

CHAPTER V

CONCLUSION

Dispersion copolymerization of styrene and methyl methacrylate in the presence of the PVP matrix polymer in an ethanol-water system is studied in order to obtain narrow size distribution of the copolymer particles. The present research is able to prepare the styrene/methyl methacrylate copolymer particles that have a narrow size distribution (Monodispersed) with a CV of smaller than 10%, which is similar to the work of Takahashi, et al. (61).

In this research, poly(styrene-*co*-methyl methacrylate) particles of 0.3 to 1.5 μm in diameter can be prepared by dispersion polymerization in ethanol/water mixture using PVP as the matrix polymer and AIBN as an initiator. The results indicating that co-stabilizer (co-matrix polymer) as previously discussed is not an essential component of reaction mixtures for preparing the narrow size distribution polymer particles in this works. Nevertheless, the matrix polymer is important for stabilizing the polymer particles and controlling the size and dispersity of the polymer particles. Dispersion polymerization system without the matrix polymer, agglomerated particles or even sheets were produced. The absence of any repulsive forces generated by barriers of soluble matrix polymer and the attractive force operating between two adjacent particles, usually called the van der waals force, are the main attribute to the rapid coalescence of the particles.

The copolymer particles controlled by the matrix polymer have a spherical shape because the aggregative nucleation mechanism will take place in dispersions if the kinetic energy of two colliding particles is larger than the energy of stabilization (the sum of the repulsive steric energy and the van der waals attraction energy) (62). In conclusions, the matrix polymer stabilizes growing oligomers against capture by particles of lower molecular weights, so it reduces the probability of capture and produces more nuclei, besides the matrix polymer participates in forming incipient nuclei and reduces interfacial tension, to reduce the probability of capture. Finally the matrix polymer prevents or limits agglomeration of small particles to form larger ones, thereafter, the total particle surface area and hence the number of particles, are limited by the amount of the matrix polymer (63).

The largest poly(styrene-*co*-methyl methacrylate) particles with a narrow size distribution of 1.5 μm ($\text{CV} = 4.75\%$) and the weight average molecular weights of 79214 with a molecular weight distribution (M_w/M_n) of 2.65 could be obtained by using 2 wt% PVP K-30 at the reaction temperature of 60°C whereas the same system containing 12 wt% PVP K-30 gave the smallest particle size with a narrow size distribution of 0.3 μm ($\text{CV} = 9.07\%$) and the weight average molecular weights of 34016 with a molecular weight distribution of 2.25. The polymerizing system of styrene and methyl methacrylate having 6 wt% PVP K-30 gave the copolymer particles with the narrowest molecular weight distribution ($\text{MWD} = 1.81$). Therefore, it is highly recommended that the matrix polymer concentration should be optimized first to achieve a narrow size distribution along with the desirable particle size of the copolymer. Additionally, the optimum reaction temperature for controlling the narrow

molecular weight distribution of the copolymer is at 70°C because the MWD produced at this temperature is 1.51. The molecular weight distributions (MWD) of most copolymer particles prepared in this research are in the range of 2-3.

The dispersion copolymerization of styrene and methyl methacrylate initiated by AIBN under various conditions emphasizes that the PVP matrix polymer concentration, the polarity of the reaction medium, the reaction temperature, the reaction time, the agitation rate and the feed ratio of styrene/methyl methacrylate significantly affect the size and dispersity of the polymer particles obtained. The size of the resulting poly(styrene-*co*-methyl methacrylate) particles decreased with increasing PVP K-30 concentration, the increasing polarity of the reaction medium, the increasing agitation rate and the high feed ratio of styrene (75%). The particle dispersity of most copolymer particles is still of a narrow size distribution. In some polymerizing conditions, the broad size distribution of PSD = 1.07-1.17 (CV>10%) was obtained, which can be illustrated by the reaction temperature of 50°C and the reaction medium having a water content of 40 parts. When a 100% water or pure ethanol was used as the reaction medium instead of a water/ethanol mixture, the copolymer particles have a broad size distribution. Using a water/ethanol mixture instead, the particle size becomes smaller and decreases with increasing water content. That is, the ratios between a good and poor solvent (expressed in terms of solubility parameters) greatly affect the particle size and size distribution.

The particle 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. In this research, the narrow particle size

distribution of the copolymers was obtained when the solvent mixture of ethanol/water contain 10-30 parts of water were used. This mixture contained 10-30 parts of water act as a good solvent for poly(N-vinyl pyrrolidone) matrix polymer. The matrix polymer can dissolve easily and its chains disentangle and then stretch freely in that medium. The expanded matrix polymer chains give the free volume (or free-space) in the matrix polymer solution, which controls morphologically the particle size of the copolymer. However, pure ethanol, pure water and a mixture contain 40 parts of water act as a poor solvent for the matrix polymer. The matrix polymer chains entangle or aggregate to become a coiled form in the poor solvent. The particle size distribution is controlled by the excluded free volume in solution of the matrix polymer, so the broad particle size distribution of the copolymer was obtained.

For particle growth, the phenomenon of the free volume within the matrix polymer chains is a main factor in controlling the particle formation. The larger the free volume in solution within the matrix polymer chains, the larger the size of the copolymer. The copolymer particles so obtained as a function of reaction time have a narrow size distribution, that is, these particles are controlled by the possibly equal free volumes of the matrix polymer chains in solution.

In addition to the investigation of various parameters mentioned above the development of surface charging of the polymer particles is also important for an application of electrophotography as a binder of the toner. The matrix polymer becomes anchored to the copolymer particles as discussed previously, although thorough washings have been carried out. Their surface properties could be dramatically affected by the nature of the matrix polymer.

Future Work

To further develop the properties of a narrow-sized distribution particles of poly (styrene-*co*-methyl methacrylate) to utilize for various applications, the future research work are suggested as below :

1. Control of the surface properties of the copolymer particles, such as surface charging by a development of a novel mixed matrix polymer system that allows an accurate control of the surface properties for applying to electrophotographic printing.
2. Improvement of mechanical stability and flow properties of the beads to attain higher separation efficiencies for use as a column packing material.

Investigation of dispersion copolymerization of the other monomers to determine the particle size and size distribution is also highly recommended.