

Nonswellable and Swellable Poly(EGDMA) Microspheres

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SYNOPSIS

In this study, nonswellable and swellable poly(ethylene glycol–dimethacrylate) microspheres, in the size range of 20–177 μm , were produced by conventional and modified suspension polymerizations of ethylene glycol–dimethacrylate (EGDMA) in an aqueous medium. Poly(vinyl alcohol) and benzoyl peroxide were used as the stabilizer and the initiator. A diluent, i.e., toluene, was included in the polymerization recipe of the modified suspension polymerization. The microspheres were characterized by optical microscopy, FTIR, and FTIR–DRS. Highly crosslinked, transparent, and nonswellable poly(EGDMA) microspheres were obtained with the conventional suspension polymerization procedure. While the modified suspension polymerization provided swellable, opaque, and crosslinked copolymer microspheres. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymer microspheres have attracted attention as carrier matrices in a wide variety of medical and biological applications, such as affinity chromatography, immobilization technologies, drug delivery systems, nuclear imaging, and cell culturing.^{1–6} Various parameters including particle size and size distribution, porosity and pore structure, surface area, swellability, and specific functional residuals (or reactive sites) are considered to describe the overall performance of polymer microspheres in these applications.

Polymer microspheres within the size range of 50 nm to 2 mm are produced by various manufacturing processes including suspension, emulsion, and dispersion polymerizations.^{7,8} Suspension polymerization is an established process of the polymer industry for the manufacturing of polymers in microsphere form, usually larger in size ($>20 \mu\text{m}$).^{7–9} When the polymer is soluble (or swellable) in its monomer mixture [e.g., polystyrene, poly(methyl methacrylate)], the resulting polymer particles obtained in suspension polymerization have a smooth surface and a relatively

homogeneous (nonporous) texture. On the other hand, when the polymer is not soluble (or swellable) in its monomer mixture [e.g., poly(vinyl chloride), polyacrylonitrile] the final particles have a rough surface and a porous structure. Porosity in the matrices of microspheres may also be created during polymerization by using diluents (or porogens) by a controllable manner, as extensively studied for polystyrene, polyacrylamide, polymethacrylates, etc.^{10–34} These studies have suggested that polymer particles with a wide range of porosities can be produced, depending on the nature and the percentage of diluent and the extent of polymer crosslinking.

Crosslinked polymer networks formed by free radical polymerization of ethylene glycol methacrylates and dimethacrylates have been found attractive as hydrogel matrices because they do swell in aqueous media to a certain extent, depending on the crosslinking density but do not dissolve,^{35,36} and their polymerization kinetics have extensively been investigated usually in bulk polymerization.^{21,37–42} These investigations have suggested that, while copolymerization of ethylene glycol monomethacrylates with small amount of dimethacrylate crosslinking agents produce homogeneous hydrophilic (swellable) materials, homopolymerizations of dimethacrylates typically yield heterogeneous glassy polymers (nonswellable).

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Recently, we aimed to prepare nonswellable and swellable polymer microspheres by homo- and copolymers of ethylene glycol–dimethacrylate (EGDMA) with acrylic acid, hydroxyethylmethacrylate, and acrylamide by conventional and modified (by using toluene as diluent) suspension polymerization processes. This first article reports preparation and characterization of the nonswellable and swellable poly(EGDMA) microspheres.

EXPERIMENTAL

Materials

EGDMA supplied from Rohm and Haas Ltd., Germany, was purified by passing through active alumina. Benzoyl peroxide (BPO) and poly(vinyl alcohol) (PVA) (88% hydrolyzed and with an average molecular weight of 96,000) (Aldrich Chem. Corp., Milwaukee, WI) were used as the initiator and stabilizer, respectively, without further purification. Toluene (Merck, A. G., Germany) was included in the polymerization recipe as a diluent, and used without further purification. Dispersion medium was distilled water.

Production of Microspheres

In order to prepare the nonswellable poly(EGDMA) microspheres, a conventional suspension polymerization procedure was applied. In a typical procedure, the dispersion medium was prepared by dissolving 200 mg of PVA within 50 mL of distilled water. The desired amount of BPO was dissolved within the monomer phase (i.e., EGDMA). This solution was then transferred into the dispersion medium placed in a magnetically stirred (at a constant stirring rate of 600 rpm) glass polymerization reactor (100 mL) in a thermostatic water bath. The reactor was flushed by bubbling nitrogen and then was sealed. Polymerization was conducted at $80 \pm 1^\circ\text{C}$ for 3 h. In this group of experiments, the effects of various polymerization parameters (i.e., the initiator and stabilizer concentrations, monomer/dispersion medium ratio, temperature, and stirring rate) on the size distribution of the microspheres, and the monomer conversion were investigated. The experimental conditions for these conventional suspension polymerizations are summarized in Table I.

The swellable poly(EGDMA) microspheres were produced with a similar procedure given above. Except, a proper amount of a diluent (i.e., toluene) was

added to the monomer phase before dissolving the initiator. In order to obtain poly(EGDMA) microspheres with different sizes and swellabilities, the relative amounts of EGDMA, water and toluene were changed.

After polymerizations, the microspheres were cleaned by the following procedure: the microspheres were allowed to settle, and the dispersion medium was removed. The microspheres were first washed with water, and the undesirable polymeric aggregates were removed by filtration (sieving). The microspheres were dispersed in water, and the dispersion was sonicated for about 10 min in an ultrasonic bath (200 Watt, Branson 200, USA). The water phase was removed and the microspheres were resuspended in ethyl alcohol. This dispersion was sonicated, ethyl alcohol was removed, and the microspheres were transferred into toluene, and were kept there by stirring about $\frac{1}{2}$ h. Toluene was removed and the microspheres were left within ethyl alcohol for about 20 min. Ethyl alcohol was removed, and the microspheres were washed with distilled water once again, then were filtered and dried in a vacuum oven at 60°C for 48 h.

Characterization of Microspheres

FTIR and FTIR-DRS Spectra

For the characterization of bulk and surface chemical structures, FTIR and FTIR-DRS spectra of the microspheres were obtained by using a FTIR spectrophotometer with a diffuse reflectance attachment (Shimadzu, FTIR 8000 Series, DR-8001, Japan). For FTIR spectra the microspheres and KBr (IR Grade) were thoroughly mixed and this mixture was pressed to form a tablet, and the spectrum was recorded. FTIR-DRS spectra were obtained with KBr-microsphere mixture in the powder form.

Microsphere Yield and Size

The dried microspheres were weighed in an electronic balance, and the microsphere yield was calculated by the following expression:

$$\text{Microsphere Yield} = (W_d/W_m) \times 100$$

Where, W_d = weight of clean and dry polymer microspheres (g); and W_m = weight of monomer initially charged to the reactor (g).

The size distribution of polymeric microspheres was obtained by screen analysis using standard

Table I Experimental Conditions for Conventional Suspension Polymerization of EGDMA

Experiment No	BPO Concentration (mg/mL)	PVA Concentration (mg/mL)	EGDMA/Water Ratio (ml/mL)	Temperature (°C)	Stirring Rate (rpm)
Effects of Initiator Concentration					
1	5.0	4.0	4/100	80	600
2	20.0	4.0	4/100	80	600
3	40.0	4.0	4/100	80	600
4	80.0	4.0	4/100	80	600
Effects of Stabilizer Concentration					
5	5.0	4.0	4/100	80	600
6	5.0	8.0	4/100	80	600
7	5.0	16.0	4/100	80	600
Effects of Monomer/ Dispersion Medium Ratio					
8	5.0	4.0	2/100	80	600
9	5.0	4.0	4/100	80	600
10	5.0	4.0	8/100	80	600
11	5.0	4.0	24/100	80	600
12	5.0	4.0	48/100	80	600
Effects of Temperature					
13	5.0	4.0	4/100	65	600
14	5.0	4.0	4/100	80	600
15	5.0	4.0	4/100	90	600
Effects of Stirring Rate					
16	5.0	4.0	4/100	65	100
17	5.0	4.0	4/100	80	600
18	5.0	4.0	4/100	90	1000

In these experiments, polymerization time was 3 h.

Tyler sieves (W.S. Tyler International Comp., Cleveland, OH).

Swellabilities of Microspheres

In order to exhibit swellabilities of the microspheres, swelling ratios of the microspheres were obtained as follows: the apparent volume of the dry microspheres (10 g) was measured within a cylindrical glass tube (100 mL). Water was added into the tube, and the microspheres were allowed to swell at room temperature for 24 h (i.e., the predetermined equilibrium swelling time) with occasional shaking, and then the volume of the swollen microspheres was measured. Swelling ratio was calculated by the following equation:

$$\text{Swelling Ratio (\%)} = \{(V_s - V_d)/V_d\} \times 100$$

Where, V_s = volume of swollen microspheres (mL), and V_d = volume of dry microspheres (mL).

RESULTS AND DISCUSSION

Nonswellable Poly(EGDMA) Microspheres

At the first part of this study, nonswellable poly(EGDMA) microspheres were produced by a conventional suspension polymerization procedure by using BPO as the initiator, and PVA with an average molecular weight of 96,000 as the stabilizer. Note that, in our preliminary studies we have tested different stabilizers such as tricalcium phosphate and PVAs with different molecular weights and hydrolysis degrees. However, we were only able to produce stable and spherical poly(EGDMA) particles with PVA with an average molecular weight of 96,000 and 88% hydrolyzed.

A typical optical micrograph of the poly(EGDMA) microspheres produced with this conventional suspension polymerization procedure is given in Figure 1. As seen in this figure, rigid, transparent, and spherical particles were obtained.

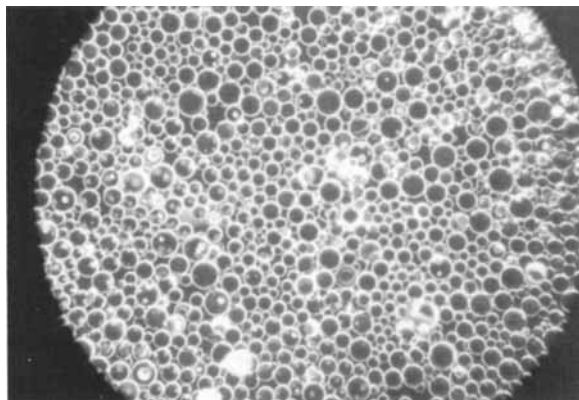


Figure 1 A representative optical micrograph of nonswellable poly(EGDMA) microspheres (Experiment No. 1, see Table I).

FTIR and FTIR-DRS spectra of the nonswellable poly(EGDMA) microspheres are given in Figure 2(A) and (B), respectively. The strong carbonyl and the aliphatic bands representing the bulk structure of poly(EGDMA) microspheres were detected in the FTIR spectra, at 1740 cm^{-1} and 3000 cm^{-1} , respectively. The hydroxyl band (at 3500 cm^{-1}) probably originated from the PVA molecules strongly entrapped in the bulk or on the outer surface layer of the microspheres during polymerization. It should be pointed out that stronger hydroxyl and aliphatic bands are observed on the surface spectrum [Fig. 2(B)] relative to the bulk structure [Fig. 2(A)], which may be an indication for the localization of PVA molecules, preferentially on the microsphere surface.

In order to produce polymeric microspheres with different size and size distributions, we changed the initiator and stabilizer concentrations, monomer/dispersion medium ratio, temperature, and stirring rate, and investigated their effects on the microsphere size distribution and yield, which are discussed in the separate sections given below. Note that none of these poly(EGDMA) microspheres produced by the conventional suspension polymerization at different experimental protocols given below exhibited any observable swellability; therefore, we called them as “nonswellable poly(EGDMA) microspheres.”

Effects of Initiator Concentration

Here, the initiator concentration was changed between $5.0\text{--}80.0\text{ mg/mL}$ while the stabilizer concentration and monomer/dispersion medium ratio were 4.0 mg/mL and $4/100\text{ mL/mL}$, respectively (Experiment Nos. 1–4, see Table I). The polymerizations

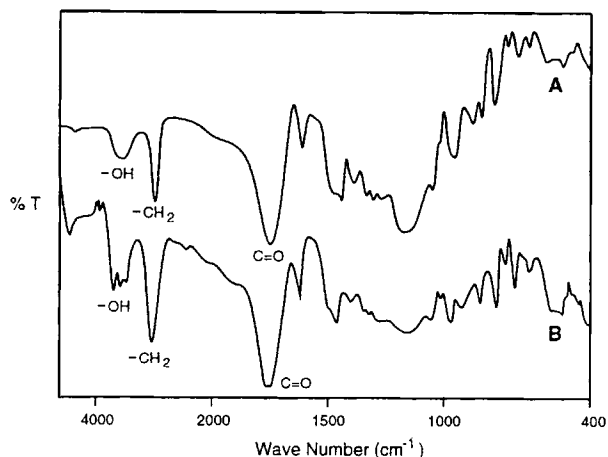
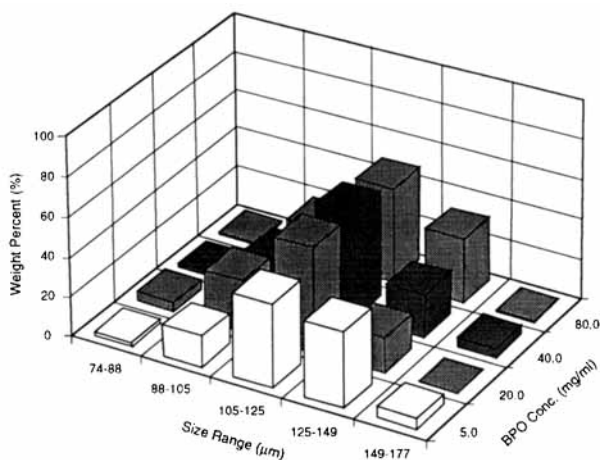


Figure 2 Spectra of nonswellable poly(EGDMA) microspheres (Experiment No. 1, see Table I): (A) FTIR; (B) FTIR-DRS.

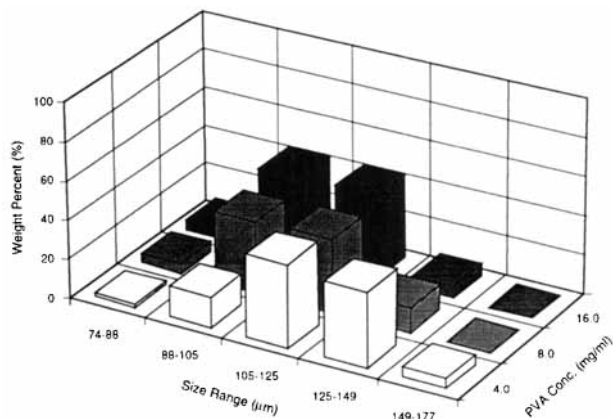
were conducted at 80°C with a stirring rate of 600 rpm for 3 h . Figure 3 shows the size distributions in bar graphs and yields of the microspheres produced in this group of experiments.

As seen here, initiator concentration did not affect the average size and size distribution significantly. About $40\text{--}50\%$ of the microspheres were in the range of $105\text{--}125\ \mu\text{m}$. Satisfactory microsphere yield values between $85\text{--}95\%$ were obtained with all initiator



BPO Conc. (mg/ml)	5.0	20.0	40.0	80.0
Microsphere Yield (%)	84.3	90.5	95.2	95.2

Figure 3 Effects of initiator concentration on size distribution of nonswellable poly(EGDMA) microspheres (Experiment Nos. 1–4, see Table I) and microsphere yield.



PVA Conc. (mg/ml)	4.0	8.0	16.0
Microsphere Yield (%)	84.3	83.3	82.9

Figure 4 Effects of stabilizer concentration on size distribution of nonswellable poly(EGDMA) microspheres (Experiment Nos. 5–7, see Table I) and microsphere yield.

concentrations, and the microsphere yield slightly increased with increasing initiator concentration, which may be explained by the increase in the radical production rate with increasing initiator concentration.

Effects of Stabilizer Concentration

Note that in the absence of sufficient stabilizer, the smaller droplets coalesce easily during the hardening stage. This produces larger and irregular particles, and may even lead to partial or full coagulation of the particles. Therefore, in this group of experiments the stabilizer concentration was changed between 4.0–16.0 mg/mL while the initiator concentration and monomer/dispersion medium ratio were 5.0 mg/mL and 4/100 mL/mL, respectively (Experiment Nos. 5–7, see Table I). The polymerizations were conducted at 80°C with a stirring rate of 600 rpm for 3 h. Figure 4 shows the size distribution of the microspheres in bar graphs and the microsphere yields.

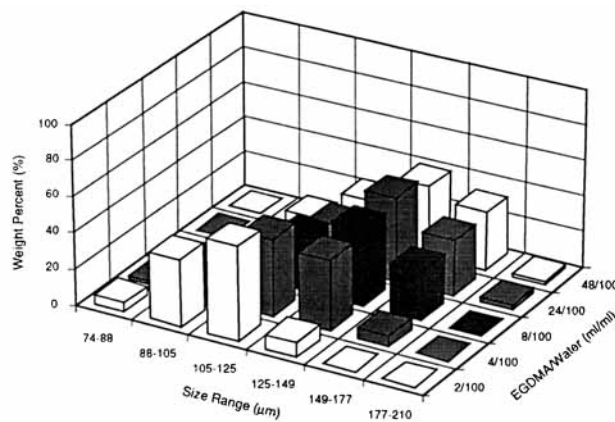
As seen in Figure 4, the average size of the microspheres decreased with increasing stabilizer concentration as also stated in the related literature.^{7,8,43–47} When the stabilizer concentration was 4.0 mg/mL, 30 and 25% of the microspheres were in the range of 105–125 μm and 125–149 μm, respectively. While 80% of the microspheres were in the range of 88–125 μm, respectively, when the sta-

bilizer concentration was 16.0 mg/mL. There was no appreciable change in the microsphere yield, which was about 83%, within the examined range of stabilizer concentration.

Effects of Monomer/Dispersion Medium Ratio

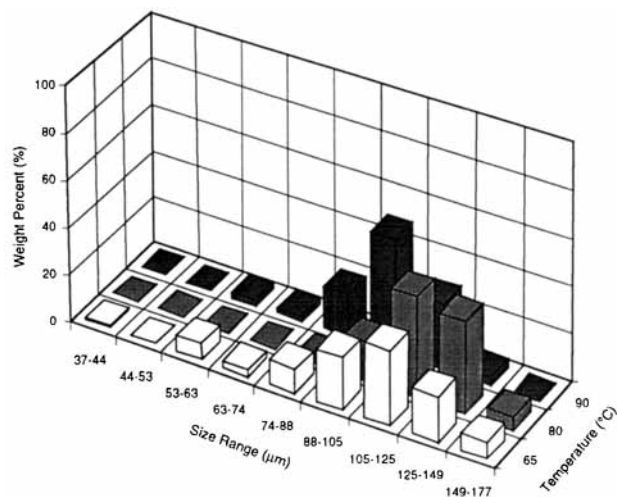
The monomer/dispersion medium ratio was changed between 2/100–48/100 mL/mL. In these experiments, the initiator and stabilizer concentrations were 5.0 mg/mL and 4.0 mg/mL, respectively (Experiment Nos. 8–12, see Table I). The polymerizations were conducted at 80°C with a stirring rate of 600 rpm for 3 h. Figure 5 shows the size distribution of the microspheres obtained in this group of studies and the microsphere yields.

As seen in Figure 5, both size and the size distribution of the microspheres increased with increasing the monomer/dispersion medium ratio, similar to results reported by others.^{7,8,43–47} The smallest microspheres with the narrowest size distribution was obtained with a monomer/dispersion medium ratio of 2/100 mL/mL, in which 40 and 35% of the microspheres were in the range of 105–125 μm and 88–105 μm, respectively. While 38 and 30% of the microspheres were in the range of 125–149 μm and 149–177 μm, respectively, when the EGDMA/water ratio was 48/100 mL/mL. The microsphere yield first increased with increasing monomer/dispersion



EGDMA/Water (ml/ml)	2/100	4/100	8/100	24/100	48/100
Microsphere Yield (%)	74.3	84.3	91.0	81.7	82.5

Figure 5 Effects of monomer/dispersion medium ratio on size distribution of nonswellable poly(EGDMA) microspheres (Experiment Nos. 8–12, see Table I) and microsphere yield.



Temperature (°C)	65	80	90
Microsphere Yield (%)	21.4	84.3	87.6

Figure 6 Effects of temperature on size distribution of nonswellable poly(EGDMA) microspheres (Experiment Nos. 13–15, see Table I) and microsphere yield.

medium ratio and then decreased. The maximum microsphere yield was 91.0%, which was obtained when the monomer/dispersion medium ratio was 8/100 mL/mL.

Effects of Temperature

The polymerization temperature was changed between 65–90°C. In these experiments, the initiator and stabilizer concentrations were 5.0 mg/mL and 4.0 mg/mL, respectively (Experiment Nos. 13–15, see Table I). The polymerizations were conducted at a monomer/dispersion medium ratio of 4/100 mL/mL with 600 rpm stirring rate. Figure 6 shows the size distribution of the microspheres and the microsphere yields.

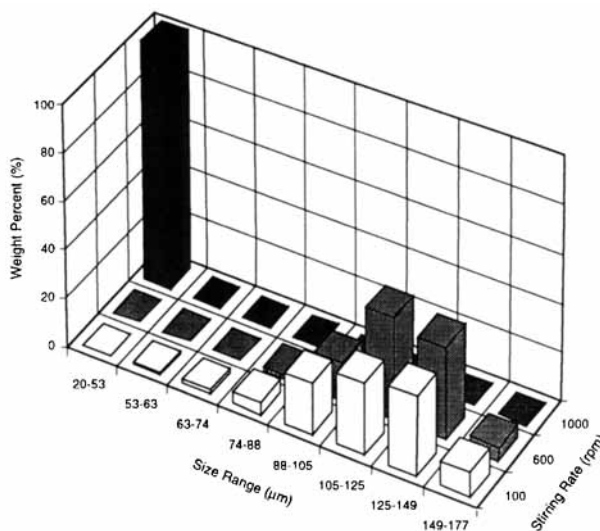
Figure 6 shows that the widest microsphere size distribution was observed at 65°C, while the narrowest size distribution was at 80°C. Average microsphere size increased when temperature was raised from 65 to 80°C, however, decreased with further increase in temperature. About 38 and 32% of the microspheres were in the range of 105–125 µm and 125–149 µm, respectively, when temperature was 80°C. As seen here, the lowest microsphere yield (21.4%) was obtained at 65°C. The microsphere yield significantly increased with increasing polymeriza-

tion temperature. Satisfactory microsphere yields (about 85%) were achieved at 80 and 90°C.

Effects of Stirring Rate

Note that among various factors influencing particle size, stirring rate (or more generally, the power of mixing) provides a relatively convenient means of particle size control for most practical purpose. Lower stirring rates may not be sufficient to establish a steady-state droplet size distribution, whereas too vigorous stirring may exceed the shear tolerance of the reactor system. Therefore, in this group of experiments, the stirring rate was changed between 100–1000 rpm. In these experiments, the initiator and stabilizer concentrations were 5.0 mg/mL and 4.0 mg/mL, respectively (Experiment Nos. 16–18, see Table I). The polymerizations were conducted at a monomer/dispersion medium ratio of 4/100 mL/mL at a polymerization temperature of 80°C. Figure 7 shows the size distribution of the microspheres, and the microsphere yields.

As shown in Figure 7, slightly narrower size distribution was obtained with the increase of the stirring rate from 100 rpm to 600 rpm, and most of the microspheres at these stirring rates were in the size



Stirring Rate (rpm)	100	600	1000
Microsphere Yield (%)	82.8	84.3	90.0

Figure 7 Effects of stirring rate on size distribution of nonswellable poly(EGDMA) microspheres (Experiment Nos. 16–18, see Table I) and microsphere yield.

Table II Microsphere Yield and Swelling Ratio Values for the Swellable Poly(EGDMA) Microspheres

Experiment No	EGDMA/Water/Toluene Ratio (ml/mL)	Microsphere Yield (%)	Swelling Ratio (%)
19	8/100/6	88.5	24
20	8/100/12	91.3	38
21	16/100/6	98.1	17
22	16/100/12	97.5	22
23	24/100/8	95.4	3
24	24/100/16	94.7	30
25	24/100/24	97.6	22

In these experiments, initiator and stabilizer concentrations, temperature, stirring rate, and polymerization time were, 5.0 mg/mL, 4.0 mg/mL, 80°C, 600 rpm, and 3 h, respectively.

range of 88–177 μm . A very significant decrease was observed when the stirring rate was 1000 rpm, similar to the literature reports.^{7,8,43–48} The size distribution became very narrow relative to the distributions obtained in other experiments, and about more than 95% of the microspheres were in the size range of 20–53 μm . The microsphere yields were in the range of 83–90%, and increased with increasing stirring rate.

Swellable Poly(EGDMA) Microspheres

Porosity and surface area (or tertiary structure) of the polymer microspheres are the most important functional characteristics in many applications.^{1–6} Porosity is determined by precipitation process that takes place during the conversion of liquid microdroplets to solid beads in the suspension medium. Control of porosity, therefore, the effective surface area, by means of a diluent (or porogen) has been extensively investigated for polystyrene, polyacrylamide, polymethacrylates, etc.^{10–34} It has been shown that the inert diluent present during the network formation may remain in the network (gel) phase throughout the polymerization, resulting in the formation of expanded network (swollen), or may separate out of the network phase, resulting in the formation of porous particles. The distribution of the diluent between network and diluent phases (diluent in the pores) at the end of the polymerization determines the total porosity of the resulting polymer and their swelling ratios in solvents. Using diluent with high solvating power (means a good solvent for the polymer) results a relatively homogeneous matrix with very low porosity, while polymerization in the presence of poor solvents (low solvency), leads to phase separation and the formation of highly porous structures. Note that in all of the applications,

the support (e.g., polymer microspheres) functions in a solvent (i.e., water in many biomedical applications) in which the matrix may swell to various extents. Under these conditions, the specific pore volume and pore size distribution in the swollen state may be substantially different those measured in the dry state.^{46–49}

In this study, we attempted to prepare swellable poly(EGDMA) microspheres (swellable in aqueous media) by following the above-mentioned literature findings, by using toluene as a diluent in the conventional suspension polymerization recipe discussed in the previous section. In all of the modified suspension polymerizations performed in this group of studies, the BPO and PVA (MW: 96,000) concentrations were 5.0 mg/mL and 4.0 mg/mL, respectively. These polymerizations were conducted in 50 mL of the dispersion medium, at 80°C with a stirring rate of 600 rpm for 3 h. In order to obtain poly(EGDMA) microspheres with different sizes and swellabilities, the relative amounts of EGDMA, water, and toluene were changed (see Table II).

Representative optical micrographs of the poly(EGDMA) microspheres (dry and swollen) produced in the existence of toluene are given in Figure 8. Note that the color of the dry swellable poly(EGDMA) microspheres was grey or yellow, and they were not transparent [Fig. 8(A)] in contrast to the nonswellable poly(EGDMA) microspheres produced by the conventional suspension polymerization (Fig. 1). The opacity and color of these microspheres is an indication of their microporous structure. The color of swellable microspheres turned to dark or light blue when they were swollen with water [Fig. 8(B)].

The FTIR and FTIR-DRS spectra of the dry swellable poly(EGDMA) microspheres are given in Figure 9(A) and (B), respectively. Notice that, the

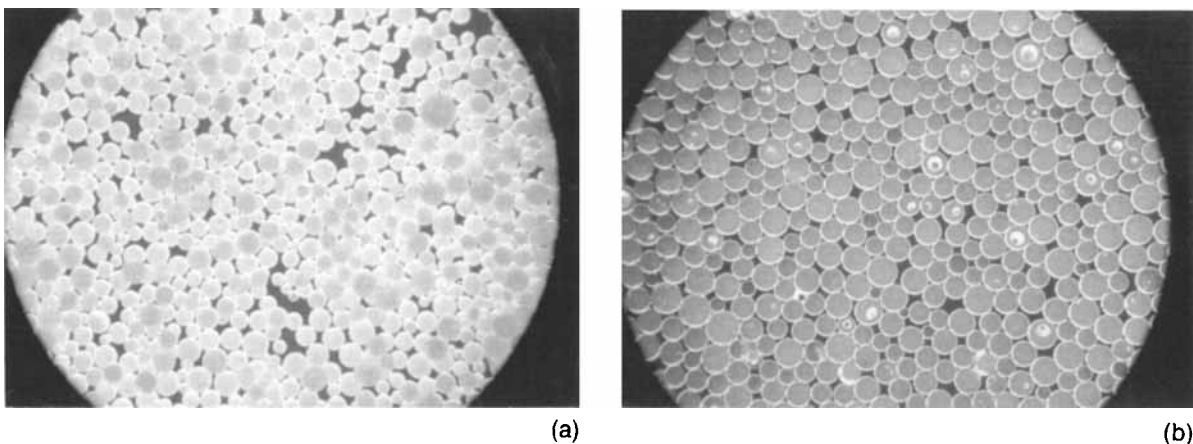


Figure 8 Representative optical micrographs of (A) dry and (B) swollen poly(EGDMA) microspheres (Experiment No. 20, see Table II).

relative intensity of the hydroxyl band was stronger in the FTIR spectrum of the swellable poly(EGDMA) microspheres [Fig. 9(A)] than that observed in the FTIR spectrum of nonswellable microspheres [Fig. 2(A)]. This may be due to the existence of diluent, which slightly enhances the entrapment of the PVA molecules within the matrix of the microspheres during polymerization. The differences in the relative intensities of the hydroxyl and aliphatic bands in FTIR and FTIR-DRS spectra of the dry swellable poly(EGDMA) microspheres may be attributed to the preferential localization of PVA molecules on the outer surface of the microspheres, similar to nonswellable poly(EGDMA) microspheres as discussed before.

Figure 10(A) shows the size distributions of two types of poly(EGDMA) microspheres, which were prepared by using the EGDMA/toluene volumetric ratios, 8/6 and 8/12 mL/mL (Experiment Nos. 19 and 20, respectively, see Table II). There was no significant difference in the particle size distribution. About 60% (by weight) of microspheres were in the size range of 88–105 μm .

Figure 10(B) gives the size distributions of the microspheres prepared by using EGDMA/toluene ratios of 16/12 and 16/24 mL/mL (Experiment Nos. 21 and 22, respectively, see Table II). Note that these microspheres were produced by using higher amounts of EGDMA and toluene in the initial polymerization medium than those discussed in Figure 10(A), but the EGDMA/toluene ratios were equal ($16/12 = 8/6$ and $16/24 = 8/12$). As seen here, a relatively wider size distribution and larger microspheres were obtained with the polymerization in which higher amount of toluene was used

(EGDMA/toluene ratio: 16/24 mL/mL). When the EGDMA/toluene ratio was 16/24 mL/mL, about 30 and 40% of the microspheres were in the range of 105–125 μm and 125–149 μm , respectively, while 60% of the microspheres were in the range of 88–105 μm when the EGDMA/toluene ratio was 16/12 mL/mL.

Figure 10(C) gives the size distributions of the microspheres prepared by using EGDMA/toluene ratios of 24/8, 24/16, and 24/24 mL/mL (Experiment Nos. 23, 24, and 25, respectively, see Table II). Note that very significant size distributions were observed when the EGDMA/toluene ratio was higher than 24/24 mL/mL. Wider size distributions may be attributed to the increase in the amount of EGDMA used. In addition, larger microspheres were

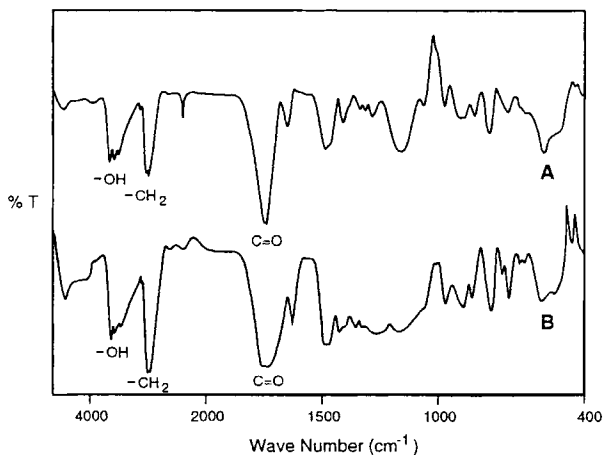


Figure 9 Spectra of nonswellable poly(EGDMA) microspheres (Experiment No. 20, see Table II): (A) FTIR; (B) FTIR-DRS.

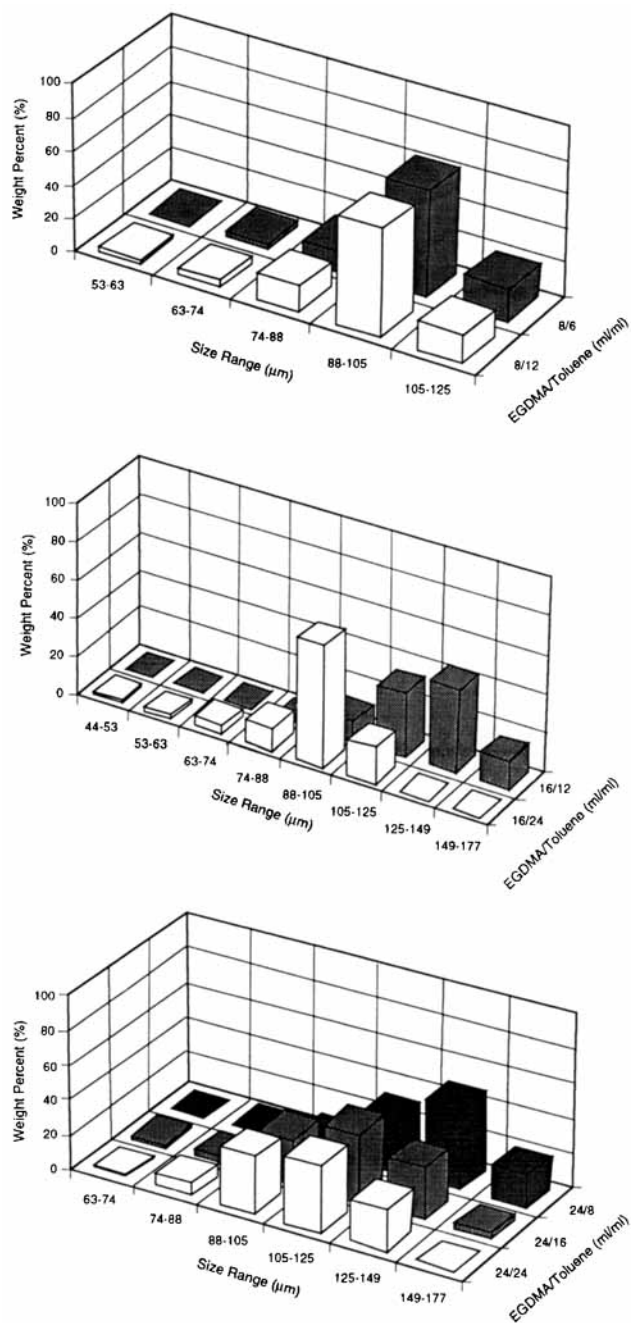


Figure 10 Size distribution of swellable poly(EGDMA) microspheres (see Table II): (A) Experiments Nos. 19–20; (B) Experiment Nos. 21–22; (C) Experiment Nos. 23–25.

obtained when the amount of toluene was increased. When the EGDMA/toluene ratio was 24/24 mL/mL, about 45% of the microspheres were in the range of 125–149 μm , while 40% of the microspheres were in the range of 105–125 μm when the EGDMA/toluene ratio was 24/8 mL/mL.

Table II gives the microsphere yield and swelling ratio values for the swellable poly(EGDMA) microspheres produced at different conditions given in Table II (Experiment Nos. 19–24). Note that high microsphere yields (up to 98%) were obtained in all cases. Slightly lower yields were observed when the amount of the monomer (i.e., EGDMA) was low (Experiment Nos. 19 and 20, see Table II).

The differences in the swellability (between 3–38%) of the poly(EGDMA) microspheres produced at different conditions were significant. Swellability of the microspheres increased by increasing amount of diluent at constant monomer concentration, similar to the general tendency reported in the related literature.^{25–33} Okay and Gürün reported that the weight swelling ratio of poly(EGDMA) networks produced by bulk polymerization was a linear function of monomer dilution.³³ In our suspension polymerization experiments, we also observed an increase in the volumetric swelling ratio with the increase of the diluent (i.e., toluene) content in the organic phase; but the relation was not a linear function. Note that at a fixed volume fraction of the diluent, the swelling ratio decreases as the crosslinker concentration in the starting monomer mixture increases. This effect is much pronounced when the crosslinker concentration is less than 10–15% in the initial mixture.^{25–33} In our study, the monomer itself is a crosslinker; thus, the polymer network is highly crosslinked and swelling is not expected; however, due to presence of diluent molecules resulting poly(EGDMA) microspheres do swell considerably in aqueous medium as shown in Table II.

CONCLUSION

At the first part of this study, nonswellable poly(EGDMA) microspheres with different size and size distributions were produced by a conventional suspension polymerization. Larger microspheres but usually with wider size distribution may be obtained by decreasing the stabilizer concentration and the stirring rate, and by increasing the monomer/dispersion volume ratio.

At the second part, swellable poly(EGDMA) microspheres with different sizes and swellabilities were produced by a modified suspension polymerization. Larger microspheres with wider size distributions were obtained when the relative amount of EGDMA was higher. Microsphere yields were more

than 90% almost in all cases. Swellabilities up to 38% were observed in these highly crosslinked structures due to the presence of a diluent.

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