



## CHAPTER 5

### CONCLUSION

A variety of crosslinked (meth)acrylate polymer particles with unique morphologies/surface features were synthesized employing SPG pore sizes of 0.9, 5.25 and 9.25  $\mu\text{m}$ . The appropriate recipe between monomer, crosslinking agent, and heptane is 70:30:70 % by weight based on the weight of the monomer and crosslinking agent.

The emulsion droplets and polymer particle sizes were dependent on the ratios between the crosslinking agent, EGDMA and heptane, that is, the trend of sizes was decreased with increasing amounts of EGDMA and heptane. The coefficient of variation (CV) close to 10% and the standard deviation ( $\sigma$ ) close to 4 were obtained from each experiment.

The amount of EGDMA and solvents, toluene and heptane, had a strong effect on the morphology/surface feature. Increasing EGDMA and heptane amounts enhancing the high degree of the macro phase separation resulted in increasingly rough surface of the polymer particles, which also affected the capacity of the solvent absorption. Poly(2-EHA-co-EGDMA) particles with the high amount of EGDMA (40%) at 45 and 70% of heptane were ruptured after swelling in solvents, toluene and heptane, because the densely crosslinked network was unable to expand freely under the swelling stress due to the decreasing balance between the diffusion and relaxation rates.

Poly(2-EHA-co-EGDMA) particles with a  $\delta$  value of 16.3  $\text{MPa}^{1/2}$  prepared in various solvent types with different solubility parameters and the chemical structures, such as heptane (a straight-chain alkane,  $\delta=15.1 \text{ MPa}^{1/2}$ ), isooctane (a branched-chain alkane,  $\delta=14.3 \text{ MPa}^{1/2}$ ) and cyclohexane (a cycloalkane,  $\delta=16.8 \text{ MPa}^{1/2}$ ) influenced the surface feature of the polymer particles and the capacity of the solvent absorption. On the basis of the partially close polymer/solvent interaction value, a good solvent resulted in the high swelling degree. The finely porous surface was also obtained. The good solvent enhanced the micro-phase separation and the good solvent was able to expand and swell the highly-crosslinked network whereas the poor solvent only

expanded the crosslinked network only. Thus, the high swelling degree along with the finely porous surface was obtained from cyclohexane as a solvent.

The monomer types with different  $T_g$  values, such as 2-EHA ( $T_g = 188$  K), 2-EHMA ( $T_g = 263$  K), lauryl acrylate ( $T_g = 270$  K), lauryl methacrylate ( $T_g = 208$  K), cyclohexyl acrylate ( $T_g = 292$  K) and MMA ( $T_g = 378$  K) influenced the surface features/morphologies and the capacity of the solvent absorption at the constant content of 30% EGDMA and 70% heptane. The monomers of 2-EHA, lauryl acrylate and cyclohexyl acrylate produced the creased surface, while 2-EHMA and lauryl methacrylate monomers produced the finely porous surface, and MMA monomer gave the particles with the spongy hollow morphology. The capacity of the solvent absorption of acrylate monomer and methacrylate monomers depended on the substituent group at the alpha-carbon atom in which a small substituent group provides higher flexibility to the chains and the stretching of the chains to absorb solvent is easier. Thus, the capacity of the solvent absorption of the acrylate monomers was higher than the methacrylate monomers because the acrylate monomers have a hydrogen atom in the alpha-carbon atom whereas the methacrylate monomers have a methyl group at the alpha-carbon atom. Besides, the highest swelling degree was obtained when lauryl acrylate was used as a monomer.

The spongy and smooth hollow morphologies were obtained which depended on the ratios between 2-EHA: MMA: EGDMA at the constant content of 70% heptane. It was found that the increase of 2-EHA improved the surface feature of the hollow spheres from the spongy hollow morphology to the smoothly hollow morphology. Decreasing amount of the hydrophilic MMA segment decreases the hydrophilic moieties, which have decreased affinity with water molecules. Thus, the smoothly hollow morphology was obtained. The capacity of the solvent absorption was not satisfactory because the surface of the hollow morphology was too hard to absorb the solvents, so the hollow polymer particles were not appropriate for applying to the solvent absorption.

The difference of the surfaces feature/morphologies between finely porous surface, creased surface, spongy hollow morphology and smooth hollow morphology, which were prepared by SPG pore  $5.25 \mu\text{m}$  exerted various effects on the capacity of the solvent absorption. It was found that the crease surface of poly(lauryl acrylate-co-EGDMA) particles with mesopores about  $44 \text{ \AA}$ , pore

volume of  $1.2 \times 10^{-4}$  ml/g and the specific surface area of  $3.37 \text{ m}^2/\text{g}$  had the highest swelling degree to 7.1 times in toluene and benzene.

The polymer particle size affects the capacity of the solvent absorption, that is, the smallest particle size obtained by SPG pore size of  $0.9 \text{ }\mu\text{m}$  gave the highest swelling degree at the same conditions whereas  $9.25 \text{ }\mu\text{m}$  gave the lowest swelling degree.

Poly(lauryl acrylate-co-EGDMA) particles were able to absorb both aliphatic hydrocarbon solvents, such as heptane, isooctane and cyclohexane, and aromatic hydrocarbon solvents, such as toluene, xylene and benzene, including the mixed solvent between the aliphatic hydrocarbon solvent and the aromatic hydrocarbon solvent, i.e. heptane and toluene. The particles did not rupture or collapse after the swelling in solvents. Therefore, the polymer particles could be used repeatedly at least 3 times. Thus, these polymer particles were appropriate to apply to the solvent absorption, especially in the aromatic hydrocarbon solvents, which yielded the highest swelling degree.