Preparation and Characterization of 2-Hydroxyethyl Methacrylate-Based Porous Copolymeric Particles

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ABSTRACT: 2-Hydroxyethyl methacrylate was copolymerized with three different comonomers, methyl methacrylate (MMA), styrene (St), and *N*-vinyl-2-pyrrolidone (NVP), respectively, to prepare porous particles crosslinked using ethylene glycol dimethacrylate (EGDMA) in the presence of an organic solvent, 1-octanol (porogen), by means of suspension copolymerization in an aqueous phase initiated by 2,2-azobisisobutyronitrile. Nano-pores were observed in the particles. The pore size and the swelling properties of these particles can be controlled by changing comonomers or adjusting the crosslinker or porogen concentration. A lower crosslinker or porogen concentration favors generating smaller pores, whereas a higher concentration of a hydrophilic comonomer, higher concentration of crosslinker, and higher porogen volume ratio promote the generation of larger pores. In addition, the effects of the porous characteristics on the swelling properties were explored. The swelling capacity of the porous particles is reduced with the increase in the crosslinker concentration; however, there is a critical porogen volume ratio, in which the maximal swelling capacity is reached. Higher porosity in the particles and higher amount of hydrophilic comonomer favor a higher swelling capacity of the particles. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3138–3145, 2007

Key words: hydrogels; pore; 2-hydroxyethyl methacrylate; methyl methacrylate; styrene; *N*-vinyl-2-pyrrolidone; particle; porosity; swelling

INTRODUCTION

2-Hydroxyethyl methacrylate (HEMA) hydrogels have been of great interest because of the biocompatibility of their three-dimensional polymeric networks, which can swell in water and retain a significant fraction of water within the structures without dissolving.[1] HEMA hydrogels have been widely used in many areas, especially in biomedical and pharmaceutical areas, such as packing materials in chromatography,[2] sorbents in controlled release or drug delivery,[3] and implanting materials in tissue engineering,[4] etc. In recent decades, how to build uniform porous structures in HEMA hydrogels has received considerable attention because the presence of the porous structures can significantly improve the performance of HEMA hydrogels in various applications.

Porous poly(HEMA) particles can be synthesized by incorporating a multi-vinyl crosslinker, and organic solvents (porogen) by means of free-radical suspension polymerization.[5–7] The crosslinker creates the three-dimensional networks; the porogen works as a good solvent for monomers but a nonsolvent for poly(HEMA), and thus it helps generating porous structures. The types and amount of the crosslinker and the porogen used in the reaction systems largely determine the porous structures and the particle morphology.

Most of the studies in porous polymer syntheses have indicated that it is the phase separation that results in the formation of porous structures in polymers. However, different procedures of the phase separation can result in different porous structures. Okay indicated that heterogeneous (porous) and expanded networks, depending on the suspension polymerization conditions, can be obtained in the polymeric particles as a consequence of the phase separation process.[8] Heterogeneous pores are those pores that exist permanently no matter whether the solvents are removed from the polymers or not. Horak et al.[6] studied the relationships between the phase separation and the porous structures of the poly(HEMA) particles by exploring the porous structures and the particle morphology using SEM, and indicated that the heterogeneous pores could be resultant from the agglomeration of the separated microgels. The expanded pores, according to Gomez et al.,[7] are nonporous networks in a dry state since the pores are collapsed during drying and solvent removal; however, they could re-expand to their previous state in a good solvent.

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In the past decade, to control the porous structures and the swelling properties of poly(HEMA), copolymerization of HEMA with various other vinyl monomers have been reported.[2,9–11] Vianna-soares et al.[2] synthesized porous poly(HEMA-MMA) particles to be used in chromatography; however, the effects of MMA content and porous structures on the performance of particles were not investigated. Brazel and Peppas[10] studied the swelling properties of poly (HEMA-MMA) and poly(HEMA-NVP), which were to be used for drug delivery. They found that the existence of MMA component in the particles can decrease the swelling capacity, and adding the NVP component can enhance the swelling capacity, so that the controlled release by adjusting monomer content could be realized. However, the polymers they synthesized were nonporous, and the range, for which the drug release could be adjusted, was limited. Therefore, although the copolymers of HEMA have been reported for many years, how to control the porous structures and the swelling properties have not been well investigated and understood. With the presence of highly porous structures, the porous HEMA copolymer particles can be used in many areas, such as being used as a carrier in the controlled drug delivery to improve drug loading capacity and control release kinetics, and being used as absorbents to enhance separation process and water treatment, and so on.

The objective of this article is to investigate the synthesis of porous copolymer particles of HEMA with MMA, St, and NVP, respectively, and to characterize the resulting copolymers as well as to study the relationships between the porous structures and the swelling properties of the polymers.

EXPERIMENTAL

Materials

Ethylene glycol dimethacrylate (EGDMA, 98%; Aldrich Chemical, Ontario, Canada), methyl methacrylate (MMA, 99%; Aldrich Chemical), styrene (St, 99%; Aldrich Chemical), *N*-vinyl-2-pyrrolidone (NVP, 99%; Aldrich Chemical), 1-octanol (99%; Aldrich Chemical), and 2-hydroxyethyl methacrylate (HEMA, 97%; Aldrich Chemical) were used without further purification. The initiator was 2,2-azobisisobutyronitrile (AIBN; Polysciences, Washington, PA). Polyvinyl-pyrrolidone (PVP, K90, weight average molecular weight: 360,000; Aldrich Chemical) and sodium dodecyl sulfate (SDS, 70%; Aldrich Chemical) were dissolved in deionized water before being used as a stabilizer and a costabilizer, respectively. Petroleum ether (95%, boiling temperature range: 30–60°C; Fisher Scientific, Ottawa, Canada) and methanol (HPLC grade; Fisher Scientific) were used to wash the polymers after reactions.

Suspension copolymerization

The organic mixture, consisting of HEMA, a comonomer (MMA, or St or NVP), EGDMA, 1-octanol, and AIBN, was stirred for 10 min using a magnetic stirrer. The dissolved oxygen in this organic mixture and in the stabilizer solution was expelled by a nitrogen purge. After the organic mixture was added into the stabilizer solution, which consisted of 0.15 g of SDS and 1.5 g of PVP in 150 mL of deionized water, the solution was stirred with an emulsion homogenizer for 3 min to disperse the organic phase in the aqueous phase and form an emulsion system. Subsequently, the emulsion was charged into a jacketed stainless steel reactor equipped with a four-pitched blade agitator at room temperature. The reaction was maintained at 70°C for 4 h under agitation with a speed of 500 rpm, followed by a filtration operation to obtain the polymeric particles. The particles were washed successively using deionized water and methanol, and then were extracted by ether using a Soxhlet extractor for 24 h. Finally, the copolymeric particles were dried in a vacuum chamber at 35°C for 3 days.

Characterization of the porous particles

Reaction parameters

The following variables are defined to facilitate analysis and discussion:

1. Crosslinker concentration

$$\mathrm{EGDMA(mol\%)} = \frac{n_{\mathrm{EGDMA}}}{n_{\mathrm{HEMA}} + n_{\mathrm{comonomer}} + n_{\mathrm{EGDMA}}} 100\% \quad (1)$$

   where n_{HEMA} and n_{EGDMA} are the moles of HEMA and EGDMA, respectively. The $n_{\mathrm{comonomer}}$ represents the moles of MMA, St, or NVP.
2. Porogen volume ratio, r

$$r = \frac{V_{\mathrm{oct}}}{V_{\mathrm{HEMA}} + V_{\mathrm{comonomer}}} \quad (2)$$

   where V_{oct}, V_{HEMA}, and $V_{\mathrm{comonomer}}$ are the volume of 1-octanol, HEMA, and comonomers, respectively.
3. Monomer molar ratio, r_H

$$r_H = \frac{n_{\mathrm{HEMA}}}{n_{\mathrm{comonomer}}} \quad (3)$$

Porous characteristics

Porous characteristics, including the porosity, the pore volume, and the porous surface area, were

obtained using mercury intrusion porosimetry (Poremaster GT-60). The contact angle between mercury and the polymers was 140°.[2] The pore size distribution function $D_v(d)$ was defined as eq. (4),[12]

$$D_v(d) = P\frac{dV_p}{dP}\cdot\frac{2}{d} \quad (4)$$

where d is the pore diameter (μm), P is the pressure (kPa), and V_p is the pore volume (mL/g or cc/g).

A LEO 1530 Field-Emission Scanning Electronic Microscope (SEM) was used to evaluate the porous morphology. The dried polymer samples were located on an electronic tape double-coated with a gold coating of 10 nm. SEM photos were taken under different levels of magnification to examine the detail of the morphology.

Swelling experiments

The swelling experiments were carried out at 25°C. The experimental methods were the same as described previously.[13]

The equilibrium weight swelling ratio (q_w) and the equilibrium volume swelling ratio (q_v) were defined as eqs. (5) and (6), respectively.

$$q_w = \frac{W_{\text{swell}}}{W_{\text{dry}}} \quad (5)$$

$$q_v = \frac{V_{\text{swell}}}{V_{\text{dry}}} = \frac{{D_{\text{swell}}}^3}{{D_{\text{dry}}}^3} \quad (6)$$

where W_{dry} is the weight of the dry polymeric particles, and W_{swell} is the weight of the swollen polymeric particles at the equilibrium state. D_{swell} and D_{dry} are the particle diameters at the equilibrium swelling state and at the dry state, respectively.

RESULTS AND DISCUSSION

Since HEMA is a hydrophilic monomer, poly (HEMA) particles are synthesized in an aqueous phase with an aid of other solvents that are not soluble in water. For instance, Horak et al.[6] used cyclohexanol to reduce the solubility of HEMA in the aqueous phase to make spherical particles. In the present studies, St, MMA, and NVP are used. MMA and St are water-insoluble monomers. Although NVP is hydrophilic, the presence of 1-octanol still can make suspension copolymerization possible. The values of the solubility parameter shown in Table I indicate that the organic phase is a homogeneous mixture because the solubility parameter values do not have much difference from each other.

TABLE I
Solubility Parameters[1,14] (MPa)$^{1/2}$

HEMA	23.2
EGDMA	18.2
MMA	18
Styrene	19
NVP	23
1-Octanol	20.9

Effect of crosslinker concentration on porous structures

The particles were synthesized at various EGDMA concentrations. The data of the specific porous surface area and the pore volume are shown in Table II. The change of the porosity with the EGDMA concentration is shown in Figure 1. The pore size distribution profiles are shown in Figure 2. It was found that the porous structures and the pore size significantly depend on the EGDMA concentration.

According to Table II and Figure 1, there are maximums in the porosity and the pore volume within the range of the EGDMA concentration, whereas the porous surface area increases with an increase in EGDMA concentration for all of the three types of HEMA copolymer particles. This is caused by the pore formation mechanism change with the increase in EGDMA concentration. Although it has been well accepted that the formation of the pores in polymers is induced by phase separation, the two types of phase separation mechanisms, termed χ-induced syneresis (at low crosslinker concentration) and ν-induced syneresis (at higher crosslinker concentration),[5] exist and they are affected by the relative amount of the crosslinker and the porogen used. At a low EGDMA concentration, the residual monomer–porogen mixture is a nonsolvent for the growing copolymer chains, whereas it could become a good solvent at higher EGDMA content.[8] The critical points (summits) of the porosity and the pore volume in the range of the EGDMA concentration reflect the transformation from χ-induced syneresis to ν-induced syneresis.

At a low crosslinker concentration, the polymeric networks are swollen by the solvent–monomer mixtures easily, so that the phase separation occurs later than the original gel point and it does not happen until the networks grow to a certain extent; the porogen separates only when the swelling capacity of the networks reaches their maximum capacity in the porogen.[8,15] Therefore, more porogen separates with the increase in the crosslink density during the course of the reaction, which then induces more pores. According to the study[5] for the synthesis of poly(HEMA-EGDMA), lower EGDMA concentration makes the reaction mixture a poorer solvent for the resultant polymers. In the present study, the porous

TABLE II
Reaction Compositions and Porous Characteristics

Batch	EGDMA (mol %)	r (mL/mL)	Pore volume (mL/g)	Surface area (m^2/g)	q_w	q_v
HM-1	3.0[a]	1	0.29	27.1	1.78	1.86
HM-2	8.8[a]	1	1.29	22.7	1.87	1.32
HM-3	17.6[a]	1	0.81	42.3	1.73	1.43
HM-4	23.4[a]	1	0.50	98.3	1.62	1.10
HS-1	3.0[b]	1	1.08	9.1	2.09	1.26
HS-2	8.6[b]	1	2.01	8.3	1.33	1.15
HS-3	18.0[b]	1	3.47	43.9	2.01	1.16
HS-4	23.9[b]	1	1.77	28.1	1.53	1.14
HN-1	3.0[c]	1	0.19	2.4	2.95	4.96
HN-2	8.4[c]	1	1.72	19.4	3.64	2.74
HN-3	17.6[c]	1	1.55	26.6	2.13	1.55
HN-4	23.4[c]	1	1.53	48.5	2.02	1.33
HM-5	23.4[a]	0.5	0.21	32.3	1.60	1.32
HM-6		0.65	1.23	30.5	2.55	1.64
HM-7		0.8	0.91	61.0	1.64	1.30
HS-5	23.9[b]	0.5	0.20	0.6	1.49	1.40
HS-6		0.65	2.01	11.9	1.58	1.51
HS-7		0.8	1.18	20.3	1.77	1.27
HN-5	23.4[c]	0.5	0.89	49.2	1.66	1.59
HN-6		0.65	1.10	92.5	2.20	1.40
HN-7		0.8	1.04	50.2	2.30	1.75

[a] HEMA and MMA, $r_H = 1.75$.
[b] HEMA and St, $r_H = 1.89$.
[c] HEMA and NVP, $r_H = 1.75$.

structures formed before the critical point was possibly induced by the incompatibility between the polymers and the reaction mixtures, i.e., so called χ-induced syneresis. If the EGDMA concentration increases further, the reaction mixture tends to become a good solvent for the polymers.[8] However, on the other hand, at a certain high crosslink density, the rigidity of the polymeric networks increases. The networks become relatively hard to be swollen so that the highly crosslinked microgels tend to separate earlier than the original gel point.[8] These microgels are agglomerated to form pores between them. Therefore, the pores, which are formed after the critical point, as shown in Figure 1, are mainly induced by the crosslinking, which is corresponding to the ν-induced syneresis.[8] Higher crosslink density induces smaller microgels and shorter polymeric segments between crosslinking points, which results in smaller pores. This is the reason that the porosity decreases when the EGDMA concentration exceeds a certain level, as shown in Figure 1.

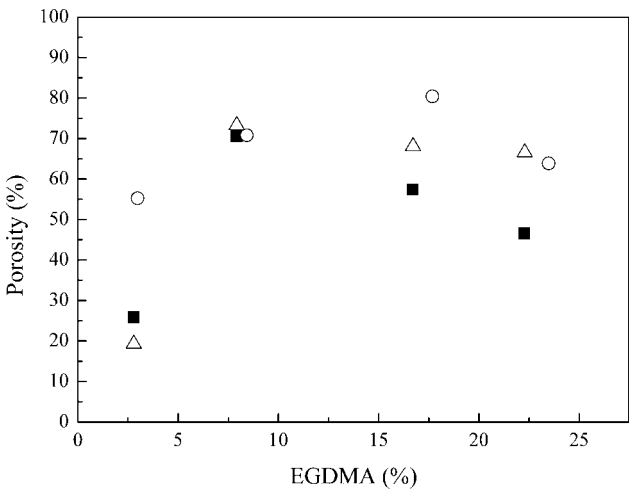

Figure 1 Effect of the crosslinker concentration on the porosity. ■: poly(HEMA-MMA), $r_H = 1.75$; ○: poly (HEMA-St), $r_H = 1.89$; △: poly(HEMA-NVP), $r_H = 1.75$. $r = 1$, agitation speed = 500 rpm, $T = 70°C$.

However, lower porosity and lower pore volume at higher EGDMA concentration do not mean fewer pores. As shown in Figure 2, the ratio of smaller pores was higher than the larger pores at a lower EGDMA concentration; however, the amount of the total pores was low according to the height of the peaks. As stated earlier, this is caused by the shrinkage or the collapse of the pores when removing porogen under χ-induced syneresis. Figure 2 also indicates that with the increase in EGDMA concentration, the pore size distribution profiles shift toward larger pores and further increase in EGDMA concentration can make the pore size distribution profiles shift back to the side of smaller pores. This also can be understood by the phase

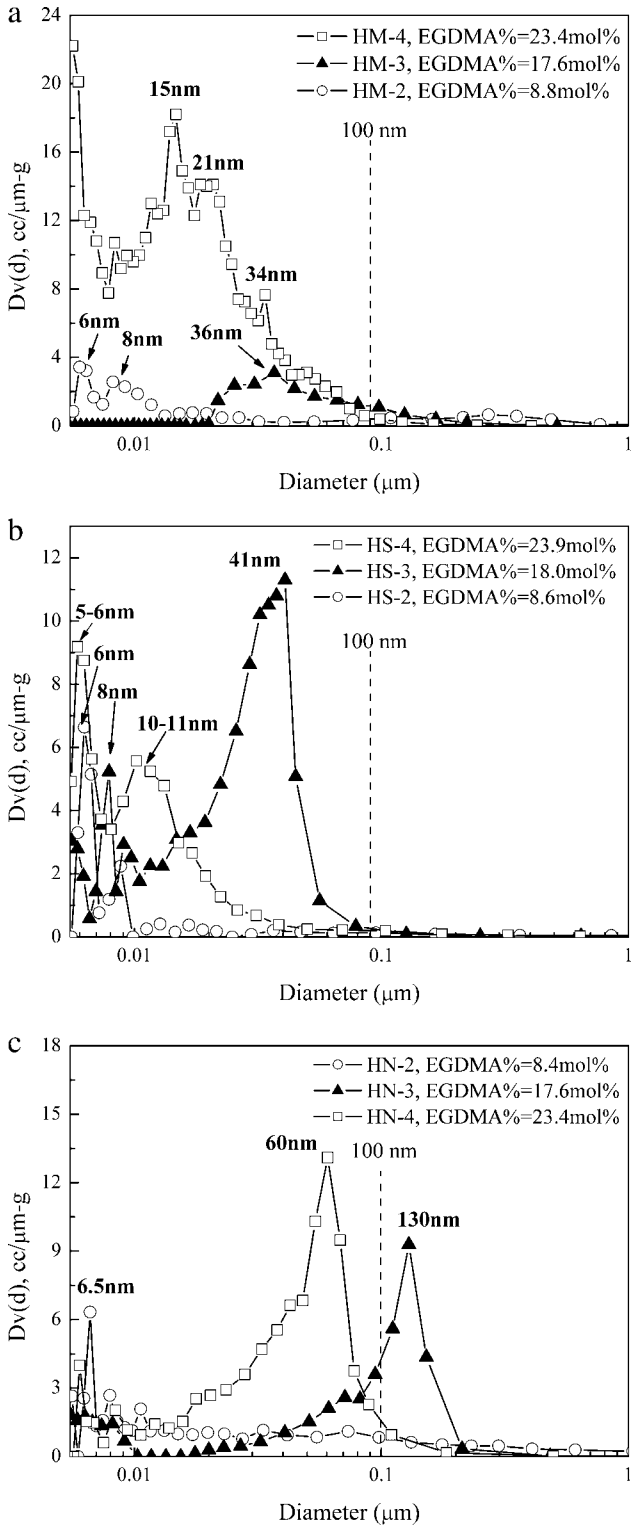

Figure 2 Pore size distributions of polymeric particles at different EGDMA concentration. (a) HEMA and MMA, r_H = 1.75; (b) HEMA and St, r_H = 1.89; (c) HEMA and NVP, r_H = 1.75; r = 1.

separation mechanism. More pores in smaller size are generated at a higher crosslink density under v-induced syneresis.[8]

Figure 2 also implies that the pore size could be controlled by adjusting EGDMA concentration and selecting comonomers. The nano-pores (diameter < 100 nm) were observed in Figure 2 except for HN-3. According to the positions of the peaks in the pore size distributions, a lower EGDMA concentration favors the formation of smaller pores. For poly (HEMA-MMA) and poly(HEMA-St), 17–18 mol % of EGDMA gives rise to the pores in the range of 35–40 nm, whereas poly(HEMA-NVP) has larger pores being 130 nm on the average. At higher EGDMA concentration, such as 23.4 mol %, poly (HEMA-MMA) exhibits a pore size of 10–30 nm, and poly(HEMA-St) has a pore size of around 10 nm, whereas poly(HEMA-NVP) shows a pore size of around 60 nm. Therefore, at higher EGDMA concentration, more hydrophilic comonomer, such as NVP, generates larger pores. In the copolymerization of HEMA and NVP, or that of EGDMA and NVP, the monomers HEMA and EGDMA are much more reactive than NVP.[16,17] For example, the reactivity ratios of HEMA and NVP in the copolymerization are 3.07 and 0.045, respectively.[17] Since HEMA and EGDMA are much more reactive than NVP, the HEMA and EGDMA enter into the copolymer much faster than NVP, and thus in the late stage of the copolymerization, the resultant polymers may have a composition close to PNVP homopolymer.[17] Such formed short PNVP chains could be soluble in the solvent. This ''internal polymer solution'' in the particles could act as a porogen. When they are washed out, some large pores can be formed.

Effect of porogen volume ratio on porous structures

Table II and Figures 3–5 show the effect of the porogen volume ratio on the porous characteristics.

Basically, for these three polymeric particles, the porosity and the pore volume decrease slightly after certain porogen volume ratio is reached. This phenomenon is similar with that observed in the synthesis of the porous poly(St-DVB) particles.[8] As stated by Okay,[8] higher solvent concentration results in the further dilution of monomer so that isochoric conditions cannot be held. According to Figure 4, for the polymers produced at higher porogen concentration, the pore size distribution shifts to the right side (larger pores) with higher peaks (more pores). This implies that loose polymeric networks are generated when a higher porogen concentration is applied. Figure 5 also proves that the polymeric networks produced at a higher porogen concentration are looser than those produced at a lower porogen concentration.

Figures 4 and 5 also indicate that poly(HEMA-St) particles have smaller pores, whereas poly(HEMA-

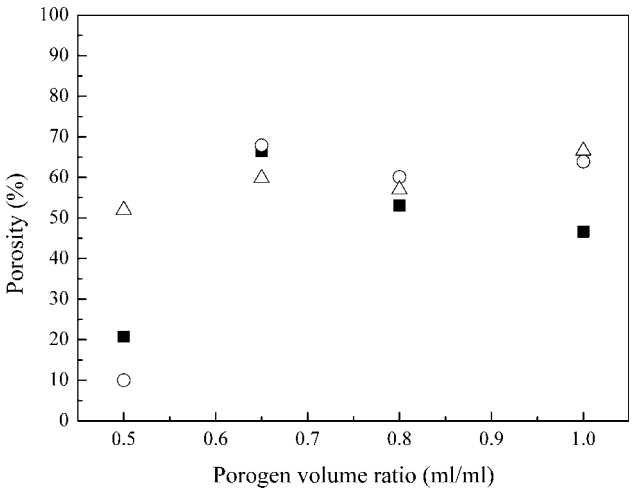

Figure 3 Effect of the porogen volume ratio on the porosity. ■: poly(HEMA-MMA), r_H = 1.75; ○: poly(HEMA-St), r_H = 1.89; △: poly(HEMA-NVP), r_H = 1.75. EGDMA% = 22.3 mol % for poly(HEMA-MMA) and poly(HEMA-NVP), EGDMA% = 23.5 mol % for poly(HEMA-St), agitation speed = 500 rpm, T = 70°C.

NVP) particles show much larger pores. Therefore, the pore size could also be controlled by adjusting the porogen ratio. Generally, in the present work, a lower porogen volume ratio generates fewer pores and smaller pore size, whereas a higher porogen volume ratio results in more pores and larger pore size.

Swelling capacity

The swelling process includes two steps. One is that solvents fill in the pores, and the other is that the solvents swell the polymeric networks.[7] Thus, the q_v is mainly determined by the properties of the polymeric networks, whereas the q_w is governed by the pore size and the amount of pores. The values of q_w and q_v are shown in Table II.

These three comonomers have different properties so that these three types of particles show different behaviors of swelling. NVP is more hydrophilic than HEMA, MMA is slightly soluble in water, and St is a hydrophobic monomer. Therefore, the swelling capacity of poly(HEMA-NVP) particles, as shown in Table II, is higher than poly(HEMA-MMA) and poly (HEMA-St) particles.

According to the analysis on the porous structures, the presence of pores has a great effect on the swelling properties. Poly(HEMA-NVP) particles have larger pores so that their swelling capacity is higher. Poly(HEMA-St) particles have the lowest swelling capacity. Even though St is more hydrophobic, some samples, such as HS-3, have higher q_w values. This could be caused by the porous structures because HS-3 has larger pores than HM-3. However, HS-3 has lower q_v values because of more rigid networks.

With the increase in the EGDMA concentration, the q_v values of these three types of particles decrease because the polymeric networks become more rigid with an increase in the EGDMA concentration, which makes them become harder to be relaxed in water. However, the changes of the q_w values indicate fluctuation resulting from the porous structures and the pore size distribution; however, it still shows a trend of decreasing. Even though the particles have more rigid networks at a higher EGDMA concentration, the q_w values still could be significant because water could be present in the pores to show higher q_w values.

The amount of porogen used in the reactions has a various effect on the swelling properties. As shown in Table II, there are maximums in the q_w and the q_v shown within the range of porogen concentration investigated. At a certain low porogen concentration, the polymeric networks can absorb more porogen and increasing porogen concentration can help increase the q_w and the q_v; however, if the porogen concentration is sufficiently high, it will promote the phase separation so that part of the porogen will separate out of the networks to produce loose networks, which will not favor the swelling of resultant polymers. This suggests that the loose networks restrict the overall swelling capacity of the polymers.

Most of the previous studies on the swelling of the HEMA copolymers were focused on the polymers which are nonporous. According to Brazel and Peppas,[10] the q_w of the nonporous poly(HEMA-NVP) containing 25 and 75 mol % of NVP is about 1.90–1.98 at 37°C, whereas q_w is around 1.60 for crosslinked poly(HEMA) with 1 mol % of EGDMA and 1–1.3 for nonporous poly(HEMA-MMA) containing 0–75 mol % of HEMA, at 37°C. In the present studies, it can be found that the q_w values are much

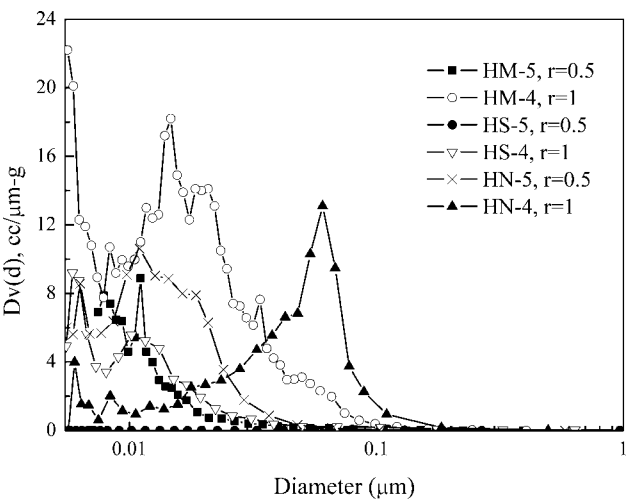

Figure 4 Pore size distribution of porous poly(HEMA-MMA), poly(HEMA-St), and poly(HEMA-NVP) particles.

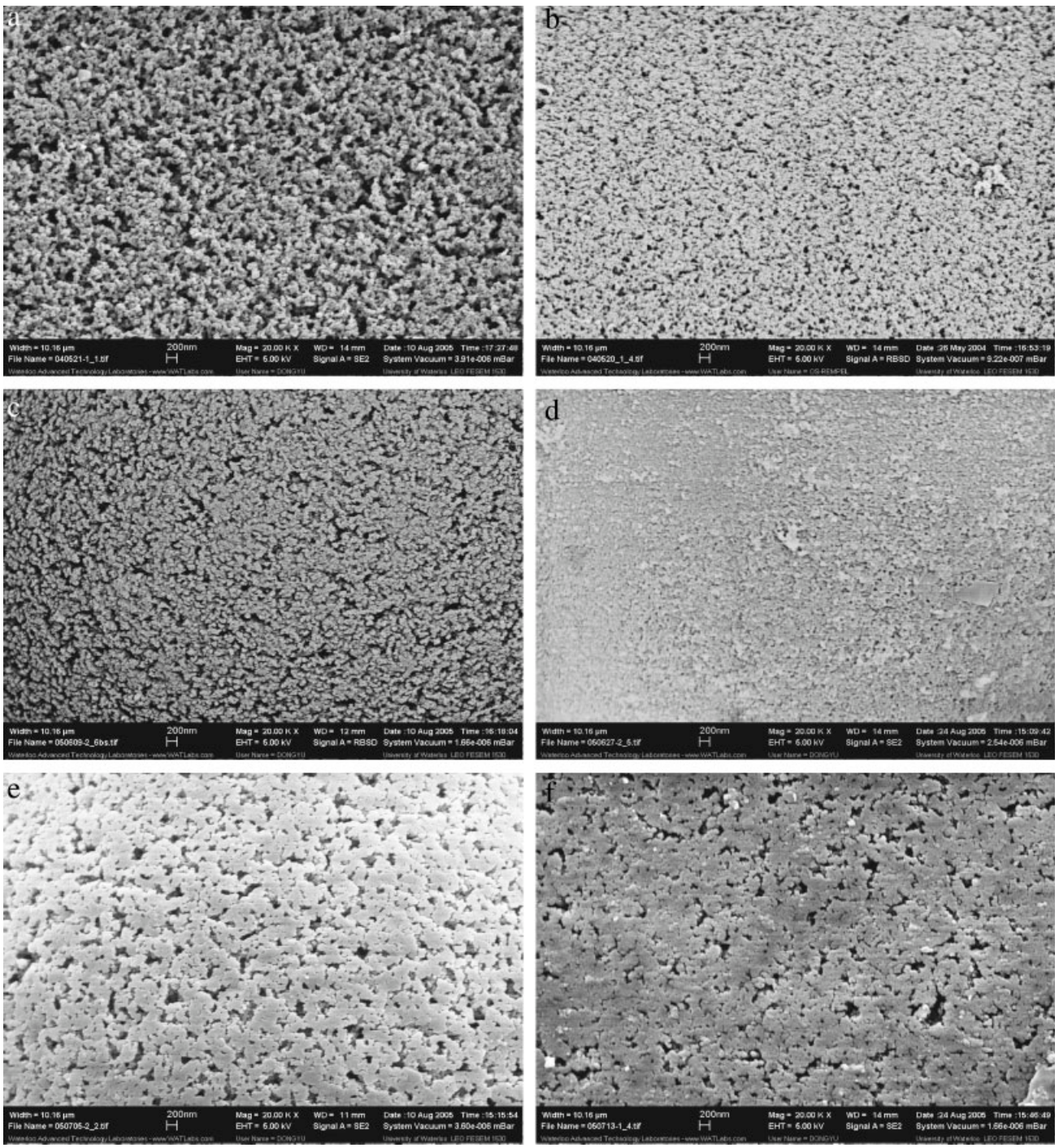

Figure 5 Porous structures of poly(HEMA-MMA), poly(HEMA-St), and poly(HEMA-NVP) particles. (a) HM-4; (b) HM-5; (c) HS-4; (d) HS-5; (e) HN-4; (f) HN-5.

higher than the reported even though the swelling experiments in the present study were carried out at room temperature.

CONCLUSIONS

The copolymer particles of poly(HEMA-MMA), poly (HEMA-St), and poly(HEMA-NVP) were synthesized by free radical suspension polymerization. Nanopores were observed in the particles. It was found that the porous structures and the swelling properties can be controlled using different comonomers and adjusting crosslinker concentrations and porogen ratios.

A hydrophilic comonomer of HEMA generates looser networks and larger pores, whereas hydrophobic one gives tighter networks and smaller pores.

A lower EGDMA concentration favors the generation of smaller pores. The pore size is larger under ν-induced syneresis than that under χ-induced syneresis.

For the polymers produced at higher porogen concentration, the pore size is bigger. The polymeric networks are more compact at lower porogen volume ratios. In the present work, a lower porogen volume ratio favors the generation of fewer pores than a higher porogen volume ratio.

NOMENCLATURE

d	Pore diameter, μm
D_{dry}	Particle diameter at dry state, μm
D_{swell}	Particle diameter at the equilibrium swelling state, μm
$D_v(d)$	Pore size distribution function, mL g^{-1} μm^{-1} or cc g^{-1} μm^{-1}
$n_{comonomer}$	Moles of MMA, St, or NVP, mol
n_{EGDMA}	Moles of EGDMA, mol
n_{HEMA}	Moles of HEMA, mol
P	Pressure, kPa
q_v	Equilibrium volume swelling ratio, mL/mL
q_w	Equilibrium weight swelling ratio, g/g
r	Porogen volume ratio, mL/mL
r_H	Monomer molar ratio, mol/mol
$V_{comonomer}$	Volume of MMA, St, or NVP, mL
V_{HEMA}	Volume of HEMA, mL
V_{oct}	Volume of 1-octanol, mL
V_p	Pore volume, mL/g or cc/g
W_{dry}	Weight of the dry polymeric particles, g
W_{swell}	Weight of the swollen polymeric particles at equilibrium state, g

Greek symbols

ν	Crosslink density
χ	Flory interaction parameter

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