Synthesis of Polymeric Microspheres Employing SPG Emulsification Technique

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SYNOPSIS

Relatively uniform polymeric microspheres, the coefficients of variation being close to 10%, were obtained by the BPO-initiated suspension polymerization of styrenic monomers. Unlike the conventional stirred-tank system, a particular microporous glass membrane (SPG) provided uniform monomer droplets continuously when monomer was allowed to permeate through the micropores. The monomer droplets were suspended in an aqueous solution containing the stabilizing agents, transferred to a stirred vessel, and polymerized. Up to 10 μm spheres, of a far narrower size distribution than those obtained by conventional microsuspension polymerization spheres, were obtained. The initial droplet size and distribution were retained with the successful suppression of secondary particle nucleation by the addition of hydroquinone in the aueous phase. Crosslinked polystyrene spheres were also synthesized in the presence of various low-molecular-weight diluents. While a good solvent, toluene, was not so effective; poor solvents, n-hexane and n-heptane, easily yielded the microporous structure, the specific surface area being as high as 160 m^2/g. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric microspheres with uniform size distribution, in particular those with diameter in the range of 10 μm, have been recognized as one of the most sophisticated materials in the industries of applied and analytical chemistry, biology, medicine, and electronics. Wide surface area, apart from its utilization as a potential adsorbent, is available to introduce functional groups for further modifications with other reagents or larger molecules. Particles having microporous structure have also been synthesized for use as carriers packed in chromatographic columns, and for the production of magnetic microspheres. The fundamental nature of charged colloidal particles finds them other promising applications such as electronic photocopying and further hybridization with other micromeritic materials.

Synthesis of these microspheres is not easy, in particular the one having uniform size. Lehigh Uni-

versity and NASA groups led by Vanderhoff and El-Aasser provided extremely uniform polystyrene (PS) spheres of up to 30 μm diameter after the successive seeded emulsion polymerizations carried out on the space shuttle under the nongravity field.[1,2] The coefficients of variation were, in most cases, less than 2%. After the space laboratory was forced to shut down temporarily, they overcame the gravity on the ground, and finally extended the particle diameter as large as 100 μm. Ugelstad et al. developed the two-stage swelling technique, which is capable of swelling the original seeds up to a thousand times in volume with monomers,[3,4] and have established commercial-scale production of a variety of uniform spheres as large as 100 μm.[5] Ohkubo et al.[6] and Yoshimatsu et al.[7] developed their own swelling techniques and provided 6–8 μm uniform spheres.

Nonaqueous phase dispersion polymerization has been well known for its capacity to provide uniform spheres of the several micrometer scale. Up to 15 μm scale was reported.[8] In commercial scale, Yamamoto et al. reported that nearly 10 μm PS spheres were produced in the mixed media of short-chain alcohol and 2-methoxy ethanol (methyl cellosolve).[9]

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Reviewing the physical and physico-chemical techniques, Panagioutou and Levendis[10] reported that 20–30 μm PS and polymethyl methacrylate (PMMA) spheres were obtained with a particular device consisting of a vibrating orifice plate and a spray drying tower. Uniformity of the size depended on the slit diameter and vibrating frequency of the orifice plate. Polymer concentration in sprayed droplets was quite low even though a possible secondary polymerization by the addition of monomer and initiator was suggested. Hou and Lloyd[11] reported that the careful phase separation procedure of nylons in theta solvent with controlled cooling for the nucleation and growth could provide monodisperse spheres in the range of 10 μm.

The recent developments being briefly summarized, however, a simple and commercially available process still seems to be desired. It would be appropriate to point out some flaws in the nonaqueous phase dispersion polymerization, namely the inevitable use of organic solvents and rather limited flexibility.

A new technique to be discussed in this article is essentially a single-stage polymerization and has a potential capacity to produce various functional microspheres with considerable monodispersity. A particular microporous glass membrane (SPG)* is fabricated using a microphase separation of the mixture of CaO — Al_2O_3 — B_2O_3 — SiO_2.[12] Spinodal decomposition yields the two phases, CaO — B_2O_3 and Al_2O_3 — SiO_2. The former can be washed out with acid, leaving a fairly uniform microporous structure. Monomer droplets, in some cases mixed with diluent solvents, are formed through the micropores, stabilized in the aqueous solution of stabilizing agents, transferred to the reactor, and then polymerized. As a first report, general polymerization procedures and the synthesis of microporous polymeric spheres will be presented.

EXPERIMENTAL

Materials

Monomers

Styrene (ST) and divinyl benzene (DVB, Kishida Chemical Co. Ltd.) were commercial grade and dis-

tilled under vacuum to remove inhibitors. Purity of the latter was about 55%, the rest consisting of 40% ethyl vinylbenzene and 5% of saturated compounds. They were stored in a refrigerator prior to use.

Solvents

Benzene, toluene, methyl alcohol, and ethyl alcohol were commercial grade and distilled prior to use. n-Hexane and n-heptane were all reagent grade and used either as received or after distillation.

Other Chemicals

Sodium lauryl sulfate (SLS) was the grade for biochemical use (Merck). Sodium sulfate (anhydride) was reagent grade. Polyvinyl alcohol (PVA) with different degree of hydrolysis [Kishida Chemical Co. Ltd., degree of polymerization (DP) = 2000, 98.5–99.4% hydrolyzed, and Kureha Co. Ltd, DP = 2000, 80.0% hydrolyzed] was used as a stabilizer. Benzoyl peroxide (BPO) with 25 wt % moisture content (Kishida Chemical Co. Ltd.) was reagent grade and used as an initiator. Hydroquinone (HQ, Kishida Chemical Co. Ltd.) was used to prevent the secondary nucleation of polymer particles in the aqueous phase. All these chemicals were used without further purification.

Polymerization

Emulsification

A diagram of the particular emulsification process is shown in Figure 1. Microporous glass membrane module (MPG, NA-I, Ise Chemical Co.) was used for the preparation of monomer emulsion. The glass membrane was an annulus cylinder (O.D. = 10 mm, L = 150 mm, and surface area = 50 cm^2), and installed in a stainless steel cylinder shown as No. 1 in Figure 1. Three different pore sizes of 1.36, 0.90, and 0.50 μm were available. A scanning electron microscopy (SEM) photograph of the cross section of the 1.36-μm glass membrane is also shown in Figure 1. The dispersion phase, mixture of monomer, solvent, and initiator, was stored in the pressure-tight stainless steel bottle (No. 2) and allowed to permeate through the membrane under appropriate pressure into the recirculating flow. The droplets were suspended in the continuous phase, an aqueous solution of PVA, SLS, sodium sulfate, and HQ, and a part of the suspension was stored in the emulsion tank (No. 3) with a gradual increase of droplet concentration. A stirrer installed in the emulsion tank was not necessarily operated for all experiments since

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* The use of two abbreviations, SPG and MPG, in the following sentences may be confusing for readers. SPG is the generally accepted abbreviation for a Shirasu microporous glass membrane, while MPG is the brand name of SPG commercialized from Ise Chemical Co. Ltd. Shirasu soil is the principal raw material to produce SPG. On behalf of the inventors, SPG is used as a general term, while the use of MPG is rather specific.
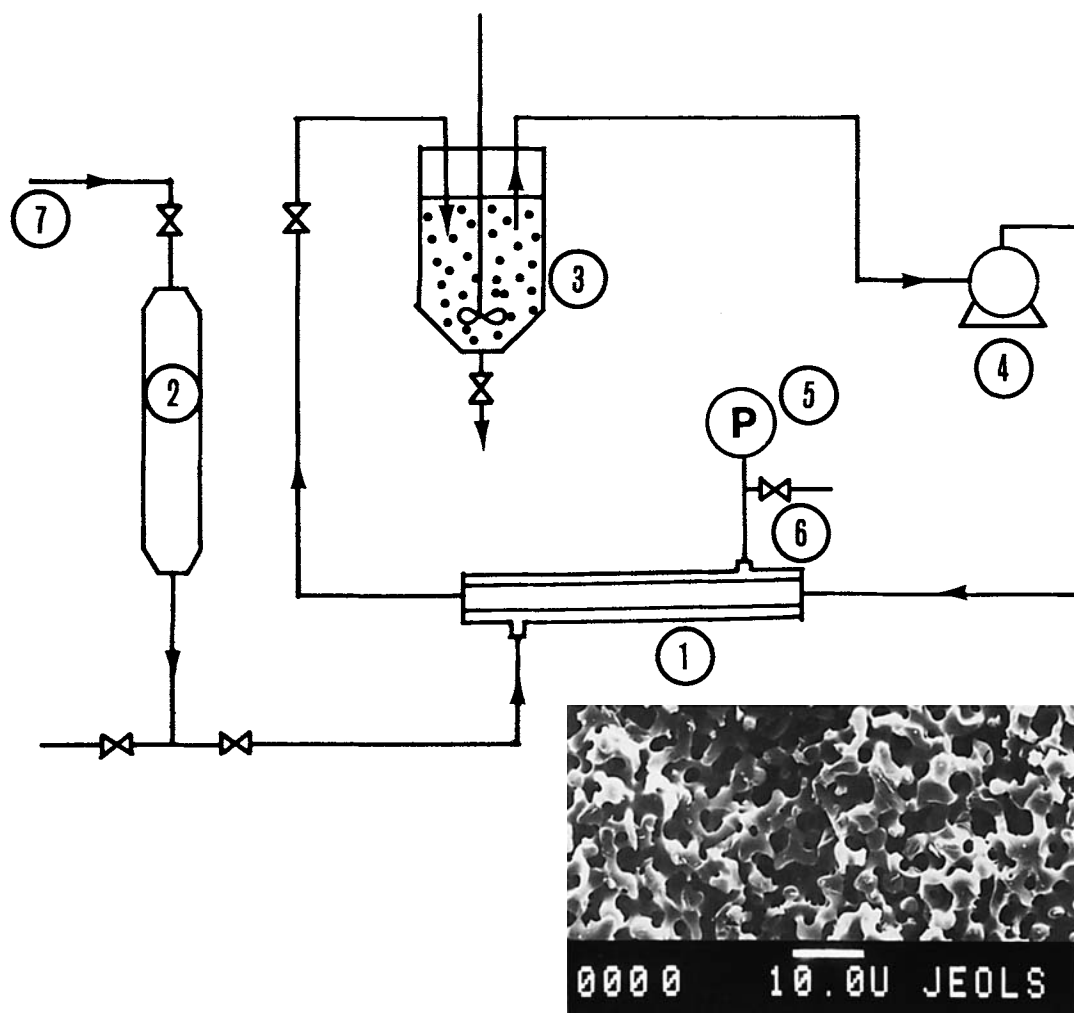
Figure 1   Diagram of emulsification by microporous glass membrane. (1) MPG module, (2) pressure bottle, (3) emulsion storage tank, (4) recirculation pump, (5) pressure gauge, and (6) purge valve. SEM photograph shows the cross-section of MPG, (7) nitrogen line.

the suspension has excellent stability. After the half volume of the dispersion phase was emulsified, the suspension stored in the emulsion tank was withdrawn and transferred to the stirred tank reactor (STR).

For maintenance after the emulsification, the recirculation loop was rinsed thoroughly with SLS solution and distilled water. Removed glass membrane was stored immersed in distilled water after extensive washing by ultrasonification. The membrane can be restored after fouling by occasional heat treatment at 773 K for 1 h.

Polymerization

As the initiator, BPO, was already mixed with monomer in the dispersion phase, efficient operation

was required to minimize the idle time. Three hundred grams of the emulsion was transferred to an ordinary glass separator flask, and gentle bubbling of nitrogen into the emulsion followed with mild agitation. After 1 h the bubbling nozzle was removed from the emulsion, the ingredients were heated to the reaction temperature, and polymerized for 24 h under the nitrogen atmosphere.

Treatment of Polymer Particles

After the polymerization, polymer particles were removed from the serum by centrifugation, washed with methyl alcohol or ethyl alcohol, and dried under vacuum. Crosslinked polymer particles, with no definite micropores observed on the surface, were swollen with benzene overnight and freeze-dried rapidly.

Analyses

Percent conversion of monomer was determined gravimetrically. Polymer was precipitated by methyl alcohol from the reaction mixture, separated by centrifugation, dried in vacuum, and the weight was measured.

Monomer droplets before polymerization and polymer particles were observed with an optical microscope. Diameters of several hundred droplets or particles were counted to calculate average diameters. General features of polymer particles were observed with SEM (JEOL, JSM-35CFII). Average diameter was mainly determined from SEM photographs, and in some experiments compared with the one calculated from an optical microscope.

Average molecular weight and molecular weight distribution were measured with gel permeation chromatography (GPC) (HLC-801, Toso Co. Ltd.) employing tetrahydrofuran (THF) as an elution solvent.

Surface area of micropores was measured with a porosimeter (Micromeritics Poresizer 9310, Shimazu) at room temperature. Average pore diameter, $\bar{d}_m$, was calculated as

$$\bar{d}_m = 4V/A \tag{1}$$

where V is volume of the sample and A is measured surface area.

RESULTS AND DISCUSSION

Polymerization Recipe

The polymerization recipe is shown in Table I. It was necessary to increase the amount of the stabi-

Table I   Polymerization Recipe

I. Continuous phase.			
MPG pore size	0.50	0.90	1.36 μm
Run No.	425	407	All
Water	450 g	450 g	450 g
Polyvinyl alcohol (PVA)	5.0 g	4.5 g	3.0 g
Sodium lauryl sulfate (SLS)	0.7 g	0.35 g	0.2 g
Sodium sulfate (Na$_2$SO$_4$)	0.1 g	0.1 g	0.1 g
Hydroquinone (HQ)	0.2 g	0.15 g	0.15 g
II. Dispersion phase (charged in the pressure bottle).			
MPG pore size	0.50	0.90	1.36 μm
Applied pressure[a]	1.05	0.7	0.50 atm
1. Standard recipe (no solvent and DVB)			
Styrene (ST)			100 g
Lauryl alcohol (LA)			5.0 g
Benzoyl peroxide (BPO, 25 wt % moisture)			2.0 g
2. Toluene solvent			
Styrene (ST)			47, 45, 40 g
Divinyl benzene (DVB)			3, 5, 10 g
Toluene (T)			50 g
3. n-Hexane solvent			
Styrene (ST)			45, 40, 35, 25, 15 g
Divinylbenzene (DVB)			5, 10, 15, 25, 35 g
n-Hexane (HX)			50 g
4. n-Heptane solvent			
Styrene (ST)		25, 20, 35	15, 12, 21 g
Divinylbenzene (DVB)		25, 20, 35	35, 28, 49 g
n-Heptane (HP)		50, 60, 30	50, 60 30 g

[a] Nitrogen pressure applied to the pressure bottle.
1. Half of the charged weight of the dispersion phase was actually emulsified.
2. 300 mL of emulsion was transferred to the reactor, and polymerized.
3. Weights of LA and BPO were fixed as in the standard recipe.
4. Polymerization temperature = 348 K.
5. Polymerization time = 24 hr.
6. Agitation rate during the polymerization = 180 rpm.

lizers in the continuous phase with decreasing micropore size in order to stabilize smaller emulsion droplets. Amounts of ingredients for the smaller pore size recipes still had to be adjusted in further experiments. The standard recipe contained only styrene, lauryl alcohol, and BPO. In each experiment emulsification was interrupted after half of the dispersion phase was emulsified through the membrane. In other words, 10 parts of the dispersion phase was actually present in 100 parts of the reaction mixture. Nitrogen pressure, to be applied to permeate the dispersion phase through the micropores, depended on the pore diameter $(\bar{d}_m)$ and was theoretically derived as follows:[13]

$$\Delta P = 4\gamma \cos \theta / \bar{d}_m \qquad (2)$$

where, ΔP is applied pressure, γ is interfacial tension between the droplet and the aqueous phase, and θ is contact angle of the droplet with the aqueous phase.

Equation (2) predicts that the required pressure is inversely proportional to $\bar{d}_m$, which is roughly satisfied by the actual nitrogen pressures shown in Table I. As the diameter of the micropore decreases, longer preparation time was necessary, nearly 2 h for 0.5 μm membrane.

According to Cheng et al.,[14] poor solvents for polystyrene such as n-heptane were effectively combined with DVB to obtain microporous structure. A good solvent, toluene, was used for comparison. The role of lauryl alcohol (LA) was not so clear as that of the long-chain hydrocarbons reported in a miniemulsion recipe,[15] however, the presence
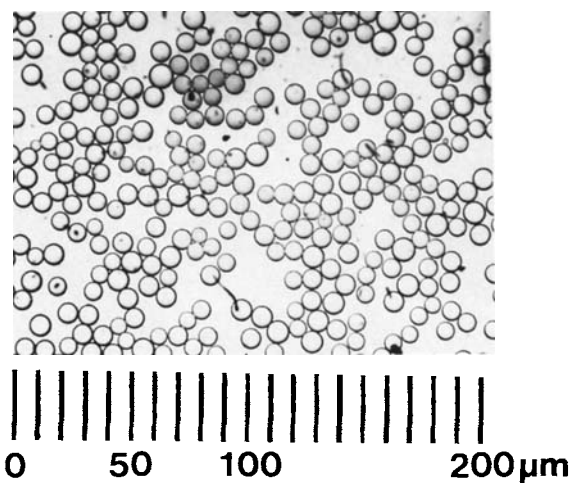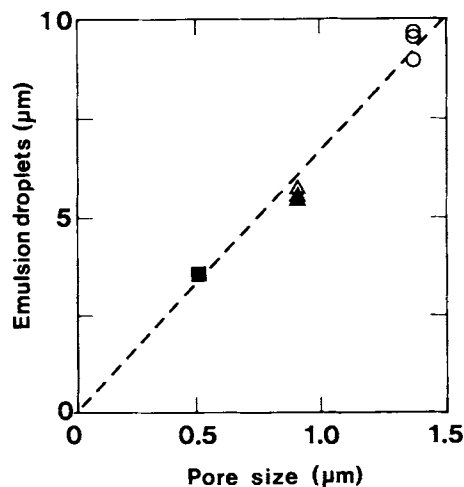
Figure 3   Average diameters of emulsion droplets as a function of micropore size of glass membrane. Different symbols indicate different MPG of same pore size.

of LA at the interface seemed to favor the stability and eventual relative monodispersity of polymer particles.

Emulsion Droplets

A photograph of emulsion droplets prepared with the standard recipe and 1.36-μm MPG is shown in Figure 2. The droplets were fairly uniform and stable. The size of the droplets changed depending on the pore size of the membrane and revealed a solid linear relationship as shown in Figure 3.

$$\bar{d}_e = 6.62\bar{d}_m \qquad (3)$$

where $\bar{d}_e$ is average diameter of emulsion droplets.

Nakashima et al.[13] reported that the coefficient was 3.25 regardless of the emulsion system and composition of the ingredients and tried to find theoretical support without success so far. The rather big difference between the two coefficients was probably due to the skillfulness of drawing glass pipes. Commercial products (MPG) used in the authors' experiments fell behind the expertise of Nakashima et al.[12] (SPG) on account of the sharpness of the edge at the opening of micropores, which was a vital factor in determining the droplet size.

Since the monomer droplets were fairly monodisperse, as can be seen in Figure 2, the number-average diameter was used for the correlation. Unless otherwise stated, the number-average diameter will be employed in the following results.

Figure 2   Photograph of emulsion droplets taken by optical microscope. Standard recipe, and 1.36 μm MPG was used.

Noncrosslinked Polymer Particles

Effect of Micropore Size of SPG

SEM photographs of polymer particles are shown in Figure 4. Various kinds of average diameters calculated for emulsion droplets and polymer particles are listed in Table II together with the selected runs of crosslinked particles discussed later. The coefficient of variation of the polymer particles was 18.8, 14.2, and 11.5% for 0.5, 0.9, and 1.36 μm membranes, respectively, showing that the polydispersity became slightly larger with the finer pore size. Despite this tendency, polymer particles obtained in all runs retained the narrow size distribution of the emulsion droplets. Run 901 shown in the extreme right columns in Table II is reference data obtained by microsuspension polymerization, employing almost an identical recipe with runs 425, 407, and 322. Emulsification was carried out using a homogenizer (Ace Homogenizer, Nissei Co. Ltd.) with an agitation rate

of 5000 rpm.[16] Comparison between the coefficients of variation clearly demonstrated an advantage of SPG emulsification technique to obtain a narrower size distribution.

As a graphical demonstration, histograms of the size distribution of emulsion droplets and polymer particles are shown in Figure 5. Considering the size shrinkage due to the density difference between styrene monomer and polymer as well as the loss of monomer due to the imperfect conversion, the size distribution of emulsion droplets was almost restored after the polymerization in run 322. No serious agglomeration between sticky droplets occurred during the whole reaction. Fairly low monomer conversion (56.0%) in run 425 was probably responsible for the post-polymerization shift of the size distribution to the left (lower size). Although sufficient initiator was present, in runs 425 and 407 the final monomer conversion was by no means complete compared to the other runs employing 1.36
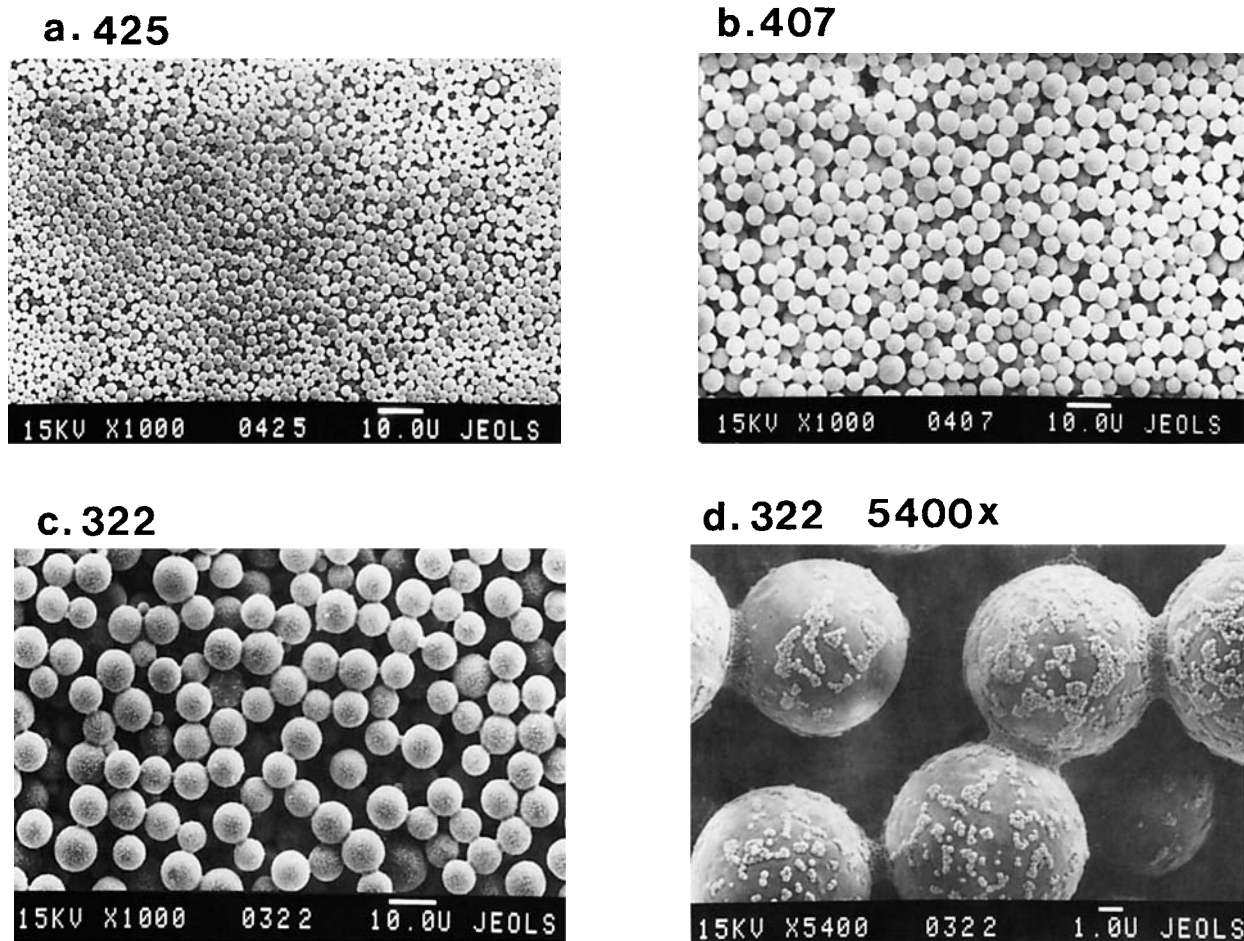
a. 425

b. 407

c. 322

d. 322 5400x

Figure 4 SEM photographs of polystyrene microspheres: (a) Run 425, $\bar{d}_{pn}$ = 2.38 μm; (b) run 407, $\bar{d}_{pn}$ = 4.88 μm; (c) run 322, $\bar{d}_{pn}$ = 8.10 μm; (d) enlarged spheres of run 322. Secondary polymer particles are clearly shown attaching on the surface.

Table II Extent of Monodispersity, Emulsion Droplets, and Polymer Particles

	425		407		322		341		343		345		347		901	
	Em.[a]	Pol.[a]	Em.	Pol.	Em.	Pol.	Em.	Pol.	Em.	Pol.	Em.	Pol.	Em.	Pol.	Em.	Pol.
Pore size (m)	0.50		0.90		1.36A[b]		1.36B		1.36B		1.36D		1.36C			
% conversion		56.0		68.4		86.8		97.0		88.2		74.8		89.4		82.1
d_n (μm)[c]	3.28	2.39	5.68	4.88	8.99	8.10	10.4	7.38	11.2	8.18	7.61	6.59	8.27	7.71	4.51	3.94
d_s (μm)[d]	3.30	2.43	5.71	4.93	9.06	8.16	10.4	7.41	11.3	8.22	7.64	6.63	8.32	7.75	5.11	4.89
d_v (μm)[e]	3.33	2.48	5.75	4.98	9.14	8.21	10.5	7.44	11.3	8.27	7.67	6.66	8.35	7.79	5.81	5.80
$d_{Saut.}$ (μm)[f]	3.39	2.57	5.81	5.09	9.30	8.32	10.6	7.51	11.4	8.36	7.73	6.73	8.42	7.86	7.53	8.17
SD (μm)[g]	0.43	0.45	0.64	0.69	1.19	0.93	1.21	0.67	1.06	0.86	0.69	0.68	0.71	0.77	2.40	2.96
CV[h]	13.1	18.8	11.3	14.2	13.2	11.5	11.7	9.08	9.46	10.5	9.07	10.3	8.59	9.99	53.2	75.1

[a] Em. = emulsion droplet. Pol. = polymer particle.
[b] Four different 1.36 μm MPGs were used.
[c] d_n = number av.
[d] d_s = surface av.
[e] d_v = volume av.
[f] $d_{Saut.}$ = Sauter av.
[g] SD = standard deviation.
[h] CV = coefficient of variation = $(SD/d_n)100$.

μm MPG. Hydroquinone may partition into the monomer-swollen particles and retard the polymerization. Also, another possibility is that hydroquinone in the aqueous phase may retard the polymerization in polymer particles, killing the radicals escaping from polymer particles. In emulsion polymerization employing an oil-soluble initiator, Nomura et al. emphasized that the radicals entering from the aqueous phase to polymer particles were singularly dominant in propagating polymer chains.[17] This mechanism may play a minor role in the polymerization of smaller polymer particles.

In run 322, PVA of 99.4% hydrolysis being used, secondary nucleation of smaller particles was definitely observed, despite the addition of hydroquinone in the aqueous phase. Enlarged photograph [Fig. 4(d)] clearly shows the accumulation of the smaller particles on the surface of larger ones, and also between the particles acting as a binding agent. In the later experiments these secondary polymer particles became unnoticeable, either on the larger particles or in the form of free secondary particles in the bulk phase, by shifting to less saponified (80%) PVA, in particular, when DVB and hydrophobic solvents were introduced in the recipe.

Considering that the secondary polymer particles of PS are highly hydrophobic, it may be difficult to assume that nearly 100% hydrolyzed PVA will function as a better stabilizing agent than the one less hydrolyzed. However, an amount of the adsorbed PVA on the surface of larger polymer particles will also decrease as the percent hydrolysis becomes higher, favoring the partitioning of free PVA chains in the aqueous phase, which may contribute to the stabilization of the secondary nucleus. Empirical addition of a small amount of SLS was chosen in our laboratory, and further investigations will follow to obtain logical explanations of the costabilization mechanism.

Crosslinked Porous Polymer Particles

Effect of Miscibility of Solvent to Base Polymer

As the three MPG yielded relatively uniform polymer particles employing the standard recipe, attention was focused on the synthesis of crosslinked microporous polymer particles. Extensive studies by Cheng et al.[14] revealed the effective use of solvents, in particular poor solvent for PS, combined with the crosslinking agent (DVB) in their seeded emulsion polymerization. As a good solvent we have chosen toluene, and n-hexane and n-heptane for poor sol-
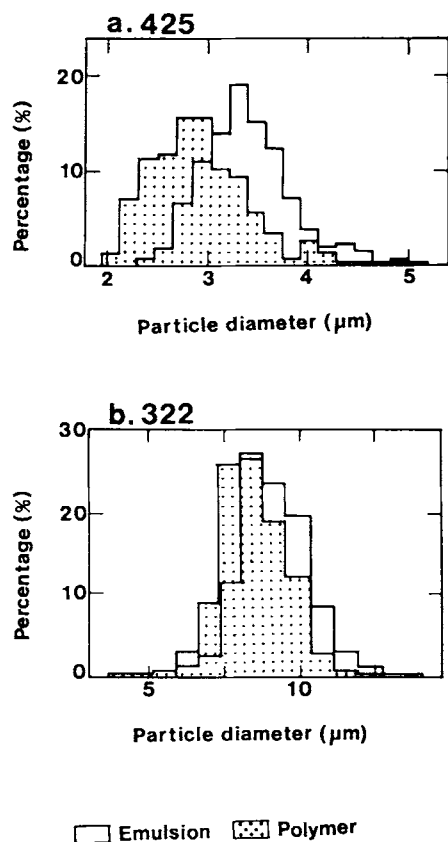
Figure 5 Histograms of size distribution: emulsion droplets and polymer particles. (a) Run 425, (b) run 322.

vents. The boiling point of n-hexane (342 K) was just below the reaction temperature (348 K), while that of n-heptane (371.6 K) was well above.

Typical SEM features of crosslinked polymer particles with different solvents are shown in Figure 6. Addition of hydrophobic solvent generally favored the monodispersity of polymer particles and prevented the nucleation of secondary polymer particles (see Table II). Run 341 and 343 compared the effectiveness of solvent to prepare microporous polymer particles with 10 wt % DVB and 50 wt % solvent in the dispersion phase. When toluene was employed as a solvent, no noticeable change was observed compared with ordinary PS particles [Fig. 6(a)]. Porous features on polymer particles appeared only after the particles were swollen with benzene and freeze-dried quickly. Measured pore size was large, and the small surface area indicated these micropores were not fully developed in the center of the sphere. On the other hand n-hexane, a poor solvent, was more effective in preparing the microporous structure [Fig. 6(b)]. It was enough to wash polymer particles with ethanol before drying in vacuum, and as shown in Table III, a surface area of 92.8 m²/g with average pore size of 0.067 μm was accomplished.

Comparison between poor solvents with 25 wt % DVB and 50 wt % solvent in the dispersion phase are shown in Figure 6(c) (run 345, n-hexane) and (d) (run 347, n-heptane). Although two photo-

Table III   Extent of Size Shrinkage of Crosslinked Polymer Particles

Run No.	ST (g)	DVB (g)	Solvent (g)		d_e (μm)	d_p (μm)	β^*	β	Monomer Conversion	A (m²/g)	d_m (μm)
425	100	0		0	3.28	2.39	0.483	0.387	56.0 (%)		
407	100	0		0	5.67	4.88	0.590	0.638	68.4		
322	100	0		0	8.99	8.34	0.748	0.798	85.8		
339	47	3	T	50	8.09	6.00	0.340	0.408	80.6	1.32ᵃ	7.28
340	45	5	T	50	9.27	6.74	0.349	0.384	82.7		
341	40	10	T	50	10.3	7.38	0.409	0.368	97.0		
342	45	5	Hx	50	10.0	6.80	0.270	0.314	74.3	21.7	0.288
343	40	10	HX	50	11.2	8.18	0.320	0.390	88.2	92.8	0.067
344	35	15	HX	50	9.51	7.76	0.297	0.543	81.8	102.4	0.075
345	25	25	HX	50	7.61	6.59	0.272	0.649	74.8	117.0	0.089
346	15	30	HX	50	8.83	7.56	0.311	0.628	85.5	139.0	0.065
347	25	25	HP	50	8.27	7.71	0.332	0.810	89.4	140.0	0.080
348	20	20	HP	60	8.32	7.31	0.255	0.678	78.1	67.1	0.218
349	35	35	HP	30	9.58	8.70	0.435	0.913	79.0	98.8	0.061
350	15	35	HP	50	8.27	7.41	0.300	0.919	80.7	157.7	0.065
351	12	28	HP	60	8.21	7.91	0.228	0.894	79.0	104.9	0.166
352	21	49	HP	30	9.47	9.24	0.508	0.929	81.6	97.3	0.067

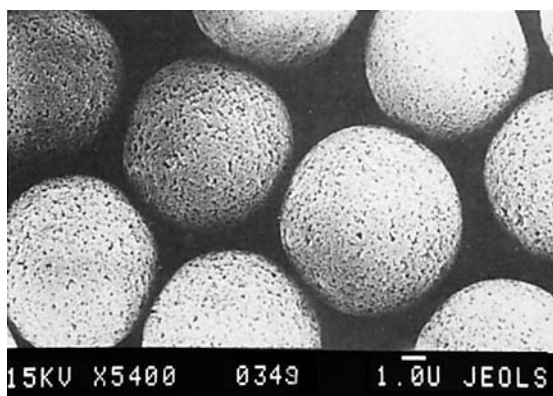ᵃ Dried sample was swollen with benzene and freeze-dried rapidly.
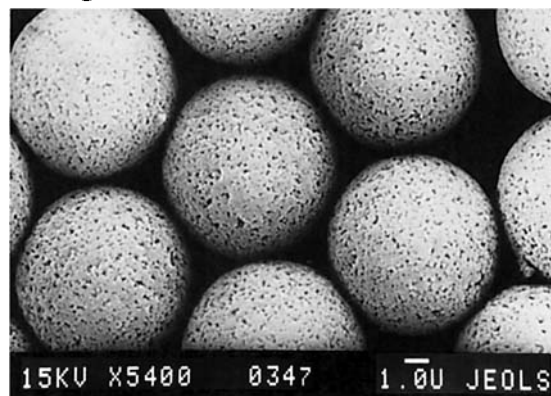
a. 341
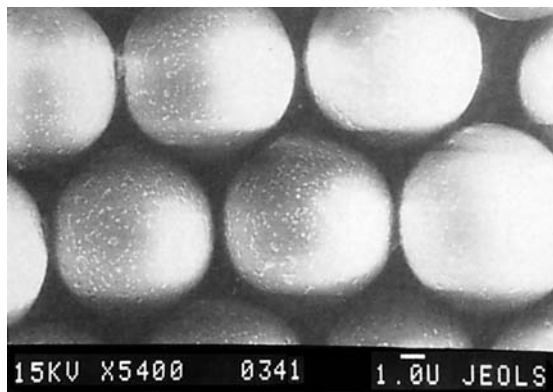
b. 343
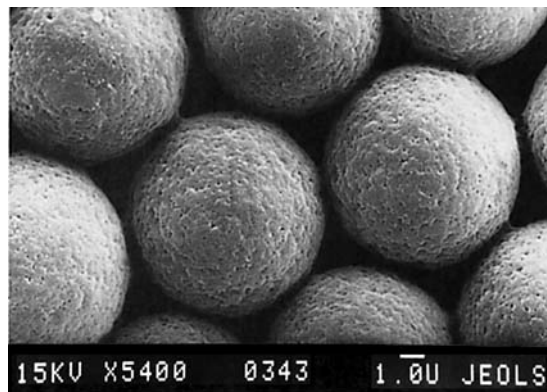
c. 345

d. 347

Figure 6 SEM photographs of crosslinked polystyrene microspheres. (a) Run 341, $\bar{d}_{pn}$ = 7.38 μm, diluent = toluene; (b) run 343, $\bar{d}_{pn}$ = 8.18 μm, n-hexane; (c) run 345, $\bar{d}_{pn}$ = 6.59 μm, n-hexane; (d) run 347, $\bar{d}_{pn}$ = 7.71 μm, n-heptane.

graphs revealed similar microporous feature, and it was difficult to distinguish the difference of the solvents, Table III indicates that n-heptane yielded the larger surface area with nearly the same pore diameter. Detailed discussion is provided in the following section.

Comparison between Figure 6(b) and (c) and the data in Table III (from run 342 to 346) clearly indicate that increasing the percentage of crosslinking monomer leads to an increase in the surface area with decreasing pore diameter. However, too much solvent (60 wt %) with a dominant amount of DVB (runs 348 and 351) yielded very brittle particles of larger pore size, and easily broken during the washing procedure. Apparently an optimal composition of DVB and the poor solvents exists to yield maximum surface area, while maintaining the mechanical strength of the particles.

Shrinkage of Polymer Particles

Size distributions of emulsion droplets and polymer particles for runs 341, 343, 345, and 347 are shown in Figure 7. While separate histograms were obtained in runs 341 and 343, two histograms almost overlapped in run 347. Run 345 yielded an intermediate profile. Assuming inert solvent (diluent) was extracted from polymer particles during the washing, the only reasonable explanation of the profiles in Figure 7(a) and (b) was that toluene (run 341) and n-hexane (run 343) were not so effective as n-heptane (run 347) as a diluent. In other words, either no appreciable voids were created (toluene) or the diluent escaped from polymer particles during the polymerization (n-hexane).

If we define β^* to evaluate the degree of shrinkage of polymer particles numerically,
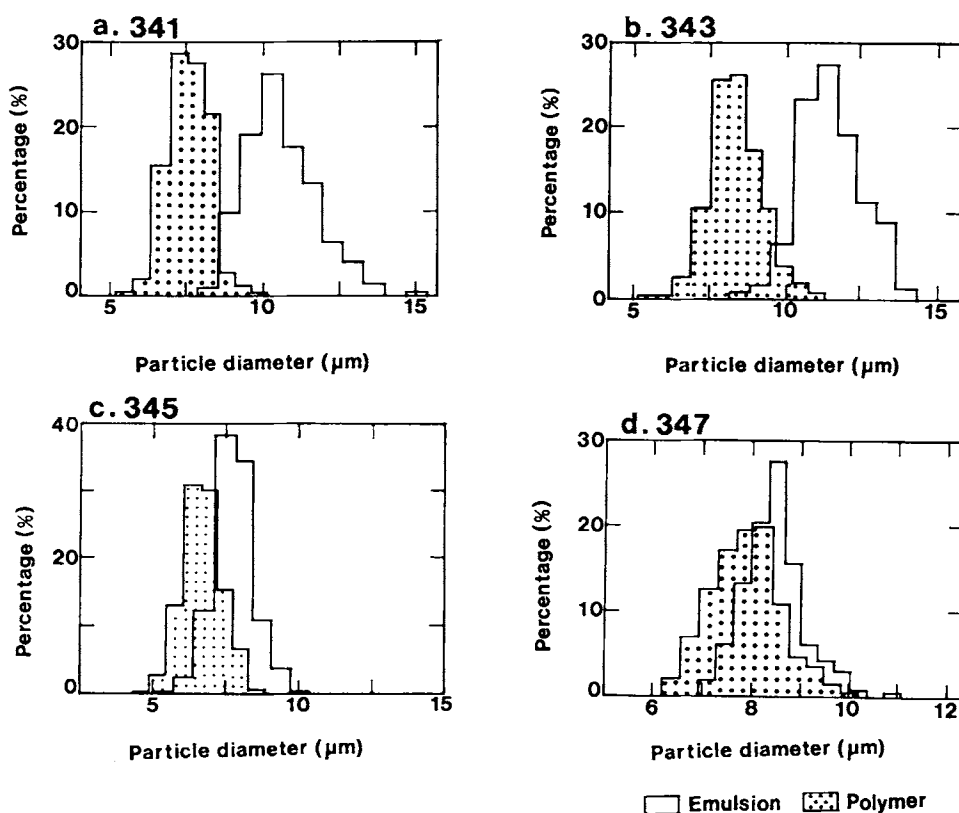
Figure 7 Histograms of size distribution: emulsion droplets and polymer particles. (a) Run 341; (b) run 343; (c) run 345; (d) run 347.

$$\beta^* = \frac{\begin{array}{c}(\text{initial monomer wt.})\\ \times\,(\%\ \text{conversion})/(\text{polymer density})\end{array}}{(\text{initial volume of dispersion phase})}\quad(4)$$
$$\times\,100$$

And also, define β as a volume ratio of polymer particles to emulsion droplets,

$$\beta = \left(\frac{\bar{d}_p}{\bar{d}_e}\right)^3 \quad (5)$$

If β was comparable with β^*, then no appreciable voids were created in polymer particles, whereas β approached unity if the diluent worked effectively. Calculated values of β and β^* are listed in Table III. Density of polymers were assumed to be 1.05 g/cm^3, and that of monomers, toluene, n-hexane, and n-heptane to be 0.905, 0.659, 0.684, and 0.866, respectively. Though some experimental errors were involved in numerical values, the outcome was straightforward; n-heptane was by far the most effective solvent to retain microporous structure. n-Hexane was not so effective unless the amount of crosslinking monomer was increased.

Toluene, a good solvent for polystyrene, was not much help in the formation of microporous structure, as reported by Cheng et al.[14] In their procedure extensive extraction by methylene chloride removed linear polystyrene as well as the diluent, leaving only a crosslinked skelton of polystyrene.

CONCLUSION

An MPG module, a particular apparatus to prepare relatively uniform monomer droplets, and succeeding suspension polymerization yielded fairly uniform polymer particles from 2 to 9 μm in size depending on the pore size of MPG. Narrow size distribution of the initial monomer droplets was retained after the polymerization even though the size of polymer particles reduced due to the difference in density and incomplete monomer conversion.

Crosslinked microporous polymer particles having maximum surface area of 160 m^2/g were obtained from the high content of crosslinking agent (DVB) and poor solvents of polystyrene. n-Heptane was a better solvent as a diluent.

Further studies will be conducted; preparation of copolymeric microspheres with functional monomers incorporated, polymerization using more hydrophilic acrylic monomers, and synthesis of composite microspheres by controlling the secondary polymer particles adsorbed on the surface of mother spheres.

As a final conclusion SPG is a promising tool to provide sophisticated polymeric microspheres with commercial potential to be used as effective carriers for proteins, enzymes, and other biologically active substances.

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