CHAPTER 4

RESULTS AND DISCUSSION

4.1 Dispersion Copolymerization of Styrene and *n*-Butyl Acrylate

Dispersion copolymerization of St and BuA in the mixture of ethanol/water in the presence of PVP and AIBN as polymeric dispersant and initiator, respectively, starts out as a clear homogeneous solution with no separate monomer phase. After a short induction period (often only within 10 minutes dependent on the given condition) a faint opalescence appears. At this stage, the dispersion of initially-formed polymer particles often has a bluish tinge by reflected light and appears red by transmitted light (Tyndall effect) [9]. At first slowly, and then faster, the opalescence whitens and eventually an opaque white latex is formed. Polymerization then continues without much further visible change until the reaction is terminated.

At the beginning of dispersion polymerization, primary radicals were produced by thermal decomposition of AIBN, which in turn react with St and BuA to form the growing oligomer chains with a reactive free radical at the end (this step is exactly conventional solution polymerization). When the oligomer chains reach to their critical chain length, they precipitate to form nuclei either by self or aggregative mechanism [21]. These nuclei are unstable and will aggregate with each other, simultaneously they adsorb the dispersant both precusor polymer (PVP) and its graft copolymer which is created in situ and finally become stable. These stabilized particles then act as a sink for sweeping the nuclei and radicals growing in the continuous phase, and thus reduce the rate of particle formation. Until the number of stable particles is high enough, no new particles are formed, and this is the end of particle formation stage. Growth of particles then proceed by

polymerization within the monomer-swollen stabilized particles (this stage is similar to the bulk polymerization). The particles continue to grow until there is no more monomer to sustain polymerization, or the reaction was terminated. From the whole mechanism of dispersion polymerization it can be implicit that dispersion polymerization proceed through both solution and bulk polymerization. The fact that particle surface is very smooth, as revealed by scanning electron microscope, supports that the polymerization continues to take place in the particles once they are formed. If the particle growth was largely dependent upon the aggregation of newly formed oligomer such smooth surfaces would not be expected [33].

In general, the polymeric dispersant, in providing a layer of polymer in dilute solution on the surface of each particle, is responsible for the stabilization of the particles against flocculation. The stability is achieved by the generation of a replusive force of a sufficient magnitude to overcome the inherent attraction manifested between particles as they approach one another.

When two polymer particles, which have polymer molecules attached to their respective surfaces, approach one another in a liquid medium in which the attached polymer molecules are soluble, then an increase in free energy will take place as the soluble polymer molecules interpenetrate or are composed. The resulting increase in the concentration of polymer segments in the zone of interpenetration will generate an osmotic pressure. To encounter this effect, solvent tends to diffuse into the regions of higher polymer concentration, forcing the particles apart until the steric barriers are no longer in contact [19].

An effective dispersant for polymer dispersions must be able to maintain a complete coverage of the particle surface. Each solvated polymeric component must be firmly attached to the surface of the particle so that it is neither desorbed from the surface nor displaced laterally when two particles collide.

As described previously, the particles become stable against flocculation when sufficient dispersants are completely adsorbed onto the particle surface.

According to Shen et al. [28], two types of dispersants may coexist, the precursor polymer (PVP) and its graft copolymer (PVP-g-P(St-co-BuA)) which is created in situ during the polymerization. When PVP is used as dispersant, the stabilizing efficiency is rather poor because it is soluble in the medium. However, it is believed that PVP which possess the active alphahydrogen can generate free radical sites through hydrogen abstraction, and these sites may then function as growth centers with upon additional polymerization of St and BuA, yielding the graft copolymer. The reactions are shown as follows:

$$AIBN \longrightarrow 2R^{\cdot} + N_2 \qquad (4.1)$$

$$(4.2)$$

$$(4.3)$$
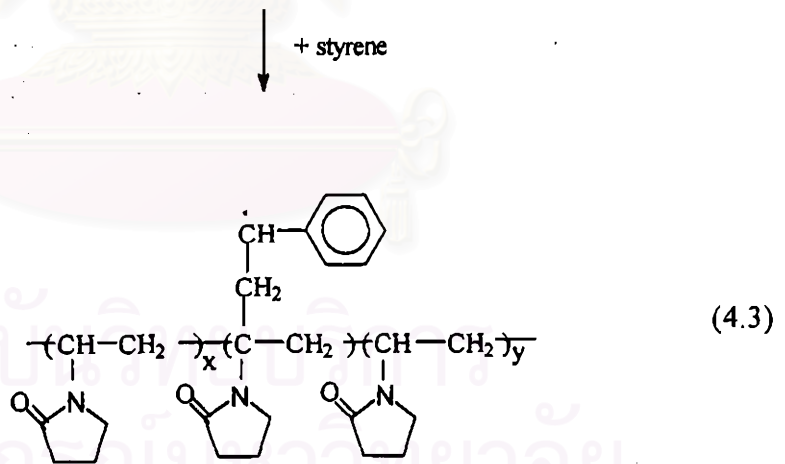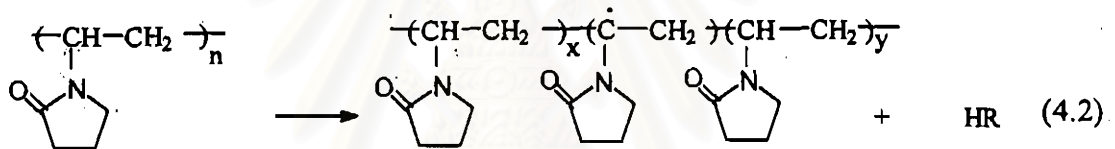
This PVP graft copolymer is very efficient for stabilization since one of the block is soluble in the medium and the other is insoluble and of the same nature as the polymer in the particles. When compared with the precursor PVP which is reversibly adsorbed on the particle, the graft PVP is chemically bound (anchored) to the particles and incapable of being desorbed [32].

In dispersion polymerization system, several parameters can control the final particle size and its distribution. These include dispersant type and concentration, solvency of reaction medium, temperature, agitation rate, monomer composition, crosslinking monomer, and polymerization time. The influences of these effects will be discussed later.

4.2 Characterization of the Functional Groups of the Copolymer

To confirm the copolymerization between styrene and n-butyl acrylate, the functional groups of the synthesized copolymer were investigated by FTIR. The spectrum of the copolymer is presented in Figure 4.1 and the absorption assignments are shown in Table 4.1, respectively. The existence of the copolymer is confirmed by comparing the copolymer spectrum with the reference peaks of the standard polystyrene and poly(n-butyl acrylate) (revealed in Figures 4.2 and 4.3).

Table 4.1 The characteristic assignment peaks for FT-IR spectrum of the poly (styrene-co-n-butyl acrylate)

	Wave Number (cm^{-1})	Assignment
Styrene	3080, 3060, 3030	=C-H aromatic stretching
	2920, 2850	C-H aliphatic stretching
	1940, 1870, 1800	mono substitute aromatic band
	1600, 1580, 1500	C=C stretching
n-Butyl acrylate	2960, 2870	C-H aliphatic stretching
	1730	C=O stretching
	1160	C-O stretching

Furthermore, the graft copolymer dispersant (PVP-g-P(St-co-BuA)) produced during the polymerization for stabilizing the particles formed, which has been mentioned above is also supported by FTIR measurement. Because this anchor graft copolymer cannot be desorbed by washing process used to clean the particles, therefore, it remains on the particle surface after washing. The existence of the anchor adsorption of the PVP graft copolymer on the copolymer surface can be analyzed by observing the additional peak of PVP that appear in the copolymer spectrum. The spectrum of PVP standard is given in Figure 4.4. Due to the overlap of the adsorption peaks of C=O in both PBuA and PVP shown in Figure 4.1, the polystyrene prepared from dispersion polymerization was used to investigate the anchoring evidence. When compared with standard polystyrene spectrum, the spectrum of our polystyrene shows an additional peak of C=O at 1670 cm^{-1} which result is in accordance with Kiatkamjornwong's previous work [32]. This indicates that there is the residual PVP on the surface of particles representing the anchor adsorption of the PVP graft copolymer.
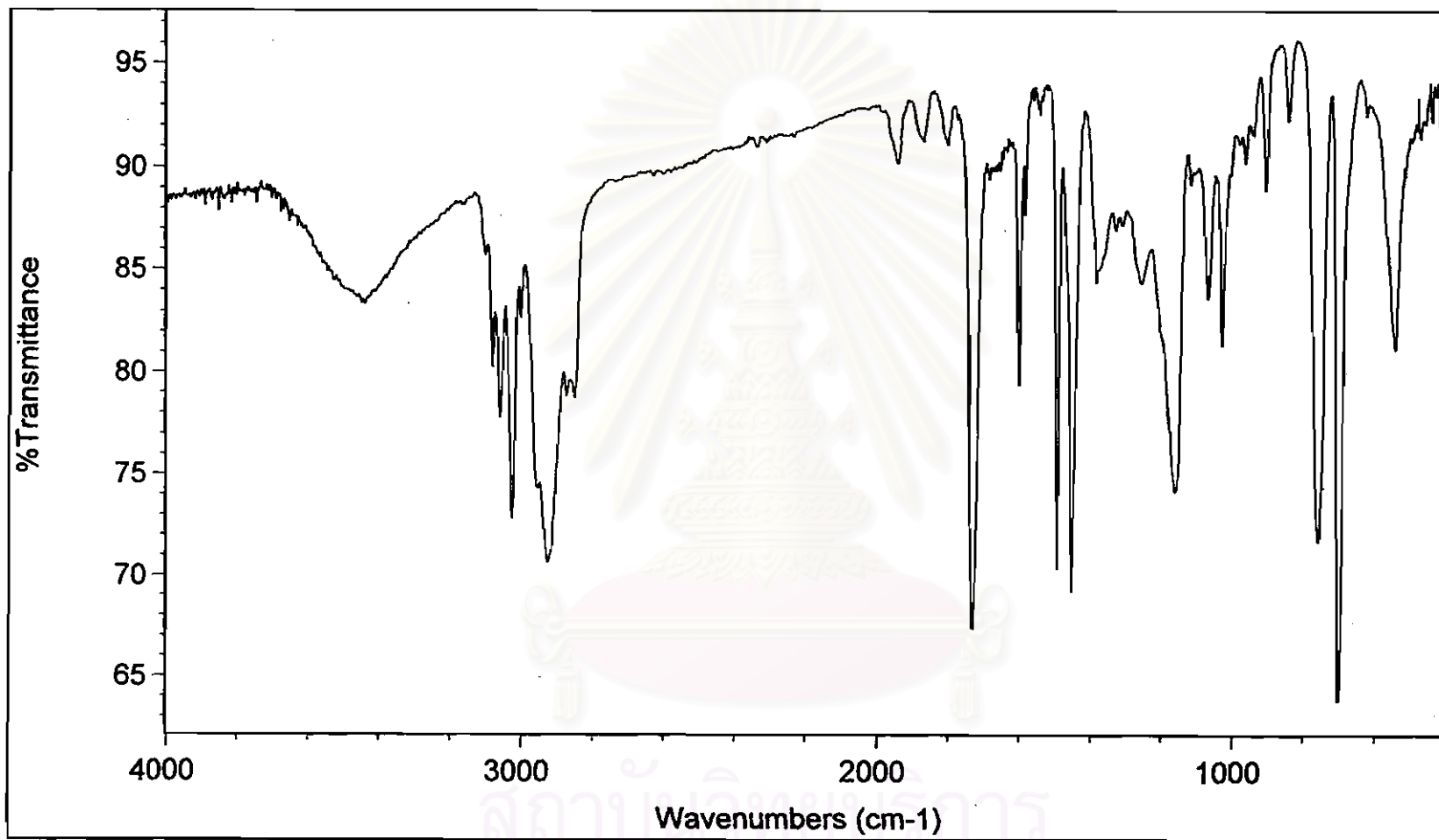
Figure 4.1 The FTIR spectrum of the poly(styrene-co-*n*-butyl acrylate) prepared by dispersion polymerization
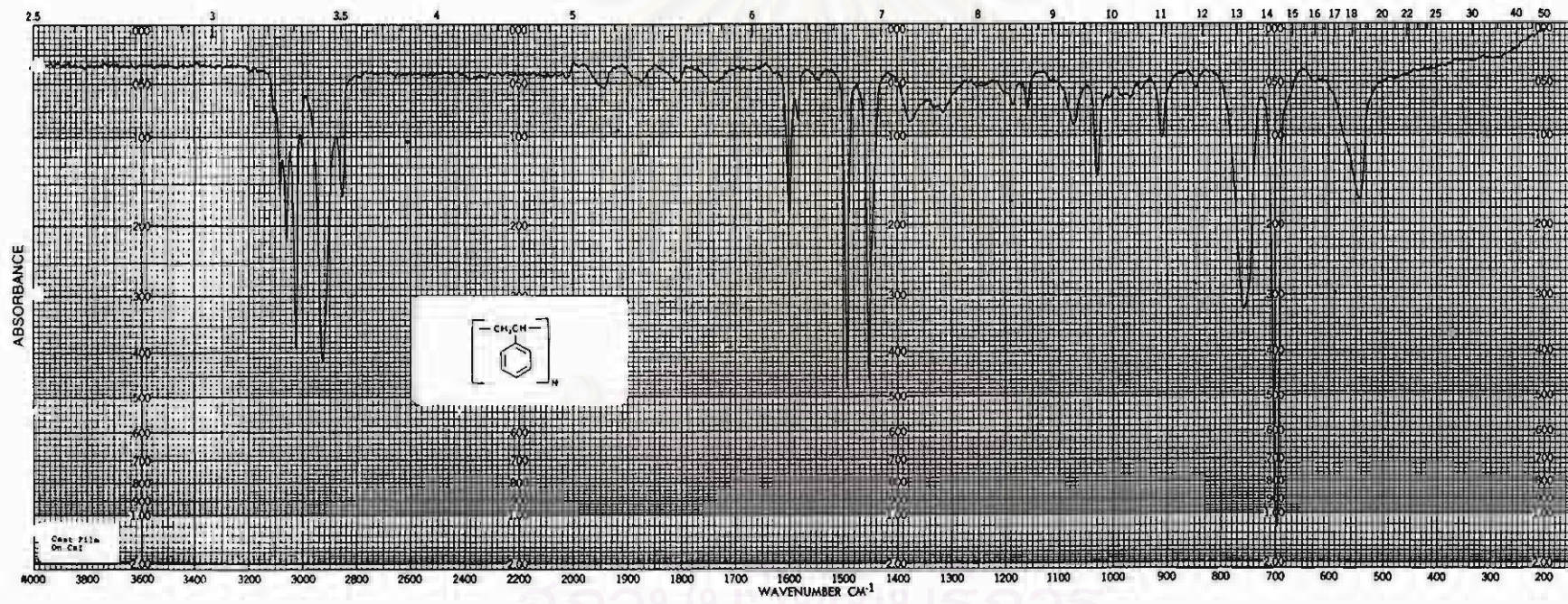
Figure 4.2 The FTIR spectrum of the polystyrene
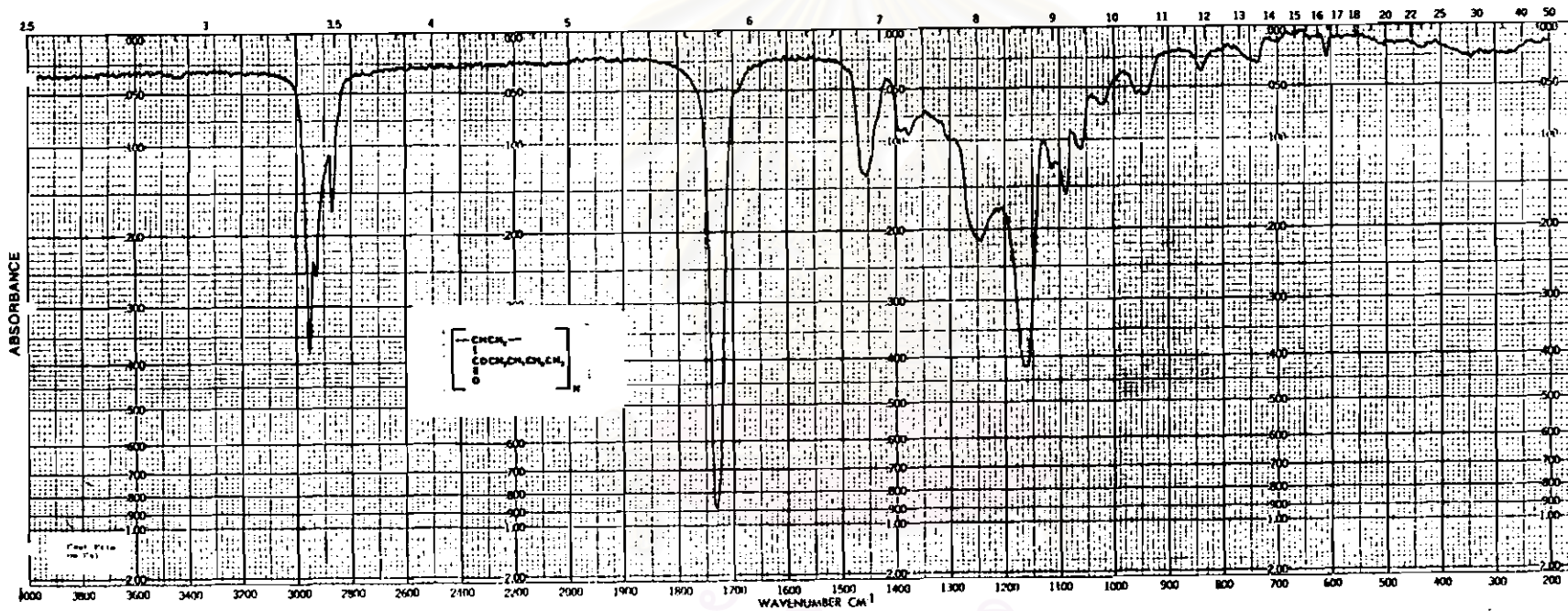
Figure 4.3 The FTIR spectrum of the poly(*n*-butyl acrylate)
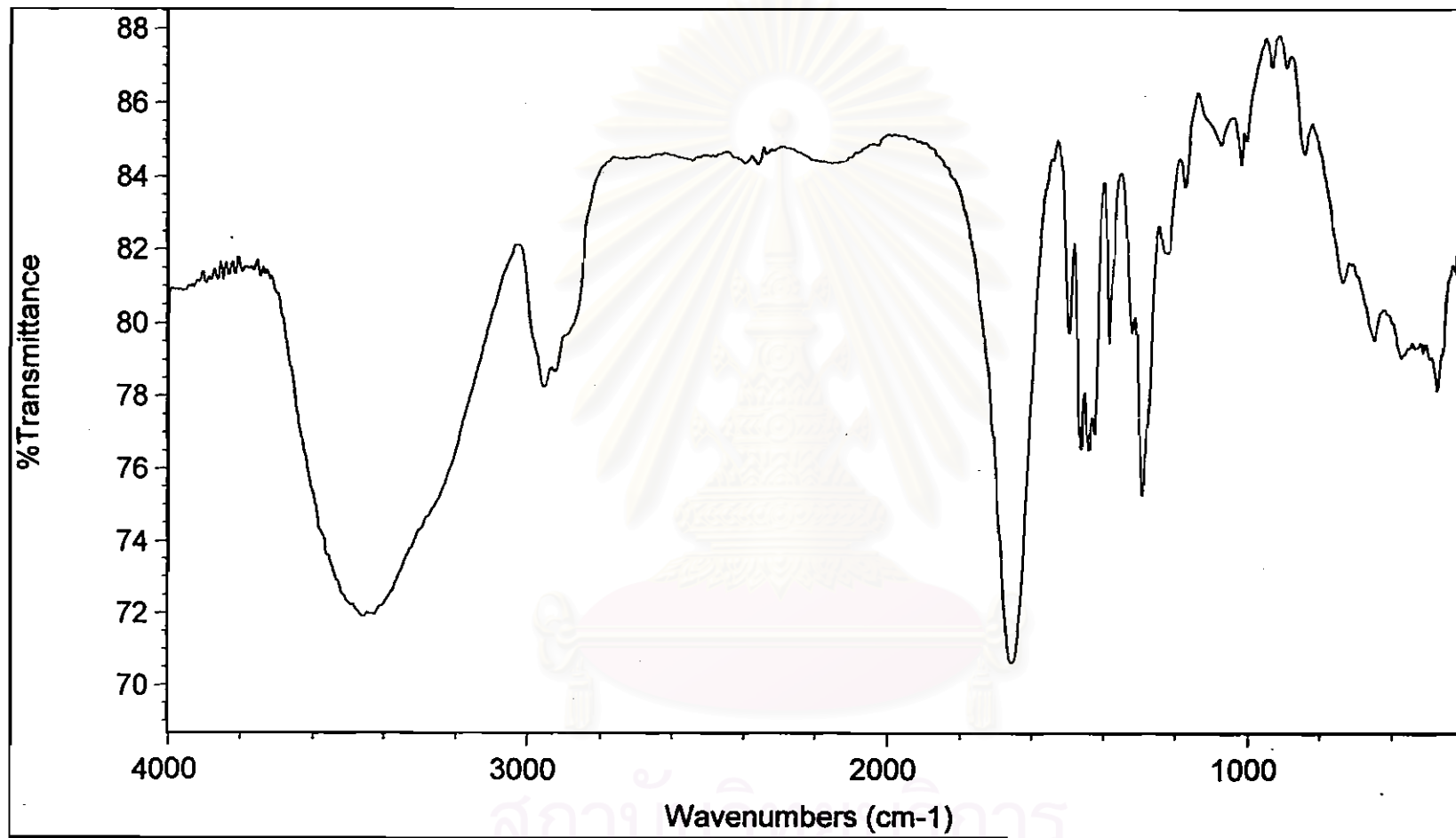
Figure 4.4 The FTIR spectrum of the poly(*N*-vinylpyrrolidone)
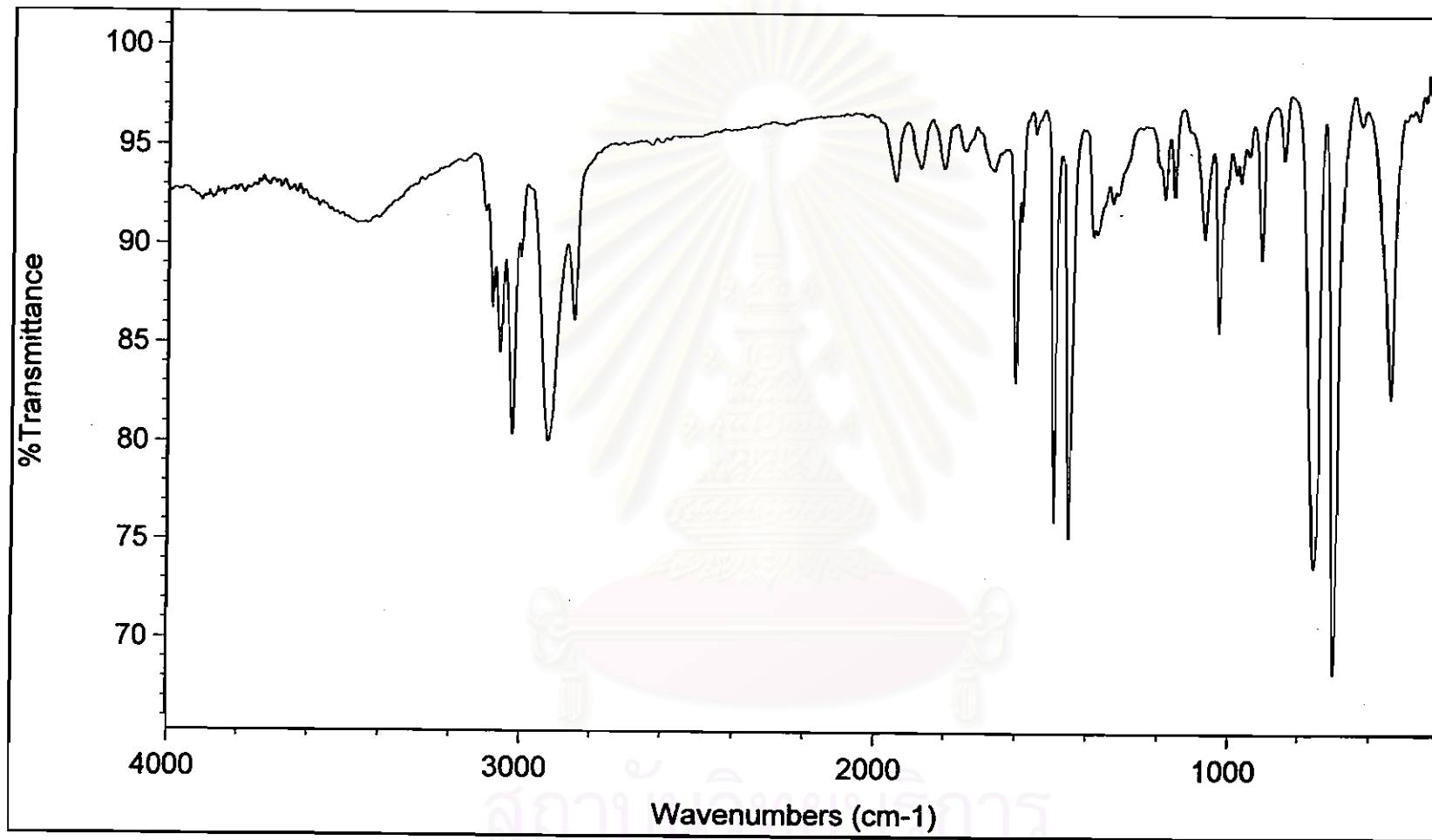
Figure 4.5 The FTIR spectrum of the polystyrene prepared by dispersion polymerization

4.3 Effect of the Concentration and Type of Dispersant on

4.3.1 The Particle Size and Size Distribution

In this study, three types of PVP were used. The viscosity-average molecular weights were 10,000, 40,000 and 360,000 g/mol, respectively. The polymerization was performed with PVP concentrations varied from 1 to 12 wt%. As shown in Figure 4.6 the particle size generally decreased with increasing PVP molecular weight for a given PVP concentration, and the particle size also decreased with increasing PVP concentration for a given PVP molecular weight. This may be explained that dispersion polymerization begins and progresses around the dispersant chains. During the nucleation period, the dispersant chains form a structure that acts as a skeleton or matrix for particle growth. The number of nuclei forming increases with increasing dispersant concentration which leads to more particles but with smaller sizes [34]. For another explanation, an increase in the concentration and molecular weight of PVP increases the viscosity of the reaction medium as shown in Table 4.2, and also increases the rate of adsorption of PVP on the particle surface. These changes would reduce the extent of nuclei aggregation and thus reduce the particle size of the resulting polymers. However, it was seen that an excess concentration beyond 8 wt% of PVP K-30 did not provide a marked decrease in particle size. This trend was also observed by Dawkins et al.[35] in dispersion polymerization of styrene in methanol media using poly(vinyl alcohol) as dispersant. They found that excess concentration of dispersant beyond 3 wt% produced little change in particle size.

Table 4.2 presents the effect of PVP concentration for each molecular weight of PVP on the particle size and size distribution of the resulting copolymers. The particle size is in the range of 0.6-1.8 μm in diameter. The largest particle size was
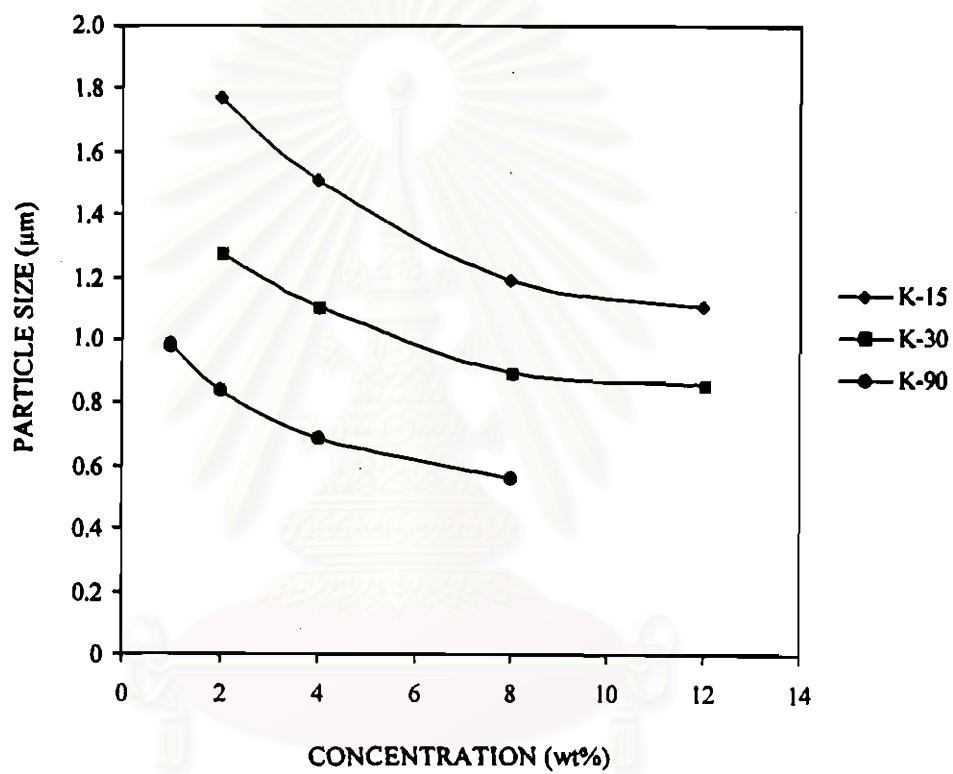
Figure 4.6 Effect of PVP concentration on the particle size of the copolymer

Table 4.2 Effect of dispersant on dispersion copolymerization of styrene and n-butyl acrylate

No.	Type	Concentration (wt%)	$\overline{D}_n$ (μm) [a,b]	CV (%) [c]	PDI [d]	$\overline{M}_n$ x 10^{-4}	$\overline{M}_w$ x 10^{-4}	$\overline{M}_w / \overline{M}_n$	Relative viscosity [e]
P1	PVP K-15	2	1.8	11.1	1.03	2.12	5.66	2.67	1.83
P2		4	1.5	4.2	1.01	2.41	6.51	2.69	2.17
P3		8	1.2	4.9	1.01	2.52	6.70	2.66	2.50
P4		12	1.1	5.00	1.01	3.10	7.56	2.43	3.33
P5	PVP K-30	2	1.3	4.3	1.01	2.57	6.72	2.61	2.00
P6		4	1.1	4.8	1.01	3.30	8.44	2.56	2.83
P7		8	0.9	4.9	1.01	3.51	9.34	2.66	5.00
P8		12	0.9	6.4	1.01	5.04	16.05	3.18	7.67

Table 4.2 Effect of dispersant on dispersion copolymerization of styrene and *n*-butyl acrylate (continued)

No.	Type	Concentration (wt%)	$\overline{D}_n$ (μm) [a,b]	CV (%) [c]	PDI [d]	$\overline{M}_n$ x 10^{-4}	$\overline{M}_w$ x 10^{-4}	$\overline{M}_w / \overline{M}_n$	Relative viscosity [e]
P9	PVP K-90	1	1.0	10.9	1.03	4.73	15.04	3.17	3.83
P10		2	0.8	10.1	1.03	3.83	11.33	2.95	8.00
P11		4	0.7	12.0	1.03	3.40	9.13	2.68	16.00
P12		8	0.6	14.2	1.05	3.30	9.04	2.74	40.83

a = Calculated diameter

b = Determined by scanning electron microscopy

c = Coefficient of variation

d = Polydispersity index

e = Viscosity of PVP in a mixed solvent of ethanol-water / viscosity of ethanol-water mixture at 25°C

obtained by using PVP K-15 at the low concentration of 2 wt%, while the smallest resulted from using PVP K-90 at 8 wt%.

Figures 4.7-4.18 shows SEM photographs of particles prepared with different concentration and molecular weight of PVP. In most cases particles with narrow size distribution were obtained, except for when a low concentration of PVP K-15 and all concentrations of PVP K-90 were used, a broad distribution was observed. At low concentration, PVP K-15 cannot sufficiently cover the surface of paricles, leading to some degree of coalescence. In this case, the number of particles would decrease, the average diameter increased, and the undesirably wide distribution was obtained. When using PVP K-90 (high molecular weight and high viscosity), it was believed that the amount of PVP graft copolymer that expected to occur during the polymerization would increase to the point where it exceeds the surface capacity or coverage requirement. This excess amount cannot be accommodated on the existing particles and is expelled from them. If excess graft is expelled, it may be able to stabilize a second crop of smaller particles growing from dead chains formed in solution but not yet captured by the large particles. In this case, the stabilized particle number count will increase and the size distribution will be broaden [26].
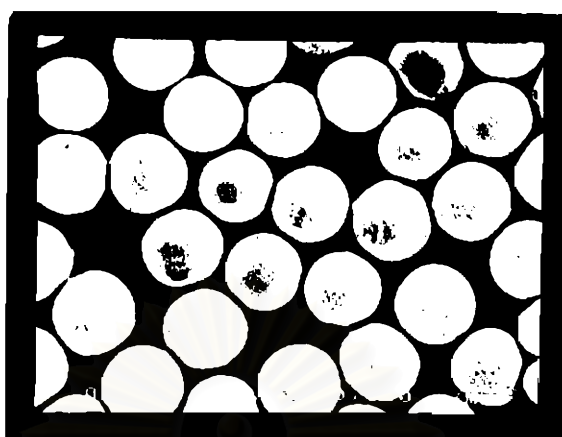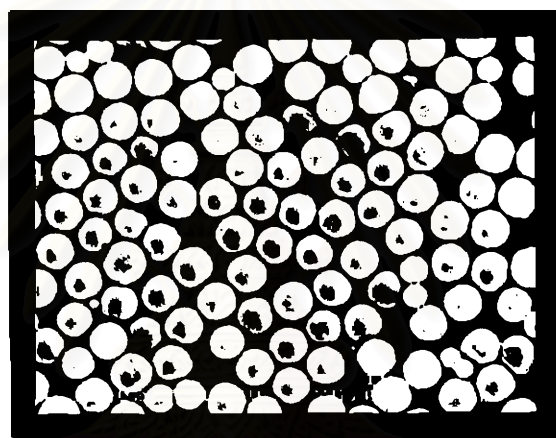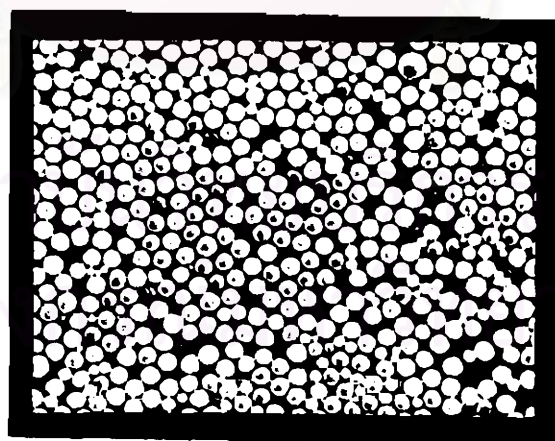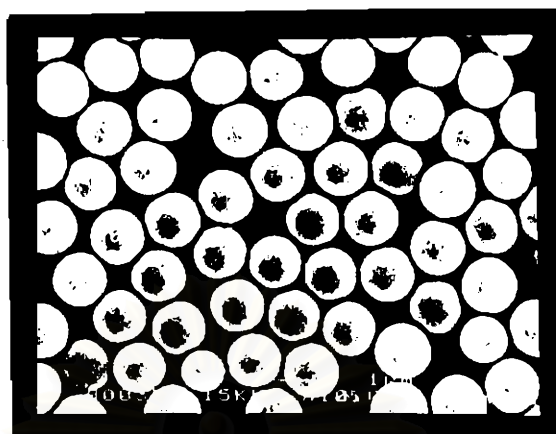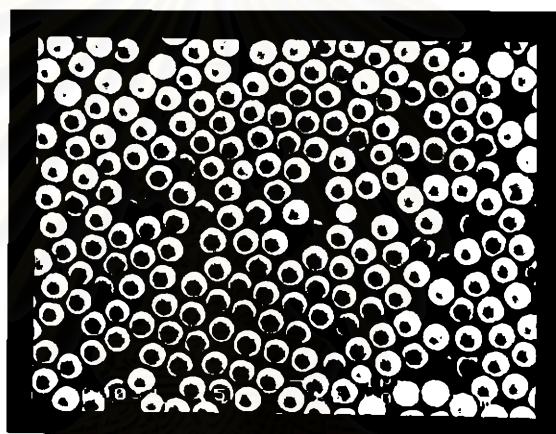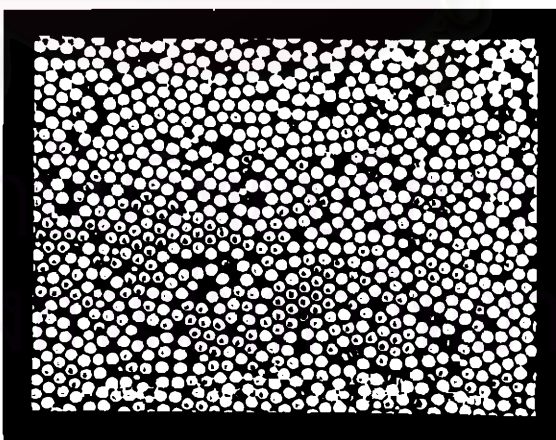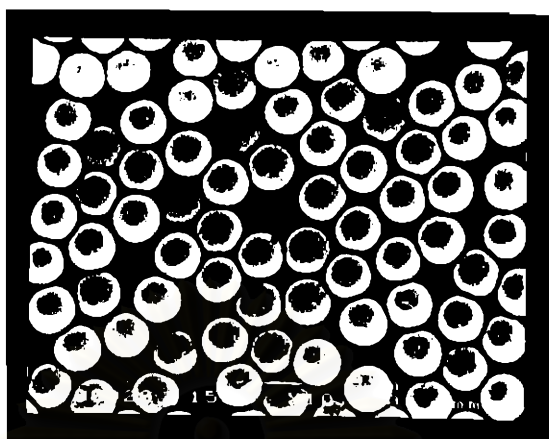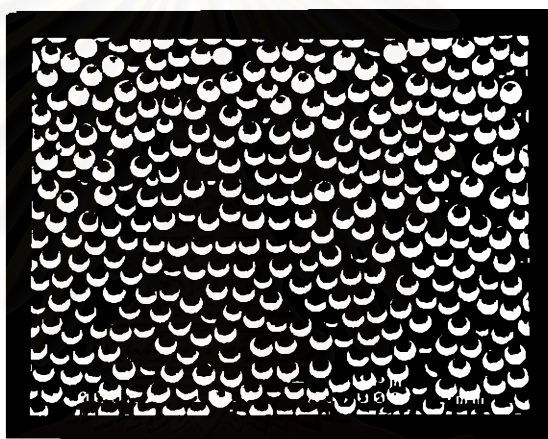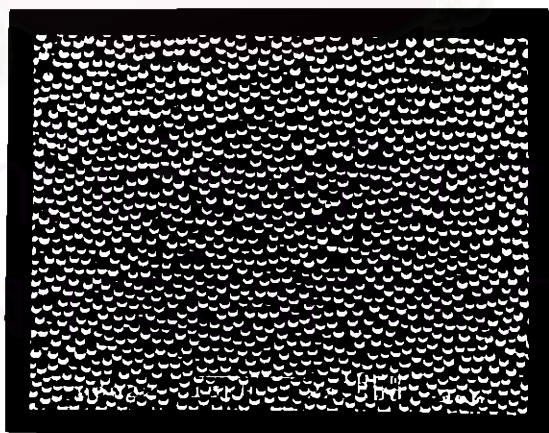
Figure 4.7 SEM photographs of the copolymer prepared with PVP K-15 at

2 wt% (a) x10,000   (b) x5,000 (c) x2,500
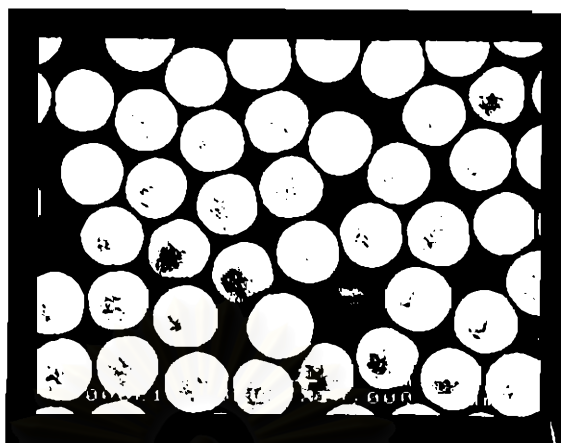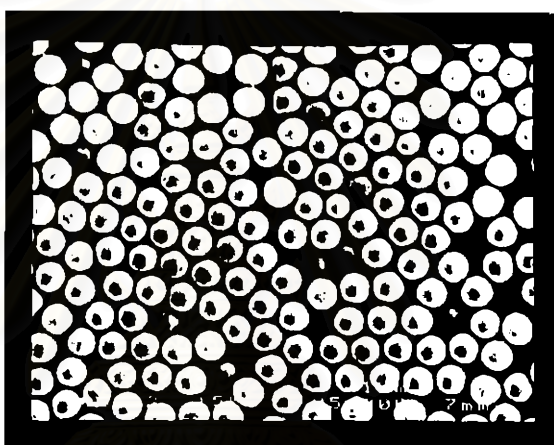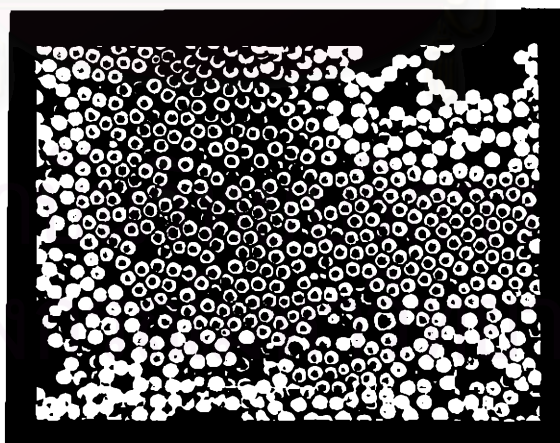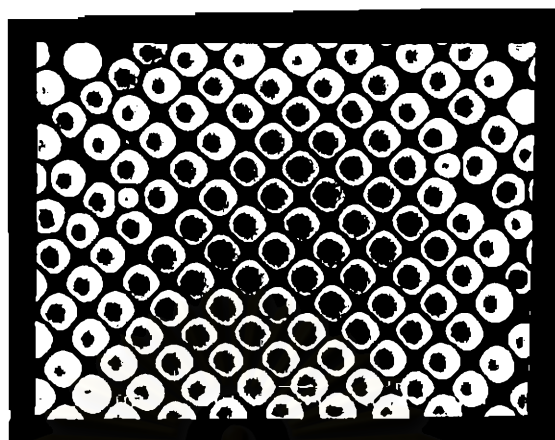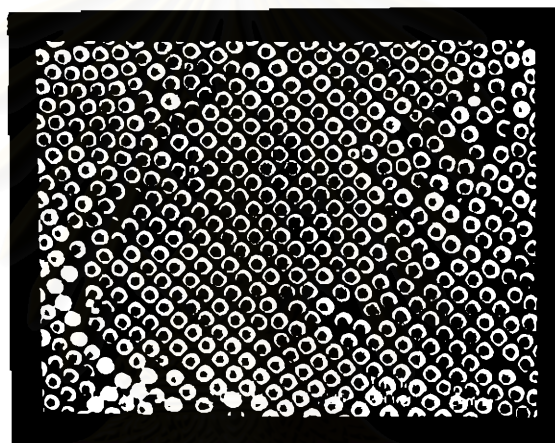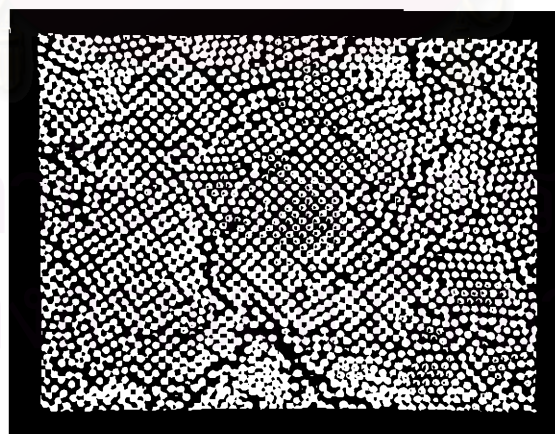
Figure 4.8 SEM photographs of the copolymer prepared with PVP K-15 at
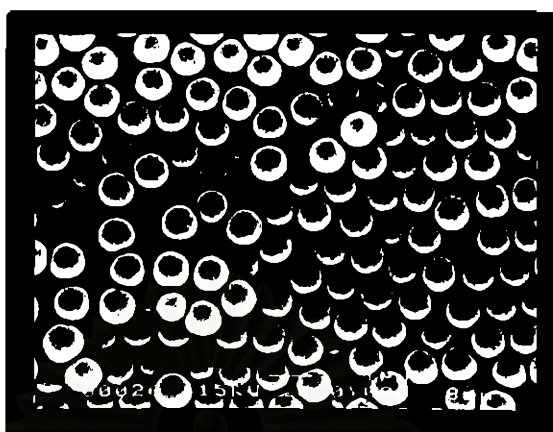
4 wt% (a) x10,000   (b) x5,000 (c) x2,500
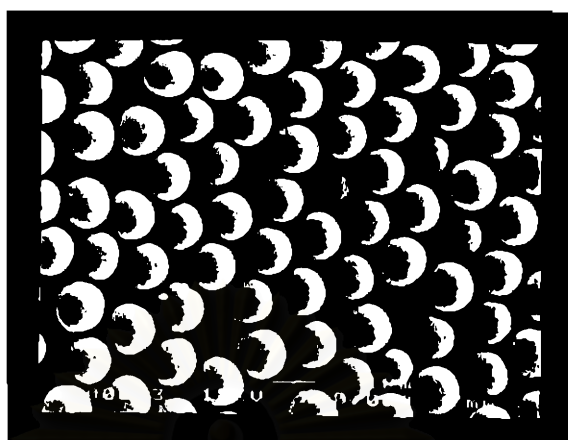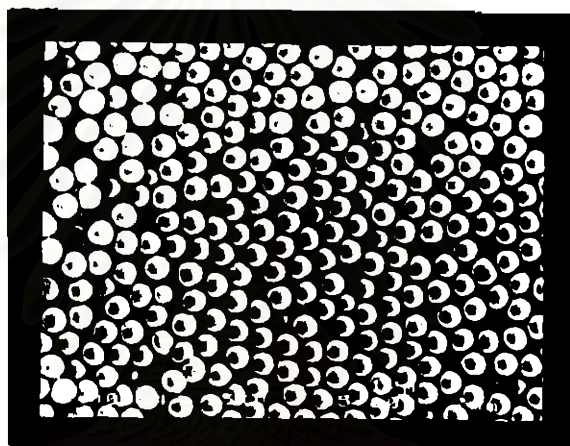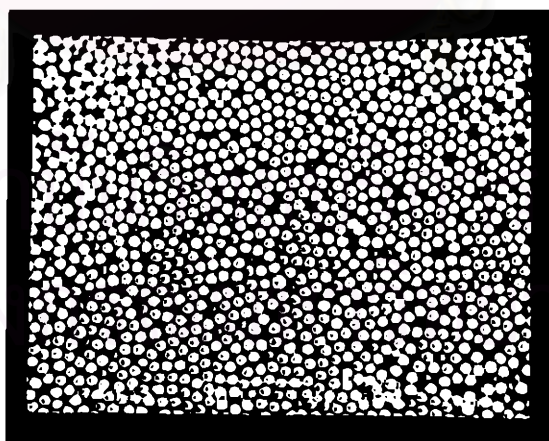
Figure 4.9 SEM photographs of the copolymer prepared with PVP K-15 at

8 wt% (a) x10,000   (b) x5,000 (c) x2,500
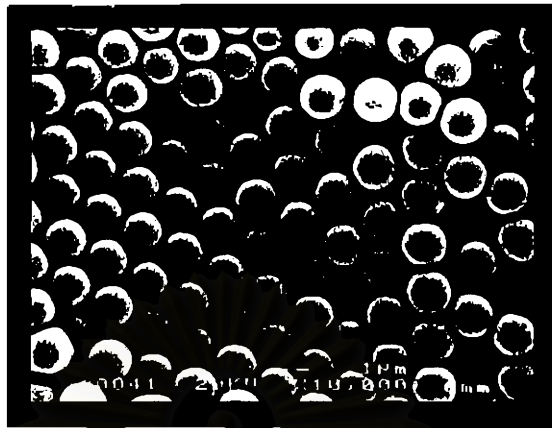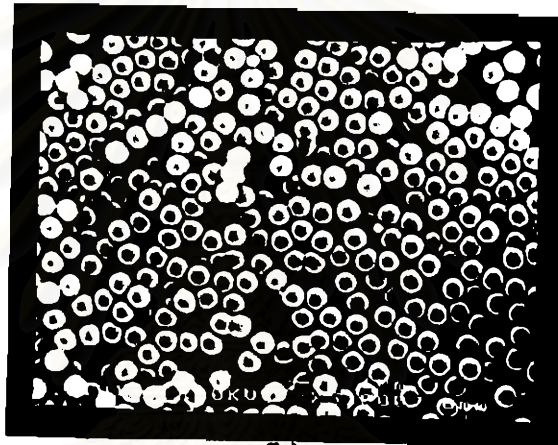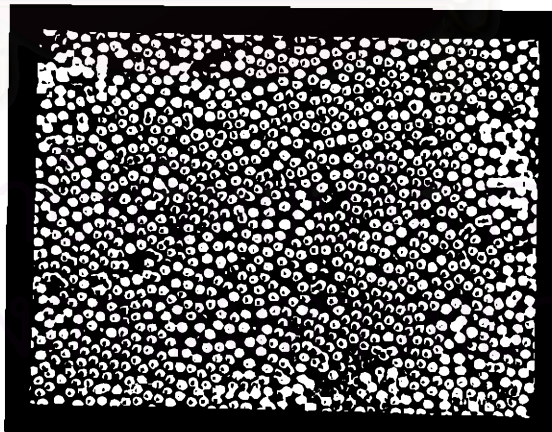
Figure 4.10 SEM photographs of the copolymer prepared with PVP K-15 at

12 wt% (a) x10,000 (b) x5,000 (c) x2,500

Figure 4.11 SEM photographs of the copolymer prepared with PVP K-30 at
2 wt% (a) x10,000 (b) x5,000 (c) x2,500

Figure 4.12 SEM photographs of the copolymer prepared with PVP K-30 at
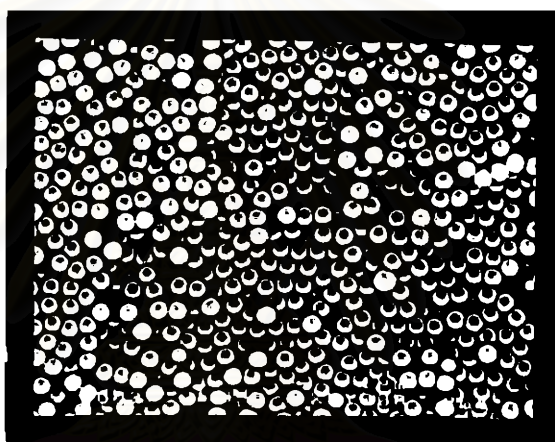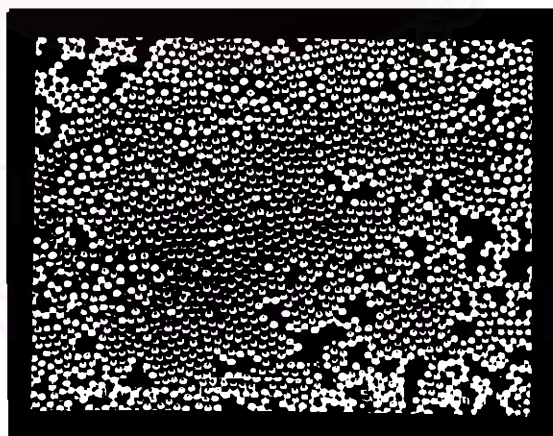
4 wt% (a) x10,000 (b) x5,000 (c) x2,500

Figure 4.13 SEM photographs of the copolymer prepared with PVP K-30 at
8 wt% (a) x10,000 (b) x5,000 (c) x2,500
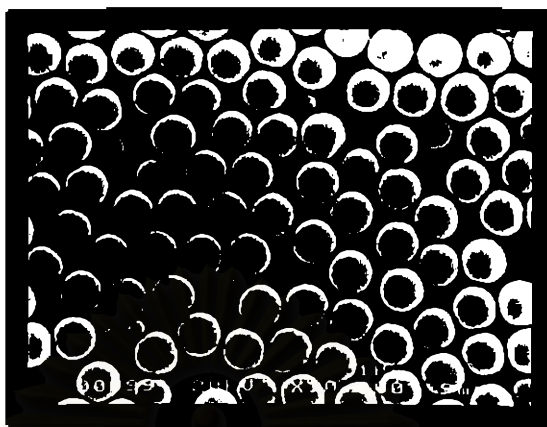
Figure 4.14 SEM photographs of the copolymer prepared with PVP K-30 at
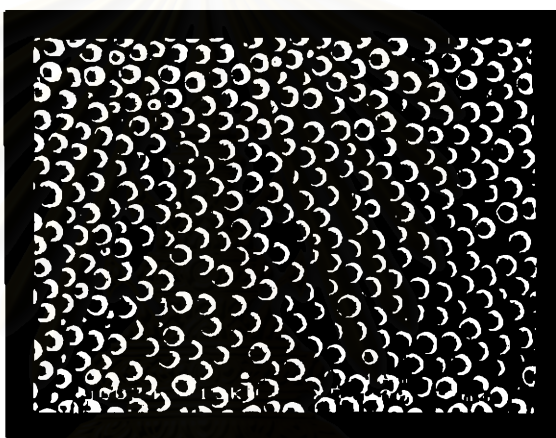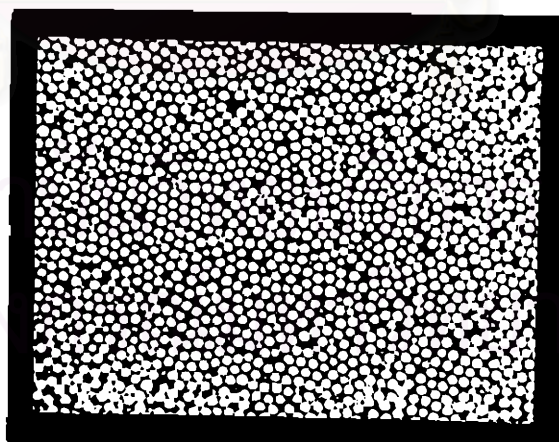
12 wt% (a) x10,000   (b) x5,000 (c) x2,500

Figure 4.15 SEM photographs of the copolymer prepared with PVP K-90 at

1 wt% (a) x10,000   (b) x5,000 (c) x2,500

(a)

(b)

(c)

Figure 4.16 SEM photographs of the copolymer prepared with PVP K-90 at

2 wt% (a) x10,000 (b) x5,000 (c) x2,500

Figure 4.17 SEM photographs of the copolymer prepared with PVP K-90 at
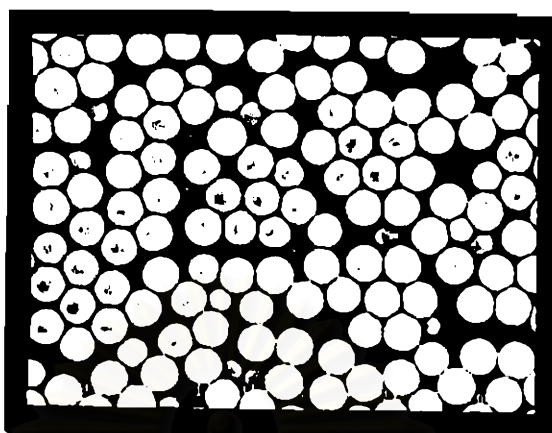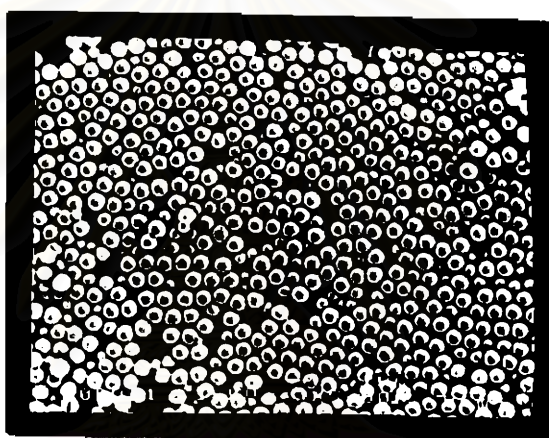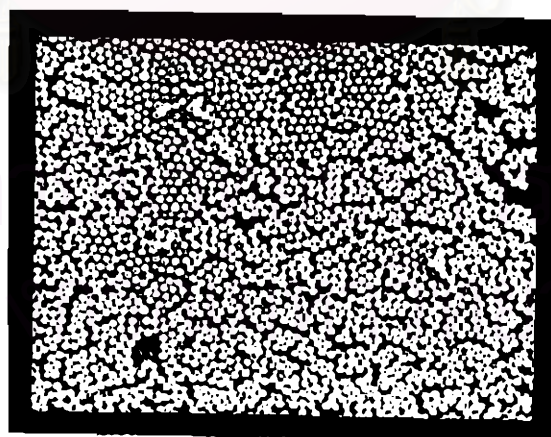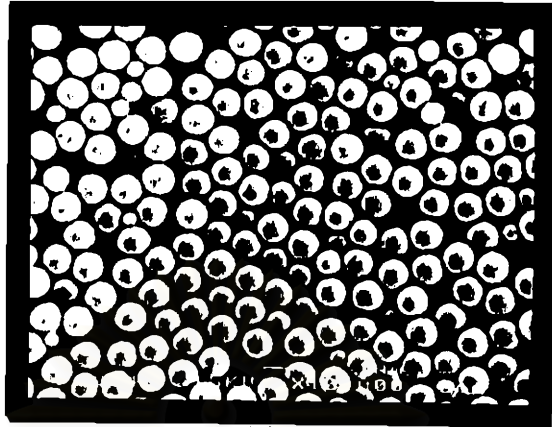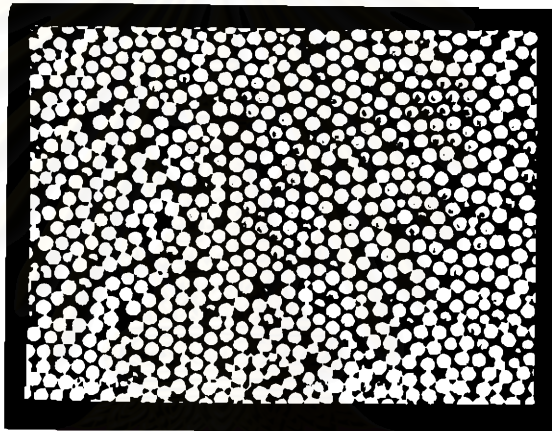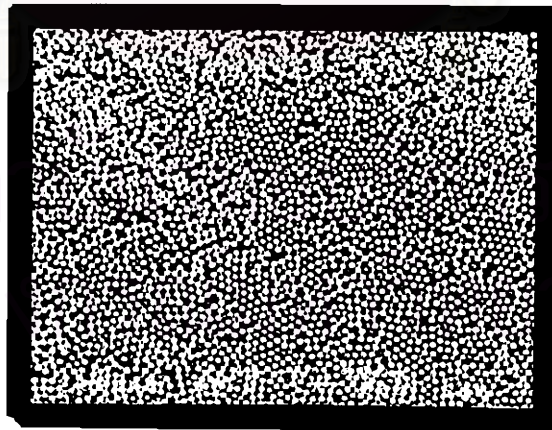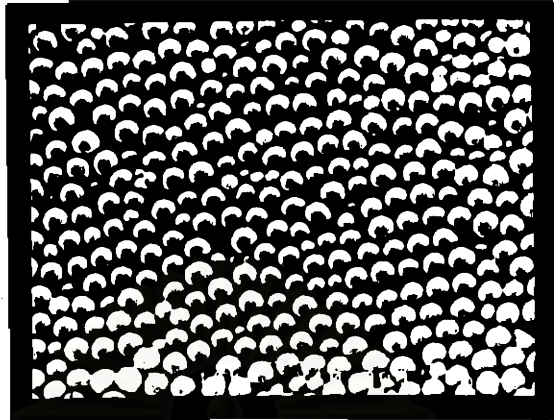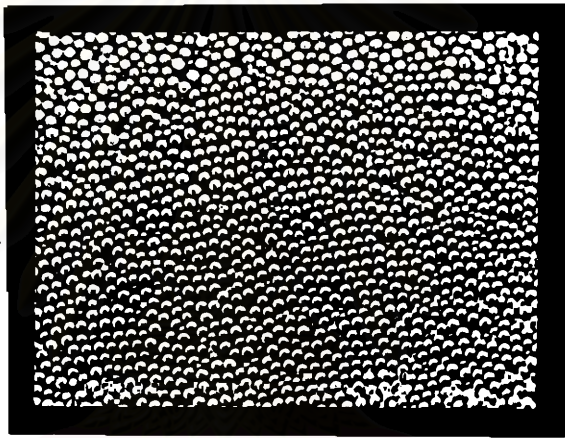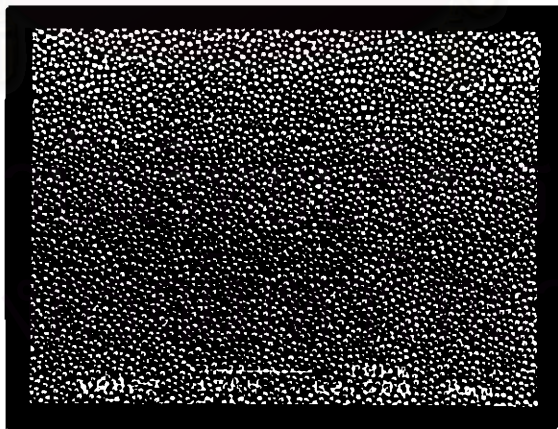4 wt% (a) x10,000   (b) x5,000 (c) x2,500

Figure 4.18 SEM photographs of the copolymer prepared with PVP K-90 at

8 wt% (a) x10,000   (b) x5,000 (c) x2,500

4.3.2 The Average Molecular Weights and Molecular Weight Distribution

The average molecular weights of the copolymer prepared with different PVP types and concentrations were shown in Table 4.2. The value of $\overline{M}_w/\overline{M}_n$ was in the range of 2.44-3.17. In most cases, the higher molecular weight was observed when the concentration of PVP increased. It could be noted that the average molecular weights inversely related to particle sizes. In other word, the average molecular weights directly related to the surface areas of the resulting particles. Higher concentration of PVP leads to small particle with great surface areas, also resulting in high molecular weight copolymers. This phenomenon can be discussed by the fact that smaller particles with their greater surface areas can grow by efficiently capturing the oligomeric radicals before they reach to critical molecular weight and terminate in the continuous phase, leading to proceed the polymerization within the particles, while large particles grow by capture of dead polymer of low molecular weight from solution. However, this trend was not seen in the systems using PVP K-90. It is probably because the excess amount of dispersant caused the secondary particles to occur, and the original particle will grow more slowly, consequently making the trend of average molecular weights changed. The relation between average molecular weights and PVP concentration is presented in Figure 4.19.
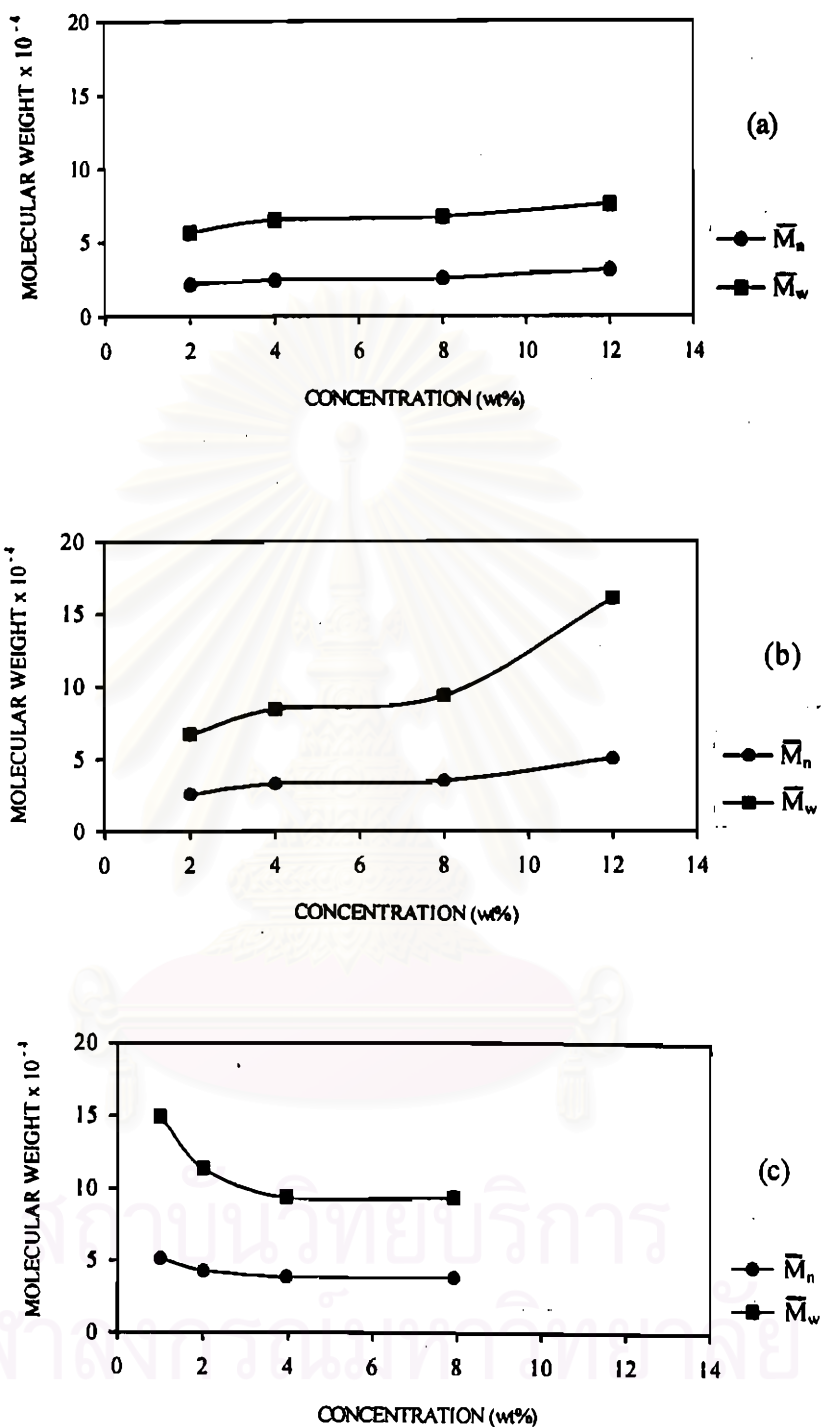
Figure 4.19 Effect of PVP concentration on the average molecular weight of the copolymer (a) PVP K-15, (b) PVP K- 30, and (c) PVP K-90

4.4 Effect of Solvency of the Reaction Medium on

4.4.1 The Particle Size and Size Distribution

The solvency of the reaction medium towards the polymer being produced plays an important role in dispersion polymerization because it controls the critical molecular weight above which the polymer will precipitate during the nucleation stage [31], and also related to the solubility properties of the polymeric dispersant affecting the stabilization of the formed particles.

In this research, the solvency of medium can be changed by addition of water to the alcohol. The content of water used was 10-30 wt%. These ranges of the reaction mixture were selected such that PVP was soluble in the initial reaction mixtures of solvent and monomer.

The solvency of the initial reaction mixture, related to its polarity, can be expressed by the overall solubility parameter (δ). The calculation of δ for a liquid mixture was performed according to the following equation [36].

$$\delta = (\sum V_i \, \delta_i^2)^{0.5} \tag{4.4}$$

where V_i is the volume fraction of each component. Neither the polymeric dispersant nor initiator was taken into account since they were presence in small quantities. The polymer produced from the monomer was not included in the calculation since it was located in a separate phase. The solubility parameters of individual components and the calculated solubility parameters for different reaction media used in this study are summarized in Table 4.3 and Table 4.4, respectively.

Table 4.3 The solubility parameters of individual component used in
dispersion copolymerization of styrene and n-butyl acrylate [37]

Component	Solubility Parameter $(MPa)^{1/2}$
Styrene	19.0
n-Butyl acrylate	18.0
Ethanol	26.0
Water	47.9

Table 4.4 The calculated solubility parameter for different reaction media

Reaction medium (ethanol/water)	Volume fraction (Vi)				Total solubility parameter $(MPa)^{1/2}$*
	Ethanol	Water	St	BuA	
100/0	0.890	-	0.084	0.026	25.3
90/10	0.816	0.071	0.086	0.027	27.5
80/20	0.740	0.146	0.087	0.027	29.6
70/30	0.660	0.223	0.089	0.028	31.6

* Calculated from equation 4.4

The effect of the solvency of polymerization mixture on particle size and size distribution is presented in Table 4.5 and Figure 4.20. The experimental results indicated that an increase in water content (equaling to an increase in the solubility parameter and polarity of the medium) led to a decrease in size of the resulting particles. Particle size decreased from 1.7 µm in pure ethanol to 0.8 µm in the medium containing 30 wt% water. Because water is a poorer solvent for poly(St-co-BuA) than ethanol, with increasing water content, the critical chain length of precipitated oligomers would decrease. This effect led to the generation of more nuclei and hence to smaller particles. On the other hand, the higher the amount of ethanol in the reaction medium, the more soluble the copolymer. Therefore, the adsorption equilibrium of the grafted PVP dispersant shifted toward a lower adsorption, and thus decreasing the area that can be stabilized with a given amount of dispersant [38]. This resulted in an increase of the particle size as the reaction medium became richer in ethanol. Obviously, the particle size is inversely proportional to the solubility parameter and polarity of the reaction medium.
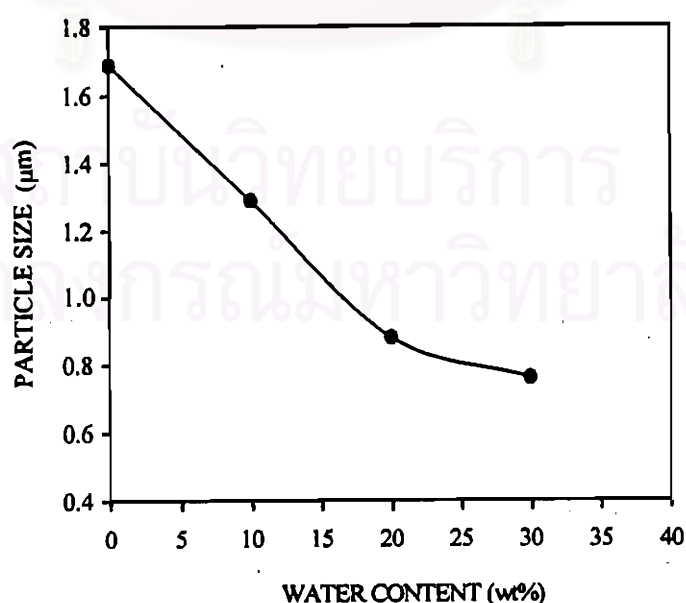

Figure 4.20 Effect of solvency of the reaction medium on the particle size of the copolymer

Table 4.5 Effect of the ethanol / water ratio on dispersion copolymerization of styrene and n-butyl acrylate

No.	Ethanol / Water	$\overline{D}_n$ (μm)^{a,b}	CV (%)^c	PDI^d	$\overline{M}_n$ x 10^{-4}	$\overline{M}_w$ x 10^{-4}	$\overline{M}_w / \overline{M}_n$
S1	100/0	1.7	11.9	1.03	1.76	3.55	2.01
S2	90/10	1.3	5.5	1.01	2.76	6.95	2.51
S3	80/20	0.9	10.7	1.03	3.46	11.04	3.19
S4	70/30	0.8	13.8	1.06	3.28	11.78	3.59

a = Calculated diameter

b = Determined by scanning electron microscopy

c = Coefficient of variation

d = Polydispersity index

Figures 4.21-4.24 revealed the SEM photographs of the polymeric particles prepared at different contents of water. It was seen that too high or to low polarity generated the particles with a broad size distribution. The size distribution remained fairly narrow when water content was about 10-20 wt%. From this experiment, it can be concluded that the favorable reaction medium for producing a monodisperse poly(St-co-BuA) shoud have the water content not higher than 20 wt%.

The result of a broad size distribution of the polymeric particles in pure ethanol medium can be described that an increase in the critical chain length would result in retardation of the particle formation [20], the step in which the oligomeric molecules nucleate by self or aggregative nucleation, which may result in the growth of the nuclei to various final sizes. Thus, fewer and larger particles will be formed, resulting in a polydisperse distribution. However, when a water content is up to 30 wt%, a broad distribution was encountered again. This effect is related to the solubility properties of the PVP in the reaction medium that influences in modifying PVP orientation, and in the number of the particles formed. As seen from Table 4.4, the medium containing 100 % ethanol with a δ equaling 25.3 $(MPa)^{1/2}$ is a good solvent for PVP ($\delta = 25.6(MPa)^{1/2}$) [39] with a $\Delta\delta$ (δ ethanol- δ PVP) value of less than 1 unit, PVP can thus dissolve easily and its chains then extend freely in the medium. Solvation, a formation of solvent-solute complex may occur. When increasing the water content up to 30 wt%, the medium becomes poorer (31.6 $(MPa)^{1/2}$) for PVP due to $\Delta\delta$ of about 6 units, PVP chains will entangle or aggregate to become a coiled structure, leading to a decrease in the adsorption rate of the dispersant and thus becoming less effective for stabilizing the particles formed. If the rate of generating nuclei in the high polarity medium was higher than the adsorption rate, the particle formation stage would extend, resulting in various particle size distributions.
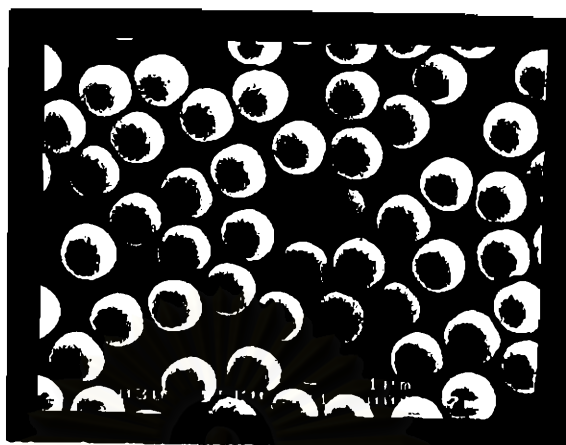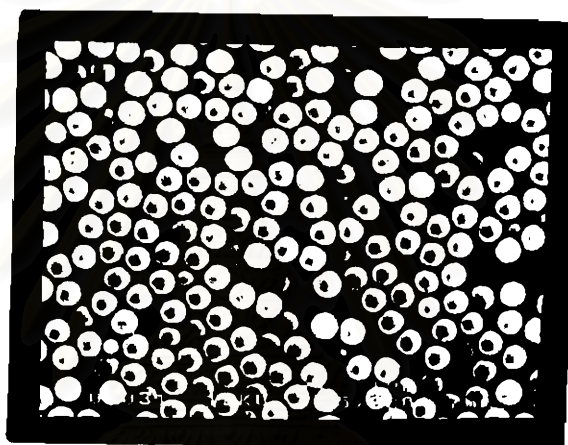
(a)
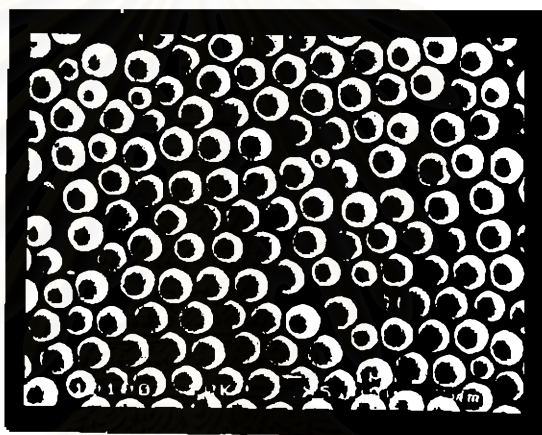
(b)
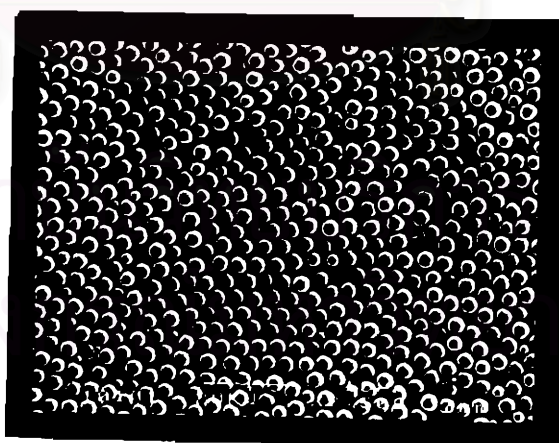
(c)

Figure 4.21 SEM photographs of the copolymer prepared in 100% ethanol
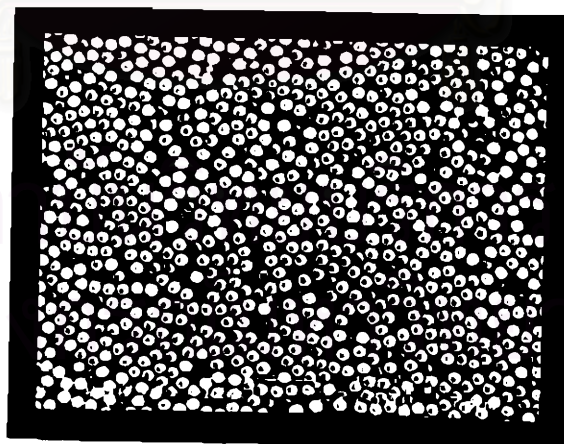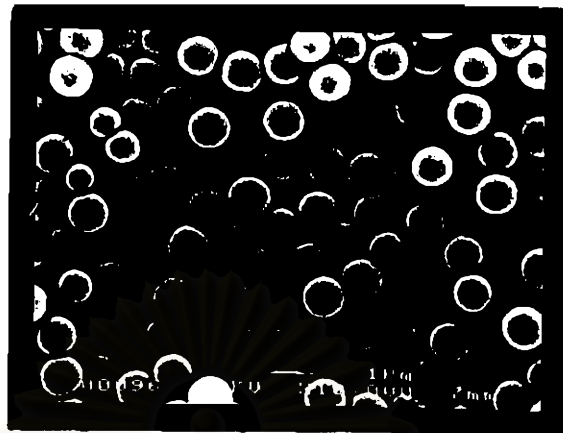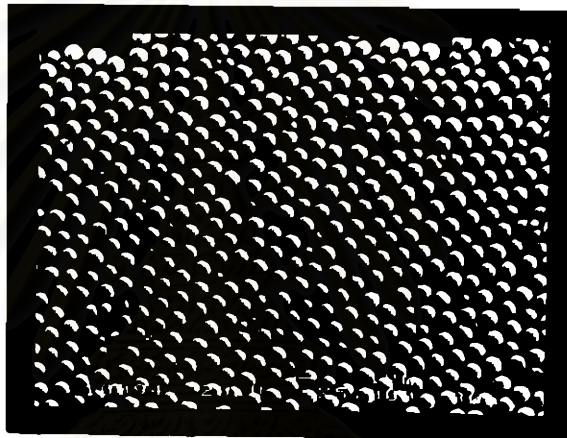
(a) x10,000   (b) x5,000 (c) x2,500

(a)

(b)

(c)

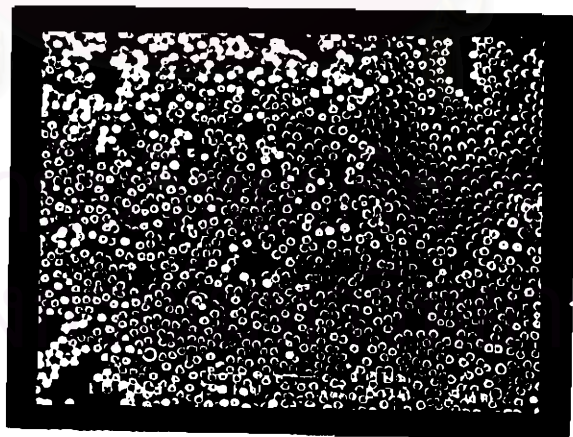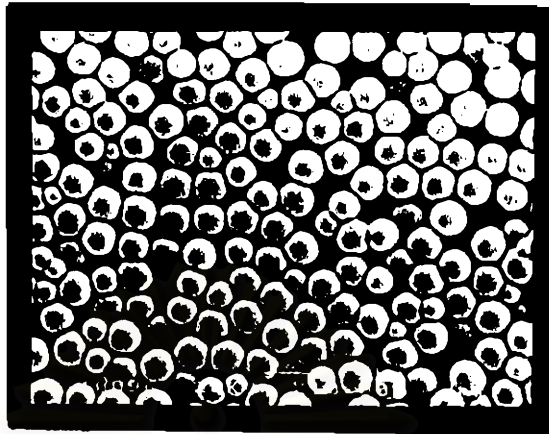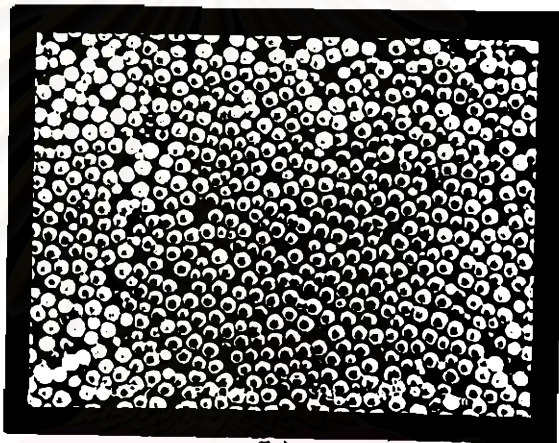Figure 4.22 SEM photographs of the copolymer prepared in ethanol/water 90/10
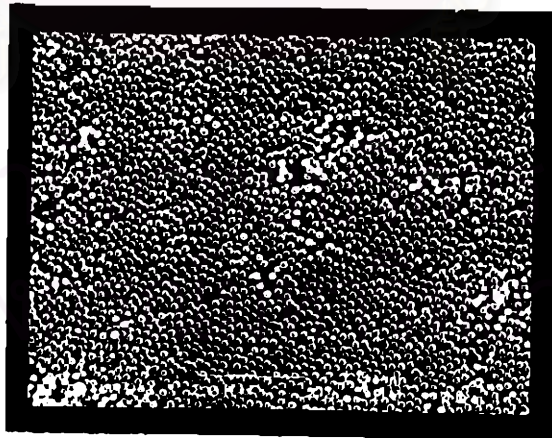
(a) x10,000   (b) x5,000 (c) x2,500

(a)

(b)

(c)

Figure 4.23 SEM photographs of the copolymer prepared in ethanol/water 80/20

(a) x10,000   (b) x5,000 (c) x2,500

Figure 4.24 SEM photographs of the copolymer prepared in ethanol/water 70/30

(a) x10,000   (b) x5,000 (c) x2,500

4.4.2 The Average Molecular Weights and Molecular Weight Distribution

Figure 4.25 presents the average molecular weights of poly(styrene-co-n-butyl acrylate) obtained by dispersion polymerization in different reaction media. The molecular weight increased with an increasing amount of water in the reaction mixture, implying an inverse correlation between the particle size and molecular weight. Values of $\overline{M_w}/\overline{M_n}$ are in the ranges of 2.01-3.59. This inverse correlation between the particle size and molecular weight, a typical characteristic for the dispersion polymerization of other systems [25, 31] can be accounted for changes of the locus of polymerization. Dispersion polymerization occurs both in solution and in the monomer-swollen particles. The molecular weight of the copolymer originating from polymerization within the particles is typically higher than that from the solution polymerization because the termination rate is reduced by the viscosity of the monomer/polymer particle medium (the gel effect) [40, 41]. With increasing water content up to 30% (the smallest polymeric particle), the highest molecular weight was obtained. After the particle formation stage, the volume fraction of polymer is higher, so the distribution coefficients of both monomer and initiator are strongly biased toward particle phase [29]. As a result, the vast majority of polymerization occurs in particle swollen monomer phase. In contrast to 100% ethanol, the less polar system, low molecular weight of the copolymers was observed, possibly because the monomer and initiator were present to a large extent in solution, and the slow particle growth occurs by capturing the dead polymer molecules already in the solution, therefore, they exhibit the lower molecular weights, a typical nature of a solution polymerization.
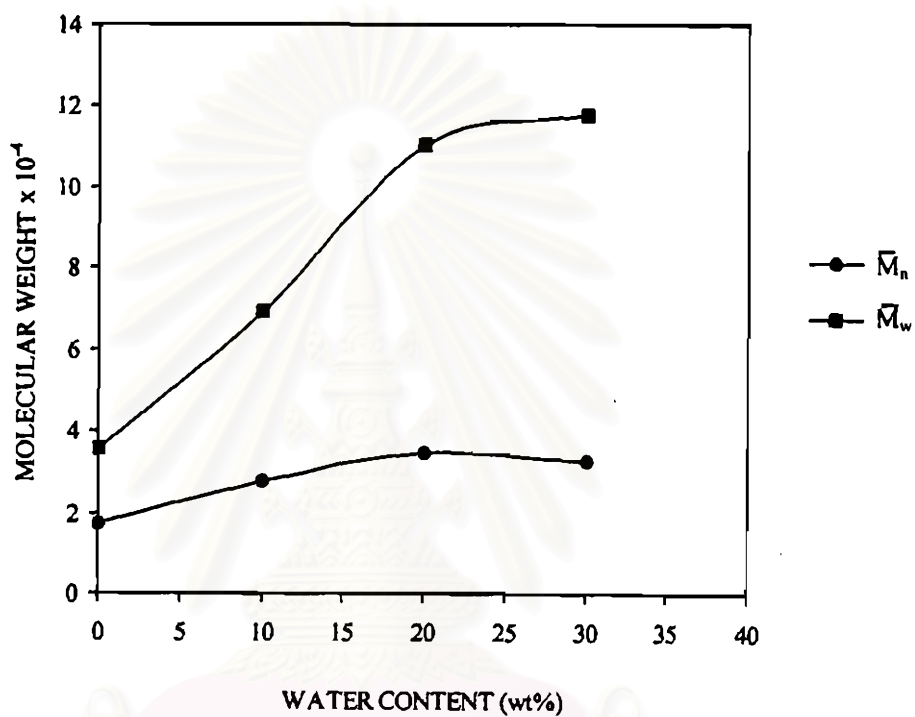
Figure 4.25   Effect of solvency of the reaction medium on the average molecular
            weights of the copolymer

4.5 Effect of Temperature on

4.5.1 The Particle Size and Size Distribution

Temperature influences the thermodynamic factors such as solubility of the oligomers formed as well as the kinetics of initiator decomposition which in turn determines the rate of polymerization and particle nucleation [23]. Furthermore, temperature also affects the viscosity of the system and the solubility of the dispersant, thereby affecting the efficiency of the stabilization. These effects have a direct impact on the particle size and the molecular weight of the resulting copolymer.

The temperature employed for this experiment was increased by a 5°C increment between 65°C and 80°C. The effects of reaction temperature on some characteristics of the resulting particles are listed in Table 4.6, and Figure 4.26 presenting a relation between particle size and temperature. It can be seen that the particle size increased from 1.1 μm at 65°C to 1.7 μm at 80°C. An increase in particle sizes with rising temperature was attributed to: (a) an increase in the critical chain length due to an increase in the solvency of the continuous phase, (b) an increase in the concentration of precipitated oligomer chains due to an increase in both the decomposition rate of the initiator and the propagation rate of oligomer radicals, (c) a decrease in the viscosity of the continuous phase, and (d) a decrease in the efficiency of the PVP graft copolymer due to its higher solubility. All of these factors can contribute to an increase in particle size [42].

According to SEM photographs of copolymer prepared at varied temperatures shown in Figures 4.27 - 4.30. It indicates that, an increase in the reaction temperature led to an increase in particle size and its particle size distribution. At high temperature, if the generation rate of the oligomeric radicals is much faster than the adsorption rate of the dispersant controlling the aggregative

Table 4.6 Effect of temperature on dispersion copolymerization of styrene and *n*-butyl acrylate

No.	Temperature (°C)	$\overline{D}_n$ (μm) [a,b]	CV (%) [c]	PDI [d]	$\overline{M}_n$ x 10^{-4}	$\overline{M}_w$ x 10^{-4}	$\overline{M}_w / \overline{M}_n$
T1	65	1.1	8.1	1.02	5.19	17.90	3.44
T2	70	1.3	5.5	1.01	2.79	6.95	2.49
T3	75	1.6	6.6	1.01	2.00	5.25	2.62
T4	80	1.7	13.5	1.04	2.19	5.35	2.44

a = Calculated diameter

b = Determined by scanning electron microscopy

c = Coefficient of variation

d = Polydispersity index

nucleation process due to the fast composition rate of the initiator, the oligomer would thus tend to aggregate and form larger particle nuclei of various sizes before enough dispersants were adsorbed to stabilize them. The chance of secondary nucleation to take place during the particle growth stage would also be increased. These factors may account for the large particle sizes with a broaden size distribution [27].
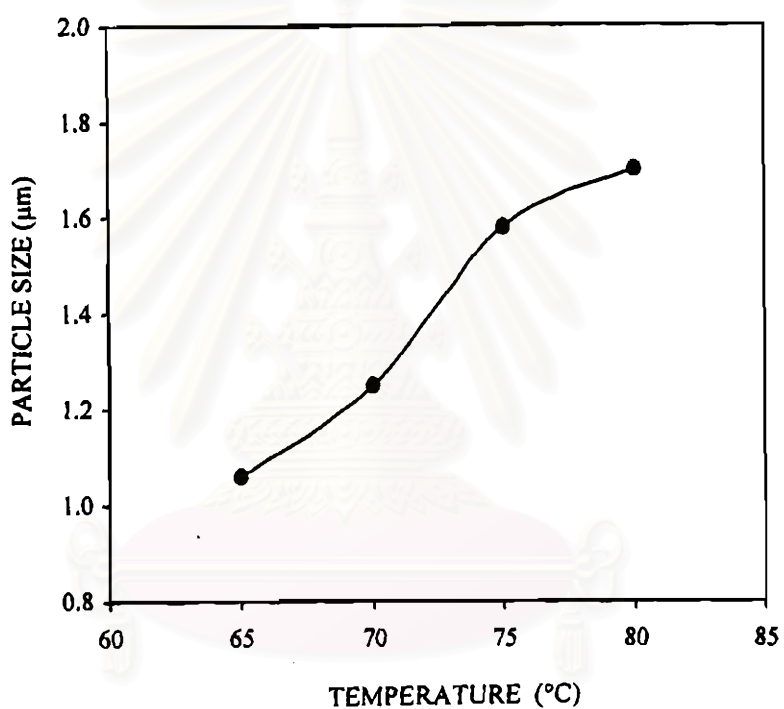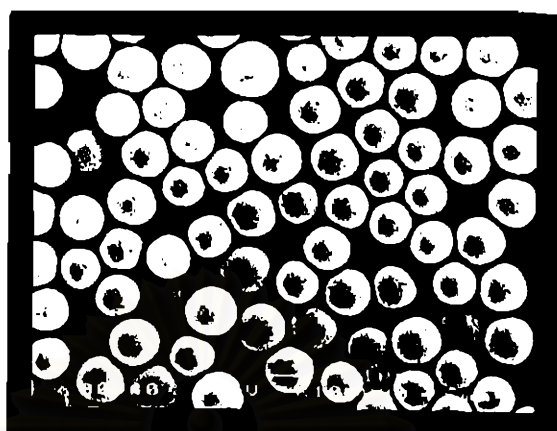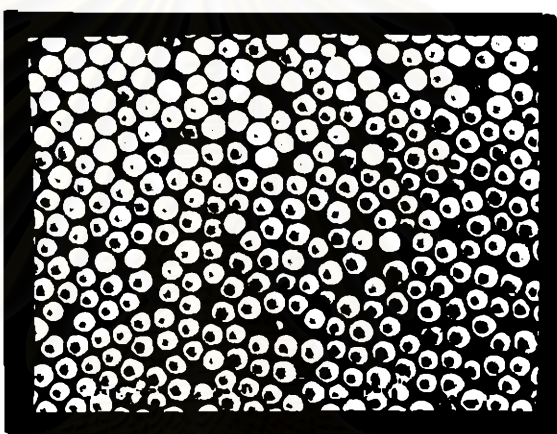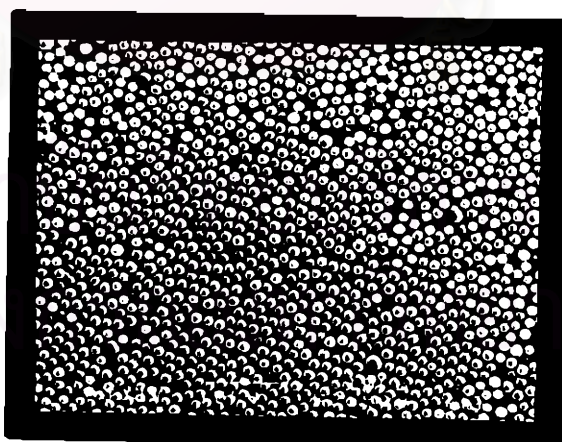

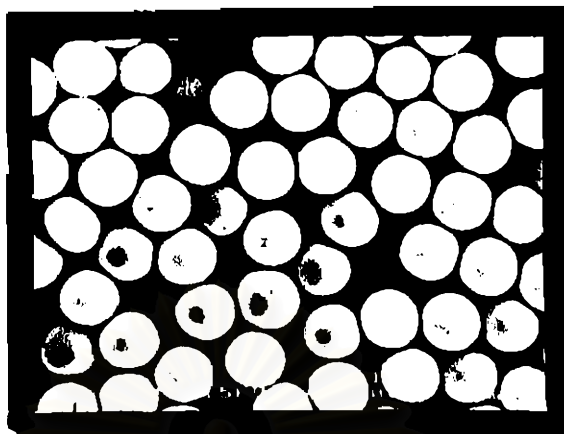Figure 4.26   Effect of temperature on the particle size of the copolymer
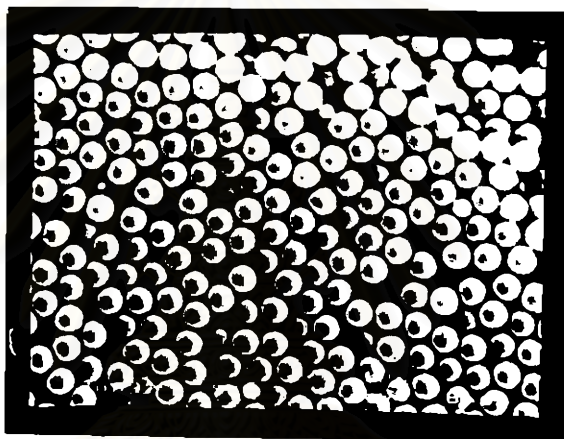
Figure 4.27 SEM photographs of the copolymer prepared at temperature 65°C

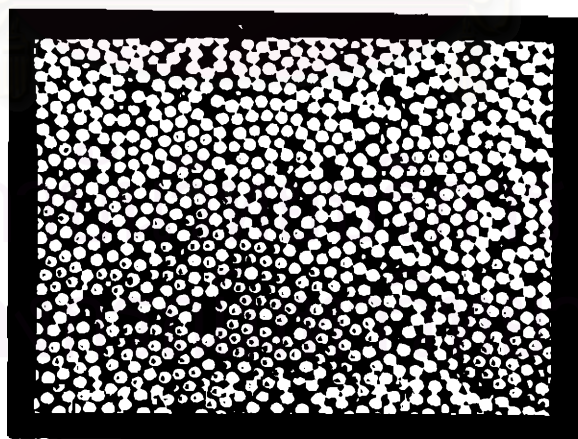(a) x10,000   (b) x5,000   (c) x2,500
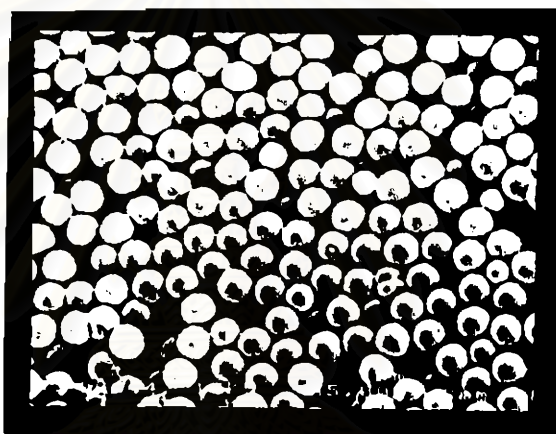
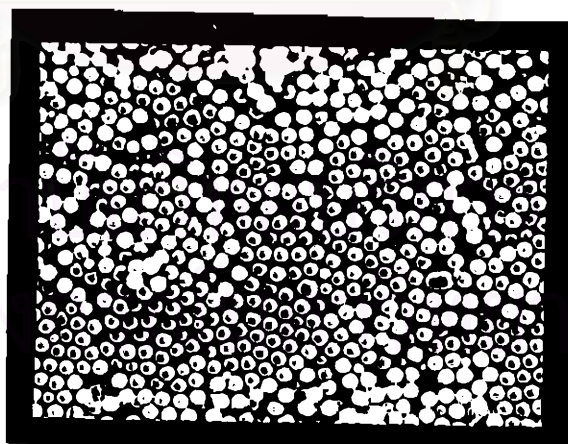Figure 4.28 SEM photographs of the copolymer prepared at temperature 70°C
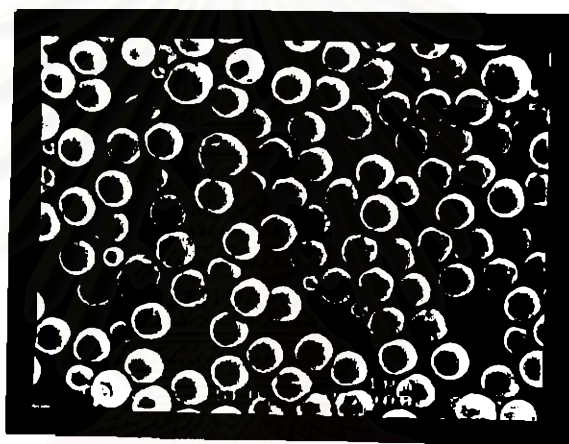
(a) x10,000   (b) x5,000 (c) x2,500

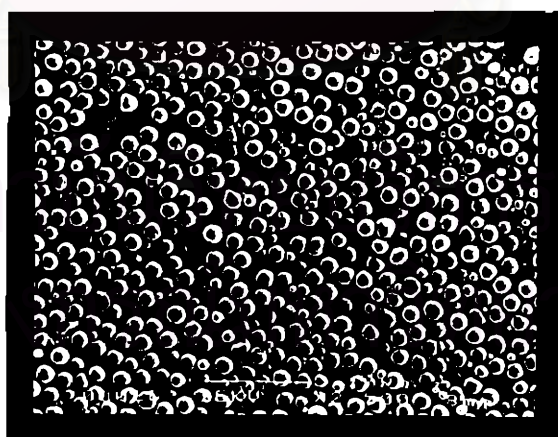Figure 4.29 SEM photographs of the copolymer prepared at temperature 75°C

(a) x10,000   (b) x5,000 (c) x2,500

Figure 4.30 SEM photographs of the copolymer prepared at temperature 80°C

(a) x10,000   (b) x5,000 (c) x2,500

4.5.2 The Average Molecular Weights and Molecular Weight Distribution

Figure 4.31 shows the relation between the average molecular weights and temperature. It is notable that, as increasing the reaction temperature, the average molecular weights were decreased. Increasing temperature will increase solubility of oligomeric chains, and thus the locus of the polymerization shifts to the continuous phase. A majority of the oligomeric radicals terminate in the continuous phase before they are captured by the existing particles, resulting in a lower molecular weight (the molecular weight is very close to that expected from solution polymerization).

For other explanations, at low temperatures, more monomers are converted to polymers per initiator per fragment than at high temperatures, where the higher rate of free radical formation will actually enhance the probability of chain termination by initiator [23]. As a result of these competing effects, the initiator becomes exhausted more quickly at high temperatures, leading to producing short kinetic chain length, i.e., the low molecular weight polymer. Additionally, at high temperatures, the acceleration of polymerization rate due to that the gel effect is smaller than that of low temperature, because the temperature reduces the viscosity of the polymerization medium with a consequent fall in polymerization rate.
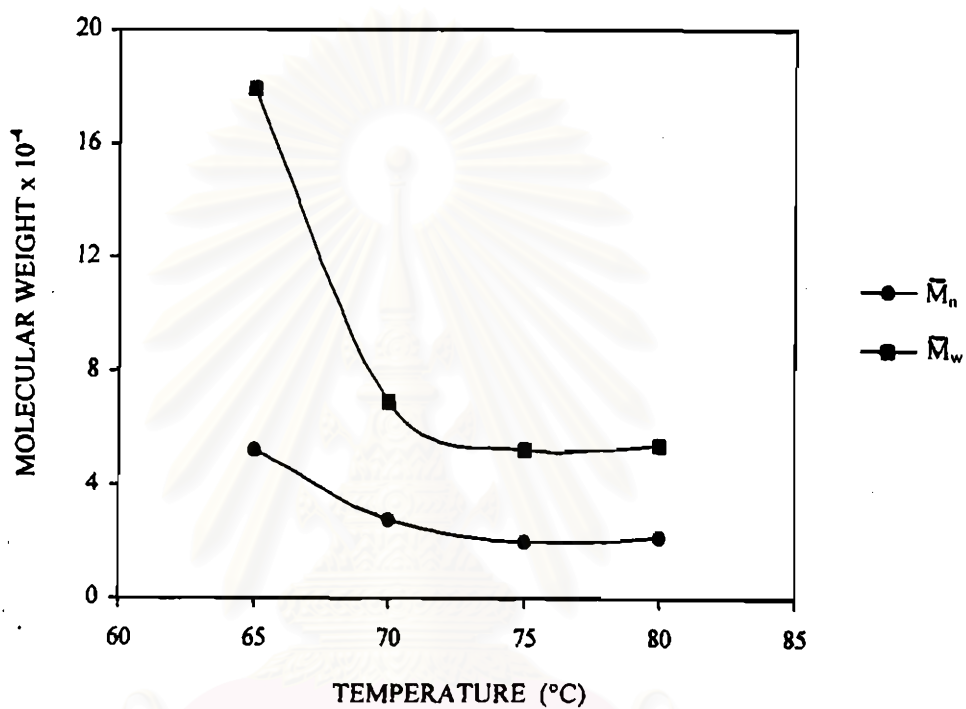
Figure 4.31 Effect of temperature on the average molecular weights of the copolymer

4.6 Effect of Agitation Rate on

4.6.1 The Particle Size and Size Distribution

All of the experiments in this research were carried out in a stirred glass reactor. The mixing of all ingredients was through the use of mechanical stirrer with semicircular anchor-type blade. Good agitation was required to ensure complete mixing of the reaction mixture and to prevent them from sedimentation to the bottom. In this study, the agitation rates investigated were 50, 100, 200 and 300 rpm. The effect of agitation rate on some characteristics of the copolymer was given in Table 4.7. It was seen that the size of the resulting particles can be effectively controlled by adjusting the agitation rate. In general, increasing the rate of agitation corresponds to increasing the shear force, which causes the particle size to decrease. Additionally, the dispersant in this system acts like a spacer or matrix between particles that inhibit coalescence. These dispersants would adsorb on the surface of particles, thus preventing the particle contact. As agitation rate increases, the space becomes smaller due to the system being more dynamic. As a result, the smaller particle will be generated [32].

The relation between the particle size and rate of agitation is shown in Figure 4.32. It presented that the particle size decreased rapidly with an increase in the agitation rate from 50 to 100 rpm, and the largest particle size of 1.5 μm was obtained at 50 rpm agitation. However, above the agitation rate of 100 rpm, any increase in mechanical force does not contribute to much reduction in particle size, but an increase in the breadth of the particle size distribution was observed (As seen in SEM photographs in Figures 4.33-4.36). This explicits that the reaction performed in a stirred reactor with high agitation rate is not efficient for producing particles with a narrow size distribution in dispersion polymerization.

Table 4.7 Effect of agitation rate on dispersion copolymerization of styrene and *n*-butyl acrylate

No.	Agitation Rate (rpm)	$\overline{D}_n$ (μm) [a,b]	CV (%) [c]	PDI [d]	$\overline{M}_n$ x 10^{-4}	$\overline{M}_w$ x 10^{-4}	$\overline{M}_w / \overline{M}_n$
A1	50	1.5	9.9	1.02	2.36	6.19	2.63
A2	100	1.2	8.0	1.02	2.75	7.08	2.57
A3	200	1.1	11.2	1.03	2.57	6.70	2.61
A4	300	1.0	15.2	1.06	1.84	4.29	2.33

a = Calculated diameter

b = Determined by scanning electron microscopy
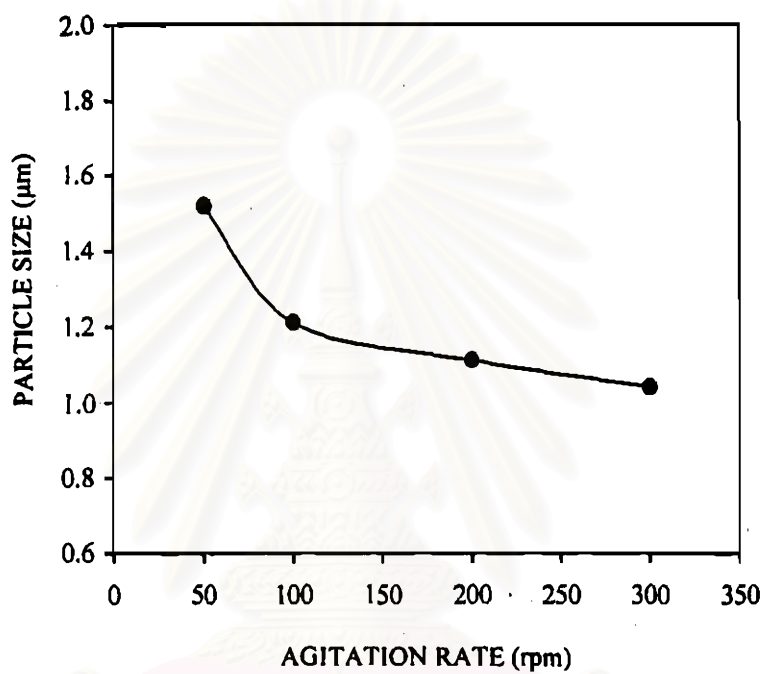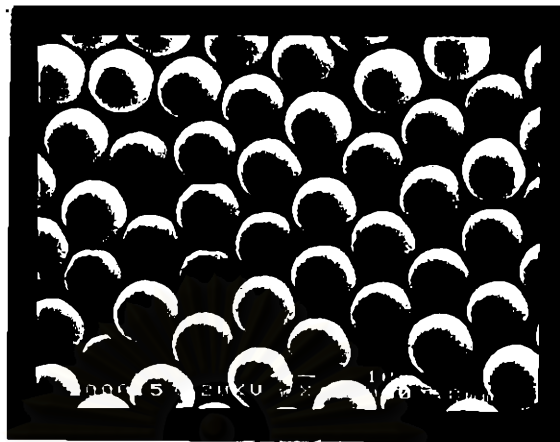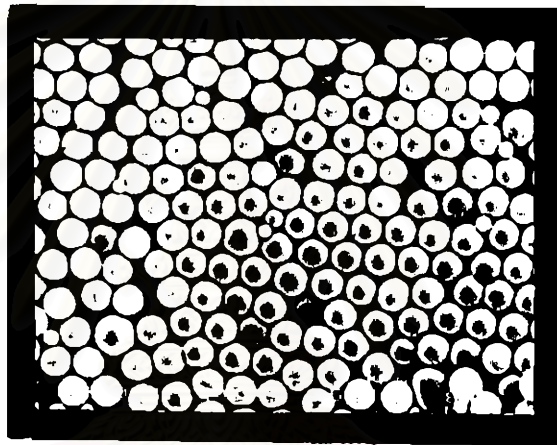
c = Coefficient of variation

d = Polydispersity index

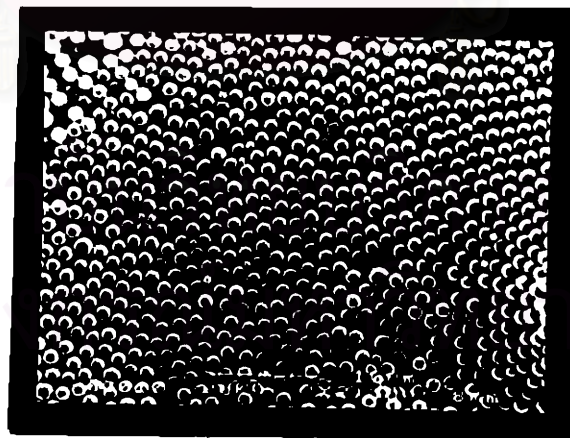Figure 4.32   Effect of agitation rate on the particle size of the copolymer

Figure 4.33 SEM photographs of the copolymer prepared at agitation rate 50 rpm

(a) x10,000 (b) x5,000 (c) x2,500

Figure 4.34 SEM photographs of the copolymer prepared at agitation rate 100 rpm
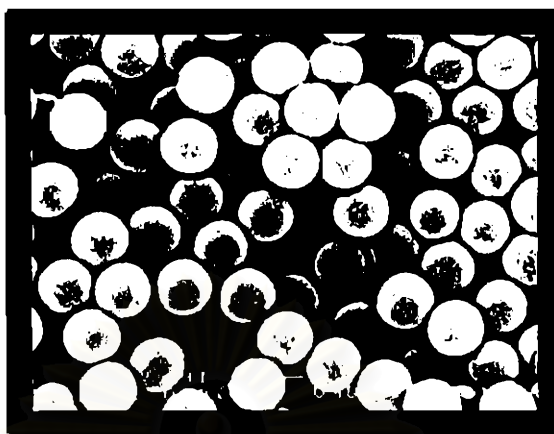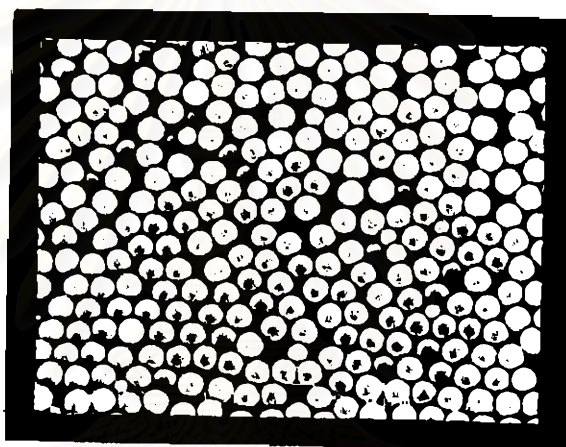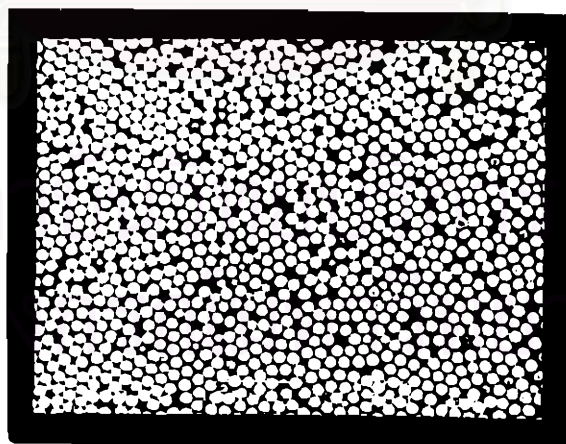
(a) x10,000   (b) x5,000 (c) x2,500

(a)

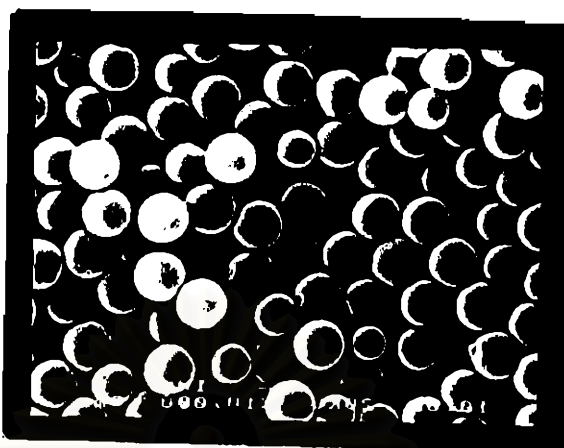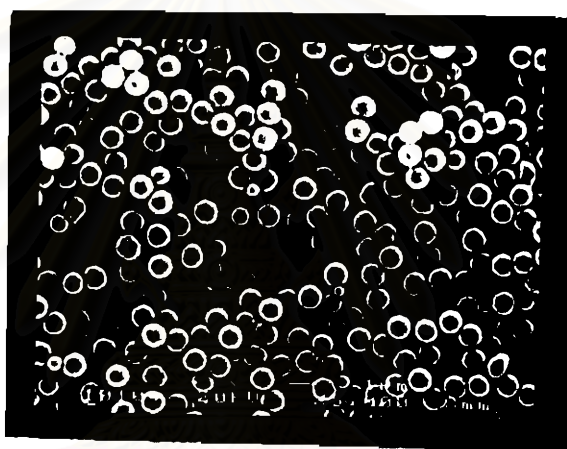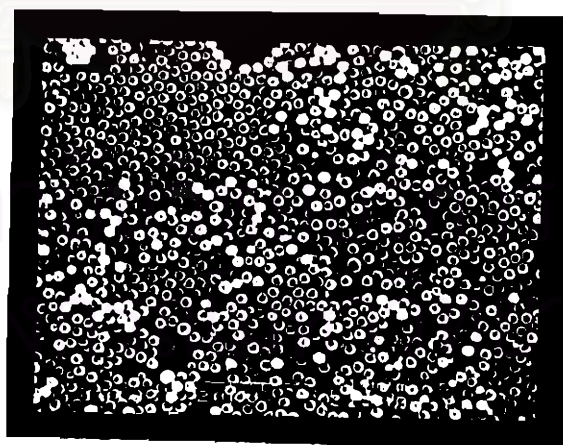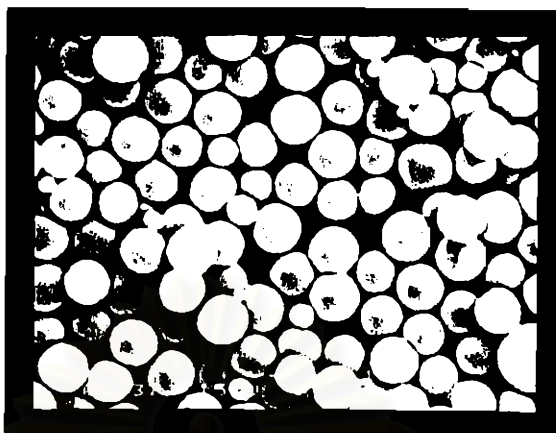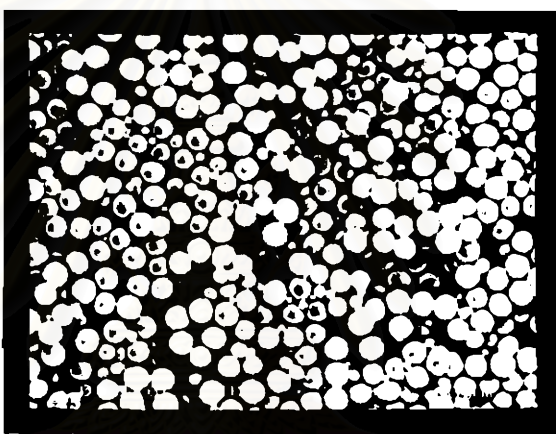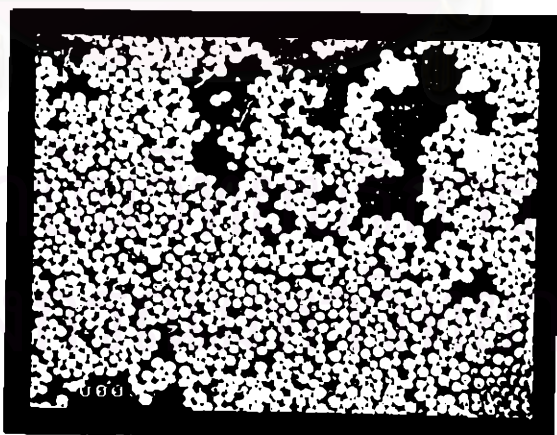(b)

(c)

Figure 4.35 SEM photographs of the copolymer prepared at agitation rate 200 rpm

(a) x10,000   (b) x5,000 (c) x2,500

Figure 4.36 SEM photographs of the copolymer prepared at agitation rate 300 rpm

(a) x10,000   (b) x5,000 (c) x2,500

4.6.2 The Average Molecular Weights and Molecular Weight Distribution

The relation between agitation rate and average molecular weights is presented in Figure 4.37. The results indicate that there are no appreciable relation between these factors. It was found that the agitation rate of 100 rpm is the appropriate condition to use for preparing high molecular weight of the copolymer. For a mild agitation rate at 50 rpm, it provided a relatively low molecular weight copolymer. This result may be discussed by the assumption that large particle can less efficiently capture oligomers in solution for further polymerization due to the smaller surface, leading to a low molecular weight. Nevertheless, when the agitation rate increases from 100 to 300 rpm, a decrease was found again. It might be due to that at a high rate of agitation, the shearing force can exert on the solution viscosity permitting faster chain diffusion in the polymer solution to increase. As a result, the rate of the chain termination is higher, thus yielding the copolymer with lower molecular weight.
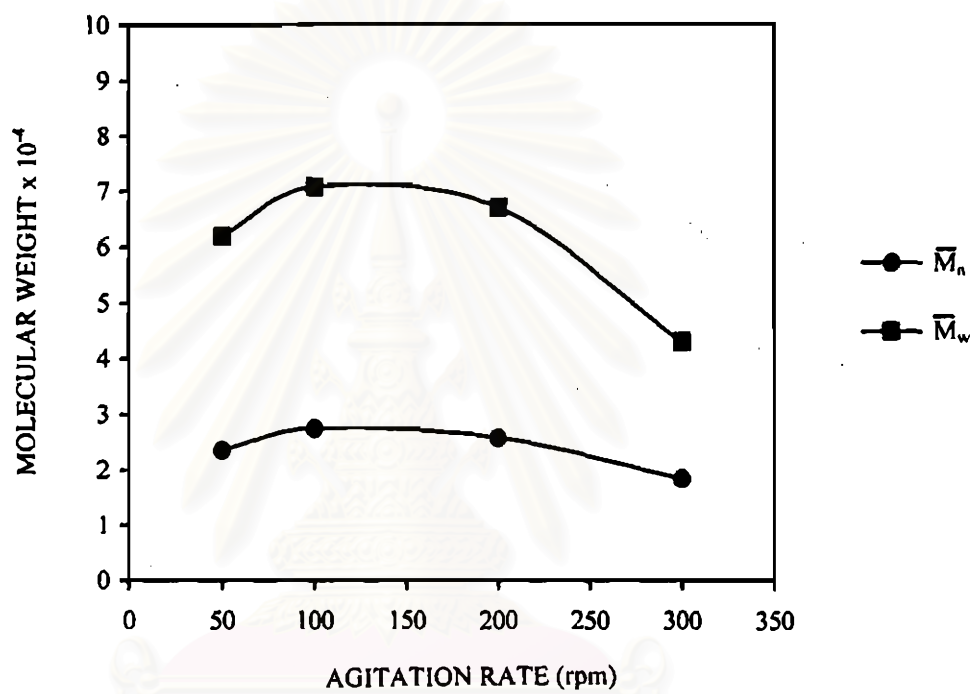
Figure 4.37 Effect of agitation rate on the average molecular weights of the copolymer

4.7 Effect of the Styrene/*n*-Butyl Acrylate Feed Ratio on

4.7.1 The Particle Size and Size Distribution

In this experiment, the copolymerizations were performed by changing the ratio between the styrene and *n*-butyl acrylate at 100/0, 95/5, 90/10, 85/15, and 80/20 mol%, respectively. The effect of the monomer composition on the particle size and distribution is presented in Table 4.8 and Figure 4.38. The result indicated that the particle size slightly increased with BuA content, whereas the particle size distribution remained narrow in all cases (as shown by SEM photographs in Figures 4.39-4.43). An increase is not significant because the amount of BuA used is limited due to its low glass temperature (-54°C) [43]. The largest particle size was obtained from 20% feed ratio of BuA, while the smallest size was obtained from homopolymer of polystyrene. Similar trend has been noted in dispersion polymerization of styrene and *n*-butyl methacrylate in an ethanol/water medium using hydroxypropyl cellulose and benzoyl peroxide as dispersant and initiator, respectively [30].

This result can be described by two main reasons: (1) the different interactions between the two monomers and the dispersant [17, 33] and (2) the change in solvency of the reaction medium [38]. For the first reason, as mentioned above, in dispersion polymerization, the in-situ grafting of PVP can occur via hydrogen abstraction process, resulting in the free radical size (PVP*) which continues to accept monomers. According to the electron donating-electron accepting theory, it was usually observed that the reactivity of an electron-donor radical would be greater with an electron-acceptor than with an electron-donor substrate [17]. For this explanation, St-PVP would have a pronounced interaction than that of BuA-PVP because styrene radical is a stronger electron donor for PVP (an electron acceptor). As a result styrene can be adsorbed much more strongly on

Table 4.8 Effect of the monomer composition on dispersion copolymerization of styrene and *n*-butyl acrylate

No.	BA (mol %) in feed	$\overline{D}_n$ (μm) [a,b]	CV (%) [c]	PDI [d]	$\overline{M}_n$ x 10^{-4}	$\overline{M}_w$ x 10^{-4}	$\overline{M}_w / \overline{M}_n$	BA (mol %) [e] in copolymer composition	T_g (°C) [f]
M1	0*	1.0	5.1	1.01	3.14	11.58	3.68	0	102.7
M2	5	1.1	3.7	1.01	3.58	9.86	2.75	4.90	91.7
M3	10	1.1	3.4	1.01	3.14	7.88	2.50	8.11	85.2
M4	15	1.2	4.0	1.01	2.82	7.59	2.69	13.10	76.0
M5	20	1.2	3.3	1.01	2.47	6.37	2.57	17.19	68.6

* = 100 mol % styrene

a = Calculated diameter

b = Determined by scanning electron microscopy

c = Coefficient of variation

d = Polydispersity index

e = Determined by NMR method

f = Glass transition temperature

the PVP* than can BuA. This contribution leads to the smallest particles with increasing styrene content.

The latter reason involves in the change of the solubility of the copolymer in the reaction medium. Comparing the polarity of styrene and *n*-butyl acrylate, the latter is more polar and also more soluble in ethanol/water medium. Increasing the relative amount of BuA in the monomer composition means to an increase in polarity of the reaction medium. Therefore, the copolymer rich in BuA is more soluble in the continuous phase than the copolymer rich in styrene, resulting in a greater importance of the polymerization in the solution, and thus the larger particle sizes with the low average molecular weight are obtained.
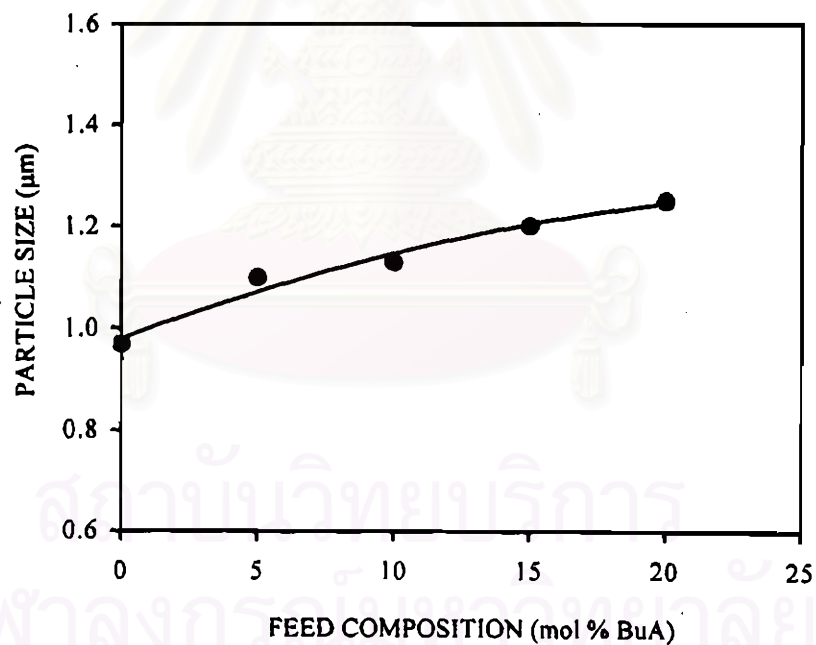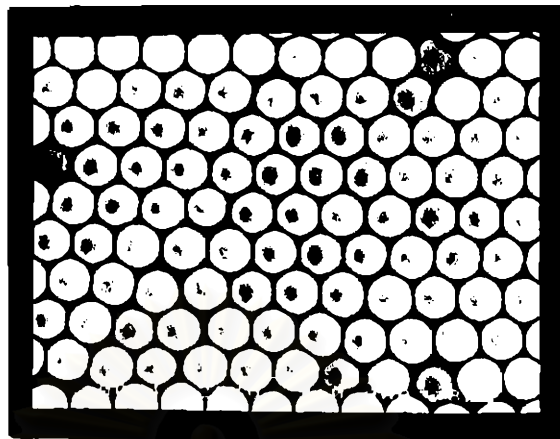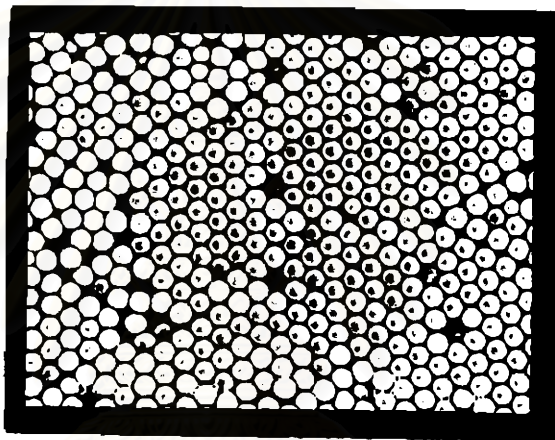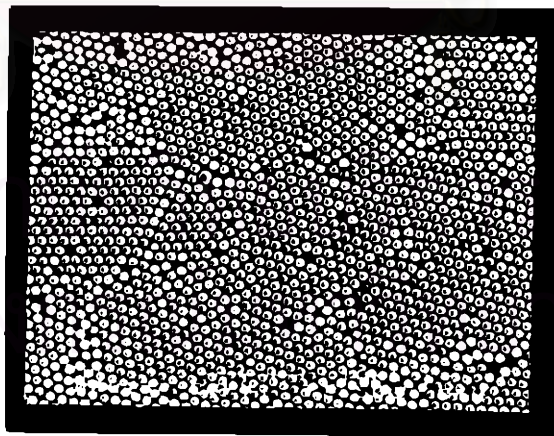
Figure 4.38 Effect of monomer composition on the particle size of the copolymer

Figure 4.39 SEM photographs of the polystyrene

(a) x10,000 (b) x5,000 (c) x2,500
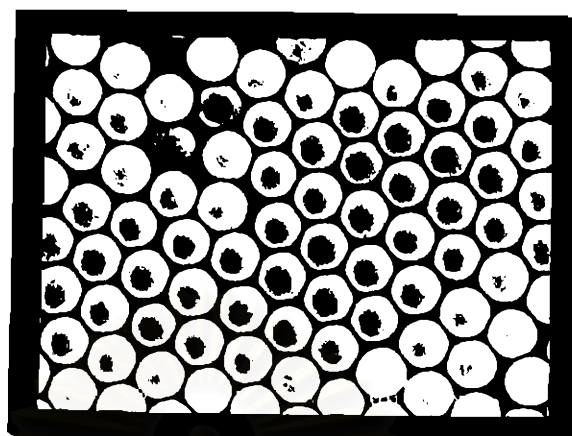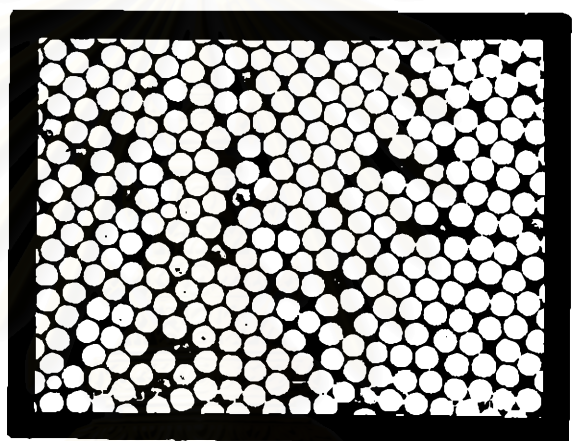
Figure 4.40 SEM photographs of the copolymer prepared with St/BuA (95/5) mol%

(a) x10,000　(b) x5,000　(c) x2,500

Figure 4.41 SEM photographs of the copolymer prepared with St/BuA

(90/10) mol%   (a) x10,000   (b) x5,000 (c) x2,500
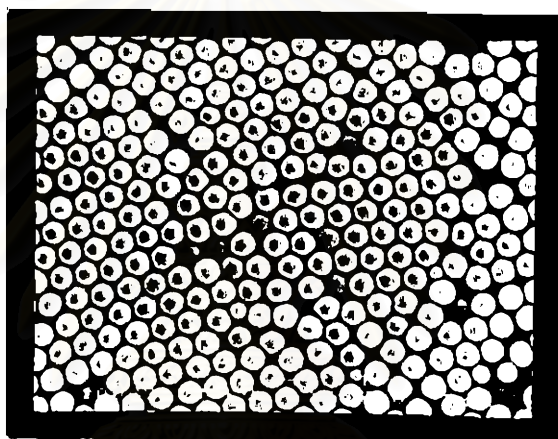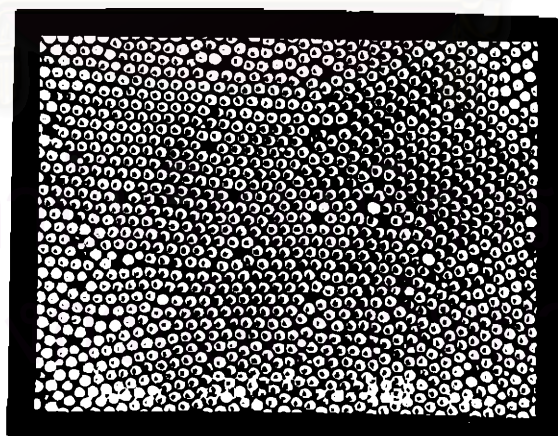
Figure 4.42 SEM photographs of the copolymer prepared with St/BuA

(85/15) mol%   (a) x10,000   (b) x5,000 (c) x2,500
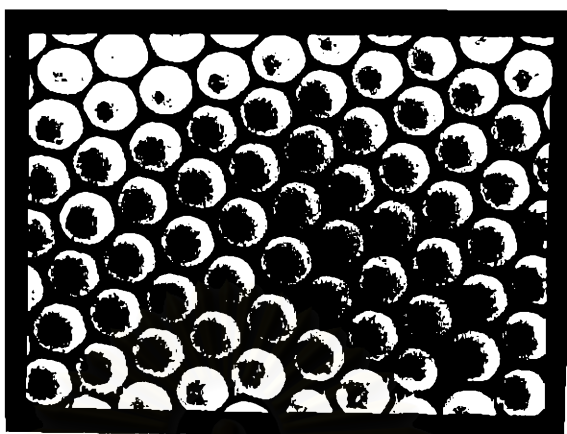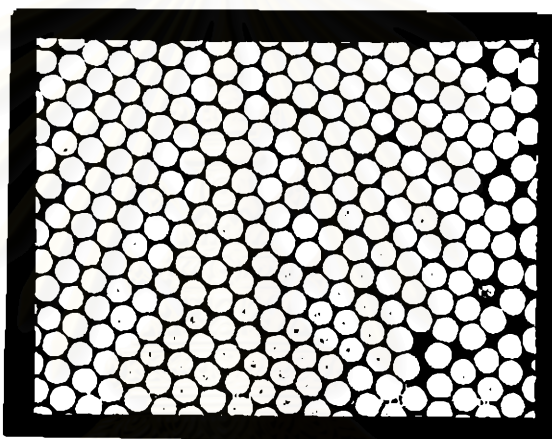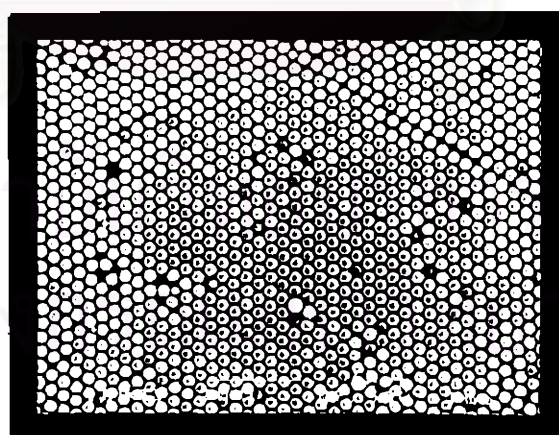
Figure 4.43 SEM photographs of the copolymer prepared with St/BuA

(80/20) mol%   (a).x10,000   (b) x5,000 (c) x2,500

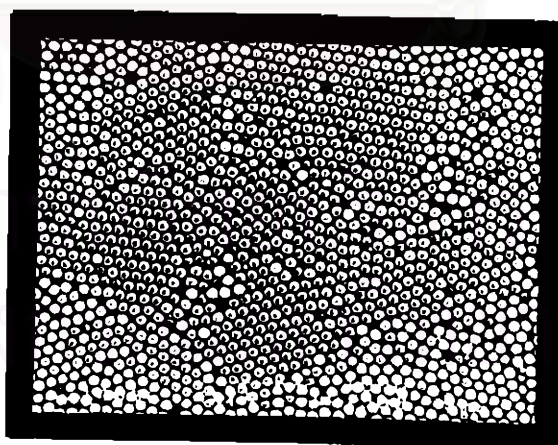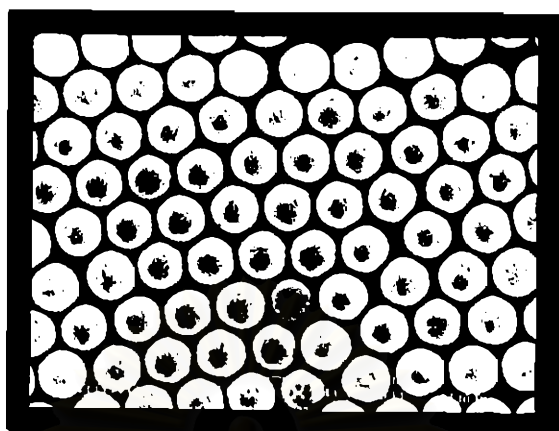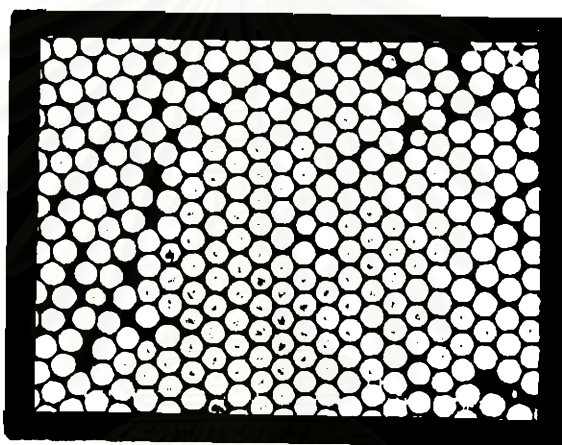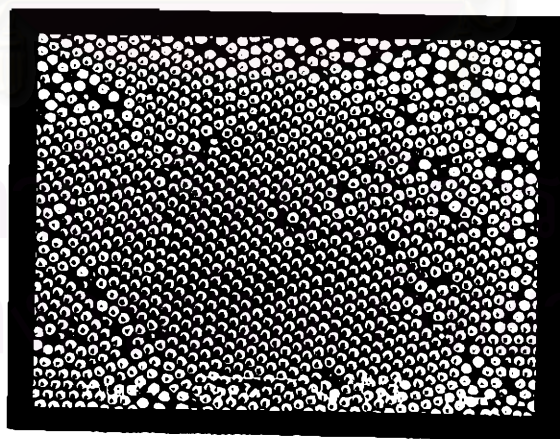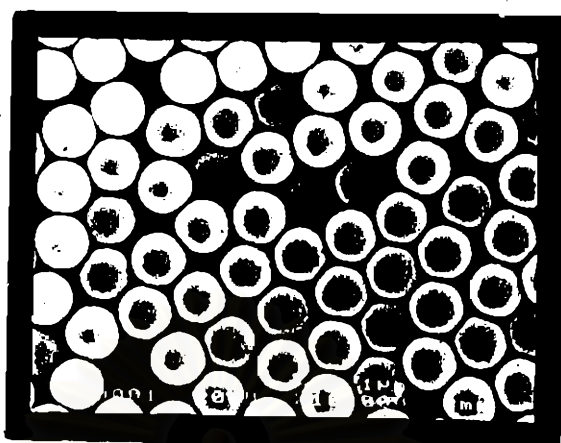## 4.7.2 The Average Molecular Weights and Molecular Weight Distribution

Table 4.8 and Figure 4.44 show the average molecular weight of resulting polymers at different copolymer compositions. The highest average molecular weight of the formed polymer was obtained from 100 mol% styrene, while the lowest molecular was obtained so far from 20 mol% BuA. It can be noted that there is a trend to decrease the average molecular weight with increasing BuA content. This observation is similar to most systems that smaller particles with great surface area can grow by capture of radicals and nuclei in the solution and further polymerization within particles (as bulk polymerization) leading to gel effect, therefore the high average molecular weights of resulting polymers are obtained from the small-sized particles.
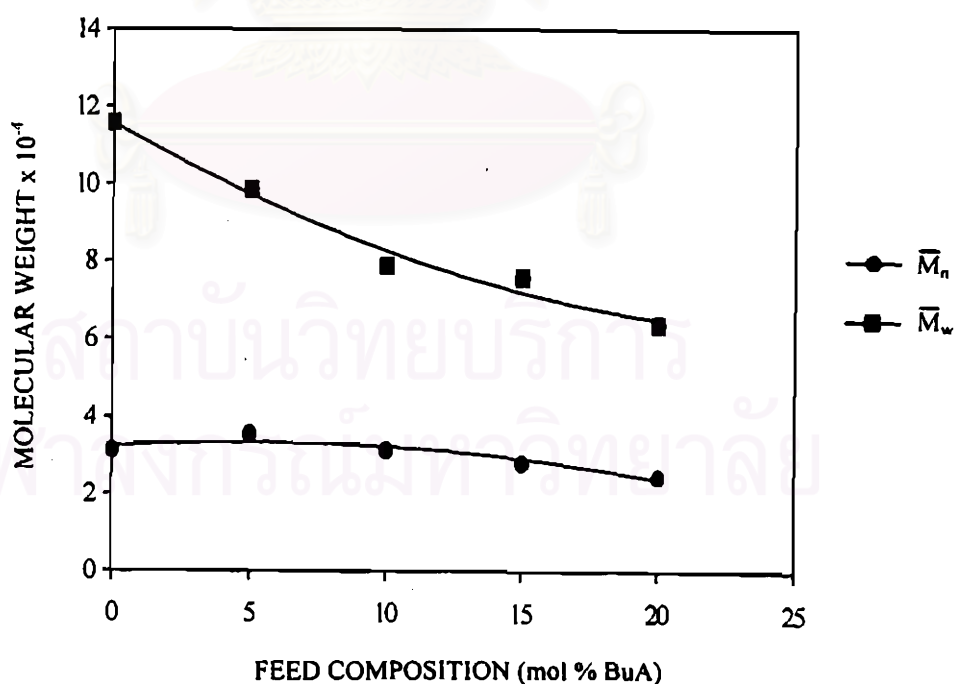
Figure 4.44   Effect of monomer composition on the average molecular weights of the copolymer

4.7.3 Glass Transition Temperature

The copolymers were investigated by DSC to identify the T_g value. The T_g values was found in the range of 68-102°C. It can be seen that varying the feed ratio of the copolymer has a direct impact on glass transition temperature of the resulting copolymers. Figure 4.45 presents the relation between T_g and BuA content. The T_g of the copolymer decreased as the amount of BuA increased. This effect is due to the lower glass transition temperature of PBuA (-54°C), the copolymer rich in BuA possess the lowest T_g at 68°C whereas the homopolymer of polystyrene has the highest T_g at 102°C.

Glass transition temperature of the copolymer is an important property in characterizing a toner resin for xerography because it corresponds to an acceptable blocking temperature, the temperature at which the toners flow into the paper. For adequate blocking, toners generally should have T_g about 50-70°C [7].
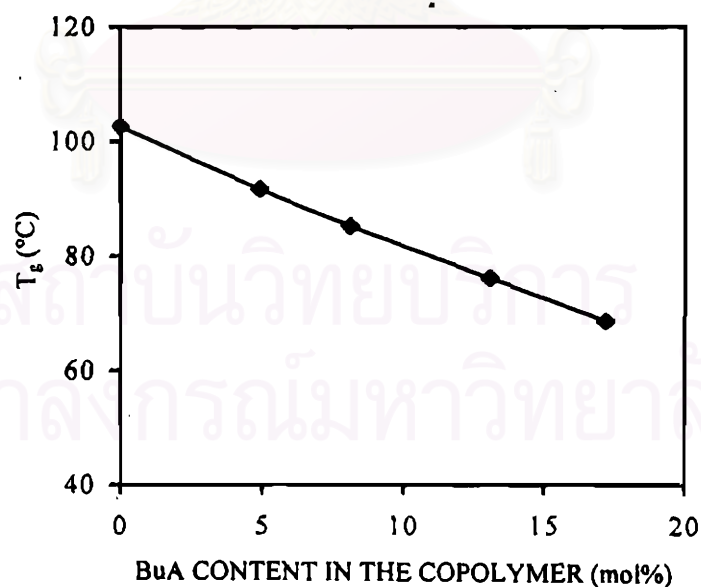
Figure 4.45   Effect of copolymer ratio on glass transition temperature of the copolymer

4.8 Effect of Crosslinking Agent on

4.8.1 Particle Morphology

In this study, ethylene glycol dimethacrylate (EGDMA) was used as a crosslinking agent. The concentration of EGDMA was varied at 0.25, 0.5, 1, 2, and 10 wt% based on the total monomer concentration. The results of dispersion polymerization in the presence of a crosslinking agent at different concentrations were revealed by SEM photographs in Figure 4.46. The experimental result indicated that the addition of crosslinking agent to produce spherical particles is limited. As the EGDMA concentration was increased from 0.25 to 1 %, the average particle size was decreased slightly and the particle uniformity remained unchanged. When 2% of EGDMA was used, partial flocculation of the particles with fused doublets (like a chubby rowing doll) occurred. Further increase in EGDMA concentration up to 10 wt% resulted in the particles with a raisin-like shape. Although these particles are not spherical, they are regular in shape (As shown in SEM Figures 4.46 d-e)

When EGDMA was incorporated to develop the network within the particle, a pendant vinyl group of EGDMA can further react with a growing chain in the region of the particle subsurface, compromising the ability of the adsorbed PVP graft copolymer chains in the function of an effective polymeric dispersant, because the reaction irreversibly links the PVP graft copolymer chain to the bulk particle phase. Once, freedom of movement has been restricted in this way, and the grafts can no longer migrate with advancing surface, it becomes redundant and unless it is replaced by fresh dispersant from the continuous phase. The particles begin to be unstable or destabilized [44].

From Figures 4.46 a-c, it indicates that at the concentration of EGDMA of less than 1%, the effect from destabilization cannot be observed. Although some
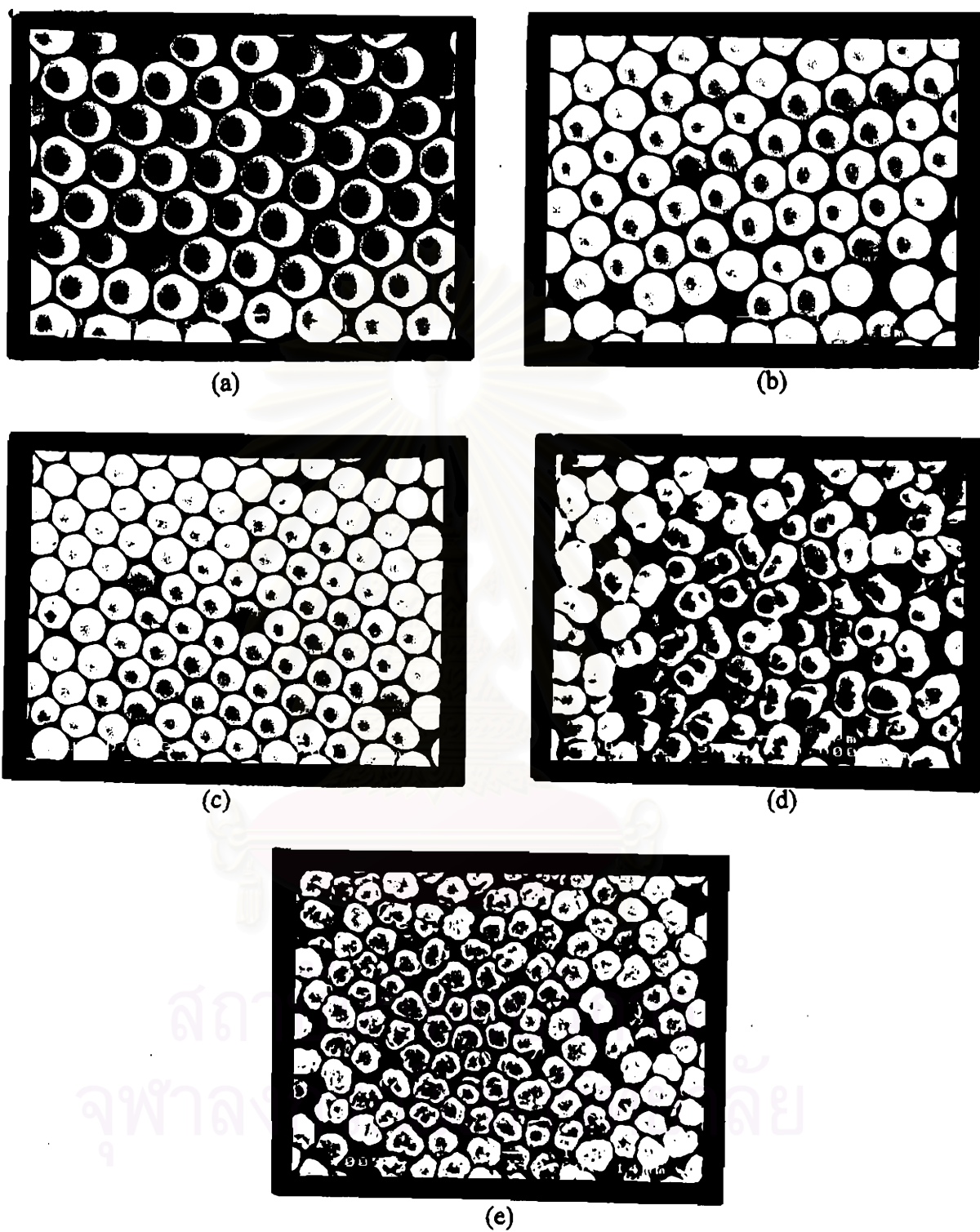
Figure 4.46 SEM photographs of the copolymer prepared with EGDMA at

(a) 0.25 wt% (b) 0.5 wt% (c) 1 wt% (d) 2 wt% (e) 10 wt%

parts of the particle are covered with the adsorbed PVP graft copolymer tied to the particle phase with EGDMA crosslinked copolymer, the gel is insufficiently crosslinked to render it rigid enough to paralyze the graft; that is, it has an elasticity that permits bound chains of PVP graft copolymer enough freedom of movement to maintain the particle stability.

As the level of EGDMA increased to 2 wt%, the deviation from sphericity becomes apparent. More graft chains at the surface are immobilized, leading to the partial flocculation of the particle to commence. To maintain their stability, particles begin to minimize surface exposure by coalescence with each other. Eventually, the resulting particles having the shape like fused doublet are formed.

However, when the concentration of EGDMA is increased up to 10 wt%, all particles seem to form as rasin-like particles with the rough surface. This may be explained that the presence of a high amount of the crosslinker would increase the degree of phase seperation during the polymerization since the particle become harder. The highly crosslinked polymers were hardly swollen by their monomers. These imply that the particles will grow by the polymerization at around the surface region and participate onto the nucleated particles, leading to the rough surface [45, 46].

4.9 Effect of Reaction Time on

4.9.1 Particle Growth

To investigate the effect of reaction time on particle growth, the dispersion polymerization was performed using the selected condition as follows: PVP K-30, 2wt%; ethanol/water, 90/10; temperature 70°C; agitation rate, 100 rpm; and St/BuA, 80/20 mol%. These conditions have been proved previously to yield the better and small-sized copolymers with a narrow size distribution. The investigation of particle growth was done by measurement of the particle size, size distribution, and average molecular weights of the copolymers formed at various reaction times of 0.5, 1, 2, 4, 6, 8, and 10 hours.

The effects of time on some characteristics of the copolymers are listed in Table 4.9, and SEM photographs of the particles so formed at different times are also shown in Figure 4.47. In the early stage, within 30 minutes, the nearly uniform particles are produced as seen in Figure 4.47 a. This indicated that the stage of particle formation is normally completed within a very short reaction time after the start of the polymerization, and its subsequent growth take place without (1) agglomeration of particles since the required dispersant are sufficiently cover onto the surface of the particles, preventing the particle contact; (2) the formation of new particles because nuclei are captured by existing particles before they are mature or stable enough to form new particles by itself. These factors lead to the narrow size distribution of the particle after the particle formation stage is complete.

Particle growth proceeds by polymerization within the monomer-swollen particles. The particle size increased from 0.4 μm at 1 hr. to 1.3 μm at 10 hours with a relatively unchanged narrow size distribution as seen in SEM photographs in Figures 4.47 a-f. The increase in particle size during the course of the polymerization would be expected to be proportional to conversion provided that (a)

Table 4.9 Effect of reaction time on dispersion copolymerization of styrene and n-butyl acrylate

Time (hrs)	$\widetilde{D}_n$ (μm) [a,b]	$\overline{M}_n$ x 10^{-4}	$\overline{M}_w$ x 10^{-4}	$\overline{M}_w / \overline{M}_n$	% Conversion [c]
0.5	0.4	0.94	1.62	1.72	2.2
1	0.5	1.14	1.86	1.63	3.9
2	0.7	1.44	2.60	1.80	11.1
4	0.9	2.33	5.11	2.18	40.7
6	1.0	2.98	7.52	2.52	51.9
8	1.2	2.86	7.02	2.45	78.7
10	1.3	2.94	8.42	2.86	82.2

a = Calculated diameter

b = Determined by scanning electron microscopy
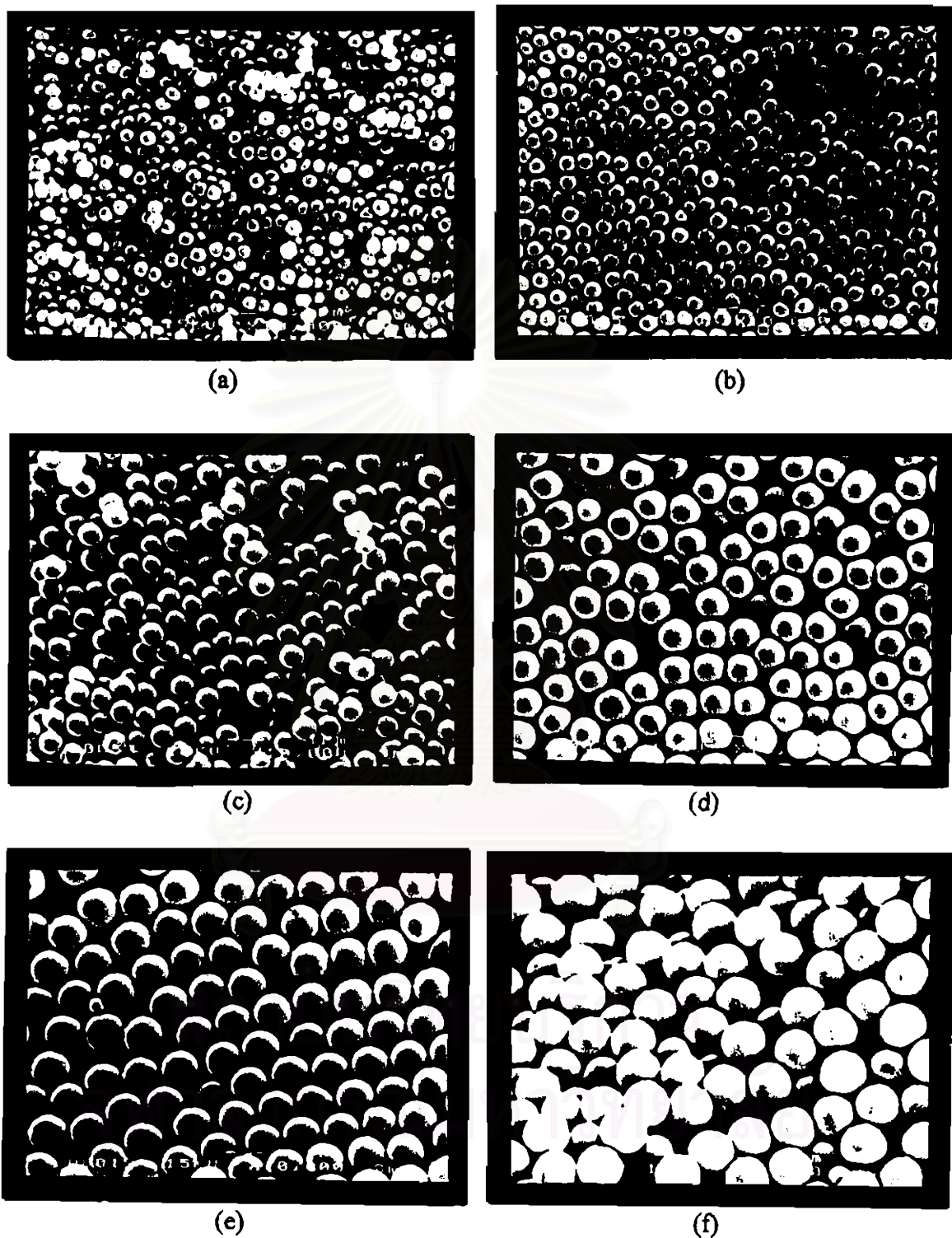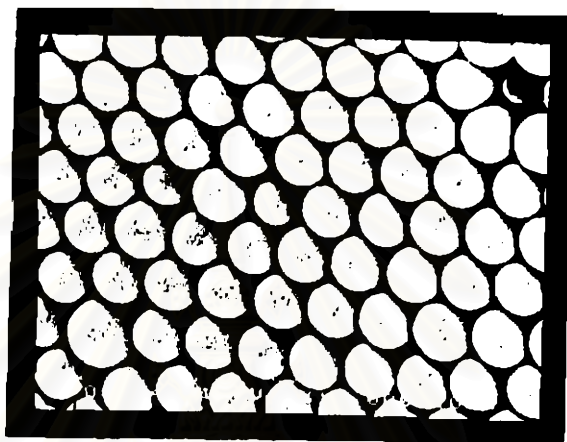
c = Determined by gravimetric method

Figure 4.47 SEM photographs of the copolymer prepared at different reaction time

(a) 0.5 hrs. (b) 1 hr. (c) 2 hrs. (d) 4 hrs. (e) 6 hrs. (f) 8 hrs.

(g)

Figure 4.47 (continued) SEM photographs of the copolymer prepared at different reaction time (g) 10 hrs.

all constant fractions of the polymer were incorporated into the particles and (b) little or no coalescence occurred between particles of the same size. The relation between particle volume (Vp) and conversion (p) is given in Figure 4.48, which shows a plot of particle volume versus conversion where the respective volume was calculated from the diameter of the particles as measured on the scanning electron micrographs. An apparently linear relationship between particle volume and conversion is observed. The linearity of the curve indicates that the number of particles is essentially constant even from the earliest stages of the reaction, and therefore nucleation must take place only in those early stages.
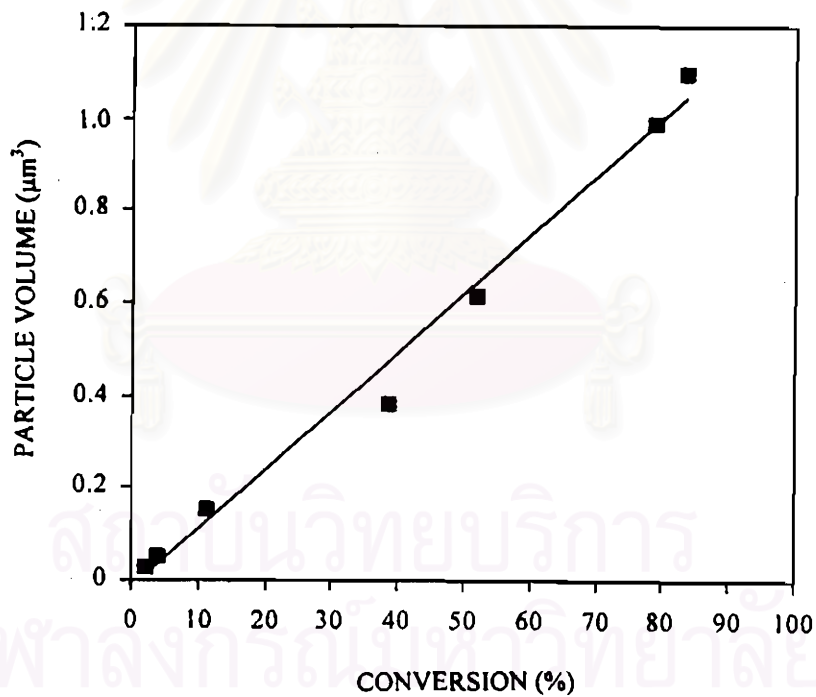

Figure 4.48   Particle volume versus conversion during growth of the copolymer particles

4.9.2 The Average Molecular Weights and Molecular Weight Distribution

From Table 4.9 it can be observed that the average molecular weights increased as a function of time. As mentioned above, due to the quick complete of the particle formation stage, most of the polymerization shift into and progress in the monomer-swollen particle phase when the polymerization time is allow to proceed. This increase in the average molecular weight might be also consistent with in auto-acceleration effect which is quiet strong in ethanol-water system [2]. The relation between the average molecular weight and reaction time was given in Figure 4.49. It was seen that the average molecular weight increased from 16,200 to 84, 600 when the polymerization times proceed from 0.5 to 10 hr, and the value of $\overline{M}_w/\overline{M}_n$ was in the ranges of 1.72-2.86 as shown in Table 4.9.
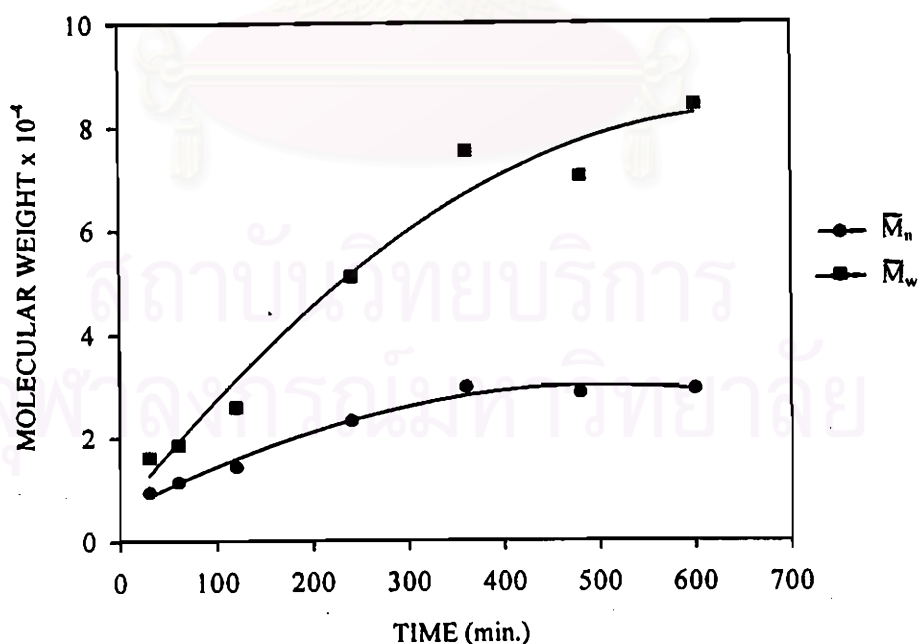

Figure 4.49   The relation between the average molecular weight and reaction time

4.10 Dispersion Copolymerization of Styrene and 2-Ethylhexyl Acrylate

In this experiment, we present a further copolymerization of St and 2-EHA in order to investigate the effect of different side chains of the acrylate monomer on the particle size and glass transition temperature of the resulting copolymers. The polymerizations were carried out by varying the mole ratios between St and 2-EHA at 95/5, 90/10, 85/15, and 80/20, respectively. The effects of the monomer composition on some characteristics of the resulting copolymer are listed in Table 4.10.

We see that the particle sizes generally increase with increasing 2-EHA content, but the particle size distribution is fairly narrow in all cases. The results are similar to our previous work of poly(St-co-BuA) in Section 4.7. However, the 2-EHA content in the mixture cannot exceed 15 mol%, as shown in Table 4.10. When 20 mol% of 2-EHA was copolymerized, the copolymer particles could not be formed as powder, hence they cannot be subject to the particle size analysis. The resulting copolymer is sticky like glue and aggregates. This indicates that the 20 mol% of 2-EHA in the copolymer composition is too high to make the particle surface of copolymer harder and non-sticky. For this reason, during the cleaning step of the particles by thorough washing with methanol, the particle surface is brought to contact, leading to the formation of aggregates.

Comparing the copolymer particles with those of St/BuA, St/2-EHA copolymer particles change marginally in particle size at a given mole ratio.(As shown in SEM photographs of Figures 4.40 to 4.43, and Figures 4.50 to 4.52). The result is very interesting because one would expect to see the decreasing particle size based on the difference in solubility parameter (δ). The extent of $\Delta\delta$ in 2-EHA ($\delta_T = 16$ (Mpa)$^{1/2}$) [37] in the given reaction medium is larger than that of BuA ($\delta_T = 18$ (Mpa)$^{1/2}$). However, we realize from the result that effect of chain length is much profound. The longer side chain of the ethyl group at the 2 position of the hexyl

Table 4.10 Effect of monomer composition on dispersion copolymerization of styrene and 2-ethylhexyl acrylate

No.	2-EHA (mol %) in feed	$\overline{D}_n$ (μm) [a,b]	CV (%) [c]	PDI [d]	2-EHA (mol %) [e] in copolymer composition	T_g (°C) [f]
E1	5	1.0	4.9	1.01	5.4	83.2
E2	10	1.2	5.2	1.01	9.6	69.2
E3	15	1.2	7.1	1.01	11.0	66.6
E4	20	*	*	*	19.2	48.5

* = Not available   d = Polydispersity index

a = Calculated diameter   e = Determined by NMR method

b = Determined by scanning electron microscopy   f = Glass transition temperature

c = Coefficient of variation
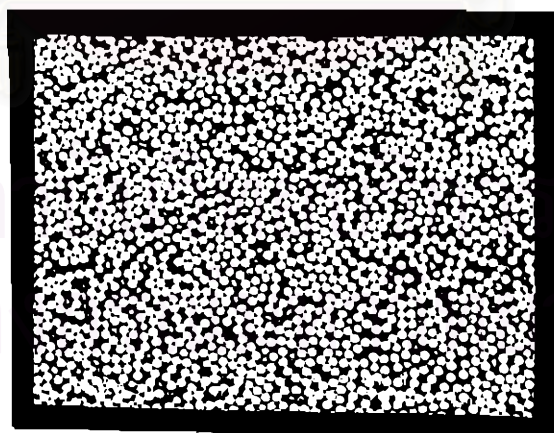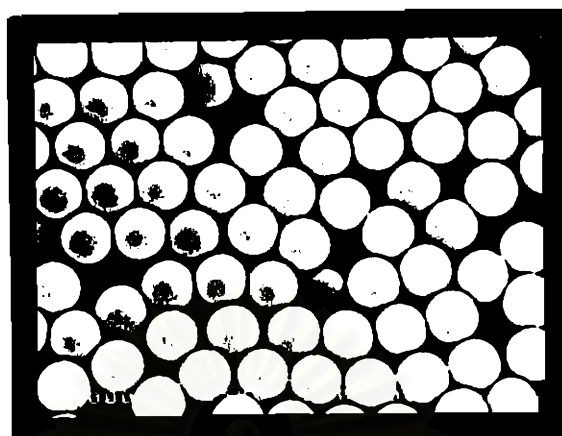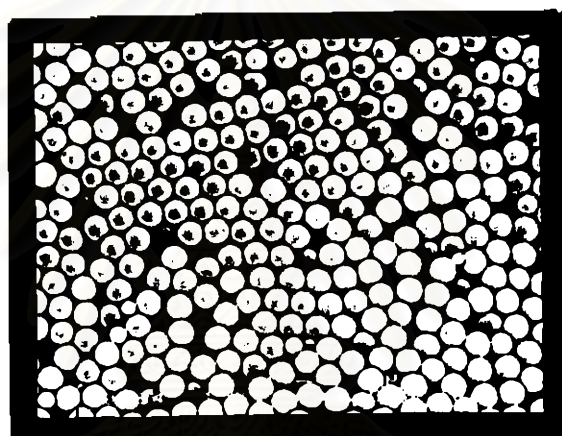
(a)

(b)

(c)

Figure 4.50 SEM photographs of the copolymer prepared with St/2-EHA
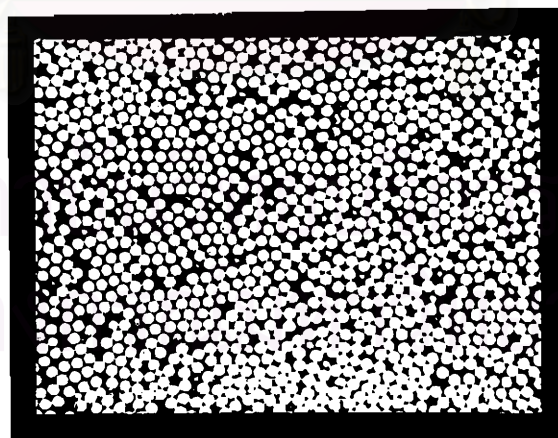
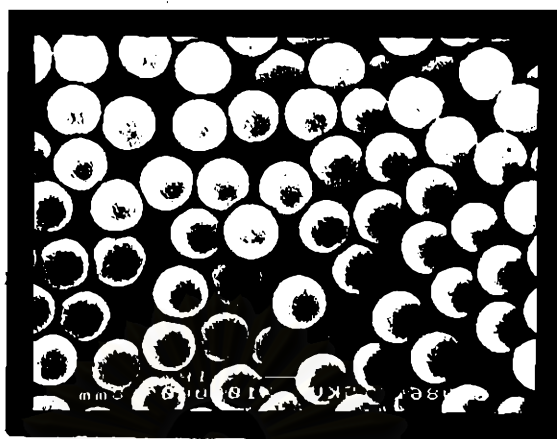(95/5) mol%   (a) x10,000   (b) x5,000 (c) x2,500
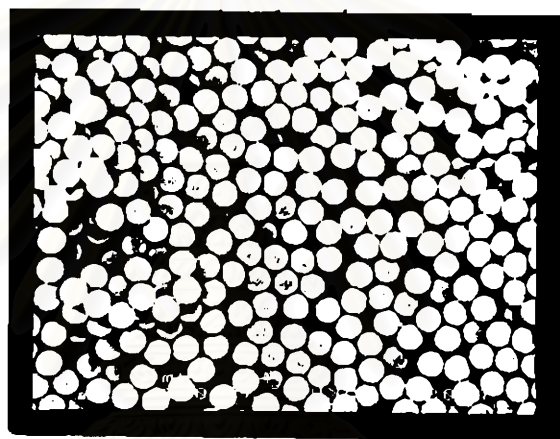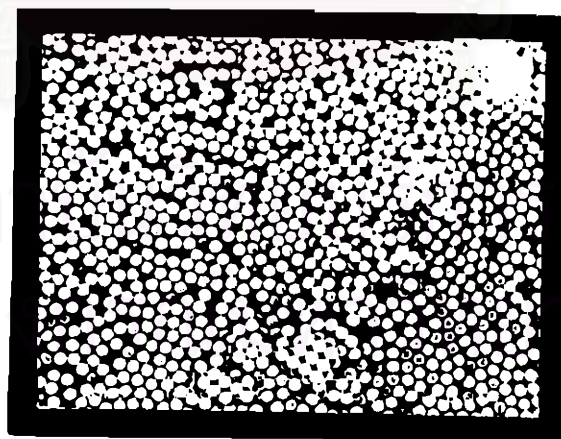
(a)

(b)

(c)

Figure 4.51 SEM photographs of the copolymer prepared with St/2-EHA

(90/10) mol%   (a) x10,000   (b) x5,000   (c) x2,500

(a)

(b)

(c)

Figure 4.52 SEM photographs of the copolymer prepared with St/2-EHA

(85/15) mol%   (a) x10,000   (b) x5,000 (c) x2,500

carbon backbone hinders the entanglement of the chain when the polymerization proceeds. The chain flexibility can be observed when its glass transition temperature is measured.

From the experimental data (Table 4.10), the difference in particle size is not significant. It is probably because the content of the acrylate monomer used in this experiment is restricted due to their low glass transition temperature (-54°C for BuA and −50°C for 2-EHA) [43]. The insignificant difference in particle size between St/BuA and St/2-EHA at a given mole ratio may be arisen from the deviation in the particle size measurement technique.

Although the effect of different side chains of the acrylate monomer on the particle size is not so dominant, the significant effect on the glass transition temperature can be inevitably observed. Comparison of the T_g values between the BuA copolymer and the 2-EHA copolymer is shown in Figure 4.53. The T_g value of both copolmyers decreases as the content of the acrylate monomer in the respective copolymer increases. However, at same mole ratio of the acrylate content, 2-EHA imposes a pronounced effect on reducing the glass transition temperature of the resulting copolmer than does the BuA. This can be explained in terms of the dependence of T_g on weight fraction, by the following relation [47].

$$T_g = W_A T_{gA} + W_B T_{gB} \qquad (4.5)$$

where the W's are weight fractions of the monomers in the copolymer. It is seen that T_g values of any random copolymer depend on both the weight fraction of monomers in the copolymer and the T_g value of each monomer. Though the T_g values of BuA and 2-EHA are nearly the same, the weight fraction of 2-EHA is much higher than that of BuA due to its higher molecular weight per mole. For this reason, at a given mole ratio the St/2-EHA copolymer would produce particles with lower T_g than St/BuA copolymer.
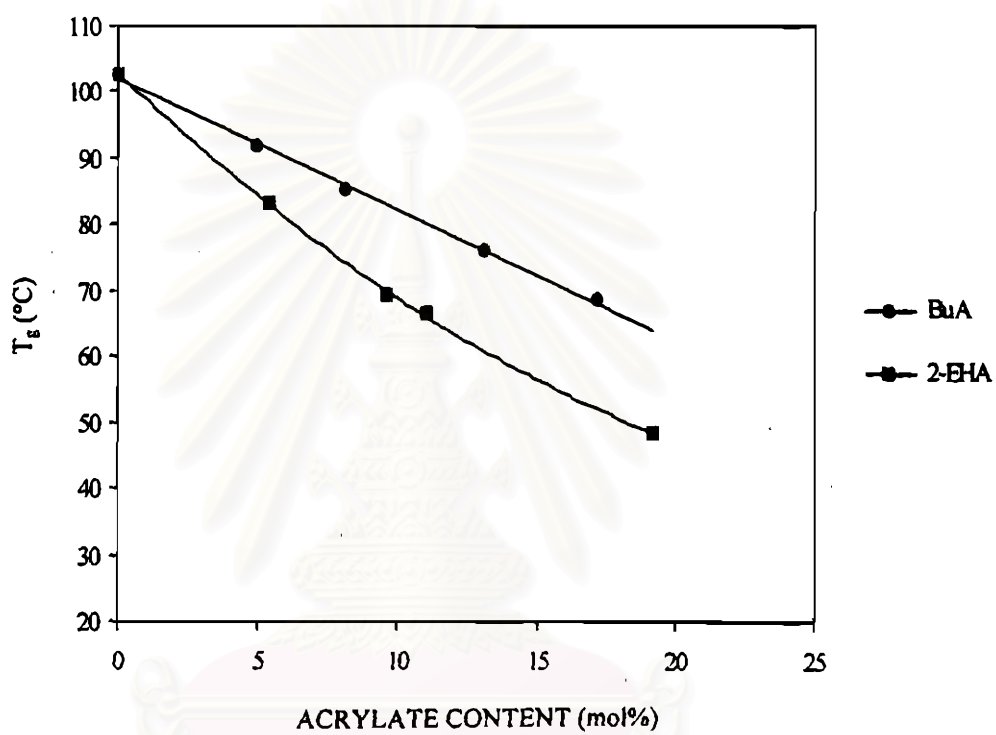
Figure 4.53   Comparison of the T_g values between the BuA copolymer and the

2-EHA copolymer