Synthesis of Uniform PMMA Microspheres Employing Modified SPG (Shirasu Porous Glass) Emulsification Technique

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SYNOPSIS

Application of the particulate microporous glass membrane (SPG) was extended to the synthesis of fairly monodisperse poly(methyl methacrylate) (PMMA) microspheres. Hydrophilic monomers have been believed to yield polymer particles of a broad size distribution when the SPG technique was employed. This difficulty was overcome by adopting the droplet swelling technique. The primary uniform emulsion composed of a mixture of hydrophobic diluent (and/or monomer), cosurfactant, and initiator was prepared with an SPG membrane and was allowed to absorb MMA (and diluent) under the principle of the degradative diffusion process from droplets in the secondary emulsion. The coefficient of variation of PMMA spheres was around 10%. Porous PMMA spheres possessing up to 185 m^2/g of specific surface area were obtained as well as one-eyed spheres and smooth and solid spheres. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In a previous article, the synthesis of fairly monodisperse polystyrene (PS) spheres using a particulate microporous glass membrane (SPG) was reported.[1] SPG, an abbreviation for Shirasu Porous Glass, is fabricated from a spinodal decomposition of the mixture $CaO-Al_2O_3-B_2O_3-SiO_2$, with a subsequent removal of the $CaO-B_2O_3$ phase by acid treatment, which leaves monosized pores in a cylindrical shell tube consisting of hydrophilic $Al_2O_3-SiO_2$.[2] Several SPG membranes, the pore size ranging from 0.5 to 5.25 μm, were used for the preparation of stable emulsions. A mixture of hydrophobic monomers, cosurfactant, diluent, and initiator was allowed to permeate through the membrane into a continuous flow of stabilizer solution, and the dispersion was stored in a vessel until a sufficient amount of the droplets was formed for polymerization. Polymerization is an ordinary suspension polymerization except that the initial

narrow-size distribution of the droplets was retained throughout the polymerization, eventually yielding polymer particles from 2.5 to 30 μm with their coefficient of variation (CV) around 10%. Crosslinking by incorporating divinylbenzene (DVB), and an addition of poor solvents as a diluent, were quite effective to create a microporous structure; specific surface area reached as high as 373 m^2/g.[3] The potential flexibility of SPG membrane for preparing uniform polymeric microspheres of various sizes has been well established. However, it has been generally believed that a broader size distribution will be obtained when more hydrophilic monomers are employed. Since SPG is essentially composed of hydrophilic $Al_2O_3-SiO_2$, hydrophilic substances easily wet its pore wall, generating a jetlike stream which leads to nonuniform droplets. For instance, methyl methacrylate (MMA) has been regarded as unsuitable to obtain uniform dispersion by employing the SPG emulsification system. However, monodisperse micron-scale PMMA spheres are in great demand commercially, in particular, as a surface modifier, additive, and lubricant for organic pigments, rubbers, cosmetics, and so on.

In this article, it is shown that the synthesis of fairly uniform PMMA microspheres becomes possible by employing a modified SPG emulsification technique which involves a particular swelling process proposed by Higuchi and Misra.[4] Meanwhile, monosized PMMA spheres of μm size have been synthesized with the nonaqueous phase dispersion (NAD) polymerization.[5,6] In the case of NAD–PS spheres, the continuous medium was always selected from the homologs of short-chain alcohols, ethyl alcohol (EtOH) being the most frequent choice. On the contrary, although some reports[7,8] classify MMA as a hydrophobic monomer, diversity of the solvents seems to reflect the more sophisticated nature of NAD–MMA polymerizations. Rather than the use of polar organic solvents, simple suspension polymerization in the aqueous phase will be preferred either in laboratories or in commercial processes for many reasons, such as flammability, toxicity, pollution, and so on.

EXPERIMENTAL

Materials

Monomers

Methyl methacrylate (MMA) and divinylbenzene (DVB, Kishida Chemical Co.) were commercial grade and distilled under vacuum to remove inhibitors. DVB is a mixture of 55% isomeric DVB, 40% ethyl vinylbenzene, and 5% of saturated compounds. Ethylene glycol dimethacrylate (EGDMA, Tokyo Chemical Industry Co.) was commercial grade and also distilled under vacuum. Acrylic acid (AA, Kishida Chemical Co.) was reagent grade, stored in a refrigerator, and used after the precipitated polymer was removed through filtration.

Solvents

Benzene (Bz), ethyl alcohol (EtOH), heptane (HP), lauryl alcohol (LA), octanol (OA), and hexanol (HA) were reagent grade. Toluene (TOL) and methyl alcohol (MeOH, Kishida Chemical Co.) were commercial grade. EtOH and TOL were distilled prior to use.

Other Chemicals

Sodium lauryl sulfate (SLS, Merck) was the grade for biochemical use. Poly(vinyl alcohol) samples (PVA, Kuraray) with different degrees of hydrolysis and degrees of polymerization (DP) were used as stabilizers: PVA-420 with DP = 2000, 80% hydro-

lyzed, and PVA-217, DP = 1700, 88.5% hydrolyzed. Benzoyl peroxide (BPO) with a 25 wt % moisture content was reagent grade and used as an initiator. Hexadecane (HD, Tokyo Chemical Industry Co.) was reagent grade and used as a hydrophobic oligomer to stabilize droplets of the primary emulsion. Sodium nitrite was reagent grade (Kishida Chemical Co.) and used as an inhibitor to prevent the nucleation of polymer particles in the aqueous phase. All these reagents were used as received.

Apparatus

A particular apparatus for emulsification with an MPG module (microporous glass, a brand name of SPG, Ise Chemical Co.) installed was already presented elsewhere[1,3]; however, because of the complexity of the procedure, a schematic diagram is shown in Figure 1. An ordinary four-neck glass separator flask was employed as a reactor and also served for the swelling process. A semicircular anchor-type blade was installed for agitation. A nitrogen inlet nozzle and a condenser were used on the cover of the flask. Nitrogen was purged from the top of the condenser.

Two-stage Emulsification

The two-stage emulsification process should be mentioned in detail: The primary (seed) emulsion contains hydrophobic solvent (Bz) and/or monomer (DVB) in which water-insoluble HD is dissolved. The secondary emulsion includes hydrophilic MMA, EGDMA as a crosslinker, and long-chain alcohols. Subsequent absorption is essentially a diffusion process of the hydrophilic substances to the hydro-
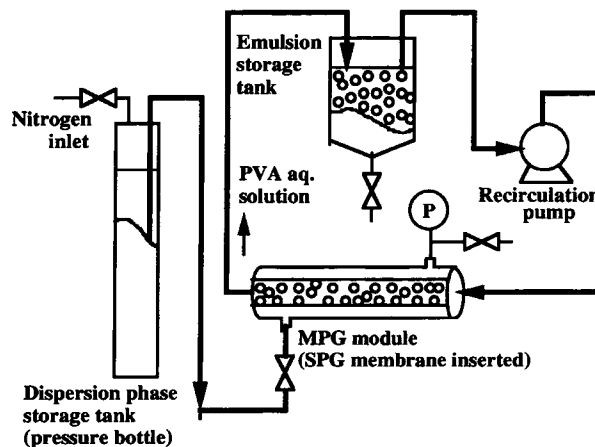
Figure 1 Schematic diagram of SPG emulsification. Preparation of primary emulsion.

phobic seed droplets. As an example, the run 371 recipe is shown in Table I and ensuing procedures will be explained referring to this recipe.

Preparation of Primary (Hydrophobic Seed) Emulsion

A mixture of 70 g of Bz, 3.0 g of BPO, and 5.0 g of HD was supplied into the pressure-tight bottle shown in Figure 1. A third of this mixture, as shown in the left column of Table I, was permeated through an SPG membrane of pore size 0.5 μm under a nitrogen pressure of 100 kPa (gauge). The droplets were stabilized by adsorbing PVA and SLS dissolved in the recirculating aqueous solution. The composition of this aqueous solution was 475 g of water, 3.0 g of PVA-217, 0.5 g of SLS, and 0.3 g of sodium nitrite, which was added to prevent the nucleation of small polymer particles. After the desired amount of the oil phase was dispersed in the aqueous phase, 150 g of the emulsion was transferred from the storage tank to the reactor. A photograph of the primary emulsion taken by an optical microscope is shown in Figure 2(a).

Preparation of Secondary (Hydrophilic) Emulsion

Each 20 g of MMA and EGDMA was emulsified in 110 g of the aqueous phase containing 0.05 g of SLS with a conventional laboratory homogenizer (Ace homogenizer, AM-11, Nissei Co.) with a rotation rate of 1.39 s^{-1} for 5 min at room temperature. The emulsion was unstable, and the entire contents were immediately added to the primary emulsion in the reactor. A photograph of the secondary emulsion is shown in Figure 2(b).

Swelling Process

The mixture of the primary and the secondary emulsion was allowed to stand for 15 min under moderate agitation of 3.0 min^{-1}. Unless the swelling ratio is too high, droplets of the secondary emulsion were rapidly absorbed in the seed droplets and almost completely disappeared. A photograph of the swollen emulsion is shown in Figure 2(c). While the droplets of the secondary emulsion were polydisperse, the final droplets retained the uniformity of the primary emulsion.

Swelling Ratio

A theoretical value of the swelling ratio can be defined as follows:

Table I Recipe of Run 371 for Two-stage Emulsification and Polymerization

Substance (g)	Primary Emulsion	Secondary Emulsion	Polymerization
Water	475	110	251.1
PVA-217	3.0	—	0.891
SLS	0.5	0.05	0.20
NaNO$_2$	0.3	—	0.089
Bz	23.3	—	6.93
BPO	1.0	—	0.30
HD	1.67	—	0.50
MMA	—	20	20
EGDMA	—	20	20
Total	504.8	150.1	300.0

Primary emulsion was prepared at a room temperature. Secondary emulsion was prepared with a conventional homogenizer of 1.39 s^{-1} agitation rate. Swelling step was carried out in the reactor under nitrogen atmosphere at room temperature.

$$S_r = 1 + \frac{\left(\begin{array}{c}\text{wt of monomers and/or solvents}\\ \text{in the secondary emulsion}\end{array}\right)}{\left(\begin{array}{c}\text{wt of hydrophobic substances}\\ \text{in the primary emulsion}\end{array}\right)} \quad (1)$$
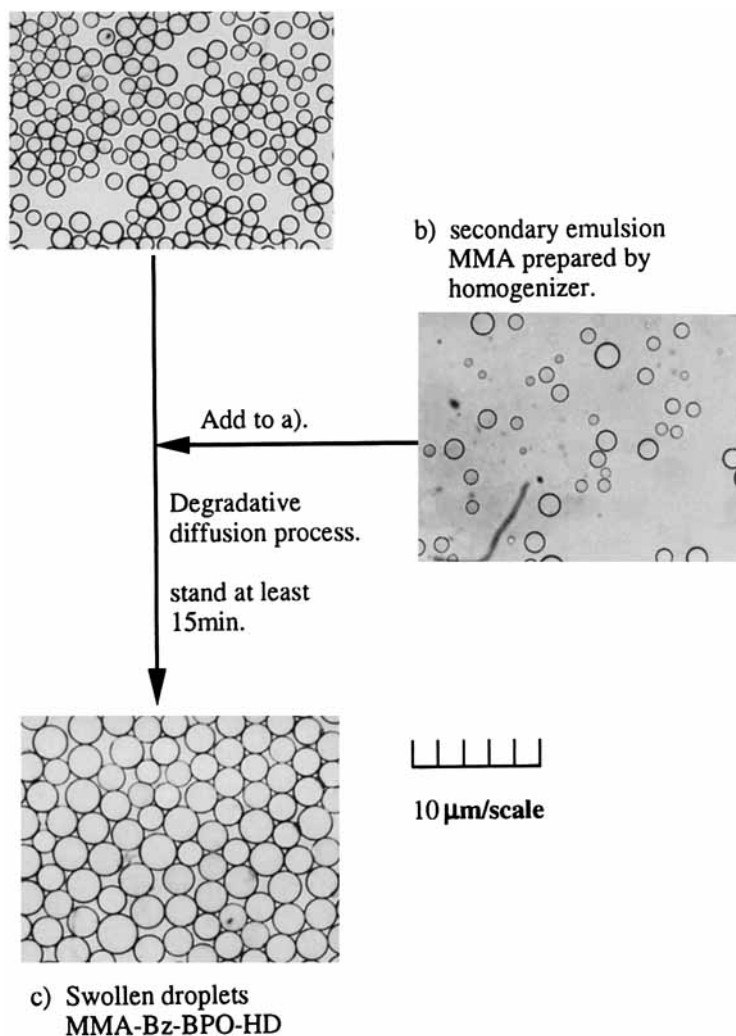
Polymerization

Because of the complexity of the swelling procedure, the actual formulation of run 371 is expressed beyond the decimal point and is shown in Table I. According to eq. (1), the swelling ratio is given as follows:

$$S_r = 1 + (20 + 20)/(6.92 + 0.30 + 0.50) = 6.18$$

After the swelling process, a gentle bubbling of nitrogen into the emulsion was continued. The bubbling nozzle was removed from the emulsion after 1 h, the ingredients were heated to a reaction temperature, normally 343 K, and polymerized for 24 h under a nitrogen atmosphere.

For the sake of efficiency, one formulation of the primary emulsion was used for two or three runs, which proceed in parallel, the amount being changed depending on the swelling ratio. Compositions of MMA, the crosslinking monomer, and solvents (diluents) and the swelling ratio were changed in the following experiments: Concentrations of PVA, SLS, NaNO$_2$, Bz, BPO, and HD varied inherently depending on the formulation ratio between the pri-

b) secondary emulsion
MMA prepared by
homogenizer.

Add to a).

Degradative
diffusion process.

stand at least
15min.

10 μm/scale

c) Swollen droplets
MMA-Bz-BPO-HD

Figure 2   Principle of preparation of monodisperse droplets containing MMA by swelling method.

mary and the secondary emulsion. Total weight of the ingredients was, in principle, set as 300 g; however, they increased as high as 420 g for the same reason.

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. After drying, the polymer particles maintained a fine powdery character.

Analyses

Percent conversion of monomer was determined gravimetrically. The polymer was precipitated by methyl alcohol from the serum, separated by centrifugation, and dried in vacuum and the weight was measured.

Droplets of the primary emulsion, those after swelling, and polymer particles were observed with an optical microscope. Diameters of several hundred droplets or particles were counted to calculate average diameters. In the later tables, d_{el} indicates the average diameter of the droplets in the primary emulsion. General features of polymer particles were

observed with SEM (JEOL, JSM-35CFII). Average diameters of polymer particles, referred to as d_p in the later tables, were mainly determined from SEM photographs. Experimentally observed ratios of the swelling can be expressed as (d_p/d_{el}),[3] and compared with the theoretical ratio, S_r, defined in eq. (1).

The surface area of micropores was measured with a porosimeter (Micromeritics Poresizer 9310, Shimadzu) at room temperature using nitrogen as an adsorbing gas. Unless polymers were highly crosslinked, average molecular weights were measured with gel permeation chromatography (GPC) (HLC-801, Toso Co.) employing tetrahydrofuran (THF) as a solvent.

RESULTS AND DISCUSSION

Uncrosslinked PMMA Spheres with One Uniform Hole

The polymerization recipe and experimental results are summarized in Tables II–V and classified based on the features of PMMA spheres obtained. In Table II, formulations which yielded unusual one-eyed spheres are summarized. These PMMA spheres unanimously possessed a uniform hole created by the phase separation of extremely hydrophobic HD from the PMMA phase.

An example of these spheres is shown in Figure 3: an SEM photograph of PMMA spheres of run 359. Notice the uniformity of the holes as well as that of the particle size. Ugelstad et al.,[9] in one of the applications of the two-stage swelling technique to seed emulsion polymerizations, showed very similar one-eyed spheres, which resulted from the fallout of PS seeds from the surrounding shell layer of polyacrylates. In common, all the runs in Table II include no crosslinking agent or polar solvents in the recipe. The extent of the phase separation became enhanced; in other words, the hole became larger, when the content of Bz was small compared to that of HD (runs 378 and 387). An addition of a small amount of AA in the later runs for the purpose of enzyme immobilization on the sphere seems to enhance the phase separation. When the particle size is large (run 389), the phase separation apparently takes place at several spots on the surface, yielding spheres with several uniform holes.

In run 381, a mixture of MMA and HP was directly added to the primary emulsion under constant agitation, instead of preparing the secondary emulsion, in order to investigate the effect of droplet size of the secondary emulsion on the swelling process.

No broadening of the size distribution or coagulation was observed during the swelling process, and one-eyed uniform spheres with a 9.1% coefficient of variation (CV) were obtained.

Replacement of Bz with HP and addition of nonpolar DVB in the primary emulsion yielded capsulelike spheres as shown in Table III. As HP has very poor miscibility with PMMA, the polymerization probably proceeded via an *in situ* mechanism, creating a skin layer of PMMA–DVB near the surface as the polymerization progressed. Resulting spheres were essentially microcapsules, containing a mixture of HP and HD (run 362) or formed a porous structure (run 363). SEM photographs of run 362 revealed collapsed spheres due to the elimination of the diluents, whereas the particles of run 363 were full of dents partly because of poor conversion.

Solid Uniform Crosslinked PMMA Spheres

The peculiar holes as shown in Figure 3 disappeared, and solid smooth spheres were obtained when crosslinking monomers were added either in the primary emulsion (DVB) or in the secondary emulsion (EGDMA). Polymerization recipes and experimental results are summarized in Table IV.

An example of uniform smooth spheres, run 371, is shown in Figure 4. When DVB was used as a crosslinker (runs 360 and 361), a couple of short hairpin cracks were observed on the surface. Obviously, EGDMA forms a homogeneous network in a sphere as shown in Figure 4. Runs 370, 379, and 385 all yielded smooth spheres as did run 371 except that the secondary nucleation of polymer particles took place to a minor extent in run 385 and covered the surface of the large spheres.

No distinct micropores were detected from an observation of SEM; however, the following calculation may reveal that these crosslinked spheres are not closely packed. Suppose an extreme case where all the Bz, HD, and unreacted comonomer were extracted from the polymer particles after the washing and drying procedure. Under the additional assumptions that no coalescence or breakup of spheres occurred during the swelling and polymerization process, and a negligible density difference exists between the two mixtures, then we obtain the following relationship:

$$\bar{d}_{\text{pcalcd}} = \left(\frac{w_{M0} \times x_M + w_{\text{BPO}}}{w_{\text{Bz}} + w_{\text{DVB}} + w_{\text{BPO}} + w_{\text{HD}}} \right)^{1/3} \bar{d}_{\text{el}} \quad (2)$$

where w_{M0} is the total weight of the comonomer; x_M, the comonomer conversion, and w_{BPO}, w_{DVB}, w_{HD},

Table II   Polymerization Recipe and Experimental Results of Uncrosslinked PMMA Spheres

Run No. SPG (μm)	Water (g)	PVA (g)	SLS (g)	NaNO$_2$ (g)	Bz (g)	BPO (g)	HD (g)	Monomer (g)	Solvent (g)	d_{el} (μm)	CV (%)	d_p (μm)	CV (%)	Conv. (%)	S_r	$(d_p/d_{el})^3$	Comment
359 1.36	278	1.18	0.13	0.039	21.4	0.79	1.97	MMA 10		7.73	10.9	8.57	13.9	90.8	1.42	1.36	Uniform H.
378 0.5	307	0.71	0.17	0.071	10.7	0.24	1.19	MMA 18 AA 0.036	—	2.39	10.6	3.01	9.24	—	2.49	2.00	Uniform H.
381[a] 0.9	311	2.08	0.21	0.21	32.9	1.38	1.73	MMA 16 AA 0.04	HP 8	5.40	10.8	4.75	9.10	85.7	1.67	0.68	Uniform and big H.
387 0.9	326	1.43	0.19	0.14	11.3	0.24	0.60	MMA 24 AA 0.12	—	—	—	5.46	11.9	39.4	2.99	—	Uniform H.
389 5.25	278	1.19	0.07	0.12	18.8	0.79	0.99	MMA 30 AA 0.15	—	—	—	34.6	11.8	93.8	2.46	—	Uniform small holes
391 1.7	378	1.19	0.11	0.12	18.8	0.40	0.99	MMA 20 AA 0.2	—	—	—	8.24	9.45	94.5	2.00	—	Uniform H.

CV = coefficient of variation, H. = single hole, AA = acrylic acid, HP = heptane. d_{el} and d_p = average diameter of the droplets in the primary emulsion and that of the polymer particles, respectively.

[a] A mixture of monomers and solvent was directly added to the reactor in order to investigate the effect of droplet size in the secondary emulsion to the swelling process.

Table III   Polymerization Recipe and Experimental Results of Deformed PMMA Spheres

Run No. SPG (μm)	Polymerization Recipe									Experimental Results							
	Water (g)	PVA (g)	SLS (g)	$NaNO_2$ (g)	HP^a (g)	BPO (g)	HD (g)	Monomer (g)	Solvent (g)	d_{el} (μm)	CV (%)	d_p (μm)	CV (%)	Conv. (%)	S_r	$(d_p/d_{el})^3$	Comment
362 1.36	269	1.24	0.13	0.041	12.4 DVB 7.24	0.83	2.07	MMA 7	—	8.52	2.94	8.62	10.4	38.2	1.31	1.04	Capsules
363 1.36	270	1.06	0.12	0.035	10.6 DVB 6.20	0.71	1.77	MMA 6	TOL 4	8.52	2.94	8.50	10.3	46.0	1.31	0.99	P. with a skin layer^b

^{a} Heptane (HP) was used instead of benzene (Bz).
^{b} P. = porous spheres.

and w_{Bz}, the weights of BPO, DVB, HD, and Bz, respectively.

Then, an apparent relative volume increase, due to the void created by extraction of Bz and unreacted monomers, can be estimated by $(d_{p\,obsd}/d_{p\,calcd})$.[3] The result is shown in Table V. Except for run 379, the relative volume increase was 65% at maximum. If Bz plays the role of an ideal diluent, the relative volume increase should be nearly equal to S_r. Bz, like TOL in the case of PS spheres,[1] was by no means an effective diluent because of its good miscibility with PMMA. The reason why only run 379 yielded such a high relative volume increase is not clear.

Porous Crosslinked PMMA Spheres

In the previous sections, it became clear that neither Bz nor HP was a good diluent to form microporous spheres; the former yielded a compact crosslinking network with few void spaces, and phase separation occurred in the runs with the latter. From the experience of these solvents, slightly polar, but essentially poor, solvents for PMMA were eventually selected. Polarity is required to prevent the phase separation in polymer particles, while poor affinity with PMMA is a primary concern for diluents. Straight-chain alcohols, OA and HA, with solubility in water at 298 K being 0.054 and 0.59 wt %, respectively, respond to these requirements. Hydrophilicity of OA and HA was adjusted by mixing with an adequate amount of heptane. The polymerization recipe and experimental results are summarized in Table VI. Specific surface area measured with a porosimeter are also shown in the last column. PMMA–DVB spheres (run 365 and from runs 367 to 369) yielded a moderately fine pore structure; however, the spheres were rather brittle and the comonomer conversion remained very low.

Switching from DVB to EGDMA as a crosslinker stabilized the reaction system, and rigid porous spheres were steadily produced. Grainy and coarse PMMA–EGDMA spheres obtained in run 375 are shown in Figure 5(a). The coarseness in Figure 5 is significant compared with the smaller and finer pores observed in PS–DVB spheres and reflects moderate values of the specific surface area. A maximum 373 m^2/g was achieved for one of the PS–DVB spheres.[3] Addition of HP (runs 369, 373, and 376) seems to enhance the coarse structure. Runs 380, 386, and 390 yielded a fine pore structure; the specific surface area of run 386 attained the highest value, 185 m^2/g. An SEM photograph of fine porous PMMA spheres (run 380) is shown in Figure 5(b).

Table IV Polymerization Recipe and Experimental Results of Crosslinked Nonporous Spheres

	Polymerization Recipe									Experimental Results							
Run No. SPG (μm)	Water (g)	PVA (g)	SLS (g)	NaNO$_2$ (g)	Bz (g)	BPO (g)	HD (g)	Monomer (g)	Solvent (g)	d_{el} (μm)	CV (%)	d_p (μm)	CV (%)	Conv. (%)	S_r	$(d_p/d_{el})^3$	Comment
360 0.5	277	1.18	0.25	0.039	9.84 DVB 9.84	0.79	1.97	MMA 10	—	2.76	10.5	2.58	12.5	52.0	1.45	0.82	S. hairpin crack[a]
361 0.5	258	0.95	0.21	0.031	7.87 DVB 7.87	0.63	1.57	MMA 32	—	2.76	10.5	3.62	8.99	84.8	2.79	2.26	S. hairpin crack
370 0.5	251	0.89	0.20	0.089	6.93	0.30	0.50	EGDMA 40	—	2.72	12.7	5.32	9.23	100	6.19	7.48	S.
371 0.5	251	0.89	0.20	0.089	6.93	0.30	0.50	MMA 20 EGDMA 20	—	2.72	12.7	5.13	9.15	91.2	6.18	6.71	S.
379 0.5	307	0.71	0.17	0.071	10.7	0.24	1.19	MMA 9, AA 0.036 EGDMA 9	—	2.39	10.6	4.35	9.02	72.7	2.49	6.03	S.
385 5.25	278	1.19	0.07	0.12	18.8	0.79	0.99	MMA 15, AA 0.06 EGDMA 15 —	—	—	—	34.6	11.2	100	2.46	—	S. small particles[b]

S. = smooth and solid spheres.
[a] Smooth solid surface except with a couple of hairpin cracks.
[b] Very small particles were observed on the smooth surface of large particles.

Table V   Apparent Relative Volume Increase of Crosslinked PMMA Spheres

Run No.	d_{el} (μm)	d_{pobs} (μm)	d_{pcalc} (μm)	S_r	$(d_{pobs}/d_{pcalc})^3$
360	2.76	2.58	2.18	1.45	1.65
361	2.76	3.62	3.43	2.79	1.18
370	2.72	5.32	4.72	6.19	1.44
371	2.72	5.13	4.57	6.19	1.41
379	2.39	4.35	2.47	2.49	5.48

One should remember that, in the runs of high swelling ratios S_r (runs 365, 372, 373, 376, and 380), average diameters of the porous spheres were unusually high, the observed swelling ratio, $(d_p/d_{el})^3$, becoming higher than S_r. Although a precise mechanism of the pore formation is not clear, water molecules may have participated in the development of the pore structure and played a minor role in the formation of the coarse structure.

Other Discussion

Relationship Between PMMA Sphere Size and SPG Pore Size

Average diameters of PMMA spheres and the primary emulsion are plotted against SPG pore size and are shown in Figure 6. Except for the porous PMMA spheres, one-eyed spheres, solid and smooth ones, and droplets of the primary emulsion can be correlated with a straight line. This tendency is understandable if one assumes that all the Bz, HD, and unreacted comonomer were extracted from the spheres and no serious breakup or coagulation developed during the polymerization. These assumptions agree with the

calculation, the result of which is shown in Table V. Naturally, microporous PMMA spheres deviated from the straight line to larger diameter. The slope of the straight line is 6.7, corresponding to the value, 6.6 (Ref. 1) and 6.0 (Ref. 3), in the case of PS spheres. The coefficient of variation was around 10% for all runs, which demonstrates that the two-stage swelling is an excellent route to obtain monodisperse PMMA spheres.

Role of Hexadecane as a Strongly Hydrophobic Additive

Hexadecane (HD) is a key substance to accomplish a successful swelling process. As mentioned earlier, the presence of HD in the droplets eventually induces phase separation in PMMA spheres. However, switching to long-chain alcohols (LA or hexadecanol) yielded a primary emulsion with a broad size distribution. As Ugelstad et al.[10] proved in their experiments, in which coalescence rates of chlorobenzene dissolving various long-chain alkanes or alcohols were investigated, long-chain alcohols are still more hydrophilic than are long-chain alkanes. For example, solubility in water is $0.17(10^{-3})$ wt %
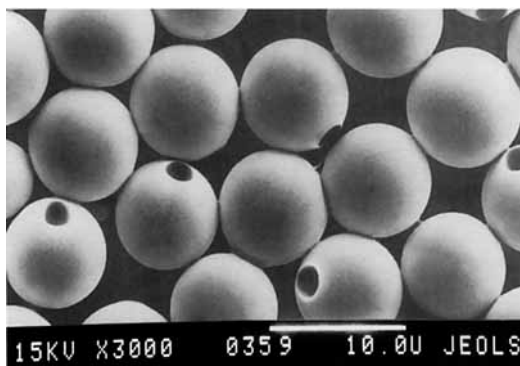
Run 359   x3000

Uncrosslinked PMMA spheres, d_p=8.57μm, CV=13.9%.

Figure 3   SEM photograph of one-eyed PMMA spheres.
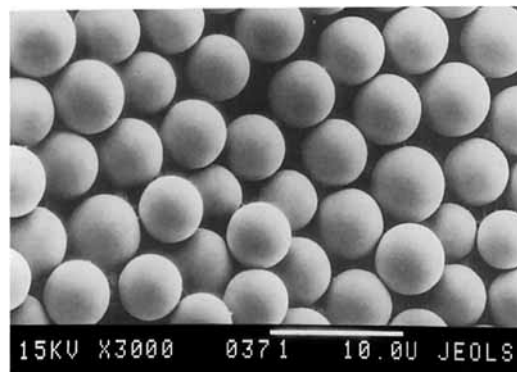
Run 371   x3000

Crosslinked solid PMMA-EGDMA spheres, d_p=5.13μm, CV=9.15%.

Figure 4   SEM photograph of crosslinked, nonporous PMMA sphere.

Table VI   Polymerization Recipe and Experimental Results of Porous PMMA Spheres

| Run No. SPG (μm)	Polymerization Recipe									Experimental Results							
	Water (g)	PVA (g)	SLS (g)	NaNO$_2$ (g)	Bz (g)	BPO (g)	HD (g)	Monomer (g)	Solvent (g)	d_{el} (μm)	CV (%)	d_p (μm)	CV (%)	Conv. (%)	S_r	$(d_p/d_{el})^3$	Comment Sp. Area[a]
365 0.5	294	0.59	0.15	0.020	4.60 DVB 10	0.79	0.33	MMA 10	LA 20	2.72	8.86	5.55	9.92	71.1	8.00	8.50	P. brittle
367 1.36	266	0.58	0.090	0.019	— DVB 8.45	0.78	0.65	MMA 9	HA 17	10.4	11.8	14.0	13.8	38.7	3.64	2.44	P. 156
368 1.36	266	0.58	0.090	0.019	— DVB 8.45	0.78	0.65	MMA 9	OA 17	10.4	11.8	14.1	15.0	51.3	3.64	1.71	P. 187
369 1.36	266	0.58	0.090	0.019	— DVB 8.45	0.78	0.65	MMA 9	OA 9 HP 9	10.4	11.8	14.4	14.0	63.2	3.64	2.65	P. 166
372 0.5	264	0.59	0.15	0.18	4.45	0.15	0.495	MMA 9 EGDMA 9	OA 12	2.81	11.3	6.04	8.40	73.4	6.89	9.93	P. 214
373 0.5	264	0.59	0.15	0.18	4.45	0.15	0.495	MMA 9 EGDMA 9	OA 6 HP 6	2.81	11.3	6.24	8.76	80.1	6.89	11.0	P. 139
375 0.9	288	1.19	0.14	0.12	8.92	0.30	0.99	MMA 1.5 EGDMA 1.5	OA 1	4.67	10.9	4.77	10.2	70.4	1.39	1.07	P. 128
376 0.9	274	0.60	0.11	0.060	4.46	0.15	0.50	MMA 9 EGDMA 9	OA 6 HP 5.5	4.67	10.9	10.4	13.7	56.1	6.78	11.0	P. 87.4
380 0.5	323	0.95	0.21	0.095	14.3	0.32	1.58	MMA 9, AA 0.036 EGDMA 9	HA 10.4	2.39	10.6	4.99	8.18	74.0	2.76	9.10	P. 138
386 5.25	278	1.19	0.070	0.12	18.8	0.79	0.99	MMA 9, AA 0.036 EGDMA 9	HA 6	—	—	34.6	11.8	77.9	2.16	—	P. 185
390 5.25	278	1.19	0.070	0.12	18.8	0.79	0.99	MMA 9, AA 0.036 EGDMA 9	HA 6	—	—	37.1	11.8	85.2	2.21	—	P. small particles[b]

P. = porous spheres.
[a] Specific surface area (m^2/g).
[b] Large porous spheres with smaller particles.
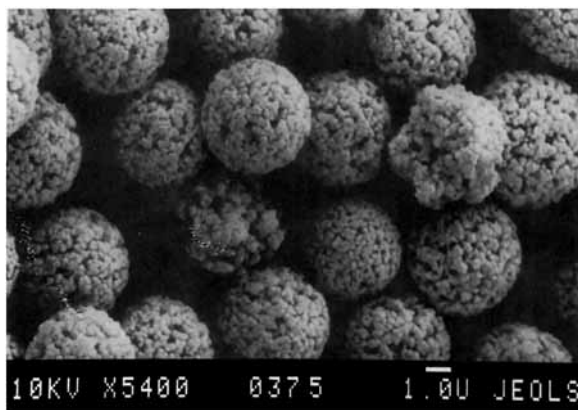
Run 375   x5400

a) PMMA-EGDMA/OA spheres.
d_p=4.77μm, CV=10.2%.
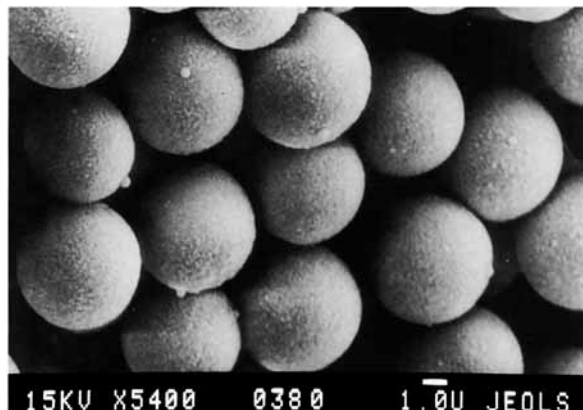
Run 380   x5400

b) PMMA-EGDMA-AA/HA spheres.
d_p=4.99μm, CV=8.18%.

Figure 5 SEM photographs of crosslinked, porous PMMA spheres.

(at 289 K) for LA and 4.1(10^{-6}) wt % (at 333 K) for hexadecanol compared to 5.9(10^{-7}) wt % (at 333 K) for HD. The phase separation was effectively suppressed by introducing a crosslinking network in the spheres, probably by limiting and distributing the phase separation in microdomains of the network.
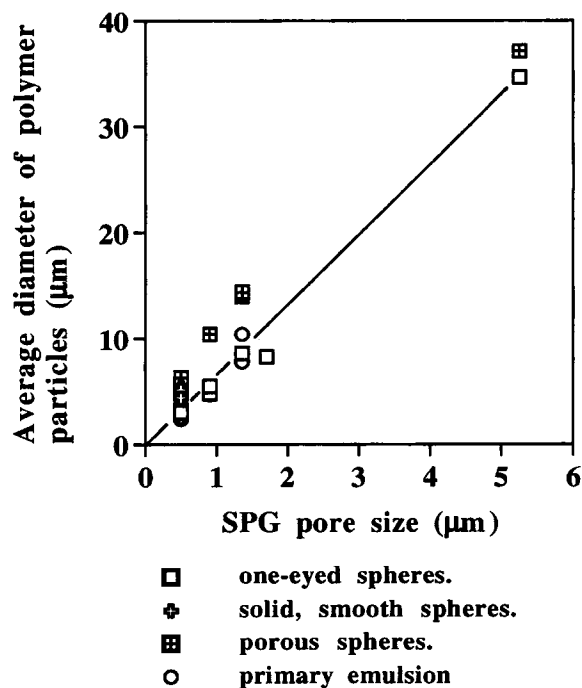

□   one-eyed spheres.
✚   solid, smooth spheres.
⊞   porous spheres.
○   primary emulsion

Figure 6 Average diameter of polymer particles plotted against SPG pore size.

Diluents

Heptane (HP), the most effective diluent to obtain porous PS spheres, promoted phase separation in the PMMA–HD–heptane system. Since HD is unreplaceable by the reason given above, hexanol and octanol were selected as intermediate substances between PMMA and HD. The phase separation was eased by the addition of these alcohols because hydroxyl end groups will have an affinity with ester groups of PMMA chains, and the alkyl group, with HD, probably lowering the interfacial energy between the PMMA and HD phase. From this consideration, long-chain esters may be attractive choices as diluents, and their effectiveness will be investigated in a future study.

Role of Sodium Nitrite as an Inhibitor of the Secondary Nucleation

To suppress the nucleation of polymer particles in the aqueous phase, sodium nitrite was used instead of hydroquinone, which colors the emulsion when MMA is present and is unsuitable. According to Fitch,[11] sodium nitrite undergoes hydrolysis and forms nitrous acid, which eventually dissociates into nitric oxide and nitric acid. Uneven numbers of electrons of nitric oxides promote the coupling with polymeric radicals. However, nitrous acid is fairly soluble in the organic phase and is capable of affecting the polymerization in polymer particles. Although monomer conversions can be achieved around 70–80% in a majority of the experiments, some runs being less, the amount of sodium nitrite

in the recipe is not directly related to the level of monomer conversion. Other factors such as enhanced phase separation (Table III), overdose of untreated solvent (runs 367, 368, and 369), and the MMA–DVB comonomer system are more likely to affect the progress of the polymerization.

Average molecular weights of uncrosslinked PMMA (run 359) in the presence of sodium nitrite were measured as $1.45(10^5)$ for M_w and $0.711(10^5)$ for M_n. In the absence of sodium nitrite (run 358, coagulated), these values were $6.69(10^5)$ and $2.06(10^5)$, respectively. Even though polymer particles, nucleated due to the absence of the inhibitor, contributed higher molecular weight polymers in run 358, the lower molecular weight obtained in run 359 confirmed that the coupling of polymeric radicals with nitric oxide actually took place in the organic phase.

CONCLUSION

Monodisperse hydrophilic PMMA spheres from 2.5 to 37 μm average diameter were obtained by employing a unique two-stage emulsion technique, in which hydrophobic droplets were swollen with a hydrophilic mixture of MMA and solvents. By this investigation, the SPG membrane extended its effectiveness and versatility to produce fairly monodisperse large polymeric spheres. Although we did not predict all the varieties of morphologies, one-eyed spheres, solid and smooth crosslinked spheres, and porous spheres were obtained depending on the polymerization formulation. The coefficient of variation of these spheres is around 10%, the same as those of hydrophobic PS spheres.

In addition to further investigations to control the particle morphology and to find more suitable diluents, future work will include incorporation of more hydrophilic monomers such as 2-hydroxyethyl methacrylate (HEMA) and N,N'-dimethylaminoethyl methacrylate (DMAEMA). In particular, the latter is interesting because it can be easily cationized by quarternarization of amino groups. Inclusion of nonpolymerizing materials in monodisperse polymeric spheres is another interest of the authors.

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