

Synthesis of 100 μm Uniform Porous Spheres by SPG Emulsification with Subsequent Swelling of the Droplets

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ABSTRACT: 100 μm porous p(styrene-*co*-divinylbenzene) (PS-DVB) microspheres were synthesized by employing a particular membrane emulsification technique, and subsequent swelling of the seed droplets. DVB dissolving a water-insoluble substance, hexadecane (HD), and an initiator was permeated through a SPG (Shirasu porous glass) membrane, and the uniform (*seed*) droplets were released to a stabilizer solution acting as the continuous phase. The average droplet size was around 30 μm , and this emulsion was mixed with a secondary emulsion of much smaller size consisting of more hydrophilic components, a mixture of styrene, middle chain alcohol (C6 to C8), dichlorobenzene, and isoamyl acetate, which promotes the degradative diffusion process of the components. After all the droplets in the secondary emulsion virtually disappeared, the seed droplets were swollen to a maximum 110 μm . Polymerization was carried out at 348 K under a nitrogen atmosphere. Uniform porous spheres of 100 μm with the coefficient of variation less than 10% were obtained. Specific surface area was 350 m^2/g . Careful controlling of the specific gravity of swollen droplets and the choice of solvents balancing between the good solvency for the polymer and polarity (solubility in water) proved vital in order that the polymerization may proceed without an extensive phase separation in the early stage, which eventually induces breakup of the droplets. The three component system, isoamyl acetate-hexanol-*o*-dichlorobenzene, provided an adequate cosolvent for these purposes. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 931–942, 1997

Key words: suspension polymerization; P(styrene-*co*-divinylbenzene); uniform microspheres; SPG (Shirasu porous glass) membrane

INTRODUCTION

Polymeric microspheres of 100 μm in diameter have been produced commercially by the suspension polymerization process in which monomer is dispersed in the form of droplets under an influence of shear force, eventually resulting in a wide size distribution. Screening of the polymer particles is an essential process when they are to be used for sophisticated purposes such as ion-exchange resins, packing materials for column chro-

matographies, spacer spheres for liquid crystal display (LCD), and so on. It is well known that the droplets should be exposed to a homogeneous shear field in order to obtain a narrow size distribution. The problem is, however, that the droplet size inevitably becomes smaller, less than 10 μm in diameter, because a brutal shear force must be applied to the dispersion system to attain a uniform shear field. Kamiyama et al.¹ fabricated a unique reactor system by which they claimed production of toner particles for xerography. Monomer droplets suspending inorganic powders, and other ingredients were passed through a high-shear line mixer before being transferred to

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a reactor. They obtained fairly uniform spheres of around 5 μm scale with this reactor system.

Extremely monodisperse polymeric spheres, of size more than 10 μm and a maximum 100 μm can be obtained by adopting the unique seeded emulsion polymerizations, one referred to as the two-stage swelling technique developed by Ugelstad et al.,^{2,3} and the other, well known as the synthesis on a space shuttle, the NASA project promoted by Vanderhoff et al.^{4,5} Besides an unrealistic setup of the latter environment, the fundamental procedure is a step-wise growth of polymer particles by emulsion polymerization without nucleation of secondary particles and development of coagulum. With the two-stage swelling technique, seed polymer particles are capable of absorbing a large amount of monomer, practically several thousands times swelling of the original volume of seed polymer particles being possible.

The principle is closely related to the degradative diffusion process reported by Higuchi and Misra.⁶ When an ordinary oil-in-water (O/W) emulsion is mixed with another emulsion containing an essentially water-insoluble substance in their droplets, eventually all the droplets in the first emulsion disappear as the ingredients dissolve in water, diffuse through the medium, and are absorbed in the droplets of the latter emulsion. Because of the presence of the water-insoluble substance, the latter droplets are stable, and no reverse diffusion will take place.

Recently, the present authors proposed a rather simpler technique for the synthesis of 2.5 to 30 μm fairly uniform spheres of polystyrene (PS), and p(styrene-co-divinylbenzene, PS-DVB).⁷ By using SPG membranes with average pore sizes being 0.5, 0.9, 1.4, 1.8, and 5.25 μm , uniform monomer droplets were formed, dispersed in an aqueous solution of polyvinyl alcohol (PVA) and sodium lauryl sulfate (SLS), and polymerized. Monomer droplets were quite stable during the polymerization with no breakup or coalescence, and retained their initial size distribution. The size of polymer particles decreased slightly due to the contraction of volume, the value of coefficient of variation (CV) being around 10%. This value is by no means comparable to the monosized particles claimed by Ugelstad et al. and Vanderhoff et al.; however, the process is far simpler than the seed emulsion polymerization, only one-step polymerization is necessary. Addition of nonsolvents to styrene-DVB comonomer yielded porous spheres with a specific surface area as high as 373 m^2/g .

The authors also proposed the synthesis of uniform hydrophilic polymethyl methacrylate (PMMA) and p(MMA-co-ethyleneglycol dimethacrylate, PMMA-EGDMA) spheres, which were regarded as difficult to produce because of the strong hydrophilicity of a SPG membrane.⁸ Because MMA is fairly soluble in water, it wets the surface of SPG membrane, and the release of uniform droplets becomes unlikely. The authors have overcome this problem by adopting the swelling technique presented by Ugelstad et al. As a primary (*seed*) emulsion, a hydrophobic solvent containing water-insoluble hexadecane (HD) was prepared by the SPG emulsification process. A secondary emulsion, its oil phase composed of hydrophilic MMA, EGDMA, and sparsely water-soluble solvents, was prepared by a conventional homogenizer, and added to the primary emulsion. The swelling was rapid under mild agitation at room temperature. Subsequent polymerization yielded uniform spheres with the same CV range as those of PS spheres.

It was a logical consequence for the present authors to realize that application of the swelling technique to the styrene droplets and subsequent polymerization will yield larger uniform spheres, probably ca. 100 μm in diameter. This article will describe in detail how the authors managed to obtain 100 μm porous and uniform PS-DVB spheres.

EXPERIMENTAL

Material

All reagents were purchased from Kishida Chemical Co., Ltd. unless stated otherwise.

Monomers

Styrene, glycidyl methacrylate, and divinyl benzene (DVB) were commercial grade and distilled under vacuum to remove inhibitors. Purity of DVB was about 55%, the rest consisting of 40% ethyl vinylbenzene and 5% of saturated compounds. They were stored in a refrigerator prior to use. Acrylic acid (AA) was reagent grade, stored in a refrigerator, and filtered to remove polymer just before formulation of ingredients.

AA was used to incorporate carboxyl groups to immobilize enzyme, and GMA was used to introduce spacer arms.

Table I Specific Gravity and Solubility in Water of Chemicals Used

Substance	Specific Gravity	Solubility in Water (wt %)
Styrene	0.9059 (293) ^a	0.03 (298), 0.053 (333)
Divinyl benzene	0.914	—
Acrylic acid	1.062 (289)	soluble
Glycidylmethacrylate	1.078 (298)	—
Hexadecane	0.775	9.0 (10 ⁻⁸) (298), 5.9 (10 ⁻⁷) (333)
Lauryl alcohol	0.825 (298)	1.7 (10 ⁻⁴) (289), 3.6 (10 ⁻⁴) (322)
Heptane	0.684 (293)	2.7 (10 ⁻⁴) (298)
Benzene	0.8787 (289)	0.171 (293), 0.260 (342)
<i>o</i> -Dichlorobenzene	1.306 (293)	—
1,2,4-Trichlorobenzene	1.463 (298)	—
Hexanol	0.8153 (298)	0.59 (298)
Octanol	0.827 (293)	0.054 (298), 0.06 (333)
Isoamyl acetate	0.876 (288)	1.40 (298)

^a Measured temperature (K).

Solvents

Benzene (Bz), *o*-dichlorobenzene (DCB), 1,2,4-trichlorobenzene (TCB), heptane (HP), hexanol (HA), octanol (OA), and isoamyl acetate (IA) were all reagent grade, and used as received except IA, which was distilled under vacuum.

DCB and TCB, good solvents of PS, were used to adjust the density of the droplets. HA and OA, poor solvents of PS, were used as a diluent to induce gentle phase separation, and finally to yield a porous structure. IA, fairly soluble in water, was used to promote the degradative diffusion of sparsely soluble substances.

Methyl and ethyl alcohol were commercial grade, and used to remove the diluents and unreacted monomer as a centrifuge medium.

Water-Insoluble Chemicals

Hexadecane (HD), and lauryl alcohol (LA) were reagent grade, and used as received. Specific gravity and solubility in water of these chemicals are listed in Table I.

Stabilizers

Polyvinyl alcohol (PVA, Kuraray Co., Ltd.) had 88.5 mol % degree of hydrolysis, and 1800 degree of polymerization (DP). Sodium lauryl sulfate (SLS, Merck) was biochemistry grade. Emulgen (polyoxyethylene nonylphenylether, 80% purity, 23 units of ethylene oxide, Kao Co. Ltd.) was briefly used. They were used as received.

Initiator

Benzoyl peroxide (BPO) with 25% moisture content was reagent grade.

Inhibitors

Hydroquinone (HQ) and 2,5-dihydroxybenzenedisulfonic acid, dipotassium salt (DHBSP, Aldrich Chemical Co, Inc.) were used to prevent secondary nucleation of polymer particles in the aqueous phase.

Electrolyte

Sodium sulfate was reagent grade, and was used as received.

Polymerization

Preparation of Seed Emulsion

The schematic diagram of a particular emulsification process using a SPG membrane and the detailed procedures were presented in previous articles.⁷⁻⁹ Only minor modifications will be mentioned in the following paragraph.

The SPG membranes of 5.25 μm pore size were used preferentially to obtain a maximum droplet size. Two formulations of the seed emulsion are shown in Table II. Depending on the swelling ratio defined in the later section, the volume fraction of organic phase to the total seed emulsion was adjusted. The nitrogen pressure applied for the permeation of dispersion phase through the mem-

Table II Formulations of Seed Emulsion (Runs 450 and 466)

Seed No.	450	466
Divinyl benzene (g)	64	20
Hexadecane (g)	16	20
Benzoyl peroxide (g)	4 (3) ^a	1.25 (0.938)
Water (g)	320	360
Polyvinyl alcohol (g)	2	2
Sodium lauryl sulfate (g)	0.05	0.05
Total weight (g)	406.1	403.3

^a Net weight of benzoyl peroxide.

brane was roughly in the range between 0.05 to 0.08 kgf/cm², never exceeding 0.1 kgf/cm². The time required for emulsification varied from 0.5 to 1 h, depending on the formulation. Two or three emulsions were finally prepared from one seed emulsion, either by changing the swelling ratio or the composition of the secondary emulsion. As shown later in Table IV, only a fraction of the seed emulsion was used as the swelling ratio became higher.

Preparation of Secondary Emulsion

A variety of formulations of the secondary emulsion are listed in Tables III and IV. Composition of the organic phase, generally containing monomers, polar solvents (promoters for the degradative diffusion process), and good solvents for PS was changed rather randomly. From run 1445 to 3450, hexanol and benzene were used as a mixed diluent. From run 1459, the importance of the specific gravity of the swollen droplets was recognized to maintain the stability of droplets during the polymerization, and addition of the heavy solvents, chlorinated benzene derivatives, became absolutely necessary. From run 1463, isoamyl acetate, which promotes the diffusion process, and enhances the extent of swelling as well, was used together with hexanol as a mixed polar solvent. A conventional laboratory homogenizer (Ace homogenizer, AM-11, Nissei Co.) was used for preparation of the emulsion with a rotation speed of 133 s⁻¹ for 15 min at room temperature. Only a small amount of sodium lauryl sulfate was used as an emulsifier because stability of the emulsion is by no means necessary; instead, a gradual degradation of the emulsion is favored during the swelling period.

Swelling Process

A preparation of the secondary emulsion was started in parallel during the final stage of the preparation of seed emulsion. A required amount of the seed emulsion was weighed in a glass separator flask of 300 mL capacity, all the seed emulsion was added, and the swelling process started under mild stirring and nitrogen atmosphere. Formulations of the seed and secondary emulsion are shown in Tables III and IV. A semicircular anchor type impeller was used with a normal agitation rate of 2.5 s⁻¹.

Swelling ratio based on recipe⁸ is defined as follows,

$$S_r = 1 + \frac{\text{(Total weight of monomers and solvents in the secondary emulsion)}}{\text{(Total weight of monomers, solvents, and HD or LA in the seed emulsion)}} \quad (1)$$

As the swelling ratio increases, the amount of seed emulsion becomes lower, only a small amount of PVA being present in the final reaction mixture. In order to compensate for this deficiency of the stabilizer, an extra stabilizer solution (shown in Table IV as the additional stabilizer solution) was prescribed and added gently to the emulsion immediately after the swelling process is over.

Polymerization

After the swelling process, gentle bubbling of nitrogen into the emulsion was started. After 1 h, the bubbling nozzle was removed from the emulsion, and fixed above the interface, thereby providing a nitrogen atmosphere in the reactor. The temperature was raised to 348 K, and the emulsion polymerized for 24 h. After the polymerization, a few grams of the emulsion were set aside for a measurement of monomer conversion. Polymer particles were removed from the serum by centrifugation, washed with methanol or ethyl alcohol, and dried under vacuum. Either this dried powder or a drop of diluted emulsion was treated for use as a SEM sample.

Analyses

Percent conversion of monomer was determined gravimetrically. The polymer was precipitated by

Table III Formulations of Seed and Secondary Emulsion (Swelling Ratio ≤ 4)

Seed emulsion			
Run No.	1445	2445	1447
Swelling ratio	2	4	4
Styrene (g)	6	6	—
Divinyl benzene (g)	6	6	6
Hexadecane (g)	—	—	1
Lauryl alcohol (g)	2	2	—
Heptane (g)	6	6	—
Benzoyl peroxide (g)	1 (0.75) ^a	1 (0.75)	0.5 (0.38)
Water (g)	130	130	40
Polyvinyl alcohol (g)	0.667	0.667	0.5
Sodium lauryl sulfate (g)	0.0167	0.0167	0.00625
Sodium sulfate (g)	0.0167	0.0167	0.0125
DHBS ^b (g)	0.0167	0.0167	0.0125
Total weight (g)	151.1	151.1	48.1
Secondary emulsion			
Styrene (g)	—	9	9
Divinyl benzene (g)	—	9	—
Glycidyl methacrylate (g)	1	2	1
Hexanol (g)	10	22	5
Benzene (g)	9	18	15
Water (g)	130	90	220
Sodium lauryl sulfate (g)	0.05	0.05	0.05
Total weight (g)	150.1	150.1	250.1
Grand total weight (g)	301.2	301.2	298.2
Specific gravity of droplets ^c	0.836	0.856	0.883

^a Net weight of benzoyl peroxide.

^b 2,5-dihydroxy-1,4-benzenedisulfonic acid, dipotassium salt.

^c Specific gravity of droplets after the swelling process.

methanol from the serum, separated by centrifugation, and dried in vacuum and the dried weight was measured.

Droplets of the seed emulsion, those after swelling, and polymer particles were observed with an optical microscope. Diameters of several hundred droplets or polymer particles were counted to calculate average diameters. In Figure 2, as shown later, d_0 indicates the average diameter of the seed emulsion, and d , that of the swollen droplets. Experimentally observed ratios of the swelling can be expressed as,

$$S_{\text{robs}} = (d/d_0)^3 \quad (2)$$

S_{robs} will be compared with S_r defined in eq. (1) in Table V as shown later.

General feature of the surface and the cross section of polymer particles were observed with SEM (JEOL, JSM-35CFII). Average diameters of polymer particles, d_p , were mainly determined from SEM photographs.

The surface area of micropores was obtained from BET measurement by using a Quantasorb Jr. (Yuasa Ionics Co. Ltd.). Adsorbent was a mixture of nitrogen and helium, the measurement being carried out at ambient temperature.

RESULTS AND DISCUSSION

Swelling of the Seed Droplets

A visual illustration of the swelling procedure is demonstrated in Figure 1. The seed emulsion (25.4 g) of run 450, $d_0 = 29.7 \mu\text{m}$ and $\text{CV} = 10.8\%$, was mixed with 175 g of the secondary emulsion. After mild stirring for 12 h at room temperature, an additional stabilizer solution was gently added. As shown in the photograph, the size of the droplets, $d = 57.9 \mu\text{m}$ and $\text{CV} = 11.1\%$, increased to almost twice the size of seed droplets. Apparently neither secondary droplets remained, nor larger droplets formed by coalescence were

Table IV Formulations of Seed and Secondary Emulsion (Swelling Ratio ≥ 8)

Seed emulsion									
Run No.	2448	3450	1459	1461	1463	1464	1465	1466	2467
Swelling ratio	8	8	8	8	8	8	16	64	64
Divinyl benzene (g)	4	4	4	4	4	4	1.6	0.25	—
Hexadecane (g)	1	1	1	1	1	1	0.4	0.25	0.5
Benzoyl peroxide (g)	0.25 (0.19) ^a	0.25 (0.19)	0.25 (0.19)	0.25 (0.19)	0.25 (0.19)	0.25 (0.19)	0.1 (0.075)	0.0156 (0.0117)	0.025 ^e —
Water (g)	20	20	20	20	20	20	8	4.5	4.5
Polyvinyl alcohol (g)	0.5	0.125	0.125	0.125	0.125	0.125	0.05	0.025	0.025
Sodium lauryl sulfate	0.05	0.0031	0.0031	0.0031	0.0031	0.0031	0.00125	0.00063	0.00063
Total weight (g)	25.8	25.4	25.4	25.4	25.4	25.4	10.1	5.04	5.05
Secondary emulsion									
Styrene (g)	11	11	11	12	11	11	—	—	—
Divinyl benzene (g)	—	—	—	—	—	—	10	11.5	11.5
Acrylic acid (g)	1	1	1	—	1	1	1	1	1
Hexanol (g)	16	23	12	15	6	8	5	5	5
Isoamyl acetate (g)	—	—	—	—	6	4	5	5	5
Benzene (g)	7	—	3	—	—	—	—	—	—
o-Dichlorobenzene (g)	—	—	8	8	11	11	9	9	—
1,2,4-Trichlorobenzene	—	—	—	—	—	—	—	—	9
Water (g)	190	140	140	140	140	140	140	160	160
Sodium lauryl sulfate	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Total weight (g)	225.1	175.1	175.1	175.1	175.1	175.1	171.1	191.6	191.6
Additional stabilizer solution ^b									
Water (g)	50	100	100	100	100	100	100	100	100
Polyvinyl alcohol (g)	1	1	2	2	2	2	2	2	2
Emulgen (80%) (g)	—	3.75	—	—	—	—	—	—	—
Sodium sulfate (g)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
DHBS ^c (g)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Total weight (g)	51.1	104.8	102.1	102.1	102.1	102.1	102.1	102.1	102.1
Grand total weight (g)	302.0	305.3	302.4	302.4	302.4	302.5	283.2	298.7	298.7
Specific gravity of droplets ^d	0.863	0.852	0.930	0.921	0.967	0.963	0.973	0.971	0.995

^a Net weight of benzoyl peroxide.^b Added after the swelling process.^c 2,5-dihydroxy-1,4-benzenedisulfonic acid, dipotassium salt.^d Specific gravity of droplets after the swelling process.^e Lauroyl peroxide was used in place of benzoyl peroxide. The polymerization temperature was 333 K.

Table V Formulations of Swollen Droplets, and Experimental Data of Seed and Swollen Emulsion, and Polymer Particles

Run No.	1445	2445	1447	2448	3450	1459	1460	2460	1461	1463	1464	2464	1465	2465	1466	2466	1467	2467
Formulation of swollen droplets																		
Styrene (g)	6	6	15	11	11	11	11	11	12	11	11	11	—	—	—	—	—	—
Divinylbenzene (g)	6	6	1	4	4	4	4	4	4	4	4	4	11.6	15	11.8	11.5	11	11.5
Acrylic acid (g)	—	—	—	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Glycidyl methacrylate (g)	1	2	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hexadecane (g)	—	—	1	1	1	1	1	1	—	1	1	1	1	1	0.25	0.5	1	0.5
Lauryl alcohol (g)	2	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hexanol (g)	10	22	5	16	23	12	12	12	15	6	8	—	5	6	5	5	5	5
Octanol (g)	—	—	—	—	—	—	—	—	—	—	—	6	—	—	—	—	—	—
Benzene (g)	9	18	15	7	—	3	3	3	—	—	—	—	—	—	—	—	—	—
Isoamyl acetate (g)	—	—	—	—	—	—	—	—	—	6	4	6	5	6	5	5	5	5
<i>o</i> -Dichlorobenzene (g)	—	—	—	—	—	8	8	8	8	11	11	11	9	11	9	9	—	—
1,2,4-Trichlorobenzene (g)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	9	9
Total weight (g)	34	56	38	40	40	40	40	40	40	40	40	40	32.6	40	32	32	32	32
Average diameter of droplets																		
Seed (μm)	28.0	28.0	36.4	31.2	29.7	32.4	30.4	30.4	28.8	29.0	31.4	31.4	29.2	29.2	32.3	32.3	26.0	26.0
CV (%)	9.63	9.63	20.8	38.0	10.8	8.94	8.56	8.56	10.2	10.9	8.70	8.70	10.9	10.9	10.0	10.0	8.70	8.70
After swelling (μm)	31.6	38.2	46.1	34.7	57.9	52.0	52.4	53.0	51.4	56.9	59.3	60.1	66.5	55.5	111	92.4	75.0	91.9
CV (%)	9.45	9.31	36.1	54.8	11.1	18.7	10.1	10.9	9.04	10.2	9.52	8.74	9.29	8.47	8.32	10.3	8.51	9.41
Swelling ratio																		
Calculated	2	4	4	8	8	8	8	8	8	8	8	8	16	8	64	32	32	64
Observed	1.44	2.54	2.03	1.38	7.40	4.13	5.12	5.30	5.68	7.55	6.74	7.01	11.8	6.87	40.6	23.4	24.0	44.2
Polymer particles																		
Average diameter (μm)	31.8	38.2	41.3	60.1	—	53.9	51.1	51.5	57.4	50.4	52.1	52.8	64.5	55.7	102	89.5	54.5	60.1
CV (%)	11.0	9.91	27.5	(14.9)	—	11.7	14.2	10.6	12.3	11.9	9.35	9.60	11.4	12.9	8.39	9.20	7.91	9.62
Coagulum formation	few	few	few	few	yes	few	few	few	few	none	none	none	few	none	few	few	few	few
Secondary nucleation	none	none	few	none	yes	none	none	none	none	none	none	none	none	none	none	none	none	none
Monomer conversion (%)	96.0	80.3	95.6	83.2	85.4	72.5	73.3	76.1	86.0	96.0	89.0	54.7	86.5	94.7	58.0	64.0	63.6	63.6
Specific surface area (m^2/g)	—	—	55.4	39.3	—	108	—	—	56.4	73.3	85.4	60.2	438	442	350	377	—	—

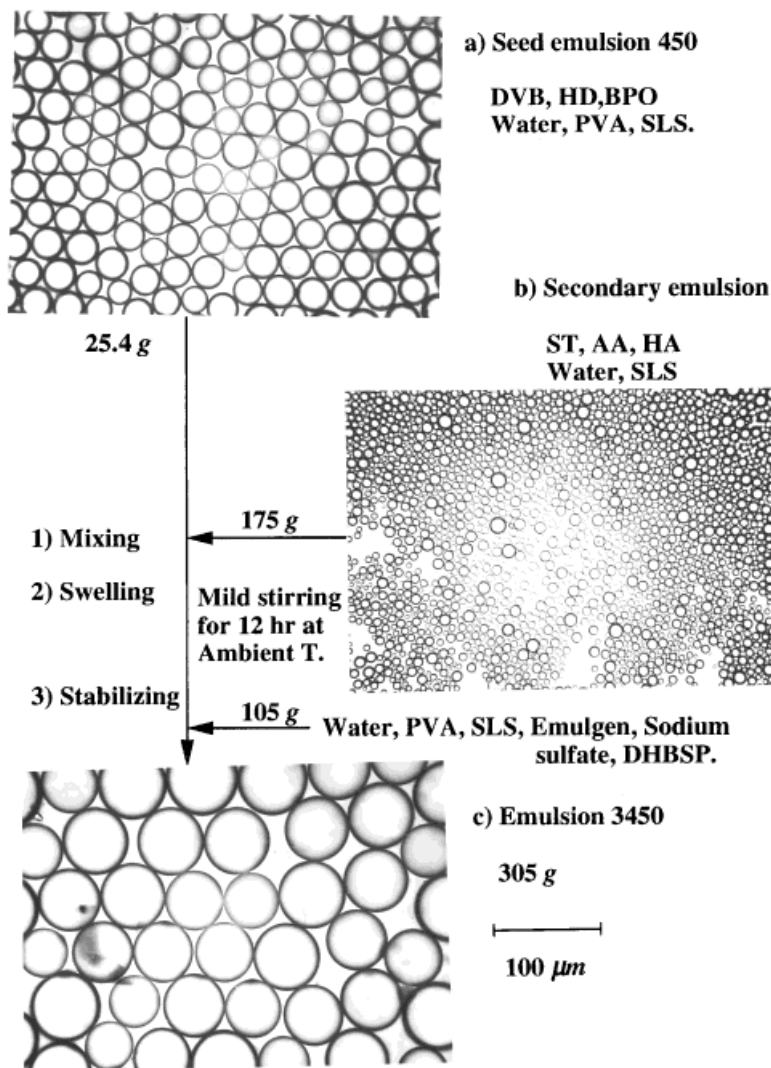


Figure 1 Optical photographs of seed, secondary, and swollen emulsion with a process of swelling (run No. 3450).

observed. As shown in Table IV, an excess amount of hexanol in the secondary emulsion promoted nearly perfect swelling.

A summary of the experimental results, after the swelling and polymerization and the formulation of swollen droplets as well, is shown in Table V. d/d_0 , a ratio of the average diameter before and after the swelling, is plotted as a function of the swelling ratio in Figure 2. A theoretical curve can be drawn from eq. (2) as a broken line in Figure 2. Effectiveness of various solvents for the swelling is compared. The symbol of run 3450 (+, HA only), almost hidden in the figure, falls on the theoretical line at $S_r = 8$. When benzene is mixed with hexanol, the observed ratios are well below the theoretical line. If attention is paid to the rows of swelling

ratio in Table V, in particular, runs with $S_r = 8$, this poor swelling tendency (run 2448) is clearly improved by a partial (runs 1459, 1460, and 2460) or complete replacement (run 1461) with dichlorobenzene. In fact, the observed swelling ratio of run 2448 is only 1.38, while those using DCB are in the range from 4.13 to 5.68. Originally, DCB was used for the purpose of increasing the specific gravity of swollen droplets. Significant progress in efficient swelling was achieved by a cosolvent of hexanol and isoamyl acetate, which accelerated the swelling process, and improved the stability of swollen droplets. Kubota et al. reported that swelling of more than thousand times in volume was possible when IA was mixed with styrene in their PS seeded emulsion polymerization.¹⁰

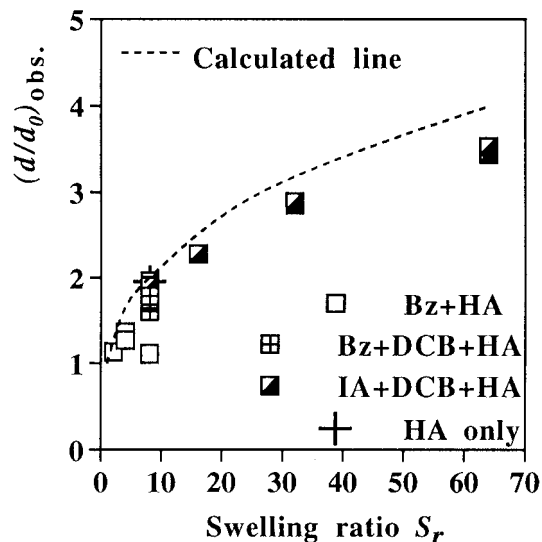


Figure 2 Observed value of d/d_0 as a function of swelling ratio.

Swelling ratios of more than 8 (16, 32, and 64) were tried, and the swelling time was reduced to a few hours from at least overnight. It became clear that the swelling is not necessarily complete; the polymerization can be started in the presence of smaller secondary droplets, which do not contain an initiator. Samples taken after the onset of polymerization showed that appreciable numbers of smaller droplets still remained in the reaction mixture. This is part of the reason why the plots of d/d_0 for IA + DCB + HA fell slightly short of the theoretical line at $S_r = 32$ and 64.

Polymer Particles

General features of polymer particles, average diameter, coefficient of variation, and specific surface area, are summarized in Table V with brief comments concerning the formation of coagulum and the nucleation of secondary particles. A maximum average diameter $102 \mu\text{m}$ was obtained in run 1466, its CV being a respectable 8.4%.

In retrospect, the final composition and the specific gravity of the swollen droplets were singularly important factors in obtaining solid polymer particles with uniform size.

Specific Gravity of the Swollen Droplets

Specific gravities of the swollen droplets were calculated by assuming the additivity of volume, and are shown in the last rows of Table III and IV. In the earlier experiments, no adjustment of the

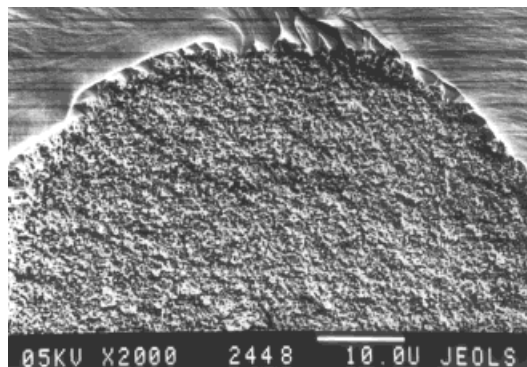
specific gravity was taken in consideration, and the omission resulted in formation of coagulum due to the creaming and eventual coalescence of the droplets, in particular, at higher swelling ratios. In the runs with a lower swelling ratio, 2 and 4, the amount of coagulum was relatively low, and no noticeable secondary nucleation was observed. The size of polymer particles remained fairly uniform in runs 1445 and 2445, becoming broader in run 1447 with a higher swelling ratio.

However, when the swelling ratio was raised to 8, regardless the final formulation of the droplets, the experiment resulted in either extensive agglomeration, clusters formation, or a polydispersity of polymer particles accompanied with secondary nucleation. Only run 2448, which used a mixed solvent dominant in hexanol, managed to yield fairly monosized particles after the smaller particles were separated by centrifugation. Because the observed swelling ratio was a mere 1.38, compared to an intended 8, the polymerization was apparently started under a nonequilibrium state of the swelling, a reasonable explanation being that the polymerization and the degradative diffusion process of smaller droplet took place in parallel during the initial stage. Heating to the reaction temperature of 348 K may have promoted further swelling.

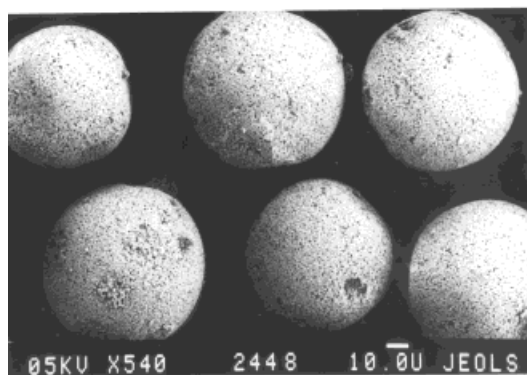
Surface features and a cross-sectional view of the polymer particles obtained from run 2448 are shown in Figure 3. A grainy structure resulting from coarse pores can be seen as well as a couple of small dents on the surface. These dents were probably formed due to the local phase separation of hexadecane, which was washed out during the washing with alcohols. Traces of spots, probably contact points with other polymer particles in clusters, are also observed on the surface. When the experiment was successful, small clusters, if any, separated easily by sonification. The specific surface area of run 2448 was a moderate $39.3 \text{ m}^2/\text{g}$, and suitable as a carrier for enzyme immobilization.¹¹

From run 449 to 458 (details not shown) no solid emulsion was formed no matter how the formulations or procedures were modified. Addition of water soluble solvents such as acetone, methoxy ethanol, and isopropanol, and other stabilizers such as carboxymethyl cellulose and polyvinyl pyrrolidone were tried with no appreciable improvements. On the contrary, raising the temperature from ambient to 348 K revealed no damage to the stability of the emulsion.

The first breakthrough was achieved by em-



a) Cross sectional view



b) Surface feature of Run 2448 spheres

Figure 3 SEM photographs of polymer particles, run 2448. Swelling ratio = 8, PS-DVB-AA/HD-HA-Bz, $d_p = 60.1 \mu\text{m}$, $A = 39.3 \text{ m}^2/\text{g}$. (a) Cross-sectional view; a grainy porous structure prevails; (b) surface feature with coarse pores and small dents.

ployment of heavier perchlorobenzene derivatives instead of benzene, which are also good solvents of styrenic polymers. From run 1459, the specific gravities were raised above 0.93, and later on, above 0.97 up to 0.995. No coalescence of the droplets due to creaming took place during the swelling nor in the earlier stage of polymerization.

Final Formulation of the Swollen Droplets

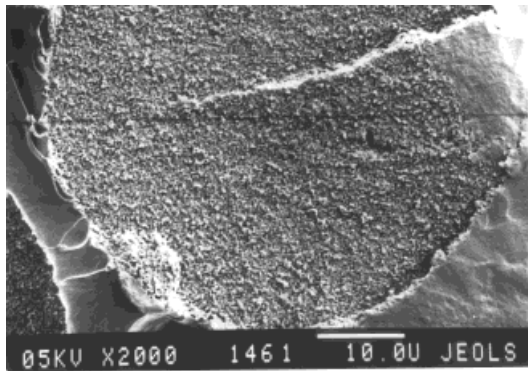
Final composition of the droplets, resulting from a combination of carefully considered formulations of the seed and the secondary emulsion, plays the other decisive role besides the specific gravity. The weight of each component in the droplets is shown in Table V.

Generally in this work, the solvent-to-monomer ratio was set at 6 : 4 to provide porous spheres. When the size of droplets was in the range of 10

μm in the previous work, the authors regarded the role of solvents as a diluent for controlling the pore size, and secondly as a promoter of the swelling, in particular, for hydrophobic monomers. However, a third and decisive factor connected to early phase separation emerged. In other words, formulations should be carefully designed in order to maintain the stability of droplets during transformation from low viscosity to viscous liquid, and finally to solid state. In the initial runs, hexanol was expected to promote the swelling, and benzene to prevent an early phase separation of crosslinked polymer chains formed at a low conversion range. As mentioned in the previous section, however, this combination failed because of a low specific gravity, and probably due to an excess percentage of hexanol. For example, run 3450 demonstrated almost flawless swelling, as shown in Figure 1, only yielding full clusters of smaller globules that were apparently formed from an enhanced phase separation. When the phase separation takes place at a low conversion range, a stagnant oil layer rich in hexanol is formed around the impeller shaft, and the initial uniform size distribution collapses. Emulgen was added in the final emulsion of the runs X 450 ($X = 1, 2, \text{ and } 3$) with an extra dosage of PVA; however, the stability was not improved.

Dichlorobenzene prevented occurrence of this undesirable phenomenon not only by increasing the specific gravity but also by interacting with hexanol to improve the compatibility between the components.

Surface features and a cross-sectional view of the polymer particles obtained from the run 1461, in which benzene was completely replaced with dichlorobenzene, are shown in Figure 4. The general features reflect those of run 2448 except for fibrous polymers sticking to the surface. Probably a thin layer rich in hexanol containing a small amount of dichlorobenzene and polymer was formed on the surface, and the fibrous structure remained after the solvents were removed by washing. Core-shell-like phase separations composed of a thin liquid shell layer and a solid core have been observed in our laboratory, PMMA-(15)/HD(2.5)-HA(15)-Bz(12.5),¹² PS(1)/LA(1),¹³ and so on. This morphology can be easily detected by observation with an optical microscope, but completely disappears after washing and drying. The specific surface area is $56.4 \text{ m}^2/\text{g}$, becoming slightly higher than that of run 2448, but remains moderate. After run 1459, from which the adjustment of specific gravity became routine, polymer



a) Cross sectional view



b) Surface feature of Run 1461 spheres

Figure 4 SEM photographs of polymer particles, run 1461. Swelling ratio = 8, PDVB-AA/HD-HA-DCB, $d_p = 57.4 \mu\text{m}$, $A = 56.4 \text{ m}^2/\text{g}$. (a) Cross-sectional view; a grainy porous structure prevails; (b) surface feature with coarse pores, fibrous polymers, and small dents.

particles retained the size and CV of the swollen droplets.

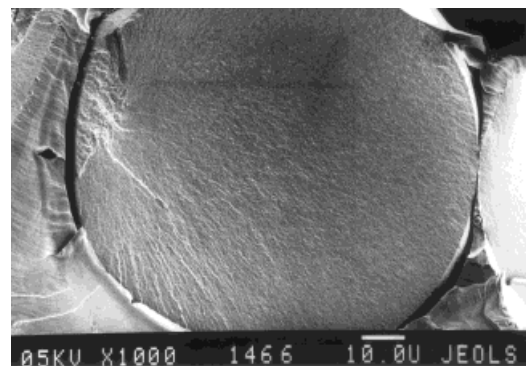
The second breakthrough was achieved by employment of isoamyl acetate, as mentioned earlier. The three-component cosolvent, isoamyl acetate–hexanol–dichlorobenzene, was so effective that runs with swelling ratios of 16, 32, and 64 were successfully carried out. As shown in Table I, isoamyl acetate is nearly three times more soluble in water, accelerates the degradative diffusion process, and is also a fairly good solvent for styrenic polymers.

Surface features and a cross-sectional view of the largest polymer particles obtained from run 1466 are shown in Figure 5. The surface looks cleaner and finer than those of runs 2448 and 1461, confirming good solvency of the three component system. The specific surface area jumped up to $350 \text{ m}^2/\text{g}$ due to the good solvency and a

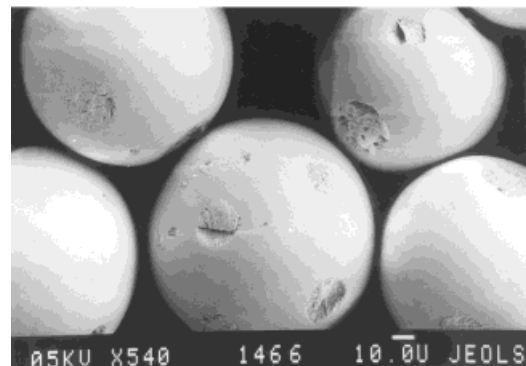
high density crosslinking network formed by a comonomer composition dominant in divinyl benzene. This value is comparable to the $373 \text{ m}^2/\text{g}$ obtained from PDVB/LA-toluene spheres.¹⁰

Incomplete Monomer Conversion

The only concern emerging from the runs with high swelling ratio is incomplete monomer conversion because the initiator concentration is forced to decrease as the ratio of seed emulsion to the secondary emulsion is getting smaller. This initiator deficiency cannot be compensated for by an addition of the initiator in the secondary emulsion, by which formation of the smaller particles will be almost certain. Screening of initiators having a high solubility in the mixture of hexadecane



a) Cross sectional view



b) Surface feature of Run 1466 spheres

Figure 5 SEM photographs of polymer particles, run 1466. Swelling ratio = 64, PDVB-AA/HD-HA-IA-DCB, $d_p = 102 \mu\text{m}$, $A = 350 \text{ m}^2/\text{g}$. (a) Cross-sectional view; a fine porous structure prevails; (b) surface feature with fine pores, and small dents. Fibrous polymers disappeared with the addition of IA.

and divinyl benzene seems to be the only realistic solution.

When trichlorobenzene was replaced with dichlorobenzene in runs 1467 and 2467, the size of the polymer particles decreased remarkably compared to the size of the swollen droplets, although the low values of CV were retained. Whether the low monomer conversion or the further improved solvency (collapsing of the cross-linking network) is responsible for this decrease remains to be investigated.

CONCLUSION

Fairly uniform porous PS-DVB spheres with average diameters ranging from 50 to 100 μm were successfully synthesized by using a SPG membrane for the formation of seed emulsion. The seed droplets were then swollen with a mixture of monomers and solvents homogenized to form minute droplets in the secondary emulsion. Careful controlling of the specific gravity and the formulation of solvents are two ultimate requirements for a successful conversion of the swollen droplets to polymer particles. The polymer particles retained uniform size distribution provided that these conditions were satisfied. Perchlorobenzene derivatives, *o*-dichlorobenzene and 1,2,4-trichlorobenzene, are recommended to increase the specific gravity of the droplets, and have good solvency for styrenic polymers. A three-component system, dichlorobenzene–isoamyl acetate–hexanol, was favored to achieve rapid swelling, and to prevent the phase separation taking place in the early stage of polymerization.

The surface of these large spheres is by no means smooth due to the presence of a few small dents, which may have been created either by a minor phase separation or by sticking with other particles. Further efforts at smoothing the surface features will be continued. However, the cross-sectional views reveal that the structure of the

polymer particles is quite homogeneous, composed of small pores that are controllable by adjusting the formulation.

The specific surface area ranges from 39.3 to 442 m^2/g .

The basic know how to synthesize uniform porous spheres of hydrophobic PS and hydrophilic PMMA with the size ranging from 2.5 to 100 μm has been established. Future investigations will be oriented to application fields for these spheres.

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