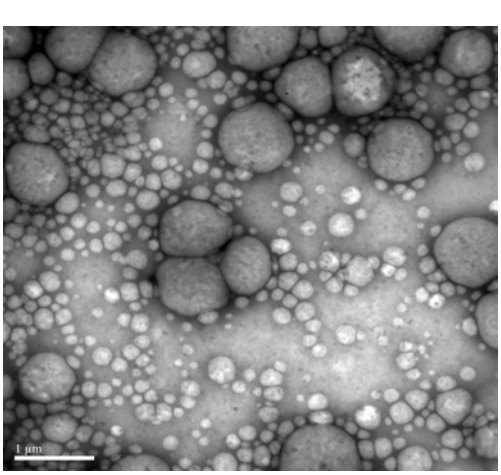
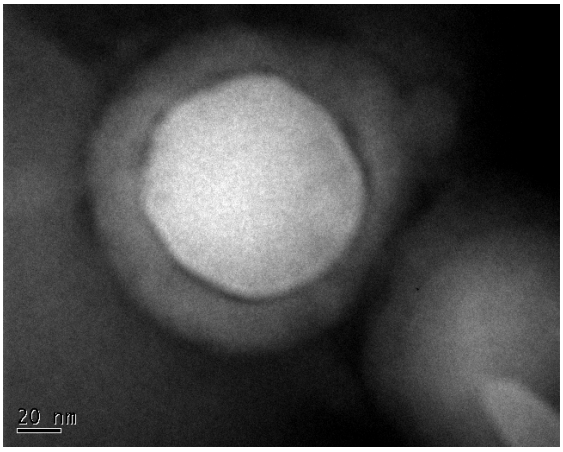
P*n*BA/PEI at pH 7





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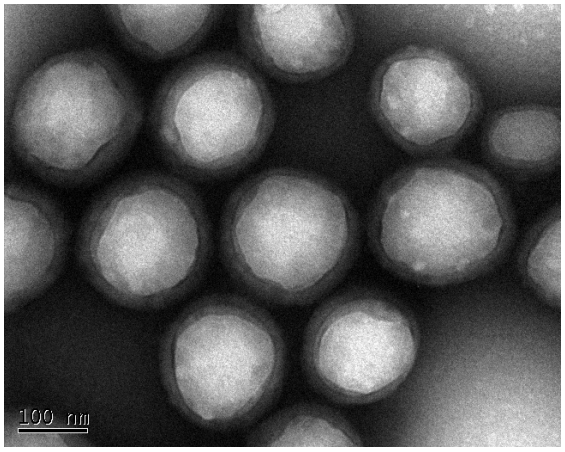
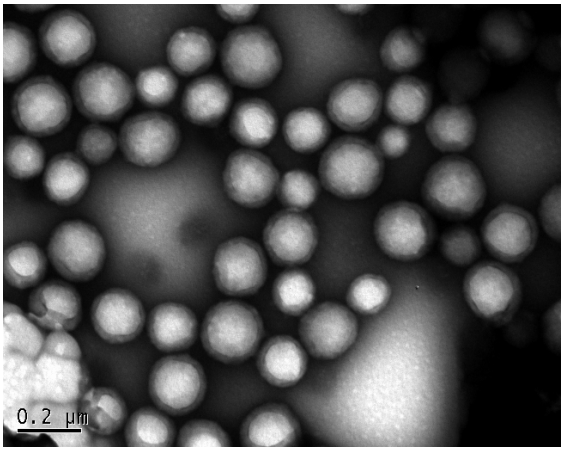
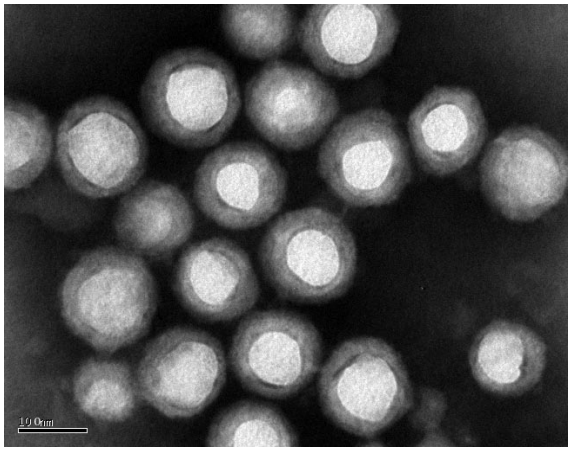
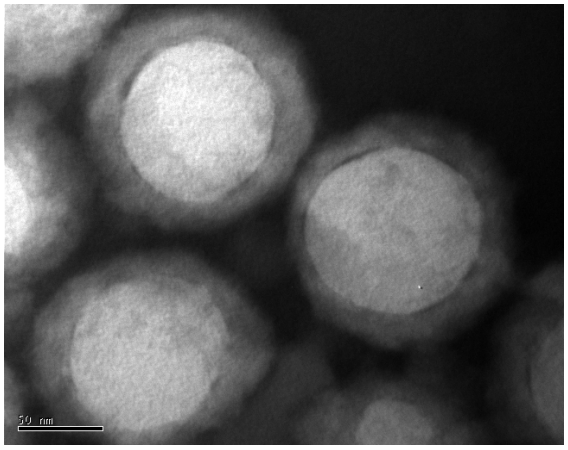


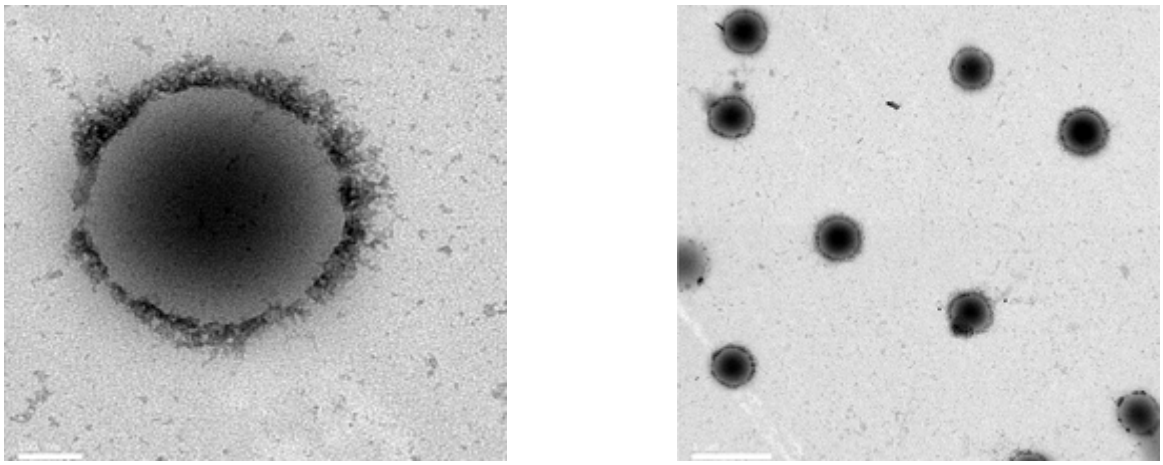


PMMA/PEI at pH 11





PEA/PEI at pH 7



PMAA/PEI pH 7

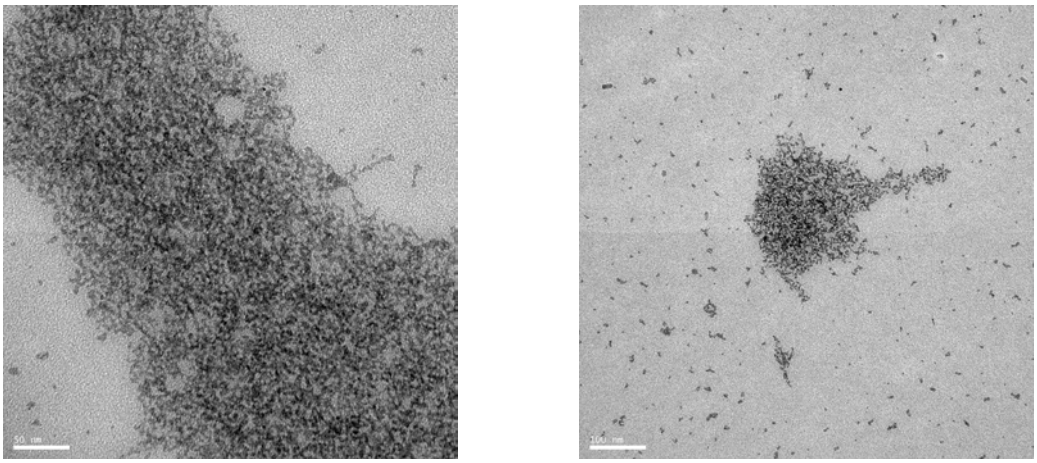


Figure 3. TEM migrographs of all latexes

- 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 ^{o}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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Elsevier Editorial System(tm) for European Polymer Journal

Manuscript Draft

Manuscript Number: EUROPOL-D-07-01140

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

Article Type: Research Paper

Section/Category:

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

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Manuscript Region of Origin:

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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^{o}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:

MC (%) = *(weight of total PMMA/weight of MMA feed) X 100*

% grafting = (weight of grafted PMMA/weight of PEI) X 100

% grafting efficiency = (weight of grafted PMMA/weight of PMMA) X 100

grafted PMMA = total PMMA - 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 cabon 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 Tgs of -54 ^{o}C and -24 ^{o}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^{o}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 Phosphotunstic acid solution. The core was in the central part of the partilcle. 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

This work was financially supported by The Thailand Research Fund (TRF) (Grant No. MRG4880124). The authors would also like to thank the National Nanotechnology Center (Thailand) for the measurement of zeta-potentials.

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Figure(s) and Table(s)

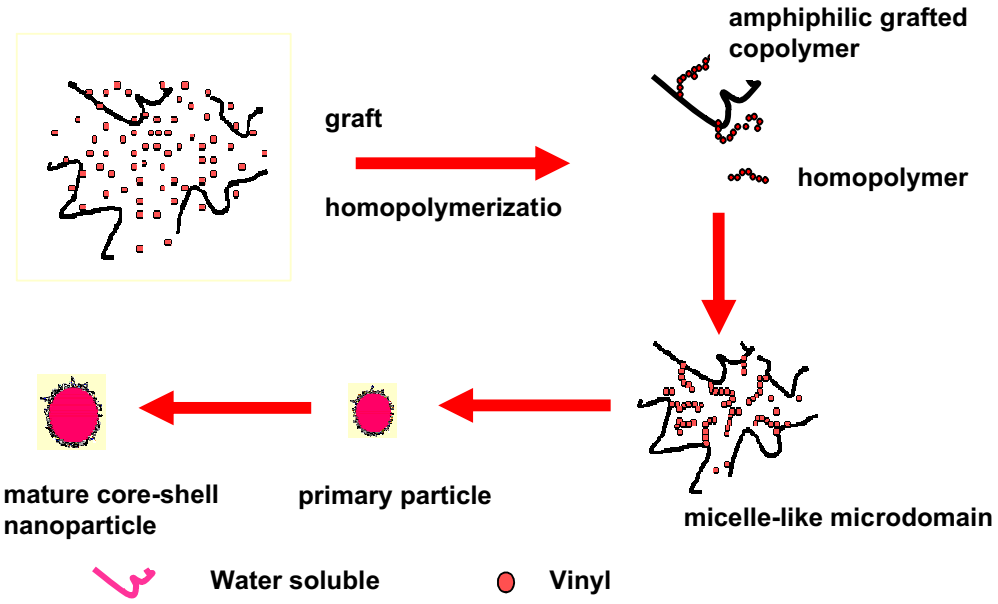


Table 1 Comparison of monomer structures and their water solubility

Monomer	**Water solubility[6]** (g/100 g water) at 60°C	**Chemical structure**
n-Butyl acrylate	0.338	$H_2C{=}C(H)COOCH_2CH_2CH_2CH_3$
Ethyl acrylate	2.13	$H_2C{=}C(H)COOCH_2CH_3$
Methyl methacrylate	2.25	$H_2C{=}C(CH_3)COOCH_3$

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

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

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

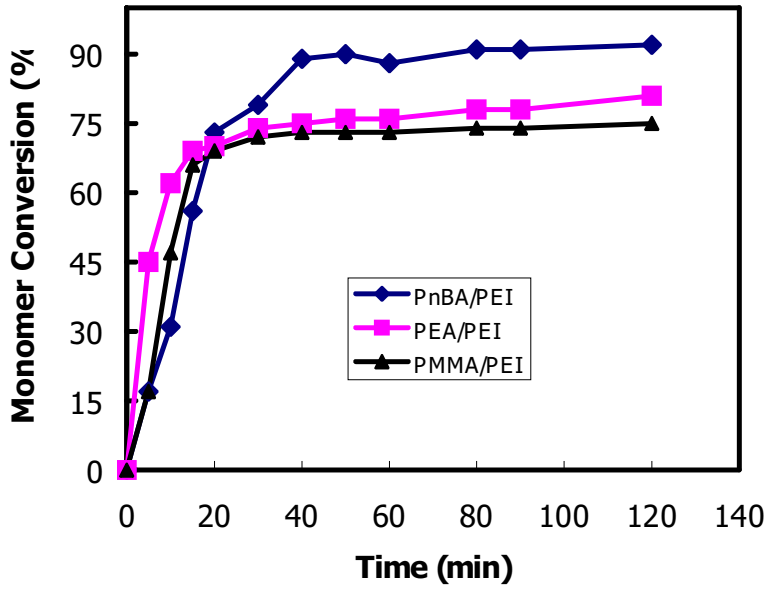


Fig. 1.The monomer conversion vs time of different monomers at pH 7

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

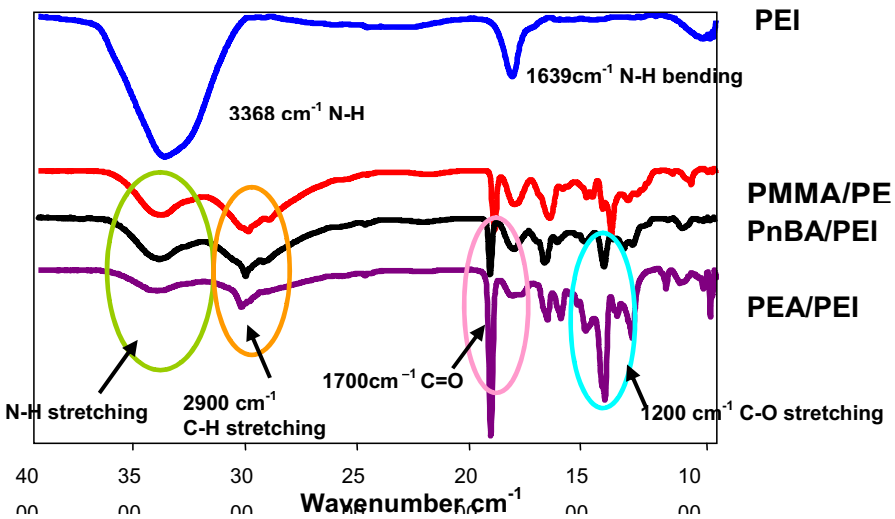
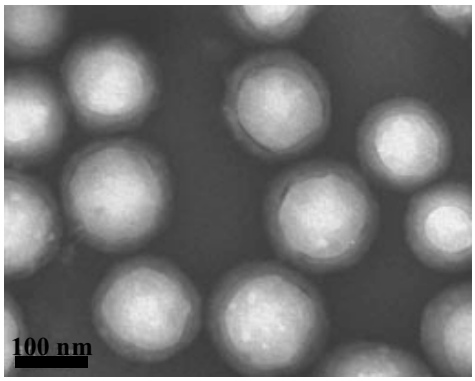
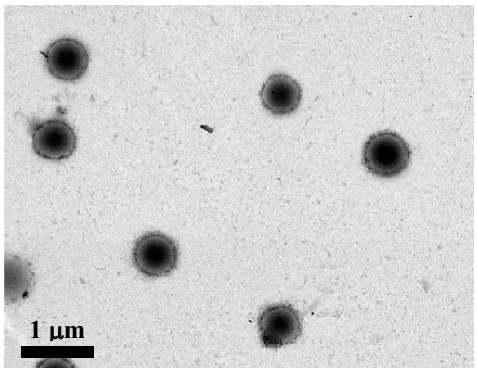


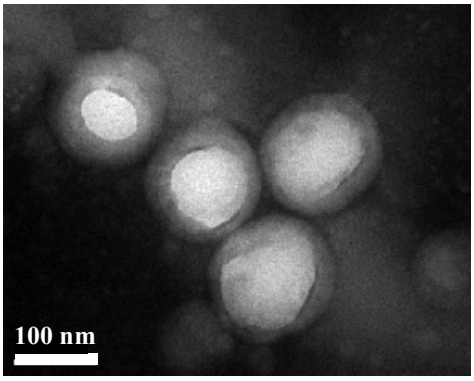
Fig. 2. The FTIR spectra of extracted grafted copolymers of PMMA/PEI, PEA/PEI, and PnBA/PEI



PMMA/PEI



PEA/PEI



PnBA/PEI

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

*** Cover Letter**

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