CHAPTER IV

RESULTS AND DISCUSSION

In this study, the styrene-divinylbenzene copolymers were synthesized by suspension copolymerization. The appropriate condition for synthesis of the styrene-divinylbenzene polymers was obtained by varying the polymerization parameters, such as the initiator concentration, crosslinking concentration, diluent concentration, reaction temperature, and time. Then the effects of these parameters on the swelling properties were investigated.

4.1 Effect of Monomer Phase Weight Fraction

The effects of monomer phase weight fraction on the average particle size, size distribution and swelling properties were investigated by varying the monomer phase weight fraction of 0.06, 0.08, 0.10, and 0.17, respectively. The other parameters were kept constant as follows:

- amount of styrene and divinylbenzene monomer (94 : 6) : 100 %wt
- initiator concentration : 0.5 %wt
- suspending agent concentration : 0.1 %wt
- reaction temperature : 70 °C
- reaction time : 10 hours
- agitation rate : 270 rpm
- Toluene : Heptane : 100 : 0

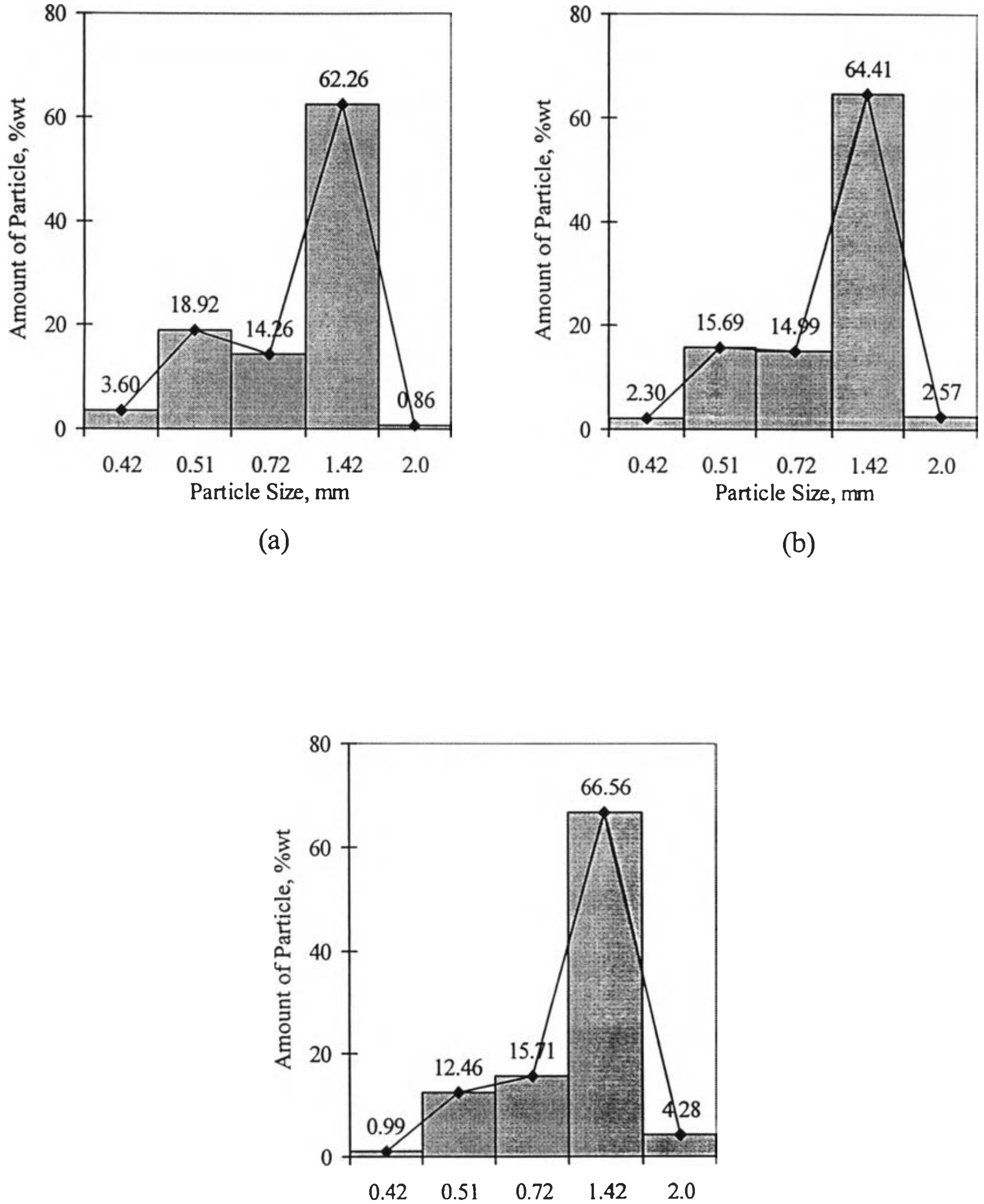
Weight fraction of the monomer phase is one of the unique characteristics of suspension polymerization, as it is the center of the reaction site in terms of concentration and stability of the oleophilic phase. Table 4.1 shows the effect of monomer phase weight fraction on the average particle size and their distribution.

Table 4.1 Effect of monomer phase weight fraction on the particle size and size distribution of styrene-divinylbenzene copolymer beads

Runs	%Conv	Particle Size Distribution					Ave. Size (mm)
		<0.42	0.42-0.59	0.59-0.84	0.84-2.0	>2.0	
M06	48	3.60	18.92	14.26	62.26	0.86	1.12
M08	50	2.30	15.69	14.99	64.41	2.57	1.16
M10	51	0.99	12.46	15.71	66.56	4.28	1.21
M17	44	-	-	-	-	-	coalesced

From Table 4.1 and Figure 4.1 upon changing the monomer phase weight fraction from 0.06, 0.08, 0.10, and 0.17, respectively, it was found that increasing the weight fraction of the dispersed phase, the average particle size increases and their distribution shift towards the large particle size. Using the monomer phase weight fraction more than 0.10, a critical point, the polymer product was coalesced as in the Run M17.

One possible explanation for the coagulated polymer may be due to the increase of the monomer ratio inside the reaction vessel, a large number of monomer droplets were generated and distributed throughout the system, while the liquid medium responsible for the heat transfer was reduced. Water is a good medium for



(a)

(b)

(c)

Figure 4.1 Bead size distribution of styrene-divinylbenzene copolymer beads under the effect of monomer phase weight fractions: (a) 0.06, (b) 0.08, and (c) 0.10.

removing heat from polymerizing droplets because it has both a high heat capacity and a high thermal conductivity. These caused the heat inside the vessel gradually accumulated to the point at which the droplets melt and agglomerate onto the propeller of the mixing shaft [28].

Table 4.2 Effect of monomer phase weight fraction on swelling properties of styrene-divinylbenzene copolymer beads

Runs	Monomer Phase Weight Fraction	$\overline{M}_c$	Crosslinking Density	Swelling Ratio
M06	0.06	11900	7.4	6.4
M08	0.08	12000	7.3	6.4
M10	0.10	12300	7.1	6.5
M17	0.17	12300	7.1	6.5

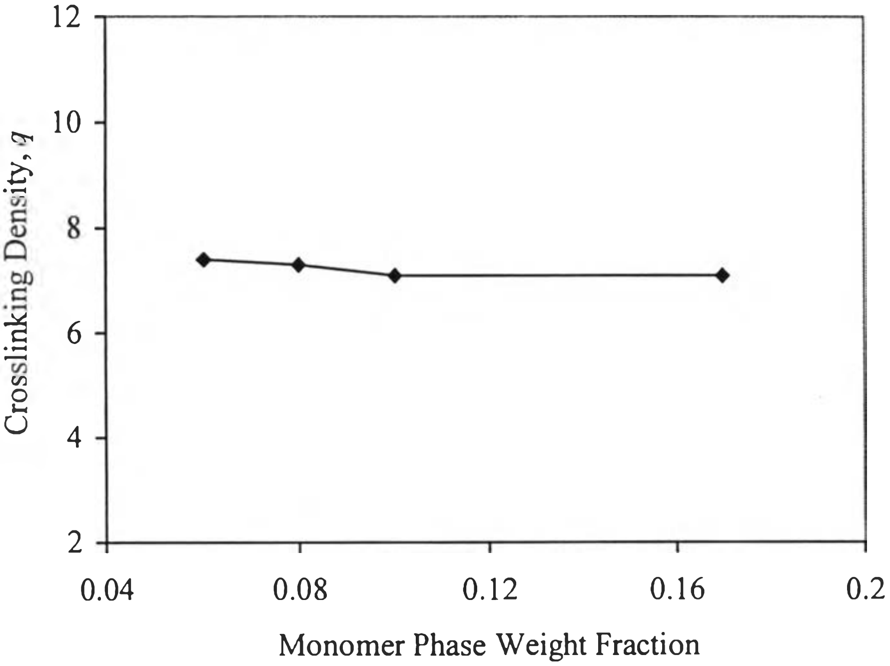


Figure 4.2 Effect of monomer phase weight fraction on the crosslinking density.

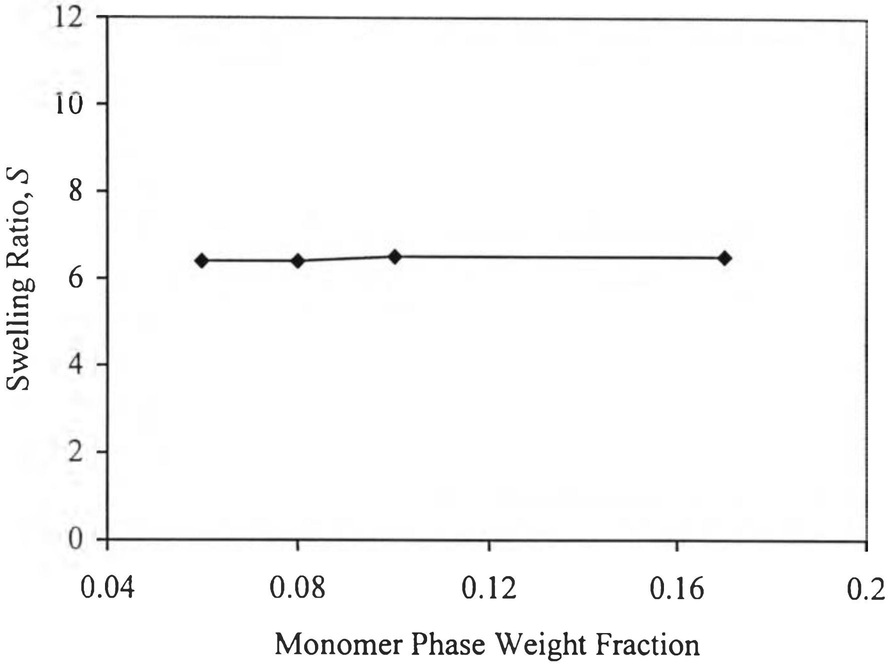


Figure 4.3 Effect of monomer phase weight fraction on the swelling ratio.

Table 4.2, Figures 4.2 – 4.3 show that varying monomer phase weight fraction from 0.06-0.17, the crosslinking density and swelling ratios of copolymers were not significantly different when the monomer phase weight fraction was increased. So these results indicated that the monomer phase weight fraction had no significant influence on the crosslinking density and swelling ratio.

4.2 Effect of Agitation Rate

The effects of agitation rate on the particle size, size distribution and swelling properties were investigated by varying the agitation rate at 200, 270, and 300 rpm. The other parameters were kept constant as follows:

- amount of styrene and divinylbenzene monomer (94 : 6) : 100 %wt
- initiator concentration : 0.5 %wt
- suspending agent concentration : 0.1 %wt
- reaction temperature : 70 °C
- reaction time : 10 hours
- monomer phase weight fraction : 0.1
- Toluene : Heptane : 100 : 0

The course of suspension polymerization and properties of the copolymer are controlled by the characteristic and intensity of stirring; this affects the average particle size and size distribution of the particles. The rate and duration of stirring enable the monomer dispersion to form specific monomer droplets. After the completion of stirring, the particles (in the absence of the stabilizer) rapidly associate into a separating oil phase. Addition of the stabilizer suppresses association of the particles and lowers the rate of the coalescence. The size of the final polymer particles depends on the size of the monomer droplets formed by dispersing the oil phase in water in the presence of the stabilizer [29].

Table 4.4 shows that increasing the rate of agitation from 200 to 270, and 300 rpm, the average particle size decreases from 1.49, 1.21, and 0.97, respectively, and their distribution shifts towards the small particle size as shown in Figure 4.4. It can be explained that an increase of agitation rate leads to increase shearing force which can disperse the oil phase to form the small droplet sizes.

Suspension polymerization uses an aqueous phase where the immiscible monomer or monomers are dispersed by agitation. If the agitation is stopped, the phases often become less dense which can rise to the top of the reactor [29].

Table 4.3 Effect of agitation rate on the particle size and size distribution of styrene-divinylbenzene copolymer beads

Runs	%Conv	Particle Size Distribution					Ave. Size (mm)
		<0.42	0.42-0.59	0.59-0.84	0.84-2.0	>2.0	
R20	50	1.08	2.64	21.43	31.27	43.58	1.49
R27	51	0.99	12.46	15.71	66.56	4.28	1.21
R30	42	5.31	27.25	21.08	46.36	-	0.97

The effect of agitation rate on the crosslinking density and swelling properties was shown in Table 4.4 and Figures 4.5 – 4.6. It was found that the swelling ratio increases slightly from 6.4 to 6.5, and 7.0 with the increasing rate of agitation from 200 to 270, and 300 rpm, respectively. Increasing the agitation rate, a larger number of smaller particles are generated. The polymer chains inside the small beads are more flexible leading to the decrease in crosslinking density, regardless of their larger surface area and resemble density. These results also led to a slight increase in the swelling ratio.

Table 4.4 Effect of agitation rate on swelling properties of styrene-divinylbenzene copolymer beads

Runs	Agitation Rate, rpm	$\overline{M}_c$	Crosslinking Density	Swelling Ratio
R20	200	12000	7.3	6.4
R27	270	12300	7.1	6.5
R30	300	14800	6.0	7.0

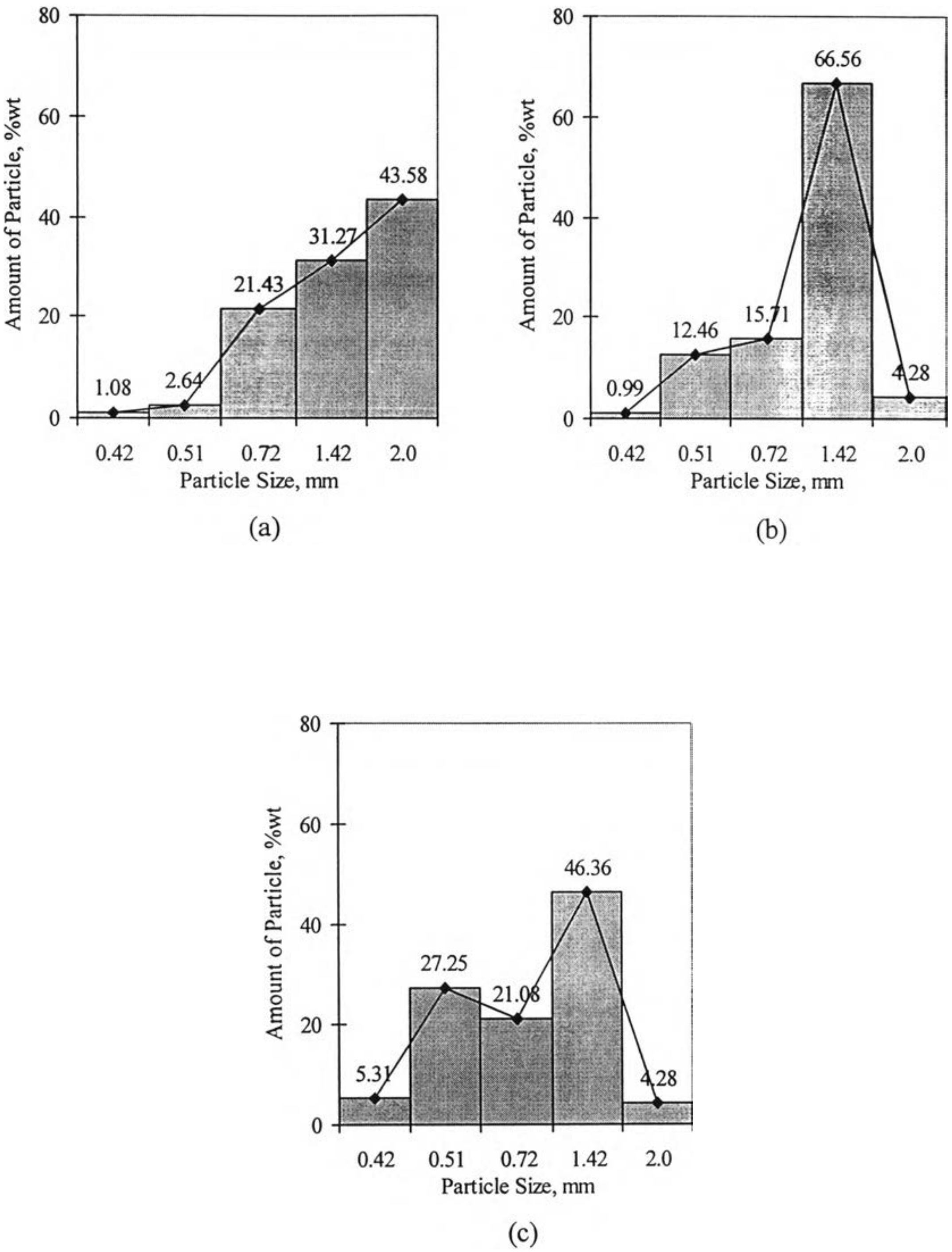


Figure 4.4 Bead size distribution of styrene-divinylbenzene copolymer beads under the effect of agitation rates: (a) 200 rpm, (b) 270 rpm, and (c) 300 rpm.

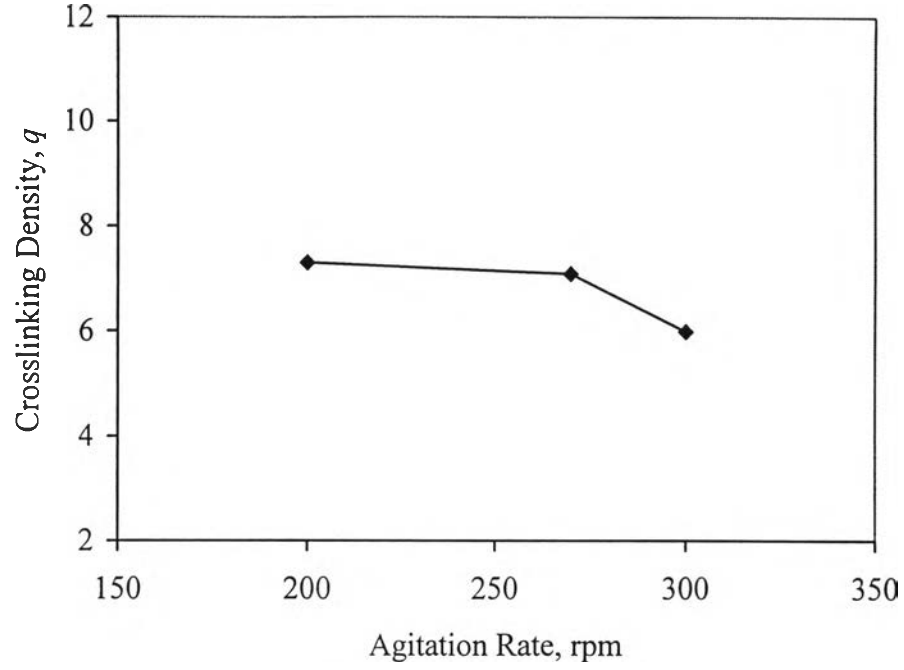


Figure 4.5 Effect of agitation rate on the crosslinking density.

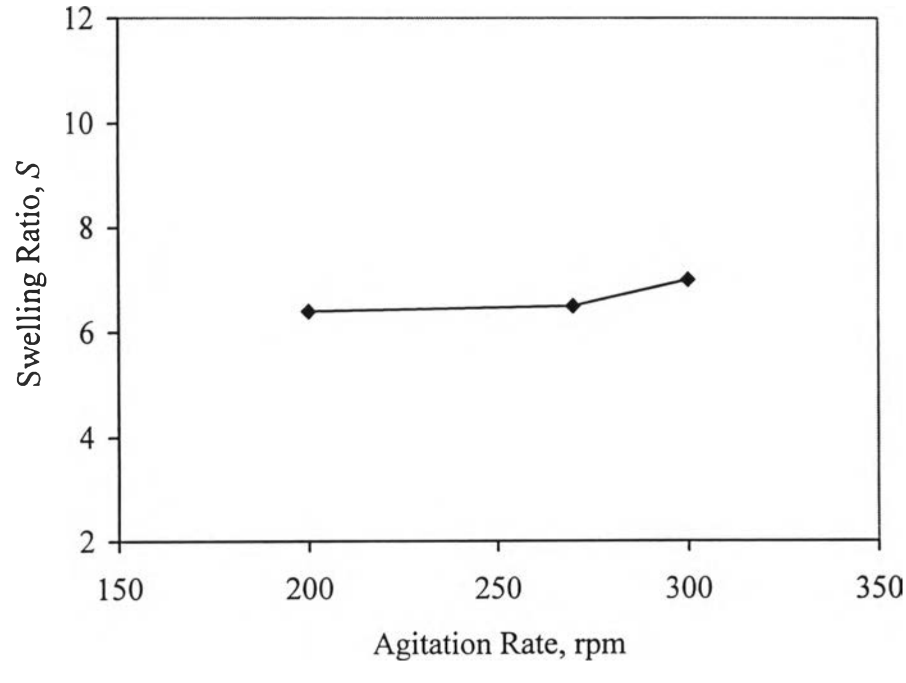


Figure 4.6 Effect of agitation rate on the swelling ratio.

4.3 Effect of Reaction Temperature

The effects of reaction temperature on the particle size, size distribution and swelling properties were investigated by varying the reaction temperature of 60, 70, and 80 °C. The other parameters were kept constant as follows:

- amount of styrene and divinylbenzene monomer (94 : 6) : 100 %wt

- initiator concentration	:	0.5 %wt
- suspending agent concentration	:	0.1 %wt
- reaction time	:	10 hours
- agitation rate	:	270 rpm
- monomer phase weight fraction	:	0.1
- Toluene : Heptane	:	100 : 0

When increasing the reaction temperature of a radical chain copolymerization, the decomposition rate of the initiator to produce a large amount of free radicals that can initiate to give many polymer radicals. It results in an increased overall conversion as shown in Table 4.5.

Table 4.5 and Figure 4.7 indicated that the effect of reaction temperature on the average particle size and size distribution. At 60 °C, the polymer particles were very soft and sticky. Then they were dried, the beads were clustered and stuck to a big fused mass (no bead formation). When the reaction temperature of the reaction increased from 70 °C to 80 °C, the average particle sizes were constant from 1.21 mm to 1.24 mm, respectively. It is probably due to that the reaction temperature is also another important parameter controlling the formation of particle. Basically, reaction temperature involves both thermodynamic and kinetic aspects of chain polymerization [30]. On the thermodynamic aspect, increasing the temperature will increase the magnitudes of ΔH and ΔS, i.e., both are possible as more heat is given. The reaction will therefore, spontaneously proceed and more copolymer will be produced. Solubility of the copolymer is enhanced at higher temperatures until the copolymer has precipitated out.

Table 4.5 Effect of reaction temperature on the particle size and size distribution of styrene-divinylbenzene copolymer beads

Runs	% Conv	Particle Size Distribution					Ave. Size (mm)
		<0.42	0.42-0.59	0.59-0.84	0.84-2.0	>2.0	
T60	34	-	-	-	-	-	fused
T70	51	0.99	12.46	15.71	66.56	4.28	1.21
T80	72	4.51	10.68	16.99	53.92	13.90	1.24

The effects of the reaction temperature on the crosslinking density, and swelling ratio of Sty-DVB copolymers are shown in Table 4.6 and Figures 4.8 – 4.9. The details of all data and calculations are shown in Appendices C, and D, respectively. As shown in Figure 4.8, it is found that crosslinking density steadily increases with increased temperature due to increases in both the decomposition rate constant of the initiator (k_d) and the propagation rate constant of the monomer (k_p), these could therefore lead to an increase in the crosslinking sites inside the beads. Increasing the crosslinking sites, chain mobility inside the beads was restricted or decreased, it causes the chain less flexible and thus an decrease in the swelling ratio as shown in Figure 4.9.

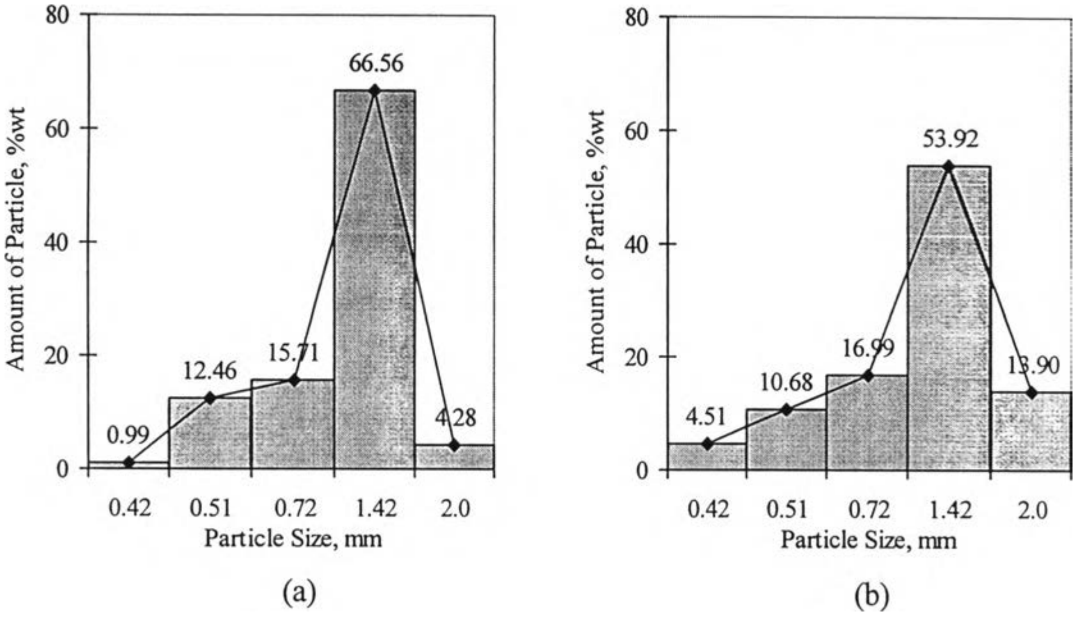


Figure 4.7 Bead size distribution of styrene-divinylbenzene copolymer beads under the effect of reaction temperatures: (a) 70 °C, and (b) 80 °C.

Table 4.6 Effect of reaction temperature on swelling properties of styrene-divinylbenzene copolymer beads

Runs	Temperature, °C	$\overline{M}_c$	Crosslinking Density	Swelling Ratio
T60	60	14900	5.9	7.1
T70	70	12300	7.1	6.5
T80	80	10600	8.3	6.1

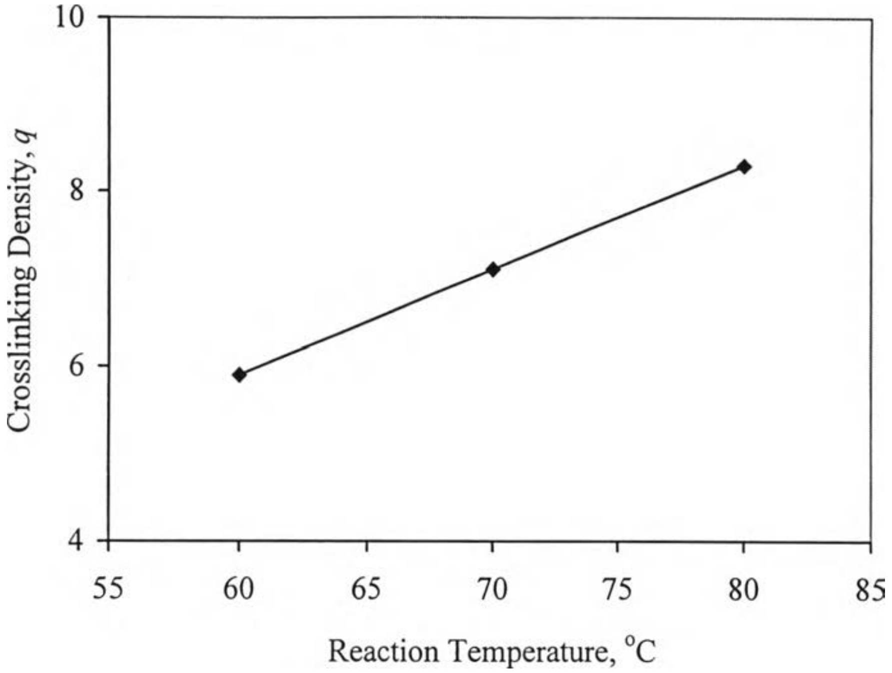


Figure 4.8 Effect of reaction temperature on the crosslinking density.

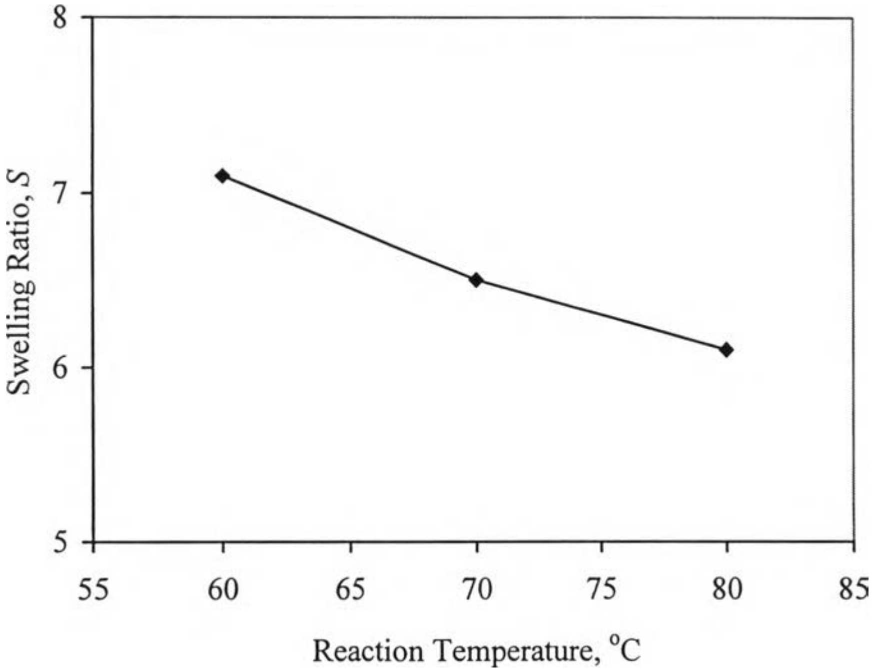


Figure 4.9 Effect of reaction temperature on the swelling ratio.

4.4 Effect of Reaction Time

The effects of initiator concentration on the particle size, size distribution and swelling properties were investigated by varying the reaction time of 6, 8, 10, and 15 hours. The other parameters were kept constant as follows:

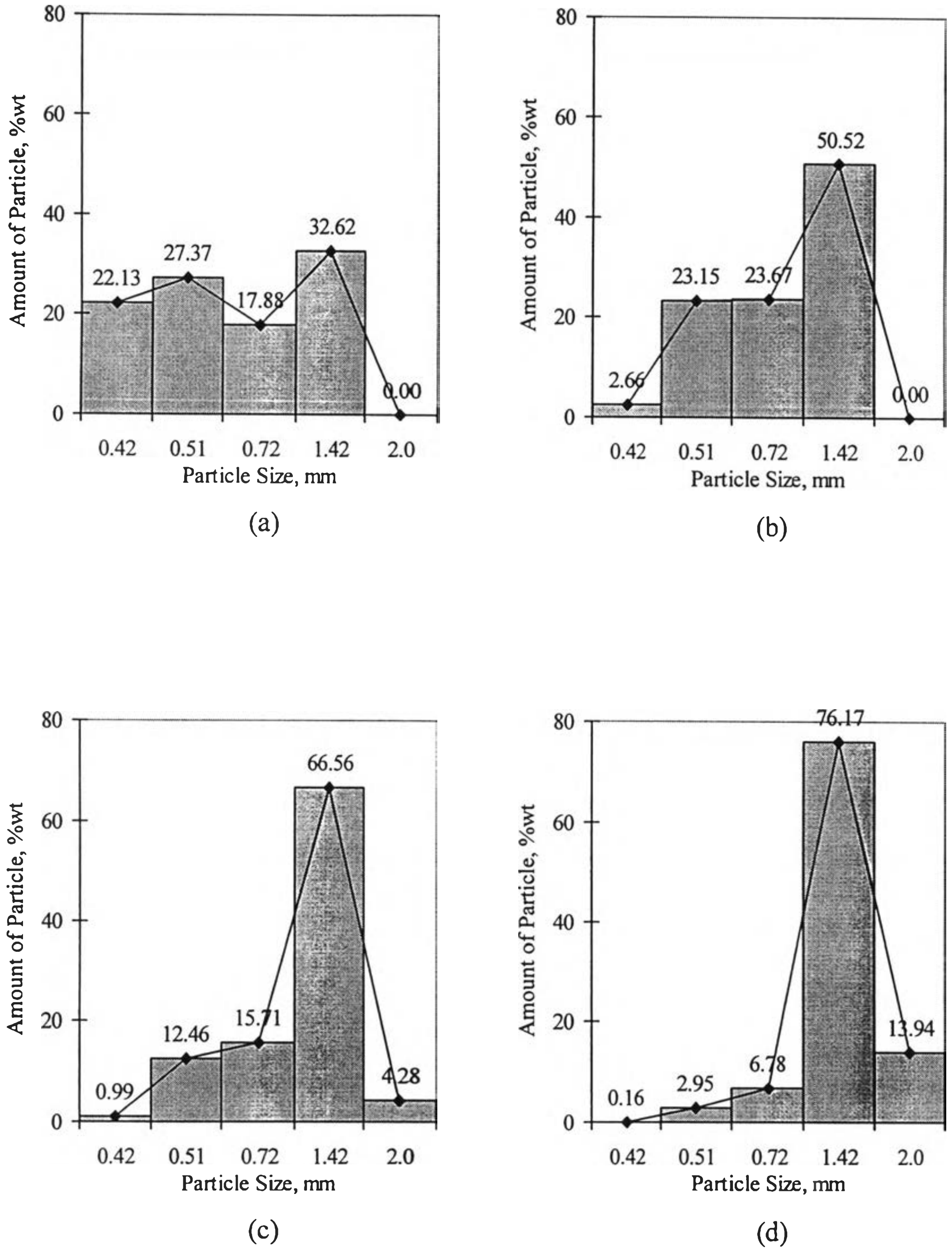
- amount of styrene and divinylbenzene monomer (94 : 6) : 100 %wt
- initiator concentration : 0.5 %wt
- suspending agent concentration : 1.0 %wt
- reaction temperature : 70 °C
- agitation rate : 270 rpm
- monomer phase weight fraction : 0.1
- Toluene : Heptane : 100 : 0

Table 4.7 shows that the polymerization time increases from 6, 8, 10, and 15 hours, respectively, the conversion increases from 24, 39, 51, and 74 %, respectively due to that the monomer was increasingly converted to the polymer. At 6 hours with a conversion of about 20 %, the copolymer particles were clustered and stuck to a big fused mass when dried. The average particle size increased with increasing the polymerization time, which particle size distribution is shown in Figure 4.10. The increased particle size at higher polymerization times due to that the microspheres were aggregated from the larger particles.

Table 4.7 Effect of reaction time on the particle size and size distribution of styrene-divinylbenzene copolymer beads

Runs	%Conv	Particle Size Distribution					Ave. Size (mm)
		<0.42	0.42-0.59	0.59-0.84	0.84-2.0	>2.0	
t06	24	22.13	27.37	17.88	32.62	-	0.82
t08	39	2.66	23.15	23.67	50.52	-	1.02
t10	51	0.99	12.46	15.71	66.56	4.28	1.21
t15	74	0.16	2.95	6.78	76.17	13.94	1.42

Table 4.8 indicates the crosslinking density and swelling ratio of Sty-DVB copolymers prepared by varying the polymerization time of 6 to 15 hours. The crosslinking density of the copolymer increases with increasing conversion with respect to the longer reaction time, as shown in Figure 4.11. On the other hand, the decreasing swelling ratio of the copolymer depends on the polymerization time, as shown in Figure 4.12, due to the increasing crosslinking density. Since the polymerization process takes a long time to reach higher conversion, the polymer chains are more entangled and the second double bonds or vinyl groups of DVB were the crosslinking sites [31]. When increasing the crosslinking sites, chain mobility inside the beads is restricted or decreased, it causes a decrease in the swelling ratio. These results also led to decreasing the diffusion coefficient of the copolymer, as shown in Table 4.8.



(a)

(b)

(c)

(d)

Figure 4.10 Bead size distribution of styrene-divinylbenzene copolymer beads under the effect of reaction times: (a) 6 h., (b) 8 h., (c) 10 h., and (d) 15 h.

Table 4.8 Effect of reaction time on swelling properties of styrene-divinylbenzene copolymer beads

Runs	Reaction Time, hours	$\overline{M}_c$	Crosslinking Density	Swelling Ratio	Diffusion Coefficient, cm^2/sec
t06	6	28900	2.8	9.7	2.60×10^{-5}
t08	8	18400	4.6	7.8	2.34×10^{-5}
t10	10	12300	7.1	6.5	2.13×10^{-5}
t15	15	9200	9.6	5.8	1.52×10^{-5}

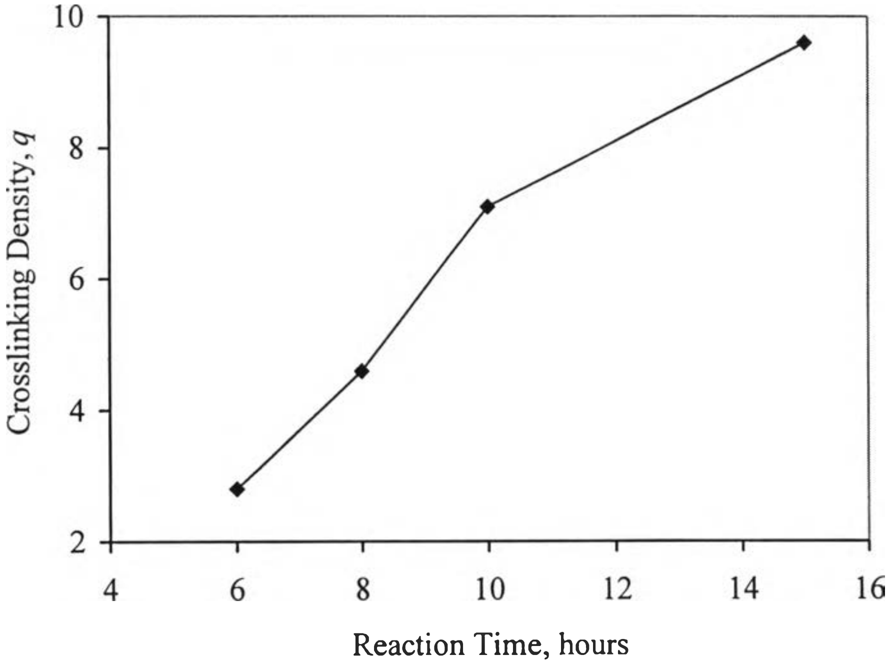


Figure 4.11 Effect of reaction time on the crosslinking density.

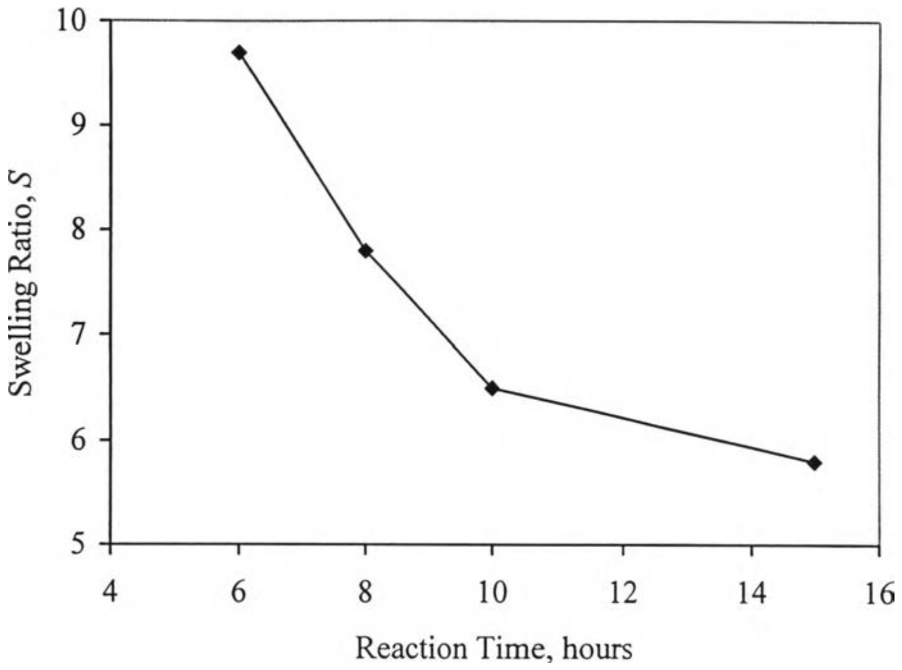


Figure 4.12 Effect of reaction time on the swelling ratio.

4.5 Effect of Initiator Concentration

The effects of initiator concentration on the particle size, size distribution and swelling properties were investigated by varying the initiator concentration of 0.1, 0.5, 1.0, and 2.0 %wt based on monomer phase. The other parameters were kept constant as follows:

- amount of styrene and divinylbenzene monomer (94 : 6) : 100 %wt
- suspending agent concentration : 0.1 %wt
- reaction temperature : 70 °C
- reaction time : 10 hours
- agitation rate : 270 rpm
- monomer phase weight fraction : 0.1
- Toluene : Heptane : 100 : 0

Table 4.9 shows the over all conversion, the average particle size and size distribution in relation to benzoyl peroxide concentration, as an initiator of these polymerization system. It was shown that the initiator concentration of the initial increase from %BPO: 0.1, 0.5, 1.0, and 2.0, respectively; based on monomer phase, the conversion increases due to more initiator radicals formed in the initiation step [30].

Table 4.9 Effect of initiator concentration on the particle size and size distribution of styrene-divinylbenzene copolymer beads

Runs	%Conv	Particle Size Distribution					Ave. Size (mm)
		<0.42	0.42-0.59	0.59-0.84	0.84-2.0	>2.0	
I01	19	0.51	13.70	27.11	58.68	-	1.10
I05	51	0.99	12.46	15.71	66.56	4.28	1.21
I10	58	1.05	8.93	17.89	67.77	4.36	1.23
I20	70	1.08	9.47	11.49	74.12	3.84	1.26

The average size and size distribution of the copolymer beads obtained as shown in Table 4.9 and Figure 4.13. It shows that the particle size increases from 1.10 to 1.26 mm. When the initiator increases from 0.1 to 2.0 %wt based on monomer phase. This has been related to the kinetic length of the polymers. The increase in benzoyl peroxide concentration at the beginning induced a great number of short kinetic chain length to result in a relatively large number of low molecular weight beads [30].

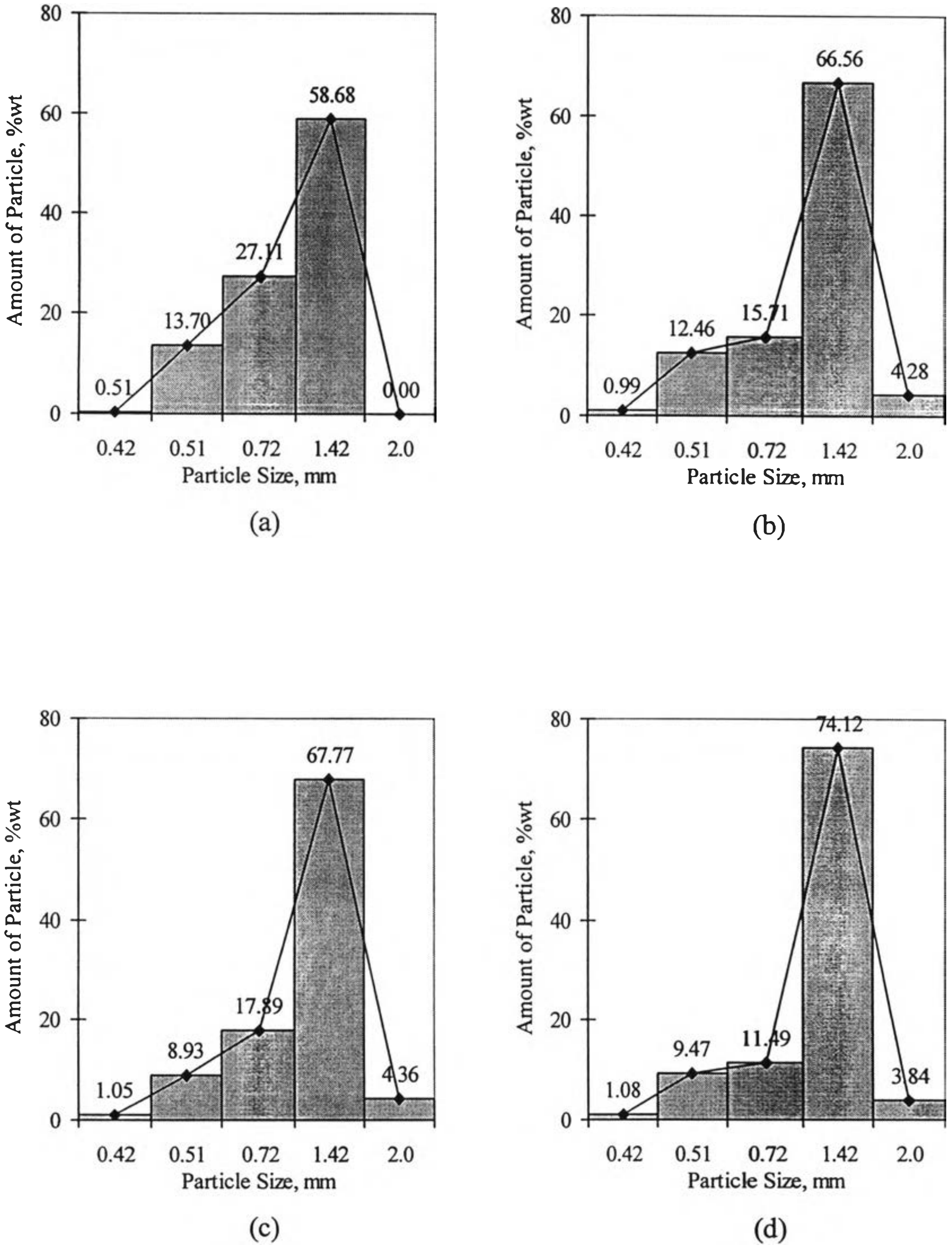


Figure 4.13 Bead size distribution of styrene-divinylbenzene copolymer beads under the effect of initiator concentrations: (a) 0.1, (b) 0.5, (c) 1.0, and (d) 2.0 BPO% based on monomer phase.

The crosslinking density and swelling ratio of the copolymer beads prepared by varying BPO concentration range of 0.1 to 2.0 % based on monomer phase as shown in Table 4.10 and Figures 4.14 – 4.15. The rate of producing primary radicals is increased when the initiator concentration increases. The crosslinking density increases due to the DVB is consumed more readily than is styrene to form radicals because it has higher reactivity than styrene. This results suggest that the increase of BPO concentration produced the increasing crosslinking sites in the polymer network, the copolymer beads are less flexible leading to the decrease in swelling ratio.

Table 4.10 Effect of initiator concentration on swelling properties of styrene-divinylbenzene copolymer beads

Runs	Initiator Concentration, %wt	$\overline{M}_c$	Crosslinking Density	Swelling Ratio
I01	0.1	30400	2.9	9.6
I05	0.5	12300	7.1	6.5
I10	1.0	10900	8.1	6.2
I20	2.0	9800	9.0	5.9

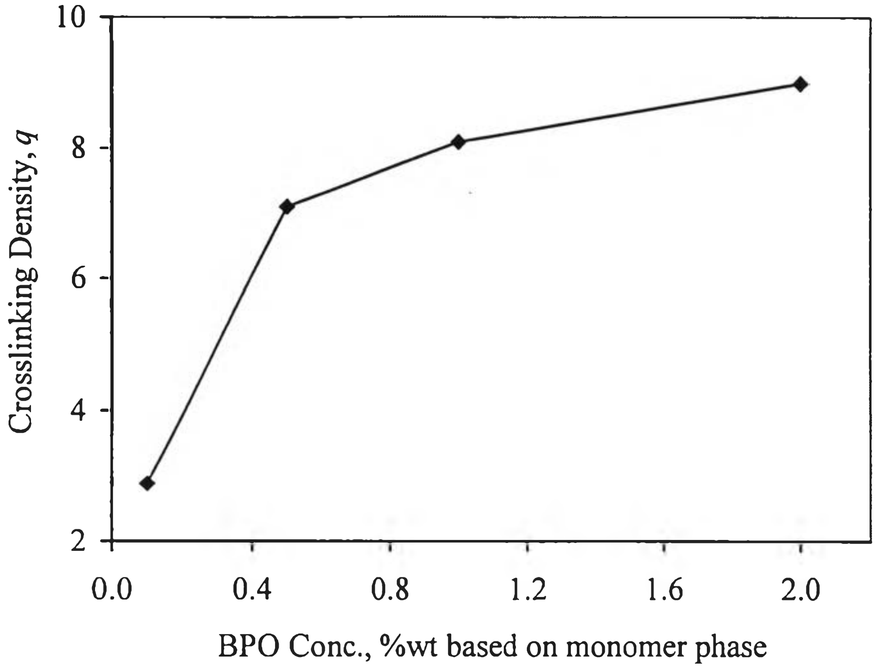


Figure 4.14 Effect of initiator concentration on the crosslinking density.

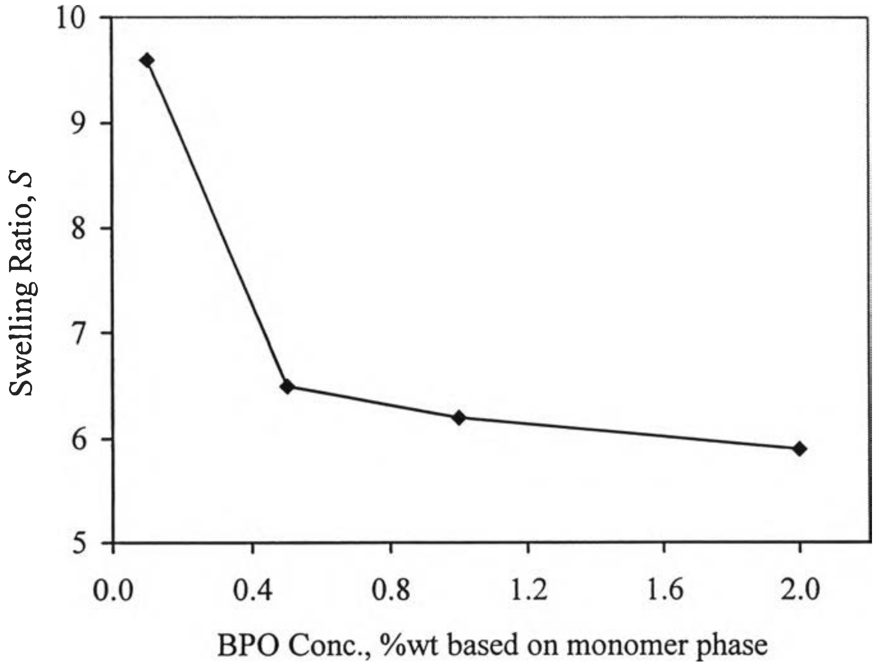


Figure 4.15 Effect of initiator concentration on the swelling ratio.

4.6 Effect of Crosslinking Agent Concentration

The effects of crosslinking agent concentration on the particle size, size distribution and swelling properties were investigated by varying the crosslinking agent concentrations of 3.0, 6.0, 9.0, 12.0, and 15.0 %wt based on monomer phase. The other parameters were kept constant as follows:

- initiator concentration : 0.5 %wt
- suspending agent concentration : 0.1 %wt
- reaction temperature : 70 °C
- reaction time : 10 hours
- agitation rate : 270 rpm
- monomer phase weight fraction : 0.1
- Toluene : Heptane : 100 : 0

To confirm the copolymerization between styrene and divinylbenzene, the functional groups and crosslinking site of divinylbenzene were investigated by FT-IR. The IR spectra of the styrene networks in KBr pellets were recorded on a Perkin-Elmer FT-IR Spectrometer 1760. The existence of the copolymer was analyzed by comparing the copolymer spectrum with the reference peak of the standard polystyrene, as shown in Appendix E. (Figures E-1 and E-2). Figures E-1 and E-2 shows that IR spectrum of both the polystyrene and the synthesized copolymer are rather similar, the assignments of the important peaks are shown in Table 4.11 [36].

Table 4.11 Important peak of the styrene-divinylbenzene copolymers beads

Wave Number, cm^{-1}	Peak Assignment
3080 – 3010	=C–H stretching (aromatic)
2960 – 2850	C–H stretching CH_3 and CH_2 (aliphatic)
2000 – 1667	Monosubstituted aromatic ring
1660 – 1640	C=C stretching (vinyl terminal)
770 – 730	Monosubstituted aromatic ring

From the IR spectrum, we found that the IR spectrum of the synthetic beads (Figure E-1) shows the peaks of *para-*, *meta-*disubstituted aromatic ring, the crosslinking bond of divinylbenzene, at 860-800 cm^{-1} and 810-750 cm^{-1}, respectively. As the result, the IR spectrum of both the synthetic beads and the polystyrene can be discriminated from each other in this region. Figure E-2 cannot show the peaks of *para-*, *meta-*disubstituted aromatic ring due to its non-crosslinking nature.

Table 4.12 shows the overall conversion, the average particle size and size distribution in relation to divinylbenzene (DVB) contents, as a crosslinking agent, for some of the copolymers prepared in this work. It shows that the overall conversion increased with increasing the DVB contents.

At % DVB of 3.0 (Run D03), the polymeric beads formed were clustered, fused, and no bead formation could be observed due to that the crosslinking agent usually helps stabilize and maintain the dimension of the beads. Thus, the small amount of the crosslinking agent is not sufficient to help the bead formation. As the DVB concentration was increased from 6-15 % (D06 to D15), the average size was decreased slightly and the particle stability remained unchanged. The particle size distribution of copolymer is then shown in Figure 4.16.

Table 4.12 Effect of crosslinking agent concentration on the particle size and size distribution of styrene-divinylbenzene copolymer beads

Runs	%Conv	Particle Size Distribution					Ave. Size (mm)
		<0.42	0.42-0.59	0.59-0.84	0.84-2.0	>2.0	
D03	39	-	-	-	-	-	fused
D06	51	0.99	12.46	15.71	66.56	4.28	1.21
D09	58	2.82	14.43	21.55	59.67	1.53	1.12
D12	66	6.23	17.39	21.71	50.96	3.71	1.07
D15	70	4.37	21.93	27.23	43.70	2.67	1.00

Figures 4.17 – 4.19 show the surface morphology of Sty-DVB copolymer bead prepared by varying the DVB content at 50, 100, and 3000 times enlargement. The effect of crosslinking agent concentration on the surface morphology of Sty-DVB copolymer beads is discussed later in Section 4.10.1.

Table 4.13 and Figures 4.20 – 4.21 show the swelling ratio and crosslinking density of the styrene-divinylbenzene beads prepared by varying the DVB concentration range of 3 to 15 %, based on the monomer content. The swelling of the beads decreased when the DVB concentration produces the increasing crosslinking density of the copolymer chain, the copolymer beads are therefore less flexible leading to the decrease in swelling ratio. These results also led to decreasing the diffusion coefficient of the copolymer, as shown in Table 4.13.

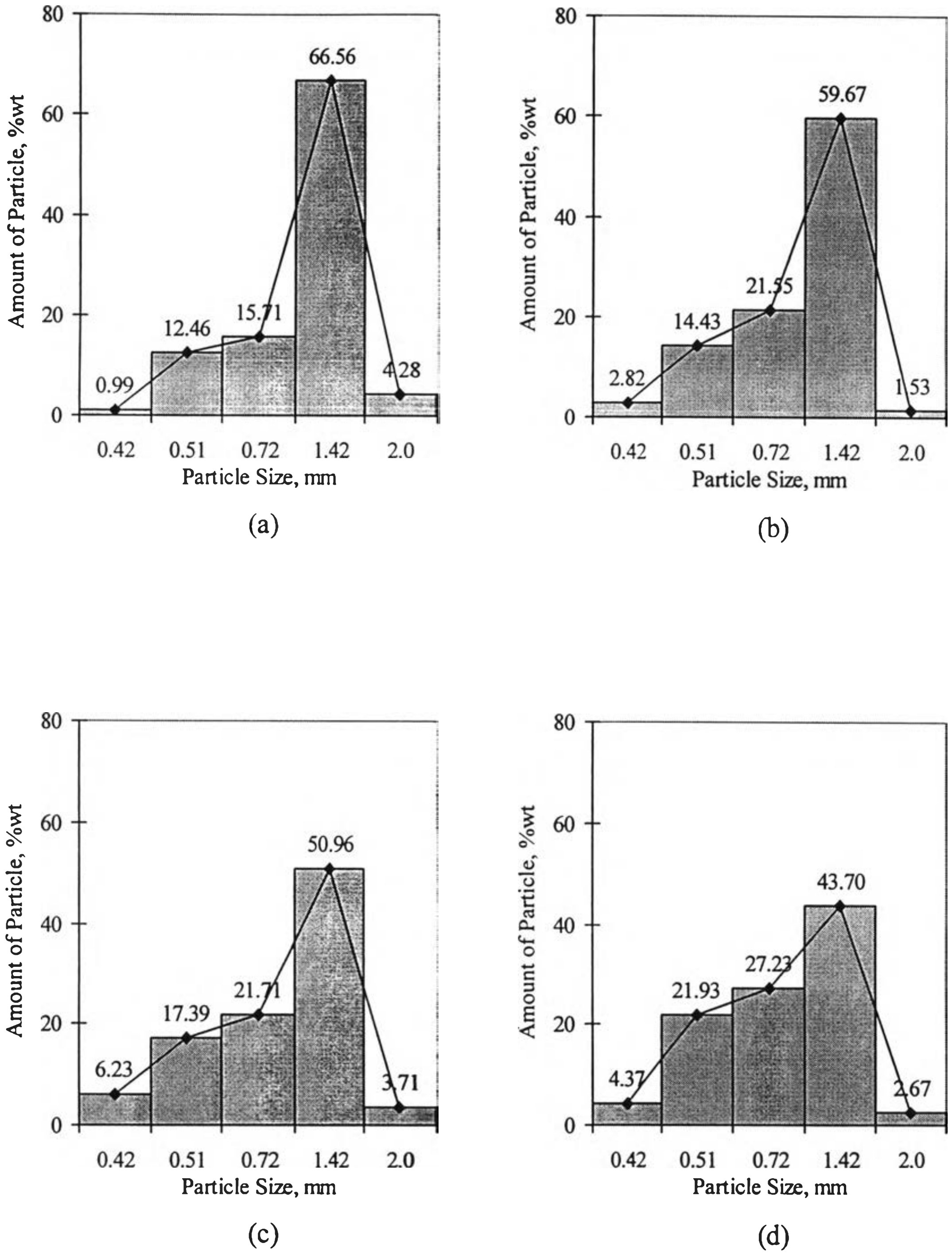
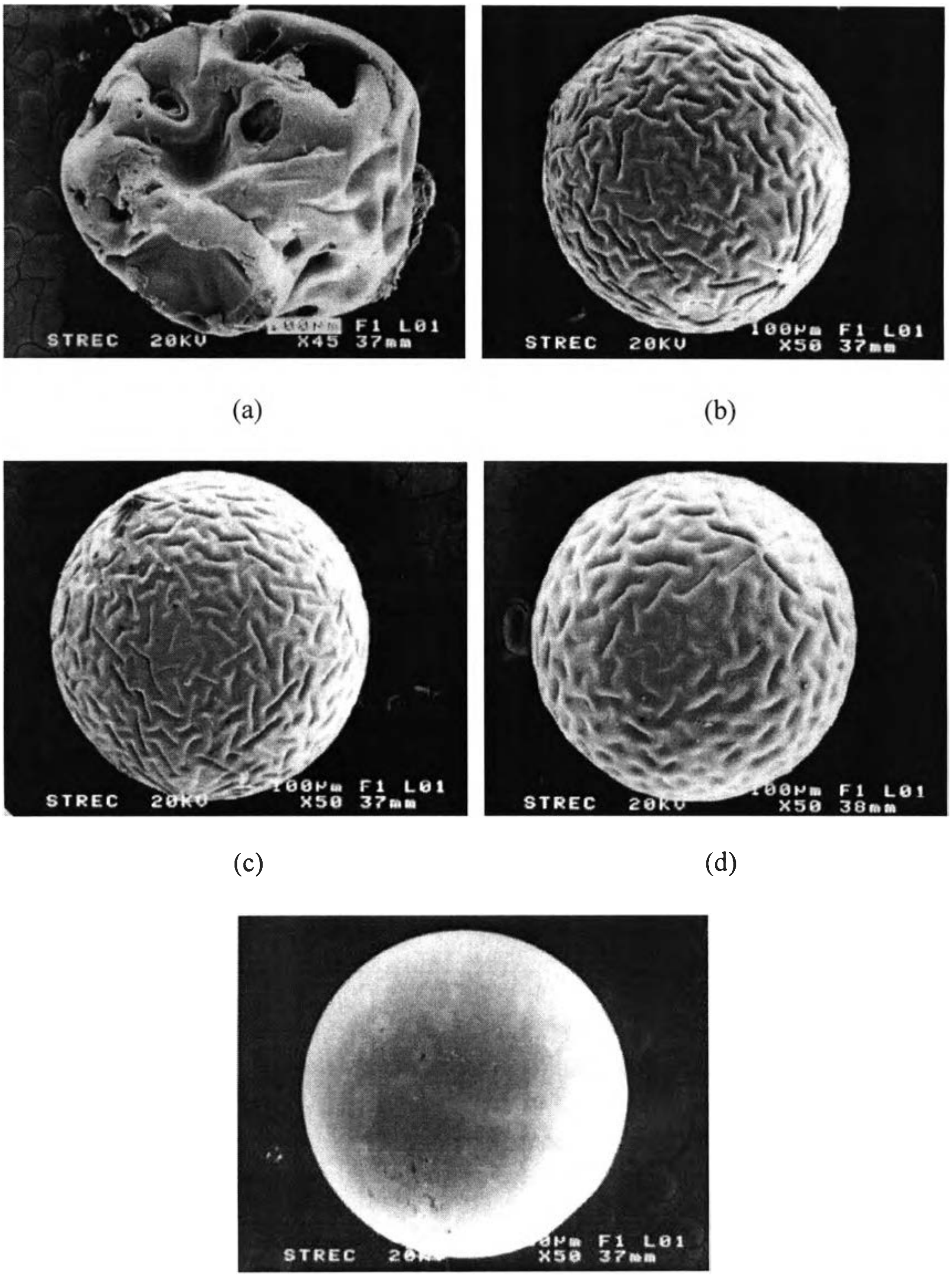


Figure 4.16 Bead size distribution of styrene-divinylbenzene copolymer beads under the effect of crosslinking agent concentrations: (a) 6.0%, (b) 9.0%, (c) 12.0%, and (d) 15.0%wt based on monomer phase.



(a)

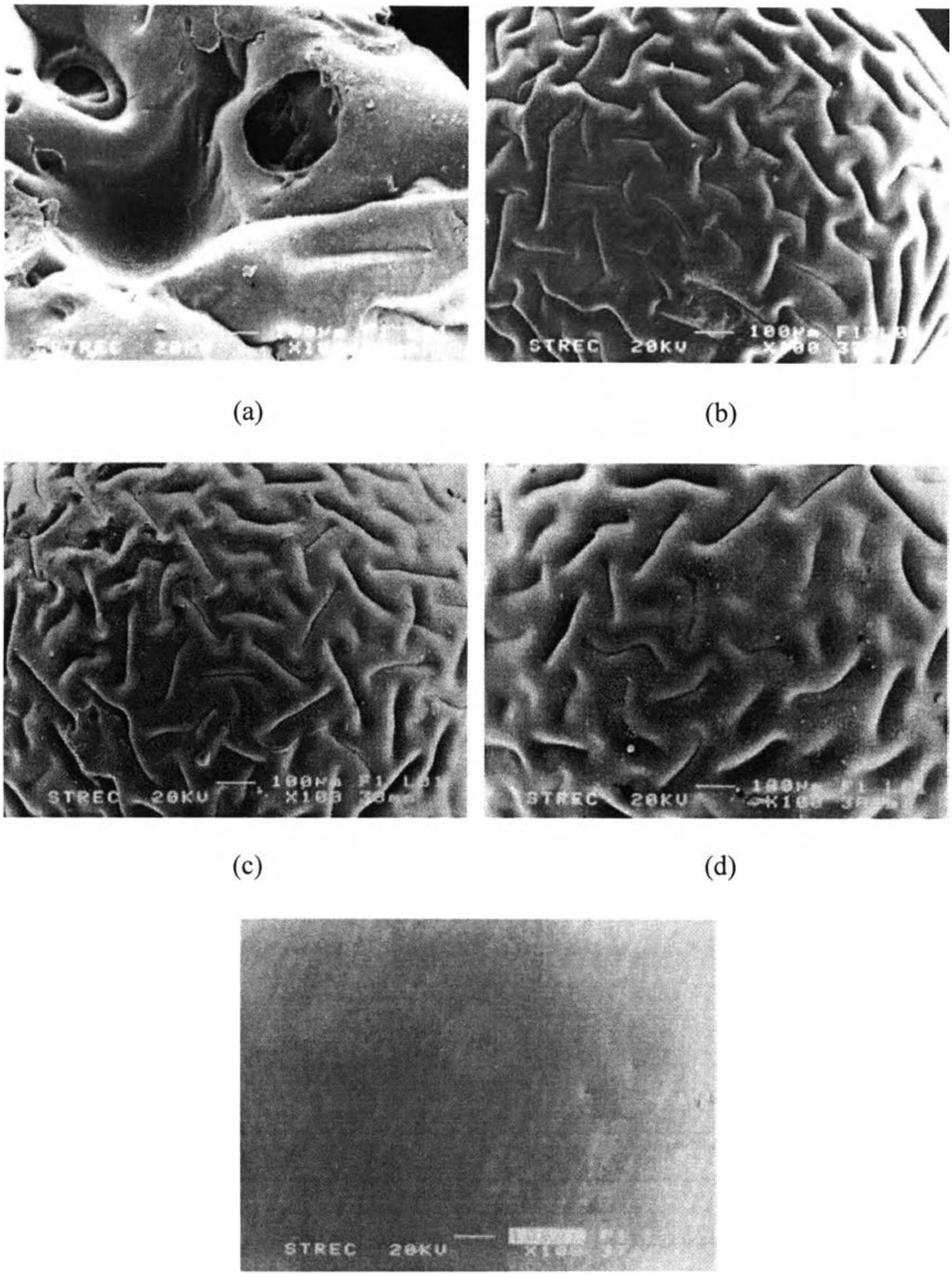
(b)

(c)

(d)

(e)

Figure 4.17 SEM photographs of the copolymer prepared at different crosslinking agent concentrations: (a) 3.0%, (b) 6.0%, (c) 9.0%, (d) 12.0%, and (e) 15.0% (×50).

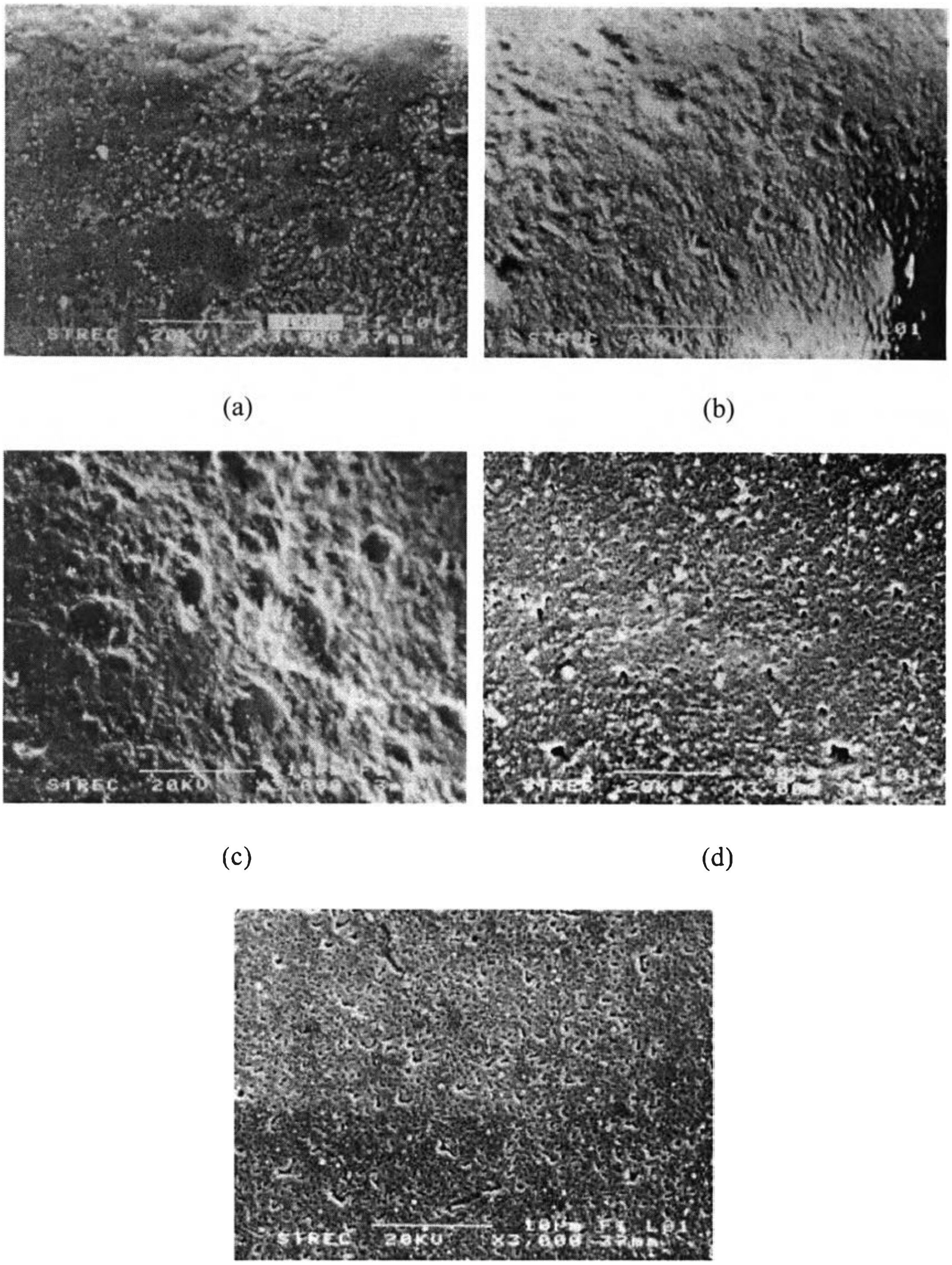


(a) (b)

(c) (d)

(e)

Figure 4.18 SEM photographs of the copolymer prepared at different crosslinking agent concentrations: (a) 3.0%, (b) 6.0%, (c) 9.0%, (d) 12.0%, and (e) 15.0% (×100).



(a) (b)

(c) (d)

(e)

Figure 4.19 SEM photographs of the copolymer prepared at different crosslinking agent concentrations: (a) 3.0%, (b) 6.0%, (c) 9.0%, (d) 12.0%, and (e) 15.0% (×3000).

Table 4.13 Effect of crosslinking agent concentration on swelling properties of styrene-divinylbenzene copolymer beads

Runs	Crosslinking Agent Conc., %wt	$\overline{M}_c$	Crosslinking Density	Swelling Ratio	Diffusion Coefficient, cm^2/sec
D03	3.0	53400	1.6	12.3	-
D06	6.0	12300	7.1	6.5	2.13×10^{-5}
D09	9.0	7900	11.1	5.5	1.66×10^{-5}
D12	12.0	5800	15.2	4.8	9.14×10^{-6}
D15	15.0	3900	22.3	4.2	2.89×10^{-6}

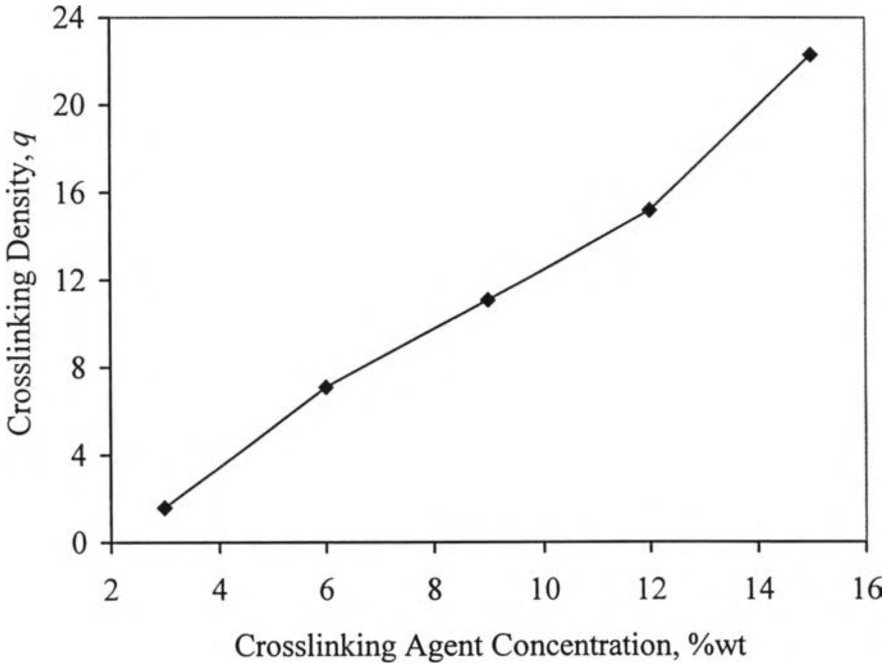


Figure 4.20 Effect of crosslinking agent concentration on the crosslinking density.

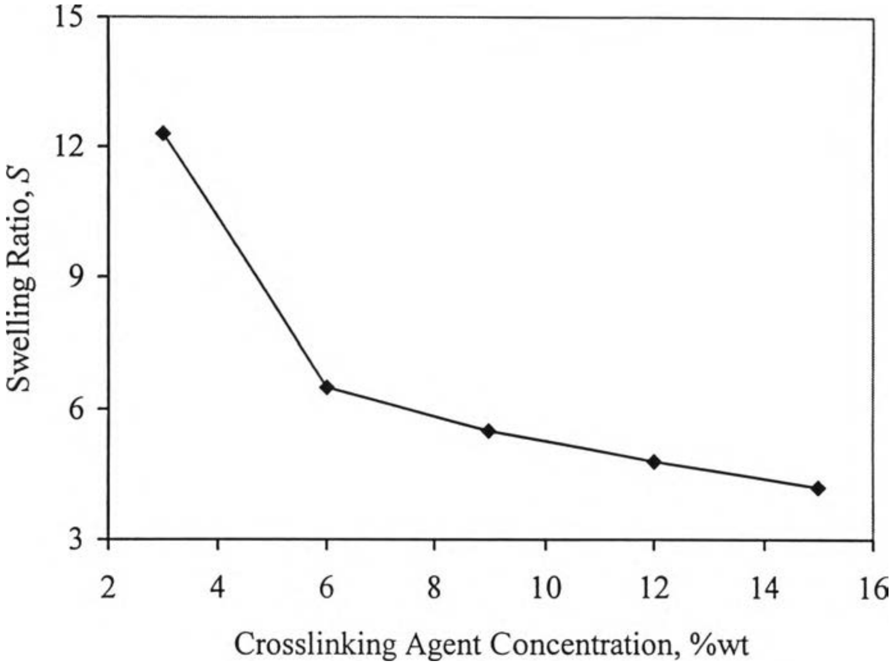


Figure 4.21 Effect of crosslinking agent concentration on the swelling ratio.

4.7 Effect of Suspending Agent Concentration

The effects of suspending agent or stabilizer concentration on the particle size, size distribution and swelling properties were investigated by varying the suspending agent concentrations of 0.05, 0.10, 0.15, and 0.20 %wt based on monomer phase. The other parameters were kept constant as follows:

- amount of styrene and divinylbenzene monomer (94 : 6) : 100 %wt
- initiator concentration : 0.5 %wt
- reaction temperature : 70 °C
- reaction time : 10 hours
- agitation rate : 270 rpm
- monomer phase weight fraction : 0.1
- Toluene : Heptane : 100 : 0

The selection of a stabilizer or suspending agent is very important in the preparation of polymer particles by suspension polymerization. The stabilizer must not only be stable in the system but also be able to cover the particle surface sufficiently to prevent coalescence [28].

In this research, poly(vinyl alcohol), PVA, with a molecular weight 100,000 and a degree of hydrolysis of 86 – 89 % was used as a stabilizer in suspension copolymerization of styrene and divinylbenzene.

Poly(vinyl alcohol) or partial by saponified poly(vinyl acetate) is a classical representative of a group of the stabilizer formed by water-soluble polymers. After dispersing the monomer phase in water, the partially hydrolysed poly(vinyl acetate) is adsorbed onto the monomer particle surface, and the particles then change gradually into polymer particles. It is localized on the surface such that the terminal acetate groups contact the surface of the oil or polymer phase, while the hydroxyl groups are oriented outwards from the interphase into the water (see Figure 4.22). The coalescence occurs due to the collisions of particle droplets in a turbulent flow, most of the collisions results in coalescence. The stabilizer, being spread over the particle surface, creates a protective layer, which prevents coalescence of the particles during collisions. In this situation, the polymer particles do not coalesce if the replusive forces prevail over the attractive ones. Collisions of these stable particles are accompanied only by overlapping of their outer layers; in the zone of mutual overlap the osmotic pressure increases (owing to the flow of water into these regions), which gradually separates the particles one from others. The rate of separation of the suspension particles, whose surface layers mutually overlap after collisions, is not interactions of the stabilizer molecules and of interactions between the stabilizer molecules and polymers or monomers [29].

Table 4.14 Effect of suspending agent concentration on the particle size and size distribution of styrene-divinylbenzene copolymer beads

Runs	%Conv	Particle Size Distribution					Ave. Size (mm)
		<0.42	0.42-0.59	0.59-0.84	0.84-2.0	>2.0	
P05	43	-	-	-	-	-	coalesced
P10	51	0.99	12.46	15.71	66.56	4.28	1.21
P15	49	14.62	21.61	22.01	41.76	-	0.92
P20	48	13.84	26.36	21.83	37.97	-	0.89

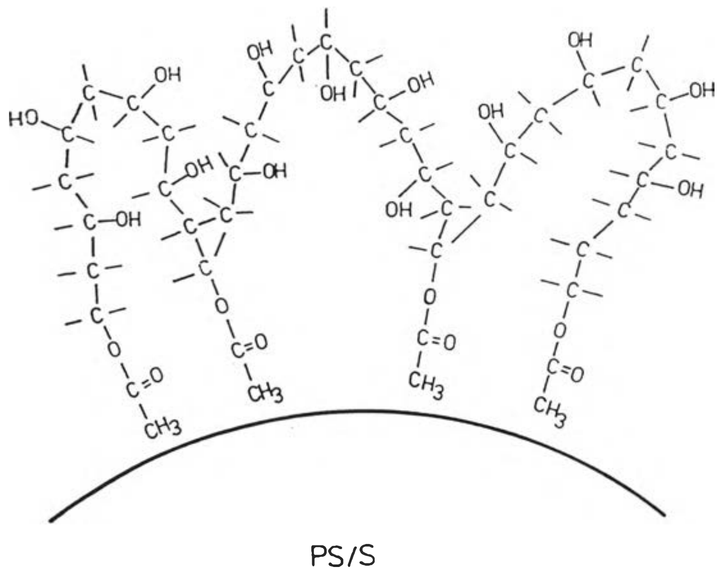


Figure 4.22 Mechanism for stabilizing polymer dispersion (polystyrene/styrene monomer) by hydrolyzed poly(vinyl alcohol) with residual acetate groups [29].

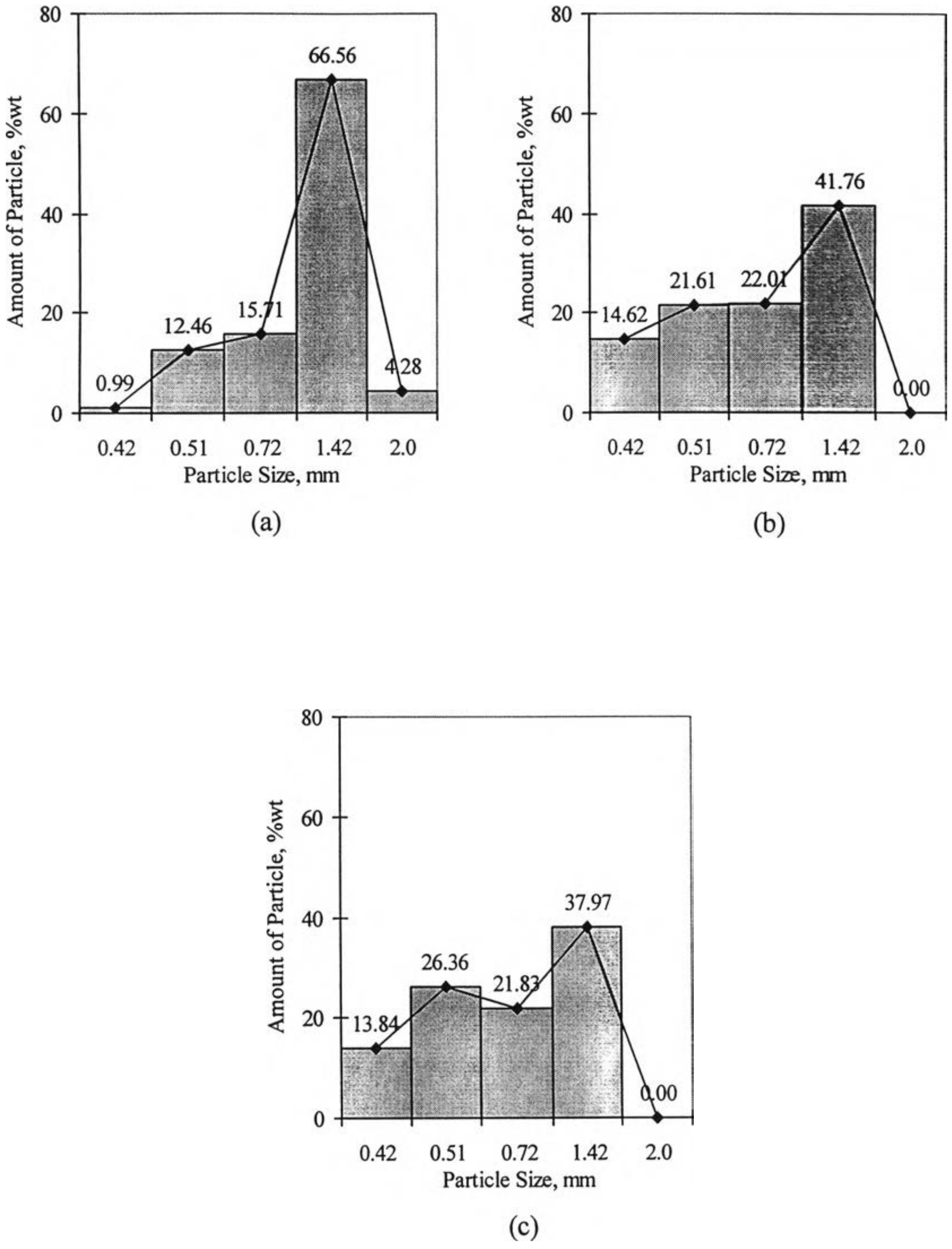


Figure 4.23 Bead size distribution of styrene-divinylbenzene copolymer beads under the effect of suspending agent concentrations: (a) 0.10%, (b) 0.15%, and (c) 0.20%PVA.

Table 4.14 and Figure 4.23 show the effect of suspending agent concentration on average particle size and size distribution. At 0.05 % PVA, the polymer droplets were coalesced due to that the amount of stabilizer is not enough to stabilize the dispersions; and the average particle size decreases from 1.21 to 0.89 mm with an increase in the suspending agent concentration. It can be described that the mutual interactions of the particles (or their surface layers) cause an increase in the viscosity of the polymer dispersion. Increasing in the concentration of the stabilizer produces an increase in viscosity of the system and, in parallel, the stability of the suspension. The increase in stability follows the formation of an efficient protective layer on the particle surface.

The effect of suspending agent concentration on swelling properties of the beads is shown in Table 4.15 and Figure 4.24. It was found that increasing the stabilizer concentrations from 0.05, 0.1, 0.15, and 0.2 % based on monomer phase, the swelling ratio of the copolymers is 5.9, 6.5, 6.9, and 8.1, respectively. Increasing the PVA concentration, a larger number of smaller particles are generated. The polymer chains inside the small beads are more flexible leading to the decrease in crosslinking density, regardless of their larger surface area and resemble density. These results also led to a increase in the swelling ratio.

Table 4.15 Effect of suspending agent concentration on swelling properties of styrene-divinylbenzene copolymer beads

Runs	Suspending Agent Concentration, %wt	Swelling Ratio
P05	0.05	5.9
P10	0.10	6.5
P15	0.15	6.9
P20	0.20	8.1

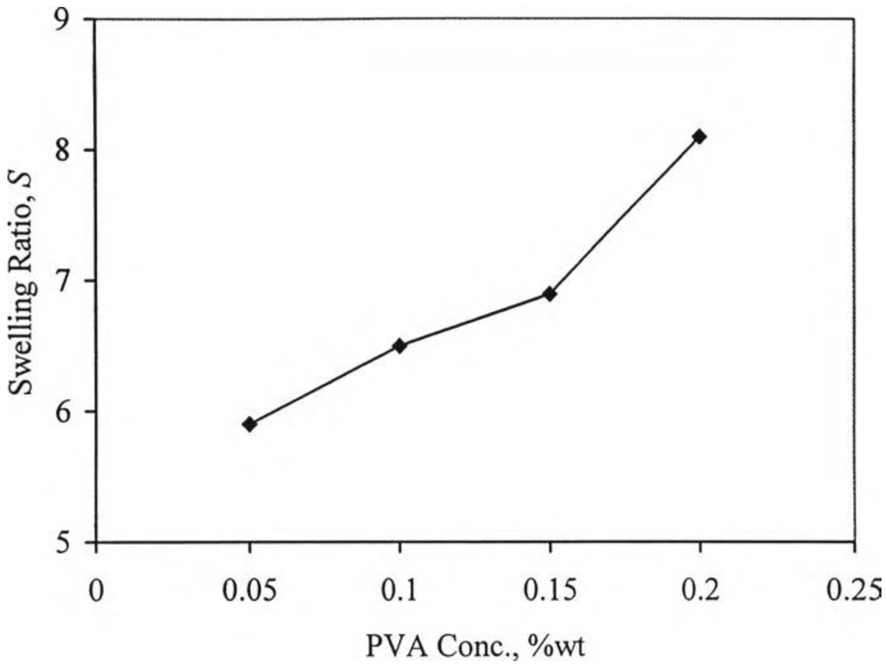


Figure 4.24 Effect of suspending agent concentration on the swelling ratio.

4.8 Effect of Diluent Compositon

The effects of diluent composition on the particle size, size distribution and swelling properties were investigated by varying the diluent composition between toluene and heptane of 100/0, 80/20, 60/40, 40/60, and 20/80 %wt based on monomer phase. The other parameters were kept constant as follows:

- amount of styrene and divinylbenzene monomer (94 : 6) : 100 %wt
- initiator concentration : 0.5 %wt
- suspending agent concentration : 0.1 %wt
- reaction temperature : 70 °C
- reaction time : 10 hours
- agitation rate : 270 rpm
- monomer phase weight fraction : 0.1

Table 4.16 shows the overall conversion, the average particle size and size distribution in relation to diluent composition (Tol/Hep), as a good solvent and bad solvent, for the newly synthesized copolymers in this work. It is shown that the overall conversion does not give any difference with the diluent composition. It is also noted that the changes in diluent composition, the average particle size of the copolymers is not also affected by the diluent composition. The particle size distribution of the copolymers is shown in Figure 4.20. The function of diluent composition between the good and poor solvent is to develop surface and interior morphology of the copolymers which is shown by scanning electron microscopy in Figures 4.26 – 4.28 (see discussion in Section 4.10.2).

Table 4.16 Effect of diluent composition between toluene and heptane on the particle size and size distribution of styrene-divinylbenzene copolymer beads

Runs	%Conv	Particle Size Distribution					Ave. Size (mm)
		<0.42	0.42-0.59	0.59-0.84	0.84-2.0	>2.0	
H00	51	0.99	12.46	15.71	66.56	4.28	1.21
H02	48	1.79	9.50	12.32	71.43	4.96	1.26
H04	49	3.33	10.91	11.87	68.23	5.66	1.24
H06	50	6.66	7.85	13.39	64.91	7.19	1.23
H08	48	8.86	9.10	12.16	47.17	22.71	1.23

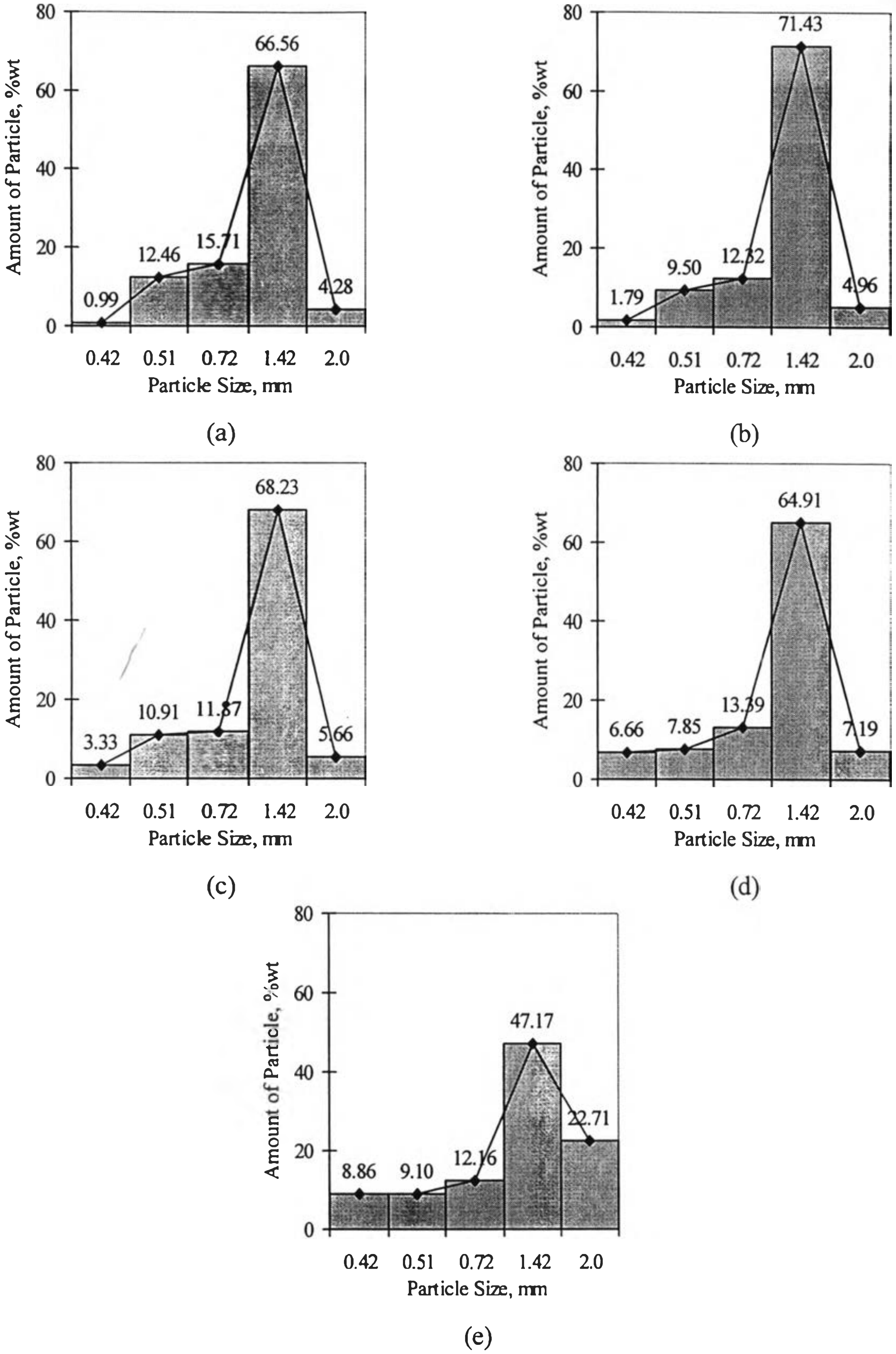
The thermodynamic affinity of the diluent for Sty-DVB copolymer determines decisively the macroporous structure formation and the swelling properties. When styrene and divinylbenzene are copolymerized in presence of a diluent which, like the monomers, solvates the copolymer, two kinds of porous structures can be obtained:

expanded or macroporous. At a low DVB content (6%), the final structure is an expanded gel [Figure 4.28 (a)], since the chains are fully solvated during the polymerization and they shrink less than those in the corresponding systems in the absence of a solvating diluent. However, the internuclear chains can collapse when the solvating diluent is removed at the later stage to result in an aggregated mass. A macroporous copolymer is only obtained when the DVB content is high. In this case, the collapse of the internuclear chains has occurred before all the solvating diluent is removed. The macroporosity of the copolymer beads is thus a result of the removal of the remaining diluent [21].

On the other hand, when the diluent is a poor solvent for the polymer chains, partial phase separation may eventually occur. As the polymerization progresses, the polymer chains are no longer extended, as in a solvating system, and there is a tendency of the growing chains to become entangled inside the nuclei. Consequently, the nuclei of the final structure are large and connected by a relatively small number of coiled and crumpled internuclear chains. When the non-solvating diluent is removed, the collapse of the system of interconnected nuclei can also occur [21].

When mixtures of solvating and non-solvating diluents are used the copolymers present porous structures with intermediary characteristics in relation to the copolymers prepared with the pure diluents [Figure 4.28 (b)-(e)]. The effects of synthetic conditions on the swelling properties are considerably more complex for copolymers obtained with diluent mixtures [21].

The solvent uptake can appear in two ways by filling the pores without affecting the gel regions (no volume change), and by chain displacement in the gel

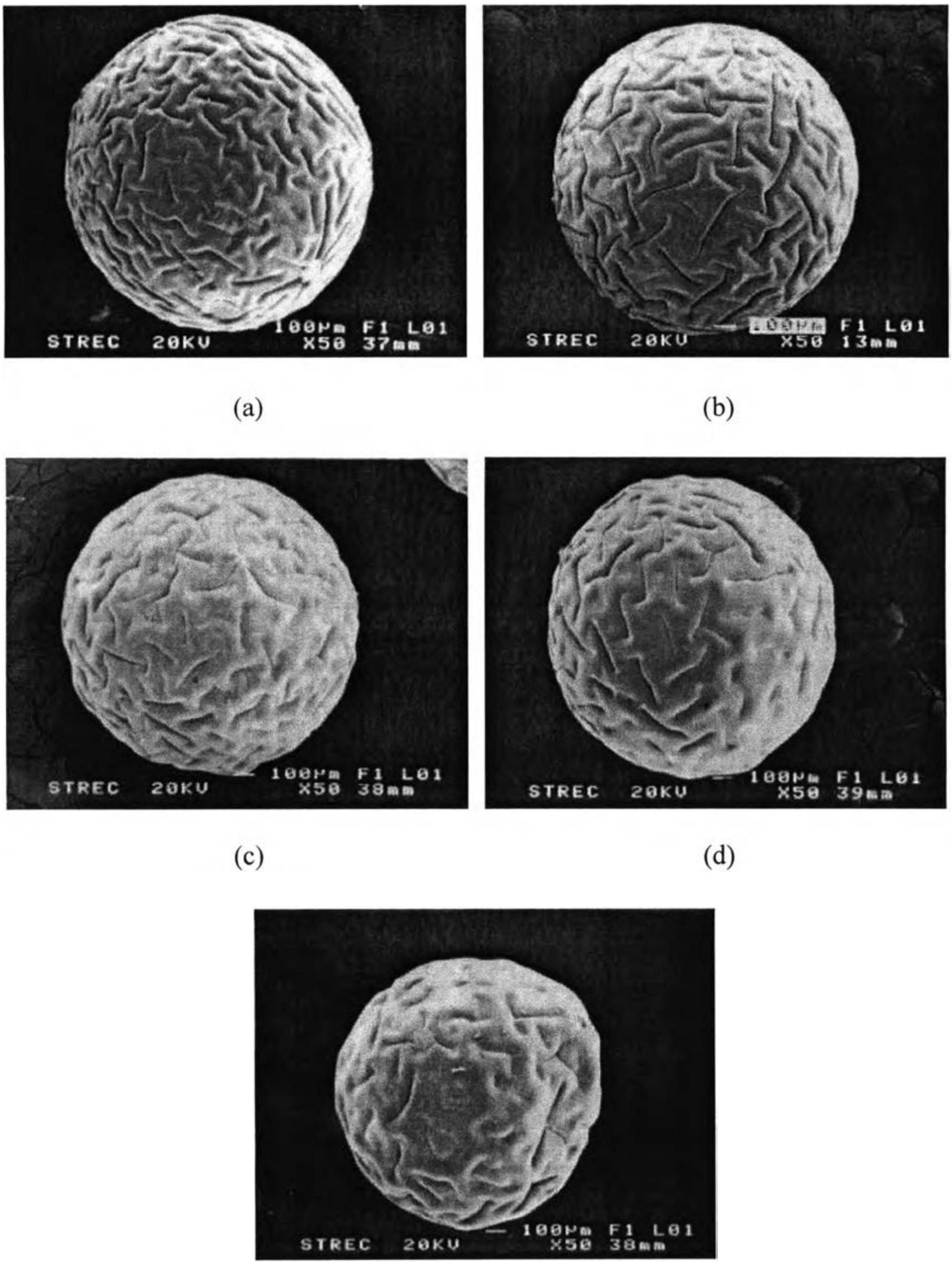


(a) (b)

(c) (d)

(e)

Figure 4.25 Bead size distribution of styrene-divinylbenzene copolymer beads under the effect of diluent composition between toluene and heptane: (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, and (e) 20/80 %wt based on monomer phase.

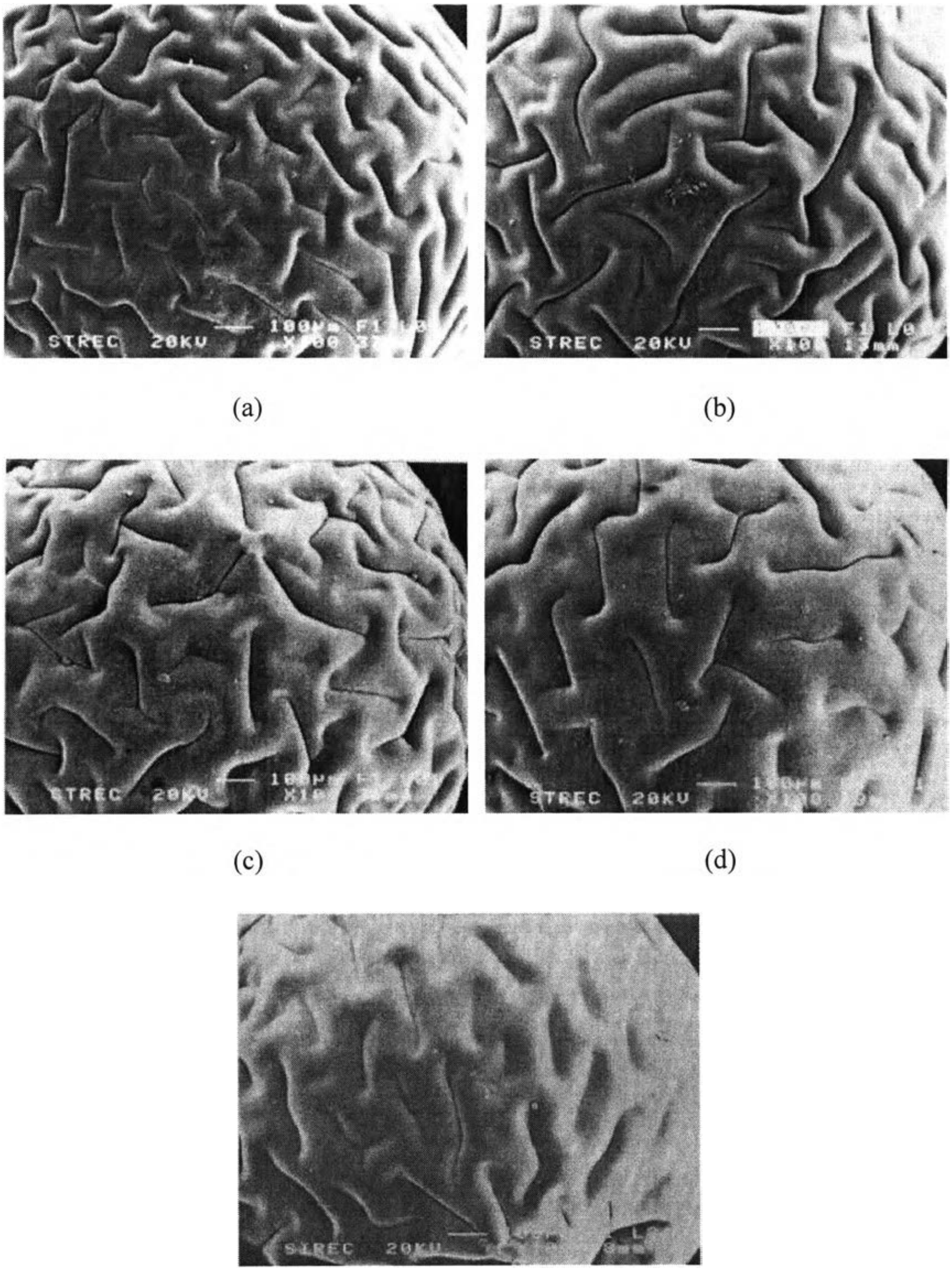


(a) (b)

(c) (d)

(e)

Figure 4.26 SEM photographs of the copolymer prepared at different toluene/heptane ratios: (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, and (e) 20/80 (×50).

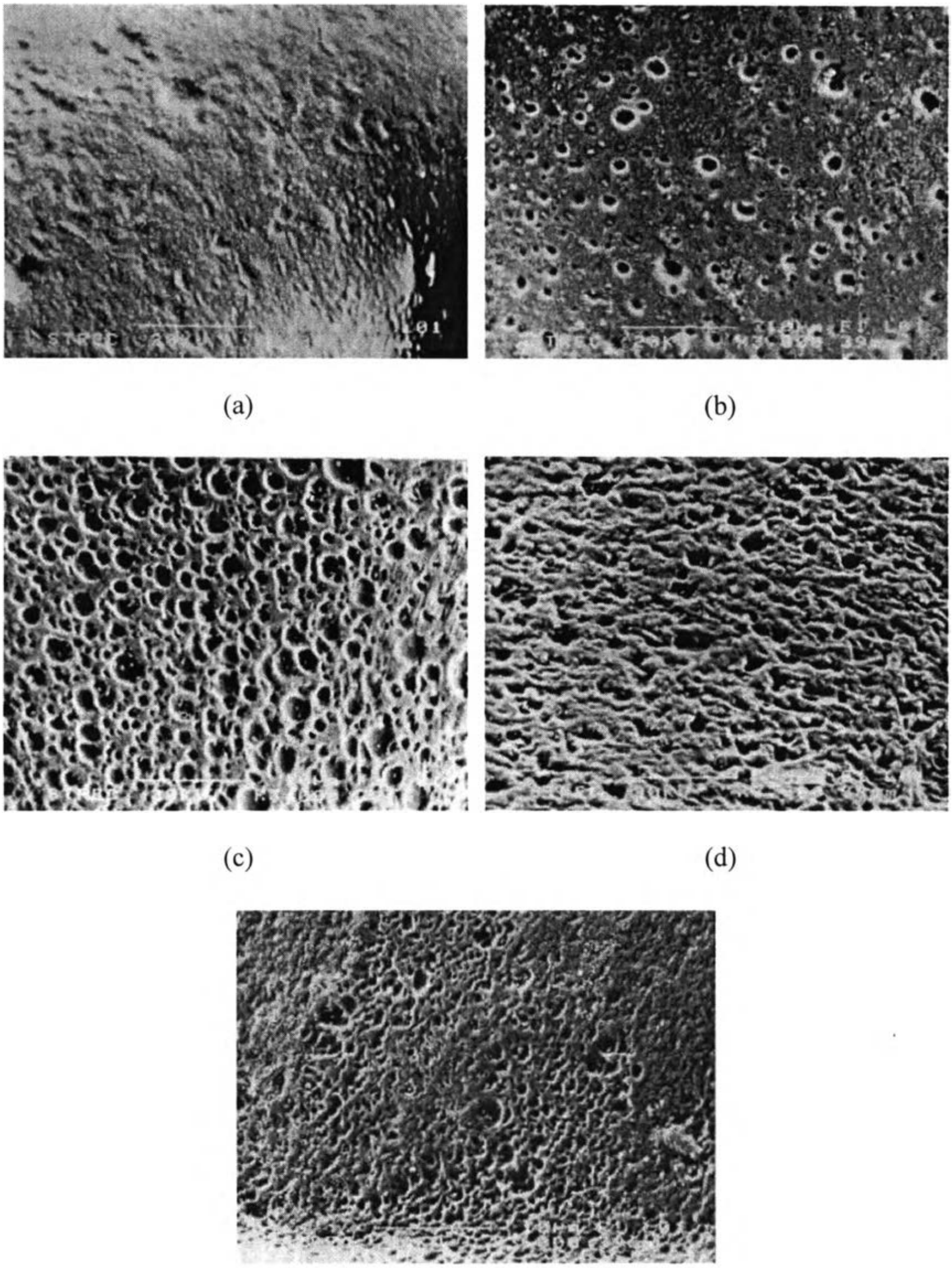


(a) (b)

(c) (d)

(e)

Figure 4.27 SEM photographs of the copolymer prepared at different toluene/heptane ratios: (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, and (e) 20/80 (×100).



(a)

(b)

(c)

(d)

(e)

Figure 4.28 SEM photographs of the copolymer prepared at different toluene/heptane ratios: (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, and (e) 20/80 (×3000).

regions that causes bead expansion. The swelling of heterogeneous network is governed by two separate processes [32]. Firstly, solvating of network chains, the main driving force of this process is the changes in the free energies of mixing and elastic deformation during the expansion of the network. The extent of network solvation is determined by the crosslinking density of the network and by the interactions between solvent molecules and the network chains. Secondly, filling of voids (pores) by the solvent, the extent of this process is determined by the total volume of (open) pores, i.e., by the volume of diluent separated out of the network phase during the polymerization.

Table 4.17 Effect of diluent composition between toluene and heptane on swelling properties of styrene-divinylbenzene copolymer beads

Runs	Diluent Composition	$\overline{M}_c$	Crosslinking Density	Swelling Ratio
H00	100/0	12300	7.1	6.5
H02	80/20	12900	6.8	6.7
H04	60/40	17400	5.1	7.6
H06	40/60	11800	7.4	6.5
H08	20/80	7700	11.4	5.6

From Table 4.17 and Figures 4.29 – 4.30 show the effect of diluent composition on crosslinking density and swelling properties of Sty-DVB copolymer beads. When the copolymers were prepared in the presence of pure toluene, the expanded gel can be obtained. The swelling of the copolymers takes place through the solvent partly taken by the gel portion of the network due to the solvating of network chains only. When the copolymers were prepared with a lower heptane portion, the copolymer structures with intermediary characteristics between expanded gel and heterogeneous porous network can be obtained. The increased swelling of the copolymers takes place through the solvent partly taken by the whole network (gel + pores) due to both the solvating of network chains and the filling of voids by the solvent. When the heptane portions increases, the copolymer structures with less gel portion and more heterogeneous network portion can be obtained [32]. The swelling of the copolymers decreased due to the polymeric chains of the copolymers prepared with higher non-solvent portion are more rigid and entangled than the chains of a gel-type one [21].

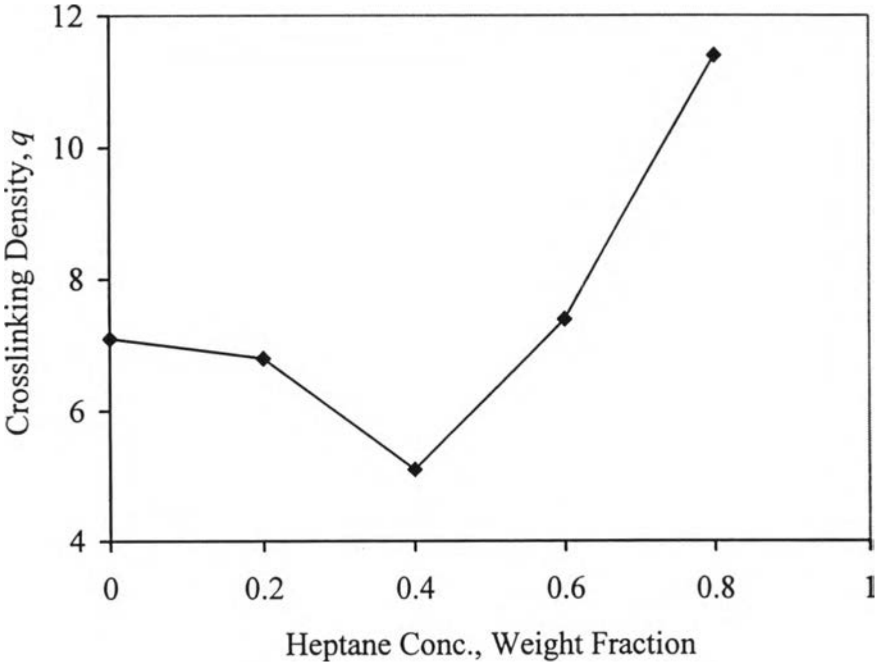


Figure 4.29 Effect of diluent composition on the crosslinking density.

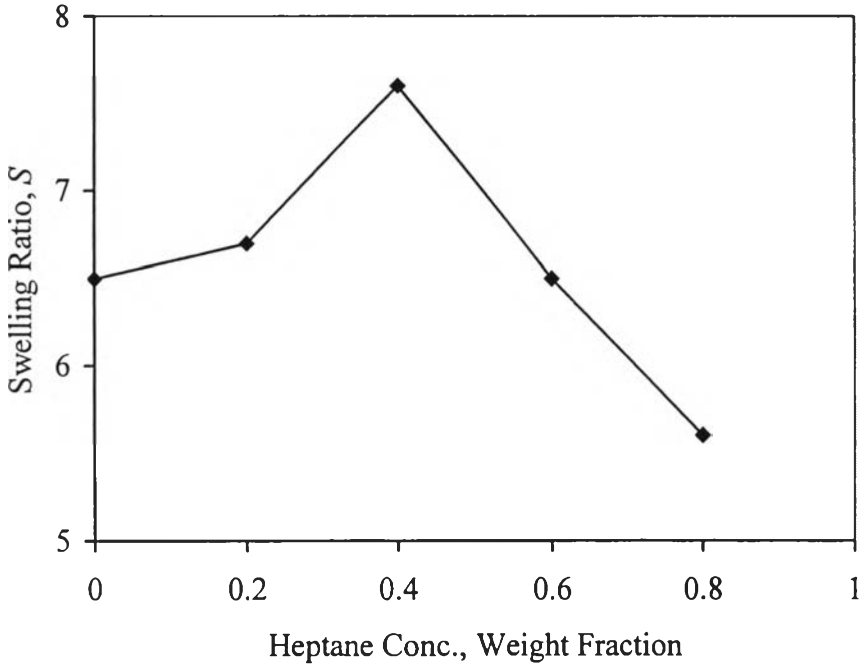


Figure 4.30 Effect of diluent composition on the swelling ratio.

4.9 Effect of the Third Comonomer

The effects of the third comonomer on the particle size, size distribution and swelling properties were investigated varying the monomer composition, styrene/divinylbenzene/*n*-butyl acrylate and styrene/divinylbenzene/2-ethyl hexyl acrylate of 94/6/0, 70/6/24, and 47/6/47 %wt based on monomer phase. The other parameters were kept constant as follows:

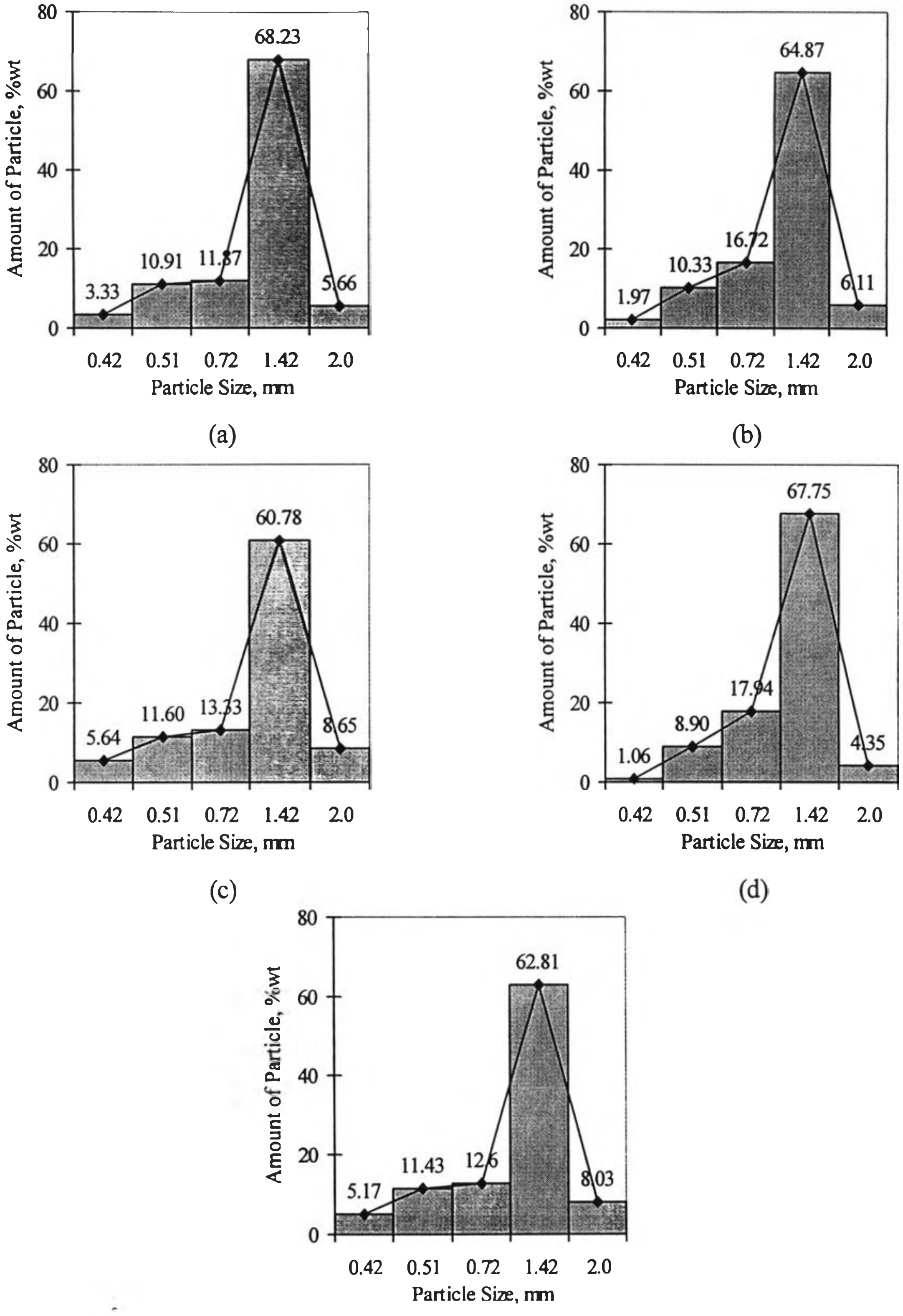
- initiator concentration	:	0.5 %wt
- suspending agent concentration	:	0.1 %wt
- reaction temperature	:	70 °C
- reaction time	:	10 hours
- agitation rate	:	270 rpm
- Toluene: Heptane	:	60:40
- monomer phase weight fraction	:	0.1

The functional groups of the synthetic terpolymer bead were investigated by spectroscopy. The FTIR spectra of styrene-divinylbenzene-*n*-butyl acrylate terpolymers (Runs B24, B47) and styrene-divinylbenzene-2-ethylhexyl acrylate terpolymers (Runs E24, E47) were presented in Appendix E (Figures E-3 to E-6). These spectra of terpolymers show the additional peaks of C=O stretching at 1730 cm^{-1} and C-O stretching at 1160 cm^{-1}, besides the peaks mentioned in the Sty-DVB copolymer spectrum (Figure E-1).

2-EHA) for the newly synthesized copolymers prepared in this work. It is shown that the overall conversion does not give any significant difference with the monomer composition. It is also noted that the changes in monomer composition, the average particle size of the copolymers is not affected by the monomer composition, either. The particle size distribution of the copolymers was shown in Figure 4.31. The surface morphology of the copolymers shown by scanning electron microscopy is in Figures 4.32 – 4.34.

Table 4.18 Effect of the third comonomer on the particle size and size distribution of polymer beads

Runs	%Conv	Particle Size Distribution					Ave. Size (mm)
		<0.42	0.42-0.59	0.59-0.84	0.84-2.0	>2.0	
PS	49	3.33	10.91	11.87	68.23	5.66	1.24
B24	50	1.97	10.33	16.72	64.87	6.11	1.22
B47	49	5.64	11.60	13.33	60.78	8.65	1.21
E24	48	1.06	8.90	17.94	67.75	4.35	1.23
E47	51	5.17	11.43	12.56	62.81	8.03	1.22



(a)

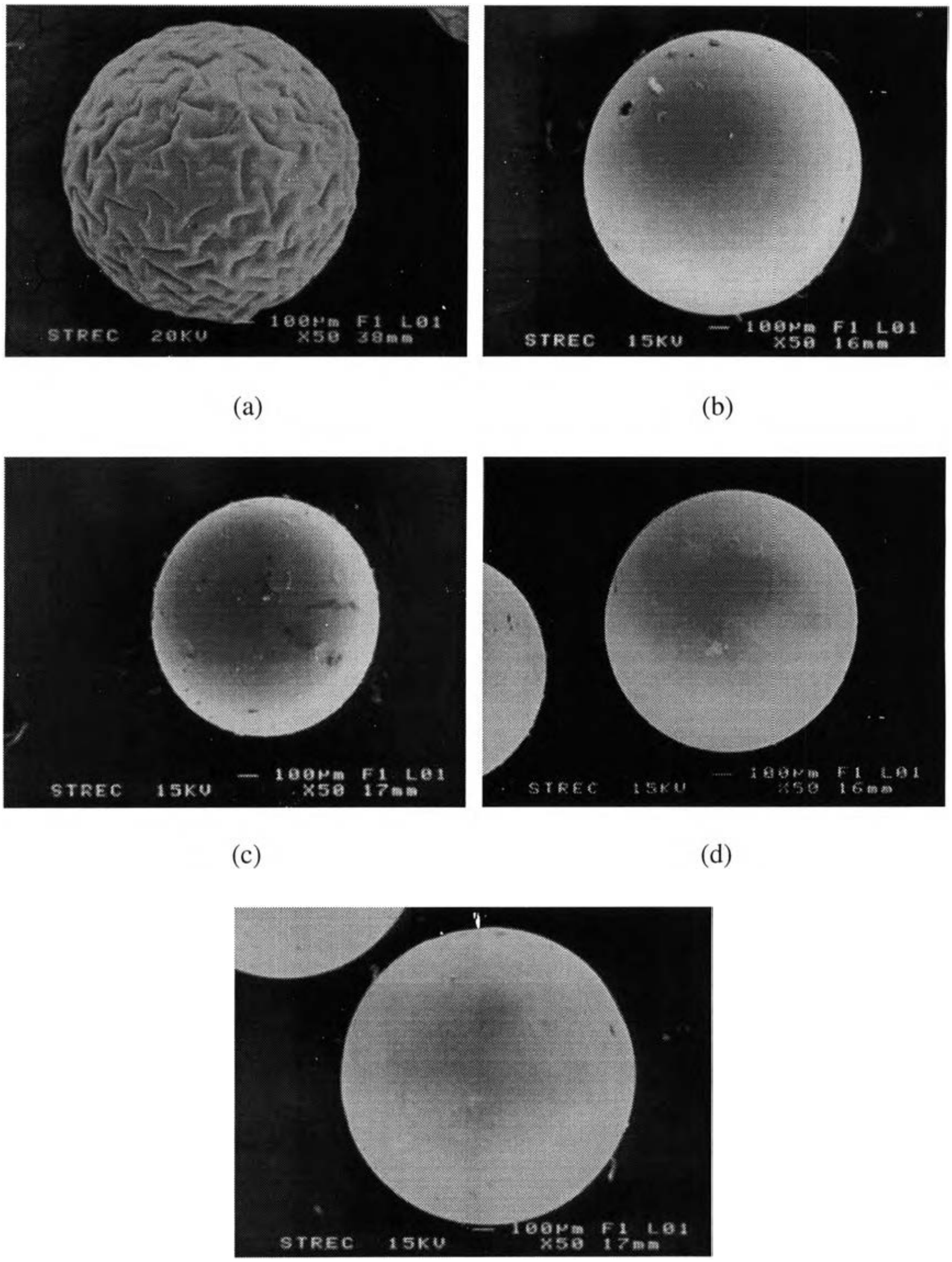
(b)

(c)

(d)

(e)

Figure 4.31 Bead size distribution of terpolymer beads under the effect of monomer composition: (a) Sty/DVB 94/6, (b) Sty/DVB/*n*-BA 70/6/24, (c) Sty/DVB/*n*-BA 47/6/47, (d) Sty/DVB/2-EHA 70/6/24, and (e) Sty/DVB/2-EHA 47/6/47.

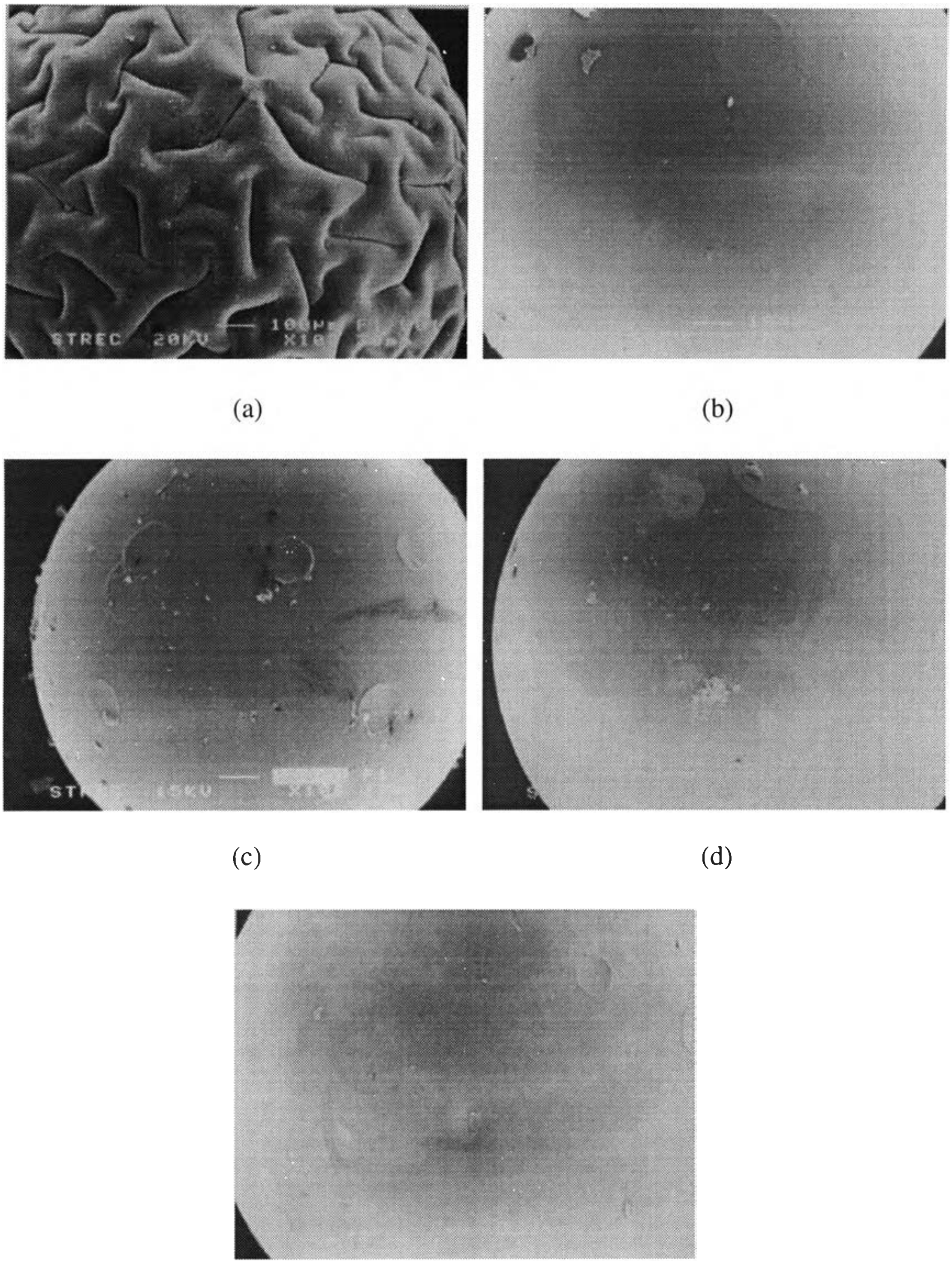


(a) (b)

(c) (d)

(e)

Figure 4.32 SEM photographs of the copolymer prepared with different third comonomers: (a) no third comonomer, (b) BA 24 %, (c) BA 47 %, (d) EHA 24 %, and (e) EHA 47 % (×50).

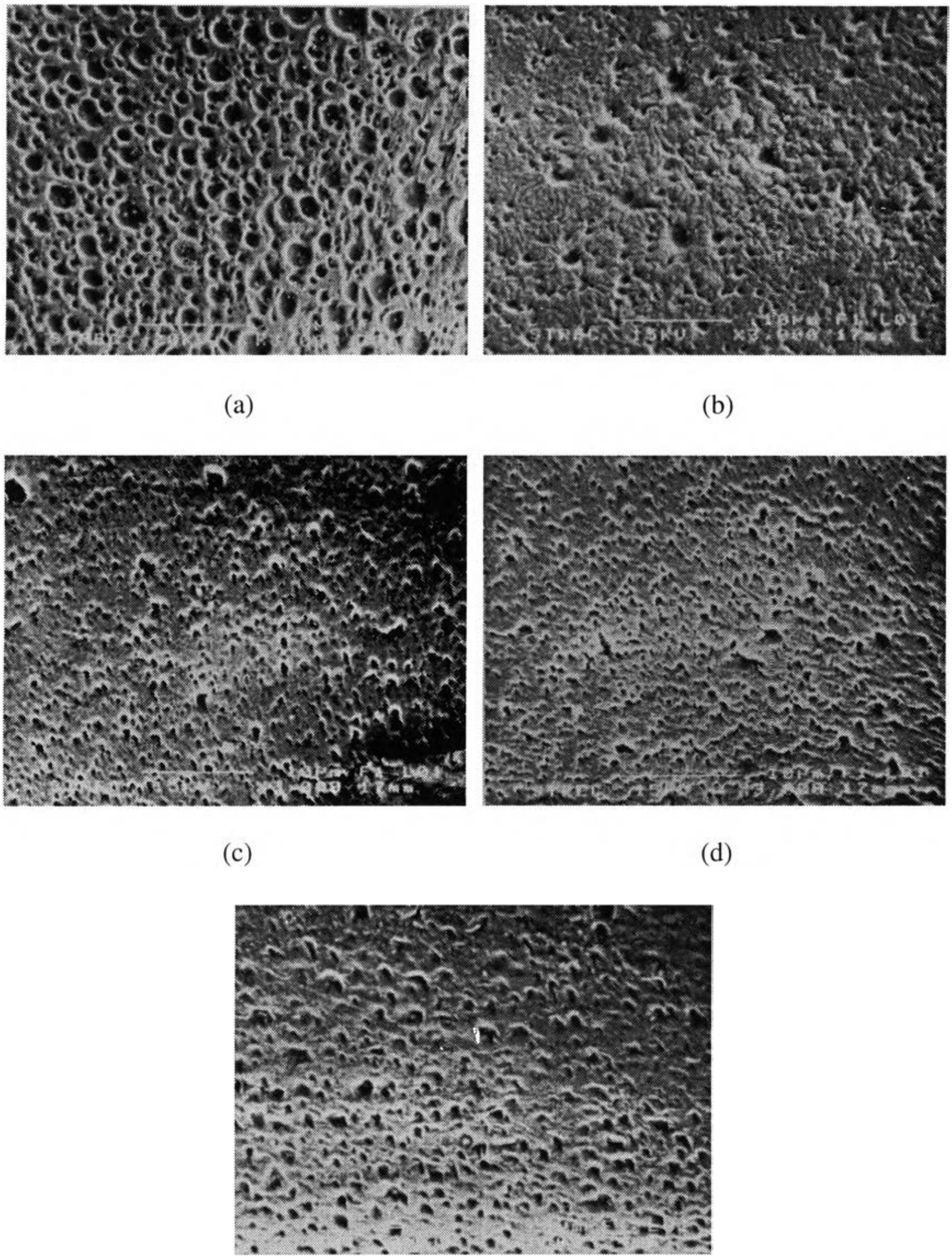


(a) (b)

(c) (d)

(e)

Figure 4.33 SEM photographs of the copolymer prepared with different third comonomers: (a) no third comonomer, (b) BA 24 %, (c) BA 47 %, (d) EHA 24 %, and (e) EHA 47 % (×100).



(a)

(b)

(c)

(d)

(e)

Figure 4.34 SEM photographs of the copolymer prepared with different third comonomers: (a) no third comonomer, (b) BA 24 %, (c) BA 47 %, (d) EHA 24 %, and (e) EHA 47 % (×3000).

The solubility parameter of a new polymer may be determined by any of several means. In this case, the polymer is cross-linked, the solubility parameter may be determined by swelling experiments. The best solvent is defined (for the purposes of the experiment) as the one with the closest solubility parameter to that of the copolymer beads. This solvent also swells the polymer at the most. Several solvents of varying solubility parameter are selected, and the cross-linked polymer is swelled to equilibrium in each of them. The swelling ratio, *S,* is plotted against the various solvent solubility parameters; the solvent that gives the maximum swelling ratio is defined as the solubility parameter of the polymer. The determination of the solubility parameter of the synthetic copolymers using the swelling experiment in various solvents is shown in Table 4.19 and Figure 4.35.

Figure 4.35 indicates that the solubility parameters of the synthetic copolymers, Runs PS, B24, B47, E24, and E47 are about 19.0, 18.8, 18.6, 18.3, and 18.2, respectively.

According to the extent of hydrogen bonding, a series of solvents used in this experiment is poorly hydrogen bonding solvents.

The results show that the highest swelling ratio of copolymer beads (Run PS) in the poorly bond solvent (chloroform) is 9.7 and the lowest ratio (hexane) is 2.0. On the other hand, when the coplymers were prepared in the presence of *n*-butyl acrylate and 2-ethyl hexyl acrylate in the monomer composition, the highest swelling ratios of copolymer beads (Runs B24, B47, E24, and E47) in the same of solvents are 8.6, 8.3, 8.2, and 7.3, respectively; and the lowest ratios are 2.2, 2.4, 2.7, and 3.2, respectively. This can be explained that only the nonpolar moiety of styrene causes

Table 4.19 Swelling ratio of the synthetic copolymer beads in various solvents

Solvent	Solubility Parameter, $(MPa)^{1/2}$				Type of Copolymer				
	δ_D	δ_P	δ_H	δ_T	PS	B24	B47	E24	E47
Hexane	14.9	0	0	14.9	2.0	2.2	2.4	2.7	3.2
Heptane	15.3	0	0	15.3	2.0	2.2	2.4	2.7	3.2
Cyclohexane	16.8	0	0.2	16.8	2.6	3.9	4.1	5.1	5.9
Trichloroethane	17.0	4.3	2.0	17.6	8.2	7.5	6.7	7.1	6.2
Carbon tetrachloride	17.8	0	0.6	17.8	8.3	7.7	7.4	7.2	6.8
Xylene	17.8	1.0	3.1	18.0	8.7	8.0	7.4	7.7	7.1
Toluene	18.0	1.4	2.0	18.2	9.3	8.1	7.9	8.2	7.3
Benzene	18.4	0	2.0	18.6	9.6	8.6	8.3	8.1	7.2
Chloroform	17.8	3.1	5.7	19.0	9.7	8.5	7.9	7.9	7.1
Chlorobenzene	19.0	4.3	2.0	19.6	9.6	8.3	7.8	7.7	6.7
Methylene chloride	18.2	6.3	6.1	20.3	8.6	8.0	7.6	7.3	6.4
Ethylene chloride	19.0	7.4	4.1	20.9	7.9	7.3	6.9	6.7	6.0

the highest maximum swelling of copolymer beads (Run PS) in the poorly hydrogen bonding solvents. Increasing the polar moiety by copolymerizing *n*-butyl acrylate and 2-ethyl hexyl acrylate monomers in the resulting copolymer chains (Runs B24, B47, E24, and E47), the maximum swelling ratio of these copolymers in the poorly hydrogen bonding solvents decreases.

Furthermore, the monomer structure of the copolymer was also considered. It is inevitably noted that adding the comonomer *n*-butyl acrylate or 2-ethyl hexyl acrylate to the Sty/DVB system is to increase the aliphatic portion to the copolymer chains; the swelling ratio of the terpolymers in the aromatic solvents, such as benzene, toluene, and xylene consequently decreased. On the other hand, the swelling ratio of these terpolymers in the aliphatic solvents, such as hexane, heptane, and cyclohexane increased, as shown in Figure 4.35.

Increasing the number of carbon atoms of acrylated vinyl monomer from *n*-butyl acrylate (C_4) to 2-ethyl hexyl acrylate (C_6) incorporated in the styrene-divinylbenzene copolymer beads enhance the absorption of the aliphatic hydrocarbon solvents of hexane, heptane, and cyclohexane. This result could be explained by the solubility parameter.

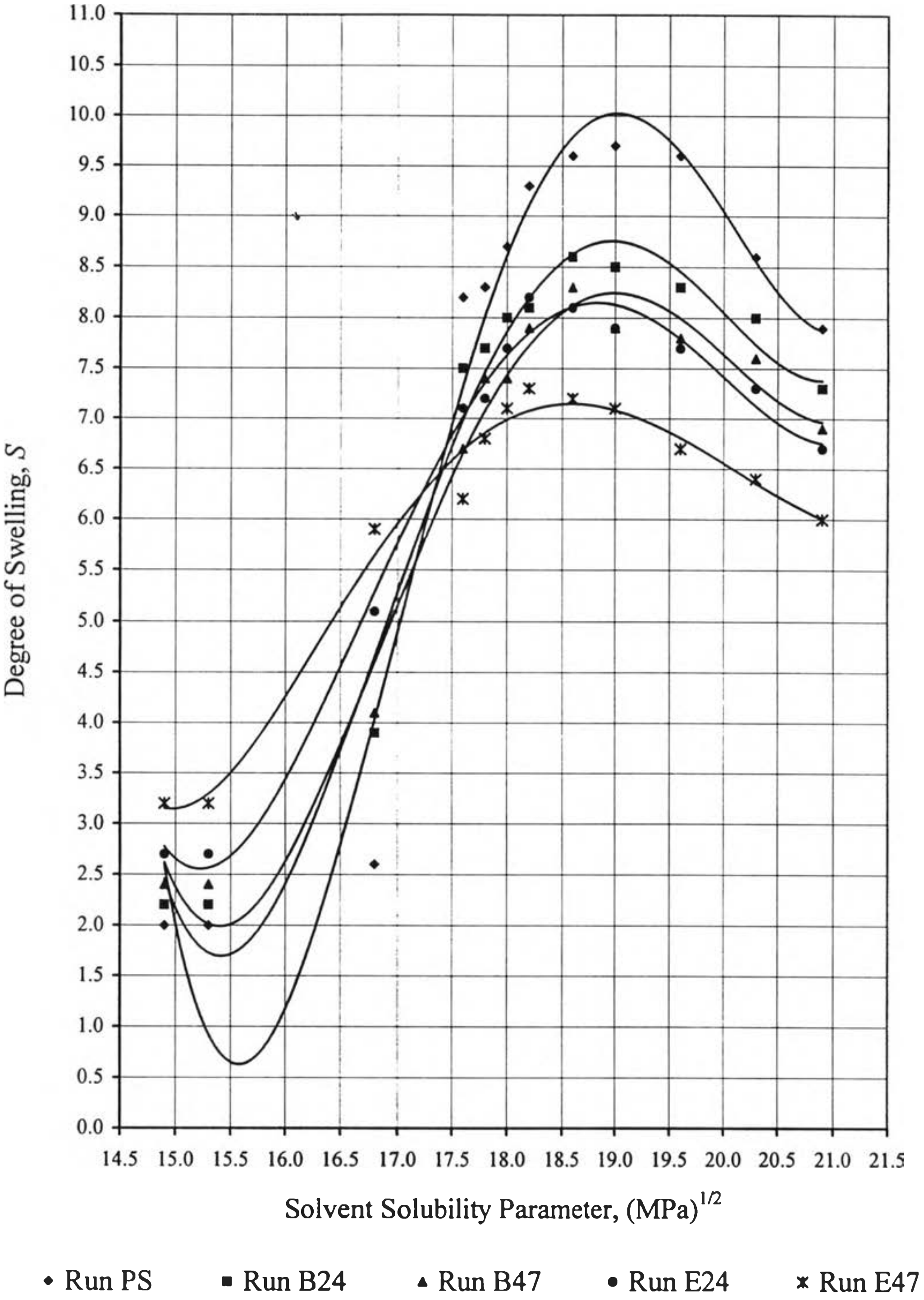


Figure 4.35 Comparative solubility parameter of synthetic copolymer beads by swelling experiments

4.10 Morphology of the Surface of Sty-DVB Copolymer

The most important factors influencing the heterogeneity of the Sty-DVB copolymer network are the type and amount of diluent as well as the amount of crosslinking agent employed in the synthesis [18]. In this work, the effects of crosslinking agent concentration and diluent mixtures were studied on the surface copolymer morphology of the copolymer.

4.10.1 The effect of the crosslinking agent concentration

Figures 4.17 and 4.18 show the surface morphology of Sty-DVB copolymer bead by the effect of crosslinking agent concentration at low magnifications 50 and 100 time enlargement. DVB of 3 % content could not successfully form the beads due to the amount of crosslinking agent was not enough to stabilize the soft surface of copolymer beads [Figures 4.17 (a) and 4.18 (a)]. In general, increase of the amount of DVB produces the increasing crosslinking density of the copolymer chain, the copolymer beads are thus less flexible leading to the decrease in shrinkage of the copolymer bead surface. The bead surfaces were getting smoother when higher crosslinking agents had been copolymerized. [Figures 4.17 (b) – (e) and 4.18 (b) – (e)]. The shrinkage of the copolymer bead surfaces in Figures 4.17 (b) – (d) and 4.18 (b) – (d) occurred because the amount of DVB was not sufficiently high for copolymerization. When the copolymers were swollen by the solvent during the solvent extraction, an imbalance tension between the bead interior and the outer surface surrounding by the extracting solvent, the removal of solvent from the copolymer beads might produce, i.e., a collapse of expanded network causes the outer surface to be shrink. This collapse phenomena of the surfaces is additionally considered as a result of the cohesive forces when the solvated polymer chains are approaching each other by loss of the solvent [31].

Figure 4.19 shows the high magnification of the surface morphology of Sty-DVB copolymer beads by the effect of crosslinking agent concentration. When styrene and divinylbenzene are copolymerized in the presence of a diluent, which behaves similarly as the monomers, solvates the copolymer, two kinds of porous structures can be obtained: expanded or macroporous. At low DVB content the final structure is a expanded gel [Figure 4.19 (a) – (c)], since the chains are fully solvated during the polymerization and they shrink less than those in the corresponding systems in the absence of a solvating diluent. However, the internuclear chains can collapse with the removal of the solvating diluent to make the approaching nuclei a compact mass. A porous copolymer is obtained when the DVB content is relatively high [Figure 4.19 (d) – (e)]. In this case, the collapse of the internuclear chains occurs before all the solvating diluent has been removed so that the porosity is a result of the removal of the remaining diluent [21]. A relatively higher crosslinking density with enhancing DVB content, as shown in Table 4.13 and Figure 4.20, results in a greater increase in the elastic-retractile force, which would cause the formation of more crosslinked microspheres. As a result, porous polymer beads were obtained.

4.10.2 The effect of diluent composition

The most important factor which controls the heterogeneity of the porous network polymers is the type and amount of diluent. Solvating diluents, generally, produce small pores while nonsolvating ones produce large pores. Therefore, the polymer-solvent interaction is the main factor in determining the pore structures. The thermodynamic affinity of the diluent for the copolymer can be predicted by the knowledge of their solubility parameters. Table 4.20 shows the effect of diluent ratio between a good solvent (toluene) and a poor solvent (heptane) on the appearance of Sty-DVB copolymer beads. Let δ_1 and δ_2 be the solubility parameters of diluent and polymer, respectively, when $|\delta_1-\delta_2| \approx 0$ or < 1.0, miscibility is favored, i.e., the diluent is a good solvent which produces expanded network gels. When $|\delta_1-\delta_2| > 3.0$ (MPa)$^{1/2}$, miscibility does not occur spontaneously so that the diluent separates out, the polymer phase then producing rather large pores. In general, diluent mixtures composed of a good and a poor solvent produce intermediate pore structures.

Table 4.20 Solubility parameters of used diluents

Mixed Toluene/Heptane	Solubility Parameter[a], (MPa)$^{1/2}$	$\|\delta_1-\delta_2\|$	Appearance of copolymer beads [b]
100/0	18.2	0.8	gel
80/20	17.5	1.5	porous
60/40	16.8	2.2	porous
40/60	16.2	2.8	porous
20/80	15.6	3.4	porous

δ_{PS}= 18.6 (MPa)$^{1/2}$ [17], δ_{DVB}= 18.0 (MPa)$^{1/2}$ [17], and $\delta_{PS/DVB}$= 19.0 (MPa)$^{1/2}$ from swelling method (see Figure 4.35)

[a] Calculation from equation 2.12

[b] From SEM

Figures 4.26 and 4.27 show the electron micrographs of the surface morphology of Sty-DVB copolymer beads by the effect of diluent compositions at the magnification of 50 and 100 times. In order to understand the effect of diluent compositions, a series of reaction was carried out at 6% DVB content in which the diluent ratio between toluene and heptane was 100/0, 80/20, 60/40, 40/60, and 20/80. All other reaction parameters including the temperature were held constant. The copolymer synthesized with Tol/Hep = 100/0 and 80/20 had deep channels regularly distributed [Figures 4.26 (a) – (c) and 4.27 (a) – (c)]. The beads obtained with larger contents of the poor solvent (heptane) had less and shallow channels with wider areas irregularly distributed [Figures 4.26 (d), (e) and 4.27 (d), (e)].

Figure 4.28 shows the electron micrographs of the surface morphology of Sty-DVB copolymer beads by the effect of diluent mixture at a high magnification of 3000. Expanded network or gel-type structures is obtained when the good solvent (toluene) is present during the network formation, remained in the gel throughout the polymerization. Expanded networks are thus nonporous [Figure 4.28 (a)]. During the removal of the diluent and drying, the expanded network reversibly collapses; on addition of a good solvent, it reexpands to its earlier state. Reducing the solvating power of the diluent mixture (toluene/heptane) by increasing the heptane fraction could produce the copolymer bead with a higher porous structure due to the occurrence of a higher phase separation [Figure 4.28 (b) – (e)]. The diluent separates partially out of the network phase during the polymerization. Thus, the diluent distributes between the network and diluent phases after synthesis. A part of the diluent acts as a pore-forming agent, whereas the other part remains in the network structure [32].

4.11 Mechanism of Porous Structure Formation

Based on the observation of particle structure, a mechanism for pore formation during Sty-DVB copolymerization by suspension polymerization has been proposed as a two-stage process [31].

4.11.1 Formation of a Macroporous Structure

The first stage in the formation of a macroporous structure is described by Kun and Kunin as a process consisting of three stages [18].

4.11.1.1 The first stage, each particle is composed of a solution of monomers, initiator, and the diluents; it is suspended in an aqueous solution and stabilized with surfactants. Since the DVB has a high reactivity ratio, during the very early stages of the polymerization, DVB-rich copolymer molecules are formed which are composed of straight chains with pendent vinyl groups [31] (During the early stages of reaction, the so called "primary" macromolecules was resulted). When a bifunctional monomer molecule is attacked by a growing radical a pendent double bond is reacted. When such a pendent double bond reacts, in turn, a branch point is formed. Further reaction leads to the increase of intermolecular linkages, with the result of formation of small crosslinked nuclei of polymer [33].

4.11.1.2 The second stage, continued polymerization yields intermolecularly crosslinked microgels and linear molecular chains that are soluble in the monomers. The monomers are transformed into crosslinked copolymer as the reaction proceeds; phase separation occurs between copolymer and linear polystyrene and diluent, which gives a copolymer-rich phase and a diluent-rich phase, the monomers being distributed between the two phases. Linear polymer used as diluent will be in a swollen state because the monomer themselves are good solvents. Since solvated and very lightly crosslinked copolymers can behave, in some respects, like a liquid, the interfacial tension at the polymer-rich phase gives it the low-energy spherical form, and the polymer is separated as a mass of microspheres [31].

4.11.1.3 The third stage, polymer macrogelation occurs and gives a gel type of particle composed of an agglomeration of microspheres. This is depicted schematically in Figure 4.36. The porous structure of these copolymers consists of globules; the smallest, rather spherical particles of about 100-200 Å in diameter are the "nuclei", and the aggregation of these nuclei results in the microspheres with diameters of 500-1,000 Å; the microspheres are aggregated again in particles of about 2,500-10,000 Å in diameter [34].

4.11.2 Pore Formation

The second stage in pore-structure formation is the binding together and fixation of the microspheres and agglomerates. As the polymerization and formation of microspheres continue, the microspheres are bound together by the polymerization of the monomers, which have a higher percentage of monovinyl components in composition, and act to solvate the microspherical polymers [31]. Primarily, internally compact crosslinked particles possessing microgel character are formed, which are linked through their peripheric double bonds to yield a gel [35]. Some fraction of the high molecular weight linear polystyrene is trapped within the microspheres and agglomerates while they are binding together; the inclusion of linear polymer is dependent on the nature of linear polymer and the extent of phase separation between the diluent phase and the copolymer phase. It is during this stage that the macroporous

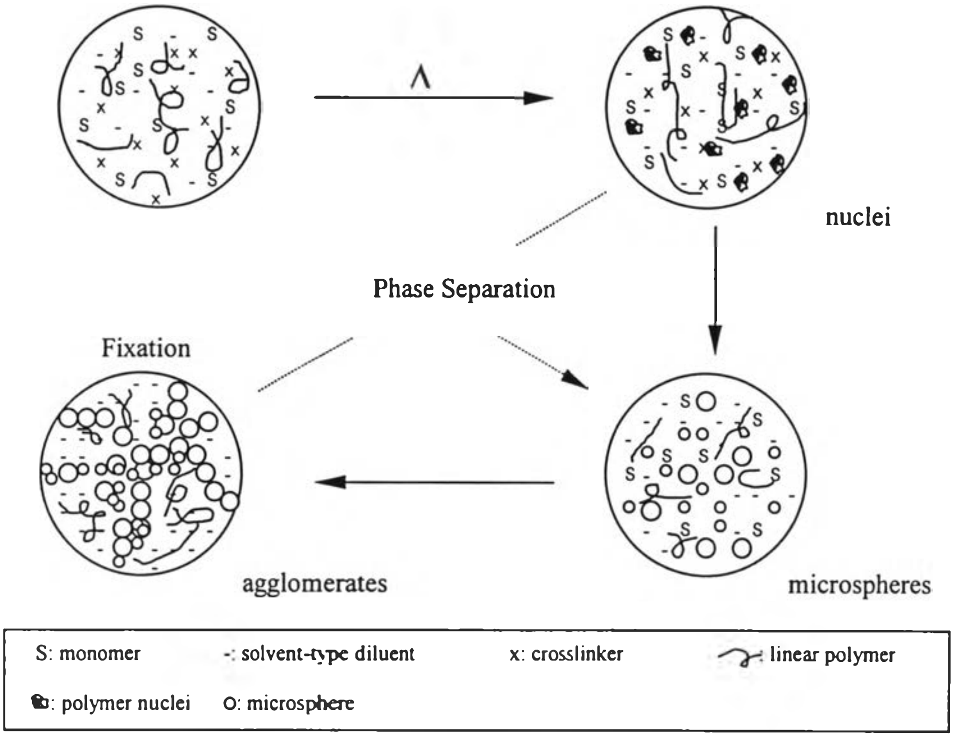


Figure 4.36 A schematic model for the process of pore formation in the copolymerization stage [31].

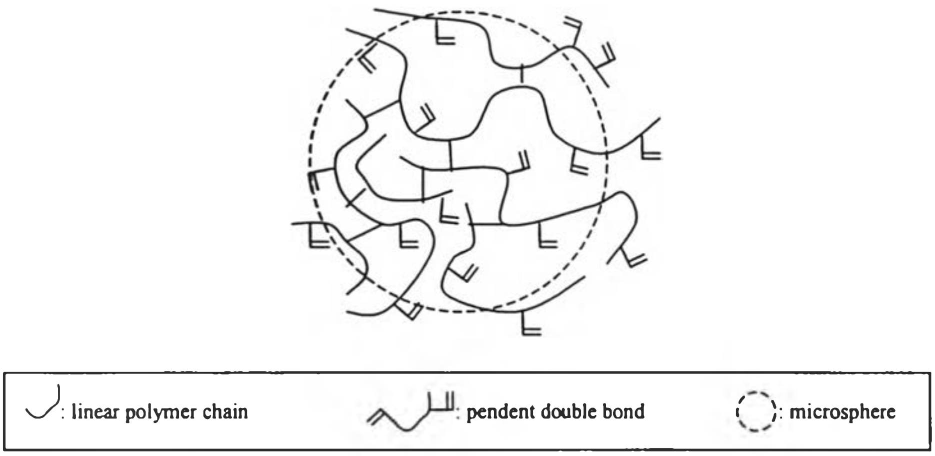


Figure 4.37 Schematic model of the internally compact crosslinked particles possessing microgel [35].

structure is actually formed. Voids between microspheres and agglomerates are filled with diluent. In the diluent phase, entanglement of linear polymer will take place, depending on the molecular weight of the polymer and interaction between solvent and linear polymer, thus explaining the sensitivity of the pore size distribution to the molecular weight of the linear polymer. After the removal of the diluents, polymer particles with macroporous structure are obtained [31].

4.12 Glass Transition Temperatures of the Copolymer

In this study, the glass transition temperatures and incremental changes in heat capacity at Tg were measured calorimetrically. The DSC thermograms of the synthetic copolymer beads with various contents of DVB are shown in Figure 4.38. The Tg values was found in the range of 99-129 °C. It can be seen that varying the DVB contents as a crosslinking agent of the copolymer has a direct impact on glass transition of the resulting copolymer. The relation between Tg and DVB contents is presented in Figure 4.41. The higher the DVB content, the higher the Tg is observed. It is believed that the limited macromolecular relaxation by crosslinks in network reduces a chain flexibility and elevates the Tg of the beads [37]. Furthermore, the DSC thermograms of the synthesized copolymer beads with various toluene/heptane ratios of 100/0, 80/20, 60/40, 40/60, and 20/80 as diluents for the monomers are shown in Figure 4.39. The Tg range is 107.09 °C, 107.43 °C, 107.91 °C, and 108.88 °C, respectively. The results indicate that the variation of toluene/heptane ratio insignificantly affect Tg of the beads.

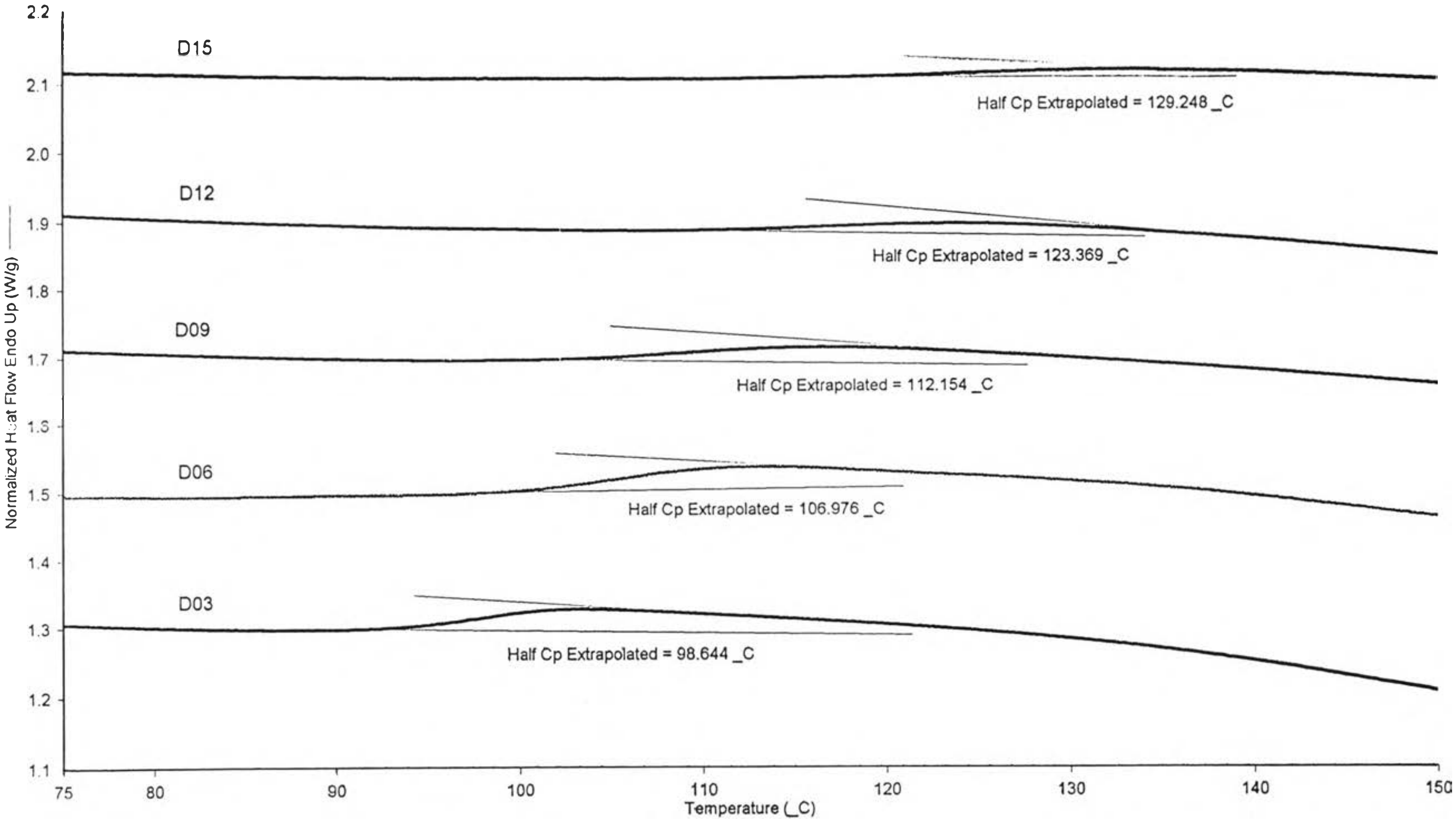


Figure 4.38 DSC traces of styrene-divinylbenzene copolymers prepared by varying crosslinking agent concentration.

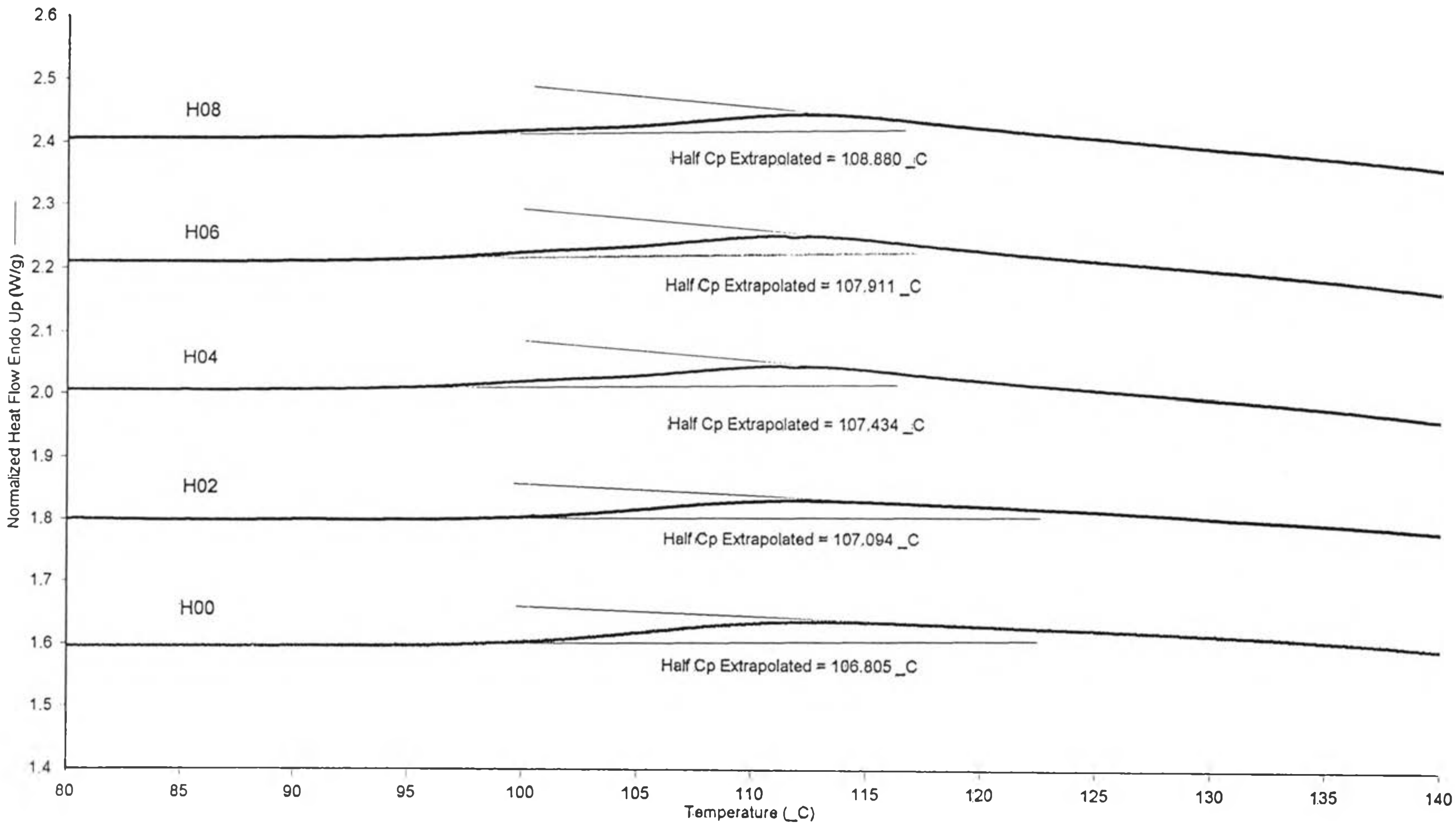


Figure 4.39 DSC traces of styrene-divinylbenzene copolymers prepared by varying diluent composition.

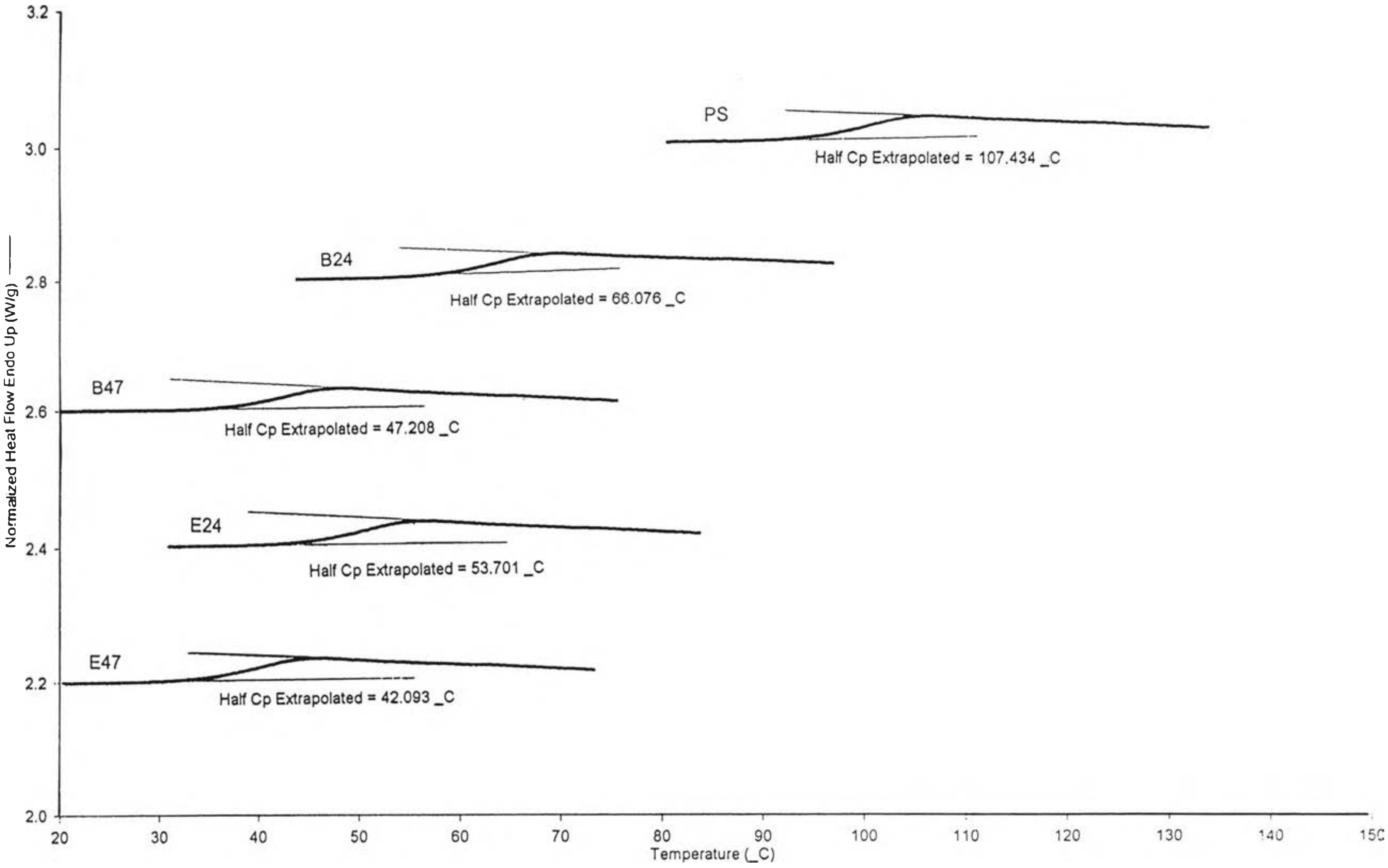


Figure 4.40 DSC traces of styrene-divinylbenzene copolymers prepared by varying monomer composition.

Finally, the DSC thermograms of the terpolymers, synthesized with different styrene/*n*-BA and styrene/2-EHA feed ratio are shown in Figures 4.40. The Tg values were found in the range of 42-107 °C. It can be seen that varying the feed ratio of the terpolymer has a direct impact on glass transition of the resulting terpolymers. Figure 4.42 presents the relation between Tg and *n*-BA content and 2-EHA content. The Tg of the terpolymer decreased as the amount of *n*-BA and 2-EHA increased. This effect is due to the low glass transition of P-*n*-BA (-54 °C), P-2-EHA (-50 °C) [38], the terpolymer rich in *n*-BA and 2-EHA possess the lowest Tg at 47.21 °C and 42.09 °C, respectively, whereas the styrene-divinylbenzene copolymer with 6 %wt DVB has the highest Tg at 107 °C.

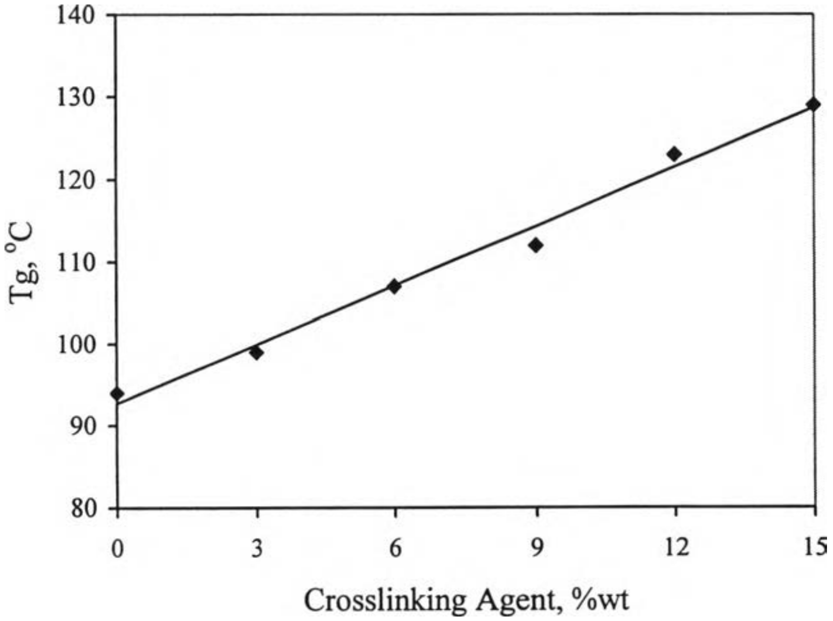


Figure 4.41 Effect of crosslinking agent concentration on glass transition temperature of the copolymer beads.

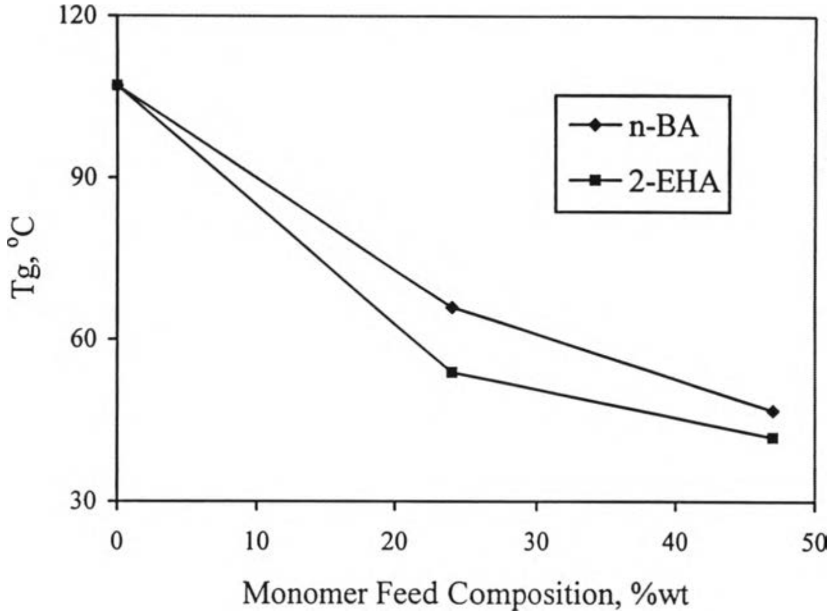


Figure 4.42 Effect of monomer feed composition on glass transition temperature of the terpolymers.

4.13 Absorption-Desorption and Diffusion Coefficient in Toluene-Heptane Solution of the Copolymer Beads [the Toluene Volume Fraction (*z*) = 0.5]

4.13.1 Absorption

The absorption of the imbiber beads in toluene-heptane solution [the toluene volume fraction (*z*) = 0.5] was determined microscopically based on an increase in bead size upon swelling in solvent mixture. Toluene and heptane are the aromatic solvent and aliphatic solvent, respectively. Appendix G shows the increase in bead diameter and volume with swelling time. Ingress of solvent mixture into a dry bead was readily visible, but the polymer continued to swell well after uniformly transparent appearance had been reached [39].

Figures 4.43, 4.45, 4.47, 4.49, and 4.51 show the variation of bead volume with swelling time. The curves comprise three stages:

I. An initial stage of the high sorption rate can be easily observed due to the solvation of network chains. The main driving force of this process is the changes in the free energies of mixing 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.

Considering the increasing of bead volume with swelling time for the beads prepared by using *n*-butyl acrylate and 2-ethyl hexyl acrylate, as the third comonomer, the initial stage of sorption was about 30 min., the bead volume increased rapidly since the network began to expand by absorbing the surrounding solvent. Finally, the swollen bead reached a stationary state in equilibrium with the surrounding solvent within 60 min. The calculation of the diffusion coefficient was demonstrated in Appendix H and the diffusion coefficient of the copolymers is shown in Table 4.21.

Table 4.21 shows that the diffusion coefficient of the copolymer beads in toluene-heptane solution [the toluene volume fraction (*z*) = 0.5] increased when the third comonomer was changed due to the chemical structures of the copolymer with the third comonomer, either *n*-butyl acrylate or 2-ethyl hexyl acrylate, contains both aliphatic portion and aromatic portion. Therefore, the absorption of toluene- heptane solution of the copolymer with the third comonomer becomes greater than the

Table 4.21 Diffusion coefficient of the copolymer beads in toluene-heptane solution [the toluene volume fraction (z) = 0.5]

Runs	Diffusion Coefficient (cm^2/sec)		
	Absorption 1st	Absorption 2nd	Absorption 3rd
PS	6.40×10^{-6}	6.26×10^{-6}	6.39×10^{-6}
B24	1.05×10^{-5}	1.03×10^{-5}	1.03×10^{-5}
B47	1.08×10^{-5}	1.06×10^{-5}	1.04×10^{-5}
E24	1.12×10^{-5}	1.10×10^{-5}	1.08×10^{-5}
E47	1.52×10^{-5}	1.52×10^{-5}	1.53×10^{-5}

Sty-DVB copolymer containing only the aromatic portion. It was noted that the diffusion coefficient of the copolymer increased with increasing the chain length of the aliphatic portion, it may be a result of the chemical nature of the long chain aliphatic portion resemble that of the heptane portion in the mixed solvent.

Table 4.22 Solubility of the synthetic copolymers

Runs	Solubility Parameter [a], $(MPa)^{1/2}$	$\lvert\delta_1-\delta_2\rvert$ [b]
PS	19.0	2.4
B24	18.8	2.2
B47	18.6	2.0
E24	18.3	1.7
E47	18.2	1.6

[a] From swelling method (see Figure 4.35)

[b] δ_2 is the solubility of toluene-heptane solution, calculated from equation 2.12

The absorption of the copolymers can be considered as a result of solvation of the network chains. The extent of network solvation is related to the interaction between solvent molecules and the network chains or the polymer-solvent interaction, which is presented in the term of solubility parameter, as shown in Table 4.22. When the difference of these parameters for polymer and solvent is smaller, the solvation is more favored, which would cause an increase in the rate of solvation of the copolymers. As a result, it also leads to an increase in the diffusion coefficient of the terpolymers as shown in Table 4.21.

4.13.2 Desorption

When a swollen bead was placed on an absorption substance such as a filter paper, the solvent diffused from the bead and got into the filter paper. It may be possible to state that the interaction between solvent and the substrate is higher than the interaction between the solvent and the polymer network. Appendix G shows the bead diameter and volume upon desorption at different times.

Figures 4.44, 4.46, 4.48, 4.50, and 4.52 show the variation of swollen bead volume with time. These curves can be divided into three stages:

I. An initial stage of the high desorption rate on the cellulosic substrate.
II. A second stage of slow desorption rate.
III. A third stage of no solvent loss (plateau) or a very low, undetectable desorption rate.

For the decrease of the swollen bead volume with time for the beads prepared using *n*-butyl acrylate and 2-ethyl hexyl acrylate, as the third comonomer. The initial

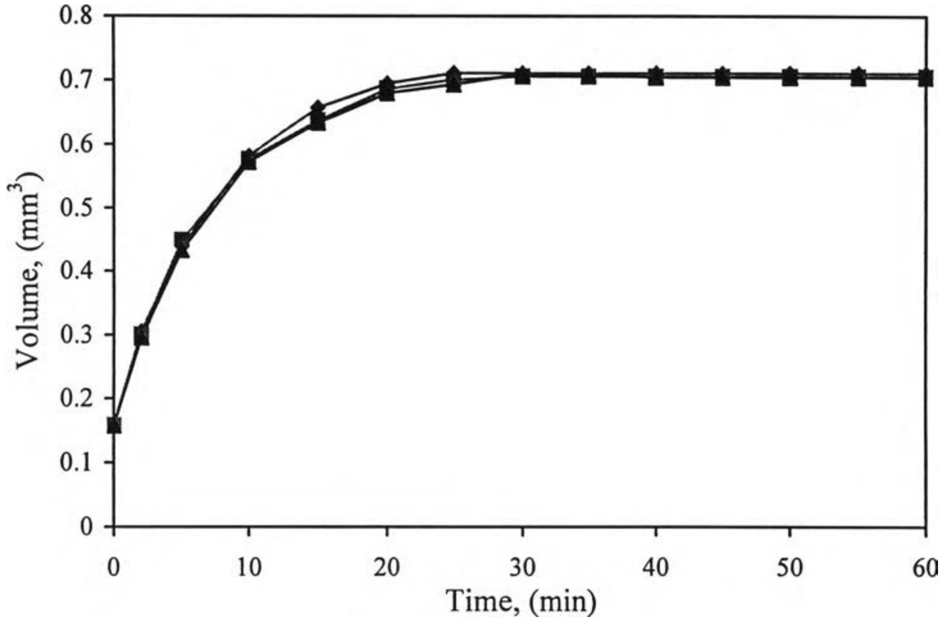


Figure 4.43 Absorption of bead with time: Run PS (The curves ■■■ and ▲▲▲ are for absorption of Run PS 2nd and 3rd)

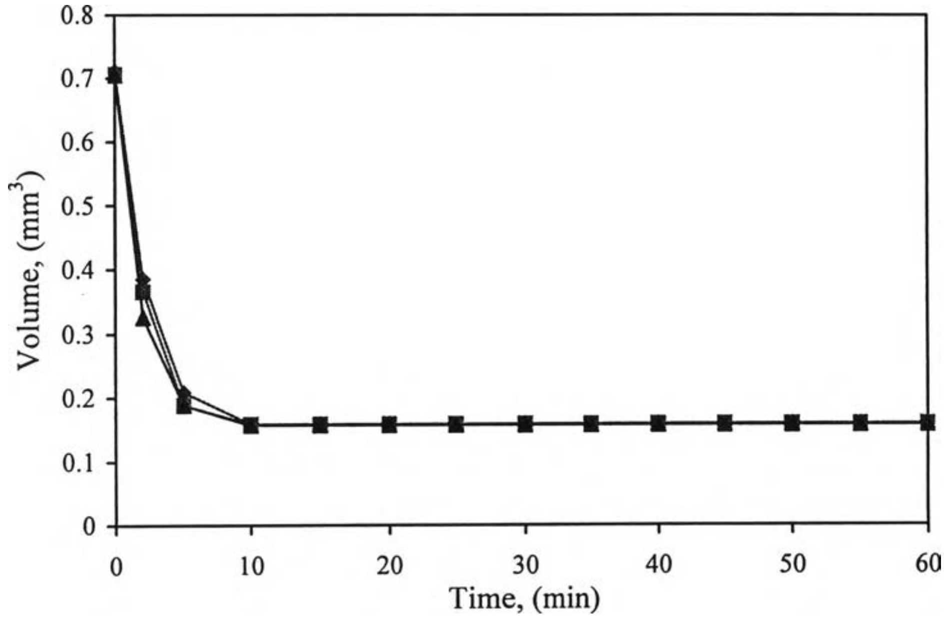


Figure 4.44 Desorption of bead with time: Run PS (The curves ■■■ and ▲▲▲ are for desorption of Run PS 2nd and 3rd)

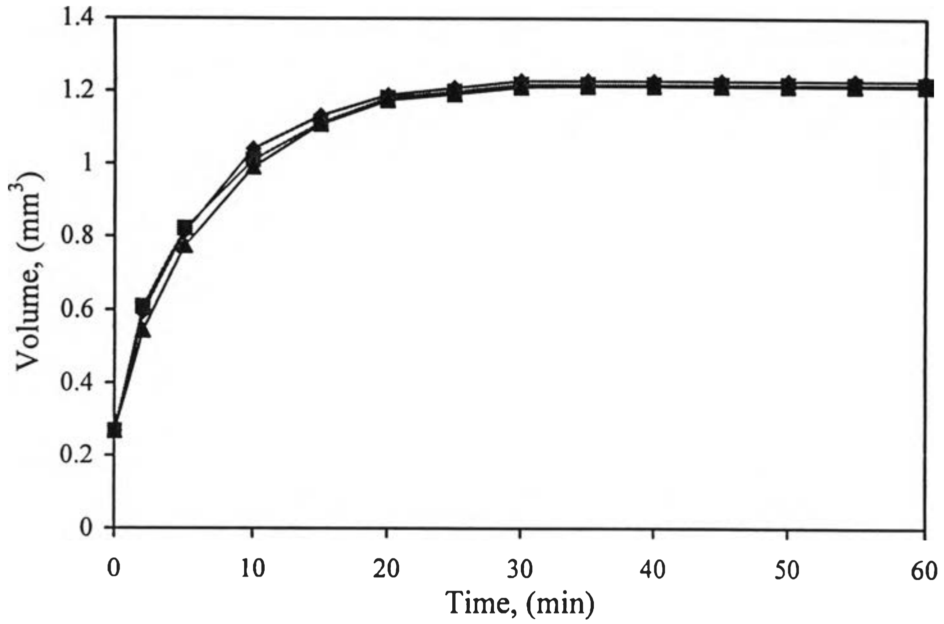


Figure 4.45 Absorption of bead with time: Run B24 (The curves ■■■ and ▲▲▲ are for absorption of Run B24 2nd and 3rd)

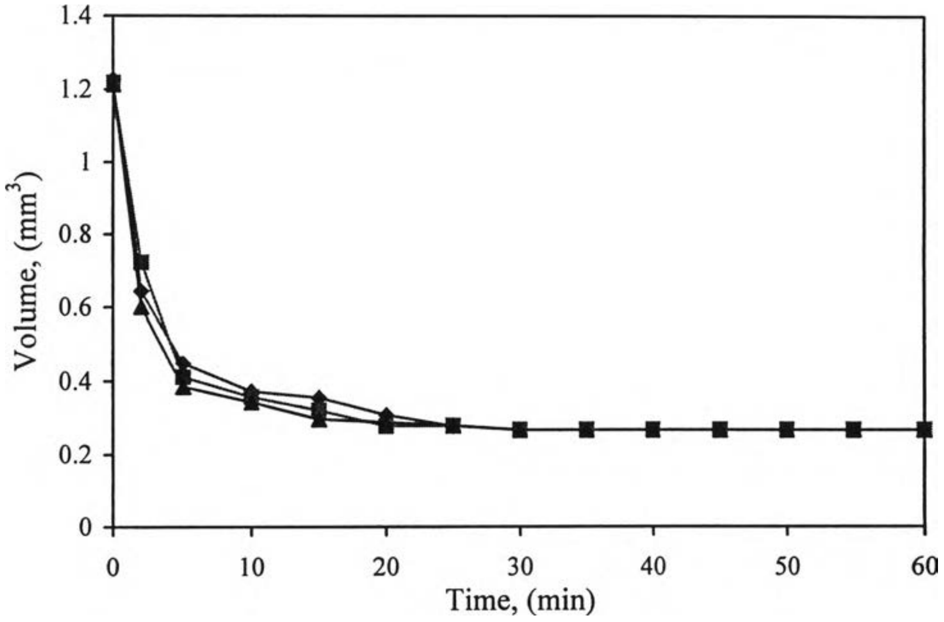


Figure 4.46 Desorption of bead with time: Run B24 (The curves ■■■ and ▲▲▲ are for desorption of Run B24 2nd and 3rd)

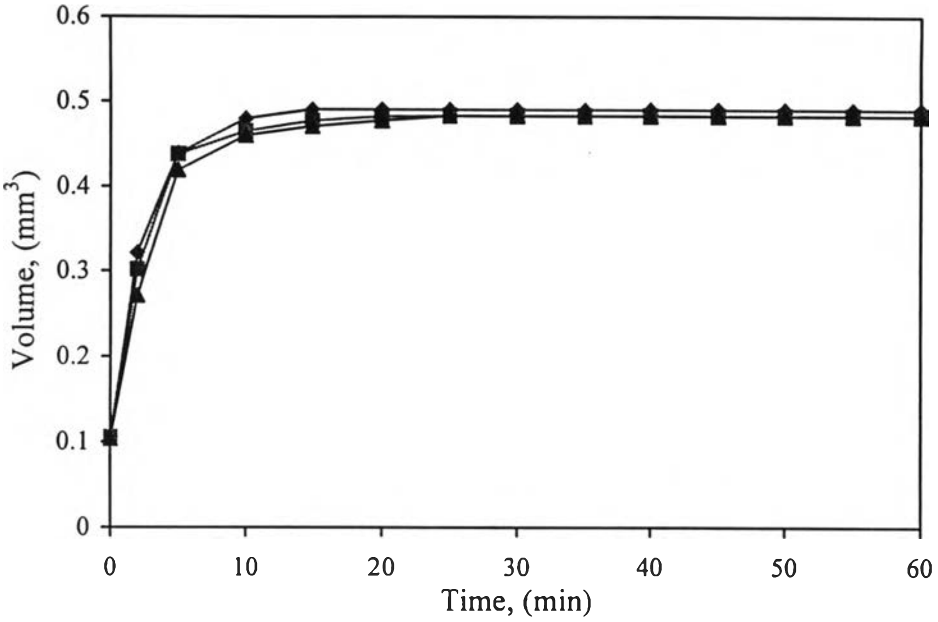


Figure 4.47 Absorption of bead with time: Run B47 (The curves ■■■ and ▲▲▲ are for absorption of Run B47 2nd and 3rd)

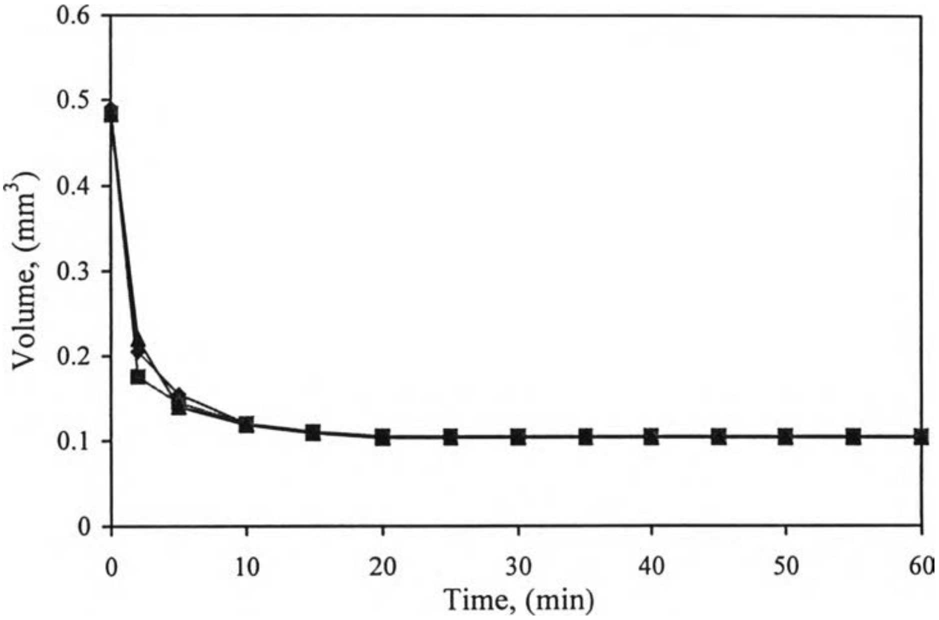


Figure 4.48 Desorption of bead with time: Run B47 (The curves ■■■ and ▲▲▲ are for desorption of Run B47 2nd and 3rd)

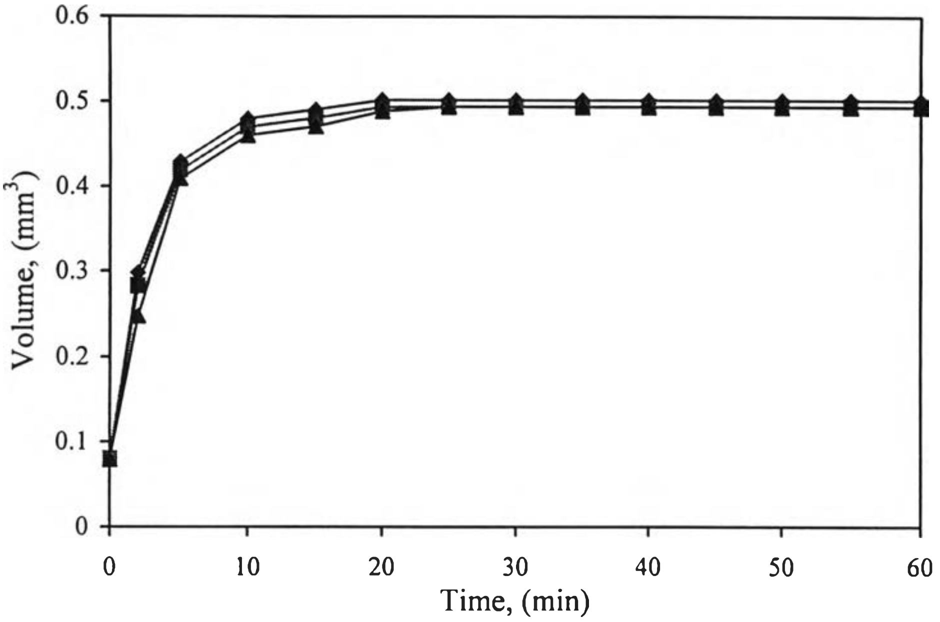


Figure 4.49 Desorption of bead with time: Run E24 (The curves ■■■ and ▲▲▲ are for absorption of Run E24 2nd and 3rd)

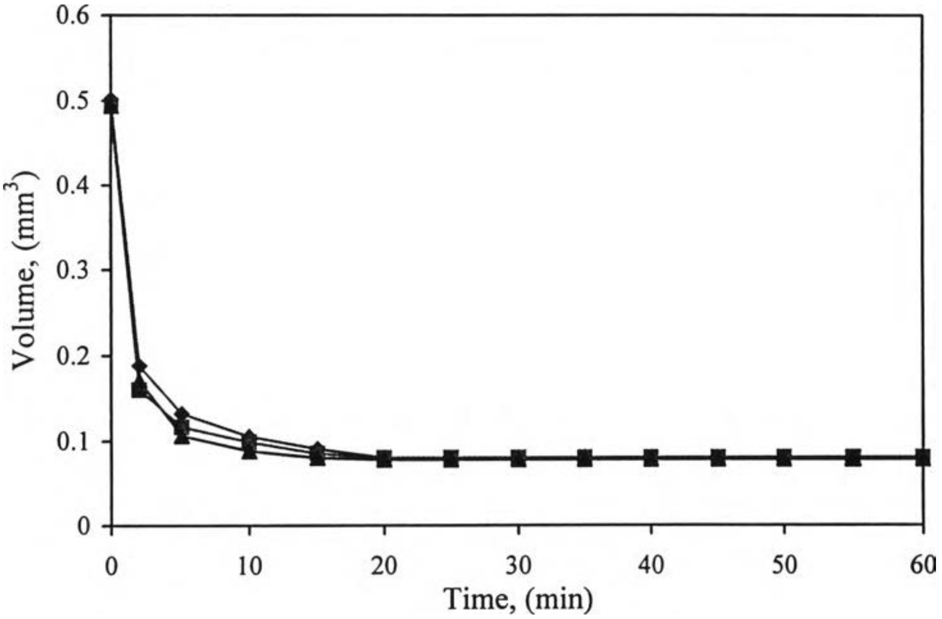


Figure 4.50 Desorption of bead with time: Run E24 (The curves ■■■ and ▲▲▲ are for desorption of Run E24 2nd and 3rd)

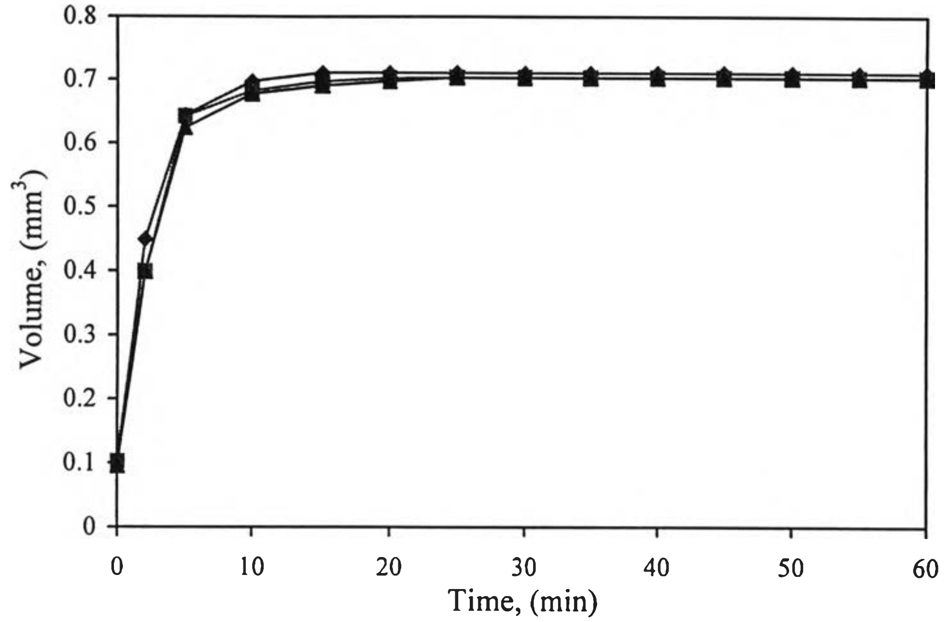


Figure 4.51 Absorption of bead with time: Run E47 (The curves ■■■ and ▲▲▲ are for absorption of Run E47 2nd and 3rd)

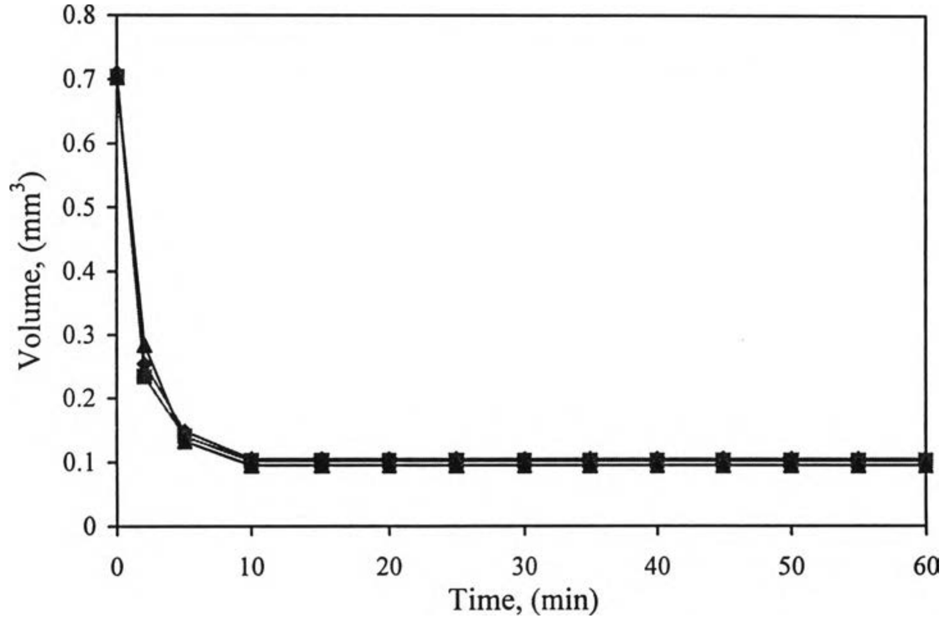


Figure 4.52 Desorption of bead with time: Run E47 (The curves ■■■ and ▲▲▲ are for desorption of Run E47 2nd and 3rd)

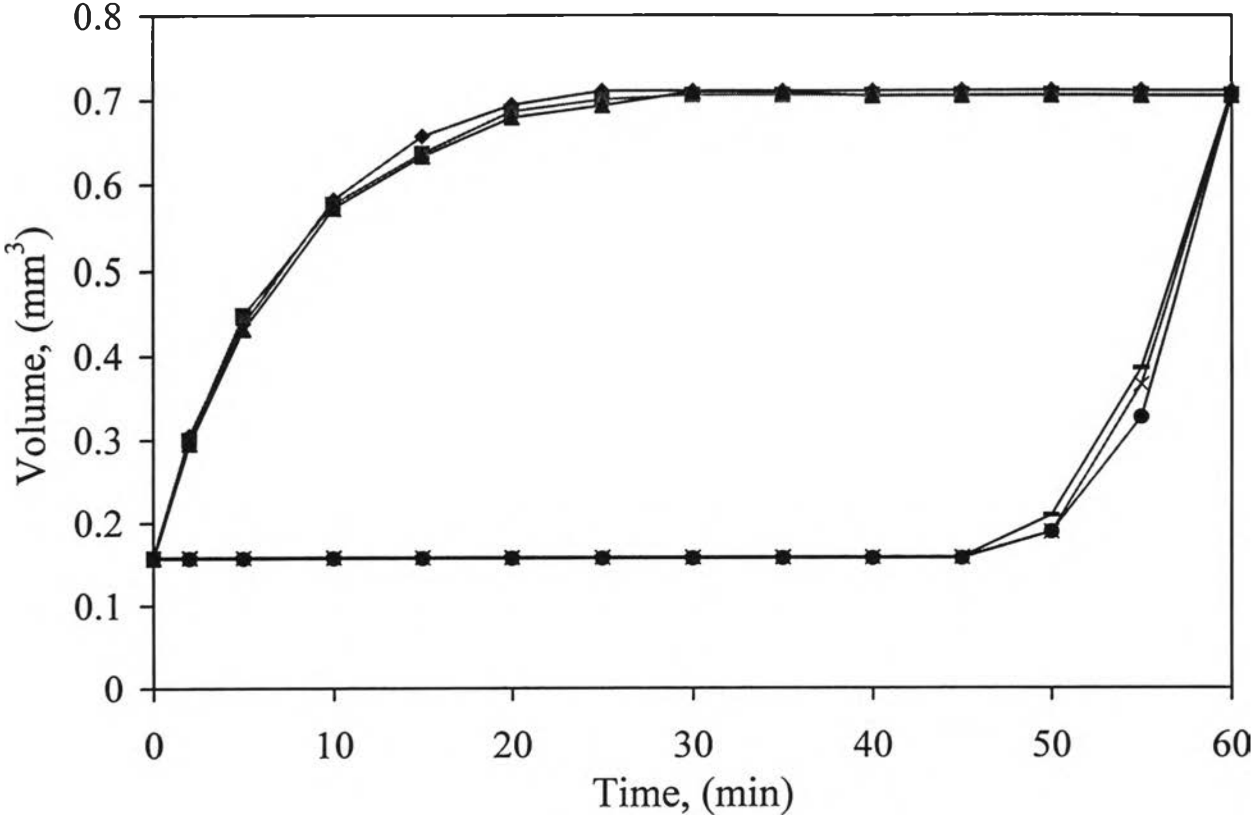


Figure 4.53 Absorption and desorption of bead with time: Run PS (The curves ■■■, ▲▲▲, ×××, and ●●● are for absorption 2nd, absorption 3rd and desorption 2nd, desorption 3rd, respectively).

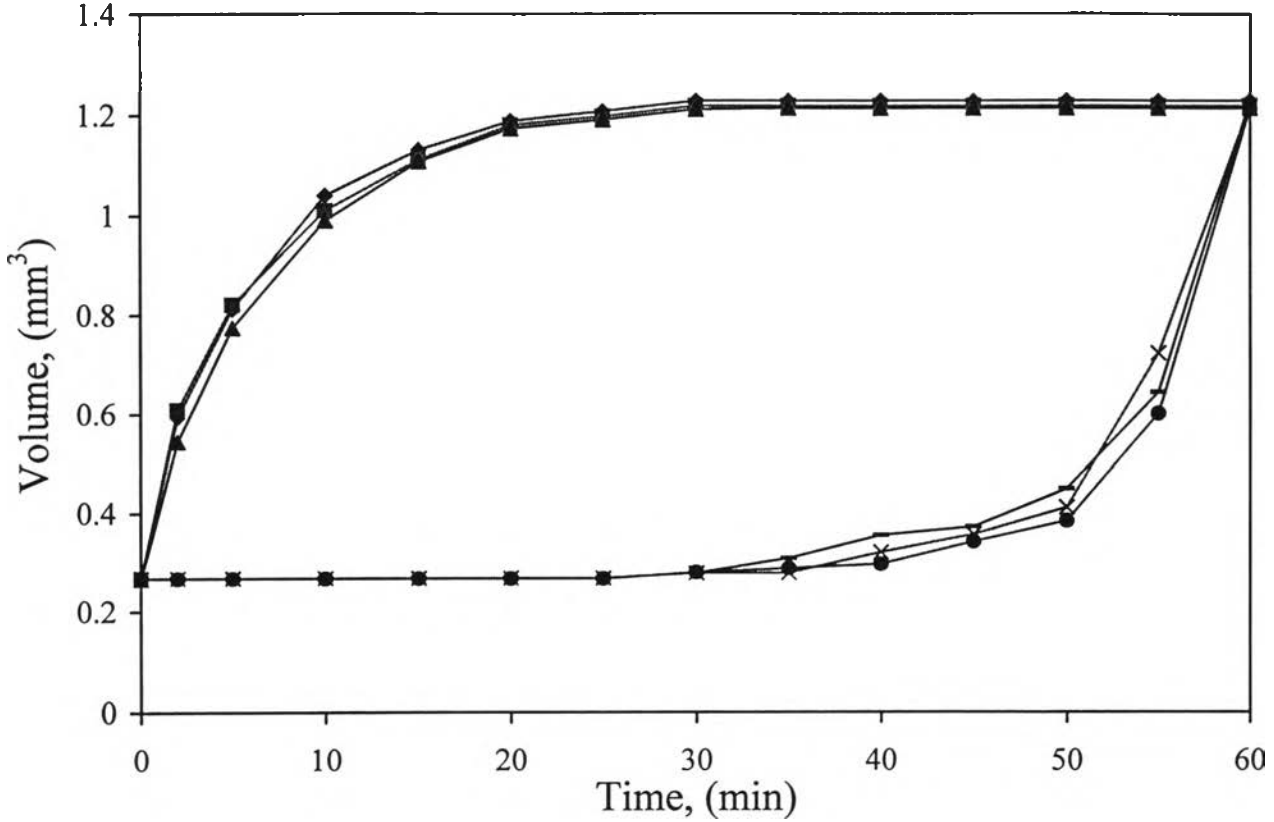


Figure 4.54 Absorption and desorption of bead with time: Run B24 (The curves ■■■, ▲▲▲, ×××, and ●●● are for absorption 2nd, absorption 3rd and desorption 2nd, desorption 3rd, respectively).

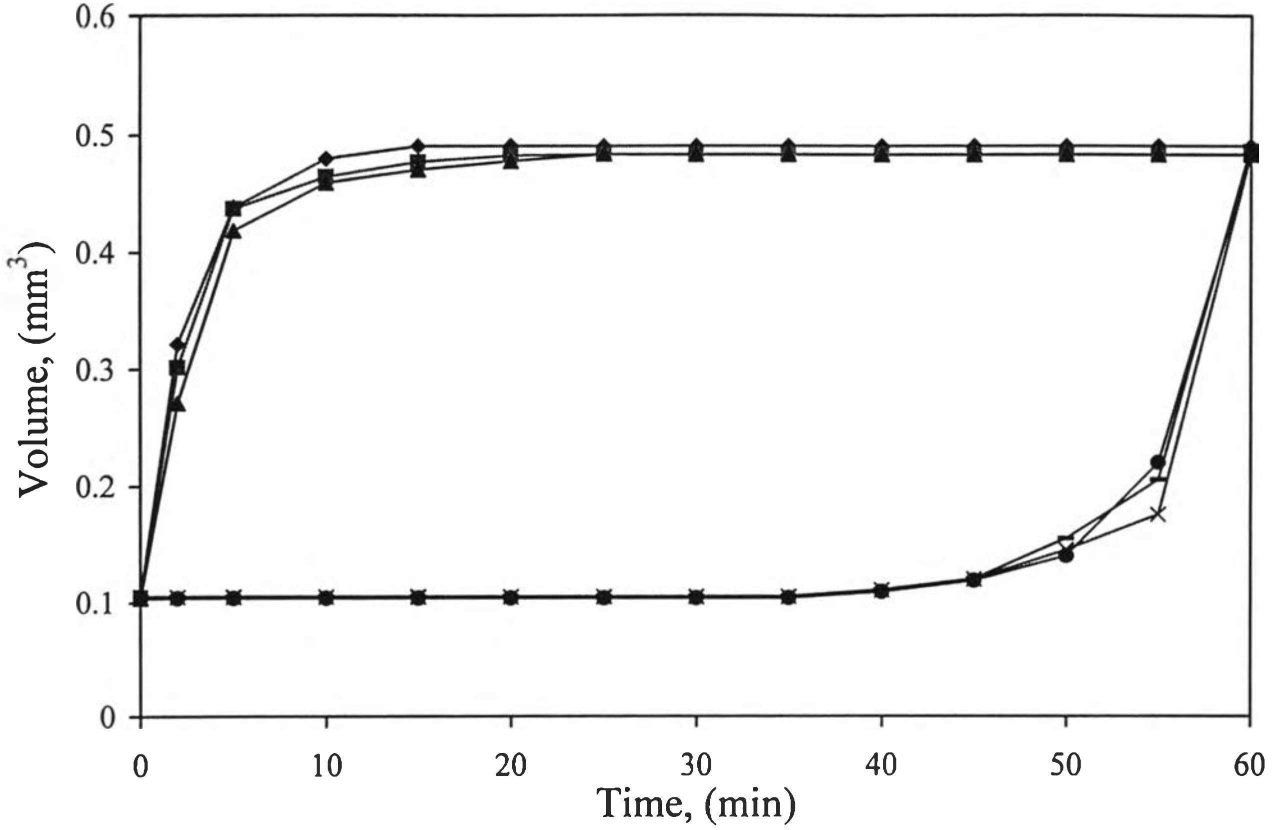


Figure 4.55 Absorption and desorption of bead with time: Run B47 (The curves ■■■, ▲▲▲, ×××, and ●●● are for absorption 2nd, absorption 3rd and desorption 2nd, desorption 3rd, respectively).

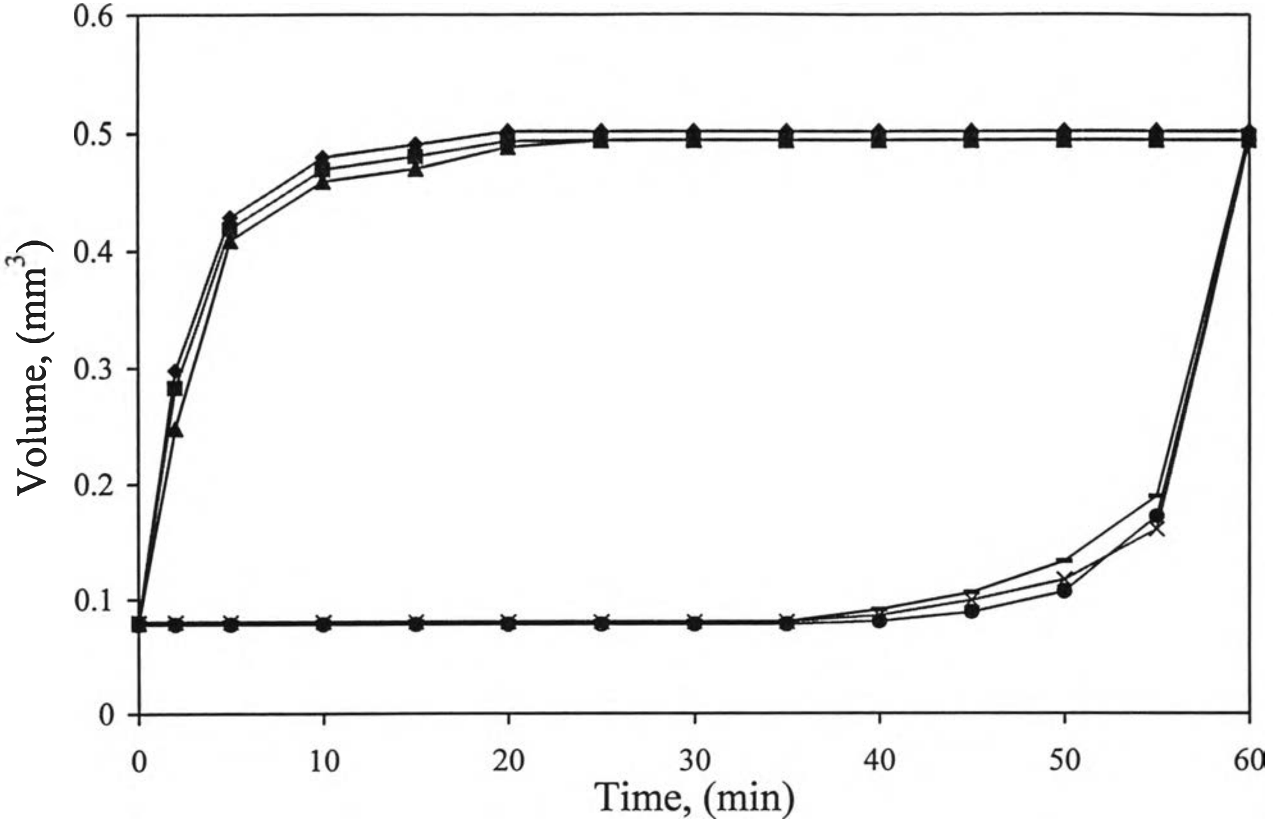


Figure 4.56 Absorption and desorption of bead with time: Run E24 (The curves ■■■, ▲▲▲, ×××, and ●●● are for absorption 2nd, absorption 3rd and desorption 2nd, desorption 3rd, respectively).

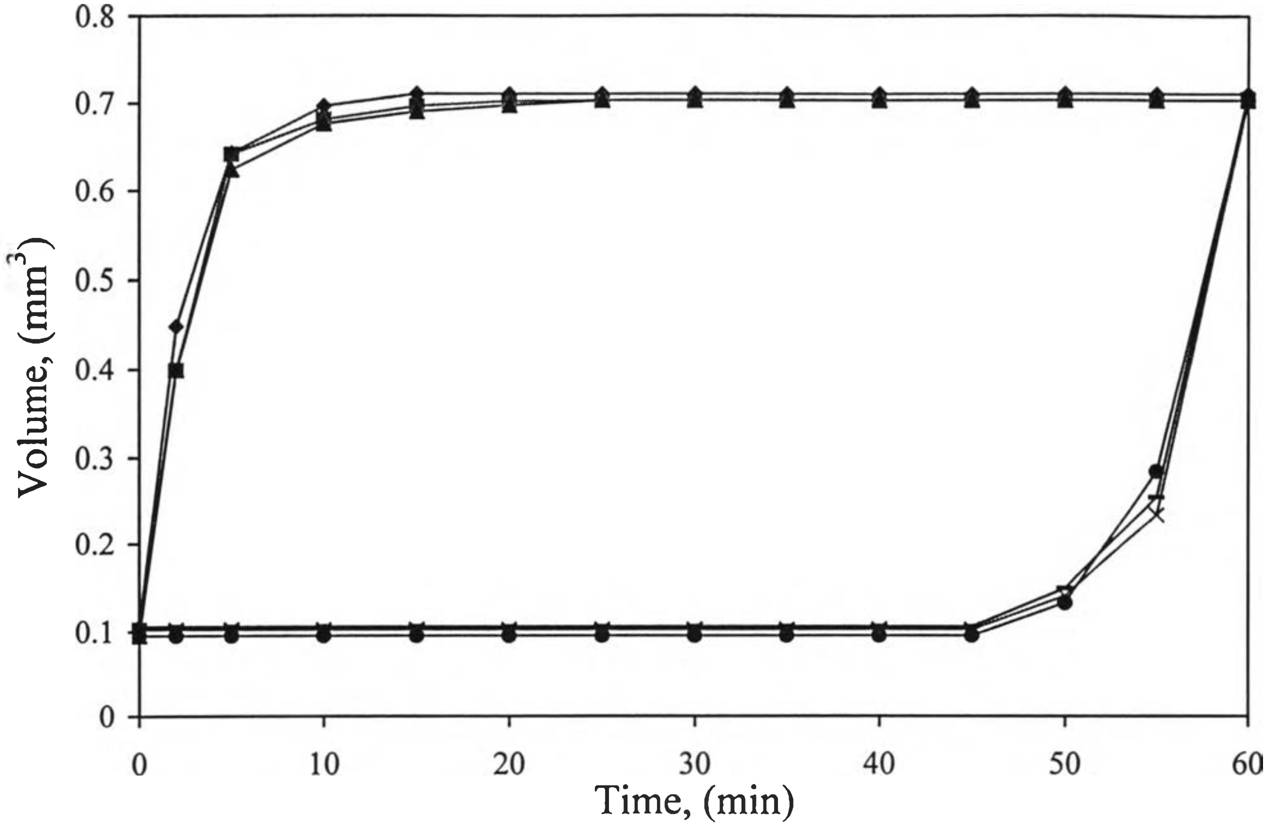


Figure 4.57 Absorption and desorption of bead with time: Run E47 (The curves ■■■, ▲▲▲, ×××, and ●●● are for absorption 2nd, absorption 3rd and desorption 2nd, desorption 3rd, respectively).

rate of desorption was about 10 min., and then the swollen bead lost all solvent within 40 min. after the start of desorption process.

The copolymer beads could be used to absorbed and desorbed toluene-heptane solution for many cycles. The repeated absorption and desorption behavior of the second and third cycles were also the same as the first cycle as shown in Figures 4.53 – 4.57. The very slightly difference of volume between first cycle absorption and second cycle absorption may be possible to state that (1) the network of the copolymer beads was changed and (2) the homopolymer was dissolved. During absorption and desorption the copolymer beads still retained their spherical shape throughout the cycles; they did not collapse after repeated uses. The copolymer beads could be applied to absorb and desorb the waste solvents and oil.

4.14 Absorption of Mixed Solvent Layer on Water Surface of the Copolymer Beads

Since the copolymer or terpolymer beads can absorb and desorb several organic solvents, they are expected to perform the same function. As such the beads should be able to absorb the spilled organic solvents or spilled oil on a water surface. The terpolymer beads (Run E47) were used for absorbing a series of mixed solvent between aromatic and aliphatic or naphthenic portion, toluene/heptane and toluene/cyclohexane at 25/75, 50/50, and 75/25 floating on the water surface. From Table 4.23, it was always found that the mixed solvent are on the water surface, the swelling ratio of the terpolymer beads is slightly larger than those of the mixed solvent without water. It may be ascribed to two effects: these mixed solvent could form an emulsified mixture with water (emulsification), and it is possible that the emulsified water is partly absorbed due to the presence of acrylate functionality, which could penetrate to the interchain vacancies of the expanded terpolymer network during absorption [24].

Table 4.23 Swelling ratio of the synthetic copolymer beads in solvent mixtures

Solvent Composition	Solubility Parameter	Swelling Ratio	
		without water	within water
Toluene	18.2	8.2	9.1
Heptane	15.3	2.7	3.2
Cyclohexane	16.8	5.1	5.8
Toluene:heptane 0.25:0.75	16.0	6.8	7.3
Toluene:heptane 0.5:0.5	16.8	7.2	7.8
Toluene:heptane 0.75:0.25	17.5	7.4	8.5
Toluene:cyclohexane 0.25:0.75	17.2	7.5	8.0
Toluene:cyclohexane 0.5:0.5	17.5	7.6	8.4
Toluene:cyclohexane 0.75:0.25	17.9	7.8	8.8

Furthermore, the swelling of the terpolymer beads (Run E47) in pure solvents and mixed solvent is also shown in Table 4.23. The result shows that the swelling ratio of the terpolymer beads (Run E47) in pure toluene was higher than those of the mixed solvent containing toluene-to-heptane ratio, and toluene-to-cyclohexane ratio of 25/75, 50/50, and 75/25. Based on the concept of solubility parameter, pure toluene is the good solvent for the copolymer beads; when the poor solvent (heptane and cyclohexane) was added into the good solvent (toluene), the solubility parameter of the mixed solvent decreases. This effect leads to a decrease in the swelling ratio.

4.15 Determination of Polymer Bead Density

The densities of styrene-divinylbenzene polymer beads were determined by the pycnometric technique which test method (ASTM D-792) was described in Appendix A. The densities of the polymer beads were reported to be, (about 1 g/cm^3), in the range of 0.9375–1.0581 g/cm^3 (see Table 4.24); the beads could therefore float on the water surface. This is to confirm that all the beads are porous when comparing to the general density of polystyrene (1.04–1.06 g/cm^3). Because of their light density and buoyancy, the absorbing beads could be removed from the water surface easily after they absorb spilled solvents to their full capacity. It is interesting that the beads of series H00–H08 have the relatively lowest density, pore properties were then investigated.

Table 4.24 The densities of the copolymers

Runs	Density g/cm^3
M06	1.0360
M08	1.0441
M10	1.0464
M17	1.0554

Runs	Density g/cm^3
P05	1.0469
P10	1.0464
P15	1.0434
P20	1.0370

Table 4.24 (continued)

Runs	Density g/cm^3
R20	1.0560
R27	1.0464
R30	1.0449
T60	1.0373
T70	1.0464
T80	1.0473
t06	1.0291
t08	1.0397
t10	1.0464
t15	1.0488
I01	1.0414
I05	1.0464
I10	1.0547
I20	1.0581

Runs	Density g/cm^3
D03	1.0496
D06	1.0464
D09	1.0463
D12	1.0399
D15	1.0357
H00	1.0464
H02	1.0364
H04	1.0266
H06	1.0129
H08	0.9375
B24	1.0245
B47	1.0232
E24	1.0199
E47	1.0179

4.16 Determination of Pore Properties of Copolymer Beads

The mercury porosimetry technique was used to investigate the average pore diameter, surface area and pore volume of the polymer porous beads. The principle of this method was described in Appendix B. In this study, the copolymer beads which have diameter in the range of 0.84-2.0 mm was selected to determined in this technique. The average pore diamemter, surface area, and pore volume of the polymer beads shown in Table 4.25 were of about 0.0133–0.0212 μm, 17.466–44.057 m^2/g and 0.0581–0.2337 cm^3/g, respectively.

Table 4.25 Pore properties of the styrene-divinylbenzene copolymer

Parameter	H00	H02	H04	H06	H08
Average pore diameter, μm	0.0133	0.0137	0.0141	0.0167	0.0212
Surface area, m^2/g	17.466	25.248	32.764	39.219	44.057
Pore volume, cm^3/g	0.0581	0.0863	0.1158	0.1634	0.2337

Table 4.25 shows the variation of pore properties, average pore diameter, surface area, and pore volume of the resulting copolymers as the diluent composition shifted from the good solvent (toluene) towards the poor solvent (heptane). We can see that increasing the fraction of heptane diluent increase the copolymer pore diameter and pore volume. When the solvating power changes, the formation of porous structure are the difference between critical concentrations for the polymer chains, to precipitate and agglomerate in the microspheres, and the entanglement degree of nuclear and internuclear chains. In the presence of a solvating diluent (toluene), the nuclear chains become less entangled. The tendency of nuclei to agglomerate favors the formation of longer and less entangled internuclear chains. The microspheres are thus rather small and the pore are consequently small (Run PS). On the other hand, when the diluent solvating power is reduced, the precipitated polymer chains tend to agglomerate rapidly to form large microspheres; consequently, the diluent molecules distribute preferentially among the microsphere agglomerates to form big pores [21, 22].