

## CHAPTER 5

### CONCLUSION

Dispersion polymerization has proved to be an efficient technique for producing monodispersed microspherical particles of high molecular weight in a single step. The present work, based on this method, was successful in preparation of poly(styrene-co-*n*-butyl acrylate) and poly(styrene-co-2-ethylhexyl acrylate) particles in the ethanol/water medium using PVP and AIBN as dispersant and initiator, respectively. The resulting particles were in the size range of 0.6-1.8  $\mu\text{m}$  with a narrow size distribution ( $CV < 10\%$ ).

Control of particle size and its uniformity was a major area of this research. Several reaction parameters involved in determining the final particle size and its distribution are thoroughly investigated. We can therefore conclude the findings as follows:

The particle size decreased as the concentration and molecular weight of dispersant increased. Significantly, the amount of dispersant should only be sufficient to cover the surface of polymeric particles formed during the polymerization. Insufficient or exceed amount of dispersant is the failure of monodispersity. These conditions are the causes of the particle coalescence and the secondary stabilization of new particles, respectively. From this research, the highly recommended dispersant is PVP K-30 at the concentrations of between 2-8 wt%.

Solvency or polarity is one of the key components to achieve monodispersity. Polarity of the reaction medium can be altered by replacing some part of ethanol with water. Increasing the polarity of the reaction medium leads to reduction in particle size, however too high or too low medium polarity would generate the particles with a broad size distribution. It was found that a reaction

medium of ethanol/water having a weight ratio of 90/10 was most suitable for producing the copolymer particles with a narrow size distribution.

The temperature is one of the main parameters that was effective on size and size distribution of the particles. Larger particles were obtained when the polymerization temperatures were high. Interestingly, the narrow size distribution of the particles remained unchanged within the temperature range of 65-75°C. Using the temperature at 80°C resulted in large particles with an undesirably broad size distribution.

It was noted that the polymerization carried out in the stirred glass reaction at different agitation rates resulted in different particle sizes. The higher the rate, the smaller the resulting particles. However, when the rate of agitation was increased up to 300 rpm, a large number of secondary particles were obtained. For this reason, it is suggested that the stirred glass reactor with a high agitation rate be not efficient in producing the uniform particles.

Control of glass transition temperature of the copolymer is one of the most interest in this research. The copolymer particles with a  $T_g$  in the range of 66-102°C can be achieved by adjusting the suitable ratio of styrene and acrylate monomers in the monomer feed. The high composition of both *n*-butyl acrylate and 2-ethylhexyl acrylate yields the particles with a lower  $T_g$ . Furthermore, the feed composition also affects the size of the final particles. Since an increase in the amount of acrylate monomers is similar to increasing the polarity of the reaction medium, thus in this case the large particles were obtained. Instead of using *n*-butyl acrylate monomer in the copolymerization, the 2-ethylhexyl acrylate copolymerization with styrene resulted in insignificant change in the particle sizes but with the significant decrease in  $T_g$  values.

The amount of crosslinking agent (EGDMA) incorporated to develop the network in the particle is limited. Less than 1% of the crosslinking agent, the particles still maintain their spherical shape; when the concentration increases

beyond this level, the odd shape of the resulting particles was observed. The reason for this phenomenon lies in the effect of destabilization of PVP and the phase separation occurred during the copolymerization.

In most cases of the experimental results, an inverse correlation between particle size and molecular weights is obtained. As the particle size decreases, the average molecular weight increases. This rationale depends mainly on the locus of the polymerization, which involves both solution and monomer-swollen particle phases. The molecular weights of particle-phase polymerization are usually higher than those in solution polymerization, because the termination rate is reduced due to the gel effect. For small particles, a higher proportion of the polymerization occurs in the particle phase, because the oligomeric radicals initiated in solution are captured more efficiently by the smaller particles due to their greater surface areas. In contrast, the large particles can grow by capturing dead polymer molecules already in the solution, thus exhibit the low molecular weight.

The focus of this work is to define the operating parameters for preparation of monodisperse micronsize particles. Future work is suggested to develop the properties of the monodispersed micron-sized polymer for use as potential materials in various applications, and it may be done as follows:

1. Incorporation of different functional groups onto the surface of particles to improve the surface properties of the polymer.
2. Copolymerization with organic dye to achieve colored particles for dry toner application in a single step of manufacturing.
3. Preparation of highly crosslinked microspheric polymer for superior heat and solvent resistant properties.