CHAPTER IV

RESULTS AND DISCUSSION

4.1 One-Stage Suspension Polymerization

In this study, the core/shell beads of styrene:methyl methacrylate were synthesized by a one-stage suspension polymerization. The appropriate condition for such a synthesis of polymer was obtained by varying the suspending agent concentration, crosslinking agent concentration, initiator concentration, diluent composition, inhibitor concentration, polymerization time, polymerization temperature and agitation rate.

4.1.1 Effect of Suspending Agent Concentration

The effects of suspending agent concentration on the average particle size, size distribution and swelling ratio were investigated by varying the suspending agent concentrations of 0.5, 0.7 and 1.0 %wt based on the aqueous phase, while the other parameters were kept constant as follows:
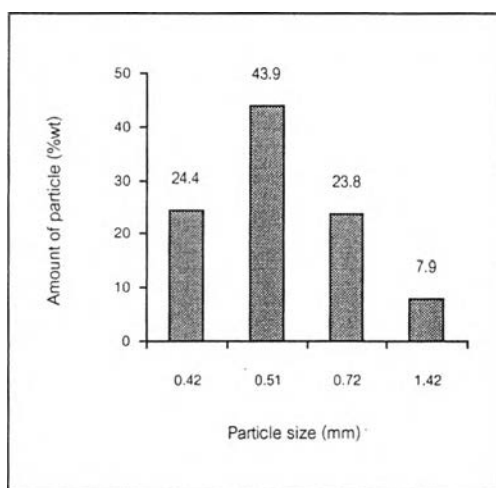
- Amount of styrene:methyl methacrylate:ethyleneglycol
  dimethacrylate monomer (46.5:46.5:7.0)   : 100 %wt
- Initiator concentration (based on the oil phase)   : 0.4 %wt
- Toluene:isooctane   : 70:30
- Inhibitor concentration (based on the aqueous phase)   : 0.11 %wt.
- Polymerization time   : 10 hours
- Polymerization temperature   : 75°C

| - Agitation rate | : 160 rpm |
| - Homogenizing time | : 10 minutes |
| - Homogenizing speed | : 2000 rpm |

Table 4.1 Effects of the suspending agent concentration on size and size distribution of the polymer beads.

Batch No.	Particle Size Distribution (mm)				
	< 0.42	0.42 – 0.59	0.59 – 0.84	0.84 – 2.0	> 2.0
S-1.0	24.4	43.9	23.8	7.9	-
S-0.7	18.9	35.8	25.6	19.7	-
S-0.5	Coagulated				

where S-1.0, S-0.7 and S-0.5 are the sample using the suspending agent concentration of 1.0 %wt, 0.7 %wt and 0.5 %wt, respectively.
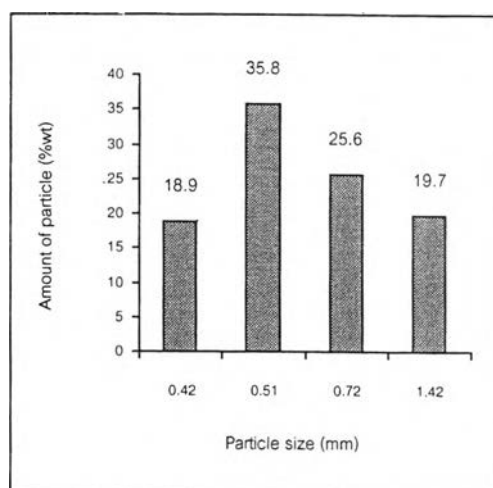
(a) S-1.0, 1.0 % PVP K-90   (b) S-0.7, 0.7 % PVP K-90

Figure 4.1 Size distribution of the copolymer beads of styrene/methyl methacrylate/ ethyleneglycol dimethacrylate under the effect of suspending agent concentrations: (a) 1.0 % and (b) 0.7 % PVP K-90

Table 4.2 Effects of the suspending agent concentration on % monomer conversion, average particle size and swelling ratio of the polymer beads

Batch No.	% MonomerConversion	Average Particle Size (mm)	Swelling Ratio
S-1.0	67.2	0.61	5.8
S-0.7	62.7	0.73	5.6

Tables 4.1-4.2 and Figure 4.1, show the effect of stabilizer concentration on the average particle sizes. The average particle sizes were found to decrease from 0.73 mm to 0.61 mm with increasing the stabilizer concentration from 0.7 % to 1.0 %wt based on the aqueous phase. It can be described that increasing the concentration increases both rate of physical adsorption of stabilizer and the viscosity of the continuous phase. These changes reduce the extent of aggregation of nuclei, resulting in smaller particles [18]. At 0.5 %wt PVP K-90, the monomer or polymer droplets were coagulated because the amount of stabilizer is not enough to stabilize the dispersion. The coalescence occurs due to the collisions of particles in a turbulent flow, most of the collisions result in coalescence. The stabilizer, being spread over the particle surface, creates a protective layer, which prevents coalescene of the particles during collisions. In this situation, the polymer particles do not coalescence if the repulsive forces prevail over the attractive ones. Collisions of these stable particles are accompanied only by overlapping the osmotic pressure increase, which gradually separates the particles one from the others. The rate of separation of the suspension particles, whose surface layers mutually overlap after collisions, is not interactions between the stabilizer molecules and polymer or monomer [4]. The swelling ratio of polymer beads is constant as already shown in Table 4.2.

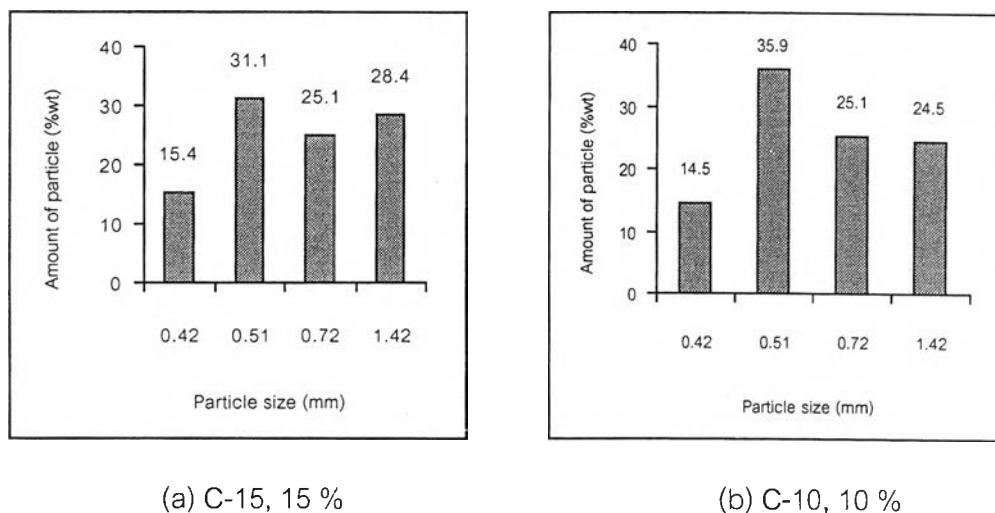## 4.1.2 Effect of Crosslinking Agent Concentration

The effects of crosslinking agent concentration on the average particle size, size distribution and swelling ratio were investigated by varying the crosslinking agent concentrations of 5, 7, 10 and 15 %wt based on the monomer phase, while the other parameters were kept constant as follows:

- Suspending agent concentration

  (based on the aqueous phase) : 0.7 %wt

- Initiator concentration (based on the oil phase) : 0.4 %wt

- Toluene:isooctane : 70:30

- Inhibitor concentration (based on the aqueous phase) : 0.11 %wt.

- Polymerization time : 10 hours

- Polymerization temperature : $75^{o}C$

- Agitation rate : 160 rpm

- Homogenizing time : 10 minutes

- Homogenizing speed : 2000 rpm

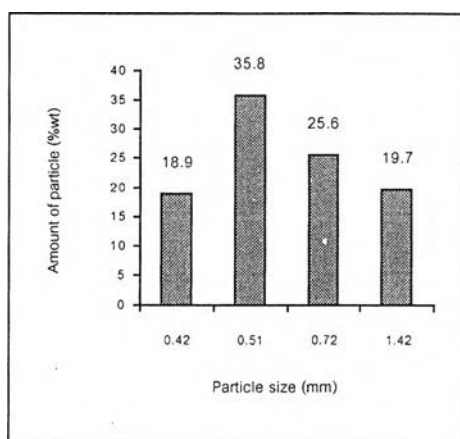Table 4.3 Effects of the crosslinking agent concentration on size and size distribution of the polymer beads.

Batch No.	Particle Size Distribution (mm)				
	< 0.42	0.42 – 0.59	0.59 – 0.84	0.84 – 2.0	> 2.0
C-15	15.4	31.1	25.1	28.4	-
C-10	14.5	35.9	25.1	24.5	-
C-7	18.9	35.8	25.6	19.7	-
C-5			Fused		

where C-15, C-10, C-7, C-5 are the sample using the crosslinking agent concentration of 15 %wt, 10 %wt, 7 %wt and 5 %wt, respectively.

(a) C-15, 15 %

(b) C-10, 10 %

(c) C-7, 7 %

Figure 4.2 Size distribution of the copolymer beads of styrene/methyl methacrylate/ ethyleneglycol dimethacrylate under the the effect of crosslinking agent concentrations: (a) 15 %, (b) 10 % and (c) 7 %wt based on monomer phase.

Tables 4.3-4.4 and Figure 4.2 indicate the effect of crosslinking agent concentration on the swelling ratio and % monomer conversion. At 5 %wt of EGDMA, There was no bead formation because the amount of crosslinking agent was not enough to stabilize the soft surface of polymer beads. As shown in Table 4.4, it was found that the swelling ratio decreases with increasing crosslinking concentration. It can be elucidated that increasing crosslinking concentration leads to a limitation of the chain mobility. It causes the chain to be less flexible, and a decline in a swelling ratio,

accordingly. On the other hand, increasing the crosslinking concentration increases % monomer conversion, because the increased crosslink density of seed particles enhanced both the degree of phase separation and the number of phase domains. The result led to the increasing % monomer conversion. In general, increase of the amount of crosslinker produces the increasing crosslinking density of the polymer chains. The polymer beads are thus less flexible leading to the decrease in shrinkage of the polymer bead surface. The bead surface was getting smoother when the higher crosslinking agent had been polymerized, as shown in Figure 4.4 [19].

Table4.4 Effects of the crosslinking agent concentration on % monomer conversion, average particle size and swelling ratio of the polymer beads

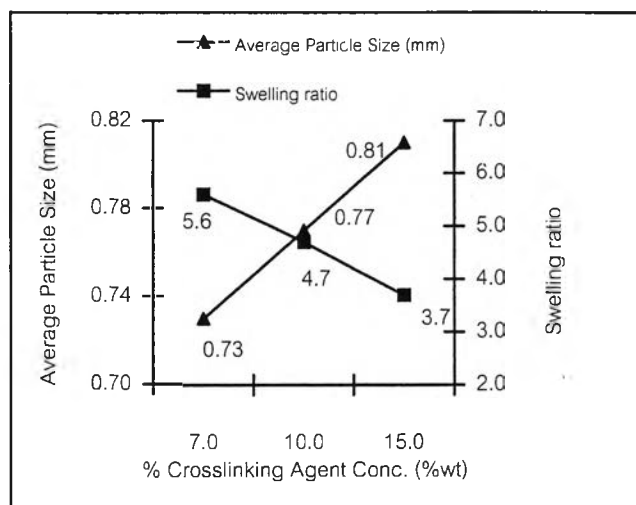| Batch No.	% Monomer Conversion	Average Particle Size (mm)	Swelling Ratio
C-15	80.1	0.81	3.7
C-10	72.8	0.77	4.7
C-7	62.7	0.73	5.6

Figure 4.3 Effects of the crosslinking agent concentration on average particle size and swelling ratio of the copolymer beads of styrene/methyl methacrylate/ ethyleneglycol dimethacrylate.
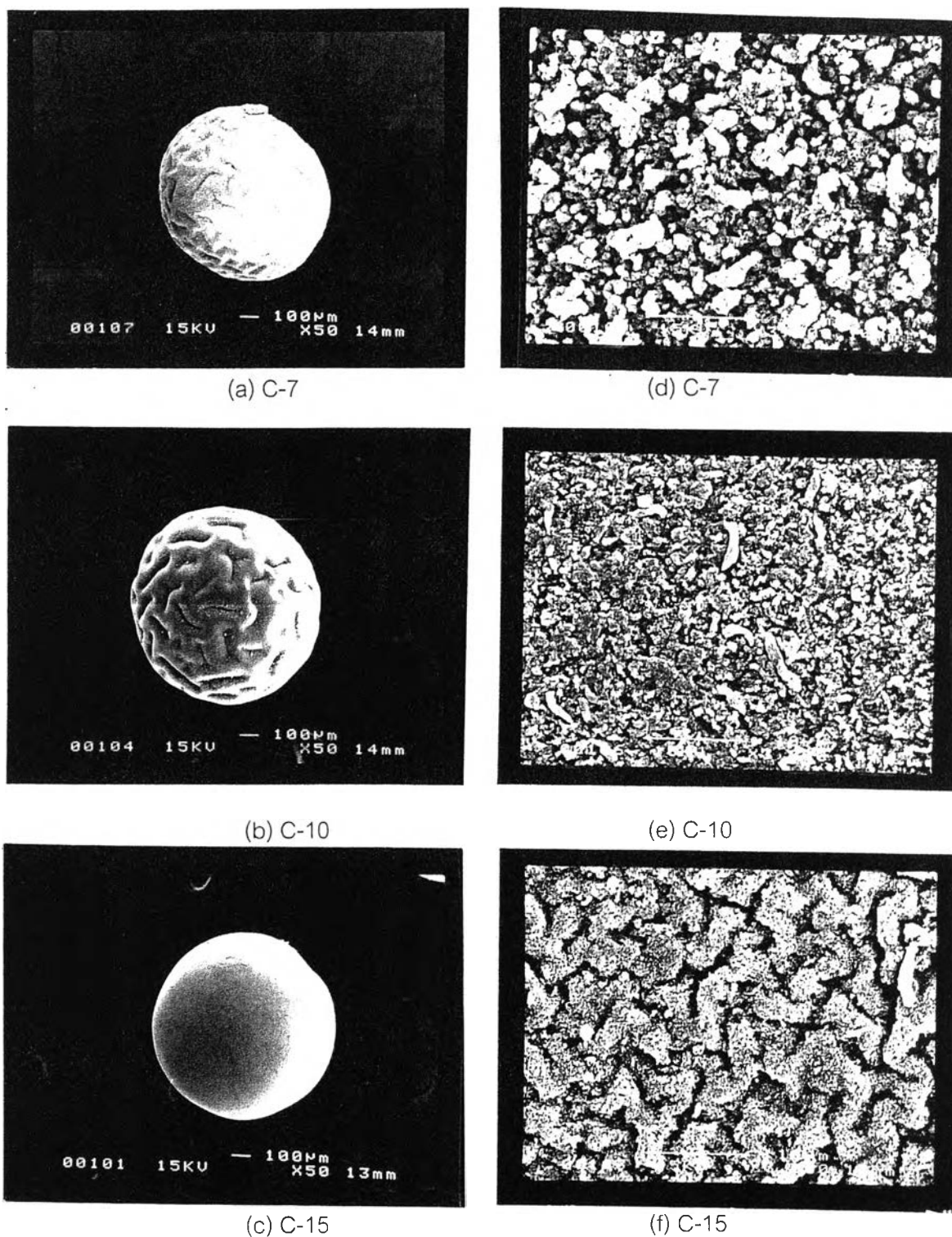
(a) C-7

(d) C-7

(b) C-10

(e) C-10

(c) C-15

(f) C-15

Figure 4.4 SEM photographs of poly(Sty-*co*-MMA-*co*-EGDMA) at different crosslinking agent concentrations: (a) 7.0 % (x50), (b) 10.0 % (x50), (c) 15.0 % (x50), (d) 7.0 % (x3000), (e) 10.0 % (x3000) and (f) 15.0 % (x3000)

4.1.3 Effect of Initiator Concentration

The effects of initiator concentration on the average particle size, size distribution and swelling ratio were investigated by varying the initiator concentrations of 0.1, 0.4, 0.6, 0.7 and 1.0 %wt based on the oil phase, while the other parameters were kept constant as follows:
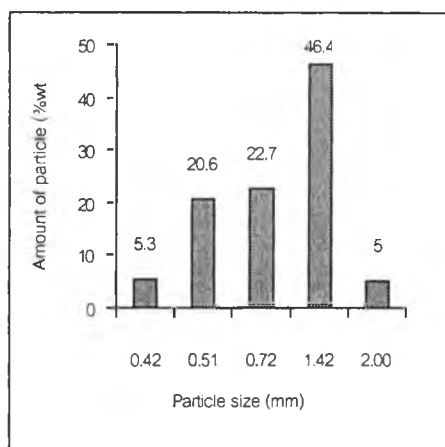
- Amount of styrene:methyl methacrylate:ethyleneglycol
  dimethacrylate monomer (46.5:46.5:7.0)   : 100 %wt
- Suspending agent concentration
  (based on the aqueous phase)   : 0.7 %wt
- Toluene:isooctane   : 70:30
- Inhibitor concentration (based on the aqueous phase)   : 0.11 %wt.
- Polymerization time   : 10 hours
- Polymerization temperature   : 75°C
- Agitation rate   : 160 rpm
- Homogenizing time   : 10 minutes
- Homogenizing speed   : 2000 rpm

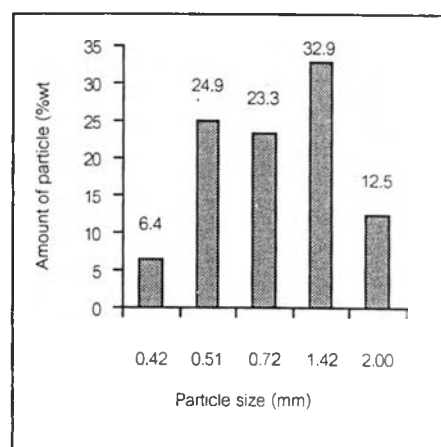Table 4.5 Effects of the initiator concentration on size and size distribution of the polymer beads.

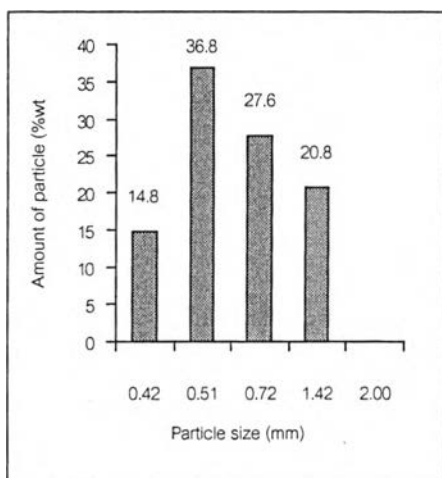| Batch No.	Particle Size Distribution (mm)				
	< 0.42	0.42 – 0.59	0.59 – 0.84	0.84 – 2.0	> 2.0
I-1.0	5.3	20.6	22.7	46.4	5.0
I-0.7	6.4	24.9	23.3	32.9	12.5
I-0.6	14.8	36.8	27.6	20.8	-
I-0.4	18.9	35.8	25.6	19.7	-
I-0.1	Coagulated				

where I-1.0, I-0.7, I-0.6, I-0.4 and I-0.1 are the sample using the initiator concentration of 1.0 %wt, 0.7 %wt, 0.6 %wt, 0.4 %wt and 0.1 %wt, respectively.
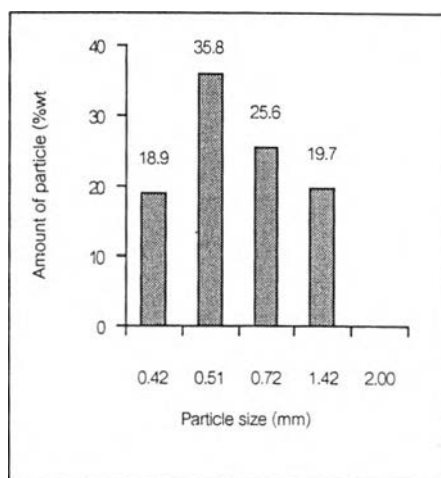

(a) I-1.0, 1.0 %

(b) I-0.7, 0.7 %

(c) I-0.6, 0.6 %

(d) I-0.4, 0.4 %

Figure 4.5 Size distribution of the copolymer beads of styrene/methyl methacrylate/ ethyleneglycol dimethacrylate under the effect of initiator concentration: (a) 1.0 %, (b) 0.7 %, (c) 0.6 % and (d) 0.4 % BPO based on the oil phase.

Table 4.6 Effects of the initiator concentration on % monomer conversion, average

particle size and swelling ratio of the polymer beads

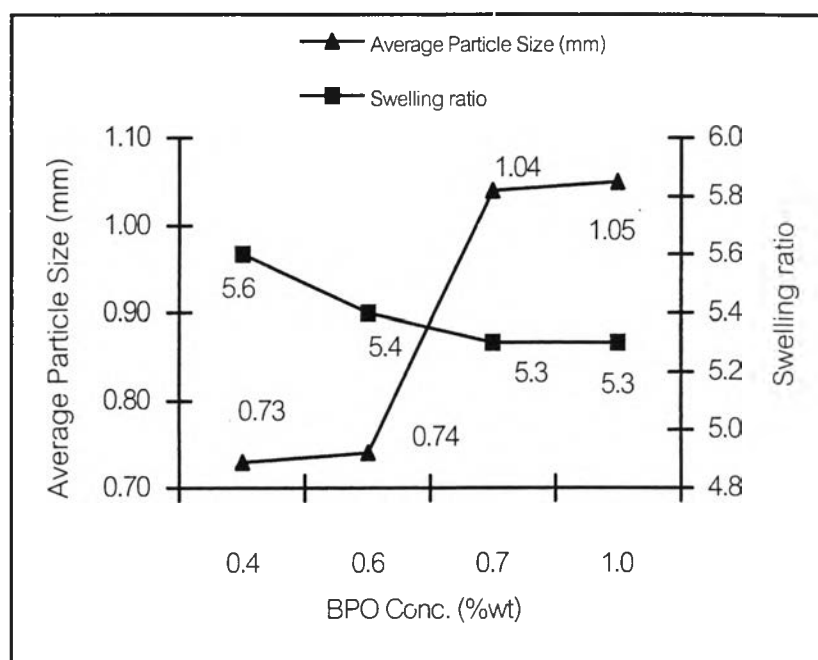| Batch No.	% Monomer Conversion	Average Particle Size (mm)	Swelling Ratio
I-1.0	78.7	1.05	5.3
I-0.7	76.8	1.04	5.3
I-0.6	72.7	0.74	5.4
I-0.4	62.7	0.73	5.6

Figure 4.6 Effects of the initiator concentration on average particle size and swelling ratio

The influence of initiator concentration on the average particle size and % conversion was shown in Tables 4.5-4.6 and Figure 4.5. The average particle sizes were found to enhance with increasing the initiator concentration. It can be explained as follows. With increasing the initiator concentration, the radical concentration increases and thus the concentration of precipitated oligomer chains also increase. Because of the increasing the initiator concentrations and the slow adsorption of the stabilizer, the aggregation process is enhanced, resulting in larger particles [20]. Moreover, the larger particles are

less likely to capture nuclei or oligo-radicals from the continuous phase simply due to the reduced total surface area and the number of particle density. Consequently, particle formation continues and this stage in the polymerization is extended.

Percentage monomer conversion was also found to increase with increasing the initiator concentration due to more initiator radicals formed in the initial step. Figure 4.6 shows the swelling ratio of the copolymer beads prepared under any concentration of the initiator is unchanged [21].

4.1.4 Effect of Diluent Composition

The effects of diluent composition on the average particle size, size distribution and swelling ratio were investigated by varying the diluent composition between toluene and isooctane of 100:0, 70:30 and 60:40 %wt based on the monomer phase, while the other parameters were kept constant as follows:

- Amount of styrene:methyl methacrylate:ethyleneglycol
  dimethacrylate monomer (46.5:46.5:7.0)   : 100 %wt
- Suspending agent concentration
  (based on the aqueous phase)   : 0.7 %wt
- Initiator concentration (based on the oil phase)   : 0.4 %wt
- Inhibitor concentration (based on the aqueous phase)   : 0.11 %wt.
- Polymerization time   : 10 hours
- Polymerization temperature   : 75°C
- Agitation rate   : 160 rpm
- Homogenizing time   : 10 minutes
- Homogenizing speed   : 2000 rpm

Table 4.7 Effects of the diluent composition on size and size distribution of the polymer beads.

Batch No.	Particle Size Distribution (mm)				
	< 0.42	0.42 – 0.59	0.59 – 0.84	0.84 – 2.0	> 2.0
D-100	36.5	32.7	21.6	9.2	-
D-70	18.9	35.8	25.6	19.7	-
D-60	Coagulated				

where D-100, D-70 and D-60 are the sample using the diluent compositon (toluene: isooctane) 100:0, 70:30 and 60:40, respectively.

Table 4.8 Effects of the diluent composition between toluene and isooctane on % monomer conversion, average particle size and swelling ratio of the polymer beads

Batch No.	% Monomer Conversion	Average Particle Size (mm)	Swelling Ratio
D-100	62.3	0.61	5.4
D-70	62.7	0.73	5.6

Tables 4.7-4.8 show the effects of composition of diluents on % monomer conversion, the average particle size and the swelling ratio. It revealed that using a composition of diluents cannot have significant effect on % monomer conversion and the average particle size, but it affects the swelling ratio of polymer beads. It can be explained as follows:

(a) When polymer is synthesized in the presence of a good solvent, toluene, the polymer chains are more expanded and less entangled. So the swelling of the bead takes place through the solvent uptake by the gel portion of network structure.

(b) In a poor solvent of i-octane, the increasing i-octane concentration enhances the polymer precipitation (entanglement of the polymer chains). Thus, the swelling of nuclei does not change. In general, the increase of isooctane concentration does not produce large modification of the network swelling [16].

(c) When polymer synthesized in the presence of a mixture of good and poor solvent, the polymer so prepared in a lower isooctane portion, its expanded gel and heterogeneous porous network occurred in the polymer structure. The increased swelling of the polymer (these) takes places through the solvent partly taken by the whole network, gel and pores, because of both the solvating of network chains and the filling of void by the solvent [22].

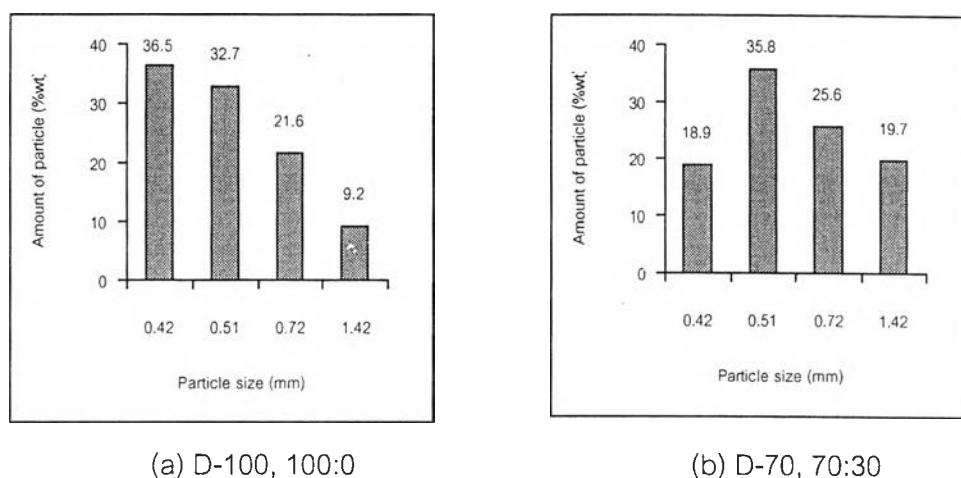(a) D-100, 100:0   (b) D-70, 70:30

Figure 4.7 Size distribution of the copolymer beads of styrene/methyl methacrylate/ ethyleneglycol dimethacrylate under the effect of diluent composition between toluene and isooctane: (a) 100:0 and (b) 70:30

Figure 4.7 shows the bead size distribution. At toluene 100 %wt, the polymer beads had broad size distribution than at toluene:isooctane 70:30. These result can be explained that toluene is a solvating diluent. The chains are fully solvated during the polymerization and less shrinkage occurs than in the corresponding systems in the absence of a solvating diluent. However, the internuclear chains can collapse with the eventual removal of the solvating diluent, so that the nuclei approached results a compact mass. From these result particle size of the beads shift towards smaller particle [23].
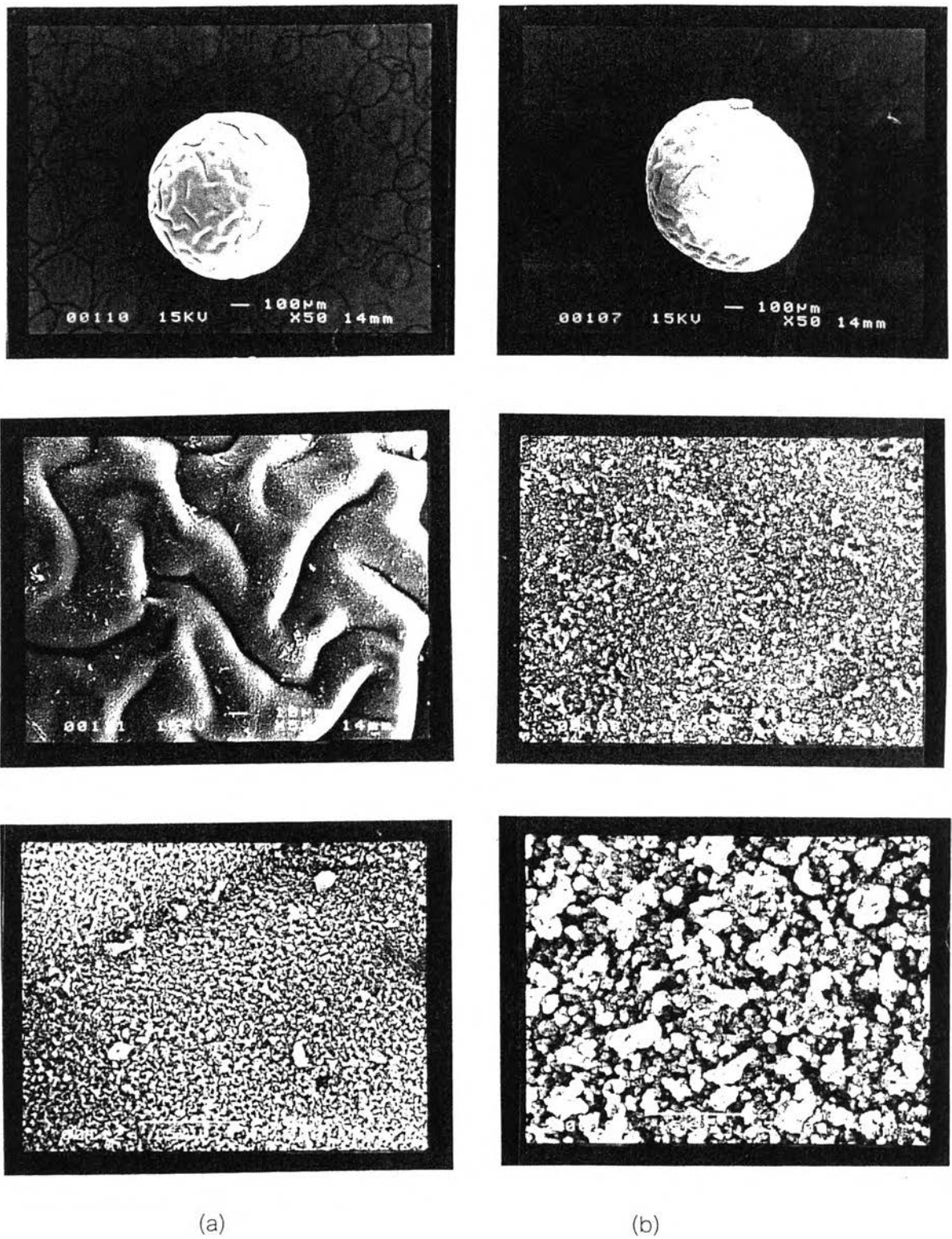
(a)　　　　　　　　　　　(b)

Figure 4.8 SEM photographs of poly(Sty-*co*-MMA-*co*-EGDMA) at different toluene:isooctane

ratios: (a) 100:0 and (b) 70:30

From Figure 4.8 (a) and (b) (at x3000), the beads prepared in a good solvent had rather rough surface with the bigger channels and more irregularly distributed than the beads obtained by 30 %wt isooctane. When styrene monomer and methyl methacrylate monomer are copolymerized by suspension polymerization in the presence of a good solvent, two kinds of porous structures can be obtained; gel or macroporous. At a low crosslinker content the final structure is an expanded gel. When the crosslinker content and dilution degree are high, a macroporous copolymer is obtained. To the other hand, when isooctane a poor solvent for the polymer chains was increased at 30 %wt, phase separation occurred during the polymerization [24] because of the polymer precipitation during the early stages of the polymerization. The precipitated polymer chains agglomerate in microspheres to become larger fixed pores, and the entanglement degree of nuclear and inter nuclear chains become greater [25].
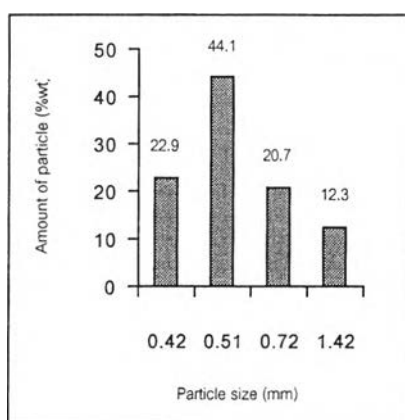
4.1.5 Effect of Inhibitor Concentration

The effects of inhibitor concentration on the average particle size, size distribution and swelling ratio were investigated by varying the inhibitor concentrations of 0.16, 0.11 and 0 %wt based on the aqueous phase, while the other parameters were kept constant as follows:

- Amount of styrene:methyl methacrylate:ethyleneglycol
  dimethacrylate monomer (46.5:46.5:7.0)   : 100 %wt
- Suspending agent concentration
  (based on the aqueous phase)   : 0.7 %wt
- Initiator concentration (based on the oil phase)   : 0.4 %wt
- Toluene:isooctane   : 70:30
- Polymerization time   : 10 hours
- Polymerization temperature   : $75^{o}C$
- Agitation rate   : 160 rpm
- Homogenizing time   : 10 minutes
- Homogenizing speed   : 2000 rpm

Table 4.9 Effects of the inhibitor concentration on size and size distribution of the polymer beads.

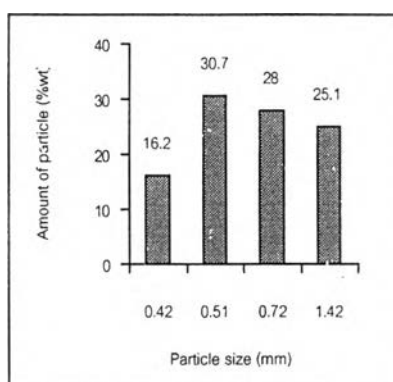| Batch No.	Particle Size Distribution (mm)				
	< 0.42	0.42 – 0.59	0.59 – 0.84	0.84 – 2.0	> 2.0
In-0.16	22.9	44.1	20.7	12.3	-
In-0.11	18.9	35.8	25.6	19.7	-
In-0	16.2	30.7	28.0	25.1	-

where In-0.16, In-0.11 and In-0 are the sample using the inhibitor concentration of 0.16 %wt, 0.11 %wt and 0 %wt, respectively.

(a) In-0.16, 0.16 %wt
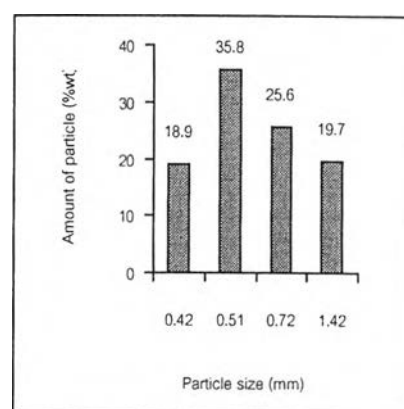
(b) In-0.11, 0.11 %wt

(c) In-0, 0 %

Figure 4.9 Size distribution of the copolymer beads of styrene/methyl methacrylate/ ethyleneglycol dimethacrylate under the effect of inhibitor concentration: (a) 0.16 %, (b) 0.11 % and (c) 0 %wt based on the aqueous phase.

Tables 4.9-4.10 and Figure 4.9 show the effect of inhibitor concentration on the average particle size and swelling ratio. In addition, the inhibitor dissolved in the continuous phase was used to prevent the secondary nucleation of polymer particles in the aqueous phase, because a part of the monomer, especially the hydrophilic monomer, will dissolve into the aqueous phase [26]. Figure 4.9 (c) shows that the second nucleation was aggregated to form larger particles because the second nucleation is not sufficiently inhibited in this system, leading to a broad size distribution of the polymer beads. The inhibitor usually decreases the average particle size because the inhibitor partition into the monomer-swollen particles that retards the polymerization in the oil phase. These phenomena result in the smaller particle size. Moreover, swelling ratio is increased since the surface of polymer increases as shown in Figure 4.10.

Table 4.10 Effects of the inhibitor concentration on % monomer conversion, average particle size and swelling ratio of the polymer beads

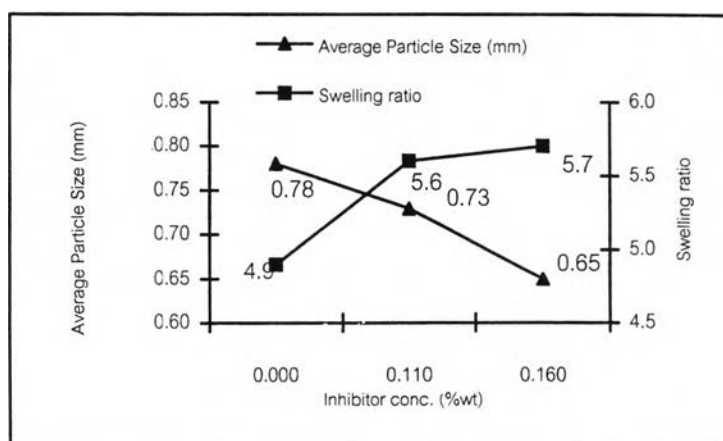| Batch No.	% Monomer Conversion	Average Particle Size (mm)	Swelling Ratio
In-0.16	63.9	0.65	5.7
In-0.11	62.7	0.73	5.6
In-0	66.5	0.78	4.9

Figure 4.10 Effects of the inhibitor concentration on average particle size and swelling ratio

4.1.6 Effect of Polymerization Time

The effects of polymerization time on the average particle size, size distribution and swelling ratio were investigated by varying the polymerization time of 6, 10 and 14 hours, while the other parameters were kept constant as follows:

- Amount of styrene:methyl methacrylate:ethyleneglycol

  dimethacrylate monomer (46.5:46.5:7.0)   : 100 %wt

- Suspending agent concentration

  (based on the aqueous phase)   : 0.7 %wt

- Initiator concentration (based on the oil phase)   : 0.4 %wt

- Toluene:isooctane   : 70:30

- Inhibitor concentration (based on the aqueous phase)   : 0.11 %wt

- Polymerization temperature   : 75°C

- Agitation rate   : 160 rpm

- Homogenizing time   : 10 minutes

- Homogenizing speed   : 2000 rpm

Table 4.11 Effects of the polymerization time on size and size distribution of the polymer beads.

Batch No.	Particle Size Distribution (mm)				
	< 0.42	0.42 – 0.59	0.59 – 0.84	0.84 – 2.0	> 2.0
T-14	16.7	32.33	28.2	22.8	-
T-10	18.9	35.8	25.6	19.7	-
T-6	17.6	33.9	24.3	24.2	-

where T-14, T-10 and T-6 are the sample from the polymerization time 14 hours,10 hours and 6 hours, respectively.

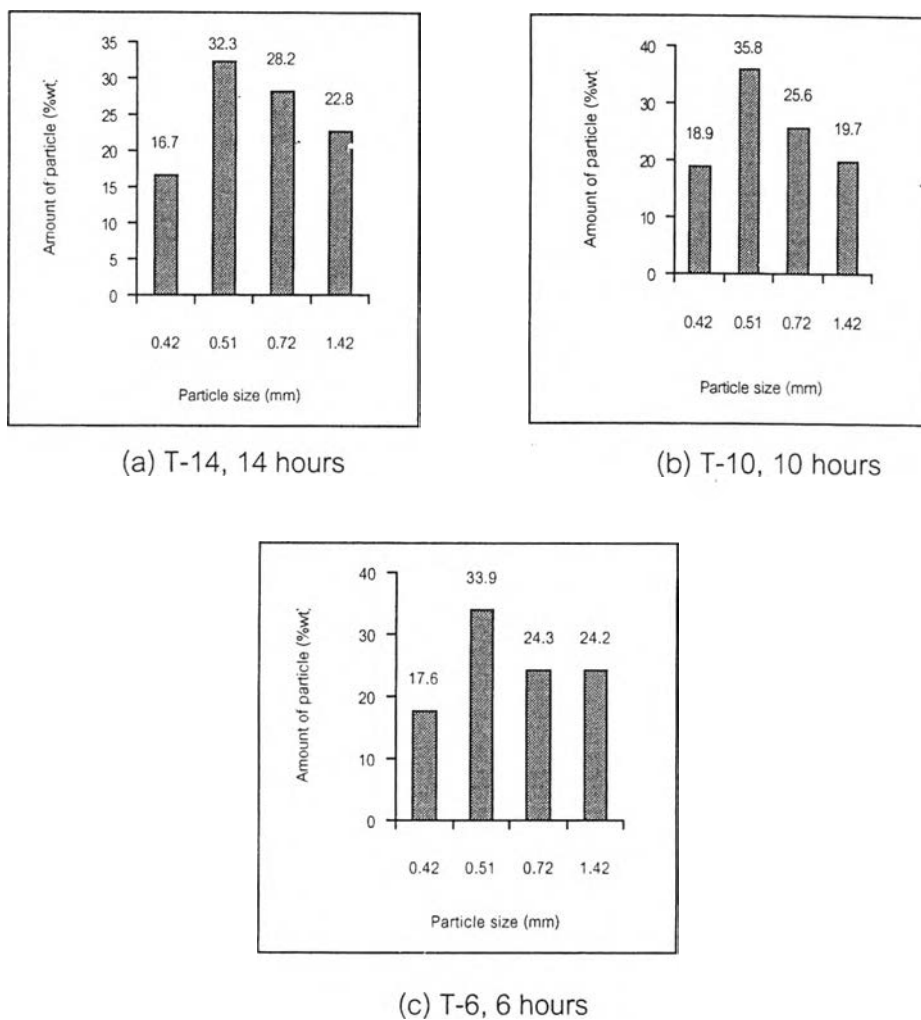(a) T-14, 14 hours

(b) T-10, 10 hours

(c) T-6, 6 hours

Figure 4.11 Size distribution of the copolymer beads of styrene/methyl methacrylate/ ethyleneglycol dimethacrylate under the effect of polymerization time : (a) 14 hours, (b) 10 hours and (c) 6 hours.

Table 4.12 Effects of the polymerization time on % monomer conversion, average particle size and swelling ratio of the polymer beads

Batch No.	% Monomer Conversion	Average Particle Size (mm)	Swelling Ratio
T-14	83.2	0.76	4.6
T-10	62.7	0.73	5.6
T-6	47.9	0.76	7.7

The effects of polymerization time on the average particle size and % monomer conversion are shown in the Table 4.12. As the polymerization time was increased from 6 to 10 and to 14 hrs, the % monomer conversion was increased from 47.9 %, to 62.7 %, and to 83.2 %, respectively. The result can be explained that the increasing time increases both the extent (amount) of the initiator radicals and the growing polymer chains. Therefore, these could lead to an increase of % monomer conversion of polymer beads [27], the average particle size is constant with increasing the polymerization reaction time. However, the swelling ratio was decreased with increasing the polymerization time. Since the polymerization process took a long time, the polymer chains were more entangled and chain mobility inside the beads was restricted or decreased. It caused an decrease in the swelling ratio from 7.7 to 5.6 and to 4.6, respectively.
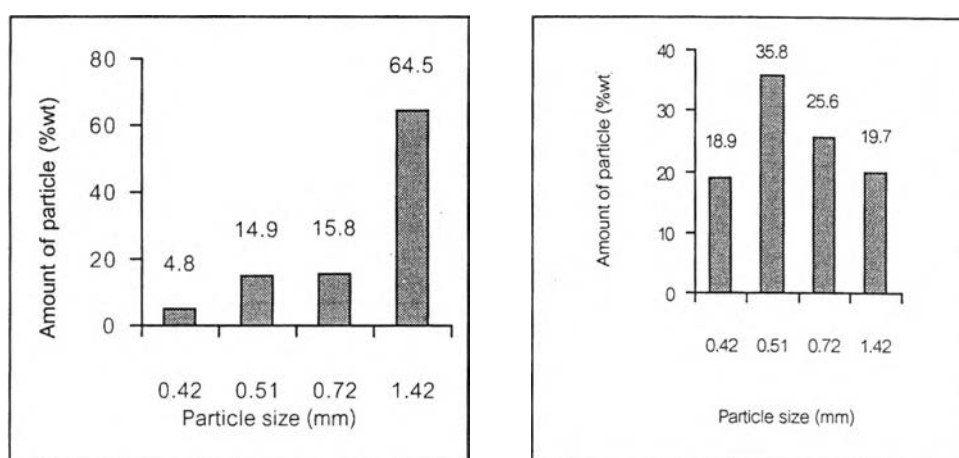
4.1.7 Effect of Polymerization Temperature

The effects of polymerization temperature on the average particle size, size distribution and swelling ratio were investigated by varying the polymerization temperature from 65, 75 to 85 $^{\circ}$C, while the other parameters were kept constant as follows:

- Amount of styrene:methyl methacrylate:ethyleneglycol
  dimethacrylate monomer (46.5:46.5:7.0)   : 100 %wt
- Suspending agent concentration
  (based on the aqueous phase)   : 0.7 %wt
- Initiator concentration (based on the oil phase)   : 0.4 %wt
- Toluene:isooctane   : 70:30
- Inhibitor concentration (based on the aqueous phase)   : 0.11 %wt
- Polymerization time   : 10 hours
- Agitation rate   : 160 rpm
- Homogenizing time   : 10 minutes
- Homogenizing speed   : 2000 rpm

Table 4.13 Effects of the polymerization temperature on size and size distribution of
the polymer beads.

Batch No.	Particle Size Distribution (mm)				
	< 0.42	0.42 – 0.59	0.59 – 0.84	0.84 – 2.0	> 2.0
T-85	4.8	14.9	15.8	64.5	2.0
T-75	18.9	35.8	25.6	19.7	-
T-65	Coagulated				

where T-85, T-75 and T-65 are the sample from the polymerization temperature 85°C,
75°C and 65°C, respectively.

(a) T-85, 85°C   (b) T-75, 75°C

Figure 4.12 Size distribution of the copolymer beads of styrene/methyl methacrylate/
ethyleneglycol dimethacrylate under the polymerization temperature : (a)
85°C and (b) 75°C

Table 4.14 Effects of the polymerization temperature on % monomer conversion, average particle size and swelling ratio of the polymer beads

Batch No.	% Monomer Conversion	Average Particle Size (mm)	Swelling Ratio
T-85	84.7	1.13	4.4
T-75	62.7	0.73	5.6

Table 4.14 shows the effects of polymerization temperature on the average particle sizes, % monomer conversion and swelling ratio. At 65°C, the polymer particles were very soft and sticky. When they were dried, there was no bead formation. When the temperature increased from 75°C to 85°C, the average particle size was increased from 0.73 mm to 1.13 mm. This increase in the particle diameter with increasing the temperature was attributed to

(a) an increase in the critical chain length due to the increase in the solvency of the continuous phase.

(b) an increase in the concentration of precipitated oligomer chains due to the increase in both the decomposition rate of the initiator and the propagation rate of oligomer radicals and oligomer chains.

(c) a decrease in the viscosity of the continuous phase [28].

The percent monomer conversion was found to increase with increasing the temperature. It can be explained that increasing the temperature increases the initial rate of polymerization. This change enhances the rate of free radical formation, resulting in higher % monomer conversion [21].

In other words, the swelling ratio was found to decrease with increasing the polymerization temperature. It can be described that the increasing temperature increases both the decomposition rate of the inhibitor and the propagation rate of oligomer radicals. All these changes produce crosslinking sites inside the polymer beads, resulting in less chain mobility. Therefore, the swelling ratio was reduced as a result of the less flexible chains.

4.1.8 Effect of Agitation Rate

The effects of agitation rate on the average particle size, size distribution and swelling ratio were investigated by varying the agitation rate from 200 rpm, 160 rpm to 100 rpm, while the other parameters were kept constant as follows:

- Amount of styrene:methyl methacrylate:ethyleneglycol

  dimethacrylate monomer (46.5:46.5:7.0)   : 100 %wt
- Suspending agent concentration

  (based on the aqueous phase)   : 0.7 %wt
- Initiator concentration (based on the oil phase)   : 0.4 %wt
- Toluene:isooctane   : 70:30
- Inhibitor concentration (based on the aqueous phase)   : 0.11 %wt
- Polymerization time   : 10 hours
- Polymerization temperature   : 75°C
- Homogenizing time   : 10 minutes
- Homogenizing speed   : 2000 rpm

Table 4.15 Effects of the agitation rate on size and size distribution of the polymer beads.

| Batch No.	Particle Size Distribution (mm)				
	< 0.42	0.42 – 0.59	0.59 – 0.84	0.84 – 2.0	> 2.0
Sp-200	43.1	44.0	10.4	2.5	-
Sp-160	18.9	35.8	25.6	19.7	-
Sp-100	Coagulated				

where Sp-200, Sp-160 and Sp-100 are the sample using the agitation rate of 200 rpm, 160 rpm and 100 rpm, respectively.

Table 4.16 Effects of the agitation rate on % monomer conversion, average particle size and

swelling ratio of the polymer beads.

Batch No.	% Monomer Conversion	Average Particle Size (mm)	Swelling Ratio
Sp-200	60.4	0.52	5.8
Sp-160	62.7	0.73	5.6
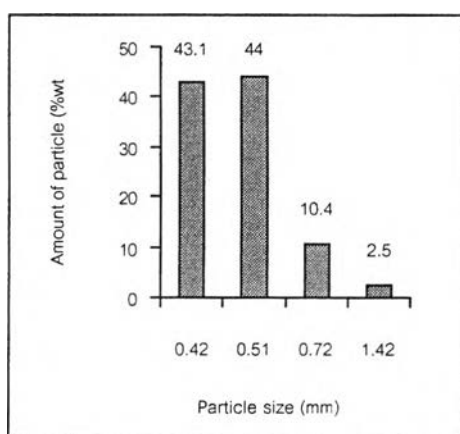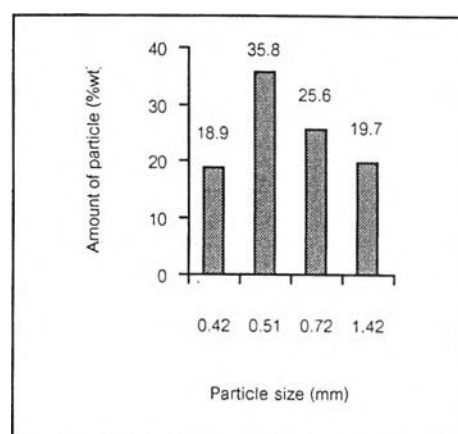
(a) Sp-200, 200 rpm   (b) Sp-160, 160 rpm

Figure 4.13 Size distribution of the copolymer beads of styrene/methyl methacrylate/
ethyleneglycol dimethacrylate under the effect of agitation rate: (a) 200 rpm.
and (b) 160 rpm.

Polymer beads were coagulated at 100 rpm. Tables 4.15-4.16 show the effect of agitation rate on the average particle size with increasing the agitation rate from 160 rpm to 200 rpm, the average particle size decreased. It can be explained that an increased agitation rate leads to an increase in shearing force, which disperses the oil phase to form the smaller monomer droplets [29].
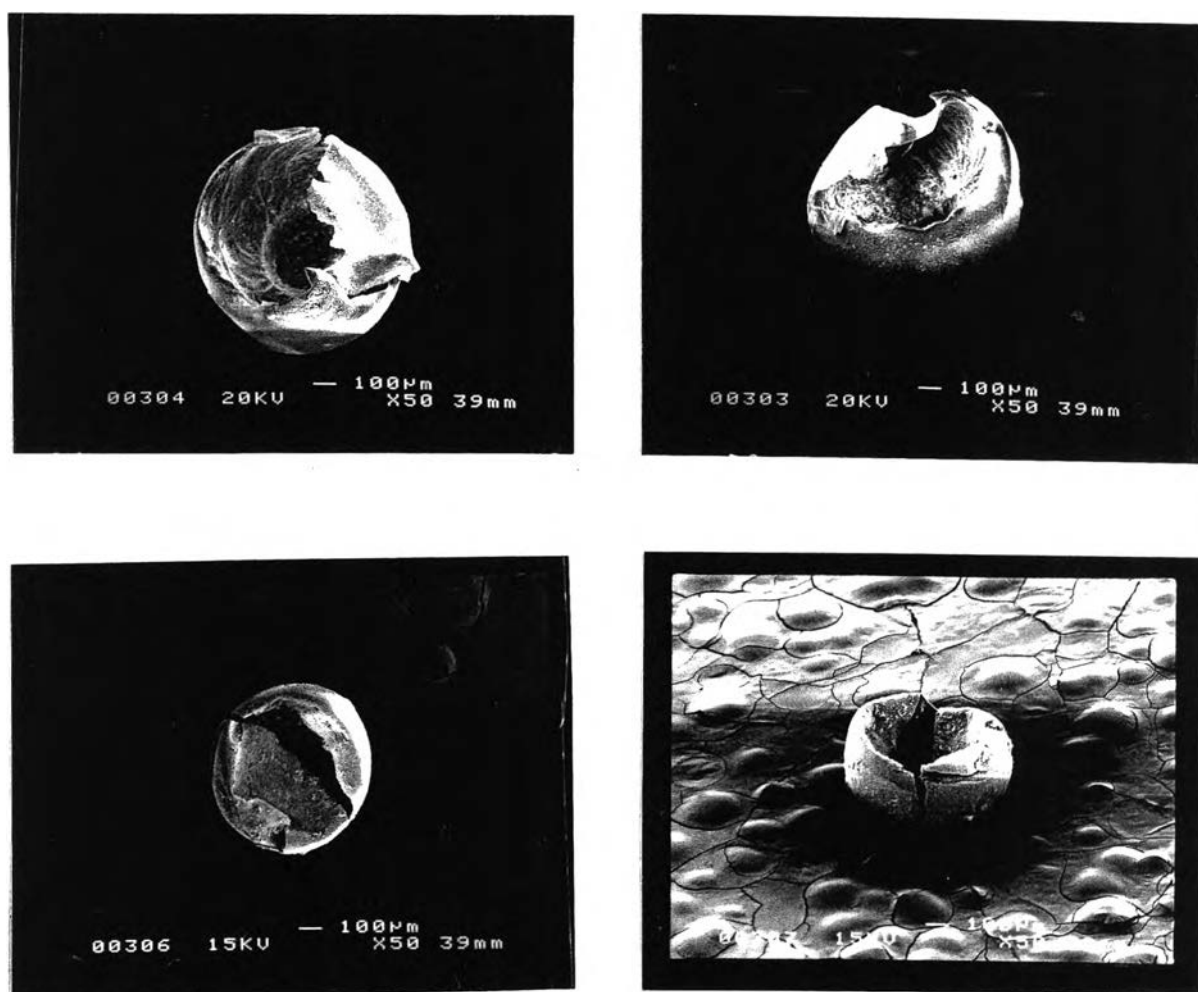
Figure 4.14 SEM photographs of poly(Sty-co-MMA-co-EGDMA) beads after extraction by cyclohexane in a soxhlet extractor for 24 hours.

Figure 4.14 shows the beads of poly(methyl methacrylate)/polystyrene, extracted by cyclohexane for 24 hours. A hollow structure inside bead particle was obtained that is poly(methyl methacrylate). The disappeared morphology of core/shell bead is polystyrene. In this study, polystyrene was dissolved in hot cyclohexane that gave a hollow structure of particle [30]. It can be assumed the polystyrene is the core and poly(methyl methacrylate) is the shell, because the latter is more hydrophilic. In the one-stage suspension polymerization, it is notable that in most cases, the morphology of polymer beads obeys thermodynamically controlled in phase separation of the polymer. The more hydrophilic polymer tends to distribute preferentially in the shell, the more

hydrophobic in the core [31]. The mechanism of morphological formation of core/shell beads is as follows. A portion of the polymeric stabilizer, PVP or poly(vinyl pyrrolidone) becomes chemically grafted on the surface of poly(methyl methacrylate) particles. Then, the poly(methyl methacrylate) is pulled out by the PVP to the outer layer of the particle close to the continuous phase. Consequently, the resulting morphology of the particle is polystyrene/poly(methyl methacrylate) core/shell type [32].

4.2 Seeded Suspension Polymerization

In this study, the syntheses of seeded copolymer of methyl acrylate/styrene and 2-ethylhexyl acrylate/styrene were carried out as a two-step reaction. The first step, poly (methyl acrylate) and poly(2-ethylhexyl acrylate) seed particles were prepared by suspension polymerization. The second step, poly(methyl acrylate)/polystyrene and poly (2-ethylhexyl acrylate)/polystyrene composite particles were synthesized by suspension copolymerization of styrene monomer onto the surface of poly(methyl acrylate) seed particles and poly(2-ethylhexyl acrylate) seed particles.

4.2.1 Seeded Suspension Polymerization of Poly(Methyl Acrylate)/ Polystyrene

Poly(methyl acrylate) seed particles were produced by suspension polymerization, which has the appropriate condition as follows:

| Composition	PMA seed	PMA/PS
- Amount of methyl acrylate:ethyleneglycol dimethacrylate monomer (85.0:15.0)	: 100 %wt	-
- PMA seed particle	-	: 3 g.
- Amount of styrene:ethyleneglycol dimethacrylate monomer (85.0:15.0)	-	: 100 %wt (10 g)

- Suspending agent concentration

(based on the aqueous phase)   : 0.2 %wt   : 0.2 %wt

- Initiator concentration

(based on the oil phase)   : 0.4 %wt   : 0.4 %wt

- Toluene:isooctane   : 80:20   : -

- Inhibitor concentration

(based on the aqueous phase)   : 0.16 %wt.   : 0.16 %wt.

- Polymerization time   : 10 hours   : 10 hours

- Polymerization temperature   : 75°C   : 75°C

- Agitation rate   : 250 rpm   : 250 rpm

Table 4.17 Size distribution of polymer beads of poly(methyl acrylate) seed and poly (methyl acrylate)/polystyrene

Batch No.	Particle Size Distribution (mm)				
	< 0.42	0.42 – 0.59	0.59 – 0.84	0.84 – 2.0	> 2.0
PMA seed	1.9	3.1	5.8	76.8	12.4
PMA/PS	-	-	-	66.2	32.8
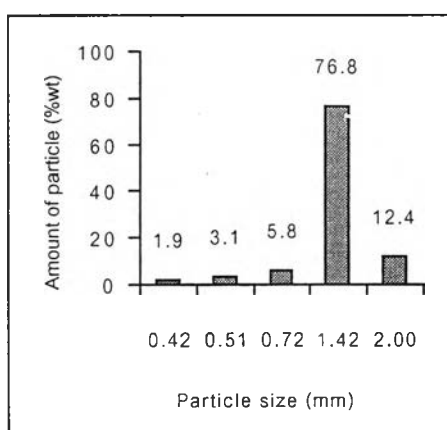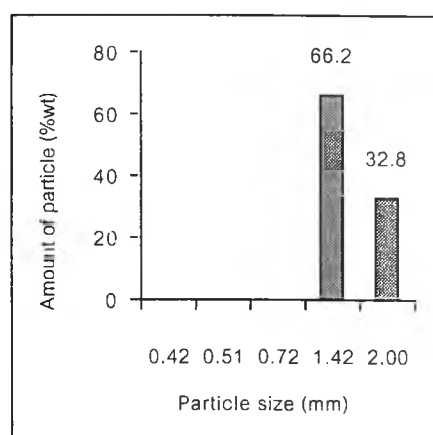
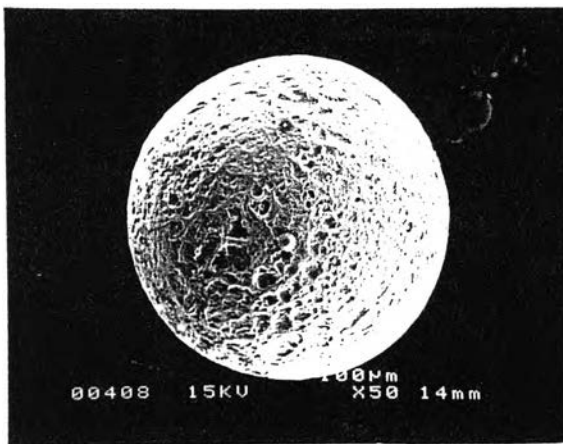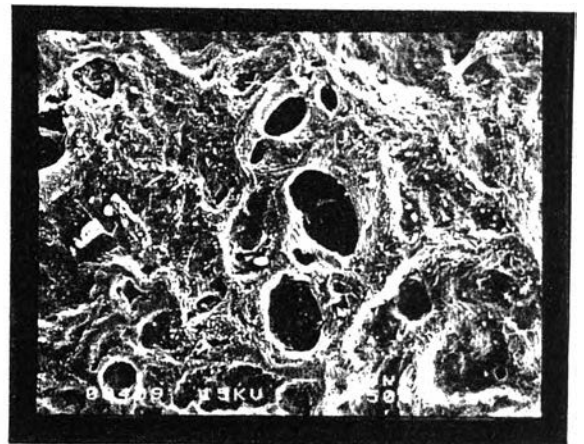(a) poly(methyl acrylate) seed   (b) poly(methyl acrylate)/polystyrene

Figure 4.15 Bead size distribution: (a) poly(methyl acrylate) seed and (b) poly (methyl acrylate)/polystyrene beads

Table 4.18 Properties of poly(methyl acrylate) seed and poly(methyl acrylate)/polystyrene in terms of percentage monomer conversion, average particle size and swelling ratio in toluene.
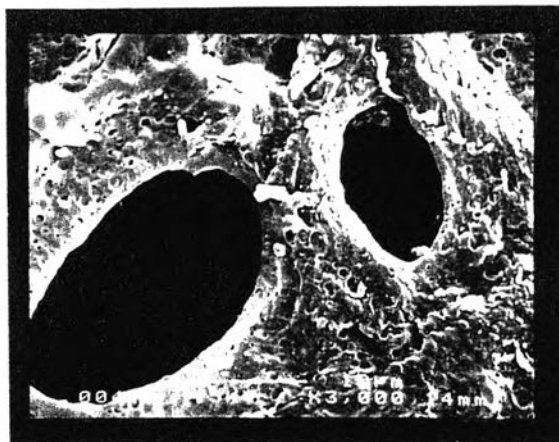
| Batch No.	% Monomer Conversion	Average Particle Size (mm)	Swelling Ratio
PMA seed	59.5	1.40	4.0
PMA/PS	49.8	1.61	2.5

(a)

(b)

(c)

Figure 4.16 SEM photographs of poly(methyl acrylate)/polystyrene (a) x50 (b) x500 and (c) x3000.

Tables 4.17-4.18 and Figure 4.15 show the % monomer conversion, bead size distribution, the average particle size and the swelling ratio of poly(methyl acrylate) seed and poly(methyl acrylate)/polystyrene. The average particle size of poly(methyl acrylate) seed is 1.40 mm and The average particle size of poly(methyl acrylate)/polystyrene is 1.61 mm. Percentage monomer conversion and swelling ratio of poly(methyl acrylate) seed and poly(methyl acrylate)/polystyrene are changed from 59.5 % to 49.8 % and 4.0 to 2.5, respectively.

Figure 4.16 shows SEM photographs of poly(methyl acrylate)/polystyrene. The polymerization process of the macroporous copolymer beads can be explained to the detail as follows: In a seeded suspension polymerizaton, a dispersed phase consisting of a monomer mixture, diluents and an initiator is dispersed in a continuous phase by a dispersing agent. The crosslinking agent is ethyleneglycol dimethacrylate, which has the high reactive ratio. Ethyleneglycol dimethacrylate rich copolymer composed of straight chains is formed in the polymerization. When the polymerization proceeds and the monomers change to the crosslinked copolymers, the formed nuclei become insoluble to both monomers and diluents, and consequently the phase separation occurs gradually between the copolymer and the diluent. Thus a copolymer rich phase becomes the spherical primary particle having a lower surface free energy. At a certain conversion of monomers, as the content of ethyleneglycol dimethacrylate monomer is higher, the formed copolymers are not able to be a nuclei and are adsorbed merely on the primary particles. Thus, the primary particles grow and agglomerate. In addition, entanglement of copolymer molecules takes place among the primary particles and the primary particles are combined and fixed. Finally, The diluent existing in agglomerates is extracted and macroporous copolymer beads are obtained [33].
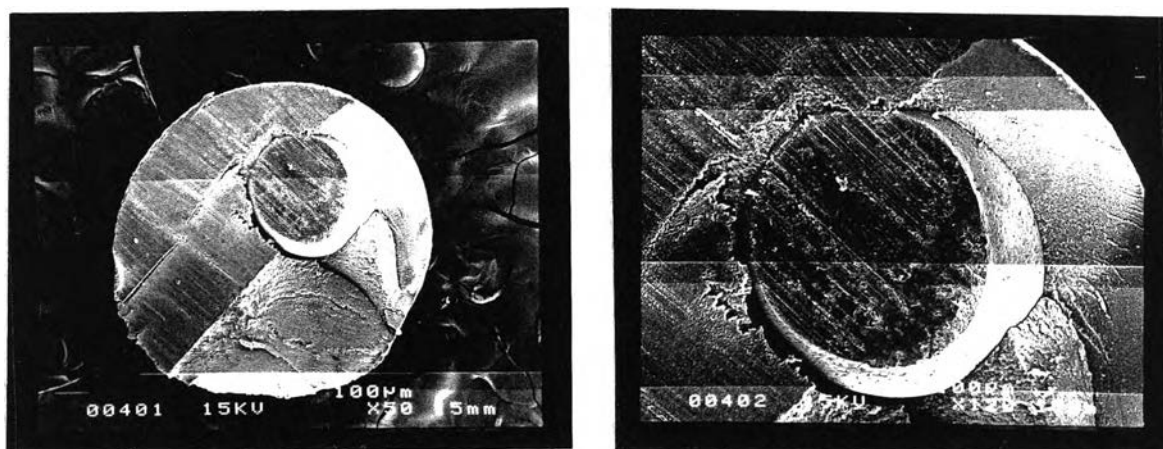
(a)   (b)

Figure 4.17 SEM photographs of cross-section of seeded poly(methyl acrylate)/poly

styrene (a) x50 and (b) x120.

Figure 4.17 shows SEM photographs of cross-section of seeded poly(methyl acrylate)/polystyrene. The core hemisphere is poly(methyl acrylate) and the shell hemisphere is polystyrene.

4.2.2 Seeded Suspension Polymerization of Poly(2-Ethylhexyl Acrylate)/Polystyrene

Poly(2-ethylhexyl acrylate) seed particles were produced by suspension polymerization, which has the appropriate condition as follows:

Composition	P(2-EHA) seed	P(2-EHA)/PS
- Amount of 2-ethylhexyl acrylate:ethyleneglycol dimethacrylate monomer (93.0:7.0)	: 100 %wt	-
- P(2-EHA) seed particle	-	: 3 g.

- Amount of styrene:ethyleneglycol

  dimethacrylate monomer (93.0:7.0)   -   : 100 %wt (10 g)

- Suspending agent concentration

  (based on the aqueous phase)   : 0.2 %wt   : 0.2 %wt

- Initiator concentration

  (based on the oil phase)   : 0.4 %wt   : 0.4 %wt

- Toluene:isooctane   : 60:40   :   -

- Inhibitor concentration

  (based on the aqueous phase)   : 0.16 %wt.   : 0.16 %wt.

- Polymerization time   : 10 hours   : 10 hours

- Polymerization temperature   : 75°C   : 75°C

- Agitation rate   : 250 rpm   : 250 rpm

Table 4.19 Size distribution of the polymer beads of poly(2-ethylhexyl acrylate) seed

Batch No.	Particle Size Distribution (mm)				
	< 1.0	1.1-2.0	2.1-3.0	3.1-4.0	> 4.1
P(2-EHA) seed	1.5	28.4	44.6	23.0	2.5

Table 4.20 Size distribution of the polymer beads of poly(2-ethylhexyl acrylate)/polystyrene

Batch No.	Particle Size Distribution (mm)				
	0.3	0.35	0.40	0.45	0.50
P(2-EHA) /PS	8.0	19.7	49.3	16.7	7.0

Table 4.21 Properties of poly(2-ethylhexyl acrylate) seed and poly(2-ethylhexyl acrylate)/
polystyrene in terms of percentage monomer conversion, average particle
size and swelling ratio in toluene.

Batch No.	% Monomer Conversion	Average Particle Size (mm)	Swelling Ratio
P(2-EHA) seed	52.0	2.5	5.9
P(2-EHA)/PS	90.7	4.0	2.9
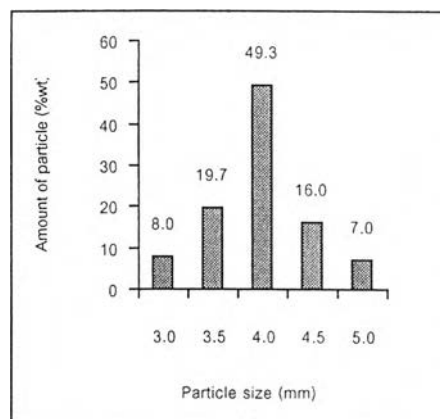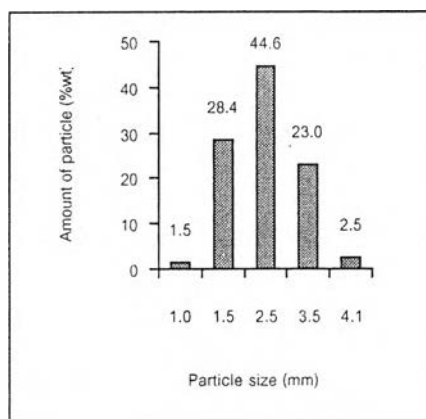
(a) poly(2-ethylhexyl acrylate) seed   (b) poly(2-ethylhexyl acrylate)/polystyrene

Figure 4.18 Bead size distribution : (a) poly(2-ethylhexyl acrylate) seed, and (b) poly
(2-ethylhexyl acrylate)/polystyrene beads

Tables 4.19-4.21 and Figure 4.18 show % monomer conversion, bead size distribution, the average particle size and the swelling ratio of poly(2-ethylhexyl acrylate) seed and poly(2-ethylhexyl acrylate)/polystyrene. The % monomer conversion and average particle size of poly(2-ethylhexyl acrylate) seed and poly(2-ethylhexyl acrylate)/ polystyrene are increased from 52.0 % to 90.7 % and 2.50 mm to 4.0 mm, respectively. The swelling ratios of poly(2-ethylhexyl acrylate) seed and poly(2-ethylhexyl acrylate)/ polystyrene are decresed from 5.9 to 2.9 because of harder polystyrene shell.
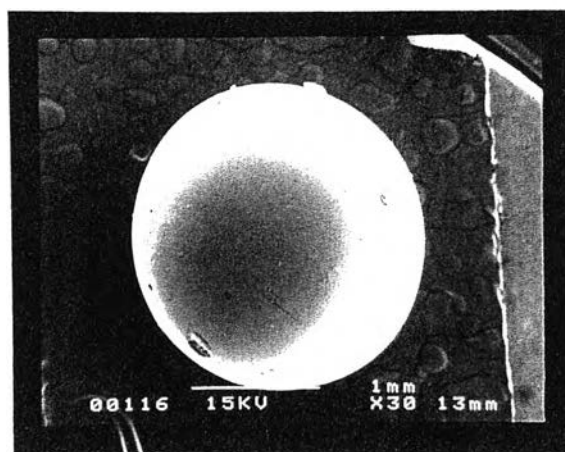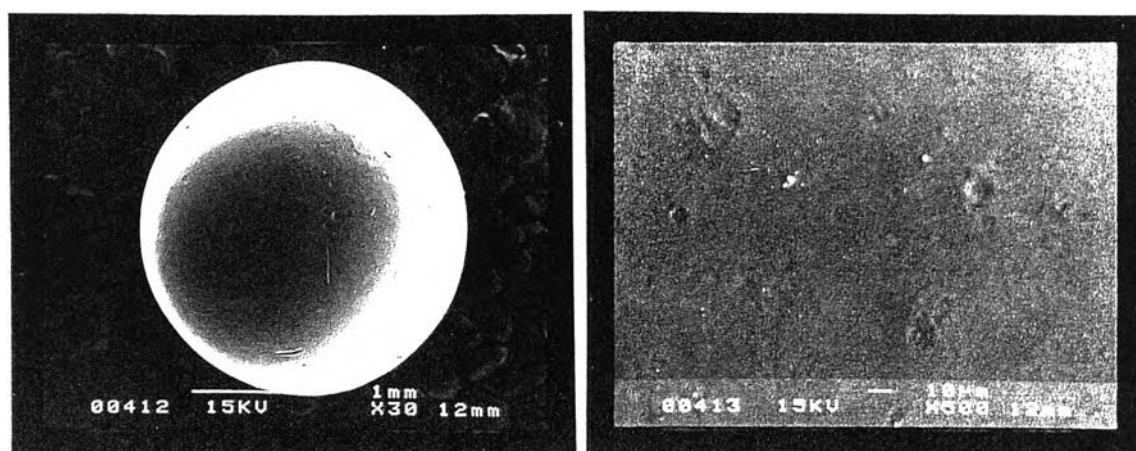
Figure 4.19 SEM photographs of poly(2-ethylhexyl acrylate) seed.

(a)   (b)

Figure 4.20 SEM photographs of poly(2-ethylhexyl acrylate)/polystyrene (a) x30 and
(b) x500

Figure 4.19 shows SEM photograph of poly(2-ethylhexyl acrylate) seed, which presented a homogeneous structure and a transparent appearance. The seed bead surface was very smooth. Poly(2-ethylhexyl acrylate)/polystyrene has a heterogeneous structure with an opaque appearance. The core/shell bead surface was smooth as shown in Figure 4.20.
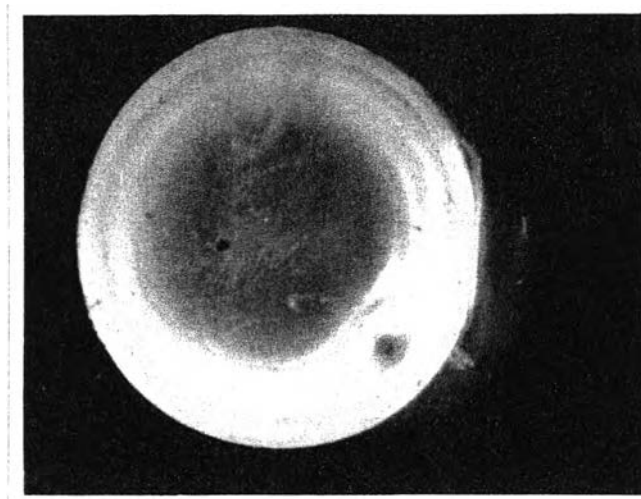
Figure 4.21 Optical photographs of cross-section of poly(2-ethylhexyl acrylate)/polystyrene (x45)

Figure 4.21 shows the cross-section of seeded poly(2-ethylhexyl acrylate)/ polystyrene. The bead has two domains parts, the central dark region is poly(2-ethylhexyl acrylate) and the white, outer region is polystyrene.

Polymer Chains   PVP   Chains
o   Monomer Molecules   Surfactant Molecules
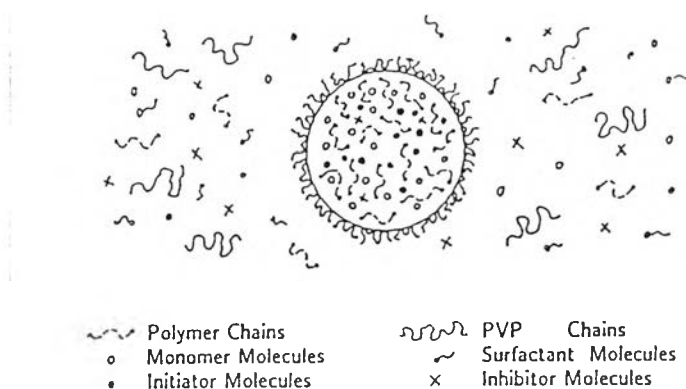•   Initiator Molecules   x   Inhibitor Molecules

Figure 4.22 Schematic representation of the polymerization system.

In the seeded suspension polymerization, the polymerization system is depicted in Figure 4.22, where large circle represents the swollen seed particle surrounded by the aqueous phase. There are three possible polymerization sites, namely in the aqueous phase, in the interior, and at the surface. Overall, the extent of

polymerization in the aqueous phase is considered to be small for three reasons: (a) most of the monomer and the initiator are concentrated inside the large particle because of their low water solubilities, (b) a large amount of water-soluble inhibitor is used, and this inhibitor is expected to reside mainly in the aqueous phase, (c) no significant amounts of secondary particles were found in the aqueous phase after polymerization. Therefore, the polymerization of styrene is expected to proceed predominantly inside the seed particles, in the interior and at the surface of particle.

Since the seed particles are large, the polymerization in the interior of the particles (referred to as internal polymerization) resembles a bulk polymerization. The polymerization near the surface (referred to as surface polymerization) is expected to follow a bulk-like polymerization mechanism with the additional effects of surface phenomena such as radical absorption and desorption [34].
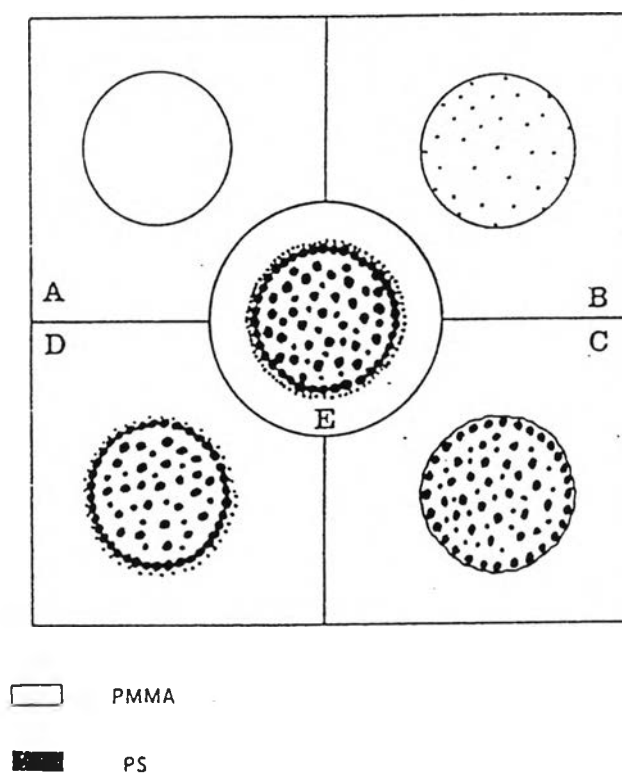

Figure 4.23 Schematic representation of formation mechanism of poly(metha)acrylate/ polystyrene composite particles.

Mechanism of the morphology development of the seeded suspension polymerization is proposed as follows, and is schematically represented in Figure 4.23. Before polymerization, the swollen poly(meth)acrylate seed particles have a uniform composition, as shown in Figure 4.23 (A). As soon as the polymerization is initiated, phase separation occurs and the polystyrene domains develops throughout the particles [i.e., in the interior and at the surface, Figure 4.23 (B)]. The existing polystyrene domains grow and new domains form until a critical concentration of styrene is reached, as shown in Figure 4.23 (C). After this point, the internal polymerization slows dramatically, while the surface polymerization does not. The polystyrene domains in the interior of the particle (the internal domain) essentially stop growing, while those at the surface continue to grow and become interconnected with one another, forming a spherical subsurface crust (the subsurface polystyrene).

With the further consumption of styrene monomer, the viscosity continuously increases, the diffusion rate of radicals is reduced and the depth of absorbed radical diffusion and radical desorption decrease. Finally, newly produced polymer chains cannot diffuse into the surface domain, as shown in Figure 4.23 (D). After that the growth of the subsurface domains essentially stops and only the surface domains continue to grow until the end of polymerization, as shown in Figure 4.23 (E).

From the above result, It can be concluded that the core is poly(methyl acylate) and the shell is polystyrene, as shown in Figure 4.17. The central dark region of bead particle is poly(2-ethylhexyl acrylate) and the white region of bead particle is polystyrene, as shown in Figure 4.21.

4.3 Absorption-Desorption in the Core/Shell Beads and Diffusion Coefficient of Toluene:Isooctane Solvents.

4.3.1 Absorption

The absorption in the core/shell beads of toluene:isooctane solvents [the toluene volume fraction (z) = 0.5] was determined based on increases in bead size

upon swelling in solvents. Appendix A shows the increase in bead diameter and volume with swelling time.

Figures 4.24, 4.26 and 4.28 show the variation of the core/shell bead volume with swelling time. These curve can be divided into three stages:

I. An initial stage of the high sorption rate can be easily observed due to the solvating of network chains. The main driving force of this process is the changes in the free energies of solvent and elastic deformation during the expansion of the network.

II. A second stage of the slow sorption rate is due to the sorption into the pore inclusive of pore structure and dimension.

III. A third stage of the plateau value because of the absorption saturation.

Figure 4.24 shows the increase of the bead volume with swelling time for the core/shell bead of poly(methyl methacrylate)/polystyrene. The initial stage of absorption take place at about 20 minutes, the bead volume increased rapidly since the network began to expand by absorpting the surrounding solvent. Finally, The swollen bead reached a stationary state in equilibrium with the surrounding solvent within 35 minutes.

The increase of the bead volume with swelling time for the core/shell bead of poly(methyl acrylate)/polystyrene is shown in Figure 4.26. The initial stage of absorption was found at about 25 minutes after the immersion. Finally, the swollen bead reached a stationary state in equilibrium with surrounding solvent within 55 minutes.

The core/shell bead of poly(2-ethylhexyl acrylate)/polystyrene also show the increase of the bead volume with swelling time in Figure 4.28. The initial stage of absorption was about 35 minutes. Finally, The swollen bead reached a stationary state in equilibrium with the surrounding solvent within 60 minutes. As a comparison, the chain flexibility of these three types of bead is, of course, totally difference. The extent of crosslinking in each case plays an important role in absorption rate.

4.3.2 Desorption

When a swollen core/shell bead was placed on the filter paper, the solvent diffused from the swollen core/shell bead into the filter paper. It may be possible that the interaction between solvent and the substrate is higher than the interaction between solvent and the polymer network. Appendix A shows the core/shell bead diameter and volume upon desorption at different times.

Figures 4.25, 4.27 and 4.29 show the variation of the swollen core/shell beads volume with time. These curve can be divided into three stages:

I. An initial stage of high desorption rate.

II. A second stage of slow desorption rate.

III. A third stage of no solvent loss or a very low undetectable desorption process.

Figure 4.25 shows the desorption of the swollen bead volume of PMMA/PS with time. The initial stage of desorption took place at about 15 minutes, and then the swollen bead lost all solvents within 35 minutes after the start of the desorption.

The desorption of the swollen bead volume of PMA/PS with time is illustrated in Figure 4.27. The initial stage of desorption was found at about 20 minutes, and then the swollen bead lost all solvent within 55 minutes after the start of the desorption.

As for poly(2-ethylhexyl acrylate)/polystyrene, the desorption of the swollen bead volume with time in Figure 4.29 shows the following. The initial stage of desorption took place within 20 minutes, and then the swollen bead lost all solvent within 60 minutes after the start of the desorption.

The absorption-desorption rate process of the polymer beads progresses with different because each polymer bead had a different content of the crosslinking agent, which affected the chain mobility.
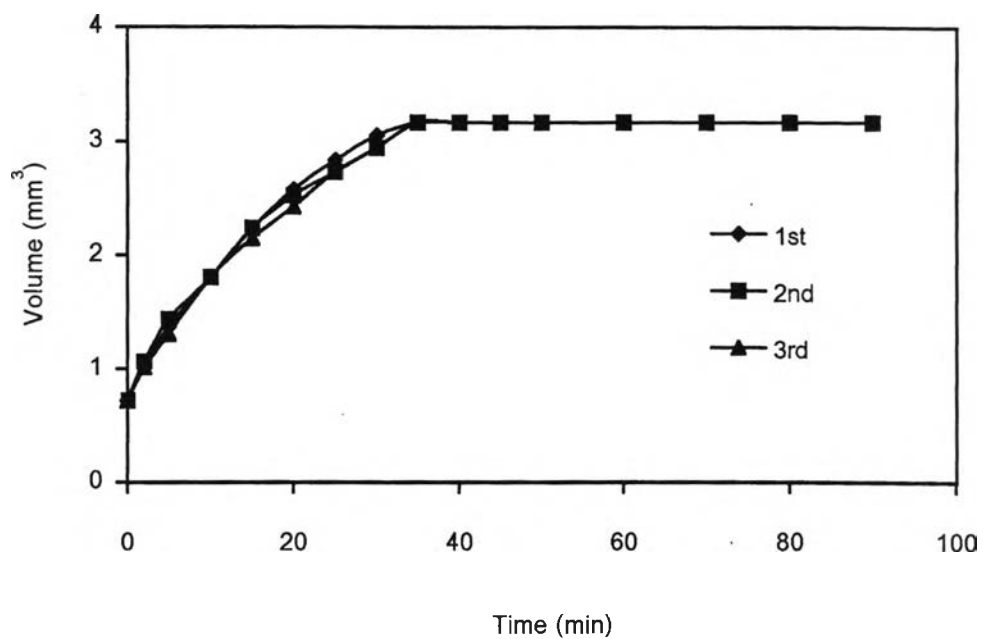
Figure 4.24 Absorption of the PMMA/PS bead by one-stage suspension
polymerization with time.

Figure 4.25 Desorption of the PMMA/PS bead by one-stage suspension
polymerization with time.

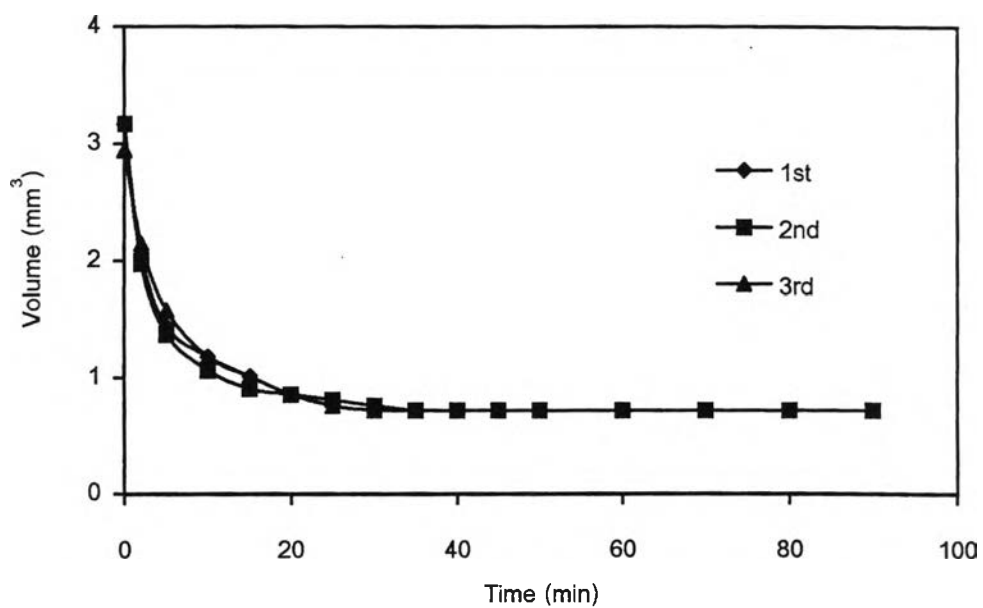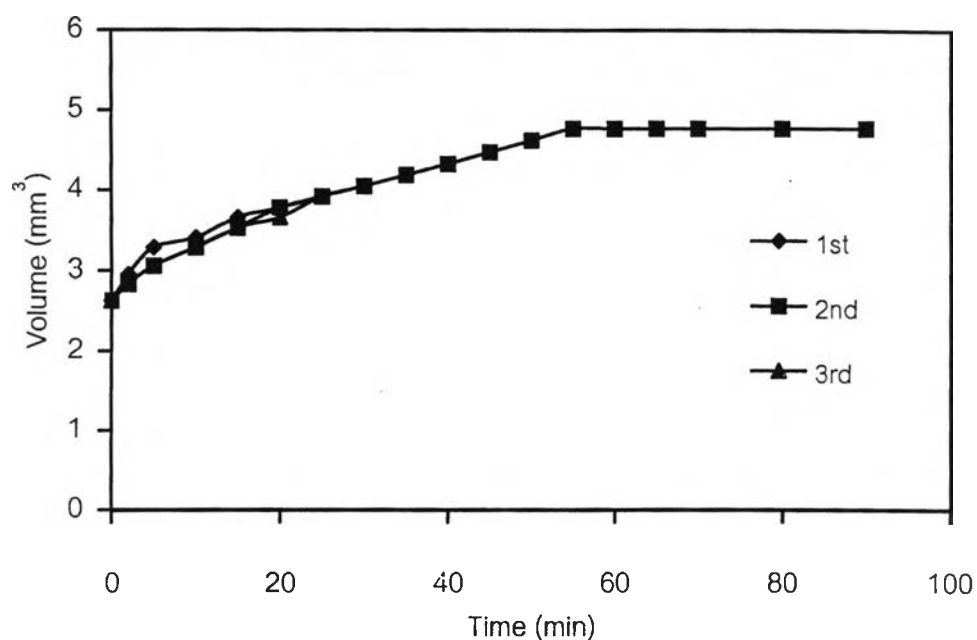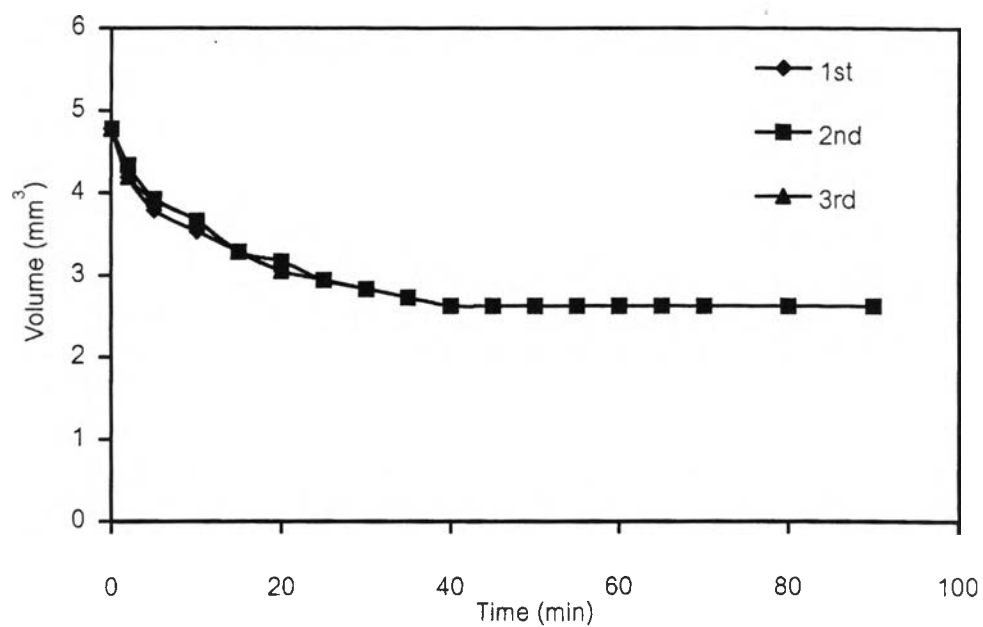Figure 4.26 Absorption of the PMA/PS bead by seeded suspension polymerization with time.

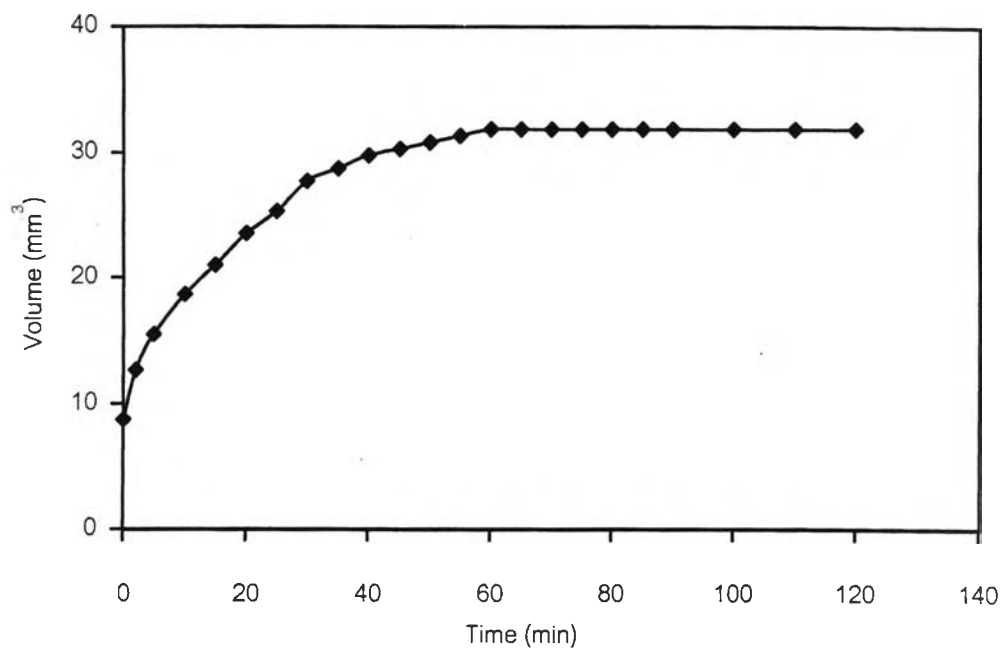Figure 4.27 Desorption of the PMA/PS bead by seeded suspension polymerization with time.

Figure 4.28 Absorption of the P(2-EHA)/PS bead by seeded suspension
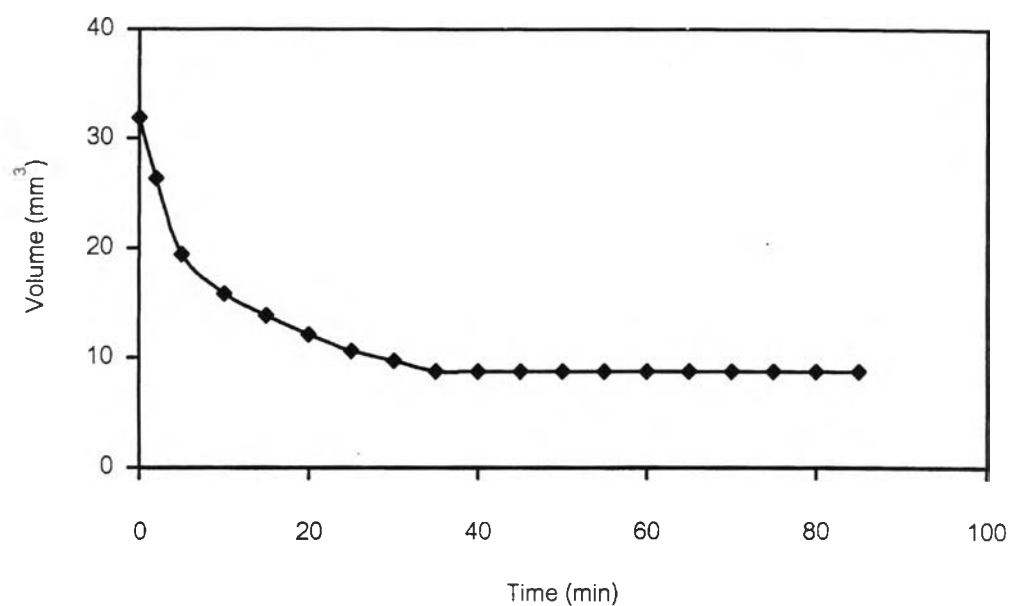polymerization with time .

Figure 4.29 Desorption of the P(2-EHA)/PS bead by seeded suspension
polymerization with time.

4.3.3 Cycle of Solvent Absorption and Desorption

The beads could be used to absorb and desorb toluene:isooctane for many cycles. The repeated absorption and desorption behavior of the second and third cycles were also the same as the first cycle. From the very slight difference that the volume of toluene:isooctane absorbed between the first cycle and the second cycle, it may be caused by: (1) The network of the core/shell beads was changed, and (2) The homopolymer was dissloved during absorption and desorption. The beads of poly (methyl methacrylate)/polystyrene by one-stage suspension polymerization and poly (methyl acrylate)/polystyrene by seeded suspension polymerization still remained spherical throughout the cycles; they did not collapse after repeated uses as shown in Figures 4.30 and 4.31. When the bead of poly(2-ethylhexyl acrylate)/polystyrene was used to absob-desorb the solvent of toluene:isooctane just one time, the bead was collapsed when the swollen bead desorbed the retained solvent onto the filter paper. It can be explained that poly(2-ethylhexyl acrylate) has a low T_g like rubber. Thus, the network structure of the bead is not strong and flexible enough for keeping the spherical structure because of the stress exerted on the bead during expansion and compression when the solvent comes in and out of the bead, as shown in Figure 4.32.

4.3.4 Diffusion Coefficient

The diffusion coefficient of solvent in the bead could be calculated from equations (4-1) and (4-2), as follows:

$$\tau = a^2/D \qquad (4-1)$$

where τ is a characteristic swelling time

a is the final radius of the fully swollen gel

D is the diffusion coefficient of the gel in the liquid

$$\ln (\Delta a_t / \Delta a_0) = const. - t/\tau \text{ (for } t/\tau > 0.25) \qquad (4-2)$$
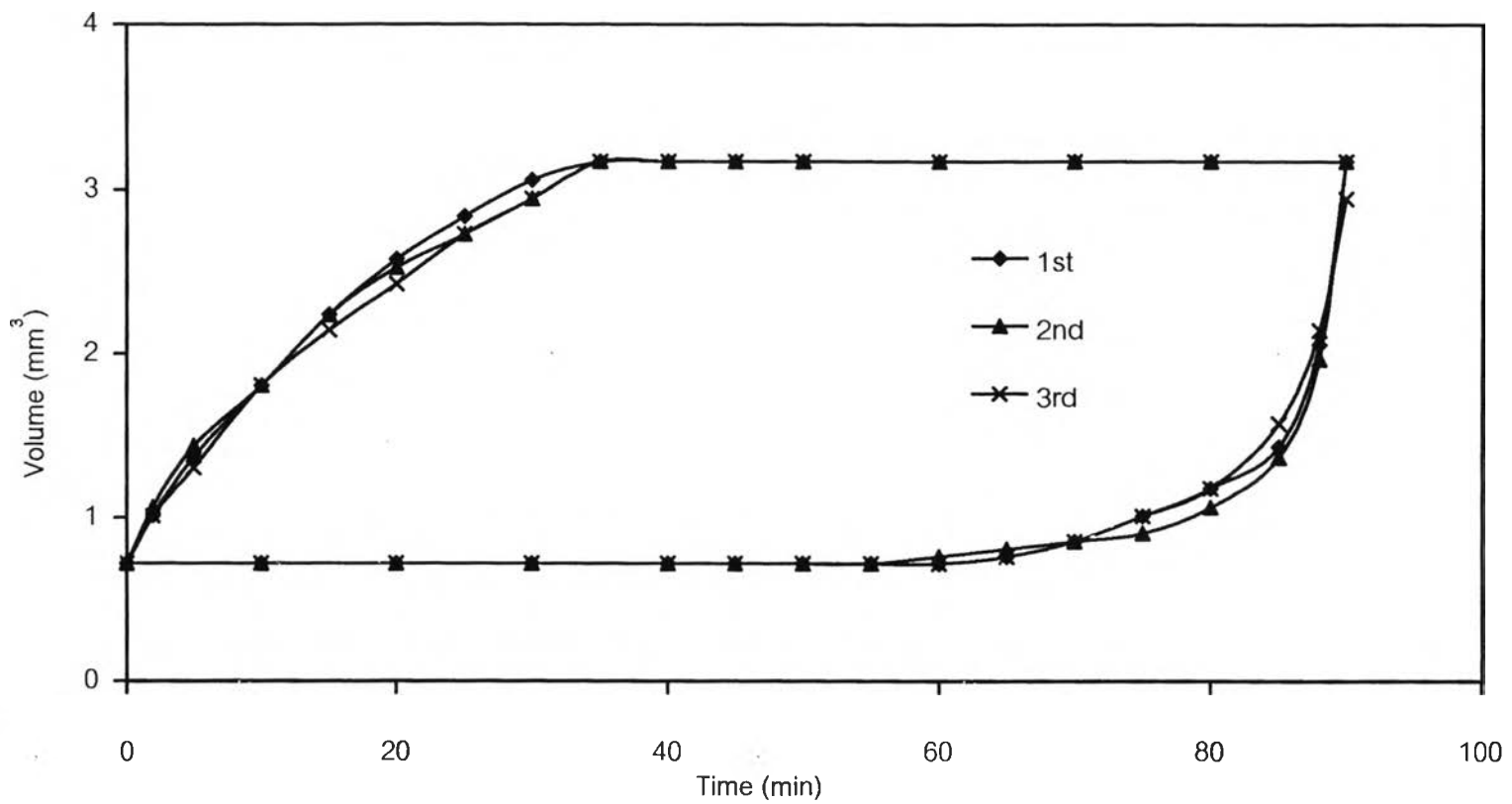
Figure 4.30 Absorption and desorption of the PMMA/PS bead by one-stage suspension polymerization with time.
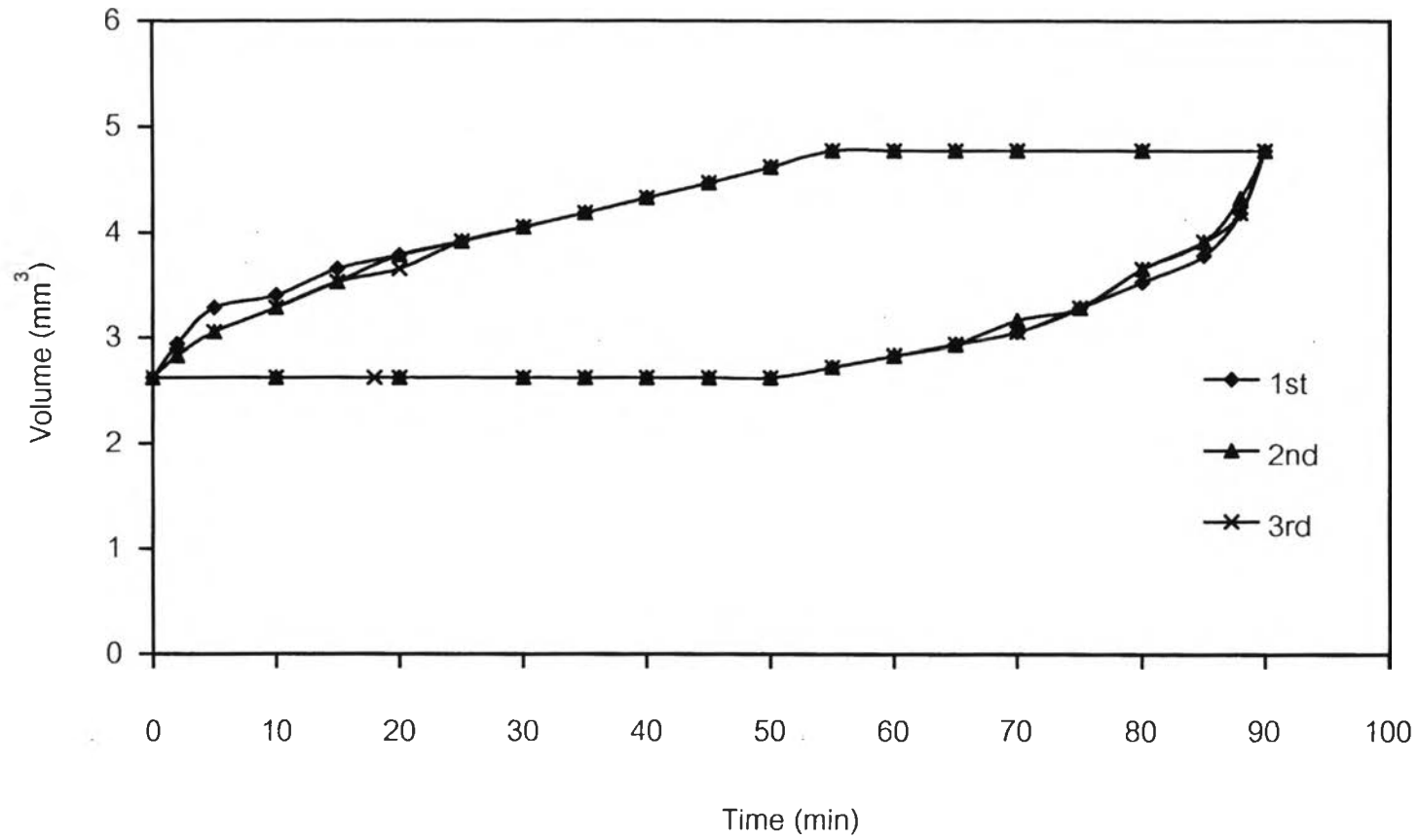
Figure 4.31 Absorption and desorption of the PMA/PS bead by seeded suspension polymerization with time.
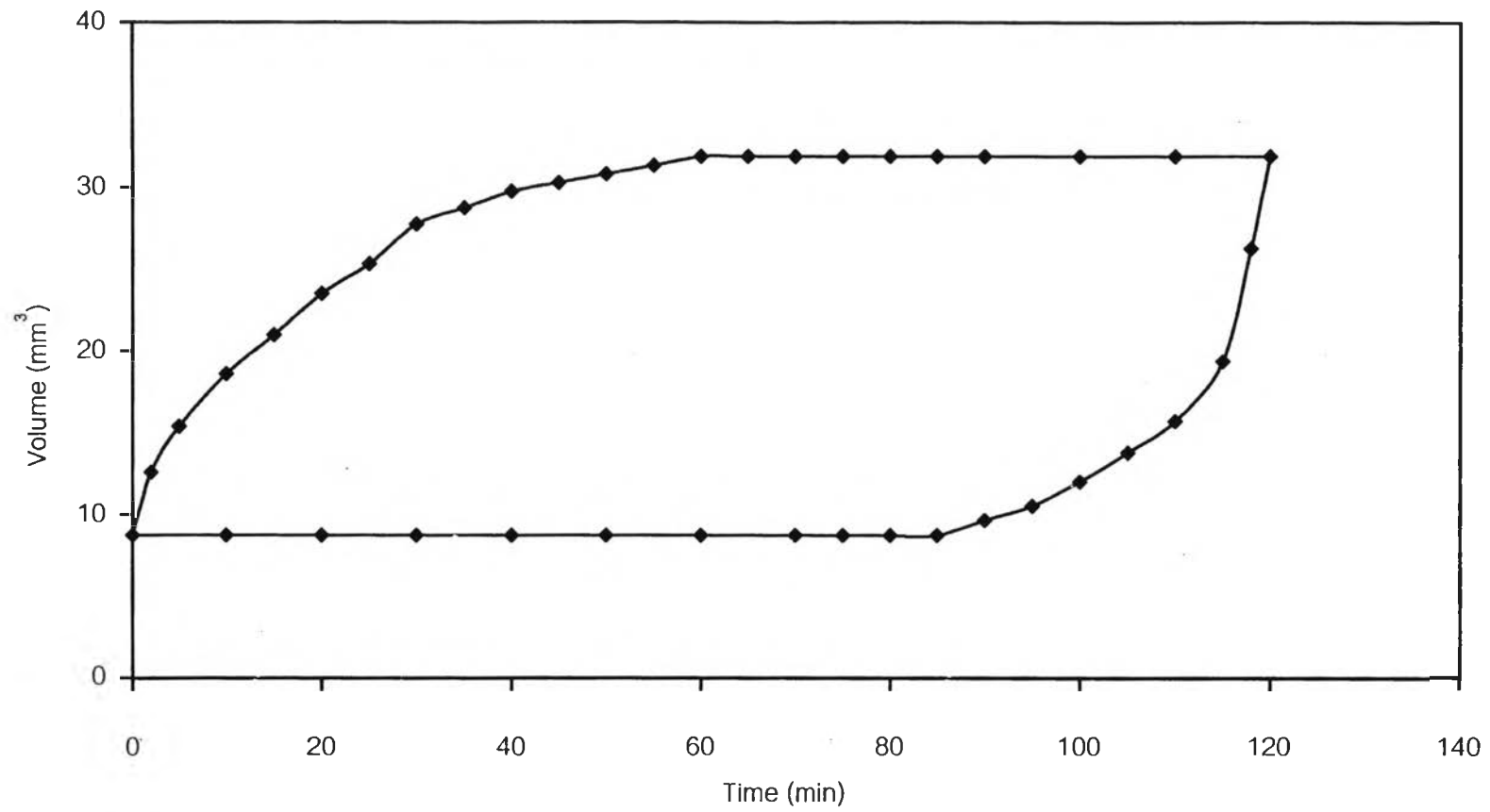
Figure 4.32 Absorption and desorption of the P(2-EHA)/PS bead by seeded suspension polymerization with time.

where Δa_t is the difference between the size (radius) at time t and that at the saturation swelling

Δa_0 is the total change in radius throughout the entire swelling process

The characteristic swelling time τ could be obtained from the slope of the ln $(\Delta a_t / \Delta a_0)$ – time plot, as shown in Appendix B.

Table 4.22 Diffusion coefficient of toluene:isooctane solvents in core/shell beads.

Runs	Diffusion Coefficient		
	1st Absorption mm^2min^{-1}	2nd Absorption mm^2min^{-1}	3rd Absorption mm^2min^{-1}
PMMA/PS	0.1737	0.1434	0.1242
PMA/PS	0.0777	0.0755	0.0711
P(2-EHA)/PS	0.7614	-	-

Table 4.22 shows the diffusion coefficient of toluene:isooctane solvents in the copolymer beads. The poly(2-ethylhexyl acrylate)/polystyrene has the higest diffusion coefficient, because it contains the long chain length of the aliphatic portion. It is noted that the chemical nature of the long chain aliphatic portion resembles that of isooctane in the mixed solvents. The diffusion coefficient of toluene:isooctane solvents in the poly(methyl methacrylate)/polystyrene is higher than in poly(methyl acrylate)/ polystyrene. The solvent absorpion of the acrylate and methacrylate polymers depends on the substituent group at the alpha-carbon atom in which a small substituent group provides higher flexibility to the chains to ease the polymer chains to absorb solvents.

4.4 Physical Properties of Swelling Ratio of Polymer Beads.

Several organic solvents of varied solubility parameters are selected to determine the approximate solubility parameter of the polymer beads.

Table 4.23 Swelling ratio of the polymer beads in various solvents

Solvents	Solubility Parameter, $(MPa)^{1/2}$				Type of Polymer Beads		
	δ_D	δ_P	δ_H	δ_T	PMMA/PS	Seeded MA	Seeded 2-EHA
i-octane	14.3	0	0	14.3	1.5	1.4	1.5
Hexane	14.9	0	0	14.9	1.5	1.4	1.5
Heptane	15.3	0	0	15.3	1.7	1.4	1.6
Cyclohexane	16.8	0	0.2	16.8	1.7	1.4	2.1
Xylene	17.8	1.0	3.1	18.0	5.3	2.0	2.7
Toluene	18.0	1.4	2.0	18.2	5.9	2.5	2.9
Benzene	18.4	0	2.0	18.6	6.6	2.5	3.0
Chloroform	17.8	3.1	5.7	19.0	6.5	7.6	5.2
Dichloromethane	18.2	6.3	6.1	20.3	5.7	6.2	4.0
1,2-Dichloroethylene	19.0	7.4	4.1	20.9	5.5	6.1	3.6
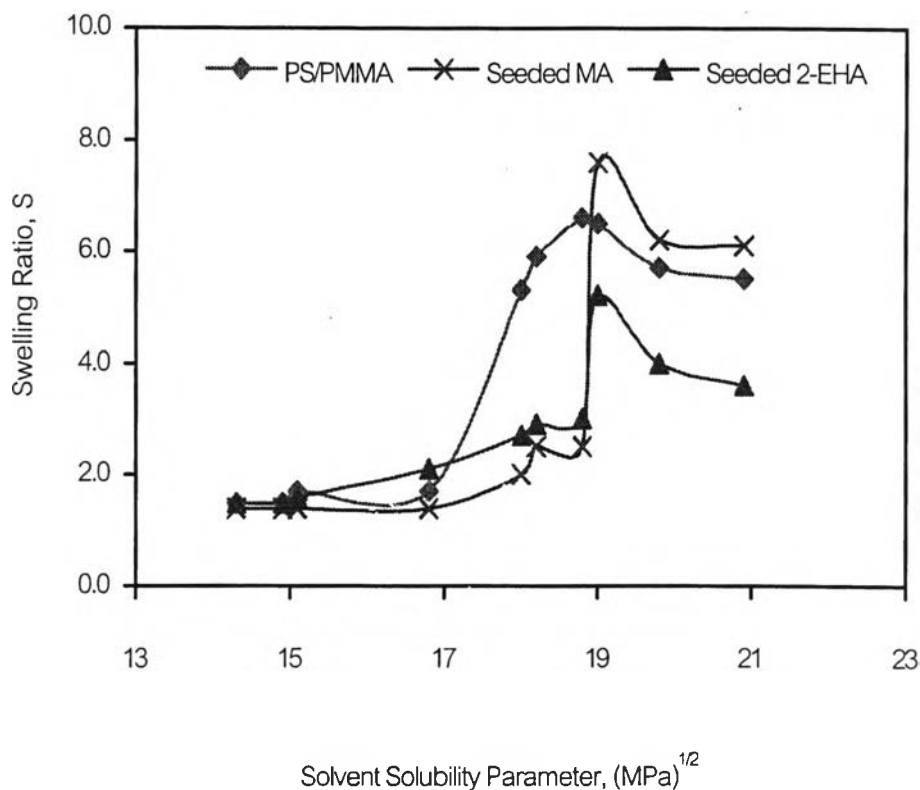
Figure 4.33 Swelling ratio of the polymer beads in various solvents.

The poly(methyl methacrylate)/polystyrene prepared by the one-stage suspension polymerization and the poly(methyl acrylate)/polystyrene prepared by seeded suspension polymerization and the poly(2-ethylhexyl acrylate)/polystyrene prepared by seeded suspension polymerization show some capacity of solvent absorption shown in Table 4.22. There are three kinds of solvent used in this study. The first kind is aliphatic hydrocarbon, namely isooctane, hexane, heptane and cyclohexane; the second one is aromatic hydrocarbon, namely xylene, toluene and benzene; the third one is halohydrocarbons, namely chloroform, dichloromethane and 1,2-dichloroethylene.

The result in Table 4.22 shows that the highest swelling ratio of the core/shell beads of poly(methyl methacrylate)/polystyrene prepared by the one-stage suspension polymerization, is 6.6 times for benzene. Additionally, the highest swelling ratio of the

core/shell beads of of poly(methyl acrylate)/polystyrene, and poly(2-ethylhexyl acrylate)/ polystyrene prepared by seeded suspension polymerization are 7.6 and 5.2 times for chloroform, respectively.

It can be seen that all core/shell beads gave the increasing swelling ratio with increasing solubility parameters of the solvents. All the beads absorbed the aromatic solvent more than the aliphatic solvent. The core/shell bead of poly(methyl methacrylate)/polystyrene prepared by the one-stage suspension polymerization had the higher swelling ratio than both of the poly(methyl acrylate)/polystyrene prepared by seeded suspension polymerization and the poly(2-ethylhexyl acrylate)/polystyrene prepared by seeded suspension polymerization. Hence, it can be concluded that the solubility parameters of the aromatic hydrocarbon solvents and polymer beads are very close (δ_T= 19.0 $(MPa)^{1/2}$). It is possible to estimated the solubility parameter of these three beads is about 19.0 $(MPa)^{1/2}$. In addition, it can be described that the limited macromolecular relaxation by crosslinks in these networks reduced the chain flexibility, resulting in a lower swelling ratio in the seeded suspension polymerization. The extent of crosslinking polymerization is the major attribute to the flexibility and relaxation of these beads.

4.5 Glass Transition Temperature of Core/Shell Beads.

In this study the glass transition temperature of core/shell beads was measured by differential scanning calorimetry. Figure 4.34 shows a DSC curve of poly(methyl methacrylate)/polystyrene bead, prepared by one stage polymerization. The curve shows that the glass transition temperature of poly(methyl methacrylate)/polystyrene was 119.4°C. This curve showing only a single point of glass transition temperature indicates that the copolymer resulting from the single-stage polymerization was compatible in every portion and polymerized together to become a one-phase polymer. We may state that the bead may not be in core/shell morphology because the glass transition temperatures of the crosslinked poly(methyl methacrylate) is 85-105°C, and that of the crosslinked polystyrene is 90-110°C. Figure 4.35 shows a DSC curve of

DSC /µV/mg

↓exo

glass transition
onset : 112.1 °C
midpt : 119.4 °C
inflpt : 120.5 °C
endpt : 126.8 °C
del cp: 1.42 mVs/(gK)

Temperature /°C

INSTRUMENT:	NETZSCH DSC 200	SAMPLE:	PMMA/PS	25.700 mg	MODE:	Dynamic
FILE:	PRANUT32.DAT	REFERENCE:	EMPTY	0.000 mg	RANGE:	-20 °C/20.0/300 °C
IDENTITY:	254	SENS-FILE:	SENSNULL.SNS		SEGM:	1/ 1
DATE/TIME:	08.06.00 15:49	CORR-FILE:			CRUC:	Pan Al, pierced lid
LABORATORY:	STREC	REMARK:			ATMOS:	N2,15;
OPERATOR:	SOPA				CORR:	000/Rg500 uV

Figure 4.34 DSC traces of crosslinked poly(methyl methacrylate)/polystyrene by one-stage suspension polymerization

Figure 4.35 DSC traces of crosslinked poly(methyl acrylate)/polystyrene by seeded suspension polymerization

DSC /µV/mg

↓ exo

glass transition
onset : 95 .3 °C
midpt : 113 .1 °C
inflpt : 110 .3 °C
endpt : 130 .9 °C
del cp: 0 .41 mVs/(gK)

glass transition
onset : - 24 .3 °C
midpt : - 21 .6 °C
inflpt : - 20 .5 °C
endpt : - 19 .0 °C
del cp: 0 .06 mVs/(gK)

Temperature /°C

INSTRUMENT:	NETZSCH DSC 200	SAMPLE:	P2-EHA/PS	20.700 mg	MODE:	Dynamic
FILE:	PRANUT22.DAT	REFERENCE:	EMPTY	0.000 mg	RANGE:	-150 °C/20.0/300 °C
IDENTITY:	252	SENS-FILE:	SENSNULL.SNS		SEGM:	1/ 1
DATE/TIME:	08.06.00 14:31	CORR-FILE:			CRUC:	Pan Al, pierced lid
LABORATORY:	STREC	REMARK:			ATMOS:	N2,15;
OPERATOR:	SOPA				CORR:	000/Rg500 uV

Figure 4.36 DSC traces of crosslinked poly(2-ethylhexyl acrylate)/polystyrene by seeded suspension polymerization

DSC /µV/mg

4.0 ↓exo

3.5

3.0

2.5

glass transition
onset : 16.3 °C
midpt : 22.6 °C
inflpt : 22.7 °C
endpt : 28.9 °C
del cp: 0.89 mVs/(gK)

2.0

1.5

1.0

-50   0   50   100

Temperature /°C

INSTRUMENT	NETZSCH DSC 200	SAMPLE:	PMA	18.100 mg	MODE:	Dynamic
FILE:	PRANUT52.DAT	REFERENCE:	EMPTY	0.000 mg	RANGE:	-100 °C/20.0/300 °C
IDENTITY:	339	SENS-FILE:	SENSNULL.SNS		SEGM:	1/ 1
DATE/TIME:	16.08.00 13:32	CORR-FILE:			CRUC:	Pan Al, pierced lid
LABORATORY:	STREC	REMARK:			ATMOS:	N2,15;
OPERATOR:	SOPA				CORR:	000/Rg500 uV
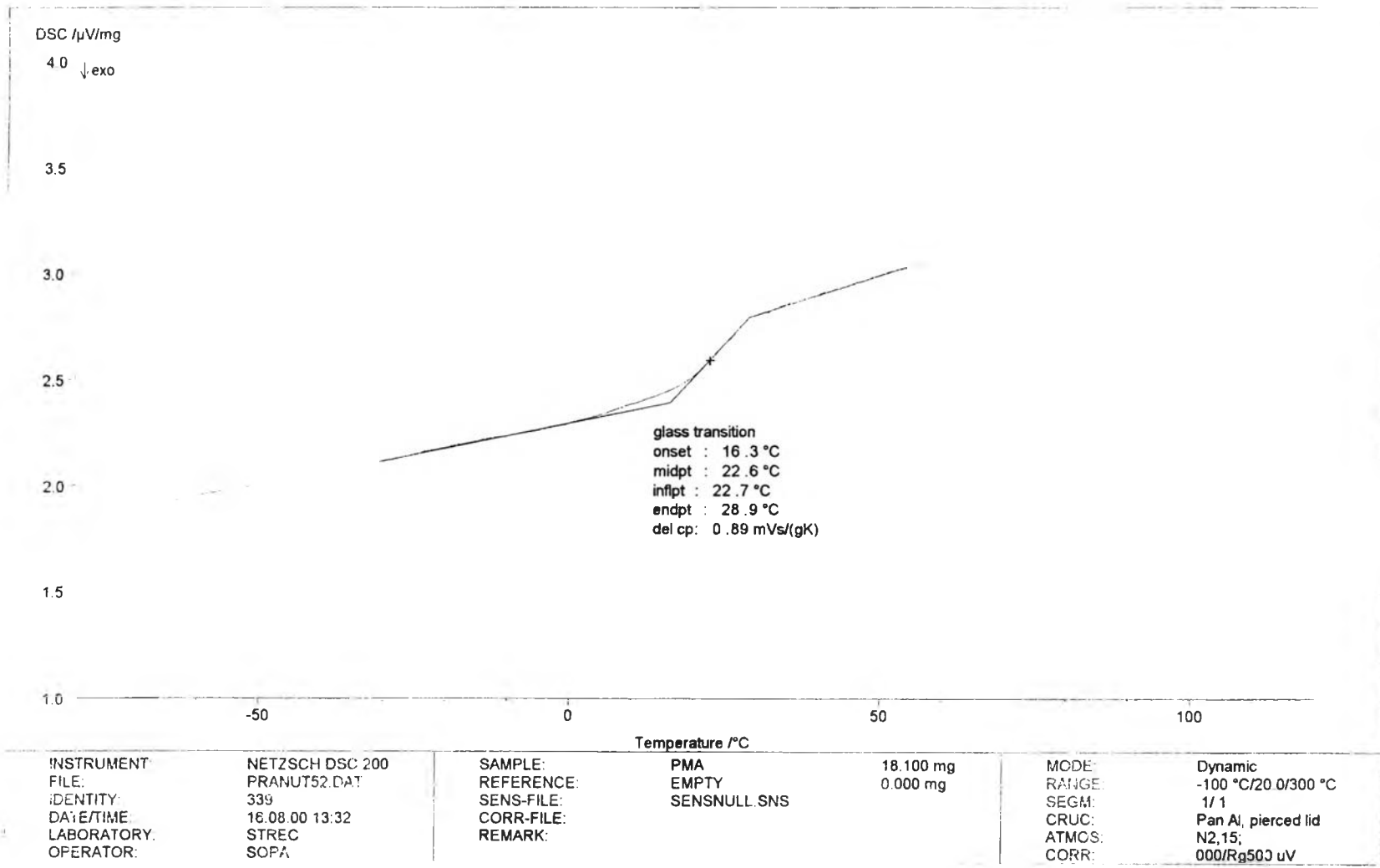
Figure 4.37 DSC traces of crosslinked poly(methyl acrylate) by suspension polymerization

DSC /μV/mg

5 ↓exo

glass transition
onset : - 66 .9 °C
midpt : - 50 .0 °C
inflpt : - 49 .4 °C
endpt : - 33 .1 °C
del cp: 1 .73 mVs/(gK)

Temperature /°C

INSTRUMENT:	NETZSCH DSC 200	SAMPLE:	P2-EHA	18.100 mg	MODE:	Dynamic
FILE:	PRANUT42.DAT	REFERENCE:	EMPTY	0.000 mg	RANGE:	-150 °C/20.0/300 °C
IDENTITY:	337	SENS-FILE:	SENSNULL.SNS		SEGM:	1/ 1
DATE/TIME:	16.08 00 11:45	CORR-FILE:			CRUC:	Pan Al, closed
LABORATORY:	STREC	REMARK:			ATMOS:	N2,15;
OPERATOR:	SOPA				CORR:	000/Rg500 uV

Figure 4.38 DSC traces of crosslinked poly(2-ethylhexyl acrylate) by suspension polymerization

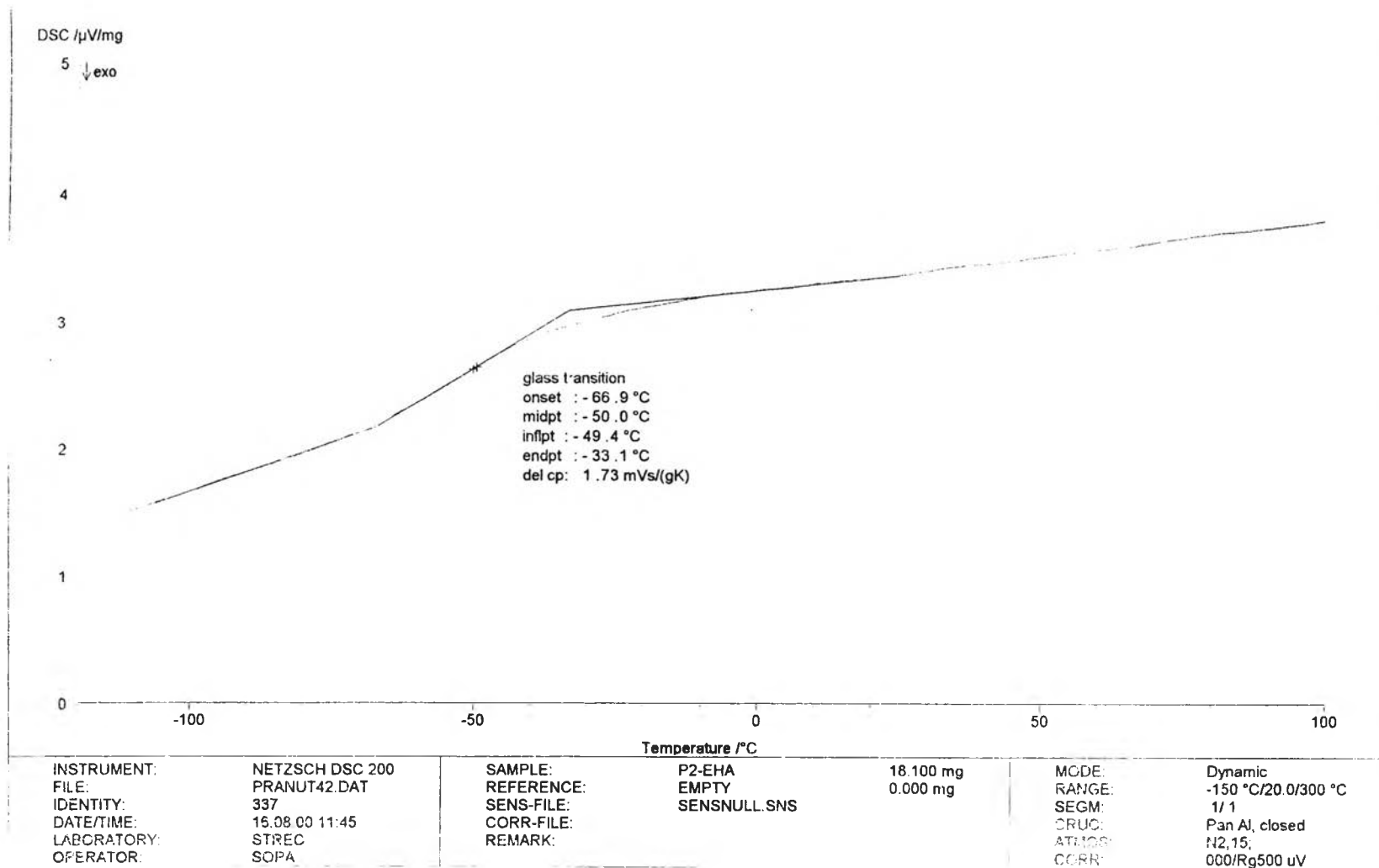core/shell bead of poly(methyl acrylate)/polystyrene, prepared by seeded suspension polymerization. The DSC shows two transitions in glass transition temperature. The higher glass transition temperature was for polystyrene at 143.4°C, and the lower glass transition temperature was the crosslinked poly(methyl acrylate) at 27.0°C, as the glass transition temperature of non-crosslinked poly(methyl acrylate) is only 10.0°C. Figure 4.36 shows a DSC curve of core/shell bead of crosslinked poly(2-ethylhexyl acrylate)/ polystyrene, prepared by seeded suspension polymerization. The DSC curve shows two transitions in the temperature profile. The higher glass transition temperature was for the crosslinked polystyrene at 113.1°C, and the lower glass transition temperature was for the crosslinked poly(2-ethylhexyl acrylate) at -21.6°C, when the glass transition temperature of non-crosslinked poly(2-ethylhexyl acrylate) is -85.0°C. [30]. Figures 4.37 - 4.38 show the DSC curves of poly(methyl acrylate) and poly (2-ethylhexyl acrylate) prepared by suspension polymerization. The curves show that the glass transition temperature of poly(methyl acrylate) and poly(2-ethylhexyl acrylate) are 22.6°C and –50.0°C, respectively.

From above results, it can be concluded that the presence of ethyleneglycol dimethacrylate, as the crosslinker in core/shell beads, had a marked effect on the higher glass transition temperature of core/shell beads. The crosslinker directly affected the glass transition temperature on the limited macromolecular relaxation that reduced chain flexibility [35].

4.6 Comparison between the One-Stage Suspension Polymerization and the Seeded Suspension Polymerization

In our research, the one-stage suspension polymerization contained the monomers, an initiator, the crosslinker and the diluent. The first step involved a production of radicals by breakdown of the initiator, which in turn reacted with monomer to form growing oligomeric chains with reactive free radicals at the end. After that the particle nuclei were formed by growth of the oligomer chains initiated in monomer solubilized in dispersant. The monomer droplets were gradually converted into

insoluble polymer particles, resulting in decreasing molar ratio of the monomers. Then, the nuclei were formed in the copolymer, which was insoluble in both the monomer and the diluent. Consequently, the phase separation occurred gradually between the crosslinked copolymer and the diluent. The copolymer rich phase became the spherical particles. The morphology of polymer beads obeyed a thermodynamically control in phase separation of polymer. The more hydrophilic polymer treads distribute preferentially in the shell, the more hydrophobic one in the core. The structure of polymer beads had homogeneous structure because all of monomer was polymerized together [36].

The seeded suspension polymerization was prepared by a series of consecutive suspension polymerization sequences with different monomer types, where the styrene monomer was polymerized in the presence of the seed particles. Mechanism of the formation was as follows: (a) the initial polymerization, styrene monomer was polymerized throughout the seed particles, (b) the polymer chain of polystyrene grew until a critical concentration of styrene monomer was reached, (c) the polystyrene in the interior of the particle stopped the polymerization reaction, while those at the surface particle polystyrene was continuous grew to form a spherical subsurface, (d) the growth of polystyrene at the subsurface stopped polymerization. On the other hand, the growth of polystyrene at the surface continued to grow until the end of polymerization. It can be concluded that the morphology of the polymer beads by seeded suspension polymerization were heterogeneous morphology [34].

4.7 Syntheses of Poly(Methyl Acrylate)/Polystyrene, Poly(2-Ethylhexyl Acrylate)/Polystyrene and Poly(2-Ethylhexyl Methacrylate)/Polystyrene by One-Stage Suspension Polymerization and Poly(Methyl Methacrylate)/ Polystyrene and Poly(2-Ethylhexyl methacrylate)/ Polystyrene by Seeded Suspension Polymerization.

The polymer beads of poly(methyl acrylate)/polystyrene were prepared by one-stage suspension polymerization. The important parameters were varied as follows: the crosslinking agent concentrations were 10.0, 15.0 and 20.0 %wt based on the monomer phase and the toluene:isooctane ratios were 100:0, 90:10, 80:20 and 70:30 %wt based on the monomer phase. The appropriate condition, which gave the spherical polymer beads, was found as follows: the suspending agent concentration was 0.5 %wt, the initiator concentration was 0.4 %wt, the crosslinking agent concentration was 15.0 %wt, the toluene:isooctane ratio was 90:10 %wt, the inhibitor concentration was 0.16 %wt, the agitation rate was 160 rpm, the polymerization temperature and time were 75°C and 10 hr, respectively. In this study, it was found that the average particle sizes were 0.71 mm and the swelling ratio was 4.4 times in toluene.

The polymer beads of poly(2-ethylhexyl acrylate)/polystyrene were prepared by one-stage suspension polymerization. The important parameters were varied as follows: the suspending agent concentrations were 0.2, 0.5, 0.7 and 1.0 %wt based on the aqueous phase, the crosslinking agent concentrations were 7.0, 15.0 and 20.0 %wt based on the monomer phase and the toluene:isooctane ratios were 100:0, 80:20, 70:30 and 60:40 %wt based on the monomer phase. The appropriate condition gave the spherical polymer beads, was found as follows: the suspending agent concentration was 0.5 %wt, the initiator concentration was 0.4 %wt, the crosslinking agent concentration was 20.0 %wt, the toluene:isooctane ratio was 70:30 %wt, the inhibitor concentration was 0.16 %wt, the agitation rate was 160 rpm, the polymerization temperature and time were 75°C and 10 hr, respectively. In this study, it was found that the average particle sizes were 1.21 mm and the swelling ratio was 3.6 times in toluene.

The polymer beads of poly(methyl acrylate)/polystyrene and poly(2-ethylhexyl acrylate)/polystyrene were extracted by cyclohexane for 24 hr. The hollow structure of the polymer beads were not found after extraction. It is assumed that there was too much crosslinking agent concentration in the feed. Therefore, it might be concluded that the morphology of poly(methyl acrylate)/polystyrene and poly(2-ethylhexyl acrylate)/polystyrene were not core/shell structure.

The polymer beads of poly(methyl methacrylate)/polystyrene were prepared by seeded suspension polymerization. The important parameters were varied as follows: the suspending agent concentrations were 0.05, 0.1, 0.2, 0.5 and 0.8 %wt based on the aqueous phase, the crosslinking agent concentrations were 1.0, 2.0, 5.0, 10.0 and 15.0 %wt based on the monomer phase, the initiator concentrations were 0.1, 0.4, 0.7 and 1.0 %wt based on the oil phase, the toluene:isooctane ratios were 100:0, 80:20, 60:40 and 50:50 %wt based on the monomer phase, the inhibitor concentrations were 0, 0.11 and 0.16 %wt based on the aqueous phase, the polymerization temperatures were $65^{\circ}C$, $75^{\circ}C$ and $85^{\circ}C$, the polymerization times were 6, 10 and 14 hr, and the agitation rates were 200, 250 and 300 rpm. The appropriate condition, which gave the spherical polymer beads was found as follows: the suspending agent concentration was 0.2 %wt, the initiator concentration was 0.4 %wt, the crosslinking agent concentration was 2.0 %wt, the toluene:isooctane ratio was 60:40 %wt, the inhibitor concentration was 0.11 %wt, the agitation rate was 250 rpm, the polymerization temperature and time were $75^{\circ}C$ and 10 hr, respectively. In this study, it was found that the average particle sizes of the seed and seeded polymers were 0.8 mm and 1.0 mm, respectively. The swelling ratios of the seed and seeded polymers were 6.4 and 4.0 times in toluene, respectively.

The cross-sectional views of the polymer beads were a homogeneous structure, so we cannot locate the part of poly(methyl methacrylate) as the core polymer and polystyrene as the shell polymer. It can be then concluded that the polymer beads of poly(methyl methacrylate)/polystyrene do not have a core/shell structure.

The polymer beads of poly(2-ethylhexyl methacrylate) were prepared by suspension polymerization. The important parameters were varied as follows: the crosslinking agent concentrations were 3.0, 5.0 and 7.0 %wt based on the monomer phase, the toluene:isooctane ratios were 100:0, 90:10 and 80:20 %wt based on the monomer phase, the suspending agent concentration was 0.2 %wt, the initiator concentration was 0.4 %wt, the inhibitor concentration was 0.11 %wt, the agitation rate was 250 rpm, the polymerization temperature and time were $75^{\circ}C$ and 10 hr, respectively.

The polymer beads of poly(2-ethylhexyl methacrylate)/polystyrene were prepared by one-stage suspension polymerization. The important parameters were varied as follows: the suspending agent concentrations were 0.5, 0.7, 1.0 and 2.0 %wt based on the aqueous phase, the crosslinking agent concentrations were 7.0, 15.0, 20.0 and 30.0 %wt based on the monomer phase and the toluene:isooctane ratios were 100:0, 90:10, 80:20 and 70:30 %wt based on the monomer phase, the initiator concentration was 0.4 %wt, the inhibitor concentration was 0.16 %wt, the agitation rate was 160 rpm, the polymerization temperature and time were $75^{\circ}C$ and 10 hr, respectively. In this study, it was found that both poly(2-ethylhexyl methacrylate), and poly (2-ethylhexyl methacrylate)/polystyrene were coagulated. The swelling ratios of poly (2-ethylhexyl methacrylate) and poly(2-ethylhexyl methacrylate)/polystyrene were 3.6 and 4.1 times in toluene, respectively. The reactivity ratios of the ethyleneglycol dimethacrylate and the styrene monomers were 0.67 and 0.39, respectively [30]. Likewise, the reactivity ratios of the styrene and the 2-ethylhexyl methacrylate monomers were 0.65 and 0.68, respectively [30]. It indicates that the ethyleneglycol dimethacrylate has the highest reactivity ratio. When the monomers were polymerized, the styrene and 2-ethylhexyl methacrylate radicals were added onto the double bonds of the ethyleneglycol dimethacrylate monomer to form the oligomer radicals. They were then grown by capture of the monomers from the monomer droplets. Consequently, the polymer particles were formed and precipitated in the aqueous phase. In this system, the toluene is a good solvent for the polystyrene, and polystyrene can dissolve in this diluent. On the other hand, the isooctane is a poor solvent, which can precipitate

poly (2-ethylhexyl methacrylate). When polymerization proceeds, the oligomers of the styrene and the 2-ethylhexyl methacrylate, which contain the free radicals, enter into the polymer particles in equimolar amounts by an alternating arrangement, because the reactivity ratio of the styrene monomer was close to that of the 2-ethylhexyl methacrylate. At the high conversion of the system, the oligomers of the styrene could not enter into the polymer particles but the oligomers of the 2-ethylhexyl methacrylate could enter. Because the glass effect, which the reaction temperature of the polymerization (75°C) was below the glass transition temperature of the polystyrene (T_g = 110°C). Therefore the polymer particles composed the rich of poly(2-ethylhexyl methacrylate) (T_g = -10°C) and the aqueous phase composed of the rich of the oligomers of the styrene. (the solubility parameters of polystyrene, poly(2-ethylhexyl methacrylate), toluene and isooctane are 18.0, 19.8, 18.2 and 14.3 $(MPa)^{1/2}$, respectively [30].