

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 SPG emulsification technique

2.1.1 Principles of membrane emulsification

The porous membrane used in this experiment is a microporous glass developed in Miyazaki-ken. Shirasu Porous Glass (SPG) membrane is made of $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$, and a phase separation between two phases of $\text{CaO-B}_2\text{O}_3$ and $\text{Al}_2\text{O}_3\text{-SiO}_2$ occurs at the second heat treatment; the former is washed out with acid, leaving a membrane with a unique microporous structure. Several SPG membranes with the pore size ranging from 0.5 to 5.25 μm were used for the preparation of stable emulsions. An SPG tube or membrane emulsification utilizes the technique of surface chemistry to disperse one of the two immiscible liquids known as a dispersion phase into another liquid called a continuous phase by applying pressure to allow the dispersion phase to permeate through the membrane of the tube. The dispersion phase contains a mixture of monomer, solvent, and initiator; and the continuous phase containing water, surfactants and inhibitor. The method can produce uniform droplet sizes in the form of both an oil-in-water emulsion (O/W), a water-in-oil emulsion (W/O), and the double emulsions of oil-in-water-in-oil (O/W/O) emulsion or water-in-oil-in-water (W/O/W) emulsion.

The membrane has higher mechanical strength and the special characteristics of interconnected structure of cylindrical micropores, ranging from submicrometer sizes up to ten micrometers. The tube is resistant to high pressure, which is used to force oil or hydrophobic liquid through the pores and it is consequently dispersed into the water phase, which is circulated through the inside of the membrane tube. The hydrophilic membrane tube was used in the present experiment while the hydrophobically modified tube can be prepared by altering its surface chemistry with a certain class of chemicals such

as a plasma polymerization of fluoride monomers. As the SPG tube itself by nature is hydrophilic, therefore, it is usually wetted in water or water dissolving surfactant to produce an oil-in-water emulsion. Whenever the dispersion of oil phase penetrates into the micropores, the following equation is usually used:

$$P_c = 4\gamma_{ow}\cos\theta/d_m \quad (2.1)$$

P_c = the minimum pressure (critical pressure) to make the oil phase to penetrate

γ_{ow} = the oil/water interfacial tension

θ = the oil/water contact angle

d_m = the average pore size of the membrane of the SPG tube

The dispersion phase does not permeate through the membrane when the pressure P is lower than P_c . However, at the moment when P has exceeded P_c , it is able to pass through the micropores for the first time, then releases a dispersion of droplets into the continuous phase. Thus, P_c is the minimum pressure where one can observe the flux of the dispersion phase.

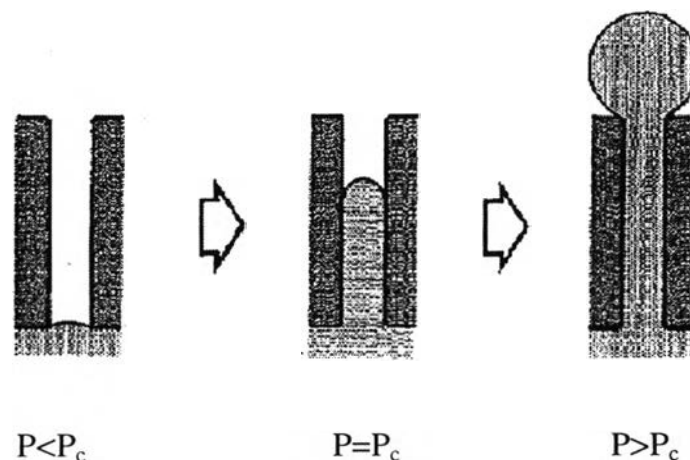


Figure 2.1 Dispersion phase intrusion into micropore and formation of droplet

The size of the droplets changes depending on the pore size of the membrane and reveals a linear relationship [8].

$$d_e = 6.62d_m \quad (2.2)$$

where d_e is an average diameter of emulsion droplets. Nakashima et al. [1] reported that the coefficient was 3.25. The rather big difference between the two coefficients was partly due to the shape of the opening of pore, which can be different when glass pipes are drawn, and also due to the differences of formulations of oil and water phases.

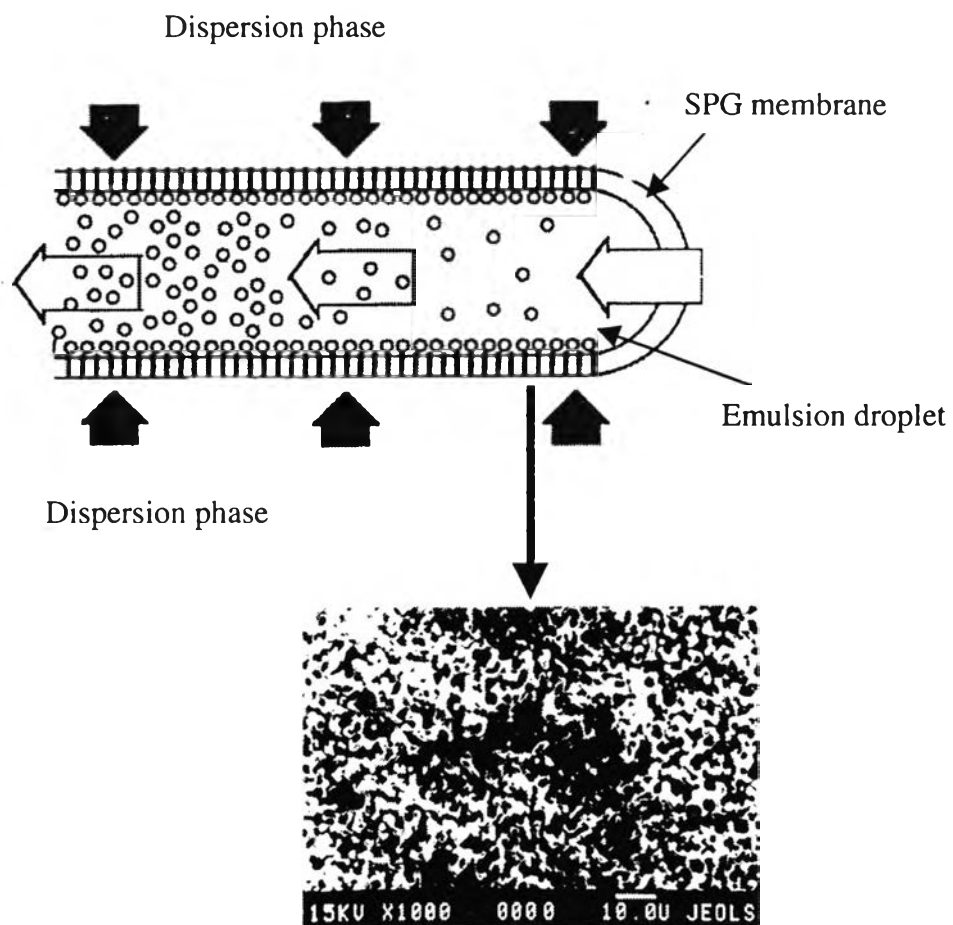


Figure 2.2 Cross section of the SPG membrane

2.1.2 Manufacturing process of SPG

The principle of the fabrication of a porous glass is generally based on phase separation during a heat treatment and dissolution of the separated phase into an acid solution. The process of manufacturing SPG is roughly illustrated in Figure 2.3.

After lime and boric acid are mixed into Shirasu soil at a fixed ratio, soda ash and magnesia are added whenever necessary. Then the mixture is heated and melted at 1250 to 1350°C to form primary glass as the precursor of SPG. This primary glass is then formed into various shapes either in tubes, fibers, beads, or plates. Next, the glasses formed are heated for several hours at 600 to 800°C. This process is very critical, for it is during this process that phase separation of the glass takes place accelerating the development of the separation phase, thereby determining the size of SPG pores. By heating the primary glass, the spinodal decomposition takes place, and the countless microphases that contain a large amount of calcium borate are separated out all over the structure of the original glass. The size of the separated glass is very small at the beginning, measuring only around 1 nm, but gradually grows up to 10,000 nm as the heating temperature goes up or the heat treatment duration becomes longer. As the calcium borate glass phase thus formed is soluble in acid, further acid treatment leaches the calcium-borate phase out of the glass into the acid, leaving the skeleton of the original glass rich in silica and alumina content.

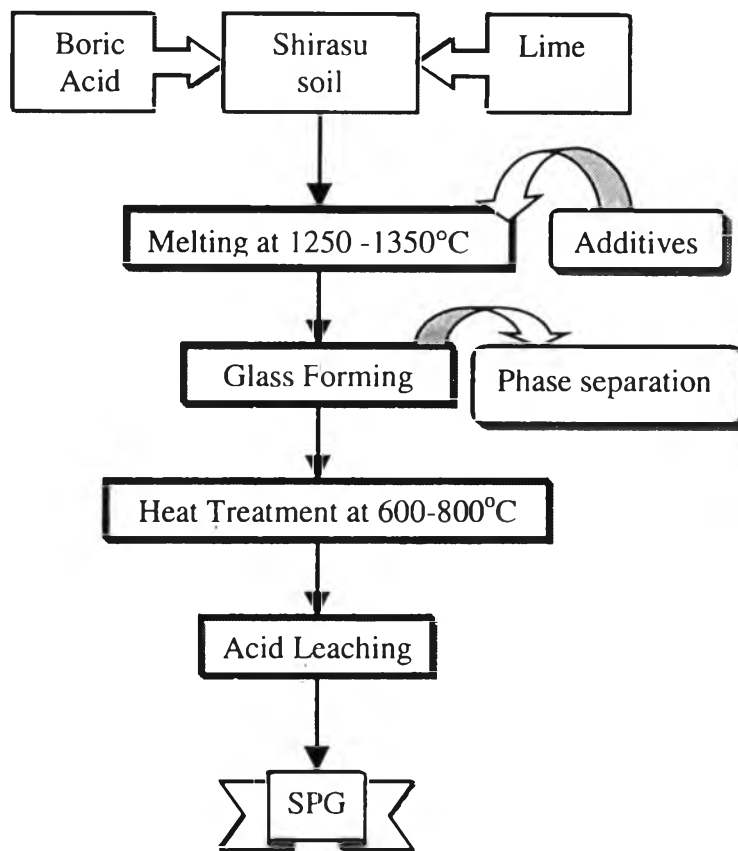


Figure 2.3 Manufacturing process of an SPG tube

2.1.3 Preparation of each emulsion types by SPG emulsification

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

The hydrophilic membrane used for this purpose must be fully wetted with the water phase, prior to the start of the membrane emulsification. This treatment can be done effectively by immersing the microporous membrane in the continuous phase and degassing it with a vacuum to remove any residual air from the micropores in the membrane. It also enables the micropores to be perfectly filled with the continuous phase. Next, the membrane now wetted with the continuous phase is carefully attached to the membrane module. Then, the dispersion phase is loaded into the storage tank, and the continuous phase, into the emulsion tank. Monodisperse emulsions can usually be obtained simply by adding anionic or nonionic surfactants alone to the continuous phase. On the other hand, if the oil phase consists of fats and

their analogues, surfactants must occasionally be added not only to the continuous phase but also to the dispersion phase.

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

A hydrophobic membrane used for the preparation of a W/O emulsion must be fully wetted with the oil phase and then the module is set on the membrane emulsification apparatus. The aqueous phase is loaded into the storage tank and the oil phase into the emulsion tank. Generally, monodisperse emulsions can be obtained by adding a nonionic surfactant to the dispersion phase and dissolving inorganic salts, etc. in the water phase.

2.1.3.3 Preparation of a double emulsion

a) Preparation of a W/O/W emulsion

W/O is prepared by the method as described in Section 2.1.3.2. Then, the W/O emulsion is loaded into the storage tank and the continuous phase into the emulsion tank. A hydrophilic membrane, which has a micropore size more than twice the diameter of water droplets in the W/O emulsion is installed. If the pore size of the membrane is equal to or smaller than the diameter of water droplets, the membrane will reject the droplets. 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 enables an easy preparation of a double emulsion.

b) Preparation of an O/W/O emulsion

The method is in contrast to the preparation of W/O/W emulsion. At first, a W/O emulsion is prepared using a hydrophobic membrane, then a W/O/W emulsion can be made easily by penetrating the W/O emulsion into a water phase through another hydrophilic membrane.

2.1.4 Applications of SPG

The SPG is used in two ways, one with no chemical treatment of the material and the other by applying chemical modification to improve the surface, which is a more sophisticated treatment.

2.1.4.1 Application to a separation membrane

Since SPG has concentrated cylindrical pores of a fixed size, which is controlled precisely to make the interconnected membrane, it provides a favorable characteristic as a highly functional separation membrane. The applications related to the membrane technology include the elimination of oil content in liquors (fusel oil), elimination of dregs in vinegar, separation of plasma in blood, regeneration of coolant oil used for the cutting machine by filtration, and application to the separation-type porous membrane of bioreactors.

2.1.4.2 Application to a packing material for HPLC

It is expected that the separation technique by the high performance liquid chromatography (HPLC) will enable the production of useful biochemical substances in an industrial scale. As a context, inexpensive and durable packing is becoming indispensable. The appropriate properties of SPG can be used in this case because it permits a chemical modification of the surface with ODS (octadecyltrichlorosilane), the modified SPG can be used in a wider pH range than the conventional silica-type packing material.

2.1.4.3 Immobilizing enzyme

The carrier for immobilized enzyme has long been drawing attentions as one of the applications of porous glass, and many patents and papers dealing with this application have been published. There are a variety of methods of immobilizing enzymes, of which the covalent bonding method is most popular. Although a number of embodiments are available, only a few cases are found in which the porous glass is used as an immobilized enzyme on

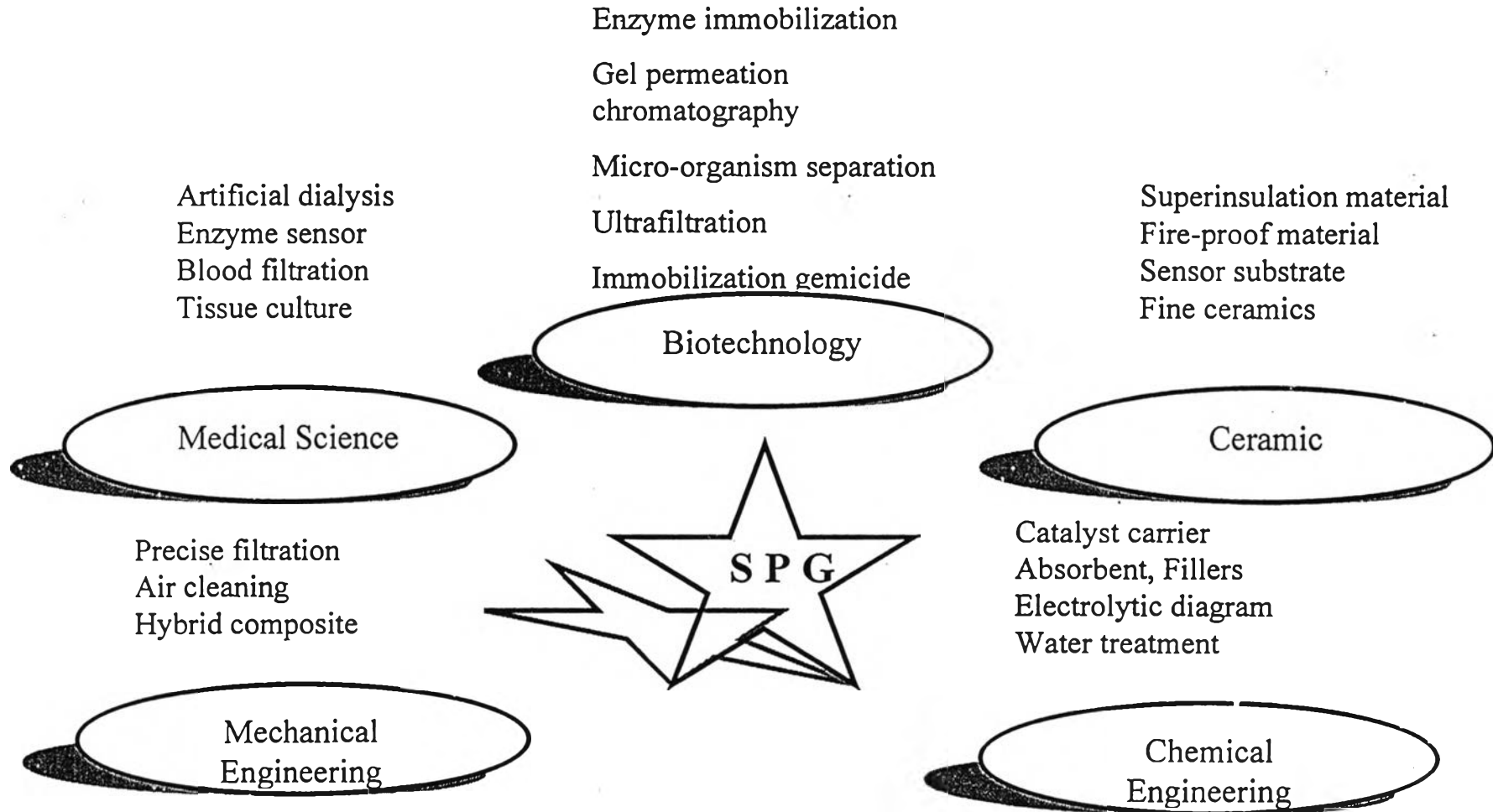


Figure 2.4 Diagram of SPG application

an industrial scale. Since this is due to the extremely high cost of the porous glass membrane as compared with that of other carriers, cost reduction is now a very important problem.

2.1.4.4 Other applications

The other application in the medical field, such as, the micro carrier for tissue culture and injection needles for blood transfusion and kidney dialysis has been used with this technique. An overall schematic flow of SPG applications is shown in Figure 2.4.

2.2 The formation of hollow bead

In suspension polymerization, each droplet of the organic phase consists of monomer, initiator and water insoluble solvent, and behaves as an individual bulk polymerization reactor. The polymerization takes place inside of the droplet that is suspended in an aqueous solution and stabilized with surfactants. In the early stage, EGDMA which is more reactive than the other noncrosslinked monomers is consumed, and copolymer molecules are formed which are composed of straight chains with $-\text{COOCH}_3$ pendant groups. Further reaction leads to the increase of intermolecular linkages. As polymerization proceeds, the crosslinked copolymer chains are no longer extended and the growing chains become entangled as insoluble in the monomer and the water insoluble solvent. The phase separation occurs between the copolymer-rich phase and the solvent rich-phase, and these result in the copolymer-rich phase precipitate in the droplet. Then, the copolymer-rich phase is repelled outwards and gradually aggregate on the surface of the droplet because the interfacial tension between the water-insoluble solvent and the continuous phase is larger than that of the interfacial tension between copolymers and the continuous phase. At the same time, water insoluble solvent moves toward inside of the droplet because the hydrophilicity of the solvent is much lower than the polymer, the solvent prefers to stay inside of the droplet. After the completion of the polymerization, the solvent is trapped inside of the bead and encapsulated by the polymer wall. When the solvent is evaporated by drying.

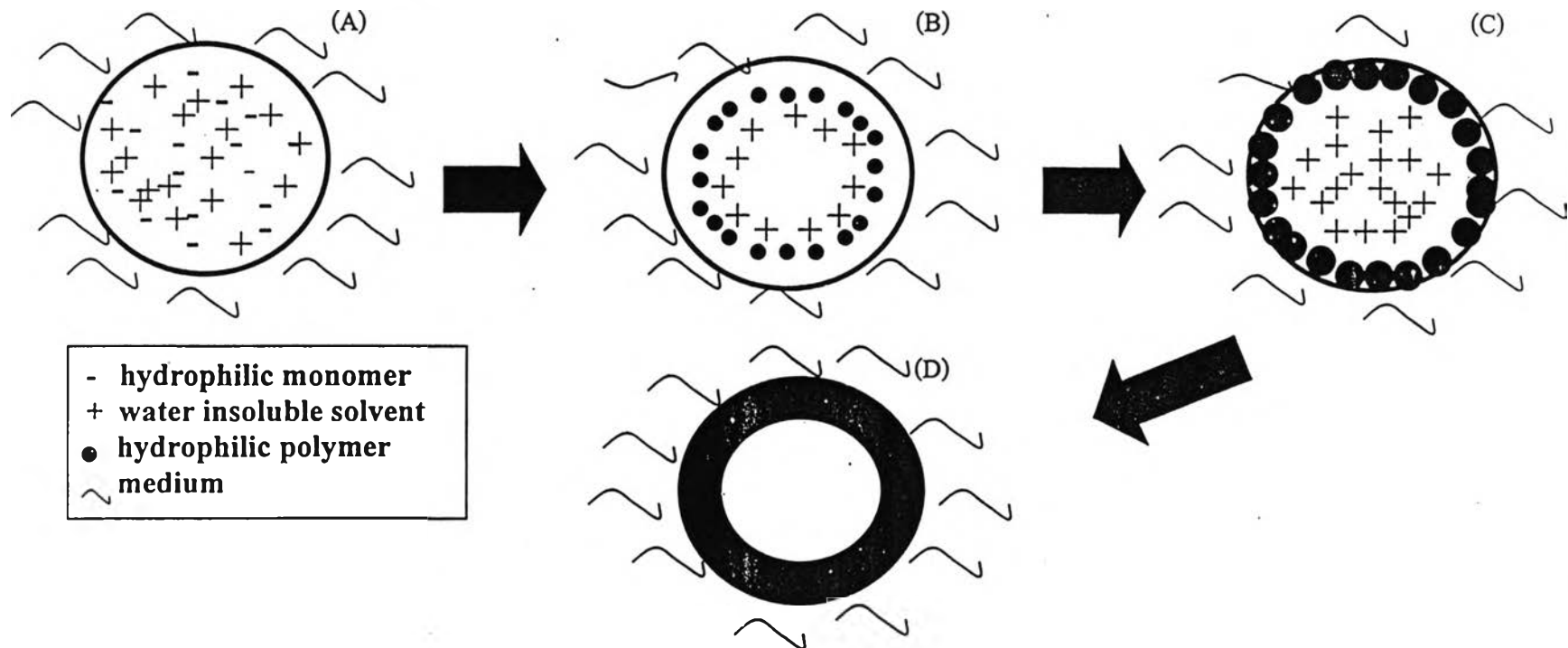


Figure 2.5 Proposed model for formation of hollow bead.

- (A) Emulsion droplet is composed of hydrophilic monomer and water insoluble solvent, which suspends in the aqueous phase.
- (B) Polymerization occurs, the hydrophilic monomer is converted to the hydrophilic polymer, which moves toward the water interface.
- (C) Precipitation process occurs, the polymer moves to the surface of particle because of its hydrophilicity while the water insoluble solvent moves to the center of the particle due to its hydrophobicity.
- (D) the water insoluble solvent was evaporated by drying and the hollow particle is obtained.

the hollow bead is then formed [16,24-25]. The mechanism of hollow bead formation is shown in Figure 2.5.

2.3 Kinetics of Absorption-Desorption

2.3.1 Absorption kinetics

Swelling is a three-dimensional expansion in which the network absorbs solvent and reaches an equilibrium degree of swelling at which the free energy decreases, because the mixing of the solvent with the network chains is balanced by the free energy increase due to the stretching of the chains [26].

The swelling degree decreases when the crosslinking agent concentration is increased because the elastic contribution of the network is a major restriction on the magnitude of the swelling. When a polymer sample is immersed in an organic liquid, the solvent molecules will diffuse into the solid polymer to produce a swollen gel. Dissolution is prevented if the attraction between neighboring polymer molecules is sufficiently great due to crosslinking or hydrogen bonding. Swelling continues until the elastic reaction of the network balances the osmotic pressure driving the solvent into the swollen polymer.

In a good solvent, the liquid-polymer interactions expand the polymer coil from its unperturbed dimensions in proportion to the extent of these interactions due to highly compatible with the polymer. In a poor solvent, the interactions are poor and coil expansion or perturbation is restricted [26]. From Hilderbrand solubility parameter, a diluent is a good solvent when $|\delta_1 - \delta_2| < 1.0$ (MPa)^{1/2} and a poor solvent when $|\delta_1 - \delta_2| > 3.0$ (MPa)^{1/2}, where δ_1 and δ_2 is the solubility parameter of the diluent and polymer, respectively [27].

At equilibrium, the swelling by a good solvent is given by Flory-Rehner equation [28]:

$$v = \frac{1}{Mc} = \frac{V_p + \chi V_p^2 + \ln(1 - V_p)}{d_r V_o \left(V_p^{1/3} - V_p/2 \right)}, \quad (2.3)$$

where v is the effective number of moles of cross-linked chains per gram of polymer

M_c is the average molecular weight between cross-links,

V_p is the volume fraction of polymer in the swollen mass,

V_o is the molar volume of the solvent,

χ is the polymer-solvent interaction parameter,

d_r is the density of the polymer

The volume fraction of the polymer in a swollen mass can be calculated by equations 2.4 and 2.5; d_s is the density of the solvent.

$$V_p = \frac{1}{1+Q} \quad (2.4)$$

$$Q = \frac{\text{wt.of solvent in gel}}{\text{wt.of gel}} \times \frac{d_r}{d_s} \quad (2.5)$$

The swelling kinetics of spherical gels is determined by the diffusion of the polymer network from Tanaka and Fillmore (TF) theory [29]. They found that the swelling of the loose polymer network was faster than the dense polymer network. The equation of the diffusion coefficient D was defined as follows:

$$D = \frac{(4U/3) + K_b}{f} \quad (2.6)$$

where U is the shear force of the polymer network alone,

K_b is the bulk modulus of the polymer network alone,

f is the frictional coefficient between the network and fluid medium.

A characteristic swelling time τ was defined by:

$$\tau = a^2/D, \quad (2.7)$$

where a is the final radius of the fully swollen gel. The rate of solvent diffusion is ruled by the surface area of the particle. Ikkai et al., [30] proposed that if the surface is smooth and dense, eq.(2.7) applies and the following equation is given,

$$\text{for dense particles,} \quad \tau = \frac{a_{\alpha}^2}{D} = \frac{d_{\alpha}^2}{4D}, \quad (2.8)$$

$$\text{for porous particles,} \quad \tau = \frac{d_{\alpha}^2}{4D_{app}}, \quad (2.9)$$

where a_{α} is the radius of the gel after swelling, d_{α} is the diameter of the gel after swelling and D_{app} is defined by:

$$D_{app} \equiv fD, \quad (2.10)$$

where f is same as the frictional coefficient in eq. (2.6).

However, the TF theory applies to the smooth spherical surface of the gel which is not applicable to a porous resin. When the dried resin is immersed in solvent, solvent molecules diffuse into the resin much faster than the case of nonporous gel, where the cavities of the porous resin are immediately filled with the solvent by capillary force. Therefore, Ikkai et al., assumed that the swelling of the porous resin particles takes place by two steps, (i) filling of the cavities with solvent by capillary force, and (ii) osmotic diffusion of the solvent into the resin. Further, they found that the filling time, t_{fill} , is much faster than that of osmotic diffusion, t_{diff} . Hence, the deterministic process of the swelling is the osmotic diffusion which can be applied to the TF theory in equation (2.7):

$$\ln \left(\frac{d_t - d_{\alpha}}{d_o - d_{\alpha}} \right) = (\text{const.}) - t/\tau \quad (2.11)$$

where d_t denotes the diameter of the particle at time t (0 , t , and α). The characteristic swelling time τ can be obtained from the slope of the $\ln(\Delta d_t/\Delta d_0)$ – time plot as shown in Figure 2.6.

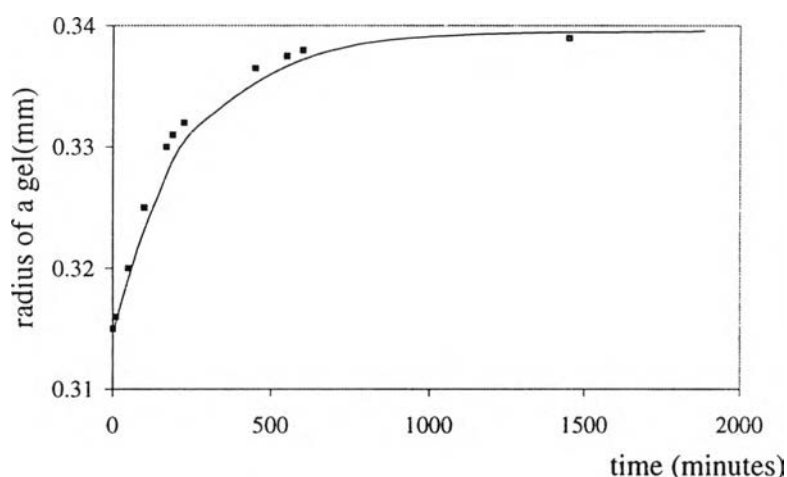


Figure 2.6 The typical swelling curve of polyamide gel in water [29].

2.3.2 Desorption Kinetics

The desorption kinetics of a bead is observed by determination of the rate of a solvent loss with an absorptive substrate such as a filter paper. The amount of solvent penetrating into the capillary pores of the substrate is proportional to the square root of the time of penetration. The capillary action enables the interaction between the bulk liquid and the polymer chains, i.e., the penetration of a liquid without a direct contact of all absorbate molecules with the polymer segments. Rideal-Washburn [31] equation describes the penetration of a liquid into capillary pores as follow:

$$I^2 = r\gamma\cos\theta/2\eta = Kt\gamma\cos(\theta/2) \quad (2.12)$$

where I is the depth of penetration

r is the radius of the cylindrical capillaries

t is the time of penetration

γ is the surface tension of the liquid

θ_l is the contact angle of the liquid on the capillary wall

η is the viscosity of the liquid

K is the effective radius of noncylindrical capillary pores including a tortuous factor

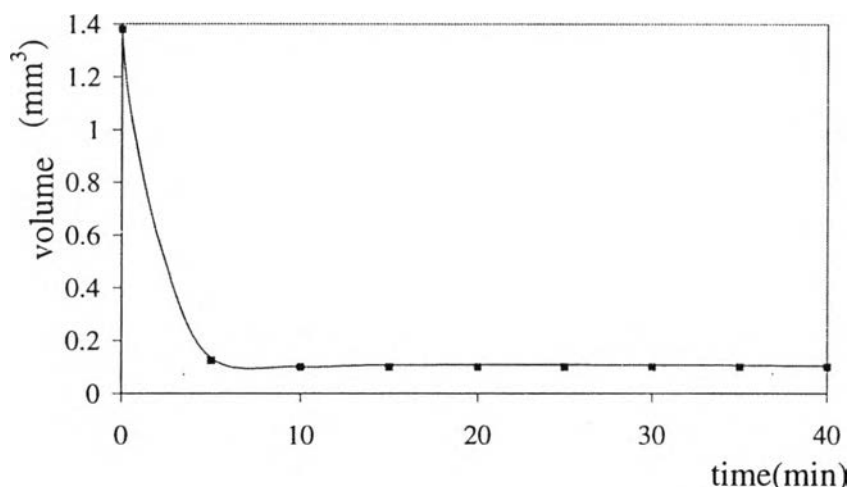


Figure 2.7 The desorption curve of poly(styrene-co-DVB) beads [31].

2.4 Literature review

As stated previously, the SPG membrane emulsification technique is a new method for preparing fairly monodisperse polymeric microspheres with the diameter ranging from several to 100 μm and their coefficient of variation (CV) of approximately 10 %.

Many articles concerning SPG technique have been recently reported [1-3, 8-10, 12]. Uniformly crosslinked microporous spheres of polystyrene in the presence of various low molecular-weight diluents, which have a maximum surface area of 160 m^2/g were obtained from a high content of crosslinking agent (divinylbenzene, DVB) and poor solvents of polystyrene. The CV of the beads was close to 10% [8]. Uniform poly(methyl methacrylate) or PMMA microspheres were studied by adopting the droplet swelling technique. The primary uniform emulsion composed of a mixture of a hydrophobic diluent (and/or monomer), a cosurfactant, and an initiator was prepared with an SPG membrane and was allowed to absorb MMA (and hydrophilic diluent) under

the principle of the degradative diffusion process from droplets in the secondary emulsion. The CV of PMMA spheres was around 10%. Porous PMMA spheres having 185 m²/g of specific surface area or more were obtained as well as one-eyed spheres, smooth, and solid spheres [9]. The applications of microspheres with average diameters from 2.5-3.8 μm of polystyrene and poly (methyl methacrylate) for a packing material and a carrier of enzyme immobilization were demonstrated. The CV was around 10% and specific surface was 370 m²/g [1]. Monodisperse poly(styrene-co-divinylbenzene) or PS-DVB spheres for toner particles were prepared with high contents of electrifying additives by combining SPG membrane emulsification with a solvent evaporation process [5]. Uniformly porous PS-DVB microspheres of 100 μm were obtained employing the SPG membrane emulsification technique, and subsequent swelling of the seed droplets. The average initial droplet size was around 30 μm; after the swelling, the droplets were swollen to a maximum of 110 μm. The CV was less than 10% and the specific surface area was 350 m²/g [12]. Likewise, the SPG membrane emulsification technique was applied for preparing monodisperse PS-DVB microspheres with/without electrifying additives for toner application [2]. The uniform microspheres containing a very hydrophilic monomer, 2-hydroxyethyl methacrylate (HEMA), can be prepared successfully using a special swelling method of uniform hydrophobic droplets, which were prepared by the SPG emulsification technique, followed by suspension polymerization. Various microspheres with different morphologies, such as, spherical, snowman-like, and popcorn-like depending on the composition of the oil phase were observed. Furthermore, the porous microspheres with a high content of HEMA was obtained employing hexanol as a porogen [3].

There are many methods for preparing the hollow particles reported in journals and patents. In 1983, hollow bead of poly(styrene-co-divinylbenzene) was prepared by seed polymerization using two different simple methods. The first method, polystyrene particles were added to a polymerization system containing styrene and divinylbenzene. The other method, a mixture of styrene and divinylbenzene was added to a system containing polystyrene particles. In the latter method, thin-walled hollow spheres were obtained but the wall thickness was able to increase by repeating the coating process [14]. A single stage emulsion polymerization of monomer in the presence of hydrocarbon was

used to produce hollow particles. The first step involved introducing an effective amount of a first charge of an organic phase to an aqueous phase. The first charge of the organic phase comprised a monomer, which was insoluble in the aqueous phase and an inert-nonpolymerizable hydrocarbon. The monomer was polymerized to produce low molecular weight polymers. The second step involved introducing a second charge of the organic phase to the aqueous phase, wherein the second charge of the organic phase comprised a crosslinking monomer. The crosslinking monomer was polymerized with the low molecular weight polymers to produce hollow particles [13]. A process of making hollow polymer latex particles was prepared by Lee et al. [15]. Core-shell emulsion polymerization without the use of acid in the swellable polymer core and in the step of shell polymerization, a strong alkaline solution, such as, sodium hydroxide was used to produce the hollow morphology. Toda et al. [18] obtained a hollow polymer by base and acid treatment method. The first step, copolymer particles having three layers were prepared by seed coating polymerization. The second step was a base treatment step by adding a base to make a pH of the latex 8 or more. The third step was an acid treatment step by adding an acid to make the pH of the latex 7 or less and then polymerization. Jo et al. [16] prepared hollow beads of poly(styrene-co-divinylbenzene) by suspension polymerization. The reaction temperature was maintained at 40 °C for 30 min to stabilize the spherical monomer droplets, and the polymerization temperature was then increased to 60, 70 or 80 °C and kept this temperature for 20 h with the rate of temperature increase of 0.5 or 1 °C/min. The amount of initiator of 0.2, 0.4 or 0.6 g, of azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO) was added as initiator. The size of the microparticles decreased with the amount of initiator. In the case of BPO as initiator, the thickness of the wall was greater and the size of the microparticles aggregated on the surface of the hollow polymer bead was smaller than that using AIBN. The thickness of the wall of the polymer bead increased with a decrease in the polymerization temperature. Lee et al. [19] reported a method for preparing the hollow polymer latex particles again in patent with the same method. Recently, Okubo et al. [17] synthesized a hollow polymer particle by suspension polymerization. Divinylbenzene and toluene were dissolved with polystyrene (PS) in an aqueous solution of poly(vinyl alcohol). Also, the effect of the molecular weight and the concentration of PS molecules on the hollow

structure were indicated. It was found that the molecular weight of PS was 9.1×10^5 and 11×10^5 with a concentration of 2.4% by weight, and the molecular weight of PS was 1.6×10^5 with a concentration of 9.1 and 13% by weight were able to produce the hollow polymer particles.

Besides, multi-hollow polymer particles were also synthesized by various methods such as emulsion polymerization with alkali and acid treatments [20,21], emulsion polymerization with an alkali and cooling method [22], and seed emulsion polymerization by alkali/acid treatment with or without acrylic acid [23].

Coutinho et al. [32] studied the effect of the diluent/polymer affinity on the porosity of styrene-divinylbenzene copolymer, the DVB content and the initial dilution of the monomers on the formation of the porous structure by suspension polymerization. The porous copolymers were obtained when a low DVB contents and large amount of diluent are employed. Besides, using a precipitant (poor solvent), such as, heptane in the system showed a good balance of properties, such as, porosity and specific area.

Coutinho et al. [33] studied the influence of the content of the crosslinking agent (DVB) and the diluents, heptane as a non-solvating diluent and diethylphthalate (DEP) as a solvating diluent, on the formation of the porous structure of ion-exchange resins based on 2-vinylpyridine and DVB. The resins were synthesized by suspension polymerization. It was found that increasing in the DVB and heptane led to increases in the final porosity of the resins with low values of specific surface area, to give macroporous beads when heptane was used. The macroporous structure was not obtained when DEP was used at any concentrations of the diluent and DVB.

Kim et al. [34] studied the effect of various parameters on styrene-DVB polymerization, such as, polymer crosslinking density, solvent chain length and temperature on the transport kinetics, absorption rate, and swelling ratio. Poly (styrene-co-DVB) samples were prepared by bulk polymerization. The transport kinetics was characterized from the Fickian second law by increasing the crosslinking agent ratio, the penetrant size and decreasing the temperature below the glass transition temperature. They found that a highly crosslinked polymer was ruptured after swelling in good solvents, such as toluene and dibutyl phthalate, especially when the temperature was decreased or the crosslinking agent ratio was increased. The transport rate increased with

decreasing the crosslinking agent level of the polymer sample or penetrant size and increasing the temperature. The swelling degree decreased slightly with increasing the penetrant size or increasing the sample crosslinking agent ratio at a constant temperature.

Rabelo et al. [35] investigated the influence of the solvent/non-solvent volume ratio, dilution degree and DVB content on the formation of porous structure and on the swelling properties of styrene-divinylbenzene copolymer by suspension polymerization. They found that toluene uptakes of macroporous copolymers were considered as a result of three contributions: filling of the fixed pores, expansion of the fixed pores and swelling of the polymeric nuclei. On the other hand, heptane uptakes could be a result of two contributions: filling of the fixed pores and expansion of the fixed pores. The expansion of the fixed pores produced an increase of the volume of the copolymer beads.

Iayadene et al. [36] studied the influence of methyl methacrylate on the mean particle diameter, porous structure, and swelling in toluene and cyclohexane by suspension polymerization of styrene-divinylbenzene with MMA as a third monomer. A DVB content of 20% wt., a diluent mixture of 80/20% vol of n-heptane/2-ethyl-1-hexanol and dibenzoyl peroxide of 40% wt. as an initiator were used in this work. They found that the pore volume increased in the presence of MMA and the absorption of toluene and cyclohexane increased as a function of MMA content.

Kolarz et al. [37] determined the influence of the following monomers on bead swelling: methyl methacrylate (MMA), butyl acrylate (BA) and vinyl acetate (VA) on the porous structure of polymers crosslinked with the multifunctional (meth)acrylates, such as, trimethylolpropane trimethacrylate (TMPMA), trimethylolpropane triacrylate (TMPA), tetramethylolpropane tetraacrylate (TMTA) by suspension polymerization. A mixture of cyclohexanol and 2-ethylhexanol was used as an inert diluent in order to obtain porous materials. The porosity and pore size distribution in the swollen state (water as a solvent) were measured using inverse size exclusion gel chromatography. They found that the copolymer crosslinked with TMPMA, methyl methacrylate segments made the polymers more rigid and highly porous. Copolymers crosslinked with TMPA had a bimodal pore size distribution with a high percentage of small pores. Likewise, MMA segments

made the network more rigid and porous in these polymers. A similar effect was observed with VA, whereas BA results in the decreased porosity.