

CHAPTER 2

RETICAL BACKGROUND

2.1 General features of polymerization process

Over the past two decades there has been considerable interest in preparation of monodisperse polymer particles since these have applications in science, medicine and industry. In general, most of the research work is concerned with the preparation of monodisperse polymer particles via polymerization process. The process is mainly divided to emulsion polymerization, emulsifier-free emulsion polymerization, dispersion polymerization, suspension polymerization, seeded emulsion polymerization, precipitation polymerization, microemulsion polymerization, and miniemulsion polymerization. The important factors of each system are divided into reaction characteristics and mechanism of nuclei growth. The character of size, and particles size distribution are shown in Table 2.1

2.2 The Theory of SPG Emulsification

SPG is an abbreviation of Shirasu Porous Glass. The membrane is fabricated from a spinodal decomposition of the mixture of $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$, with a subsequent removal of the $\text{CaO-B}_2\text{O}_3$ phase by an acid treatment. This membrane possesses a unique porous structure in a cylindrical shape of the membrane, consisting of hydrophilic $\text{Al}_2\text{O}_3\text{-SiO}_2$. The pore sizes of SPG membrane ranging from 0.5 to 5.25 μm were used for the preparation of stable emulsion. The cross section of membrane was shown in Figure 2.1

SPG emulsification method uses the surface chemistry of a membrane to disperse one of two immiscible liquid (referred to as a dispersion phase which is consisted of a water-insoluble monomer and an initiator) into the another phase (referred to as a continuous phase which is consisted of water and a stabilizer) by applying pressure to permeate through the membrane.

Table 2.1 Comparison of characteristics of different polymerization processes

	Microemulsion	Emulsion	Emulsifier-free emulsion	Miniemulsion	Dispersion	Seeded emulsion	Precipitation	Suspension
•Continuous phase	water or organic	water and organic	water	water	water or organic	water or organic	organic	water
•Solubility of Monomer in the continuous phase	low	low			high	low		low
•Surfactant	ionic	ionic and non-ionic including polymeric surfactant	ionic	ionic	polymeric free radical ionic	ionic	absent	ionic
•Mechanism of particle polymerization	free radical	free radical	free radical	free radical		free radical	free radical	free radical
•Product formed	stable latex	stable latex	stable latex	stable latex	stable latex	stable latex	stable particle	bead
•Size (µm)	< 0.1	0.1-2.0	0.01-0.3	0.05-0.5	0.1-15		1-8	100-10,000
•Size distribution	broad	narrow	narrow	narrow	narrow	narrow	narrow	broad

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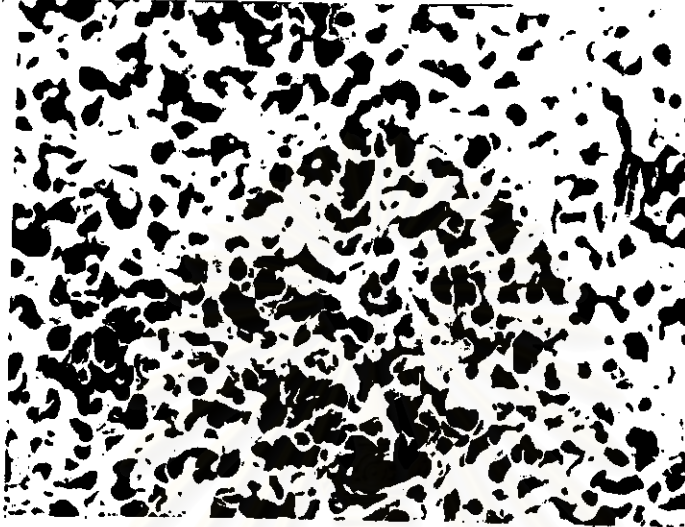


Figure 2.1 Cross section of membrane from SEM image

2.2.1 The formation of droplets

When the pressure is applied to the dispersion phase, the liquid is penetrated into the micropores. The protrusion of liquids, depends on the pore diameter (\bar{D}_m) and the pressure to be applied is theoretically derived as follows:

$$P_c = 4\gamma \cos \theta / \bar{D}_m \quad (2.1)$$

Where P_c is the minimum pressure or critical pressure in which the dispersion phase is pushed out; γ is the interfacial tension between droplets and the aqueous phase and θ is contact angle of the droplets and aqueous phase.

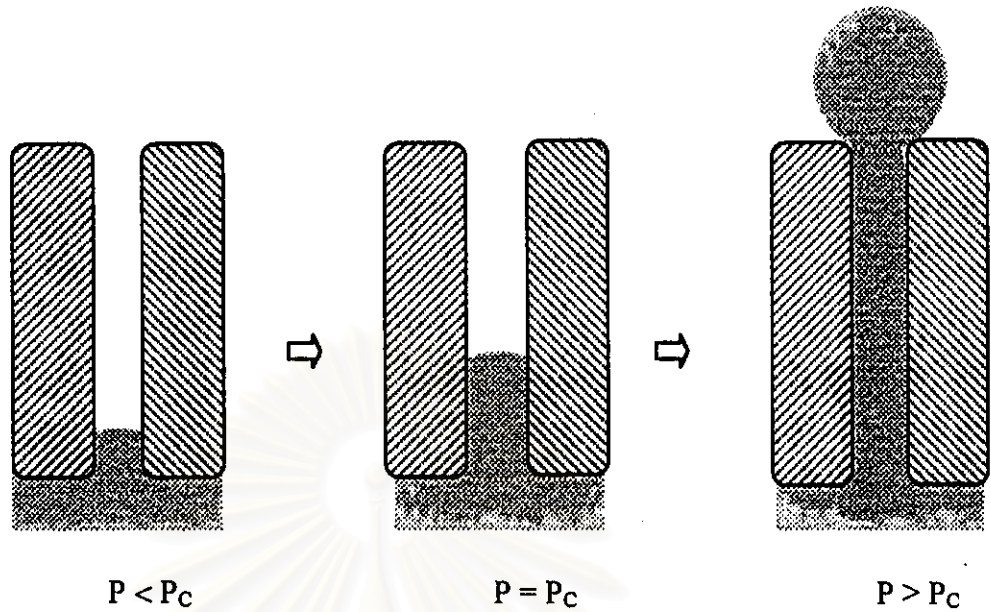


Figure 2.2 Applied pressure corresponding to formation of the emulsion droplets

As shown in Figure 2.2, when the applied pressure is lower than P_c , the dispersion phase does not permeate through the membrane. In contrast, when the applied pressure is higher than P_c , it is able to protrude the dispersion phase through the membrane pore. The creation of droplets into the continuous phase occurs. The size of emulsion droplets change depending on the pore size of the membrane as shown in Figure 2.3 and the equation follows the correlated \bar{D}_e .

$$\bar{D}_e = 6.62\bar{D}_m \quad (2.2)$$

Where \bar{D}_e is an average diameter of emulsion droplets. The coefficient 6.62 was presented by Omi et al. [5], which is demonstrated in Figure 2.3. Also, Nakashima et al. [3] claimed that the coefficient was 3.25. The difference of this value is probably due to the difference in the opening of micropores as reported by Omi et al. [5]

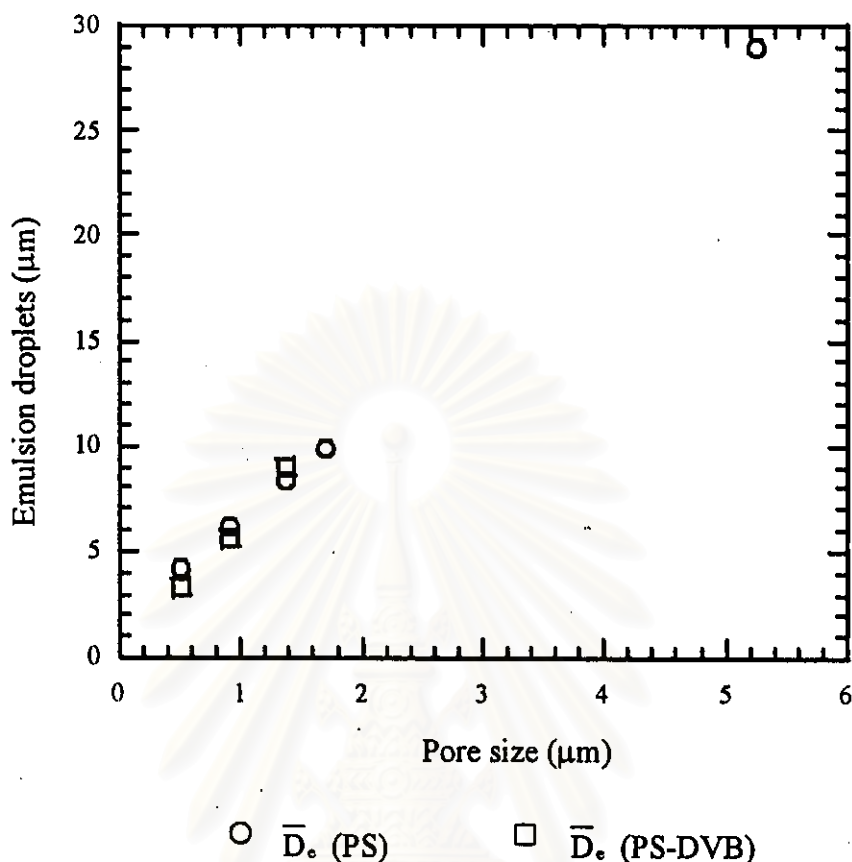


Figure 2.3 Average diameters of emulsion droplets as a function of pore size of SPG membrane (Data from Ref. [5] by permission of Omi)

2.2.2 Preparation of each emulsion type by SPG emulsification

2.2.2.1 Preparation of an oil-in-water (O/W) emulsion

An ordinary membrane, composed of $\text{Al}_2\text{O}_3\text{-SiO}_2$ is used. The microporous membrane has a hydrophilic property by itself. For the continuous phase usually water is used. The membrane is set in the stainless steel module and immersed in the continuous phase. Then, the dispersion phase is loaded into the emulsion tank. Dispersion phase is a hydrophobic substance as a water insoluble monomer or an organic solvent, monodisperse emulsion droplets can be obtained by an emulsifier and a stabilizer added in the continuous phase.

2.2.2.2 Preparation of water-in-oil (W/O) emulsion

The preparation of W/O emulsion has been done by using a hydrophobic membrane. The membrane can be modified by heating the hydrophilic type membrane at 437 K for 48 h. in a vacuum heating. Then, it is dipped in toluene to which 5% by volume of octadecyltrichlorosilane (ODS) was added, and heated with reflux at 383 K for 8 h. The membrane was rinsed in dried toluene which 1% by volume of trimethylchlorosilane (TMS) was added at room temperature for 2 h. Membrane was rinsed in dried toluene, a hydrophobic membrane is obtained.

The hydrophobic membrane wetted with the oil phase is set in the module and immersed in the oil phase. The water phase was loaded into the storage tank. Generally, monodisperse emulsion droplets can be produced by adding a non-ionic emulsifier to the oil phase and dissolving inorganic salts in the water phase.

2.2.2.3 Preparation of a double emulsion

a) Preparation of W/O/W emulsion

First, W/O emulsion was prepared by the method as described in Section 2.2.2.2. Then, the W/O emulsion was loaded into the storage tank and the water phase into an emulsion tank. A hydrophilic membrane, which has a micropore size more than twice the diameter of water droplets in W/O emulsion is installed. Selection of a microporous membrane with a pore size in a reasonable proportion to the diameter of the water droplets in the W/O emulsion can ease the preparation of a double emulsion. If the pore size of membrane is equal to or smaller than the diameter of water droplets, the droplets will be rejected by the membrane.

b) Preparation of O/W/O emulsion

This method is in contrast to the preparation of W/O/W emulsion as described in Section 2.2.2.3a. The procedure is similar to the W/O/W emulsion and the O/W emulsion was first obtained and passed the O/W emulsion to the membrane which contain the oil. The double emulsion was prepared.

2.3 Literature Review

Monodisperse micron size polymer particles have attracted attentions since Vanderhoff et al. prepared polystyrene particles with a highly uniform size in 1955 [9]. Monodisperse particles are widely used in the industries in variety of fields including chemistry, medicine and xerography. Monodisperse particles having highly porous structure and the size range from 1-50 μm have been applied with liquid chromatography [10]. High monodispersity leads to uniform solid phase as column packing material for chromatographic separation, which can improve separation efficiency and flow properties. In medical fields, the preparation of monodisperse particles with the incorporation of up to 40% magnetite have been used for cell separation, including the separation of cancerous from normal cell particles. With some extent of electrostatic properties, the charging behavior of toner can be controlled through physical factor such as the particles size of the toner [11]. Thus, the applications in xerography were included.

Control of particle size having uniform size has been a major area of interest. The attempt to prepare micron-size particles has been to break up monomer droplets into the micron size range by homogenization in presence of a stabilizer and subsequently the monomer is polymerized by suspension polymerization [12]. This method cannot achieve monodispersity because of the inherent size distribution in a mechanical step.

Ugelstad et al. [13,14] developed two step swelling method in which the small monodisperse particles as seed are swollen with monomer, followed by polymerization. The seeds can be swollen to thousand times larger in volume than the original. This method allows the preparation of the high monodispersed particles more than 50 μm and the standard deviation is less than 2%. Polymerization which is capable of preparing uniform polymer particles in micron diameter range was then developed. The polymerization reaction was carried out in a series of alcohol. Monodisperse polystyrene spheres were formed in the particle size range of 1-6 μm by a single step process. Monodisperse polystyrene latexes up to 1 μm in size were prepared by Sudol et al. [15] with a successive seeding method. Okubo et al. [16] also prepared micron-size monodisperse polymer particles successively by seeded polymerization utilizing the dynamic monomer swelling method and the dynamic

swelling method with a cooling process [17]. Polystyrene particles above 5 μm were prepared by using dispersion polymerization in an ethanol-water medium.

Dispersion polymerization in organic media has been an alternative route to the preparation of small and monodisperse polymer particles. As discussed by Barrett [9,18]. The process is different from emulsion polymerization in several factors. These include the use of a polymeric stabilizer instead of an ionic surfactant and the presence of a single phase at the beginning of polymerization. The reaction medium is organic solvent, not only non solvent for forming polymers but also for solubility soluble properties for the stabilizer. Barrett has reported the preparation of monodisperse poly(methyl methacrylate) particles with the size of 1 μm in hydrocarbon media.

Almog et al. [19] reported the formation of monodisperse polystyrene and poly(methyl methacrylate) by using quarternary ammonium salt surfactants in conjugation with the steric stabilizer. Polystyrene as large as 5 μm was prepared. Ober et al. [20] presented the use of nonionic cellulosic derivatives as steric stabilizers in the dispersion polymerization of styrene. Particles up to 10 μm can be prepared without the use of an electrostatic co-stabilizer.

Tseng et al. reported that uniform polystyrene particles in 1 to 10 μm in size range and up to 40% solid contents have been prepared by polymerizing styrene in ethyl alcohol by using an anionic surfactant, a nonionic surfactant, a long chain alcohol and monomer [21]. Okubo et al. reported that micron-size monodisperse polymer microsphere of PS having crosslinked structures and vinyl groups were produced by dispersion polymerization in ethanol-water medium [22].

In emulsion polymerization system, Hansen et al. [23] prepared styrene-in-water emulsions by applying the emulsifier system as a mixture of sodium hexadecyl sulphate (SHS) and hexadecanol (HD). Styrene latex which has a size lower than 2 μm was obtained. The improved emulsification of the monomer by addition of fatty alcohol resulted in the initiation of polymerization taking place under certain conditions mainly in the monomer droplets.

Rodriguez et al. [24] synthesized styrene-methylmethacrylate copolymer by miniemulsion copolymerization, using hexadecane as the cosurfactant. The use of different concentrations of hexadecane and ultrasonification time in the preparation of ST-MMA emulsion resulted in different particle size of the final latex. As the

amounts of hexadecane and ultrasonification time were increased, the particle size decreased. These effects have been reduced to an increase in the initial number of droplets in the nucleation stage.

Goodwin et al. [25] prepared monodisperse polystyrene by emulsifier-free polymerization. Polystyrene in a wide range of particle diameters from 100 to 1000 nm was prepared by a single-stage process in the absence of added surface active agents. Various parameters of ionic strength, monomer concentration, initiator concentration and temperature were studied. The ionic strength of the aqueous phase dissolved in a surface active agent has influenced on the diameter of the particles. Thus, varying the ionic strength can control the particles size. Also, monomer concentration, temperature and the initiator concentration revealed the significant influences on the size of particle.

Gu et al. [26] applied an emulsifier-free emulsion polymerization for preparation of polystyrene particles in an aqueous media. A single stage polymerization technique was examined under various reaction conditions. The cationic and anionic surfactants were added to control the stability of particles. The change in addition time of the surfactant affected the coefficient of variation of particles size distribution and by changing monomer concentration affected the average particle size. Monodisperse polystyrene particles were obtained with the average size of 3.3 μm .

Parth et al. have described the preparation of polymer colloids by chemical reactions in aerosols. A procedure was developed in which polymer colloid can be prepared by polymerizing aerosol droplets of a monomer with an initiator in the vapor state. The formation of poly(p-tertiarybutyl styrene) and polyurea particles can be generated by direct reaction of liquid droplets in the absence of any other additives [27,28].

Panagiotou and Levendis [29] reported that monodisperse particles of polystyrene and polymethylmethacrylate in the size range of 30 to 60 μm were produced by using an acoustically excited aerosol generator. The device consists of a vibrating orifice plate and a spray drying tower. The liquid was oscillated at a high frequency, which is the vibration created an instability of small liquid droplet. Uniformity of the droplet sizes was controlled by the size of orifice, the oscillator

frequency and the liquid feed rate. By this method, production of low molecular weight polymers is a disadvantage.

Kumakura [30] described a preparation method of monodisperse polymer microspheres with a hydrophilic property by utilizing an irradiation method hydrophilic microspheres of poly(ethylene glycol), poly(hydroxyethyl methacrylate), and poly(methacrylic acid) were synthesized. The microsphere diameter was 0.3-1.0 μm in which the irradiation was carried out without catalyzer by use of γ -ray.

The successful techniques are usually based upon polymerization. In summary they can be classified into four major processes: successive seeded emulsion polymerization, emulsifier-free polymerization, two-step swelling technique, and chemical reactions in aerosols. Considering the application to using microspheres for toner particle which size is usually in a range 7-10 μm . Dispersion polymerization in organic media or non-aqueous phase dispersion polymerization (NAD) is also included as a means of preparing the microspheres. It is easy to synthesize particles having an average particle size of 7 μm or less with a narrow size distribution, but it is difficult for inner additives to be contained in each particle. Also the use of high amount of organic solvent causes pollution to environments. Therefore, a technique that simple ingredients, an easy procedure, short reaction time, can be used with a wide range of polymer is an important alternative to the traditional techniques. Omi et al. prepared polystyrene particles with 2 to 9 μm in size by using a particular microporous glass membrane, the SPG to control the size of monomer droplets. Employing the SPG emulsification technique followed by a suspension polymerization process, crosslinked polystyrene particles having surface area of 160 m^2/g and standard of deviations of diameters close to 10% was prepared [5].

Omi et al. prepared monodisperse hydrophilic poly(methyl methacrylate) by modifying the two-stage emulsion technique, in which SPG emulsification technique was used to prepare seed hydrophobic droplets. Seed droplets were swollen with a hydrophilic mixture of methyl methacrylate monomer and solvents, and followed by polymerization. Hydrophilic PMMA from 2.5 to 37 μm average diameter were obtained. The coefficient of variation of PMMA spheres was around 10% [6,7,31].

Omi et al. reported that 100 μm porous poly(styrene-co-divinylbenzene) microspheres were synthesized by employing SPG emulsification technique and subsequent swelling of seed droplets. Divinylbenzene, hexadecane and initiator was

permeated through a SPG membrane and uniform seed droplets were stabilized in the continuous phase. The average droplet size was around 30 μm , mixed with secondary emulsion consisting of hydrophilic components of styrene and additives, the smaller size of secondary emulsion promoted the degradative diffusion process. After all the secondary emulsion was absorbed completely, the seed droplets were swollen to a size 110 μm . Uniform porous sphere of PS-DVB of 102 μm with the coefficient of variation less than 10% was obtained. Polarity of solvent and controlling of the specific gravity of swollen droplets were the important parameter which prevented the break up of droplets during the polymerization [8]. Furthermore, by adding a small amount of acrylic acid or glycidyl methacrylate into the monomer, the synthesized polymer were applied for immobilizing carriers of glucoamylase (GluA) as reported by Omi et al. [32].

Hatate et al. reported that poly(styrene-co-divinylbenzene) microspheres containing electrifying additives were prepared successfully by SPG emulsification technique. The effect of Sumiplast Blue S as a coloring additive and E-81 as a charge control agent on the triboelectric properties were studied. The synthesized polymer particles were used for toner particles [33,34].