CHAPTER 1

INTRODUCTION

1.1 Scientific Background and Rationale

Various polymers are produced as spherical particles ranging in sizes from 0.01 μm in emulsion process to 1000 μm in suspension process. The middle range of about 10-μm particles is not a mass-produced product but is used in many fields [1].

Recently, the micron-range size particles have received great interest because the demand of these potential particles with their uniformity has increased for use in special application such as toners, instrument calibration standards, standards for the determination of pore size and the efficiency of filters, column packing materials for chromatographic separation, support materials for biochemicals, and so on [2]. Several techniques have been developed to produce micron-size particles with narrow size distribution. Typically, suspension polymerization technique is used to prepare particles in required size ranges, but the resulting particles usually lack of uniformity. To reduce the polydispersity, particles require size-classification steps. The alternative approaches, successive seeded emulsion and two-stage swelling methods developed by Vanderhoff [3] and Ugelstad [4] are accomplished in obtaining monodisperse micron-size particles. When compared with the classical suspension polymerization both efficient techniques avoid size classification, but they are more complicated and time consuming. Therefore these techniques are not attractive for the large scale production.

Dispersion polymerization is the process overcoming aforementioned problems because of the simplicity of process requiring only one step polymerization. This method is a useful process for preparing particles in the 0.1 to 15 micron in diameter range with a narrow size distribution [5]. Unlike emulsion or suspension process, in dispersion polymerization, the monomer is completely miscible with the medium and the final polymer particle is insoluble under the same condition. Various monomers have been used in this technique. Selection of monomer depends on the performance expected for the resulting particle. For example, the dispersion polymerization of styrene and butyl methacrylate allows for control of the glass transition temperature of final copolymer particle [6]. This control may be particularly important for the preparation of suitable ultrafine particle toner.

One of the various applications of microsphere particle is the use of dry toners. Toners consist of binder (polymerized resin), pigments, charge controlling agents and additives [7]. Toner particle sizes are generally 3-8 μm in diameters [8]. Since toners were introduced in the mid-1950 there has been a steady trend toward smaller particle size because the smaller particle has given better print images with higher resolution and less roughness. Together with its uniform size distribution make it possible to impart a much more even charge on the particles and the particles become easier to control within the machine as they are transferred onto the paper. So, the particle size and size distribution are important parameters strongly influencing the quality of toners.

If the prediction holds, by the end of this decade, the technology for producing toner will attract considerable attention on super-fine particles with a narrow size distribution. Therefore, the interest in micron size particle with controlled uniformity for use as toner resins has led the present research to study in details of the dispersion polymerization of styrene and acrylate monomers.

1.2 Objectives of the Research Work

1. To synthesize the super-fine polymeric particles of styrene/*n*-butyl acrylate, and styrene/2-ethylhexyl acrylate by dispersion polymerization.
2. To prepare copolymer particles with a narrow size distribution.
3. To investigate the effect of important parameters on particle size, size distribution and average molecular weight of the copolymer.
4. To characterize the properties of the copolymer.

1.3 Scope of the Research Work

In this research work, the focus is to synthesize super-fine copolymer of styrene and *n*-butyl acrylate with controlled particle size and size distribution using the dispersion polymerization technique. Polymer particles were prepared in the mixed solvent of ethanol and water in the presence of poly(*N*-vinylpyrrolidone) and azo-bisisobutyronitrile as matrix polymer (or stabilizer) and initiator, respectively. Since the matrix polymer is one type of dispersant, in dispersion polymerization technique, this matrix polymer generally functions as a dispersant. We hereafter shall call it a dispersant.

The influences of different reaction parameters, i.e., dispersant type (PVP K-15, 30, 90), dispersant concentration, solvency of the reaction medium, reaction temperature, agitation rate, comonomer types and their feed ratio, reaction time, and crosslinking agent on particle sizes and size distribution of the resulting polymer were investigated.

Then, characterizations of the copolymers were performed by scanning electron microscopy (SEM) to measure particle sizes and size distribution, gel permeation chromatography (GPC) to determine average molecular weight and molecular weight distribution, fourier-transform infared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR) to elucidate copolymer composition. And finally, differential scanning calorimetry (DSC) technique is used to study thermal properties of the copolymer.

In addition, the correlation between particle size and average molecular weights of the copolymers was also demonstrated. The obtained results can be used to generalize the suitable conditions for achieving particles with required sizes, size distribution and average molecular weight.

1.4 Content of the Research Work

This thesis consists of 5 chapters. The first chapter deals with the background, the interest and the scope of this research work. Chapter 2 provides the theory of dispersion polymerization technique and related theories that are important for understanding. Additionally, it includes the literature reviews of previous works that give beneficial information and trends for the work. The experimental in Chapter 3 describes about chemical, equipment, apparatus, procedure, and reaction parameters investigated in this work. The results and discussion are explained in Chapter 4. The effects of various reaction parameters on particle sizes, size distribution and average molecular weights were shown and discussed in details. Finally, the summary and suggestion are given in Chapter 5. From this work, it is possible to prepare the super-fine polymeric particles in the size range of 0.6-1.8 μm with high molecular weight and narrow size distribution (CV<10%) for use as a toner resin in the future.