block ที่สำคัญสำหรับนาโนเทคโนโลยีอีกด้วย¹⁻³ อนุภาคนาโนที่กำลังได้รับความสนใจอย่างมากชนิดหนึ่งคืออนุภาคนาโน ที่มี morphology แบบ core-shell ชนิด แอมฟิฟิลิก (amphiphilic) กล่าวคือ อนุภาคจะประกอบด้วยส่วน เปลือก (shell) ห่อหุ้มส่วนที่เป็นแกน กลาง (core) ไว้ ซึ่ง core และ shell จะมีความแตกต่างทางด้าน hydrophilicity ทำให้เกิดลักษณะ amphiphilic ขึ้น นั่นคือมีส่วนที่เป็น hydrophobic และ hydrophilic อยู่ภายในอนุภาคเดียวกัน morphology แบบ core-shell ส่งผลให้อนุภาคนาโนดังกล่าวมีสมบัติเด่นหลายประการ อาทิ การที่มีขนาดเล็กในระดับนาโนเมตร ทำให้สามารถที่จะแพร่ผ่าน หรือถูกดูดซึมโดยเยื่อเลือกผ่าน หรือเยื่อที่มีรูพรุน ขนาดเล็กได้ ส่วนเปลือกมีหน้าที่ปกป้องส่วนที่เป็นแกนกลางจาก สิ่งแวดล้อมภายนอก และยังอาจจะ ทำหน้าที่เป็น carrier สำหรับ active principles เล็กๆ เช่น ยาสำคัญ สี เป็นต้น นอกจากนี้ส่วนแกนทำ หน้าที่เป็นตัวค้ำจุนโครงสร้างของอนุภาค และที่สำคัญส่วนแกนนี้ทำหน้าที่เหมือน carrier สำหรับโมเลกุลเล็กๆ ได้เช่นเดียวกัน ยิ่งไปกว่านั้นสมบัติ แอมฟิฟิลิก ยังก่อให้เกิด การผสมผสาน physical properties ของส่วน hydrophilic และ hydrophobic ทำให้มีสมบัติที่ดีกว่า ส่วนใดส่วนหนึ่งที่แยกกัน การเตรียมอนุภาคนาโนแบบ core-shell ชนิดแอมฟิฟิลิกทำได้หลายวิธี เช่น step-by-step deposition of polyelectrolytes⁴, shell-crosslinked knedle (SCK) micelles⁵, graft copolymerization of hydrophilic monomers onto reactive hydrophobic seeded particles⁶, หรือ copolymerization of hydrophilic macromonomers or surfmer through hydrophobic monomers⁷ อย่างไรก็ตามวิธี เหล่านี้ มีข้อจำกัดอยู่หลายประการ เช่น ใช้วิธีการสังเคราะห์ที่ซับซ้อน หลายขั้นตอน ต้องเตรียมในสารละลายเจือจางสูงทำให้ได้ส่วนที่เป็นของแข็ง (solids content) ต่ำซึ่งไม่เหมาะสมกับการประยุกต์ใช้ ในอุตสาหกรรม หรือจำเป็นที่จะต้องมีขั้นตอนเพิ่มมากขึ้นเพื่อกำจัดผลิตภัณฑ์ปนเปื้อนที่เกิดขึ้นระหว่างการเตรียม

ในโครงการวิจัยนี้ จะใช้วิธีการสังเคราะห์อนุภาคนาโนแบบ core-shell ชนิดแอมฟิฟิลิก โดย ปฏิกริยา graft copolymerization ของไวนิลมอนอเมอร์บนพอลิเมอร์ template ที่มีหมู่อะมิโนอยู่ใน โครงสร้าง และละลายน้ำได้ ซึ่งเป็นวิธีที่ผู้ขอทุนได้ทำการวิจัยในขณะศึกษาในระดับปริญญาเอก⁹⁻¹⁰ วิธีนี้มีข้อดีหลายประการนอกจากการที่ไม่เป็นพิษกับสิ่งแวดล้อมเนื่องจากทำปฏิกิริยาในตัวกลางที่เป็นน้ำ แล้ว ยังเป็นวิธีการสังเคราะห์ ที่ง่าย ไม่ซับซ้อนยุ่งยาก และไม่จำเป็นต้องเติมสารลดแรงตึงผิว (surfactant) ทำให้ได้ผลิตภัณฑ์ลิกซ์ที่บริสุทธิ์กว่าการสังเคราะห์ด้วย emulsion polymerization แบบเดิม

และจากระบบตัวอย่างที่ได้ศึกษาไปแล้ว คือ ระบบของการ graft poly(methyl methacrylate) (PMMA) บน PEI ดังนั้นในการวิจัยที่จะทำในโครงการนี้จะเป็นการขยายผลไปสู่การสังเคราะห์ด้วยการใช้ วิธีดังกล่าวกับไวนิล มอนอเมอร์ชนิดอื่นที่มีความแตกต่างกันทั้งทาง ด้านโครงสร้างเคมี หรือสมบัติทางกายภาพ เช่น ความชอบน้ำ หรือความมีขั้ว มาใช้ในการสังเคราะห์อนุภาค core-shell โดยยังคงใช้ PEI เป็นองค์ประกอบพื้นฐาน ซึ่งการปรับเปลี่ยน ชนิดของมอนอเมอร์ นอกจากจะเป็นวิธีหนึ่ง ที่จะสามารถปรับเปลี่ยนสมบัติของอนุภาคนาโนที่สังเคราะห์ได้แล้ว ยัง คาดหวังว่าจะได้ข้อมูลที่สำคัญในการปรับใช้กระบวนการวิธีให้เหมาะสมกับไวนิลมอนอเมอร์ชนิดอื่น และเข้าใจกลไกการ เกิดอนุภาคจากการวิเคราะห์ผลของการใช้มอนอเมอร์ที่มีต่อการสังเคราะห์ด้วยวิธีนี้

2. วัตถุประสงค์ของโครงการ

1. สังเคราะห์อนุภาคนาโน แบบ amphiphilic core-shell ที่มี shell เป็น PEI และ core เกิดจากไวนิล มอนอเมอร์ ชนิดที่แตกต่างกัน
2. ทำการวิเคราะห์สมบัติทางกายภาพของอนุภาคนาโนที่สังเคราะห์ได้ เช่น ขนาดของอนุภาค และการกระจายของขนาด หรือโครงสร้างพื้นฐาน (morphology) ของอนุภาค
3. ศึกษาผลของความแตกต่างของโครงสร้างทางเคมีของมอนอเมอร์ ที่มีต่อสมบัติของอนุภาคนาโน และกลไกการเกิดอนุภาค

3. ระเบียบวิธีวิจัย

1. สังเคราะห์ อนุภาคนาโน โดยใช้ PEI กับไวนิลมอนอเมอร์ ซึ่งแบ่งเป็น 3 กลุ่มใหญ่ๆ ตามได้แก่ มอนอเมอร์ที่มีขั้วต่ำ (ละลายน้ำได้น้อยมาก หรือไม่ละลาย) มอนอเมอร์ที่ละลายได้บางส่วน และมอนอเมอร์ที่ละลายน้ำได้ โดยจะนำตัวอย่างมาศึกษากลุ่มละ 2-3 ตัว พร้อมทั้งศึกษาผลของปัจจัยของ ปฏิกริยาที่มีผลต่อ % conversion^{**} เช่น อุณหภูมิ ความเข้มข้นของตัวเริ่มปฏิกริยา เวลาของการทำ ปฏิกริยา และ ค่า pH ของ reaction medium
2. ทำการ characterize อนุภาคนาโนที่สังเคราะห์ได้ โดยวัด
 - particle size และ size distribution โดย particle analyzer
 - particle morphology โดย Transmission electron microscopy (TEM)
3. ศึกษาประสิทธิภาพของปฏิกริยา graft copolymerization โดยการทำการทดลองหา pure graft copolymer ที่เกิดขึ้นโดยใช้วิธีการสกัด soxhlet extraction^{***} หลังจากนั้นทำการคำนวณ % grafting efficiency^{****} และพิสูจน์สูตร โครงสร้างทางเคมีของ graft copolymers ด้วยเทคนิค Fourier transform infrared spectroscopy (FTIR)
4. วิเคราะห์ผลการทดลอง

5. สรุปและเขียนรายงานเพื่อนำเสนอ

* จะทำการสังเคราะห์ลาเทกซ์ของอนุภาคนาโนใน water-jacketed flask ที่ต่อเข้ากับเครื่อง water-circulating bath ที่เชื่อมกับ thermometer, condenser , magnetic stirrer และ nitrogen inlet นำพอลิเมอร์ template ไปละลายน้ำ แล้วเทใส่ลงใน water-jacket flask พร้อมทั้งใส่มอนอเมอร์ที่ purified แล้วตามลงไป ทำการกำจัดออกซิเจนโดยการ purge ด้วย nitrogen gas เป็นเวลา 30 นาที ก่อนที่จะเติม t-butyl hydroperoxide (TBHP) ซึ่งเป็น initiator ลงไป มีการควบคุมอุณหภูมิ และให้ปฏิกิริยาดำเนินไปภายใต้บรรยากาศของไนโตรเจน

$$** \% \text{ Conversion} = \frac{\text{weight of monomer polymerized}}{\text{weight of monomer used}} \times 100$$

weight of monomer used

***Soxhlet extraction การสกัดที่ตัวทำละลายอยู่ในระบบที่สามารถระเหยกลายเป็นไอ โดยการให้ความร้อน และมีการควบแน่นกลับมาเป็นของเหลวเพื่อสกัดพอลิเมอร์แล้วระเหยกลายเป็นไอ ย้อนไปมาอย่างต่อเนื่อง)

$$**** \text{ Grafting Efficiency} = \frac{\text{Weight of the polymer grafted}}{\text{Weight of the total monomer polymerized}} \times 100$$

4. แผนการวิจัยตลอดโครงการในแต่ละช่วง 12 เดือน

กิจกรรมที่จะดำเนินการ	เดือน											
	1	2	3	4	5	6	7	8	9	10	11	12
1.สังเคราะห์อนุภาคนาโนพร้อมทั้งศึกษาผลของปัจจัยของปฏิกิริยาที่มี ผลต่อ % conversion เช่น อุณหภูมิ ความเข้มข้นของตัวเริ่มปฏิกิริยา เวลาของการทำปฏิกิริยา และ ค่า pH ของ reaction medium	x	x	x	x	x	x	x	x				
2. characterize อนุภาคนาโนที่สังเคราะห์ได้ - particle size และ size distribution โดย particle analyzer				x	x	x	x	x	x	x		

- particle morphology โดย Transmission electron microscopy (TEM)												
3. ศึกษาประสิทธิภาพของปฏิกิริยา graft copolymerization โดยการทำการทดลองหา pure graft copolymer ที่เกิดขึ้นโดยใช้วิธีการ สกัด soxhlet extraction หลังจากนั้น ทำการคำนวณ % grafting efficiency และพิสูจน์สูตรโครงสร้าง ทางเคมีของ graft copolymers ด้วย เทคนิค Fourier transform infrared spectroscopy (FTIR)			x	x	x	x	x	x	x			
4. วิเคราะห์ผลการทดลอง									x	x	x	
5. สรุปและเขียนรายงานเพื่อนำเสนอ											x	x

5. ผลงาน/หัวข้อเรื่องที่คาดว่าจะตีพิมพ์ในวารสารวิชาการระดับนานาชาติในแต่ละปี

Synthesis of Polyethyleneimine-based Core-Shell Nanoparticles from Various Vinyl Monomers

คาดว่าจะตีพิมพ์ในวารสารต่อไปนี้

- JOURNAL OF APPLIED POLYMER SCIENCE Impact factor = 1.017 หรือ

- EUROPEAN POLYMER JOURNAL Impact factor = 1.765 หรือ

- POLYMER Impact factor = 2.34 หรือ

6. งบประมาณ ต่อ 2 ปี

รายการ	จำนวนเงิน		
	ปีที่ 1	ปีที่ 2	รวม
1. หมวดค่าตอบแทน			
- ค่าตอบแทนหัวหน้าโครงการ (10,000 บาท/เดือน)	120,000	120,000	240,000
2. หมวดค่าวัสดุ เช่น			
ค่ามอโนเมอร์ และสารเคมีอื่นๆ	33,000	33,000	66,000
ค่าเครื่องแก้ว และวัสดุสิ้นเปลืองอื่นๆ	33,000	33,000	66,000
ค่าวัสดุอุปกรณ์วิทยาศาสตร์	15,000	15,000	30,000
ค่าวัสดุสำนักงาน	2,000	2,000	4,000
3. หมวดค่าใช้สอย เช่น			
ค่าจ้างในการใช้เครื่องมือวิเคราะห์	20,000	20,000	40,000
ค่าใช้จ่ายในการเดินทางไปปฏิบัติงานนอกสถานที่	7,000	7,000	14,000
ค่าจัดทำรายงานและส่งตีพิมพ์ในวารสารต่างๆ	5,000	5,000	10,000
ค่าส่ง fax และไปรษณีย์	5,000	5,000	10,000
4. หมวดค่าจ้าง	-	-	-
ฉ. หมวดค่าครุภัณฑ์	-	-	-
รวมงบประมาณที่เสนอขอ			480,000

รายละเอียดโครงการ

ชื่อโครงการ (ภาษาไทย) อิทธิพลของไวน์ิลมอนอเมอร์ต่อการเกิดเป็นอนุภาคนาโน แบบ core-shell ที่มี Polyethyleneimine (PEI) เป็นองค์ประกอบหลัก

(ภาษาอังกฤษ) Effects of Vinyl Monomers on the Formation on Polyethyleneimine-based Core-Shell Nanoparticles

ชื่อหัวหน้าโครงการ (ภาษาไทย) นาย พันธุ์ญา สุนันทบุรณ์ (อาจารย์)

(ภาษาอังกฤษ) Mr. Panya Sunintaboon

(ตำแหน่งทางวิชาการ) อาจารย์

ระยะเวลาดำเนินงาน 2 ปี

เวลาทำงานวิจัยในโครงการประมาณสัปดาห์ละ 20 ชั่วโมง

สถานที่ติดต่อ

ที่ทำงาน ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล

ถนนพระราม 6 กรุงเทพฯ 10400 หรือ

สาขาวิทยาศาสตร์และเทคโนโลยีพอลิเมอร์ ห้อง SC4-413 ตึกวิทย 3-4

คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล ต. ศาลายา อ. พุทธมณฑล จ. นครปฐม 73170

โทรศัพท์ 02-441-9816-20 (ต่อ 1138) โทรสาร 02-441-9322, หรือ 02-354-7151

E-mail scpsu@mucc.mahidol.ac.th

ชื่อนักวิจัยที่ปรึกษา (ภาษาไทย) นางสาวประมวล ตั้งบริบูรณ์รัตน์

(ภาษาอังกฤษ) Miss Pramuan Tangboriboonrat

(ตำแหน่งทางวิชาการ) ศาสตราจารย์

สถานที่ติดต่อ

ที่ทำงาน ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล

ถนนพระราม 6 กรุงเทพฯ 10400

โทรศัพท์ 02-201-5135 โทรสาร 02-354-7151

E-mail scptb@mucc.mahidol.ac.th

ชื่ออธิการบดี ศาสตราจารย์นายแพทย์ พรชัย มาตังคสมบัติ

การเปิดบัญชีโครงการ

ชื่อบัญชีโครงการ MRG48-พันธญา สุนันทบุรณ์

เลขที่บัญชี

ธนาคาร กรุงไทย จำกัด (มหาชน)

สาขา สาขาย่อยองค์การเภสัชกรรม

ผู้มีอำนาจสั่งจ่าย

1. นายพันธญา สุนันทบุรณ์ (หัวหน้าโครงการ)
2. นายทินกร เตียนสิงห์ (อาจารย์ภาควิชาเคมี)
3. นางสาวสุภาวดี มนต์สถาพร (อาจารย์ภาควิชาเคมี)

Effects of Vinyl Monomers on the Formation on Polyethyleneimine-based Core-Shell Nanoparticles

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Effects of Vinyl Monomers on the Formation on Polyethyleneimine-based Core-Shell Nanoparticles

1. Introduction

A branched PEI, a cationic water-soluble polymer, can be synthesized by cationic polymerization from aziridine monomer. The commercially available PEI has 1°, 2°, and 3° amine groups in the ratio of 1:2:1. Because each amine has the potential to be protonated, this renders PEI to behave like a cationic sponge with an effective buffer through a wide pH range. PEI has been used in many fields, such as paper production, water purification, or cosmetic manufacture [1]. In 2002, Li *et al* have reported the new route to amphiphilic core-shell polymeric nanoparticles via an emulsifier-free emulsion graft-copolymerization of methyl methacrylate (MMA) from both synthetic and natural amino-containing water-soluble polymers, including PEI. In this synthetic method, a small amount of *t*-butyl hydroperoxide (TBHP) was used to form the redox pairs with amino groups on such polymers to generate free radicals capable of propagating MMA. [2]. Reasonable grafting and particle formation mechanism for PMMA-core particles prepared by this method was established [2,3]. The hydroperoxide (TBHP) initially interacts with amino groups on the polymer backbone, leading to a formation of redox pairs. An electron is then transferred from nitrogen to TBHP giving a nitrogen cation radical and an alkoxyl radical (RO•). A proton is subsequently lost from the nitrogen, resulting in an amino radical that can initiate the graft copolymerization of MMA. Homopolymerization is also expected due to the polymerization initiated by alkoxyl radical fragments. Once MMA is polymerized from an amino-bearing polymer to a certain chain length, amphiphilic macroradicals can be formed and they behave like surface-active substances, which can self assemble and phase separate to form micelle-like microdomains. The further polymerization of MMA takes place within these microdomains, and core-shell nanoparticles are finally formed. The polymerization is similar to a conventional emulsion polymerization, except that no surfactant is added. Therefore, this procedure is called a surfactant-free emulsion polymerization. Stability of the particles comes from the steric, or electrostatic repulsions, or the combination of both effects (electrosteric repulsion) due to the presence of an amino-containing polymer on the surface of the particles.

Well-defined amphiphilic core-shell particles with amino surface based on PEI shell and PMMA cores were prepared with a size range of 60-160 nm in diameter. The latex product of PMMA/PEI core-shell particles can be achieved in high concentration up to 22% solids content indicating a commercial viability for a wide variety of amphiphilic core-shell

nanospheres. Moreover, PMMA/PEI nanoparticle has been demonstrated to be useful in gene and drug carriers for intracellular delivery [4, 5].

Due to the effective initiation of polymerization by PEI/amine and the versatile application of polymer latexes formed from this system, herein, we report the preparation various core-shell nanoparticles based on PEI. The effect of vinyl monomers with various water solubility and polarity on the formation of core-shell nanoparticles was investigated.

2. Experimental

- *Materials*

Methyl methacrylate (MMA), ethyl acrylate (EA), and *n*-butyl acrylate (nBA) supplied from Fluka, were purified by treating with 10% sodium hydroxide solution followed by washings with distilled water to remove inhibitor. Styrene (St) and methacrylic acid (MAA) (Merck) were purified by passing through a column packed with Alumina. *t*-Butyl hydroperoxide (TBHP) was used as an initiator without further purification. PEI (Mw 750,000) obtained from Aldrich was also used without further treatment. Distilled water was used throughout the experimental work.

- *Emulsion polymerization*

The emulsion polymerization was performed in a sealed water-jacketed flask equipped with nitrogen inlet and temperature-controlled circulating bath. A typical method of emulsion polymerization is as follow: the predetermined amount of 10 % PEI aqueous solution and distilled water were added to the flask. The mixture was degassed with nitrogen gas for 30 min. Then, the certain amount of monomer and initiator was added to the mixture. The reaction temperature was kept at 80 °C and the mixture was bubbled by nitrogen throughout the course of polymerization.

- *Polymer Latex Characterization*

Monomer conversion (MC) was determined the gravimetric method from the following equation:

$$\begin{aligned}\text{MC (\%)} &= (\text{weight of total PMMA/weight MMA feed}) \times 100 \\ \text{\% grafting} &= (\text{weight of grafted PMMA/weight of PEI}) \times 100 \\ \text{\% grafting efficiency} &= (\text{weight of grafted PMMA/weight of PMMA}) \times 100\end{aligned}$$

$$\text{grafted PMMA} = \text{total PMMA} - \text{homo-PMMA}$$

The particle sizes and distributions were determined with the Malvern Mastersizer 2000 particle analyzer by using dynamic light scattering principle.

-TEM measurement

The nanoparticle morphology was observed using transmission electron microscope (TEM). A drop of latex samples diluted with DI water was dried on the formva-coated copper grid. Then the samples were stained with 2% phosphotungstic acid aqueous solution for 3 min. A transmission electron microscope (Tecnai G2 Sphera, at an accelerating voltage of 80 kV) was utilized to observe the morphology and size of particles.

-ζ-potential measurement

The electrostatic surface charge of the polymer particles was deduced from their from their electrophoretic mobility evaluated using zetasizer nano-ZS (Malvern, UK) in 1mM NaCl solution at room temperature.

-ATR-FTIR analysis

After purified by soxhlet extraction using dichlormethane (LABSCAN, AR) as a solvent, grafted copolymers of their corresponding latexes were characterized by an ATR-FTIR (EQUINOX 55, Bruker) (32 scans at 4 cm⁻¹ resolution). The spectra were collected by using a Ge crystal with single reflection mode.

Table 1 Comparison of monomer structures and their water solubility

Monomer	Water solubility[6] (g/100 g water) at 60 °C	Chemical structure
Styrene	0.237	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{C}_6\text{H}_5 \end{array}$
<i>n</i> -Butyl acrylate	0.338	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$
Ethyl acrylate	2.13	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{COOCH}_2\text{CH}_3 \end{array}$
Methyl methacrylate	2.25	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{COOCH}_3 \end{array}$
Methacrylic acid	soluble	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{COOH} \end{array}$

3. Results and Discussion

- Mechanism of particle formation

The initiation starts from the generation of the free radicals resulted from a redox interaction between PEI and TBHP, and this process also yields other active free radicals capable of propagating vinyl monomers in the system. As the polymerization proceeds, the vinyl monomer molecules polymerizes on the PEI and with themselves giving the amphiphilic grafted oligomers and the concurrent homopolymers, respectively. As a result, the hydrophilicity of PEI solution decreases rapidly. At a certain amount of vinyl monomers grafted onto PEI, phase separate occurs, as can be observed from the solution mixture turning to milky dispersion, which would be at the early course of polymerization. Amphiphilic grafted oligomers formed then aggregate to be micelle-like domains. The inner part of domains was composed of grafted- and homo-vinyl oligomeric chains that are more hydrophobic, and the outer part was composed of the hydrophilic PEI. Due to the hydrophilicity of PEI, the micelle-like aggregates results from this path are stabilized in the aqueous medium. Once formed, these micelle-like domains start to provide the loci for vinyl monomers to be concentrated because of hydrophobic-hydrophobic interaction between the inner part and the monomers, which would accelerate polymerization. Polymerization continues in these loci and particles are growing[7]. This particle formation mechanism fits quite well with the polymerization of hydrophobic monomers, such as styrene or high alkyl acrylates.

The mechanism of particle formation for moderate to high solubility in water, however, is believed to be a little different. It is that the particle nucleation and oligo-radical formation take place simultaneously. Free radical fragments decomposed from an initiator and capable of reacting with monomers to form primary radicals, are generated in the aqueous phase. Those primary radicals grow up to a critical chain length resulting in precursor particles after phase separated from the aqueous phase without forming micelle-like domains as in the above mechanism[8]. These primarily formed particles have insufficient colloidal stability, therefore, they have to coagulate to form the stable primary particles. Then the monomers diffuse from their droplet phase and penetrate to the newly formed particles in order to swell them and propagation is continued [9].

It is clearly seen that PEI plays a major role in this amine/TBHP-initiated emulsifier-free emulsion polymerization. PEI acts as a co-initiator by working with TBHP to generate

free radicals capable of propagating vinyl monomers, and a stabilizer for latex particles via steric and electrosteric stabilization when protonated.

In this study, some of the vinyl monomers with various polarities and water solubility were selected to show their effect on the emulsifier-free emulsion polymerization in this system. The polymerizations were conducted at two stages of the PEI solution; 1) at the normal PEI solution in water (pH 11) , and 2) at the some degree of protonation of PEI (pH 7) adjusted by concentrated HCl. The results are displayed in Table 1.

St, a non-polar and highly hydrophobic monomer, yielded stable latexes at both pHs 7 and 11, but the conversions were much different (~20% and 80% at pHs 7 and 11 respectively). At pH 7, PEI is protonated and possesses more charges, which would be too rigid for styrene to incorporate leading to a lower St conversion compared to the less charged PEI at pH 11.

MMA can also result stable latexes at both pHs, however, with the comparable monomer conversions. Stable latexes from both nBA and EA can be prepared only at pH 7. At pH 11, the nucleophilicity of amine groups on PEI might be so strong that ester groups on both acrylate monomers could be hydrolyzed. The hydrolysis is not taking place for their methacrylate analogues as can be seen that stable latexes of methyl methacrylate can be prepared in both pHs with reasonable MMA conversions. In the case of MAA, although the monomer conversions were quite good at both pHs, stable latex products cannot be obtained. Instead, gel products were resulted.

Table 2 The resulted latexes prepared at pHs 7 and 11

Latex	pH of PEI solution	% MC	D_v (nm)	ζ -potential (mV)	Remarks
PS/PEI	7	22	128	65.0±1.4	Stable latex
	11	80	108	24.6±0.2	Stable latex
PnBA/PEI	7	92	398	67.1±1.0	Stable latex
	11	-	-	-	No latex obtained
PEA/PEI	7	61	182	60.9 ±1.0	Stable
	11	-	-	-	No latex obtained
PMMA/PEI	7	79	176	62.7±1.5	Stable latex
	11	89	126	54.2 ±0.7	Stable latex
PMAA/PEI	7	69 ^a	-	-	Gel product obtained
	11	67 ^a	-	-	

Conditions: monomer/PEI = 4/1 by weight; TBHP = 0.1 mM; Temp 80 °C; reaction time 2 hrs.

^a at the reaction time of 1 h

- ζ -potential measurement

The result is also shown in Table 1. The zeta-potentials of all latexes at pH 7 were in very close values around 61-67 mV. On the other hand, the zeta-potential of the PMMA/PEI latex at pH 11 was only 54.2 mV. This result strongly confirms the existence of the PEI amino groups on the particle surfaces, and the degree of protonation of PEI affects the strength of particles' surface charges, and lead to the high stability of particles.

- Kinetics of Polymerization

The kinetics of polymerization of PnBA/PEI, PEA/PEI, PMMA/PEI, and PS/PEI latexes prepared from the solution of PEI pH 7 were compared. From Figure 1, it could be seen that the steady monomer conversions for all monomers were attained in less than 1 h without the trace of induction period. This indicates the distinctly effective free radical generation of PEI/TBHP redox pair. However, the steady monomer conversion of each monomer was different from the others.

Because of the difference of distribution coefficient of monomers in polymer particle/water phase, the polymerization behaviors of these selected monomers are quite different. In the case of nBA, the distribution coefficient value is bigger due to its low water solubility (0.338 g/100 g water at 60 °C). However, probably due to the polar ester group on it, nBA still have an affinity with active radical on PEI, resulting in graft copolymerization and a formation of primary polymer particles. Once primary polymer particles are formed, they absorb monomer faster because these are the most probable sites for such hydrophobic monomer to be concentrated. After nucleation, polymerization takes place mostly in the monomer-swollen particles. The radicals in particles were separated rendering them difficult to terminate, their life time is extended, and the concentration of them is increased [10], resulting in a high monomer conversion up to 92 %. However, this effect would be less pronounced for other polar monomers with more water solubility as can be observed from the decrease in monomer conversions of EA, MMA, or MAA as shown in Table 1 and Fig. 1.

In the case of styrene, even though it has low water solubility (0.237 g/100 g water at 60 °C) and, of course, the distribution coefficient value should be large, however, the monomer conversion was only 22 %. This contradiction would be explained by the difference in polarity of the monomer and the reaction medium. At pH 7, amino groups on

PEI are protonated resulting in many positive charges on it. Dissolved PEI at this stage causes the ionic strength and polarity of the medium to be increased. Because of this, the difference between the polarity of the medium and styrene is so high that causes a large surface tension. Therefore, polymerization of styrene in this condition could be impeded as can be seen from the low monomer conversion. Moreover, unlike BA, styrene is also lack of any polar groups in its structure, which might help reduce a surface tension between two phases.

MMA and EA, the polar monomers and having close values of water solubility (2.25 and 2.13 respectively), exhibited the change of monomer conversion similar to BA, except that their steady monomer conversions were lower. This could also be explained that these two polar monomers are more water-soluble. Their distribution coefficient is lower compared to that of nBA, and some amount of monomers might be dissolved in the water phase leading the lower concentration of monomers in the polymerization site and eventually lower monomer conversion.

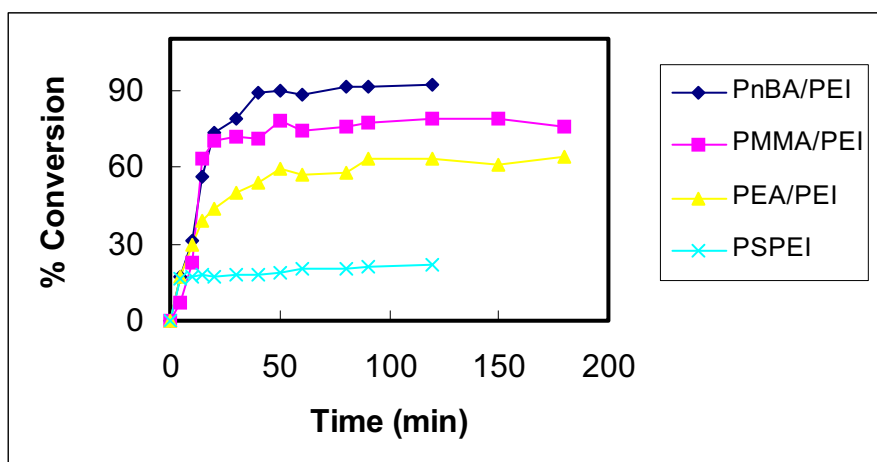


Figure 1. Monomer conversions vs time at pH 7

- Grafting copolymerization

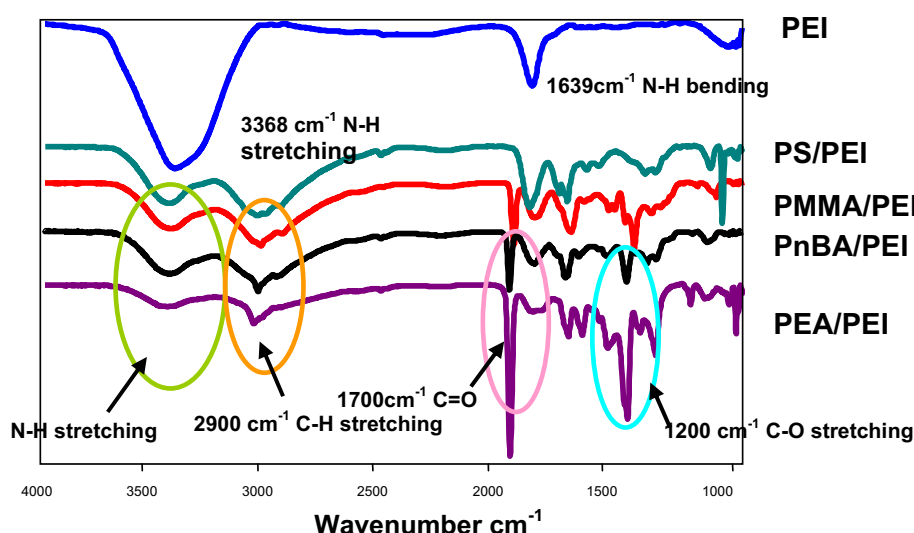
From the mechanism of the polymerization and the particle formation mentioned above, the formation of homopolymer cannot be excluded. Dried latexes prepared at pH 7 were extracted by using the soxhlet extractor with dichlormethane to remove the corresponding homopolymer. The % grafting and grafting efficiency were calculated and the result are displayed in Table 2. PnBA/PEI yielded the highest % grafting and % grafting efficiency, which were 218, and 67 % respectively. This indicates the competition between the graft copolymerization and homopolymerization.

Table 3 Grafting and grafting efficiency of the latex prepared at pH 7

Latex	% Grafting	% Grafting efficiency
PnBA/PEI (pH7)	218	67
PEA/PEI (pH7)	184	59
PMMA/PEI (pH7)	150	48
PS/PEI (pH7)	22	25

- FTIR of grafted copolymers

After soxhlet extraction to remove their corresponding homopolymers, all pure grafted copolymers of PS/PEI, PnBA/PEI, PEA/PEI, and PMMA/PEI were characterized by ATR-FTIR spectroscopic analysis. Pure PEI was also analyzed for a comparison. All spectra are shown in **Figure 2**. It can be seen that, for PS/PEI copolymer, there appeared the characteristic signals of N-H stretching and N-H bending at 3370 and 1639 cm^{-1} respectively, which are similar to the signals found in the pure PEI. In addition, there was a C=C stretching signal at 1453 cm^{-1} , which should be assigned to a signal of the corresponding aromatic part of styrene. For PnBA/PEI, PEA/PEI, and PMMA/PEI copolymers, there were a combination of signals of PEI as mentioned above, and the signals of C=O stretching and C-O stretching around 1730 and 1150 cm^{-1} , respectively. Therefore, these ATR-FTIR spectra are strong evidence to show that grafted copolymerization actually took place in all systems.

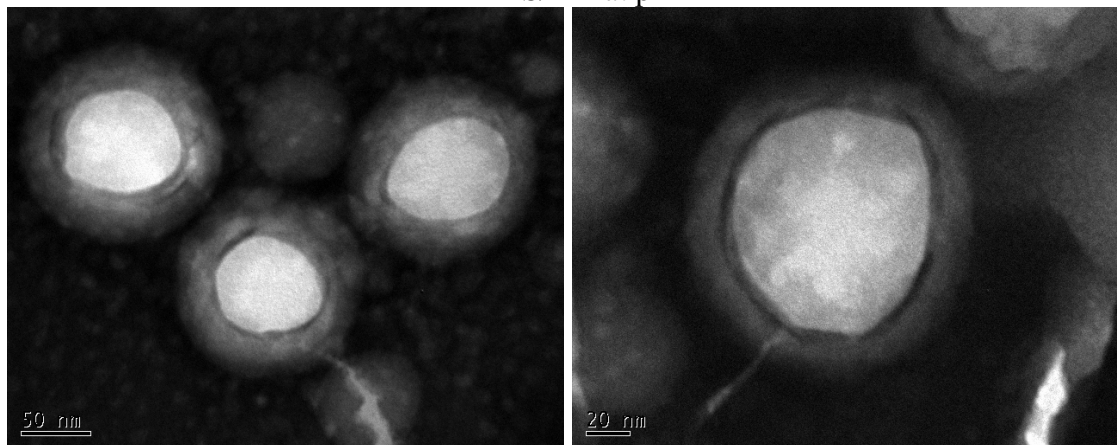
**Figure 2.** FTIR of grafted copolymers of the corresponding latexes prepared at pH 7

- Particle size and morphology

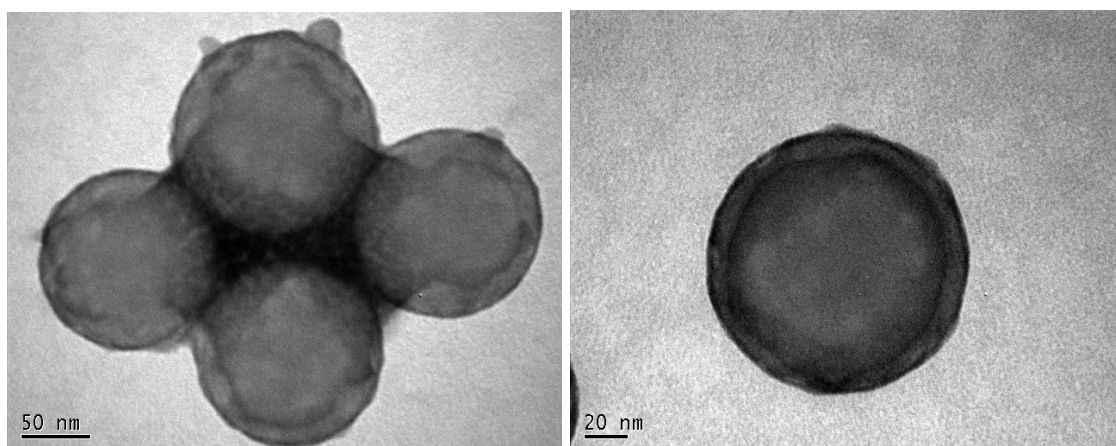
The particle sizes of all latexes were determined by the particle size analyzer and the results are shown in Table 2.

Transmission electron microscopy (TEM) is a useful technique providing a very important information of particle size and morphology. Core-shell imprints of all types of particles were clearly illustrated as shown in Figure 3. For nBA/PEI particles, there are the observation of small particles together with large particles. This could a trace of first formed small particles, which were too small to have colloidal stability. So that they coagulated to be larger particles to restabilize their colloidal entity. In the system of PMAA/PEI core-shell particles could not be obtained. Instead, the network of amphiphilic PMAA/PEI was obtained as also shown in Figure 3.

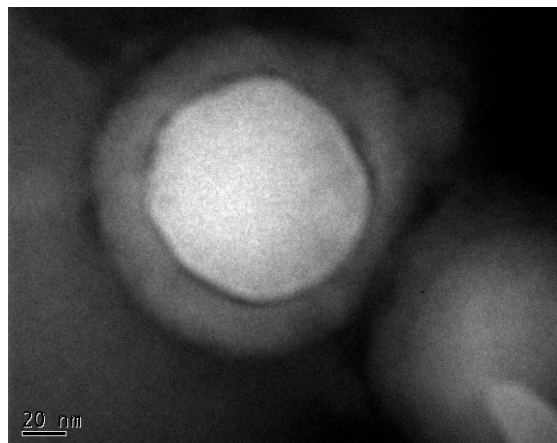
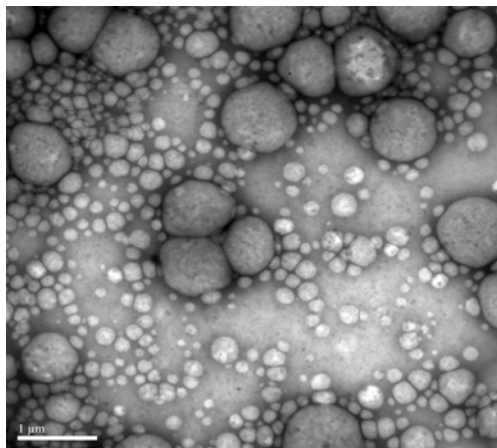
PS/PEI at pH 11



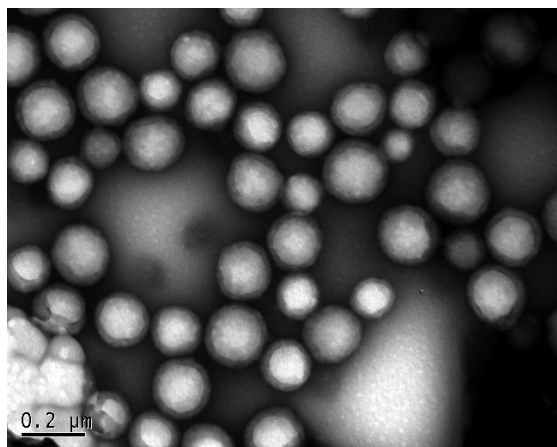
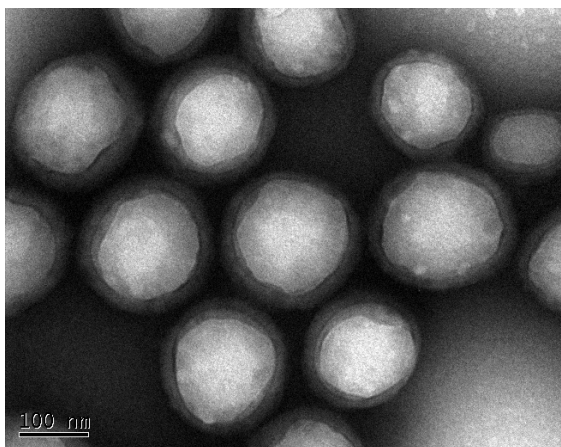
PS/PEI at pH 7



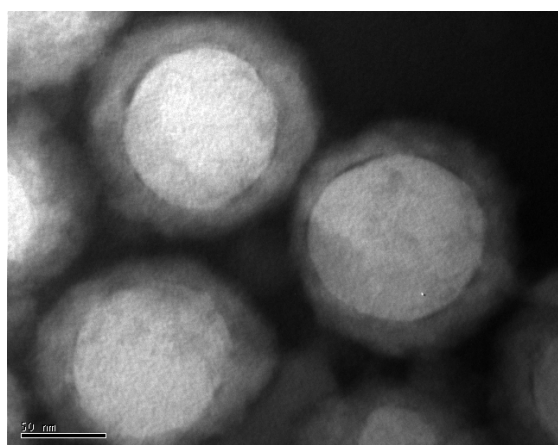
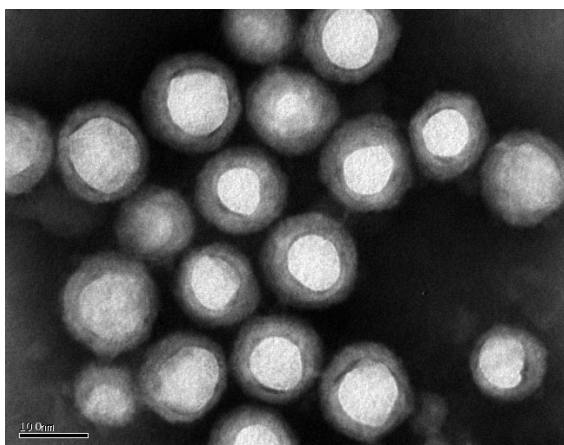
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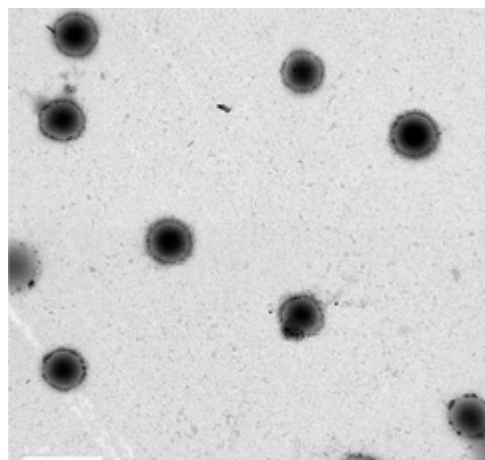
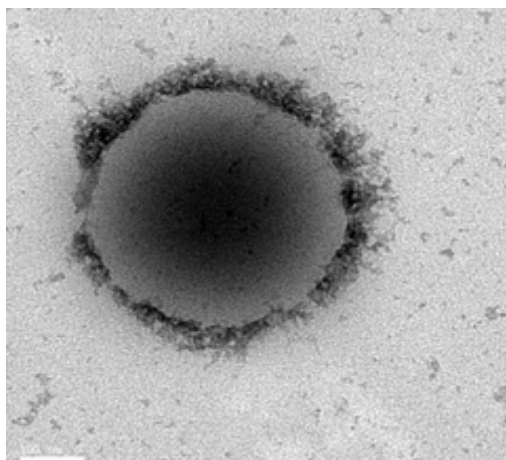
PMMA/PEI at pH 7



PMMA/PEI at pH 11



PEA/PEI at pH 7



PMAA/PEI pH 7

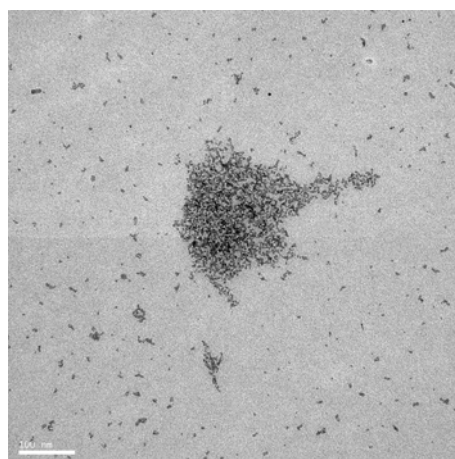
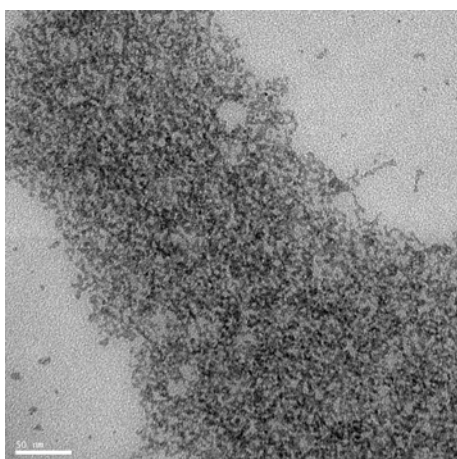


Figure 3. TEM micrographs of all latexes

- Effect of cosolvent

Table 4 Effect of ethanol on monomer conversion and size of PS/PEI

Amount of Ethanol (g)	% MC	Dv (nm)
0	21	139
10	19	141
15	17	187
20	22	238
30	32	338

Conditions: St/PEI = 4/1 by weight; pH of PEI =7, TBHP = 0.1 mM; Temp 80 °C; reaction time= 2 h.

The effect of ethanol as a co-solvent was investigated in the system of PS/PEI. Various amounts of ethanol were added to replace water before conducting each polymerization. In the presence of ethanol, St conversions were not much affected. However, the particle sizes were dramatically influenced. As the amount of ethanol increased, particle sizes tended to be larger. The result is shown in Table 4. The increased ethanol content can increase the solubility of styrene and the corresponding oligomers in the continuous phase [11]. Almog et al.[12] and Kawaguchi et al [13] also found that the particle size increased linearly with decreased solubility parameter differences between the polymer and the dispersing media due to the retardation of nucleation by increasing the solubility of the oligomers in the dispersing media.

4. Conclusion

The core-shell nanoparticles with the PEI shell and various cores including PMMA, PEA, PnBA, PS, PMAA were prepared. Variation on the degree of PEI protonation by adjusting pHs, polarity and water solubility of the vinyl monomers played a major role on the polymerization behavior of PEI/TBHP-initiated emulsion graft copolymerization. The particle size of the latexes were also affected by protonation degree of PEI and type of vinyl monomers. Zeta-potentials were only subjected to PEI. Core-shell morphology of the latex were clarified by TEM. Moreover, the effect of ethanol as a cosolvent was investigated in the PS/PEI system.

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Corresponding Author: Dr. Panya Sunintaboon, Ph.D.

Corresponding Author's Institution: Mahidol University

First Author: Panya Sunintaboon, Ph.D.

Order of Authors: Panya Sunintaboon, Ph.D.; Panya Sunintaboon; Sasitorn Sirisrimungkorn; Sitthi Duangphet; Pramuan Tangboriboonrat

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Amphiphilic nanoparticle latexes possessing n-butyl acrylate, ethyl acrylate, and methyl methacrylate cores with polyethyleneimine (PEI) shell were prepared by the emulsifier-free emulsion polymerization initiated by an PEI/t-butyl hydroperoxide(TBHP) redox couple. The dramatic effects of polarity and hydrophobicity of the vinyl monomers, and degree of protonation of PEI on the formation and properties of particles were illustrated. Monomer conversions (81-92 %), particle sizes (114-186 nm), grafting percentages (150-218%), and grafting efficiency percentages (48-67%) were varied and very subject to the type of monomers and protonating degree of PEI. In addition, the protonating degree of PEI strongly influenced the surface charge of the particles, indicating by the zeta-potential measurement ranging from 54 to 67 mV. The graft

Effect of vinyl monomers on the formation of polyethyleneimine (PEI)-based core-shell nanoparticles by the emulsifier-free emulsion polymerization

Panya Sunintaboon*, Sasitorn Sirisrimungkorn, Sitthi Duangphet, Pramuan Tangboriboonrat

Department of Chemistry, Faculty of Science, Mahidol University,

Salaya, Nakornprathom 73170, Thailand

Abstract

Amphiphilic nanoparticle latexes possessing *n*-butyl acrylate, ethyl acrylate, and methyl methacrylate cores with polyethyleneimine (PEI) shell were prepared by the emulsifier-free emulsion polymerization initiated by an PEI/*t*-butyl hydroperoxide (TBHP) redox couple. The dramatic effects of polarity and hydrophobicity of the vinyl monomers, and degree of protonation of PEI on the formation and properties of particles were illustrated. Monomer conversions (81-92 %), particle sizes (114-186 nm), grafting percentages (150-218%), and grafting efficiency percentages (48-67%) were varied and very subject to the type of monomers and protonating degree of PEI. In addition, the protonating degree of PEI strongly influenced the surface charge of the particles, indicating by the zeta-potential measurement ranging from 54 to 67 mV. The graft copolymers from the corresponding latexes were characterized by an ATR-FTIR, which showed the combination of characteristic signals from both PEI and grafted acrylate and methacrylate polymers. Core-shell morphology of the particles was clarified by TEM micrographs.

Keywords: amphiphilic; polyethyleneimine; nanoparticles; vinyl monomers; core-shell; emulsifier-free

1. Introduction

A branched polyethyleneimine (PEI), a cationic water-soluble polymer, is widely used in many fields, such as paper production, water purification, or cosmetic manufacture [1]. Recently, it has yielded significantly greater success in terms of cell transfection, and appeared as a possible alternative to viral and liposomal routes of gene delivery. Due to the fact that amine groups are especially useful for the covalent immobilization of biologically active macromolecules, the design and controlled fabrication of composite nanoparticles with PEI shell are of great interest. Among several methods used in preparation of the hydrophobic core-PEI shell nanoparticle, Li *et al* have reported the new route based on an emulsifier-free emulsion graft copolymerization of methyl methacrylate (MMA) from amino-containing water-soluble polymers, including PEI. In this method, a small amount of *t*-butyl hydroperoxide (TBHP) was used to form the redox pairs with amino groups on such polymer to generate free radicals capable of propagating MMA [2]. An electron is then transferred from nitrogen to TBHP giving a nitrogen cation radical and an alkoxyl radical (RO•). A proton is subsequently lost from the nitrogen, resulting in an amino radical that can initiate the graft copolymerization of MMA. Homopolymerization is also expected due to the polymerization initiated by alkoxyl radical fragments. Once MMA is polymerized from an amino-bearing polymer to a certain chain length, amphiphilic macroradicals can be formed and they behave like surface-active substances, which can self-assemble and phase separate to form micelle-like microdomains. The further polymerization of MMA takes place within these microdomains, and well-defined amphiphilic core-shell nanoparticles with a size range of 60-160 nm in diameter are finally formed. The polymerization is similar to a conventional emulsion polymerization, except that no surfactant is added. Stability of the particles comes from the steric, or electrostatic repulsions, or the combination of both

effects (electrosteric repulsion) due to the presence of an amino-containing polymer on the surface of the particles. The latex product of PMMA/PEI core-shell particles can be achieved in high concentration up to 22% solids content indicating a commercial viability for a wide variety of amphiphilic core-shell nanospheres. Moreover, PMMA/PEI nanoparticle has been demonstrated to be useful in gene and drug carriers for intracellular delivery [3, 4].

Due to the effective initiation of polymerization by PEI/amine and the versatile application of polymer latexes formed from this system, herein, we report the preparation of core-shell nanoparticles based on *n*-butyl acrylate (nBA), ethyl acrylate (EA), and methyl methacrylate cores and PEI shell. The effect of the vinyl monomers with different water solubility and polarity on the formation of core-shell nanoparticles was investigated. The grafting and particle formation mechanisms for core-shell particles were established [2,5].

2. Experimental

2.1 Materials

MMA, EA, and nBA (Fluka, Purum) were purified by treating with 10% sodium hydroxide solution followed by washing with distilled water to remove inhibitor. St and MAA (Merck, Purum) were purified by passing through a column packed with alumina (Fluka, chromatography grade). TBHP (Fluka, Purum) and PEI (Mw 750,000) (Aldrich, AR) were used without further purification. Distilled water was used throughout the experimental work.

2.1 Emulsifier-free emulsion polymerization

The emulsion polymerization was performed in a sealed water-jacketed flask equipped with nitrogen inlet and temperature-controlled circulating bath. In this method, the predetermined amount of 10% PEI aqueous solution and distilled water were added to

the flask. The mixture was degassed with nitrogen for 30 min. Then, the certain amount of monomer and initiator was added to the mixture. The reaction temperature was kept at 80°C and the mixture was bubbled by nitrogen throughout the course of polymerization. pH of the 10 % PEI aqueous solution was adjusted using concentrated hydrochloric acid.

2.3 Polymer latex characterization

Monomer conversion (MC) and grafting reaction were determined by the gravimetric method from the following equations:

$$\text{MC (\%)} = (\text{weight of total PMMA} / \text{weight of MMA feed}) \times 100$$

$$\% \text{ grafting} = (\text{weight of grafted PMMA} / \text{weight of PEI}) \times 100$$

$$\% \text{ grafting efficiency} = (\text{weight of grafted PMMA} / \text{weight of PMMA}) \times 100$$

$$\text{grafted PMMA} = \text{total PMMA} - \text{homo-PMMA}$$

These equations are also applied to other monomers.

The particle size and size distribution were determined with a particle size analyzer (Malvern; Mastersizer 2000) by using dynamic light scattering principle.

2.4 TEM measurement

The nanoparticle morphology was observed using transmission electron microscope (TEM; Tecnai G2 Sphera, at an accelerating voltage of 80 kV). The specimen was prepared from drying a drop of latex sample diluted with water on the formva-coated copper grid. Then the sample was stained with 2% phosphotungstic acid (EMS, AR) aqueous solution for 3 min.

2.5 Zeta-potential measurement

The electrostatic surface charge of the polymer particles was deduced from their electrophoretic mobility evaluated using the Zetasizer (NanoZS nanoseries, Malvern Instruments, UK) in 1mM NaCl solution at room temperature.

2.6 ATR-FTIR analysis

After purified by soxhlet extraction using dichlormethane (LABSCAN, AR) as a solvent, grafted copolymers of their corresponding latexes were characterized by an attenuated total reflectance-fourier transformed infrared spectrophotometer ATR-FTIR (EQUINOX 55, Bruker) (32 scans at 4 cm^{-1} resolution). The spectra were collected by using a Ge crystal with single reflection mode.

3. Results and discussion

As described above, PEI is a very important factor for the initial grafting reaction, particle formation, and then particle stabilization in this emulsion polymerization system. The process of particle nucleation and growth corresponding to the present work is illustrated in Scheme 1.

Scheme 1

When PEI is treated with *t*-butyl hydroperoxide (TBHP) at 80°C , the generated free radicals on the amine nitrogens trigger the graft copolymerization of vinyl monomers. The *t*-butoxy radical fragments obtained initiate a homopolymerization of monomers or abstract hydrogen atoms from PEI backbone forming PEI macroradicals that propagate vinyl monomers as well. At a certain point, the amphiphilic grafted macroradicals which behave like surfactants and/or a hydrophobic homopolymer generated *in-situ* would self-assemble to form micelle-like domains. The microdomains or primary particles are the sites for accumulation and further emulsion polymerization of vinyl monomers. Finally, the well-defined, amphiphilic core-shell nanoparticles are formed with PEI as a shell and a vinyl polymer as a core [5,7].

Since each monomer has its own specific characters in emulsion polymerization, specific technological operation is required. The effect of three homologous vinyl monomers with different water solubility, i.e., MMA, EA, and nBA, on this particular

emulsion polymerization system was investigated. The results in Table 2 are the comparison of the graft-copolymerizations of the three monomers onto the PEI at two different degree of protonation.

Table 2

It was observed that at pH 11, which is a normal condition of PEI dissolved in distilled water, only PMMA/PEI core-shell nanoparticle latex was formed with monomer conversion up to 90%, whereas nBA and EA did not result any latex. It is possibly due to the fact that nBA and EA have small alkyl ester groups, which cannot protect them from elimination at their acyl carbon atoms by the nucleophilic primary and secondary amines of PEI[8]. To lessen this effect, the nucleophilicity of PEI aqueous solution was then decreased by carefully adding concentrated HCl until its pH was dropped to 7. At this pH, stable latexes were formed from all three monomers with reasonable monomer conversions as also shown in Table 2. It was noticed that MMA monomer conversion at pH 11 (89%) was higher than that at pH 7 (75%). This could be explained that at pH 7, some amine groups of PEI converted to ammonium cations upon adding HCl. The result agreed well with our previous report on the polymerization of MMA onto various amino-containing water-soluble polymers, mentioning that primary amines are the most reactive to activate the radical generation on amine nitrogen after forming redox pairs with TBHP and quaternary amines are the least reactive ones to generate free radical capable of propagate MMA [2]. It was also observed that the change of pH significantly affected the size of PMMA/PEI particles. At pH 11 the diameter of PMMA/PEI particle was 129 nm, while at pH 7 its size was 173 nm. By lowering the pH of the medium, some amines are transformed to ammonium cations that could attribute to the expansion of the PEI shell layer resulting in a larger particle. The ammonium cations could bring more

charges to the particle surface that enhanced the particle stability through an electrostatic repulsion. More charges of PMMA/PEI latexes at pH 7 were confirmed with a zeta-potential of +62.7 mV compared to +54.2 mV at pH 11.

At pH 7, the size of PnBA/PEI particles was 114 nm, while those of PEA/PEI and PMMA/PEI particles were comparable, 186 and 173, respectively. The very small size of PnBA/PEI particles might be influenced by the low water solubility of nBA during the particle formation. From the mechanism mentioned above, the phase separation and aggregation of the micelle-like microdomains took place at a certain point. At that point, there should be certain units of monomers grafted on the PEI. For a low water-soluble nBA, the phase separation might occur at a very short length of a corresponding hydrophobic PnBA grafted on the PEI, leading to a smaller particle. In contrast, the longer corresponding PEA and PMMA grafted onto the PEI would be required for a phase separation resulting in a larger particle. However, the PnBA/PEI and PEA/PEI nanoparticles had a tendency to coalesce at a later stage of polymerization, resulting in larger particles that can be observed from the bimodal size distribution by the particle size analyzer and TEM (data not shown). This coalescence might occur because PnBA and PEA have low T_{gs} of -54 °C and -24 °C[9]. At the polymerization conditions, the polymer formed were so rubbery that accelerated their coalescence upon contact [10].

As already mentioned that at pH 7, stable core-shell nanoparticles can be obtained from all three monomers. The changes of monomer conversion with time on the polymerization of PnBA/PEI, PEA/PEI, and PMMA/PEI latexes were investigated and the data are displayed in Fig. 1.

Fig. 1

It was noticed that the steady monomer conversions for all monomers were attained in less than 1 h without any trace of induction period. This indicates the distinctly effective free radical generation of PEI-TBHP redox pair. However, the steady monomer conversions were 75%, 81%, and 92% for PMMA/PEI, PEA/PEI, and PnBA/PEI latexes, respectively, which seemed that monomers with higher water solubility tend to have higher initial rate of polymerization. This reminded that grafting reaction takes place on PEI in the aqueous phase and the preference between PEI and monomer might play an important role. The higher water solubility, the more polarity, and the more preference between PEI and monomer to come to contact and accelerate the propagation.

Although a more water soluble monomer gives a higher initial rate of monomer conversion before approaching a steady state, however, its monomer conversion at a steady state was lower than that having lower water solubility. In the case of nBA (0.338 g/100 g water at 60°C), its distribution coefficient value in a polymer particle and a medium is very high and this also makes it difficult to react with PEI resulting in lower initial rate of propagation. However, once primary polymer particles are formed after phase separation, they absorb monomer faster because they are the most probable sites for such hydrophobic monomer to be concentrated at this moment. After the formation of primary particles, polymerization takes place mostly in these monomer-swollen particles. The radicals in particles were separated rendering them difficult to terminate, their life time is extended, and their concentration increases [11], resulting in a high monomer conversion up to 92%. However, this effect would be less pronounced for other polar monomers with more water solubility as can be observed from the decrease in monomer conversions of EA, and MMA at plateau as shown in Table 1 and Fig. 1. Concerning MMA and EA having close values of water solubility (2.25 and 2.13 respectively), the

change of monomer conversions was similar to BA, except that their initial rates of polymerization were higher and steady monomer conversions were lower. This could also be explained that their distribution coefficient values are lower compared to that of nBA. The monomers partially dissolved in the aqueous phase leading to the lower concentration of monomers in the polymerization site and eventually lower monomer conversion.

- Grafting copolymerization

From the mechanism of the polymerization and the particle formation already mentioned, the formation of homopolymers cannot be excluded. Dried latexes prepared at pH 7 were extracted by using a soxhlet extractor with dichloromethane as an extracting solvent to remove the corresponding homopolymers. The %grafting and grafting efficiency were calculated and the results are displayed in Table 3. It was observed that the grafting and grafting efficiency percentages are in the order of PnBA/PEI > PEA/PEI > PMMA/PEI. PnBA/PEI particles yielded the highest % grafting and grafting efficiency (218 and 67% respectively) that directly reflected the competition between graft-copolymerization and homopolymerization. It is more likely that the more water-soluble monomer tends to promote a homopolymerization. The result in Table 3 indicated that a type of monomer would also affect the grafting reaction.

Table 3

- FTIR analysis of grafted copolymers

After soxhlet extraction to remove their corresponding homopolymers, all grafted copolymers of PnBA/PEI, PEA/PEI, and PMMA/PEI were characterized by ATR-FTIR spectroscopic analysis and the spectra are shown in Fig. 2.

Fig. 2

It can be seen that there appeared the characteristic signals of N-H stretching and N-H bending at 3370 and 1639 cm^{-1} respectively, for PnBA/PEI, PEA/PEI, and PMMA/PEI copolymers, which are similar to the signals found in the pure PEI. Moreover, the signals of C=O stretching and C-O stretching ca. 1730 and 1150 cm^{-1} , respectively, were also observed for all three grafted copolymers. Therefore, these ATR-FTIR spectra are the strong evidence to show that grafted copolymerization actually took place in all systems.

- Morphology of the resulted latexes

Transmission electron microscopy (TEM) is a useful technique providing a very important information of particle morphology. Core-shell imprints of all types of particles were clearly illustrated as shown in Fig. 3. The PEI shell is represented by a dark periphery around the particle resulted from being stained with a Phosphotungstic acid solution. The core was in the central part of the particle. Particle size including a core diameter and shell thickness can also be determined.

Fig. 3

4. Conclusions

In this emulsifier-free emulsion polymerization system, the PEI and type of monomer play an important role in the characteristics of polymerization, and the mechanism of particle formation. Degree of protonation of PEI could affect graft-polymerization of each monomer, and the particle surface charges. nBA, EA, and MMA having different water solubility, affected the initial rates of polymerization, steady monomer conversions, and grafting reaction. The grafting copolymers were confirmed by FTIR spectra. TEM micrographs revealed core-shell morphology of the formed nanoparticles.

Acknowledgements

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Figure(s) and Table(s)

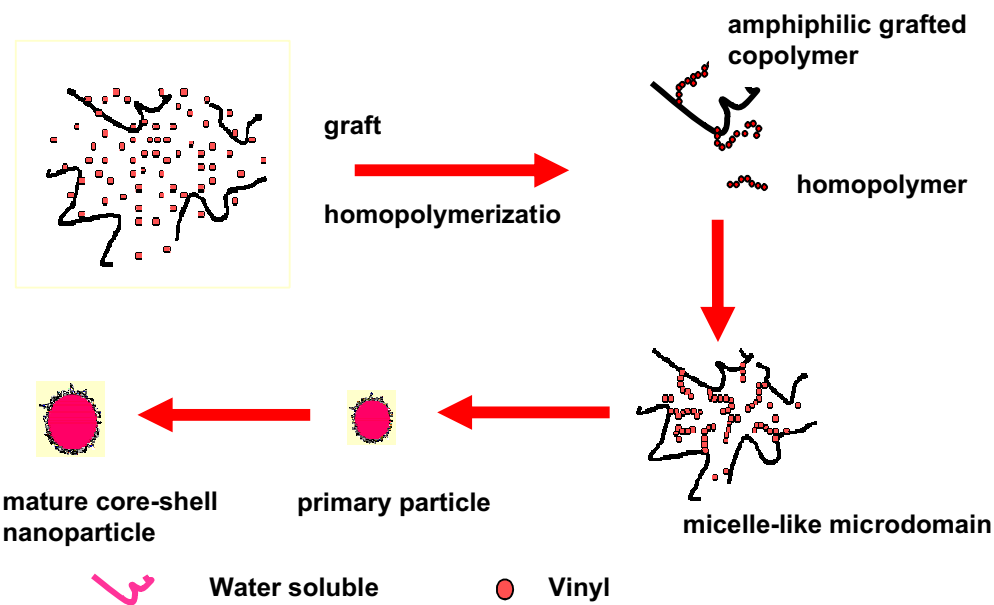


Table 1 Comparison of monomer structures and their water solubility

Monomer	Water solubility[6] (g/100 g water) at 60°C	Chemical structure
<i>n</i> -Butyl acrylate	0.338	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$
Ethyl acrylate	2.13	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{COOCH}_2\text{CH}_3 \end{array}$
Methyl methacrylate	2.25	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{COOCH}_3 \end{array}$

Table 2. The resulted latexes prepared from MMA, EA, and nBA with PEI at pH 11 and 7

Latex	pH of PEI solution	% MC	D_v (nm)	ζ -potential (mV)	Remarks
PMMA/PEI	11	89	129 $\pm$ 4	54.2 $\pm$ 0.7	Stable latex
	7	75	173 $\pm$ 4	62.7 $\pm$ 1.5	Stable latex
PEA/PEI	11	-	-	-	No latex obtained
	7	81	186 $\pm$ 27	60.9 $\pm$ 1.0	Stable
PnBA/PEI	11	-	-	-	No latex obtained
	7	92	114 $\pm$ 15	67.1 $\pm$ 1.0	Stable latex

Conditions: monomer/PEI = 4/1 by weight; TBHP = 0.1 mM; Temp 80 °C; reaction time 2 hrs.

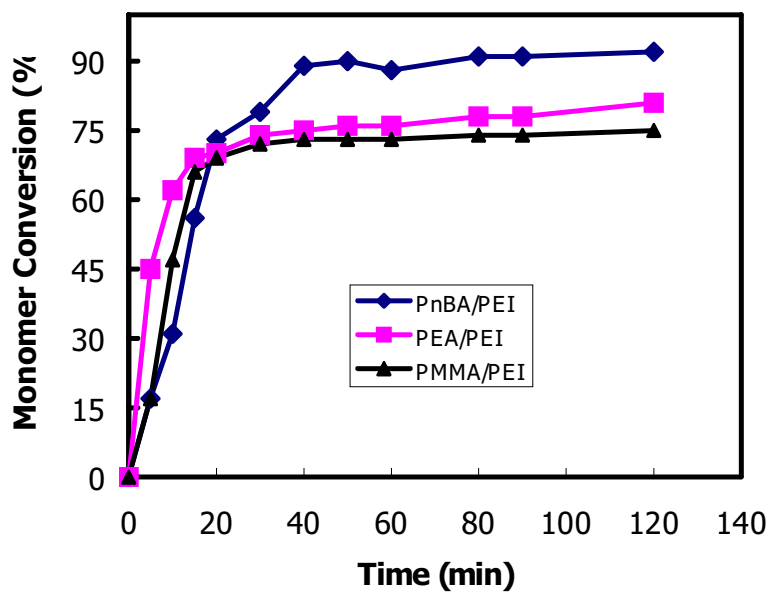


Fig. 1. The monomer conversion vs time of different monomers at pH 7

Table 3. The %grafting and %grafting efficiency of the 3 latexes prepared from PEI pH 7

Particle	% grafting	% grafting efficiency
PnBA/PEI	218	67
PEA/PEI	184	59
PMMA/PEI	150	48

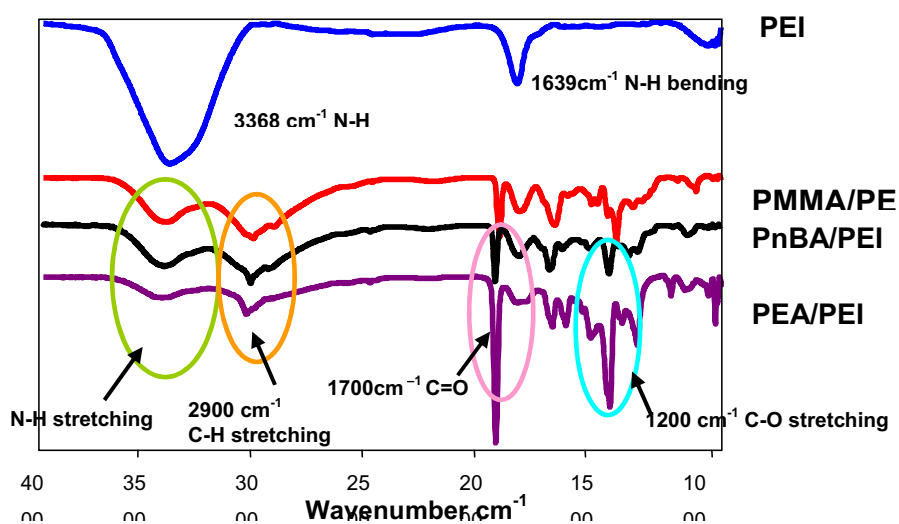
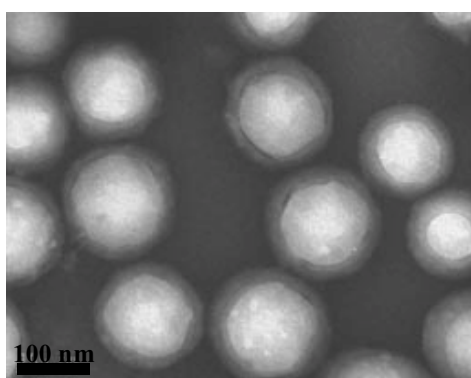
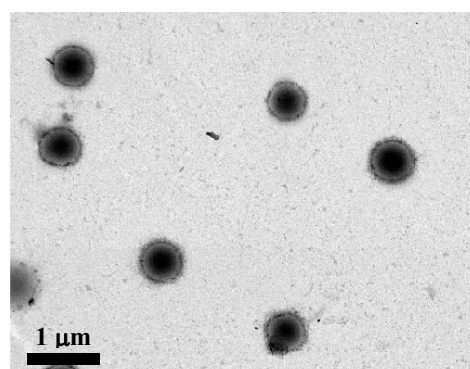


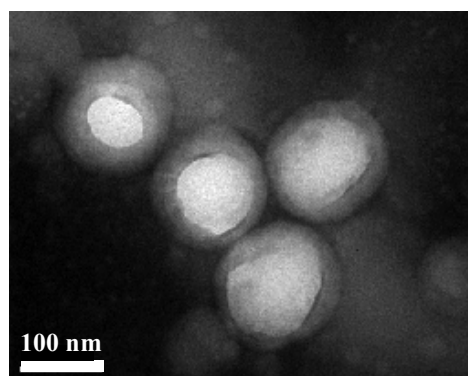
Fig. 2. The FTIR spectra of extracted grafted copolymers of PMMA/PEI, PEA/PEI, and PnBA/PEI



PMMA/PEI



PEA/PEI



PnBA/PEI

Fig. 3. The TEM micrographs of PMMA/PEI, PEA/PEI, and PnBA/PEI core-shell nanoparticles

Dear Editor

My name is Panya Sunintaboon (Ph.D.), currently working at Department of Chemistry, Faculty of Science, Mahidol, University, Thailand. I would like to take this opportunity to submit my research paper to be reviewed for being published as an article in the European Polymer Journal. The topic of the paper is “Effect of vinyl monomers on the formation of polyethyleneimine (PEI)-based core-shell nanoparticles by the emulsifier-free emulsion polymerization”. To be honest, this is my first time to submit paper to this journal. If some mistakes should happen, I have to apologize. In addition, it would be so kind, that you will please let me know any corrections or any critical decision as soon as possible. I hope that we will enjoy working together on the publication process.

Best regards,

Panya Sunintaboon