



CHAPTER 1

INTRODUCTION

1.1 The significant importance of SPG emulsification technique

Polymeric microspheres with monodisperse size have long been recognized as one of the most sophisticated materials in industries of applied analytical chemistry, printing and biomedical field, such as, packing materials of GPC (Gel Permeation Chromatography) [1], toner particles [2], biomedical material [3], and carriers of enzyme immobilization [4]. There are many techniques for preparing monodisperse particles, such as, seeded emulsion polymerization, dispersion polymerization, and two-step swelling technique. However, the time required for preparing particles may take half a day to several weeks depending upon the method being used [5]. For example, the seed polymerization method involves several steps and needs a long time to complete, and it is difficult to incorporate a very hydrophilic monomer into microspheres if water is used as continuous phase. In addition, a simple suspension polymerization method is often used to prepare large-size microspheres in the aqueous phase, but the size distribution of microspheres is very broad [3].

In 1988, a microporous glass membrane or Shirasu Porous Glass (SPG) membrane was fabricated by Nakashima et al [6, 7]. SPG membrane has a uniform microporous structure, which is able to offer the droplets with a narrow size distribution and takes a shorter time to prepare polymer particles. The SPG membrane provides many varieties of sophisticated applications, such as, food processing, drug delivery system (DDS) for cancerous therapy, ultra-filtration device and air-sparger for cell culture, and etc. The membrane emulsification method uses the surface (chemistry) of a microporous membrane to disperse one of two immiscible liquids (the disperse phase) into another liquid (the continuous phase) by applying adequate pressure to cause the dispersion phase

to permeate through the membrane. The dispersion phase is composed of monomer, initiator, solvent and water insoluble additive, and the continuous phase consists of surfactant, emulsifier, inhibitor and water. Suspension polymerization is a subsequent method after the emulsification method. The coefficient of variation (CV) of polymeric microspheres about 10% and the size ranging from 2 to 100 μm were obtained by this method.

The SPG membrane with different pore sizes ranging from 0.5 to 5.25 μm has produced a variety of monosized spheres, and has also demonstrated several successful applications of these spheres [8-12].

Hollow polymer latex particles having uniform microvoids or hemispherical particles with void centers were obtained. The hollow polymer latex particles with a center void have greater utility in coatings than those structures having microvoids or hemispherical particles with void center [13]. Furthermore, the hollow particle offers a high surface area [16] and the structure has a light scattering property more efficiently than a corresponding particle of uniform density. The light scattering properties are related to the difference in refractive index between the shell and the internal void [13,14]. Hollow particles provide many of applications such as opacifying plastic pigments for various coatings, gloss-enhancing plastic pigments for paper and paper-board coating and microencapsulations for controlled release agents [14]. In addition, hollow particles may have potential applications as a low weight packing material, new catalyst or reagent supports and encapsulation of macromolecules, such as, enzyme [15]. The methods of preparing hollow particles have been reported [13-19] and also the productions of multi-hollow polymer particles have been prepared [21-23].

Recently, Okubo et al. [17] prepared hollow polymer particles by suspension polymerization of divinylbenzene and studied the effect of the molecular weight and concentration of polystyrene on the hollow structure.

The objective of this research is, accordingly, to synthesize hollow acrylate or methacrylate beads by the new technique of the SPG membrane emulsification technique, and followed by the subsequent suspension polymerization using various amounts and the types of monomers, crosslinking agent, and solvents. The hollow beads so produced will be further modified for absorbing paraffinic solvents as well as aromatic solvents.

1.2 Objectives of the research work

The objectives of this work fall into the following categories:

1. To obtain the crosslinked poly(meth)acrylate polymers with a variety of morphologies by SPG emulsification and suspension polymerization.
2. To study the effects of monomers, crosslinking agents and inert solvents on the particle formation and the swelling degree.
3. To determine the solvent-absorption capacity of the resulting polymer.
4. To characterize the properties of the synthesized polymers.

1.3 Scope of the research work

Parameters affecting the particle formation and the swelling degree, such as, the ratios of monomer and crosslinking agent, mixed solvent contents, and the monomer types are studied. In summary, the factors to be investigated in this research work are as follows:

1. Effect of the ratios of monomer and crosslinking agent on the swelling degree and particle morphology.
2. Effect of the solvent amount on the swelling degree and the particle morphology.
3. Effect of the monomer types on the swelling degree and the particle morphology.
4. Effect of the solvent types on the swelling degree and the particle morphology.
5. Effect of the monomer types and crosslinking agent amounts on the thermal properties.

Instrumental techniques were employed to characterize the copolymer obtained from each experiment as the following:

1. Emulsion droplet sizes are observed by an optical microscopy.
2. The surface features of polymer particles and the diameter of polymer particles are observed by a scanning electron microscope (SEM).

3. Copolymer composition is elucidated by Fourier transform infrared spectroscopy (FT-IR)

4. Thermal properties of the resulting polymer are done by differential scanning calorimetry (DSC) technique.

5. The porosity, the pore size distribution and the specific surface area of the resulting polymers are measured by a porosimeter (PROSORP VAS-3000)