

CHAPTER V

CONCLUSION

Many scientific and industrial applications require the use of polymeric particles of controlled size. Recently, there have been increasing activities in the development of new methods of preparing polymer particles with a well-defined size range in the vicinity of 2-10 μm . One of the most successful methods was the synthesis of superfine PS by dispersion polymerization in the presence of PMVE matrix polymer, the recent work of Prof. N. Ogata et al. Based upon this idea, the present work was investigated to prepare the micron size poly(styrene-co-methyl methacrylate) at various feed ratios and solvent mixing ratios.

In a dispersion polymerization, the reaction requires that all of the monomers, initiator, and stabilizer are soluble in the solvent as one phase, thus, the reaction mixture starts out as a homogeneous solution and that the resulting polymer precipitates as a spherical polymer. Among the dispersion copolymerizations, it should be noted that, the copolymerization systems of 25 mole% styrene feed at 0 and 20 weight% ethanol appeared to be a two-phased system and it remained as such until the end of the reaction. Therefore, these two systems could not be explained by using the theory of dispersion polymerization.

Together with the dispersion copolymerization, the solution and bulk copolymerizations were also carried out in order to investigate a particle formation. By comparing the copolymer composition, there was no difference among these three copolymerizations. Therefore, the copolymer composition may be not the major factor of the particle formation mechanism and the questions still demand further investigation for the other parameters such as the extent of polymerization in order to obtain more information of the particle nucleation and the particle size range.

The solution and bulk copolymer particles could not be obtained in the spherical shape. This was because of the absence of the PMVE matrix polymer, that was used as a steric stabilizer and particle size controlling agent. Particle stability is achieved by the interposition of repulsive force of a sufficient magnitude to overcome the inherent attractive force of electromagnetic origin; therefore, in the absence of any repulsive forces, the particles rapidly aggregate. Consequently, the spherical styrene-

co-methyl methacrylate polymer can be synthesized only by using the dispersion polymerization in the presence of a particle size stabilizer (or a matrix polymer).

Dispersion copolymers were produced in the size range of 1-5 μm . The particle size and dispersity of the resulting copolymer were controlled by varying the monomer feed ratios, mixed solvent ratios between ethanol and n-hexane and the reaction temperatures.

By varying the feed ratio of St/MMA in the dispersion copolymerization, it was found that, the particle size and size distribution decreased with increasing the styrene feed. This would be due to the difference in polarity of the two monomers and the matrix polymer. Based on the electron accepting-electron donating theory, the electron donating styrene monomer could form a stronger interaction with the electron accepting PMVE. Therefore, styrene radical was adsorbed much stronger on PMVE matrix than the MMA radical, which contributed to the smaller particles in high styrene content systems. The higher weight-average molecular weights were obtained in the styrene and methyl methacrylate homopolymerizations and molecular weights decreased in the copolymerizations. The number-average molecular weight, on the other hand, was not significantly sensitive to the styrene feed.

The size and size distribution of the resulting copolymers were mainly controlled by changing the morphology of the matrix polymer in solution which was caused by varying the mixed solvent polarity. The smaller particle size was obtained when increasing the ethanol concentrations. This can be explained in terms of solubility parameters. The solubility parameter of the PMVE matrix is rather close to the solubility parameter of ethanol than n-hexane. In the other words, ethanol acts as a good, polar solvent and n-hexane acts as a poor, non-polar solvent for the PMVE matrix. The PMVE matrix polymer can dissolve easily and its chains stretch freely in ethanol but entangle or aggregate to become a coiled structure in the poor solvent of n-hexane. The conformation of the PMVE chains gives a volume (or free-space) change in the polymer solution. This resulted in more free spaces between chains in poor solvent dispersion system, which allows the fast growth of particles among the PMVE chains. The greater the free volume between the PMVE chains, the larger the copolymer particle sizes. Therefore, the free volume of the system is a controlling factor of particle growth. It is anticipated that equal free volumes of the polymer chains give a narrow particle size distribution.

Temperature of the copolymerization is another important factor. The lower and upper temperature limits for this dispersion copolymerization were 50 and 64°C, respectively. At 40°C, the reaction did not occur due to thermodynamic effect of energy requirements to decompose the initiator, and on the other hand, the reaction

gave the agglomerated particles at 73°C. When increasing the reaction temperatures, the average particle size and size distribution were also increased due to that the small particles obtained initially can combine easily at high temperatures caused by the soften particle surfaces. Expansion of the agglomeration of the small particles can occur spontaneously to form huge aggregates and finally a continuous film as in the 73°C system. In all cases, the higher average molecular weight was found in the small-sized particles.

To further develop the synthesis of small particle size with a narrow size distribution, suggestions arisen from the present research are the following:

1. Effect of flow rate of the monomers feeds on copolymer composition and particle size should be considered so as to design the required composition of copolymer to be further used as a toner.
2. The extent of copolymerization can provide insight information of the particle formation, such as, the period of particle formation and the number of big and small particles at various reaction times of polymerization. Careful investigations on the extent of copolymerization should be pursued.
3. Determination of the appropriate amount of PMVE matrix polymer to prevent particle flocculation should also be investigated.