# CHAPTER 4

# RESULTS AND DISCUSSION

In this work, the effects of solvent and crosslinking agent concentrations on the polymeric microsphere morphology and the degree of the polymer swelling were the prime targets to investigate. The SPG pore sizes of 0.90, 5.25 and 9.25 μm were used. The resulting polymers were characterized for the following properties: surface properties, particle size, surface area (BET), pore size distribution measurement, porosity and thermal properties.

## 4.1 Effect of the crosslinking agent (EGDMA) on properties of polymer particles

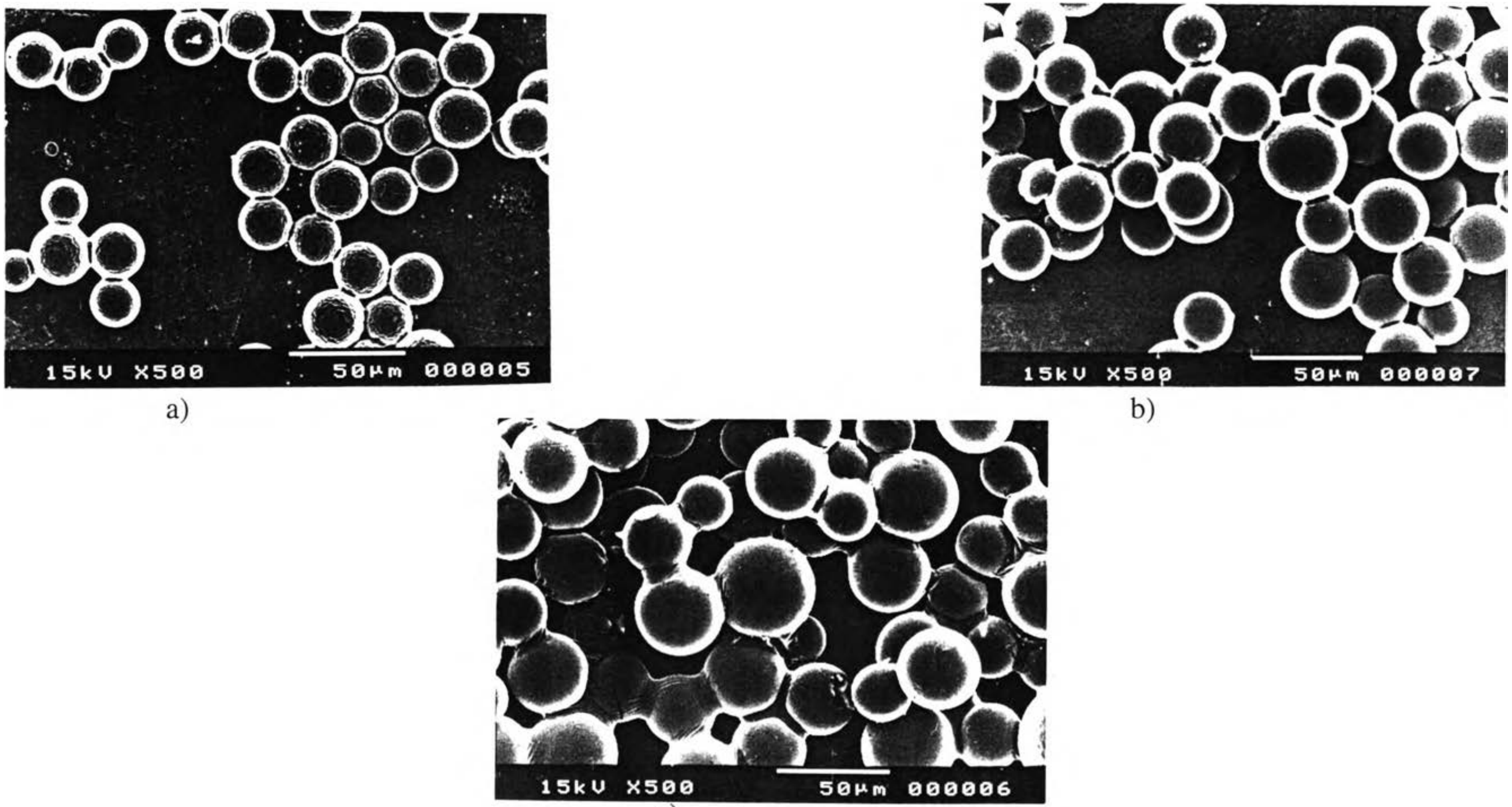
### 4.1.1 The surface feature of polymer particle microspheres

The resulting polymers, synthesized with 20% by weight of EGDMA and 70% by weight of solvents, heptane and toluene, based on the total weight of the monomer and crosslinking agent adhered together and coagulated because a small amount of the crosslinking agent could form networks between the particles as shown in Figure 4.1. The amount of EGDMA was not enough to overcome the rubbery nature (low Tg) of 2-EHA, and the particles adhered together, forming a neck-like structure. The solid powder was obtained when the concentration of EGDMA was increased more than 20% based on the total weight of the monomer and crosslinking agent because the high amount of crosslinking agent was used to form high Tg networks successfully and the particles did not coagulate.

Table 4.1 shows the effect of EGDMA concentration at 35, 45 and 70% by weight of heptane based on the total weight of the monomer and crosslinking agent. We found that an increase in EGDMA concentration resulted in higher, coarse porous spheres as shown in Figure 4.2. The sample no. 8 in Figure 4.2 gave an interesting morphology because the walls of the polymer particles almost collapsed. Increasing in the crosslinking agent concentration resulted in an increase in the elastic-retractile force, which would cause the formation of a more crosslinked microsphere and gave a higher degree of phase separation [40]

### 4.1.2 The degree of the polymer swelling

As shown in Table 4.1 the percentage by weight of EGDMA concentration was varied with 20, 30, 35 and 40% based on the weight of the monomer and crosslinking agent at a constant content of the solvent. The results of solvent swelling of these polymer particles prepared with the ratio of solvent and crosslinking agent are shown in Figure 4.3. When toluene was used as penetrant at the constant amounts 35 and 45% weight of heptane, the highest swelling degree was obtained at 30% of EGDMA but at 70% weight of heptane, there was no trend for the swelling degree. However, the polymer particle was ruptured after swelling at 70% weight of heptane with 40% weight of EGDMA (Sample no. 8) because increasing in the amount of crosslinking agent resulted in a decrease in the polymer chain mobility and free volume [34]. Kim et al. [34] also obtained ruptured samples after swelling in a good solvent if the highly crosslinked samples were used, because the relaxation rate was not as fast as the diffusion rate. In the case of heptane used as penetrant, the highest swelling degree was obtained at 30% weight of EGDMA with 35 and 45% weight of heptane but at there was no trend for the swelling degree at 70% weight of heptane as well.



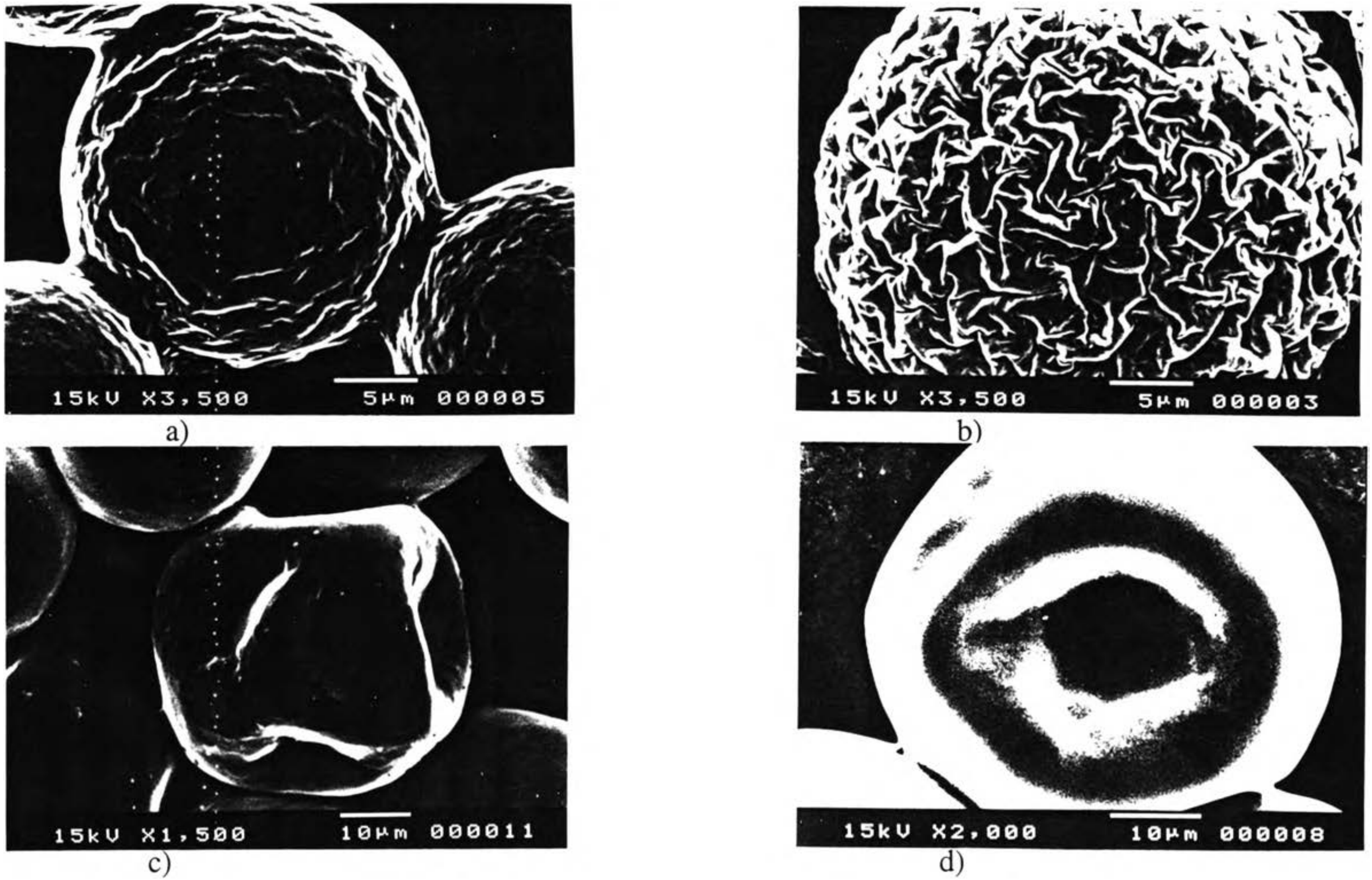
a) b) c)

**Figure 4.1** SEM photographs of poly(2-EHA-co-EGDMA) at 20% EGDMA by various concentrations of heptane, a) 70% heptane, b) 45% heptane, c) 35% heptane.

**Table 4.1 Effect of EGDMA concentration at 35%, 45% and 70% heptane on polymer swelling.**

| Sample No. | 2-EHA (g) | EGDMA (g) | Toluene (g) | Heptane (g) | Bead appearance | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Before swelling | After swelling | Swelling degree in toluene | Swelling degree in heptane |
| 6 | 8.0 | 2.0 | 3.5 | 3.5 | Smooth surface | Not ruptured | 3.1 | 2.8 |
| 4 | 7.0 | 3.0 | 3.5 | 3.5 | Finely porous | Not ruptured | 4.1 | 3.5 |
| 10 | 6.0 | 4.0 | 3.5 | 3.5 | Coarse surface | Not ruptured | 3.3 | 2.8 |
| 7 | 8.0 | 2.0 | 2.5 | 4.5 | Smooth surface | Not ruptured | 3.2 | 2.9 |
| 1 | 7.0 | 3.0 | 2.5 | 4.5 | Finely porous | Not ruptured | 3.9 | 3.9 |
| 10 | 6.0 | 4.0 | 2.5 | 4.5 | Creased surface | Ruptured | 3.2 | 2.8 |
| 5 | 8.0 | 2.0 | 0 | 7.0 | Coarse surface | Not ruptured | 3.4 | 3.7 |
| 3 | 7.0 | 3.0 | 0 | 7.0 | Creased surface | Not ruptured | 4.1 | 3.3 |
| 11 | 6.5 | 3.5 | 0 | 7.0 | Dented surface | Not ruptured | 3.6 | 3.2 |
| 8 | 6.0 | 4.0 | 0 | 7.0 | Dented surface | Ruptured | 4.1 | 3.6 |

**Continuous phase:** $H_2O$, 230 g; PVA-217, 2.5 g; SLS, 0.1 g, and $NaNO_2$, 0.03 g;
Methyl palmitate, 1.0 g, and ADVN, 0.2 g were added in the dispersion phase
Polymerization temperature 343 K, polymerization time 24 h., and agitation rate 160 rpm.
SPG pore size 5.25 μm.



a)
b)
c)
d)

**Figure 4.2** SEM photographs of the surface of poly(2-EHA-co-EGDMA) at 70% heptane with various concentrations of EGDMA, a) 20%, b) 30%, c) 35%, d) 40%.

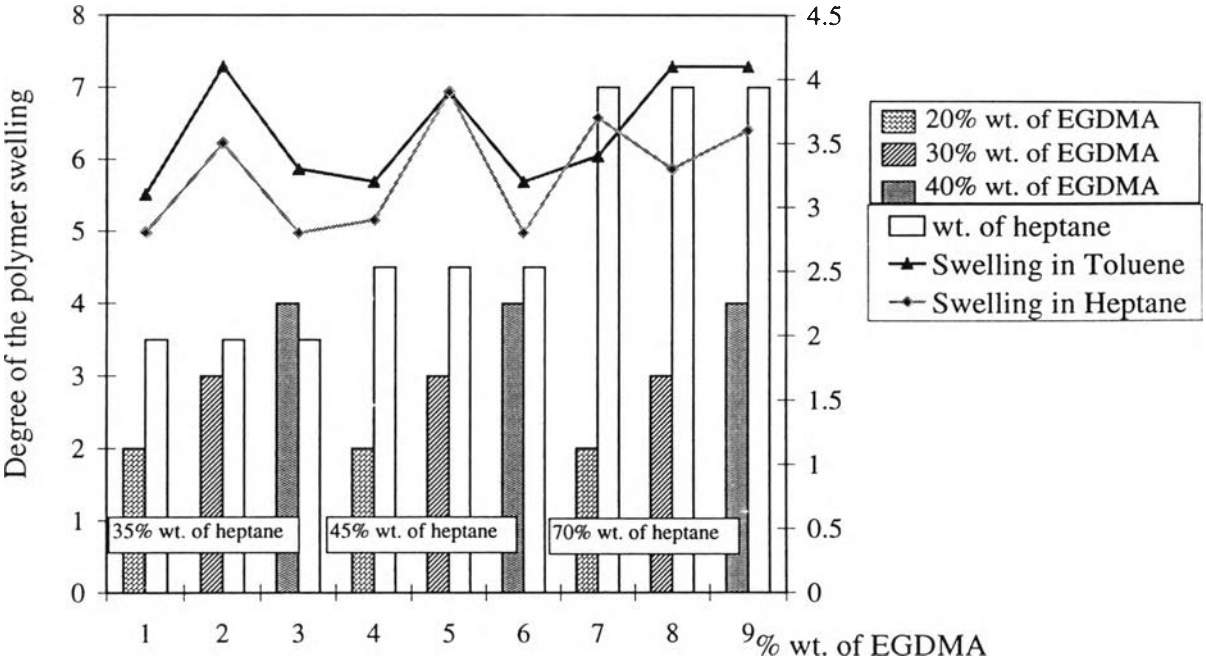


**Figure 4.3** The effect of heptane concentration on the degree of polymer swelling at 20, 30 and 40% of crosslinking agent.

### 4.1.3 The size of emulsion droplet and polymer particle

The relationship between the sizes of the emulsion droplets and the polymer particles with increasing in the amount of EGDMA at a constant content of heptane is shown in Table 4.2. Also, the coefficient variation close to 10% and the standard deviation were displayed. With increasing the amount of EGDMA to 20%, 30% and 40% at the 35% and 45% heptane by weight based on the total weight of the monomer and crosslinking agent, we found that the trend of the emulsion droplet size and the polymer particle size was decreased because a rigid network structure was formed and the mobility of the chain was decreased. Whereas at 70% heptane, increasing the amount of EGDMA resulted in a decrease in the emulsion droplets and polymer particle sizes because heptane is a poor solvent for the polymer and unable to swell the polymer chains. After the polymerization, the polymer droplet size was smaller than the emulsion droplet size because of the shrinking of the polymer chains and increasing density of the polymer.

Table 4.2 Effect of EGDMA at 35%, 45% and 70% heptane on the size of emulsion droplet and polymer droplets

| | | | | Emulsion droplets | | | Polymer particles | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Sample No.** | **2-EHA (g)** | **EGDMA (g)** | **Heptane (g)** | **$d_n$ (μm)** | **CV (%)** | **σ** | **$d_n$ (μm)** | **CV (%)** | **σ** | **Monomer conversion (%)** |
| 6 | 8.0 | 2.0 | 3.5 | 36.32 | 13.65 | 4.96 | 32.63 | 17.33 | 5.65 | 82 |
| 4 | 7.0 | 3.0 | 3.5 | 36.79 | 11.90 | 4.38 | 32.14 | 15.48 | 4.98 | 115 |
| 9 | 6.0 | 4.0 | 3.5 | 34.14 | 9.82 | 3.35 | 31.05 | 11.54 | 3.58 | 125 |
| 7 | 8.0 | 2.0 | 4.5 | 36.62 | 10.83 | 3.97 | 30.70 | 12.45 | 3.82 | 81 |
| 1 | 7.0 | 3.0 | 4.5 | 34.08 | 12.47 | 4.25 | 28.01 | 13.73 | 3.85 | 92 |
| 10 | 6.0 | 4.0 | 4.5 | 34.45 | 12.82 | 4.42 | 24.72 | 12.15 | 3.00 | 109 |
| 5 | 8.0 | 2.0 | 7.0 | 27.79 | 10.22 | 4.42 | 23.52 | 9.59 | 3.4 | 156 |
| 3 | 7.0 | 3.0 | 7.0 | 32.48 | 11.46 | 3.72 | 28.54 | 10.79 | 4.1 | 100 |
| 8 | 6.0 | 4.0 | 7.0 | 36.19 | 12.88 | 4.66 | 34.84 | 9.80 | 3.41 | 100 |

$d_n$ = number average diameter, CV = coefficient of variation, σ = standard deviation

## 4.2 The effect of solvent on the properties of polymer particles

### 4.2.1 The surface feature of polymer particles

In this work, toluene ($\delta$ = 18.3 MPa$^{1/2}$) as a good solvent and heptane ($\delta$ = 15.1 MPa$^{1/2}$) as a poor solvent were used to study the morphology of the particles.

Table 4.3 shows the effect of solvent concentration, with the constant content of crosslinking agent, on the bead appearance before and after the solvent swelling. We found that increasing the concentration of heptane resulted in a higher coarse surface of the particles as shown in Figure 4.4 (batches no.1-4). This result could be confirmed by Cheng et al. [40]. They found that the presence of nonsolvent would enhance the phase separation and structure inhomogeneity. Furthermore, Omi et al. [11] found that when a poor solvent was added in the recipe, a porous structure in polymeric spheres was obtained in the present of a crosslinking agent, because a micro-phase separation occurred during the polymerization.

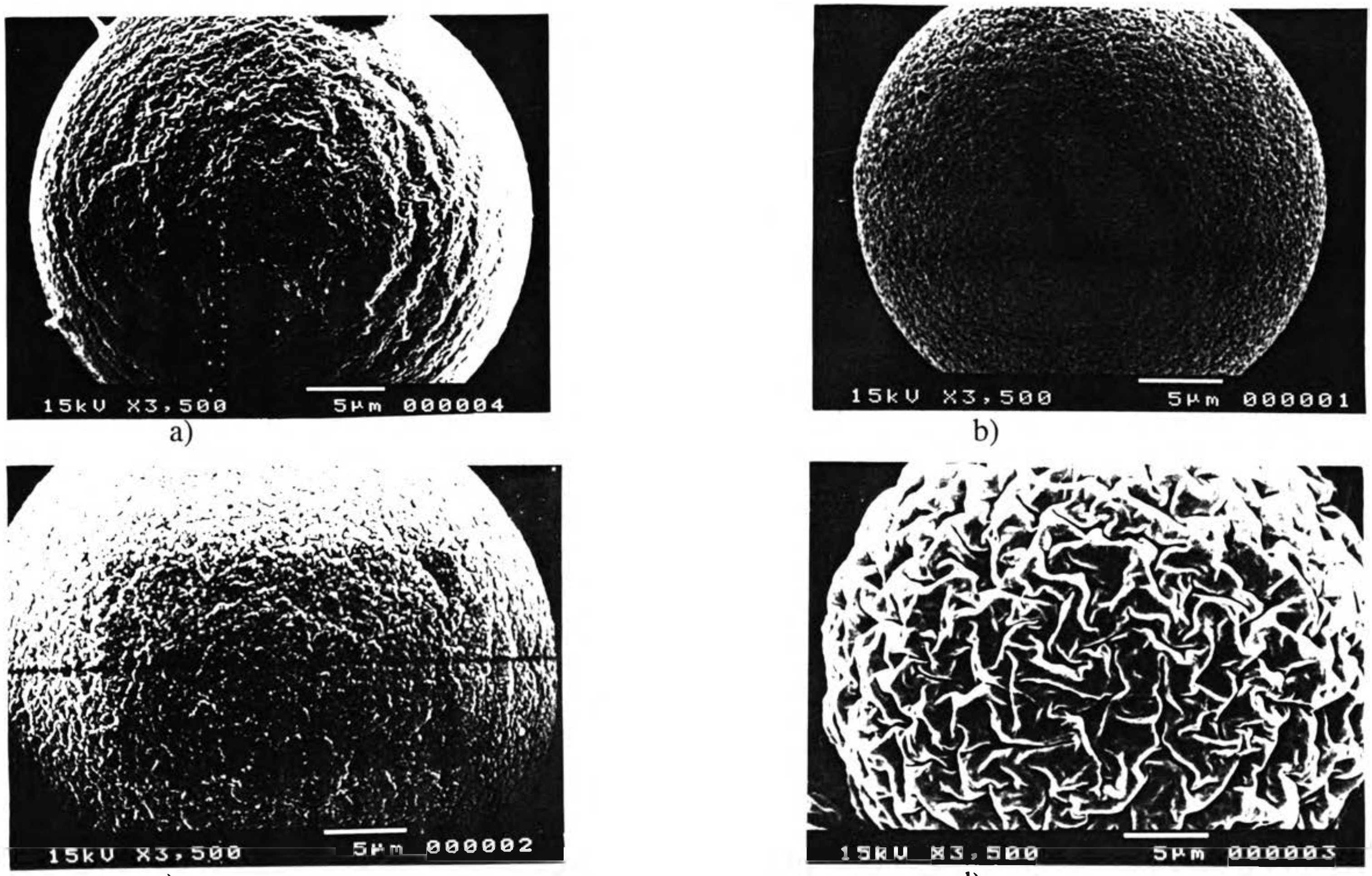
### 4.2.2 The degree of polymer swelling

Both the transparent bead and opaque beads were obtained using toluene and heptane as a penetrant. In Table 4.3, the effect of the ratio between the good solvent and poor solvent on the swelling degree was not clear. However, the highest value of the solvent swelling of the polymeric microspheres in toluene was obtained when the highest percentage of the poor solvent, heptane, was used at the constant concentrations of the crosslinking agent at 30% EGDMA as shown in Figure 4.5. As for the trend of the swelling in heptane, it was found that as in the cases of toluene, the highest swelling degree was obtained at 70% by weight of heptane at the each constant amount of EGDMA. The polymeric sphere did not rupture after the solvent swelling in both solvents.

Table 4.3 Effect of solvent concentrations at 20%, 30% and 40% EGDMA.

| Sample No. | 2-EHA (g) | EGDMA (g) | Toluene (g) | Heptane (g) | Bead appearance | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Before swelling | After swelling | Swelling degree in toluene | Swelling degree in heptane |
| 6 | 8.0 | 2.0 | 3.5 | 3.5 | Smooth surface | Not ruptured | 3.1 | 2.8 |
| 7 | 8.0 | 2.0 | 2.5 | 4.5 | Smooth surface | Not ruptured | 3.2 | 2.9 |
| 5 | 8.0 | 2.0 | 0 | 7.0 | Coarse surface | Not ruptured | 3.4 | 3.7 |
| 4 | 7.0 | 3.0 | 3.5 | 3.5 | Finely porous | Not ruptured | 4.1 | 3.5 |
| 1 | 7.0 | 3.0 | 2.5 | 4.5 | Finely porous | Not ruptured | 3.9 | 3.9 |
| 2 | 7.0 | 3.0 | 1.5 | 5.5 | Finely porous | Not ruptured | 3.1 | 2.8 |
| 3 | 7.0 | 3.0 | 0 | 7.0 | Creased surface | Not ruptured | 4.1 | 3.3 |
| 9 | 6.0 | 4.0 | 3.5 | 3.5 | Coarse surface | Not ruptured | 3.3 | 2.8 |
| 10 | 6.0 | 4.0 | 2.5 | 4.5 | Creased surface | Ruptured | 3.2 | 2.8 |
| 8 | 6.0 | 4.0 | 0 | 7.0 | Dented surface | Ruptured | 4.1 | 3.6 |

**Continuous phase:** $H_2O$, 230 g; PVA-217, 2.5 g; SLS, 0.1 g, and $NaNO_2$, 0.03 g;
Methyl palmitate, 1.0 g, and ADVN, 0.2 g were added in the dispersion phase
Polymerization temperature 343 K, polymerization time 24 h., and agitation rate 160 rpm.
SPG pore size 5.25 μm.



a) b) c) d)

**Figure 4.4** SEM photographs of the surface of poly(2-EHA-co-EGDMA) with various ratios of heptane:toluene, a) 3.5:3.5, b) 4.5:2.5, c) 5.5:1.5, d)7.0:0.

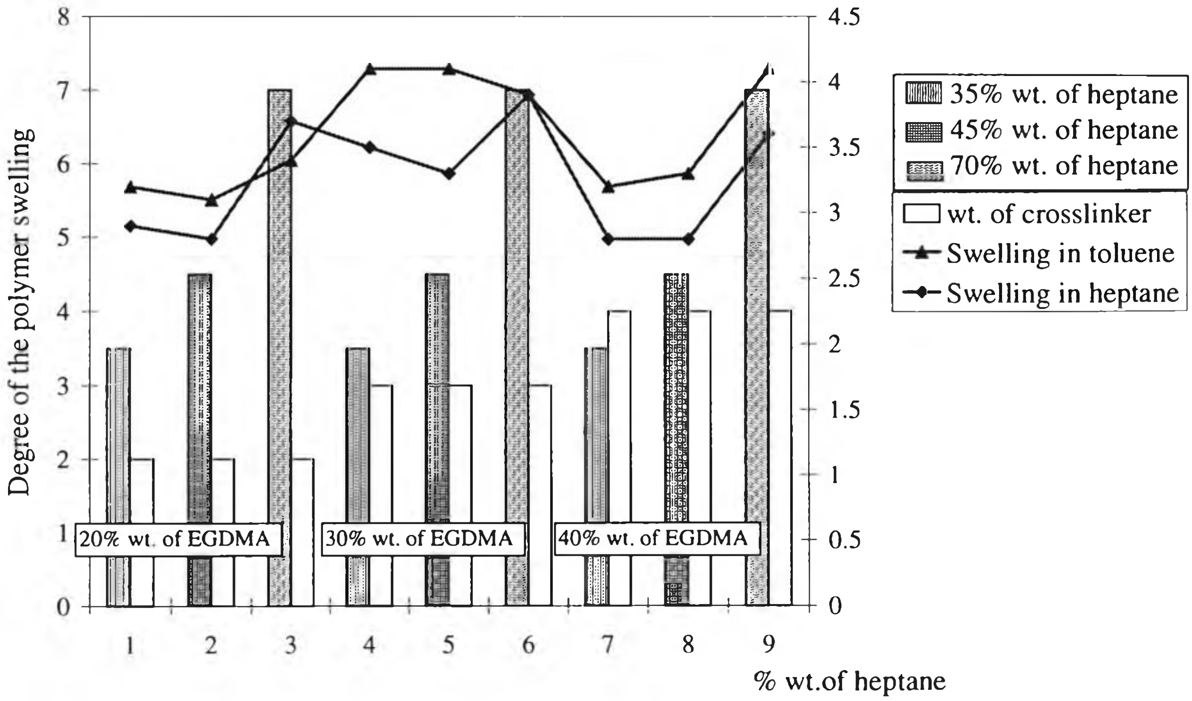


**Figure 4.5** The effect of the crosslinking agent concentrations on the degree of polymer swelling at 35, 45 and 70% of heptane.

### 4.2.3 The size of emulsion droplet and polymer particle

When the amount of heptane was increased from 35% to 45% and to 70% at the constant amount of EGDMA at 20%, 30% and 40% by weight based on the weight of the monomer and crosslinking agent as shown in Table 4.4, it was found that when increasing the amount of heptane at the constant 20% and 30% by weight of EGDMA, the trend of an emulsion droplet size and polymer droplet size were decreased due to the increasing rigid network and decreasing chain mobility. However, increasing the amount of heptane at 40% by weight of EGDMA resulted in an increase of the emulsion droplet and polymer particle size. After the polymerization, the polymer particle size is smaller than the emulsion droplet size because of the shrinking of the polymer chains and increasing density of the polymer.

### 4.2.4 The effect of the diluent types

The polymer/solvent interaction is an important factor in determining the pore size distribution and the solubility parameter theory has been applied to explain the porous structure patterns and the swelling properties of macroporous network polymers synthesized in the presence of different diluent systems.

$\delta_1$ and $\delta_2$ are the solubility parameters of the diluent and polymer, respectively. When $|\delta_1-\delta_2| \cong 0$, miscibility is favoured, i.e., the diluent is a good solvent which produces expanded network gels or small pores. In general, when $|\delta_1-\delta_2| > 3.0$ MPa$^{1/2}$, miscibility does not occur spontaneously so that the diluent separates out the polymer phase producing rather large pores [27].

The solvent type was changed in terms of the differences in chemical structure and the solubility parameter from heptane (straight-chain alkane, $\delta$ = 15.1 MPa$^{1/2}$) to isooctane (branched-chain alkane, $\delta$ = 14.3 MPa$^{1/2}$), and to cyclohexane (cycloalkane, $\delta$ = 16.8 MPa$^{1/2}$) [41] as shown in Table 4.5. The solubility parameter of 2-EHA, EGDMA and copolymer are 15.9 MPa$^{1/2}$, 17.5 MPa$^{1/2}$ and 16.3 MPa$^{1/2}$, respectively. The calculation of the solubility parameter of monomers and copolymer are shown in Appendix A and B, respectively. Polymerization was carried out with a recipe containing 70% 2-EHA and 30% EGDMA by weight based on the weight of the monomer and crosslinking agent. Figure 4.6 shows the surface feature of polymer particles when the solvent type was changed. It was found that the surface of the polymer was finely porous when cyclohexane, a good solvent, was used. In the case of isooctane, the surface of the polymer microspheres with coarse pores was obtained because isooctane was a poor solvent for this polymer. The degree of the polymer swelling is in accordance with the solubility parameter of the solvent, the closer the polymer solubility parameter approaching to that of the solvent, the greater the solvent swelling of the polymer. The polymer particle size was decreased after polymerization because of the shrinking of polymer chains and increasing density of the polymer. Figure 4.7 shows the polymer swelling degree in toluene and heptane by the various solvent types. It was found that the capacity of the solvent absorption of the polymer particles in toluene was higher than heptane and the highest swelling degree was obtained when cyclohexane was used. Besides, the coefficient variation was close to 10% and the standard deviation close to 4 was obtained.

**Table 4.4 Effect of solvent at 20%, 30% and 40% EGDMA**

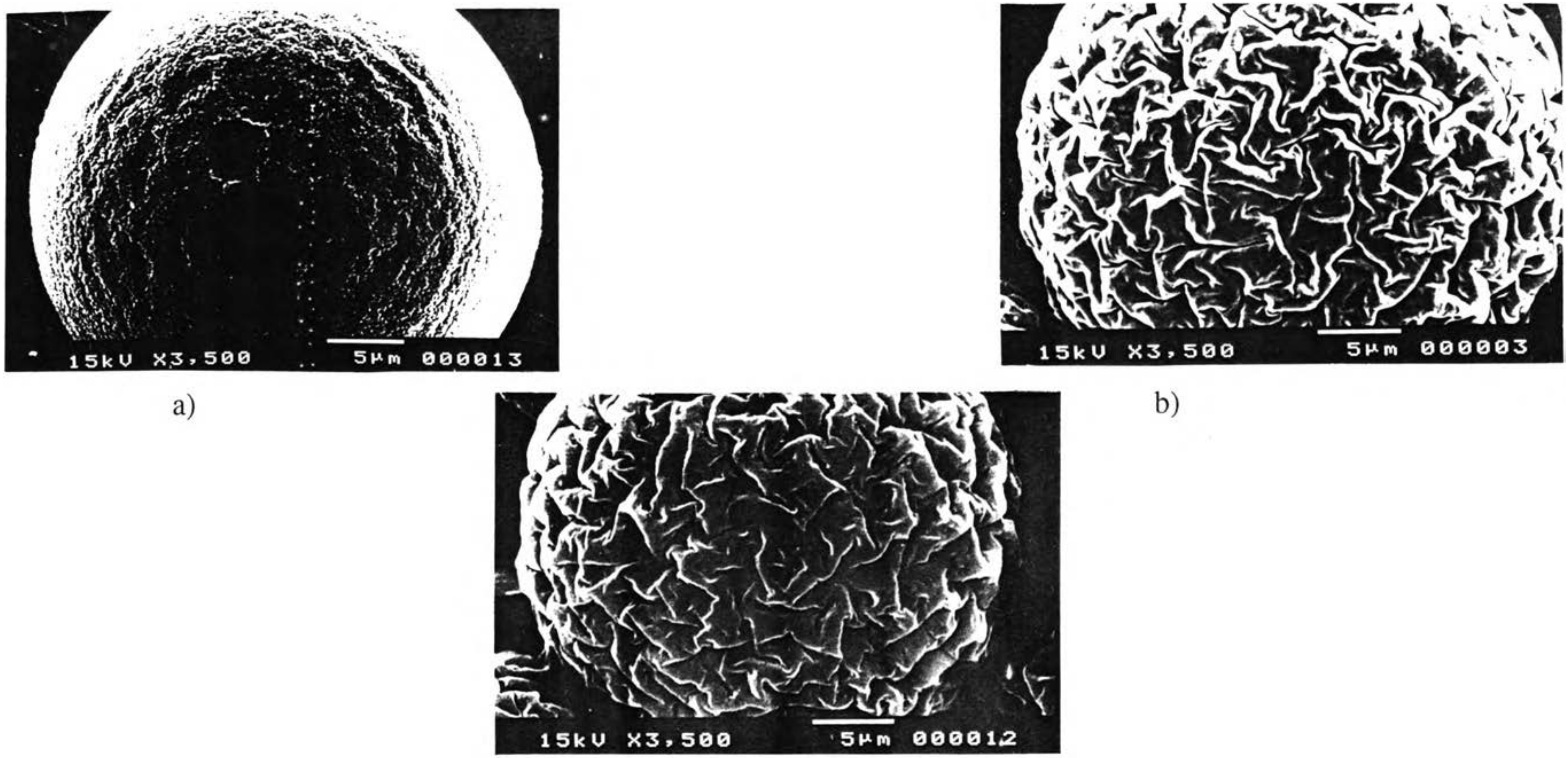
| Sample No. | 2-EHA (g) | EGDMA (g) | Heptane (g) | Emulsion droplets | | | Polymer particles | | | Monomer conversion (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $d_n$ (μm) | CV (%) | σ | $d_n$ (μm) | CV (%) | σ | |
| 6 | 8.0 | 2.0 | 3.5 | 36.32 | 13.65 | 4.96 | 32.63 | 17.33 | 5.65 | 82 |
| 7 | 8.0 | 2.0 | 4.5 | 36.62 | 10.83 | 3.97 | 30.70 | 12.45 | 3.82 | 81 |
| 5 | 8.0 | 2.0 | 7.0 | 27.79 | 10.22 | 4.42 | 23.52 | 9.59 | 2.26 | 156 |
| 4 | 7.0 | 3.0 | 3.5 | 36.79 | 11.90 | 4.38 | 32.14 | 15.48 | 4.98 | 115 |
| 1 | 7.0 | 3.0 | 4.5 | 34.08 | 12.47 | 4.25 | 28.01 | 13.73 | 3.85 | 92 |
| 3 | 7.0 | 3.0 | 7.0 | 32.48 | 11.46 | 3.72 | 28.54 | 10.79 | 3.08 | 100 |
| 9 | 6.0 | 4.0 | 3.5 | 34.14 | 9.82 | 3.35 | 31.05 | 11.54 | 3.58 | 125 |
| 10 | 6.0 | 4.0 | 4.5 | 34.45 | 12.82 | 4.42 | 24.72 | 12.15 | 3.00 | 109 |
| 8 | 6.0 | 4.0 | 7.0 | 36.19 | 12.88 | 4.66 | 34.84 | 9.80 | 3.41 | 100 |

$d_n$ = number average diameter
CV = coefficient of variation
σ = standard deviation

Table 4.5 Effect of the solvent types at 30% EGDMA and 70% solvent

| Sample No. | 2-EHA (g) | Types of solvent | δ (MPa$^{1/2}$) | Bead appearance |  |  |  | Emulsion droplets |  |  | Polymer particles |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Before swelling | After swelling | Swelling degree in toluene | Swelling degree in heptane | $d_n$ (μm) | CV (%) | σ | $d_n$ (μm) | CV (%) | σ |
| 12 | 7.0 | isooctane | 14.3 | Creased surface | Not ruptured | 3.2 | 3.0 | 33.42 | 12.57 | 4.20 | 30.96 | 11.03 | 3.41 |
| 3 | 7.0 | heptane | 15.1 | Creased surface | Not ruptured | 4.1 | 3.3 | 32.48 | 11.46 | 3.72 | 28.54 | 10.79 | 4.1 |
| 13 | 7.0 | cyclohexane | 16.8 | Finely porous | Not ruptured | 4.3 | 3.3 | 35.45 | 11.76 | 4.17 | 30.86 | 16.46 | 5.08 |

**Continuous phase:** $H_2O$, 230 g; PVA-217, 2.5 g; SLS, 0.1 g, and $NaNO_2$, 0.03 g;
Methyl palmitate, 1.0 g, and ADVN, 0.2 g were added in the dispersion phase
Polymerization temperature 343 K, polymerization time 24 h., and agitation rate 160 rpm.
SPG pore size 5.25 μm.
$d_n$ = number average diameter
CV = coefficient of variation
σ = standard deviation



a) b) c)

**Figure 4.6** SEM photographs of the polymer beads of 2-EHA crosslinked with EGDMA with various solvent types at 70% monomer and 70% solvent; a) Isooctane, b) Heptane, c) Cyclohexane.

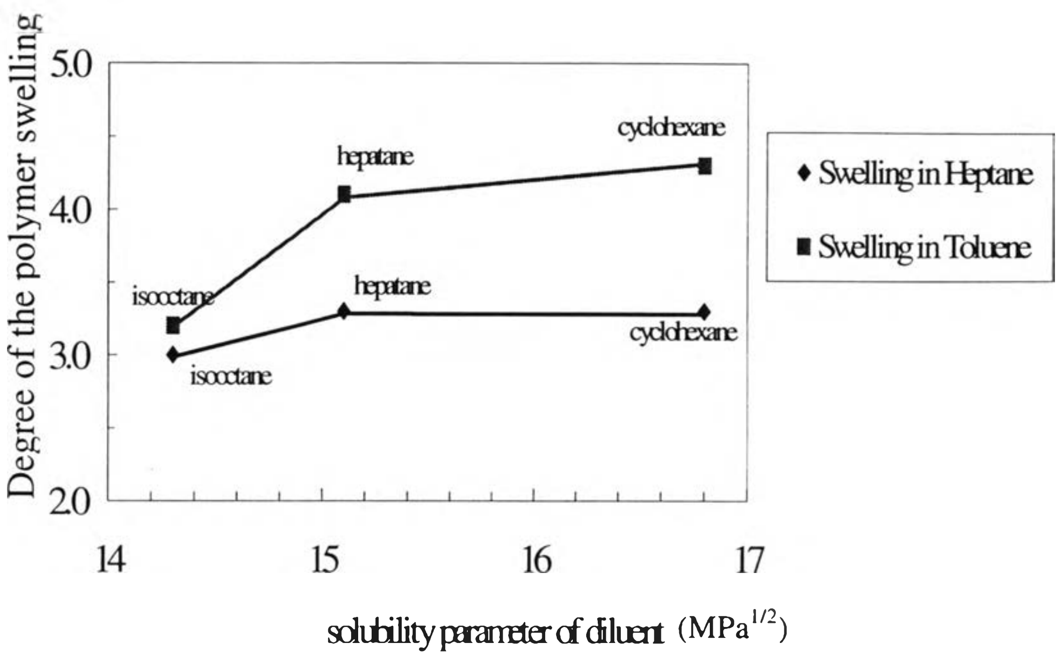


**Figure 4.7** The effect of solvent type on the degree of polymer swelling.

## 4.3 Effect of the monomer types on properties of the polymer particles

### 4.3.1 The surface feature of microspheres and the degree of the polymer swelling

The monomer type was changed with respect to the chemical structure and the glass transition temperature (Tg) from 2-EHA (Tg = 188 K) to 2-EHMA (Tg = 263 K), laurylacrylate (Tg = 270 K), lauryl methacrylate (Tg = 208 K), cyclohexylacrylate (Tg = 292 K), and MMA (Tg = 378 K) [42]. Polymer particles were synthesized with 30% EGDMA and 70% heptane by weight based on the weight of the monomer and crosslinking agent as shown in Table 4.6. A variety of surface features with each monomer type are shown in Figure 4.8. The relationships between Tg, the surface feature of polymer particles and the capacity of the solvent absorption were not absolutely clear. In the case that cyclohexylacrylate and MMA were used as monomers in which Tg of MMA was higher than cyclohexylacrylate, it was found that PMMA microspheres with dented surface and hollowness inside were obtained, while polycyclohexylacrylate microsphere had revealed crease surface. Besides, the capacity of the solvent absorption of PMMA microsphere was lower than polycyclohexylacrylate microsphere due to the higher Tg resulted in the decrease of the free volume and the flexibility of the polymer chains. The capacity of the solvent absorption of PMMA microspheres in heptane can not be measured because there were some particles floating on the surface of the solvent, or in other words, PMMA microspheres could not absorb heptane because of the incompatibility between MMA and heptane. MMA monomer is a relatively hydrophilic substance while heptane is hydrophobic. The swelling degree was decreased with increasing the amount of MMA as shown in Figure 4.9 and from Figure 4.10, it was found that the wall of PMMA sphere composed of many globules became too hard to absorb the solvent. Acrylate and methacrylate monomers, such as 2-EHA, lauryl acrylate, 2-EHMA, and lauryl methacrylate were used consequently. The polymer microsphere with creased surface and fine pores was obtained using the acrylate monomers and the methacrylate monomers, respectively. The capacity of the solvent absorption of the acrylate monomers was generally higher than that of the methacrylate monomer. In the cases of 2-EHA and 2-EHMA, where Tg of 2-EHA is lower than 2-EHMA, the capacity of the solvent absorption was higher with 2-EHA than 2-EHMA because the free volume of 2-EHA is larger. On the other hand, for lauryl acrylate and lauryl methacrylate, where Tg of lauryl acrylate is higher than lauryl methacrylate, the solvent absorption capacity of lauryl acrylate was higher than the other. This result can be explained by the effect of crosslinking degree that the capacity of the solvent absorption increased because the extent of the crosslinking degree of lauryl acrylate is lower because its molecular weight is smaller than lauryl methacrylate.

The different structures between the acrylate monomer and the methacrylate monomer are a substituent group of $-CH_3$ at the alpha-carbon atom. Acrylate monomer has a hydrogen atom in the alpha-carbon atom whereas methacrylate monomer has a methyl group as a substituent. Therefore, the acrylate monomer can absorb the solvent better than the methacrylate monomer because a smaller substituent group provides the higher flexibility to the chains and the stretching of the chains to absorb a solvent is much easier. In a consideration of the side chain group between lauryl acrylate and 2-EHA, it was found that the longer side chain resulted in the higher degree of the solvent absorption because of the decreasing polymer polarity.

The hollow morphology is the goal of this research. In Figure 4.10, a hollow morphology was obtained. In order to improve the capacity of the solvent absorption, the composition between MMA and EGDMA was hence changed from 30% to 20% and 40% EGDMA as shown in Table 4.7. Regardless of the amount of EGDMA, an improved hollow morphology was retained but the capacity of the solvent absorption was not changed. Thus, MMA plays an important role in the capacity of the solvent absorption. The cross sections of the hollow microspheres of poly(MMA-EGDMA) with 30% to 20% and 40% EGDMA at 70% heptane are shown in Figure 4.10.

**Table 4.6 Effect of monomer types on bead appearance and swelling behavior at 70% monomer and 70% heptane**

| Sample No. | Type of monomers | Tg (K) | Bead appearance | | | |
|---|---|---|---|---|---|---|
| | | | **Before swelling** | **After swelling** | **Swelling degree in toluene** | **Swelling degree in heptane** |
| 3 | 2-EHA | 188 | Creased surface | Not ruptured | 4.1 | 3.3 |
| 15 | 2-EHMA | 263 | Finely porous | Not ruptured | 3.6 | 3.0 |
| 25 | Lauryl acrylate | 270 | Creased surface | Not ruptured | 5.3 | 4.1 |
| 24 | Lauryl methacrylate | 208 | Finely porous | Not ruptured | 3.1 | 2.8 |
| 14 | Cyclohexylacrylate | 292 | Creased surface | Not ruptured | 3.3 | 3.2 |
| 16 | MMA | 378 | Spongy hollow particle | Not ruptured | 3.2 | N |

**Continuous phase:** $H_2O$, 230 g; PVA-217, 2.5 g; SLS, 0.1 g, and $NaNO_2$, 0.03 g;
Methyl palmitate, 1.0 g, and ADVN, 0.2 g were added in the dispersion phase
Polymerization temperature 343 K, polymerization time 24 h, and agitation rate 160 rpm.
SPG pore size 5.25 μm.
N means the swelling degree could not be measured.

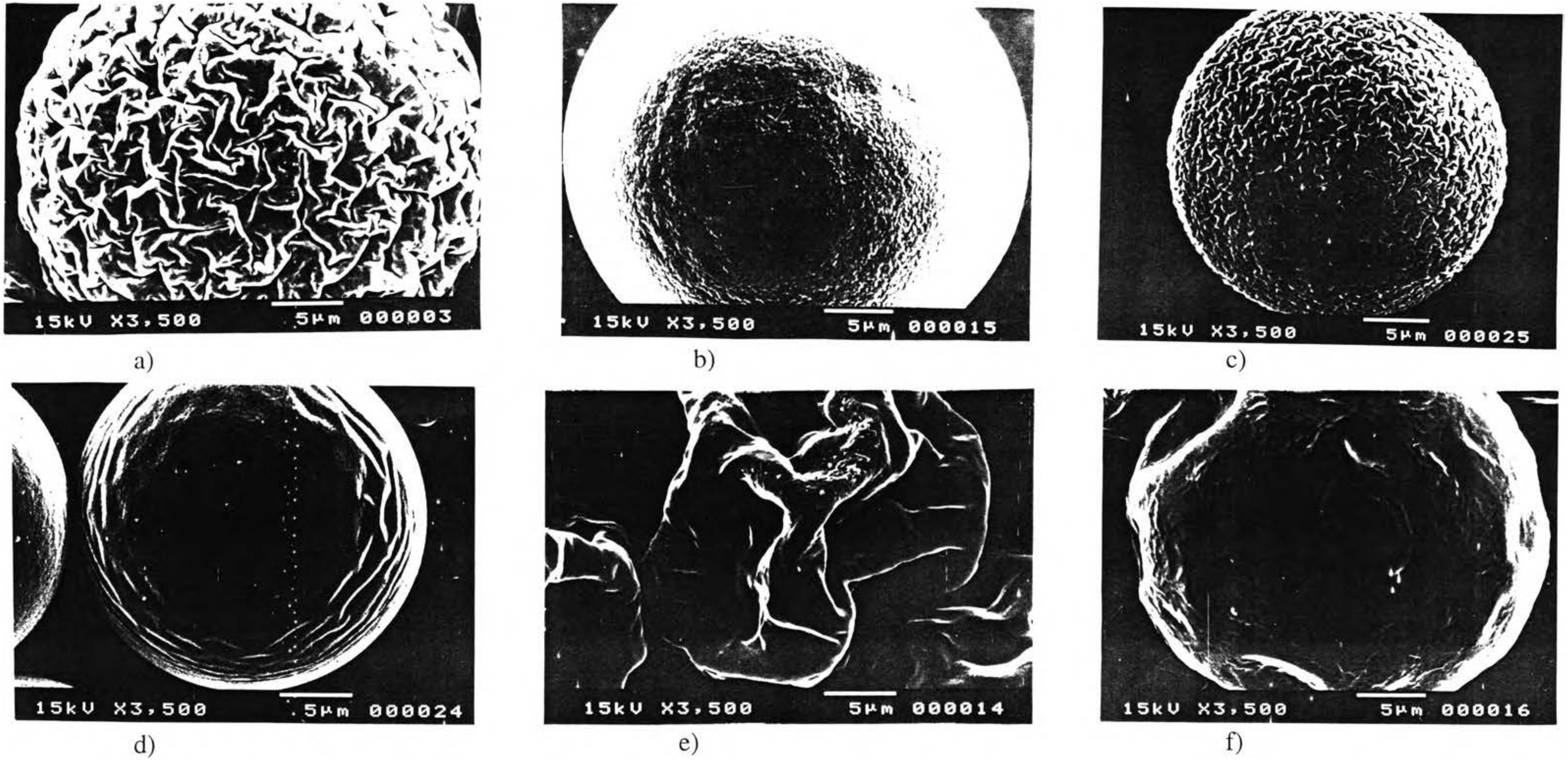


**Figure 4.8** SEM photographs with various monomer types at 70% monomer and 70% heptane; a) 2-EHA, b) 2-EHMA, c) lauryl acrylate, d) lauryl methacrylate, e) cyclohexylacrylate, f) MMA

**Table 4.7 Effect of the monomer compositions at 70% heptane**

| Sample No. | MMA (g) | EGDMA (g) | Bead appearance | | | |
|---|---|---|---|---|---|---|
| | | | Before swelling | After swelling | Swelling degree in toluene | Swelling degree in heptane |
| 22 | 8.0 | 2.0 | Spongy hollow particle | - | N | N |
| 16 | 7.0 | 3.0 | Spongy hollow particle | Not ruptured | 3.2 | N |
| 23 | 6.0 | 4.0 | Spongy hollow particle | - | N | N |

**Continuous phase:** $H_2O$, 230 g; PVA-217, 2.5 g; SLS, 0.1 g, and $NaNO_2$, 0.03 g;
Methyl palmitate, 1.0 g, and ADVN, 0.2 g were added in the dispersion phase
Polymerization temperature 343 K, polymerization time 24 h., and agitation rate 160 rpm.
SPG pore size 5.25 μm.
N means that the swelling degree could not be measured.

### 4.3.2 The size of emulsion droplets and polymer particles

The relationships among the monomer types and the emulsion droplets and the polymer particle sizes at 70% by weight of monomer and 70% by weight of heptane based on the weight of the monomer and crosslinking agent, respectively, are shown in Table 4.8. The effect of the acrylate and methacrylate monomers on the emulsion droplet size and the polymer particle size or in other words, the acrylate and the methacrylate droplet size were almost same with the acrylate and the methacrylate polymer particle size, respectively. The three types of side chains of monomers were used in this research, such as, MMA and lauryl methacrylate containigng straight side chains, 2-EHA has a branched side chains and cyclohexylacrylate has a cycloaliphatic side chain. The biggest droplet size and particle size were obtained from MMA monomer because the hydrophilic MMA segments could be emulsified form which water molecules could diffuse into the MMA droplets. The water solubility value of MMA is 1.5 g/ 100 g water at 30°C [39]. The CV close to 10% was obtained in each monomer. The majority of the monomer conversion was nearly 100% but in the case of cyclohexylacrylate was only 50%, because some portion of the polymer was lost in the precipitation step during the measurement of monomer conversion. Some part of them floated onto the surface of the supernatant and they were lost in the effluent.

In comparison between the monomer structure (except MMA) with emulsion droplet size, it was found that the emulsion droplet size depended greatly on the type and length of branching side chains: cycloaliphatic side chains and straight side chains, because of the increasing chain mobility. After the polymerization, the particle sizes of the polycyclohexylacrylate and PMMA were increased. Table 4.9 shows the effect of monomer compositions between MMA and EGDMA at 80%, 70% and 60% by weight of MMA with 70% by weight of heptane. We found that increasing the amount of MMA resulted in an increased droplet size and polymer particle size as well.

**Table 4.8 The relationship between the monomer types and the size of emulsion droplet and polymer particle**

| | | **Emulsion droplets** | | | **Polymer particles** | | | |
|---|---|---|---|---|---|---|---|---|
| **Sample No.** | **Type of monomers** | **$d_n$ (μm)** | **CV (%)** | **σ** | **$d_n$ (μm)** | **CV (%)** | **σ** | **Monomer conversion (%)** |
| 3 | 2-EHA | 32.48 | 11.46 | 3.72 | 28.54 | 10.79 | 4.1 | 100 |
| 15 | 2-EHMA | 33.89 | 10.40 | 3.52 | 29.82 | 11.48 | 3.42 | 103 |
| 25 | Lauryl acrylate | 28.35 | 11.88 | 3.37 | 24.00 | 10.62 | 2.55 | 98 |
| 24 | Lauryl methacrylate | 28.03 | 10.18 | 2.85 | 23.40 | 12.20 | 2.86 | 110 |
| 14 | Cyclohexylacrylate | 27.15 | 9.38 | 2.55 | 30.10 | 8.63 | 2.60 | 50 |
| 16 | MMA | 31.79 | 11.53 | 3.67 | 37.02 | 11.84 | 4.38 | 106 |

$d_n$ = number average diameter
CV = coefficient of variation
σ = standard deviation

**Table 4.9 Effect of the monomer compositions at 70% heptane**

| | | | Emulsion droplet | | | Polymer particle | | |
|---|---|---|---|---|---|---|---|---|
| Sample No. | MMA (g) | EGDMA (g) | $d_n$ (μm) | CV (%) | σ | $d_n$ (μm) | CV (%) | σ |
| 22 | 8 | 2 | 31.84 | 12.86 | 4.09 | 37.99 | 16.73 | 6.36 |
| 16 | 7 | 3 | 31.79 | 11.53 | 3.67 | 37.02 | 11.84 | 4.38 |
| 23 | 6 | 4 | 28.45 | 9.55 | 2.72 | 30.75 | 8.33 | 2.56 |

$d_n$ = number average diameter, CV = coefficient of variation, σ = Standard deviation

## 4.4 Effect of the third monomer on properties of polymer particles

### 4.4.1 The microsphere morphology and the degree of the polymer swelling

Table 4.10 shows the effect of MMA as the third monomer at 30% EGDMA and 70% heptane by weight based on the weight of the monomer and crosslinking agent by the various ratios between 2-EHA and MMA. At 14%, 35% and 56% by weight of MMA, the dented surfaces with hollow morphology were obtained with increasing the amount of MMA. The capacity of toluene absorption did not depend on the amount of MMA, however, its capacity of heptane absorption was decreased with increasing the amount of MMA due to the decrease of chain flexibility and the polarity as shown in Figure 4.9.

Referring to the experiments summarized in Table 4.10, the morphology of polymer microsphere (sample no.17) had the dented surface with hollowness inside. A high swelling degree, SD in toluene=3.8 and SD in heptane=3.4, of poly(2-EHA-co-MMA-co-EGDMA, 35%:35%:30%) microspher was obtained but the polymer microspheres were ruptured after the swelling in toluene and heptane. The higher swelling degree was obtained with decreasing the amount of EGDMA and the polymer microspheres were not ruptured after the swelling in toluene and heptane as shown in Table 4.11. The high mobility of polymer chains occurred and could expand its chains after the swelling in solvents at low amount of EGDMA.

The hollow morphology microsphere was still not obtained at 10% EGDMA, but the highest swelling degree was achieved. The loosely crosslinked polymers were easier to expand and increased the volume after the swelling in solvents than the densely crosslinked polymers. The cross sections of the hollow microsphere are shown in Figure 4.10. There are two types of wall structure in hollow microspheres: a spongy hollow microsphere (samples no.16, 19, 22 and 23) and a smooth hollow microsphere (samples 17 and 20).

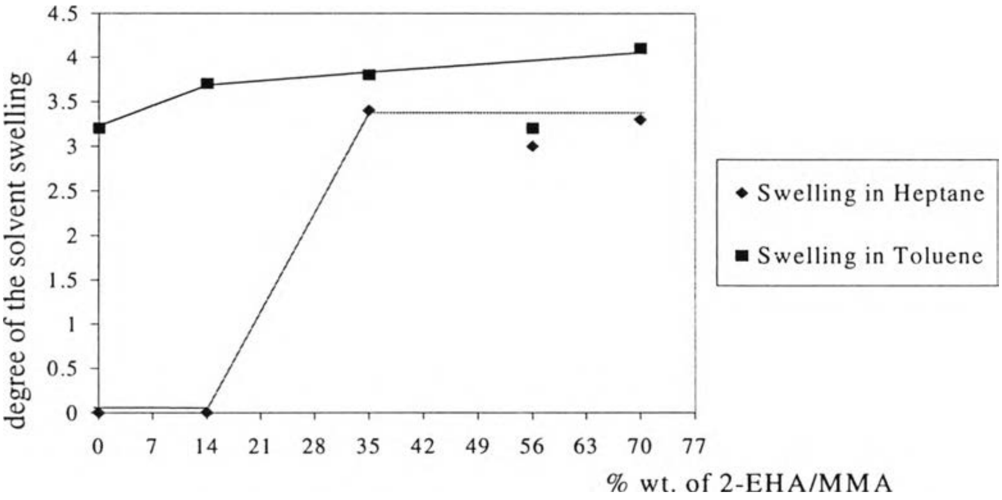


**Figure 4.9** Effect of the monomer compositions on degree of the solvent swelling.

Table 4.10 Effect of the monomer compositions at 30% EGDMA and 70% heptane

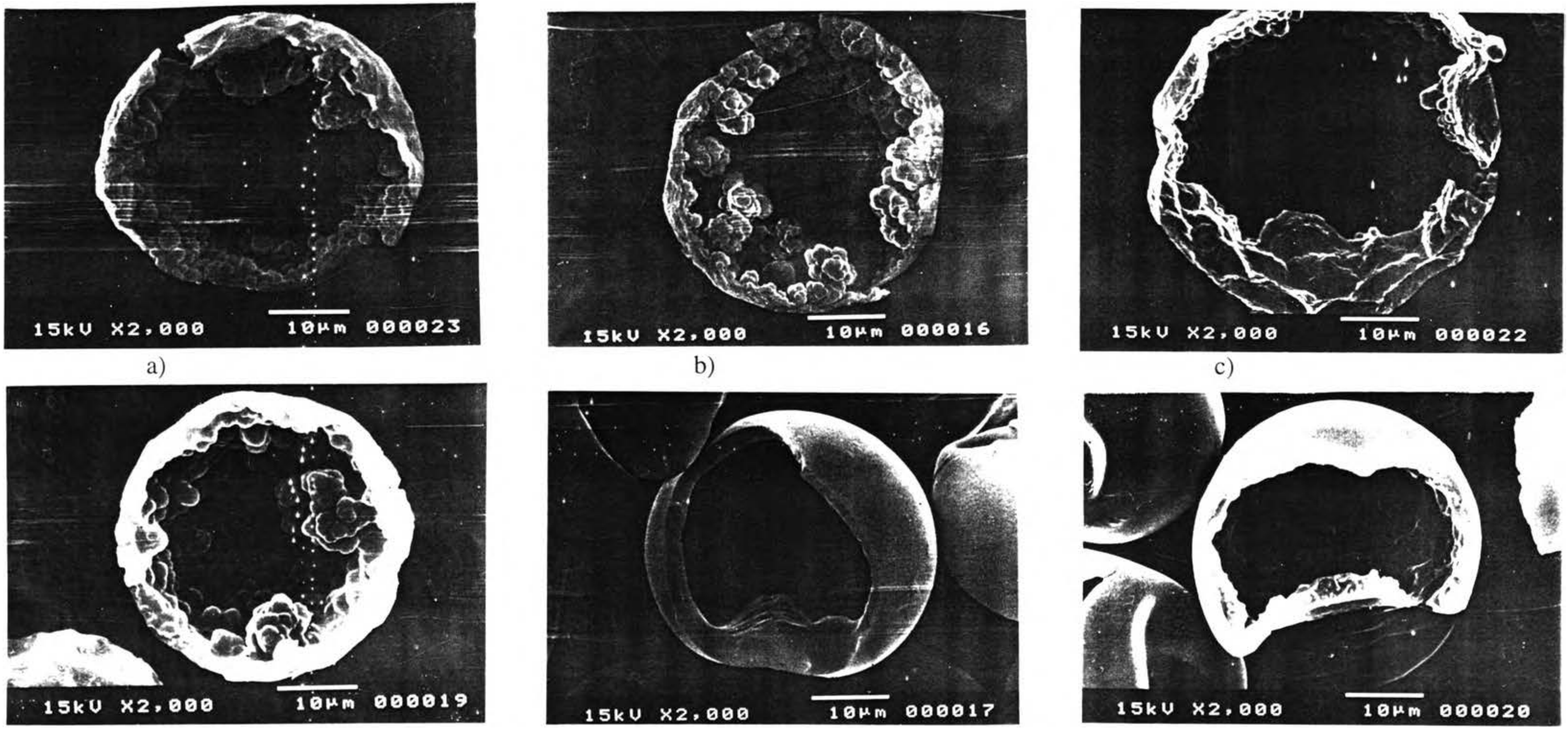
| Sample No. | 2-EHA (g) | MMA (g) | EGDMA (g) | Bead appearance | | | |
|---|---|---|---|---|---|---|---|
| | | | | **Before swelling** | **After swelling** | **Swelling degree in toluene** | **Swelling degree in heptane** |
| 3 | 7.0 | 0 | 3.0 | Creased surface | Not ruptured | 4.1 | 3.3 |
| 18 | 5.6 | 1.4 | 3.0 | Creased surface | Not ruptured | 3.2 | 3.0 |
| 17 | 3.5 | 3.5 | 3.0 | Smooth hollow particle | Ruptured | 3.8 | 3.4 |
| 19 | 1.4 | 5.6 | 3.0 | Spongy hollow particle | Not ruptured | 3.7 | N |
| 16 | 0 | 7.0 | 3.0 | Spongy hollow particle | Not ruptured | 3.2 | N |

**Continuous phase:** $H_2O$, 230 g; PVA-217, 2.5 g; SLS, 0.1 g, and $NaNO_2$, 0.03 g;
Methyl palmitate, 1.0 g, and ADVN, 0.2 g were added in the dispersion phase
Polymerization temperature 343 K, polymerization time 24 h., and agitation rate 160 rpm.
SPG pore size 5.25 μm.
N means that the swelling degree could not be measured.

**Table 4.11 Effect of the monomer compositions at 70% heptane**

| Sample No. | 2-EHA (g) | MMA (g) | EGDMA (g) | Bead appearance | | | |
|---|---|---|---|---|---|---|---|
| | | | | Before swelling | After swelling | Swelling degree in toluene | Swelling degree in heptane |
| 17 | 3.5 | 3.5 | 3.0 | Smooth hollow particle | Ruptured | 3.8 | 3.4 |
| 20 | 4.0 | 4.0 | 2.0 | Smooth hollow particle | Not ruptured | 3.9 | 2.7 |
| 21 | 4.5 | 4.5 | 1.0 | Creased surface | Not ruptured | 5.1 | 3.9 |

**Continuous phase:** $H_2O$, 230 g; PVA-217, 2.5 g; SLS, 0.1 g, and $NaNO_2$, 0.03 g;
Methyl palmitate, 1.0 g, and ADVN, 0.2 g were added in the dispersion phase
Polymerization temperature 343 K, polymerization time 24 h., and agitation rate 160 rpm.
SPG pore size 5.25 µm.



a) b) c)

d) e) f)

**Figure 4.10** SEM photographs of hollow particles of various monomer compositions of 2-EHA:MMA:EGDMA at 70% heptane: a) 0:6.0:4.0, b) 0:7.0:3.0, c) 0:8.0:2.0, d)1.4:5.6:3.0, e)3.5:3.5:3.0, f) 4.0:4.0:2.0.

### 4.4.2 The sizes of emulsion droplet and polymer particle

Table 4.12 shows the effect of the amount of the third monomer on droplet sizes by varying the ratios between 2-EHA and MMA at 30% by weight of EGDMA and 70% by weight of heptane. It was found that increasing the amount of MMA resulted in an increase of the droplet size. The polymer particle size was increased after the polymerization because the hydrophilic MMA segments promoted the absorption of water molecules into the polymer particles, leading to increase in the droplet sizes. Table 4.13 shows the effects of the composition of the monomer and crosslinking agent on the droplet sizes. It was found that the trends of the emulsion droplet sizes and polymer particle sizes were similar as shown in Table 4.12.

**Table 4.12 Effect of the monomer composition at 30% EGDMA and 70% heptane**

| | | | **Emulsion droplet** | | | **Polymer particle** | | |
|---|---|---|---|---|---|---|---|---|
| **Sample No.** | **2-EHA (g)** | **MMA (g)** | **$d_n$ (μm)** | **CV (%)** | **σ** | **$d_n$ (μm)** | **CV (%)** | **σ** |
| 3 | 7 | - | 32.48 | 11.46 | 3.72 | 28.54 | 10.79 | 4.1 |
| 17 | 5.6 | 1.4 | 26.15 | 11.81 | 3.09 | 31.83 | 14.11 | 4.49 |
| 19 | 3.5 | 3.5 | 27.58 | 12.99 | 3.58 | 31.13 | 11.82 | 3.68 |
| 18 | 1.4 | 5.6 | 33.62 | 12.03 | 4.04 | 36.14 | 14.05 | 5.08 |
| 16 | - | 7 | 31.79 | 11.53 | 3.67 | 37.02 | 11.84 | 4.38 |

**Table 4.13 Effect of EGDMA at 2-EHA:MMA, 1:1 and 70 % heptane**

| Sample No. | 2-EHA (g) | MMA (g) | EGDMA (g) | Emulsion droplet $d_n$ (μm) | CV (%) | σ | Polymer particle $d_n$ (μm) | CV (%) | σ |
|---|---|---|---|---|---|---|---|---|---|
| 21 | 4.5 | 4.5 | 1.0 | 30.20 | 9.71 | 2.93 | 28.79 | 11.23 | 3.23 |
| 20 | 4.0 | 4.0 | 2.0 | 27.33 | 9.35 | 2.56 | 29.18 | 9.20 | 2.68 |
| 17 | 3.5 | 3.5 | 3.0 | 26.15 | 11.81 | 3.09 | 28.64 | 10.26 | 2.94 |

$d_n$ = number average diameter, CV = coefficient of variation, σ = Standard deviation

## 4.5 Absorption kinetics

In general, the typical absorption kinetic curve consists of three stages: (i) a short initial stage of high absorption rate, (ii) a longer stage of constant slow absorption rate, and (iii) a third stage of the plateau value [28-29,34]. However, the swelling curve in this research had only the second and third stages, because the first stage took place to completion very rapidly and could not be measured. The swelling curves of poly(lauryl acrylate-co-EGDMA) particles in heptane prepared by the SPG pore size of 5.25 μm using the same recipe as in the sample no. 25, with various times: a) 1-10 min, and b) 6-48 hr, respectively, are shown in Figures 4.11 a and b, in which the swelling degree reached a constant from 1 min to 2 days.

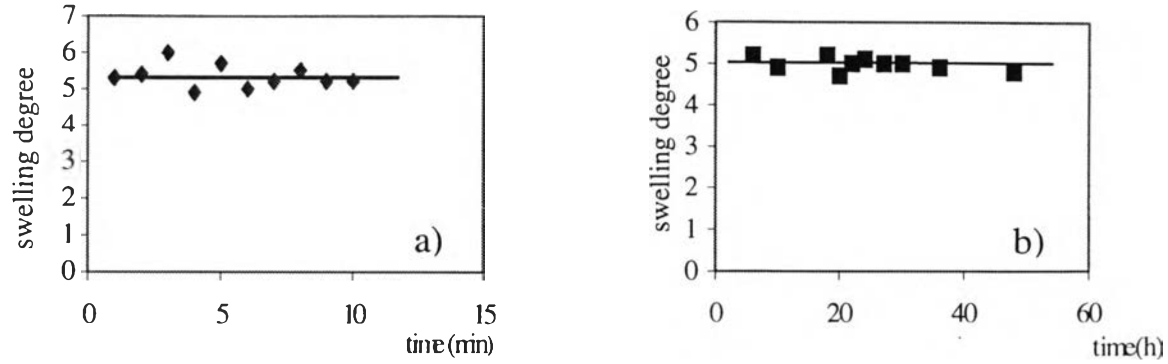


**Figure 4.11** The swelling degree curve of poly(lauryl acrylate-co-EGDMA) particles against the swelling times: a) 1-10 min, b) 6-48 hr, respectively.

### 4.5.1 Effect of particle size on the capacity of the solvent absorption

From all the solvent absorption results, it was found that lauryl acrylate as monomer had the highest swelling degree and did not rupture after swelling in heptane and toluene. Thus, lauryl acrylate was appropriate to use for the following objectives. The SPG pore sizes of 0.9, 5.25 and 9.25 μm were used in this research to study the effect of the polymer particle size on the capacity of the solvent absorption. Lauryl acrylate of 70% by weight as monomer, EGDMA with 30% by weight as crosslinking agent and 70% by weight of heptane as solvent based on the weight of the monomer and crosslinking agent, were used with various SPG pore sizes. The recipes of both phases are shown in Table 4.14. The polymer particle size, the CV close to 10%, the standard deviation, and monomer conversion are shown in Table 4.15. The effect of the polymer particle size on the capacity of the solvent absorption against the elapsed time is shown in Figure 4.12. It was found that the highest swelling degree was obtained with the smallest particle size and the lowest swelling degree was achieved from the largest particle size. From Figure 4.12, the average swelling degree at various particle sizes was obtained as shown in Table 4.16. The relationship between the average swelling degree and the polymer particle size is shown in Figure 4.13. The swelling degree was increased with decreasing the particle size, thus, the capacity of the solvent absorption was dependent on the polymer particle size only at the same recipe and reaction condition.

**Table 4.14 The recipe of the polymerization**

| Sample no. | SPG pore size (μm) | Lauryl acrylate (g) | EGDMA (g) | Heptane (g) |
|---|---|---|---|---|
| 26 | 9.25 | 7 | 3 | 7 |
| 25 | 5.25 | 7 | 3 | 7 |
| 27 | 0.9 | 7 | 3 | 7 |

**Continuous phase:** $H_2O$, 230 g; PVA-217, 2.5 g; SLS, 0.1 g, and $NaNO_2$, 0.03 g: Methyl palmitate, 1.0 g, and ADVN, 0.2 g were added in the dispersion phase: Polymerization temperature 343 K, polymerization time 24 hr., and agitation rate 160 rpm.

**Table 4.15 The effect of SPG pore size on polymer particle size**

| Sample No. | SPG pore size (μm) | $d_n$ (μm) | CV (%) | $\sigma$ | Monomer conversion (%) |
|---|---|---|---|---|---|
| 26 | 9.25 | 45.36 | 12.04 | 5.46 | 90 |
| 25 | 5.25 | 24.00 | 10.62 | 2.55 | 98 |
| 27 | 0.9 | 4.81 | 9.81 | 0.47 | 95 |

$d_n$ = number average diameter, CV = coefficient of variation, $\sigma$ = Standard deviation

**Table 4.16 The relationship between swelling degree in toluene and particle size**

| SPG pore size (μm) | Particle diameter (μm) | swelling degree |
|---|---|---|
| 9.25 | 45.36 | 4.5 |
| 5.25 | 24.00 | 5.0 |
| 0.9 | 4.81 | 7.5 |

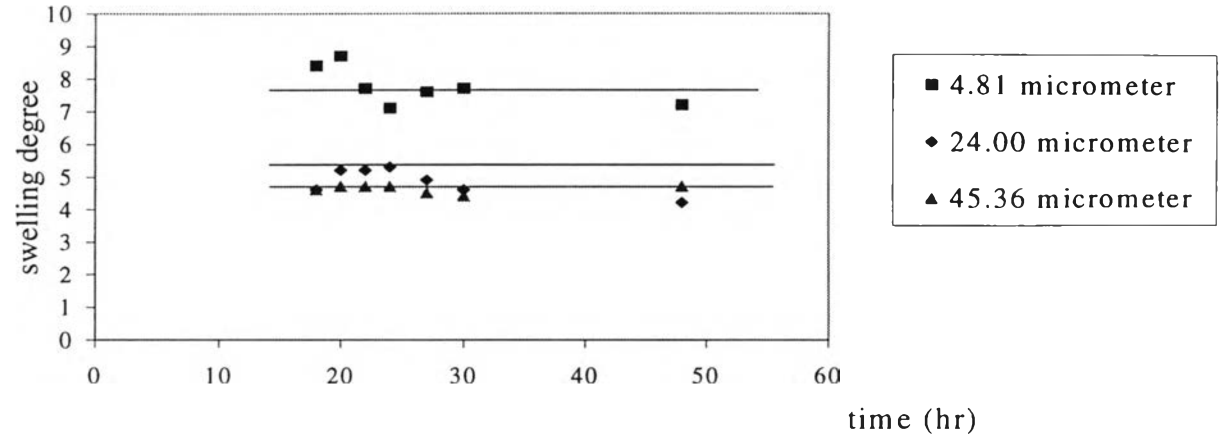


**Figure 4.12** Effect of poly(lauryl acrylate) particle size on swelling degree in toluene as a function of time.

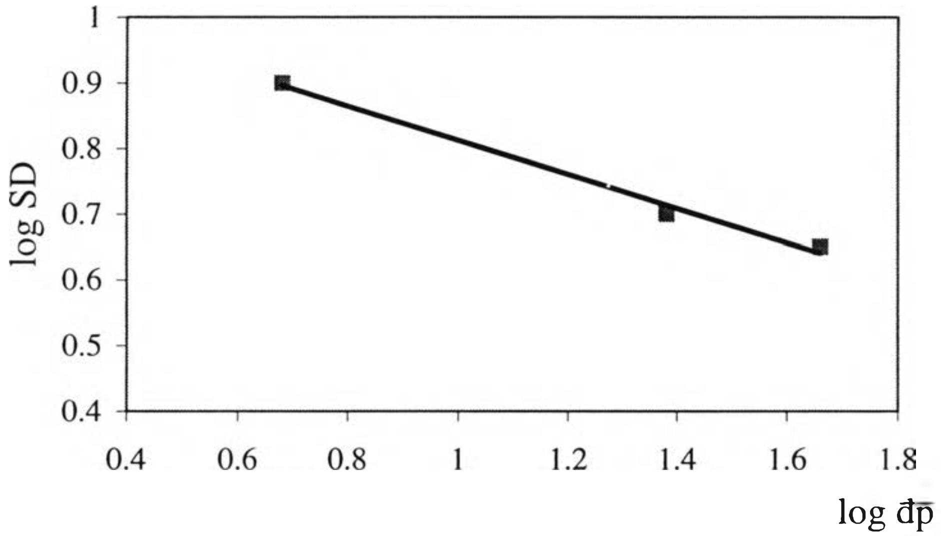


**Figure 4.13** Dependence of swelling degree on particle size

The capacity of the solvent absorption was dependent on the particle size, which can be explained by the relationships between specific surface area and average particle diameter by the following equation.

$$\frac{A}{W/\rho_p} = \frac{6}{\bar{d}_p} \qquad (4.1)$$

where A is the specific surface area ($m^2/m^3$)

W is the polymer particle weight (g)

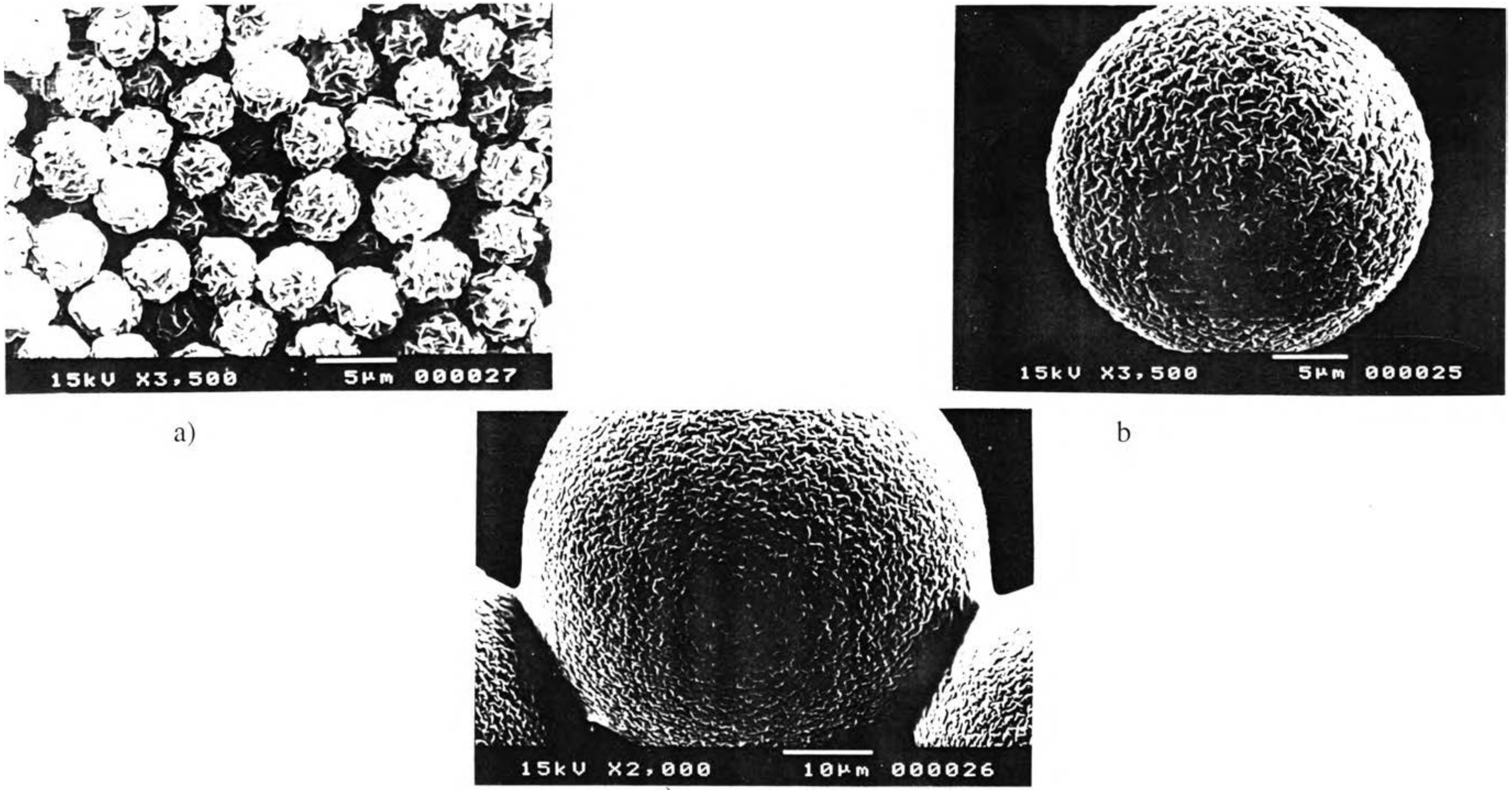
$\rho_p$ is the density of polymer particles ($g/cm^3$)

$\bar{d}_p$ is the average particle diameter (µm)

From the equation 4.1, A $\alpha$ $1/\bar{d}_p$ that the increasing of the surface area is related with the decrease of average particle diameter which corresponds to the increasing capacity of solvent absorption with the decreasing average particle diameter as shown in Fig.4.13. This result was similar to the experiment of Ikkai et al. [30] and Enscore et al [43]. Enscore et al. explained that the absorption of the large sizes happened only in the outer shell of the spheres because of either an inherent anisotropy in the large spheres or an anisotropy induced at some radial position by the prior swelling of the outer shell of the large sphere. Figure 4.14 shows the surface feature of the polymer particles prepared with the SPG pore size of 0.9, 5.25 and 9.0µm. The feature of creased surface was still remained even though the SPG membrane of other pore size was used.

### 4.5.2 Effect of absorption times on the capacity of the solvent absorption

Poly(lauryl acrylate-co-EGDMA) particles prepared with an SPG pore size of 5.25 µm was used to test the capacity of the solvent absorption with various time intervals in heptane. The polymer particles were swollen in heptane for three times as shown in Figure 4.15. It was found that the highest swelling degree was obtained at the third absorption and the lowest swelling degree was the first absorption. However, the swelling degree remained unchanged, and the polymer sphere was not deformed or collapsed after the third absorption. The third time swelling degree was higher than the second and the first times can be explained by the hysteresis. Hysteresis is the viscoelastic nature of copolymer chains, that is, the copolymer chains were not shrunk to the original chain length after swelling in solvent and drying. Thus, this polymer was appropriate for applying to repeated uses in solvent absorption.



a)

b

c)

**Figure 4.14** SEM photographs of surface features of poly(lauryl acrylate-co-EGDMA) particles with various SPG pore sizes: a) 0.9 µm, b) 5.25 µm, c) 9.25µm.

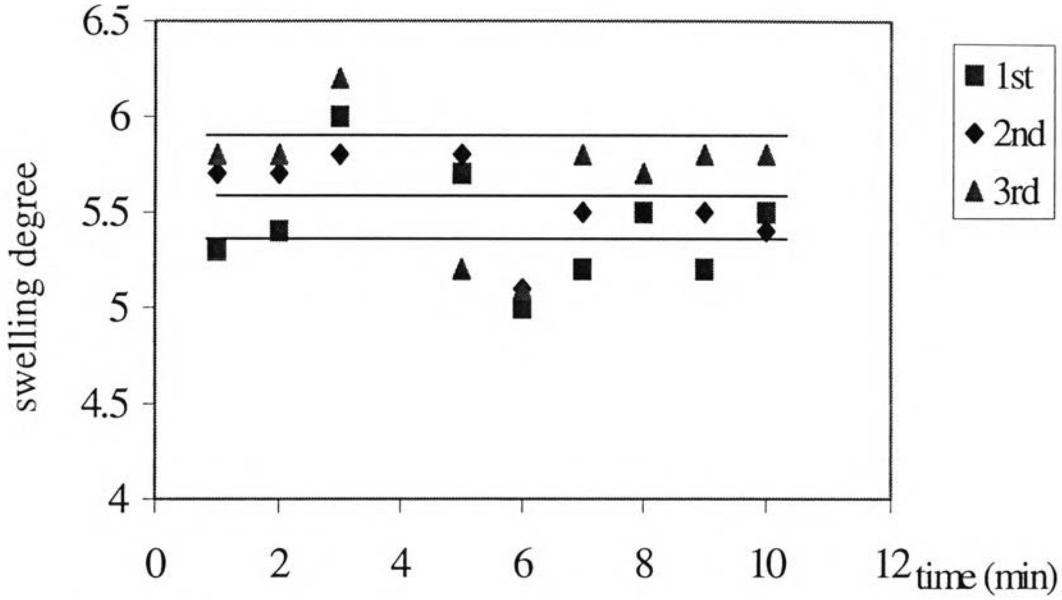


**Figure 4.15** The swelling degree of poly(lauryl acrylate-co-EGDMA) prepared with a SPG pore size of 5.25 µm and the repeated stage as function of time.

### 4.5.3 Effect of penetrant types on the capacity of the solvent absorption

The capacity of the solvent absorption of poly(lauryl acrylate-co-EGDMA) particles prepared with the SPG pore size of 0.9 µm with various penetrant types in a series of aliphatic hydrocarbon solvents, such as isooctane, heptane, dodecane and cyclohexane, and aromatic hydrocarbon solvents, such as toluene, xylene and benzene. Besides, the mixed solvents between toluene and heptane (50:50 by weight) were also measured at room temperature after 10 minutes of immersion. The calculations of average value of the solubility parameter of copolymer and the mixed solvents are shown in Appendix B. The basic physical properties and the swelling degree of each penetrant are shown in Table 4.17.

Figure 4.16 shows the capacity of the solvent absorption by various penetrant types with respect to their solubility parameters. The solubility parameter value seems to be a major factor influencing the capacity of the solvent absorption.

**Table 4.17 Physical properties of penetrants and swelling degree**

| penetrant | Solubility parameter[41] (MPa$^{1/2}$) | Density at 25°C[41] (g/cm$^3$) | Molecular weight | Swelling degree |
|---|---|---|---|---|
| Isooctane | 14.3 | 0.692 | 114.23 | 5.0 |
| Heptane | 15.1 | 0.684 | 100.21 | 5.2 |
| Dodecane | 16.2 | 0.750 | 170.34 | 5.6 |
| Cyclohexane | 16.8 | 0.779 | 84.16 | 6.2 |
| Xylene | 18.0 | 0.860 | 106.17 | 6.9 |
| Toluene | 18.2 | 0.867 | 92.14 | 7.1 |
| Benzene | 18.8 | 0.878 | 78.11 | 7.1 |
| Mix TH[a] | 16.5 | - | - | 6.0 |

[a] the mixed solvents between tolulene and heptane with 50:50 % by weight

However, the polymer particles were able to absorb the aromatic hydrocarbon solvent more than the aliphatic hydrocarbon solvent, despite (the fact that) the acrylic chains composing the polymer particles are relatively polar.

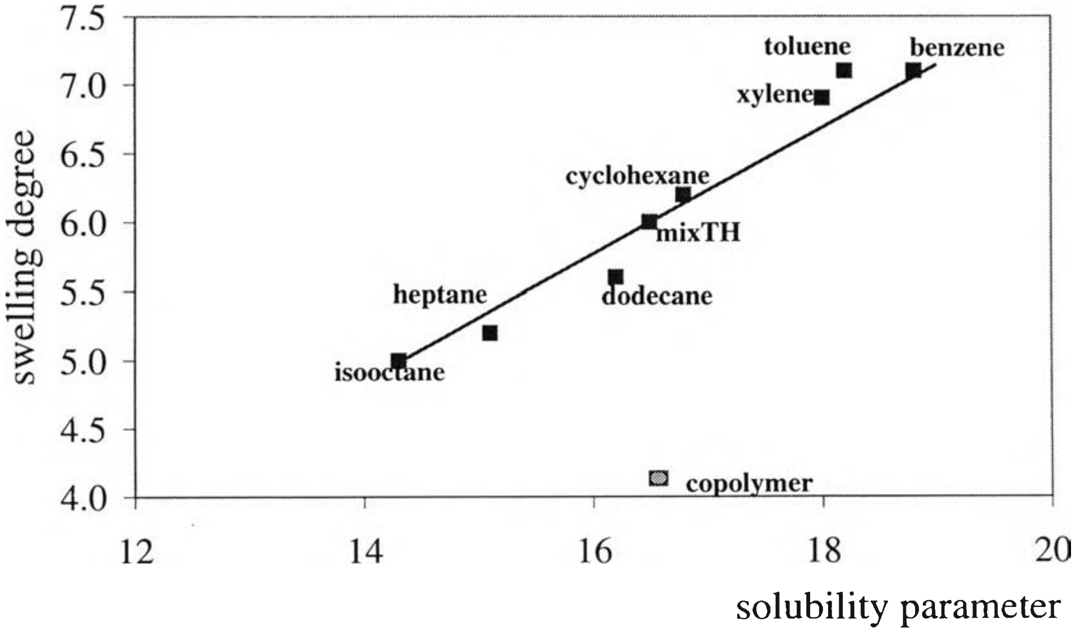


**Figure 4.16** Capacity of the solvent absorption with various solvents

## 4.6 Other characterizations

### 4.6.1 Porosity of the beads

The porosimeter (PROSORP VAS-3000) was used to measure the porosity, the pore size distribution and the specific surface area of the four polymer particles as follows:

1. The finely porous surface particle of poly(2-EHMA-co-EGDMA): 2-EHMA: EGDMA, 70%:30%, respectively by weight based on the weight of the monomer and crosslinking agent(sample no.15).
2. The smooth surface hollow particle of poly(2-EHA-co-MMA-co-EGDMA): 2-EHA: MMA: EGDMA, 35:35:30%, respectively by weight based on the weight of the monomer and crosslinking agent(sample no. 17).
3. The spongy surface hollow particle of poly(2-EHA-co-MMA-co-EGDMA): 2-EHA: MMA: EGDMA, 14:56:30%, respectively by weight based on the weight of the monomer and crosslinking agent(sample no. 19).
4. The creased surface particle of poly(lauryl acrylate) luaryl acrylate: EGDMA, 70%:30%, respectively by weight based on the weight of the monomer and crosslinking agent(sample no.25).

The surface feature and morphologies of these polymer particles are shown in Figure 4.17.

The data of the specific surface area, the pore volume, the particle diameter are shown in Table 4.18, and the pore size distribution curve of each sample is shown in Figure 4.18.

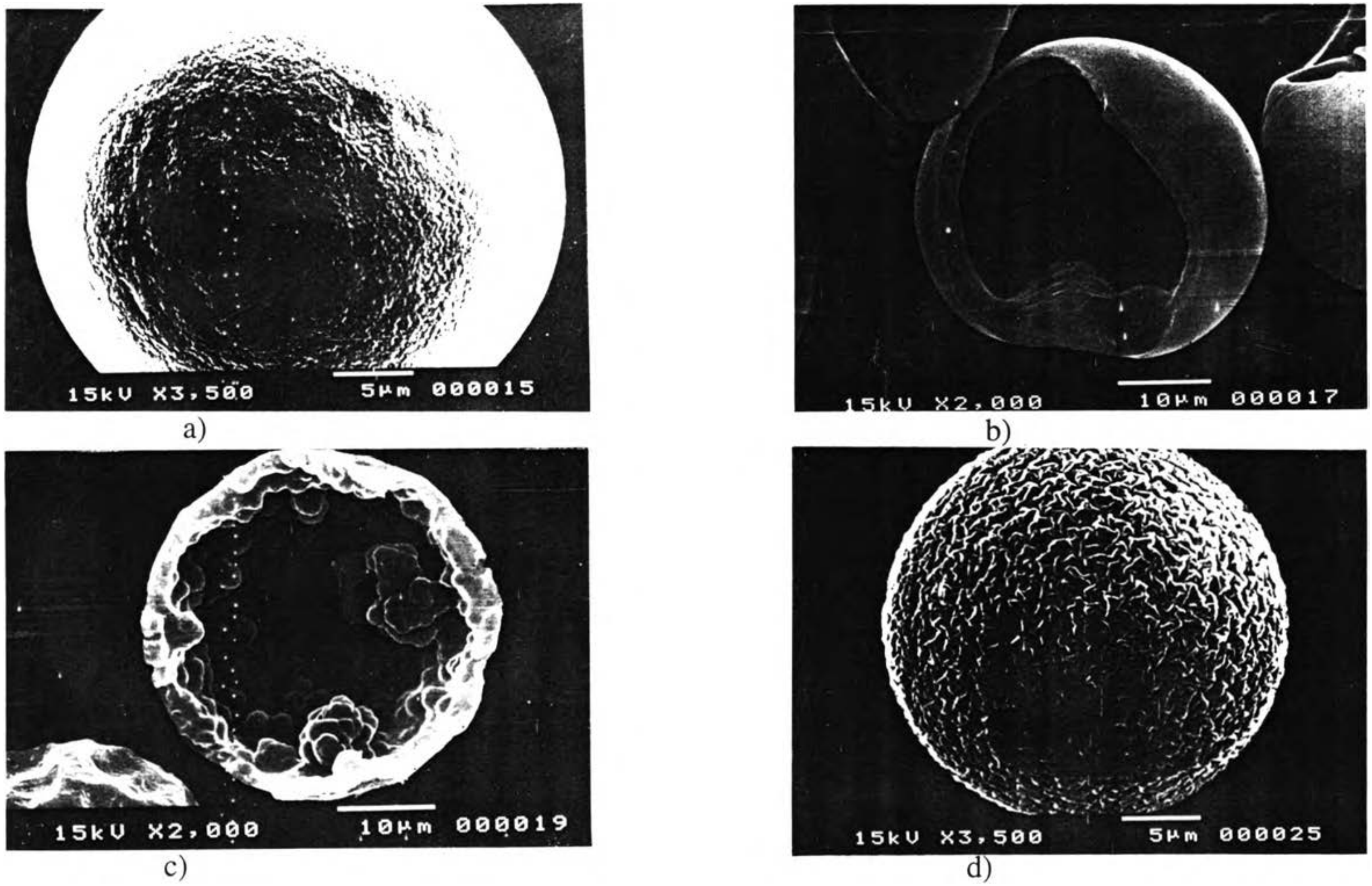


**Figure 4.17** SEM photographs of the polymer particle microspheres of various surface features and morphologies used in the porosity measurements: a) finely porous surface, b) smooth hollow morphology, c) spongy hollow morphology, d) creased surface.

**Table 4.18 Characteristics of polymer particle surface and pore**

| Sample no. | Character of polymer particle | Specific surface area ($m^2/g$) | Pore volume $(ml/g)10^{-4}$ | Pore diameter ($A^o$) |
|---|---|---|---|---|
| 15 | Finely surface | 30.40 | 9.4, 1.16-4.6 | 27, 68.5-940 |
| 17 | Smoothly hollow | 3.00 | 1.3 | 46 |
| 19 | Spongy hollow | 3.67 | 1.1 | 41 |
| 25 | Creased surface | 3.37 | 1.2 | 44 |

The pore size distribution of sample no.15, with the finely porous surface, gave one sharp peak and a wide range of pore volume and pore diameter whereas the others possessed only one sharp peak of the pore volume and the pore diameter. Virtually, no samples possessed an appreciate amount of pore volume. All of the samples gave the mesopore except sample no.15, which possessed both mesopore and a little macropore. Besides, the highest of the specific surface area was also obtained from sample no.15 and the lowest one was obtained from sample no.17, which was the smooth hollow morphology. However, the highest swelling degree was observed from sample no.25, having the creased surface, and the lowest one was obtained from sample no.15. It indicated that the creased surface with the lower specific surface area was able to absorb more solvents, such as toluene and heptane, more than the finely porous surface, which had the higher specific surface area. Thus, in this case, the capacity of the solvent absorption was only dependent on the type of monomer.

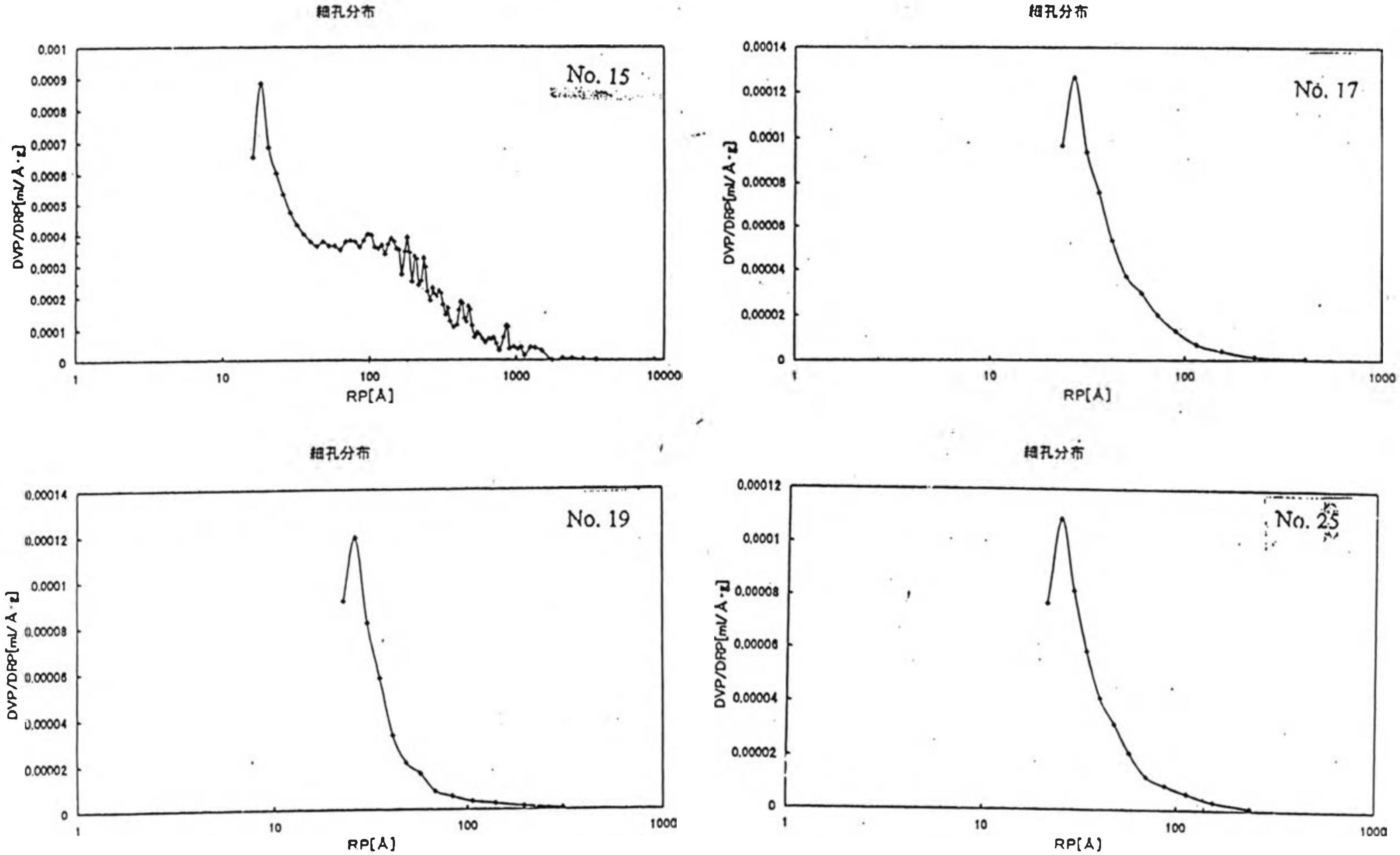


Figure 4.18 The pore size distribution of the polymer particles.

### **4.6.2** Glass transition temperature of the polymer particles

A cross-link has the opposite effect to a decrease in molecular weight: as the cross-link density increases, the free volume of a sample decreases, and the glass transition temperature increases correspondingly[26] .

In general, the presence of a crosslinking agent in a sample increases its Tg relatively to an uncrosslinked sample because of the restricted motion of the chain segments near crosslinked sites [42]. From the data as shown in Table 4.19, it was found that the crosslinked copolymers using 2-EHA, 2-EHMA and lauryl methacrylate as monomers, the Tg values of the crosslinked polymers were higher than those of homopolymers. In contrast, in the case of lauryl acrylate, cyclohexyl acrylate and MMA as monomers, the Tg values of the crosslinked polymers were lower than their corresponding homopolymers. It indicated that the intramolecular bonding of the latter crosslinked polymers had repulsieve force, which made the chains more flexible and easy to rotate, and thus the low Tg crosslinked polymer was obtained. The DSC curves of the crosslinked polymers are shown in Figure 4.19. Figure 4.20 shows the DSC curves of poly(2-EHA-co-MMA-co-EGDMA) with various ratios of 2-EHA and MMA with the constant content of 30% EGDMA based on the weight of the monomer and crosslinking agent. It was found that increasing the MMA amounts resulted in an increase of the Tg value of the crosslinked polymers.

**Table 4.19 Glass transition temperature of the homopolymers and their crosslinked copolymer**

| *Type of polymer* | *Tg (°C)* |
|---|---|
| P(2-EHA) | -85.0[a] |
| P(2-EHA-EGDMA, 70:30%) | -0.8[b] |
| P(2-EHMA) | -10.0[a] |
| P(2-EHMA-EGDMA, 70:30%) | 8.5[b] |
| P(Lauryl acrylate) | -3.0[a] |
| P(Lauryl acrylate-EGDMA, 70:30%) | -18.1[b] |
| P(Lauryl methacrylate) | -65.0[a] |
| P(Lauryl methacrylate-EGDMA, 70:30%) | 29.0[b] |
| P(Cyclohexyl acrylate) | 19.0[b] |
| P(Cyclohexyl acrylate-EGDMA, 70:30%) | 16.7[b] |
| P(MMA) | 105.0[a] |
| P(MMA-EGDMA, 70:30%) | 24.7[b] |
| P(2-EHA-MMA-EGDMA, 56:14:30%) | -2.8[b] |
| P(2-EHA-MMA-EGDMA, 35:35:30%) | 24.7[b] |
| P(2-EHA-MMA-EGDMA, 14:56:30%) | 24.7[b] |

[a] data from polymer handbook [42],

[b] data from the experiment

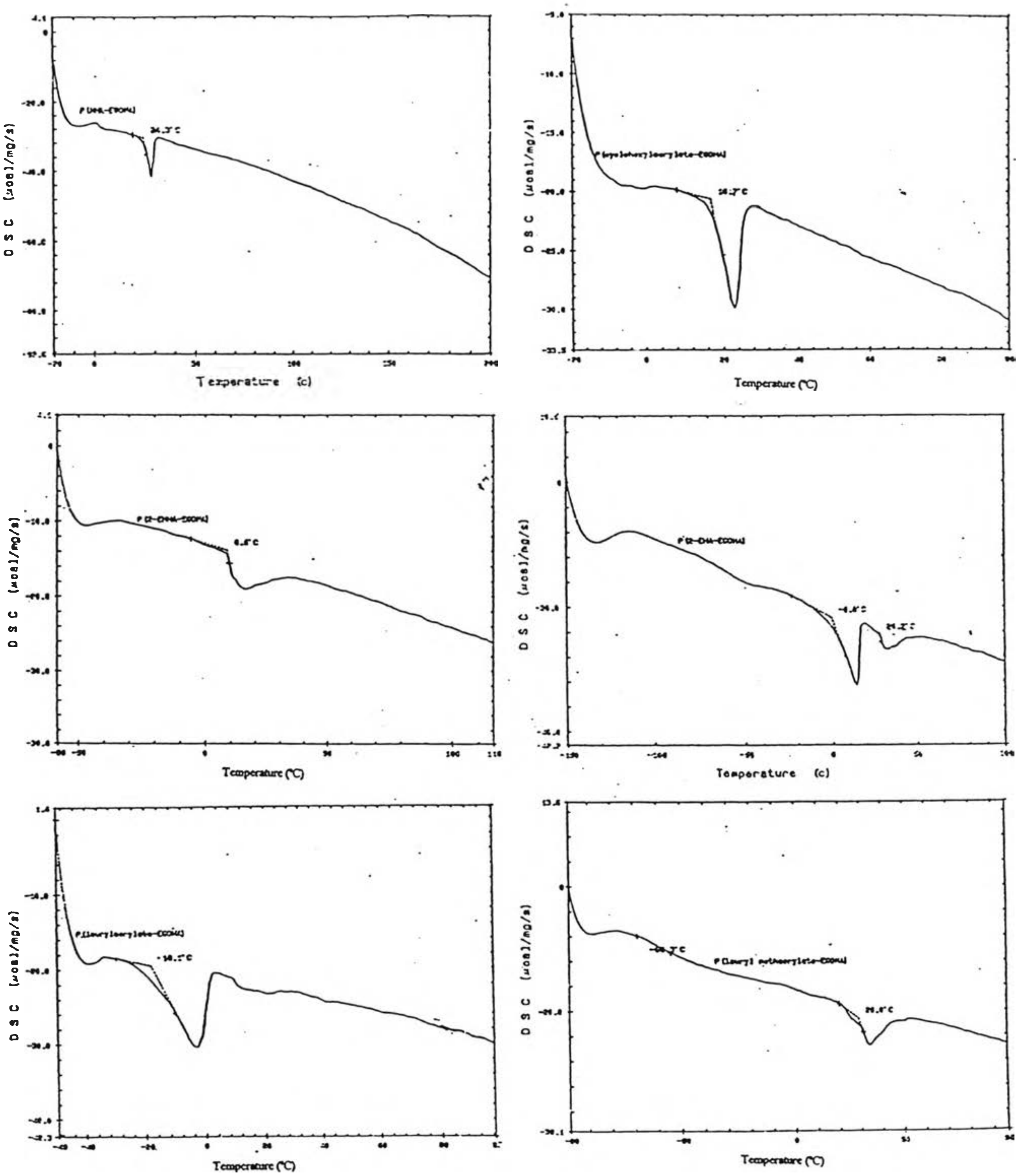


**Figure 4.19** The DSC curves of crosslinked polymers; a) poly (MMA-co-EGDMA) particles, b) poly (cyclohexylacrylate-co-EGDMA) particles, c) poly (2-EHMA-co-EGDMA) particles, d) poly (2-EHMA-co-EGDMA) particles, e) poly (laurylacrylate-co-EGDMA) particles, f) poly (lauryl methacrylate-co-EGDMA) particles.

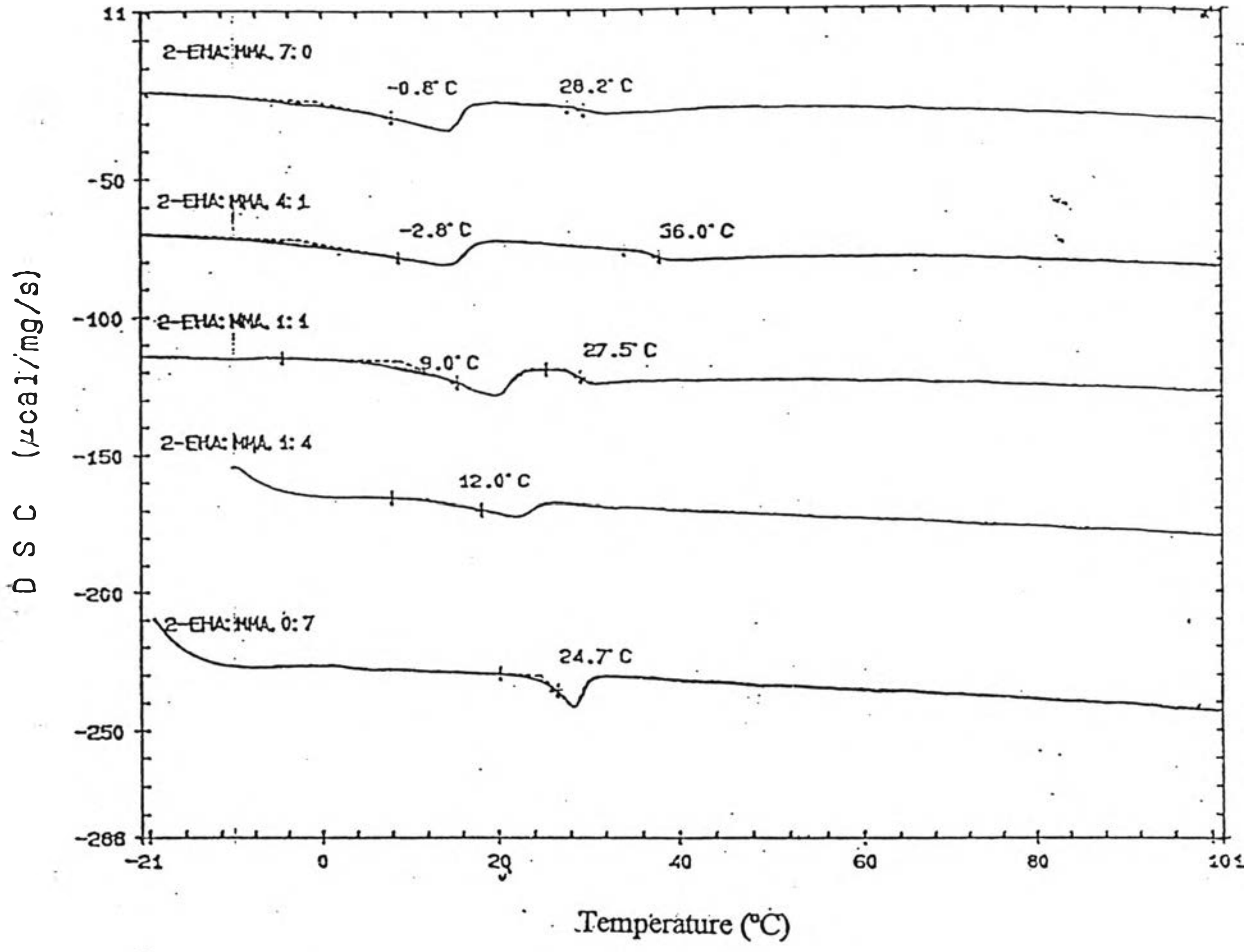


**Figure 4.20** The DSC curves of poly(2-EHA-co-MMA-co-EGDMA) particles with various ratios of the comonomers at the constant content of 30% EGDMA