Effect of Porogenic Solvent on the Porous Properties of Polymer Monoliths

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ABSTRACT: Polymer monoliths with open pores and median pore size of about 15 nm–3 μm have been successfully synthesized by photoinitiated polymerization of butyl methacrylate and ethylene glycol dimethacrylate monomers. The solubility of the monomers in a porogenic solvent is determined by Hildebrand solubility parameter, and it is found that it has great effect on the pore size of the polymers synthesized. Polymers with larger pores are usually generated with poorer solvents for the monomers. However, polymers with different pore sizes and porosities have been obtained using porogenic solvents with similar Hildebrand solubility parameters. The evaporation rate of the porogenic solvents might be another critical factor affecting the properties of the polymer monoliths. Moreover, the effect of water as a cosolvent on the pore size and porosity of the polymers have also been investigated. Polymers with larger pore size have been prepared with the presence of water due to the occurrence of earlier phase separation in the polymerization. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Porous polymers have attracted a lot of attention since a few decades ago due to their wide applications in the fields of catalysts, adsorbents, chromatography, separation and so on.[1,2] The recently developed plastic microfluidic system technology has further made the study of porous polymers becoming of great scientific as well as technological interest.[3,4] Generally, there are two basic applications of porous polymers in plastic-based microfluidic devices; one is to increase the efficient mixing of liquids by forming porous walls on open channels of microfluidic chips[5] and the other is to achieve desired functions such as prefiltering, sample concentration, and selective transport of liquids by implementing porous monolith in microchannels.[6]

There are many ways to develop porous polymer monoliths, for example, phase-separation micromolding,[7] high-internal phase emulsion polymerization,[8,9] block copolymer,[10] and particle or polymer leaching.[11] Svec[12] has also summarized the preparation methods for porous polymer monoliths in a review article. Among these approaches, porous polymers synthesized by photoinitiated free radical polymerization[13] are more suitable to microfluidic applications as a monolith can be *in situ* formed in a defined position of a flow channel by using a photomask, and further integration procedures are not needed.

Photoinitiated polymerization uses photosensitive initiator to start polymerization of monomers. The reaction can be conducted at room temperature and completed in a few minutes of time. Controlling the porous properties of the porous polymer in terms of porosity, pore size, and pore size distribution is vital for filtration, separation, and other applications.[14,15] In our previous publication,[16] we reported to synthesize polymers of butyl methacrylate (BMA) and ethylene glycol dimethacrylate (EDMA) in the presence of porogenic solvent of methanol by photoinitiation. It was found that the UV intensity and starting solution composition, including initiator fraction, EDMA crosslinking monomer fraction as well as porogen concentration, affected the porous properties of the polymers very much. Polymer monoliths with various open pores, which have great potential for microfluidic applications, were obtained by tuning these parameters.

Besides the concentration of reagents and processing parameters, the type of porogenic solvent also plays a very important part in determining the porosity and pore size of polymers. This is because the solubility of monomers in the porogenic solvent affects very much on the onset of phase separation of polymers formed from the starting solution during the free radical polymerization. For example, Rohr et al.[17] obtained acrylic polymer monoliths with pore size of 1.0 and 10.7 μm,

Table I. Hildebrand Solubility Parameter of the Materials[20]

Material	Hildebrand solubility parameter (MPa$^{1/2}$)
Ethylene glycol dimethacrylate (EDMA)	17.39
Butyl methacrylate (BMA)	16.80
60% EDMA + 40% BMA	17.15
Methanol	29.60
Decanol	19.43
Ethanol	26.00
50% decanol +50% methanol	24.52
50% ethanol + 50% methanol	27.80

respectively, by using a binary porogens of a mixture of 1-dodecanol and cyclohexanol as well as a mixture of methanol and hexane.

In this article, we continue our previous work.[16] The influences of type, concentration, and evaporation rate of porogenic solvents on the porosity, pore size, and pore size distribution of the methacrylic polymer monoliths will be studied. Moreover, the effect of water as a cosolvent on the porous properties of the polymers will also be investigated.

EXPERIMENTAL

Materials
The starting solution consisted of monomers, initiator, and porogenic solvent. Two types of acrylic monomers were used: BMA and EDMA. EDMA is a divinyl monomer; it also acted as a cross-linking agent to synthesize the cross-linked copolymers of BMA and EDMA. UV-light-sensitive compound of 2-dimethoxy-2-phenylacetophenone was used as an initiator. A single solvent or a mixture of solvents, which can dissolve the monomers while not the copolymers formed, was used as a porogenic solvent. Several types of solvents with different degree of solubility for the monomers were used to study their effects on the porous properties of the polymers. All the materials used were obtained from Sigma Aldrich.

Preparation of Porous Polymer Monolith
The monomers and initiator were dissolved in the porogenic solvent to form the starting solution. The starting solution was mixed and placed into a UV reactor (technodigm, UV flood UVF 400) equipped with UV lamp of 365 nm in wavelength. The UV intensity used was evaluated by an irradiance meter (UV cure plus II, EIT Instrument EIT Instrument Markets). The time for the polymerization was 15 min at room temperature. The monoliths formed, which usually took the shape of container, were circular disks with diameter of about 40 mm and thickness of about 1–2 mm in this work.

Characterization of the Porous Polymer
The morphology of the porous polymer was observed by several SEMs (depending on the pore size of the samples): extended pressure scanning electron microscopes (SEM, Carl Zeiss EVO 50), conventional SEM (Carl Zeiss Stereo Scan S360), and field emission scanning electron microscope (FESEM, Jeol JSM

6340F). For all the SEMs, micrographs with different magnifications were taken to get a comprehensive understanding of the morphology of a polymer monolith. The porous properties of the polymer monolith such as porosity, pore size, and pore size distribution were determined using mercury intrusion porosimetry (AutoPore IV 9500, Micromeritics Instrument Corporation). It is noted that only open pores can be accessed by the mercury in this instrument; thus, the information obtained are all for open pores.

RESULTS AND DISCUSSION

Effect of Porogen Type
Two types of monomers are used in this work: BMA with one vinyl group and EDMA with two vinyl groups, the latter also acts as cross-linking agent. Therefore, the polymerization and cross-linking of BMA and EDMA occur simultaneously in the reaction. The cross-linked polymers formed precipitate from the solution after becoming insoluble in the porogenic solvent—phase separation occurs at this moment. The precipitated polymers form nuclei and finally grow into porous polymer matrix with the further polymerization and cross-linking.[18,19]

The porous properties of the polymers developed depend greatly on the onset of phase separation during the early stage of the polymerization and cross-linking, while the solubility of the monomers in the porogenic solvent is one of the main factors determining the occurrence of the phase separation. The solubility of monomers in solvents can be evaluated using Hildebrand solubility parameters (δ), which provides a numerical estimation of interaction degree between materials. Materials with similar solubility parameters will be able to interact with each other, resulting in solvation, miscibility, or swelling. Table I lists the Hildebrand solubility parameters of the monomers and porogenic solvents used in this work.[20] Mixture of solvents is also used in the work to vary solubility parameter of porogen and to compare its effect with the individual solvent. The
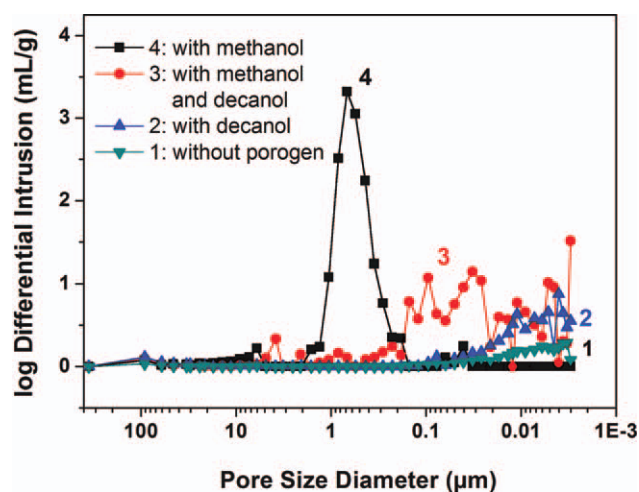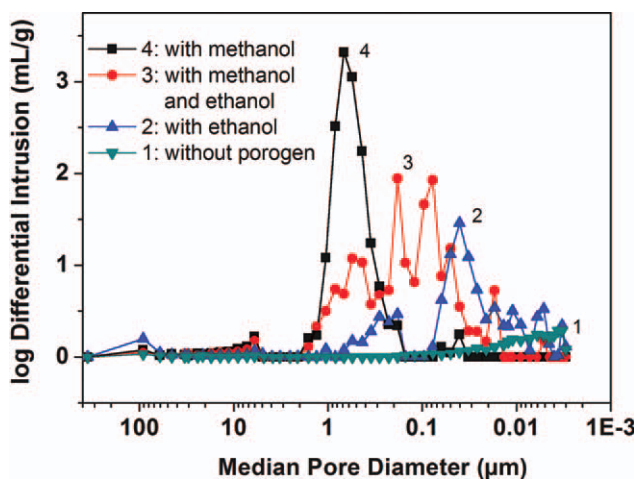

Figure 1. Pore size distribution of the polymers obtained with porogen of methanol and decanol (BMA/EDMA = 40/60, porogen fraction = 55%, initiator fraction = 4%, and UV intensity = 63.57 mW/cm^2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. Pore size distribution of the polymers obtained with porogen of methanol and ethanol (BMA/EDMA = 40/60, porogen fraction = 55%, initiator fraction = 4%, and UV intensity = 63.57 mW/cm^2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solubility parameter of a mixture is calculated by averaging the Hildebrand values of the individual solvents with weight percentage. BMA and EDMA have a similar Hildebrand solubility parameter of about 17 MPa$^{1/2}$, the solvents selected have a broad range of Hildebrand solubility parameters, and they are arranged from smallest to biggest as follows: decanol, methanol + decanol, ethanol, methanol + ethanol, and methanol. Decanol with δ of 19.43 MPa$^{1/2}$ has the most similar Hildebrand solubility parameter to the monomers, while methanol with δ of 29.6 MPa$^{1/2}$ has the furthest solubility parameter to the monomers. Thus, among the solvents used, decanol is the best solvent for the monomers. and methanol is the worst solvent for the monomers.

Figures 1 and 2 show the pore size distribution of the polymers with different types of porogens obtained from mercury porosimetry, and Table II tabulates the porosity and median pore size of the polymers obtained. It is noted that the porosity of the polymers has been corrected with a corresponding blank run. The blank run uses the sample with the same composition as the testing samples, but with no addition of porogenic solvent. The blank correction is necessary due to the compressible

Table II. Porous Properties of the Polymers Obtained with Different Types of Porogens

Porogenic solvent	Porosity (%)	Median pore diameter (μm)
Methanol	51.09	0.67
Decanol	28.96	0.014
Ethanol	36.09	0.049
50% methanol + 50% decanol	38.17	0.042
50% methanol + 50% ethanol	37.07	0.18

BMA/EDMA = 40/60, initiator = 4%, porogen fraction = 55%, and UV intensity = 63.57 mW/cm^2.
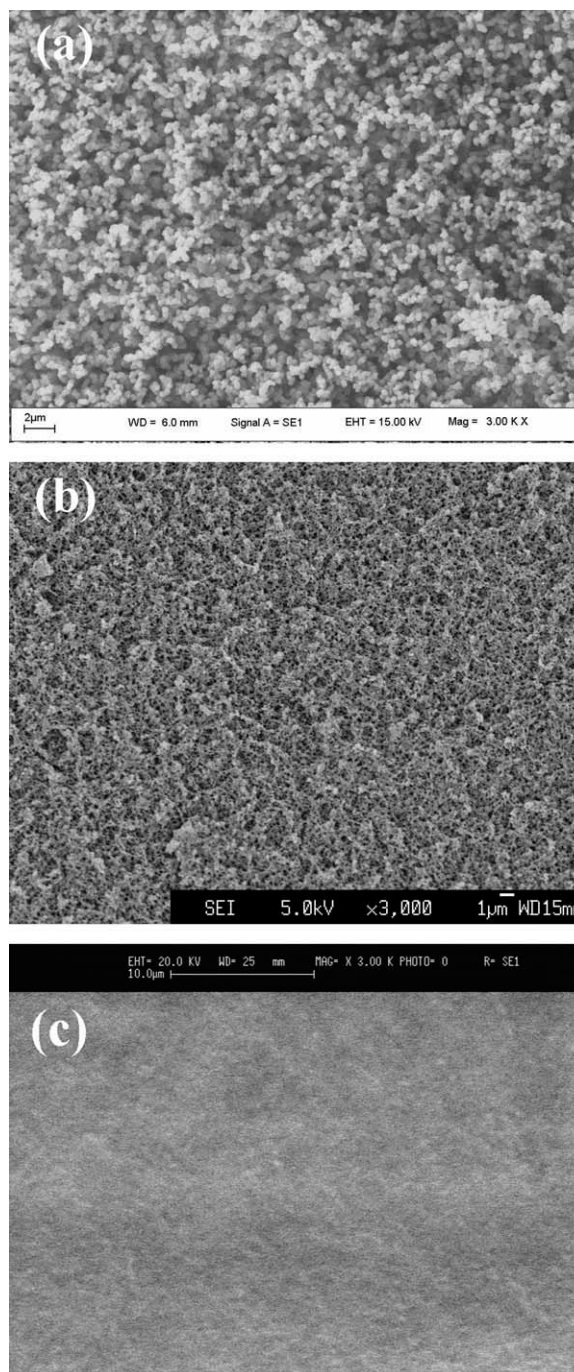

Figure 3. SEM images of the polymers obtained with different types of porogens (BMA/EDMA = 40/60, porogen fraction = 55%, initiator fraction = 4%, and UV intensity = 63.57 mW/cm^2) (a) methanol, (b) methanol + decanol, and (c) decanol.

nature of polymers.[21] It can be seen from the figures and table that the polymer monoliths obtained contain only small amount of small pores when a good solvent of decanol is used as a porogen. On the other hand, polymers synthesized have high porosity and large pores when a poor solvent of methanol is used as a porogen. The properties of the polymers are in between of the polymers obtained with the individual solvents when a mixture of methanol and decanol or mixture of

Table III. Porous Properties of the Porous Polymers with Different Concentrations of Water

Water content (%)	Porosity (%)	Median pore size (μm)
0	51.09	0.67
15	45.29	2.79
25	33.15	2.42

BMA/EDMA = 40/60, initiator = 4%, methanol fraction = 55%, and UV intensity = 63.57 mW/cm^2.

methanol and ethanol is used as a porogen. Nevertheless, the pore size distribution of the polymers with mixture of the porogens is broader than the polymers obtained with the single porogenic solvent.

With a good solvent for the monomers as a porogen, the phase separation of the polymers formed from the initiating solution occurs at later stage of the polymerization and cross-linking when compared with that using a poor solvent. The precipitated polymers form nuclei, and the nuclei compete with the monomers in solvation to the solvent during the subsequent reaction. In the situation of a good solvent for the monomers, the local monomer concentration in the solvent is higher than that in nuclei. Thus, the sizes of the nuclei and the corresponding particles are small, and the pores formed between the particles are also small. In the situation of a poor solvent for the monomers, the nuclei are better solvent to the reagents, and the monomers prefer to swell in the nuclei rather than in the solvent. As a result, the further polymerization and cross-linking are mainly in these swollen nuclei, and the particles grown from nuclei are large in size, same as the pores.

Figure 3 shows the SEM images of the porous polymers with methanol, decanol, and mixed solvents of methanol and decanol. The pores obtained from methanol are obviously much larger than those from the other two porogens. Nevertheless, it is noted that the pore size from SEM is much larger than that
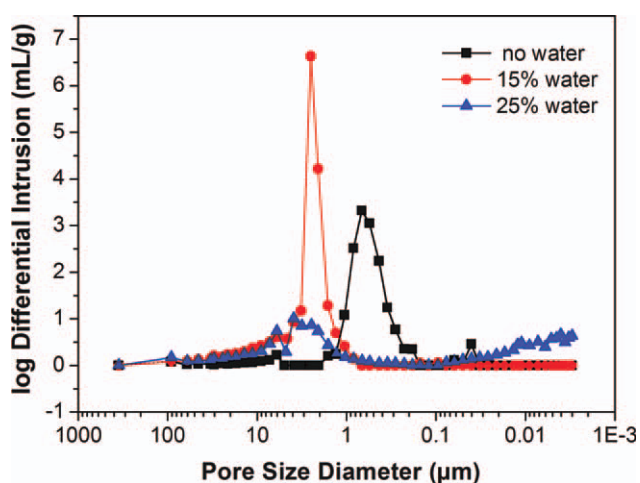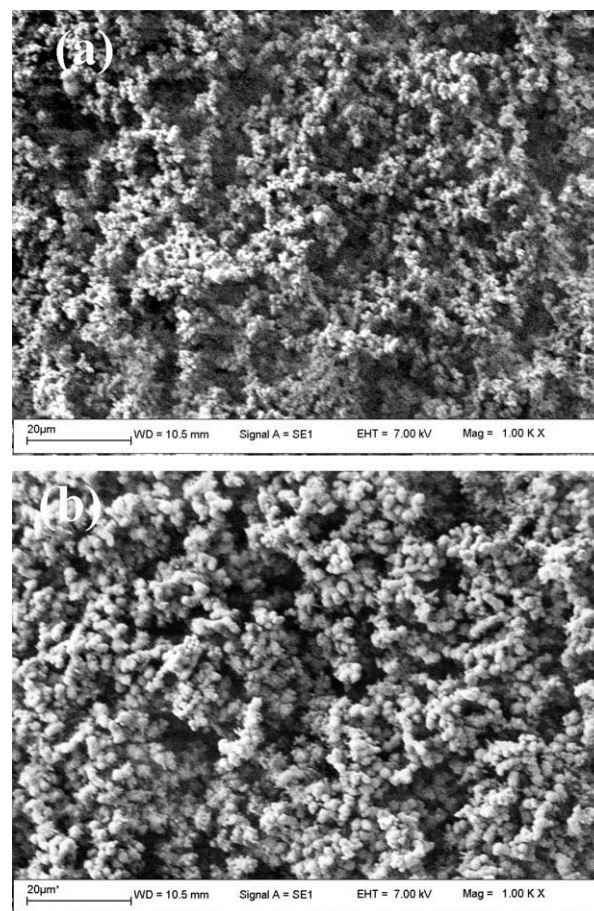

Figure 5. SEM images of the polymers with different contents of water (BMA/EDMA = 40/60, methanol fraction = 55%, initiator fraction = 4%, and UV intensity = 63.57 mW/cm^2): (a) with 15% of water and (b) with 25% of water.

obtained from mercury intrusion for all the three samples, this is because the pore size measured with porosimetry is the largest entrance or throat toward a pore while SEM reveals the cavity size of a pore.
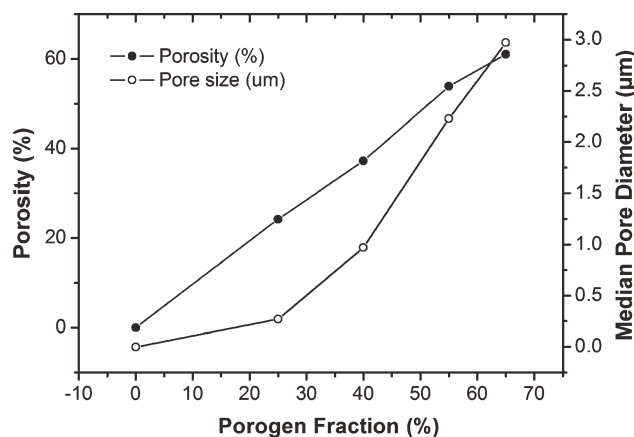

Figure 4. Pore size distribution of the polymers with different water concentrations (BMA/EDMA = 40/60, methanol fraction = 55%, initiator fraction = 4%, and UV intensity = 63.57 mW/cm^2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. Porosity and pore size of the polymers as a function of methanol fraction (BMA/EDMA = 50/50, initiator fraction = 3%, and UV intensity = 63.57 mW/cm^2).
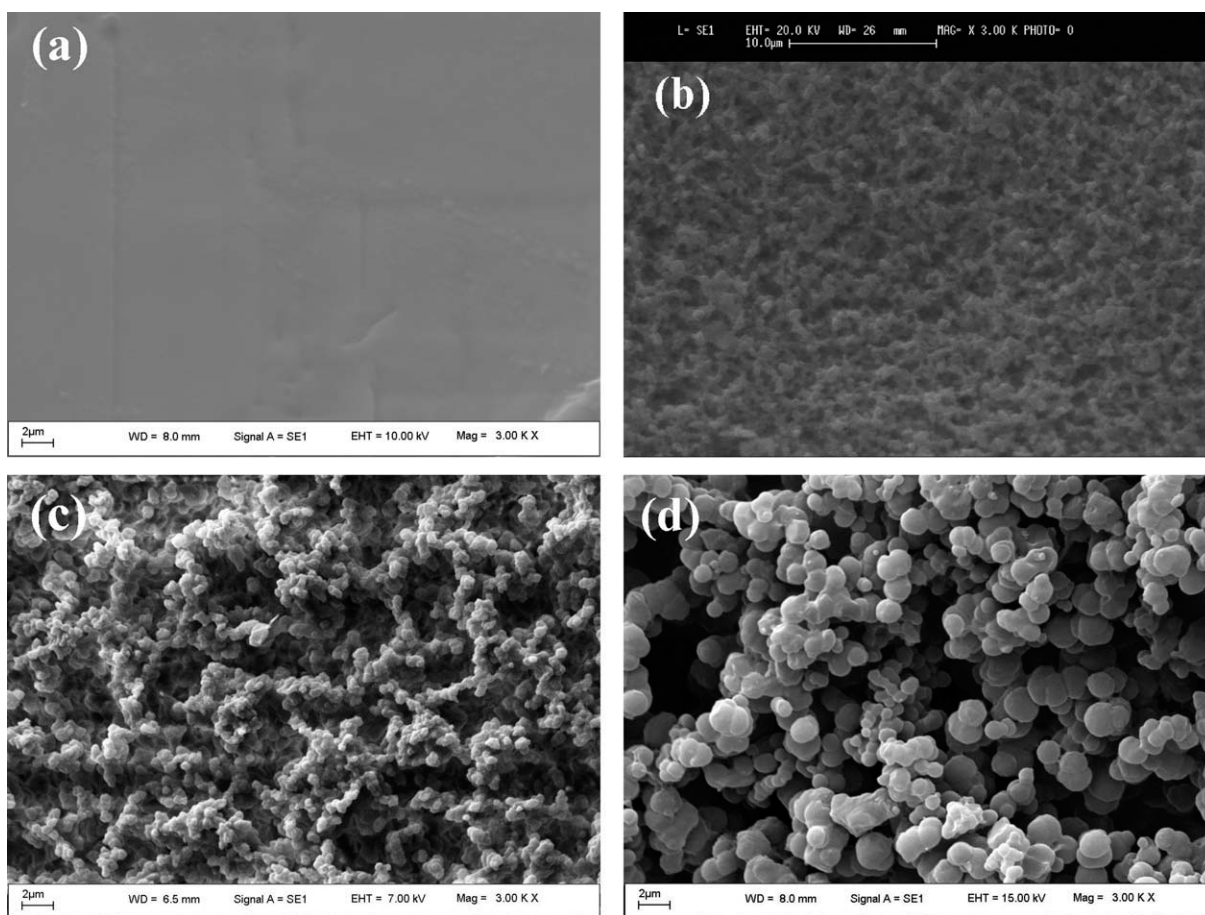
Figure 7. SEM images of the porous polymers with different methanol fractions (BMA/EDMA = 50/50, initiator fraction = 3%, and UV intensity = 63.57 mW/cm^2): (a) without addition of methanol, (b) methanol = 25%, (c) methanol = 55%, and (d) methanol = 65%.

It is obvious in Figure 2 that the pore size distribution shifts to the smaller size side when ethanol is used as a porogen compared to methanol. With ethanol, polymer produced has pore
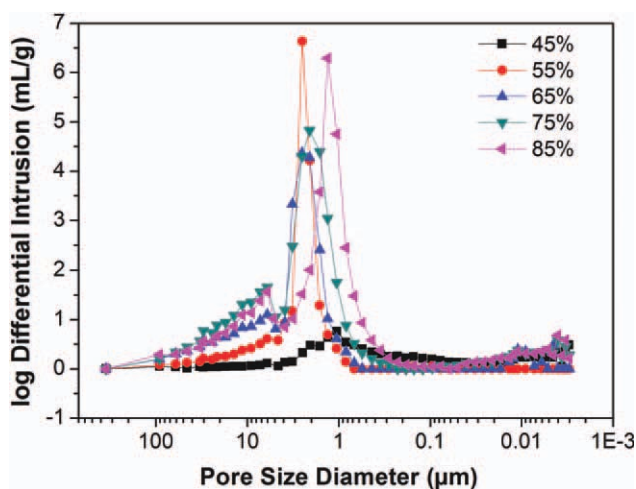

Figure 8. Effect of methanol fraction on the porous properties of the polymers in the presence of 15% water (BMA/EDMA = 40/60, initiator fraction = 4%, and UV intensity = 63.57 mW/cm^2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

size of about 0.049 μm and porosity of about 36.09%; with methanol, polymer produced has pore size of about 0.67 μm and porosity of about 51.09%, the median pore size with methanol is about 14 times larger than that with ethanol. However, the solubility parameter of ethanol is only slightly smaller than that of methanol—about 26.0 MPa$^{1/2}$ for ethanol and 29.6 MPa$^{1/2}$ for methanol, respectively. There are some other factors, besides solubility parameter, which affect the porous properties very much. Further investigations are needed to determine the factors; nevertheless, one of them might be evaporation rate. Evaporation rate for methanol and ethanol is about 5.9 and 1.4, respectively (evaporation rate of n-butyl acetate is standardized as 1.0[22,23]). Additionally, vapor pressures for methanol and ethanol are about 97.68 and 44.6 mm Hg at 20°C. Therefore, methanol evaporates much faster than ethanol at room temperature. Actually, the reaction temperature is higher than room temperature as temperature of the UV chamber increases with UV irradiation during the polymerization. It is about 63°C after 15 min of the reaction under UV intensity of about 63.57 mW/cm^2. With higher evaporation rate than ethanol, more methanol porogen is removed before the polymerization completes, which leaves more open pores behind. Moreover, phase separation during polymerization occurs earlier with methanol, and this results in the formation of larger pores. Similar phenomenon

Table IV. Porous Properties of the Porous Polymers with Different Porogen Concentrations

Porogen fraction (%)	Porosity (%)	Median pore size (μm)
45	28.30	0.63
55	45.29	2.79
65	51.72	3.13
75	61.30	2.78
85	54.41	1.64

BMA/EDMA = 40/60, initiator = 4%, UV intensity = 63.57 mW/cm^2, and water fraction = 15%.

has also been observed with other types of porogens in this work. Hildebrands solubility parameter for the mixture of methanol and ethanol is about 27.8 MPa$^{1/2}$, which is slightly higher than that of ethanol, but the median pore size of the resultant polymer increases greatly from about 0.049 μm with ethanol to 0.18 μm with the mixture of methanol and ethanol.

Effect of Water as a Cosolvent

Hildebrand solubility parameters for monomers and water are about of 17 and 47.5 MPa$^{1/2}$, respectively. Thus, if water is used as a solvent, it will have a great impact on the occurrence of the phase separation and consequently on the pore properties of the polymers obtained. Water is not able to dissolve the polymers formed from BMA and EDMA, but it is also not a good solvent for the monomers due to hydrophobic nature of the monomers; it can only be used as a cosolvent with other organic solvents such as methanol. In this work, the porous structure of the polymer monoliths formed with methanol and various amount of water is compared to that formed with only methanol as a porogenic solvent. Table III and Figure 4 show the porous properties of these polymers. Polymers with 0 and 15% of water (weight percentage of total amount of reagents and solvents) show narrow pore size distribution, while polymers with 25% of water show two types of pores; one is small pores around 0.01 μm and the other is big pores around 4 μm. The median pore sizes for the polymers with water are obviously larger than the polymer without water, but the porosity of the polymers decreases with increasing water fraction. The solubility of monomers of BMA and EDMA in methanol is adversely affected with the presence of water, which accordingly affects the porous properties of the polymers. Figure 3(a) shows SEM of polymer monolith without addition of water, and Figure 5 shows the morphology of the polymers with different amounts of water. The pores are larger for the polymers with water, which is consistent with the results obtained from mercury intrusion.

Effect of Porogen Concentration

The porogenic solvent concentration is another factor used to tune the porous structure of the polymers. Figure 6 shows effect of the fraction of porogenic methanol on the porosity and pore size of the polymers, and Figure 7 shows the SEM images of the polymers with different fraction of methanol.

With no addition of porogenic methanol, there are no pores observed in SEM. With increase in methanol fraction, both pore

size and porosity of the polymers increase. This is understandable as methanol occupies more spaces at higher fraction; thus, higher porosity and larger pores can be obtained after it is removed. Nevertheless, the polymerization reaction becomes difficult when methanol fraction is increased up to 75% and beyond. The monomers are separated by the large amount of
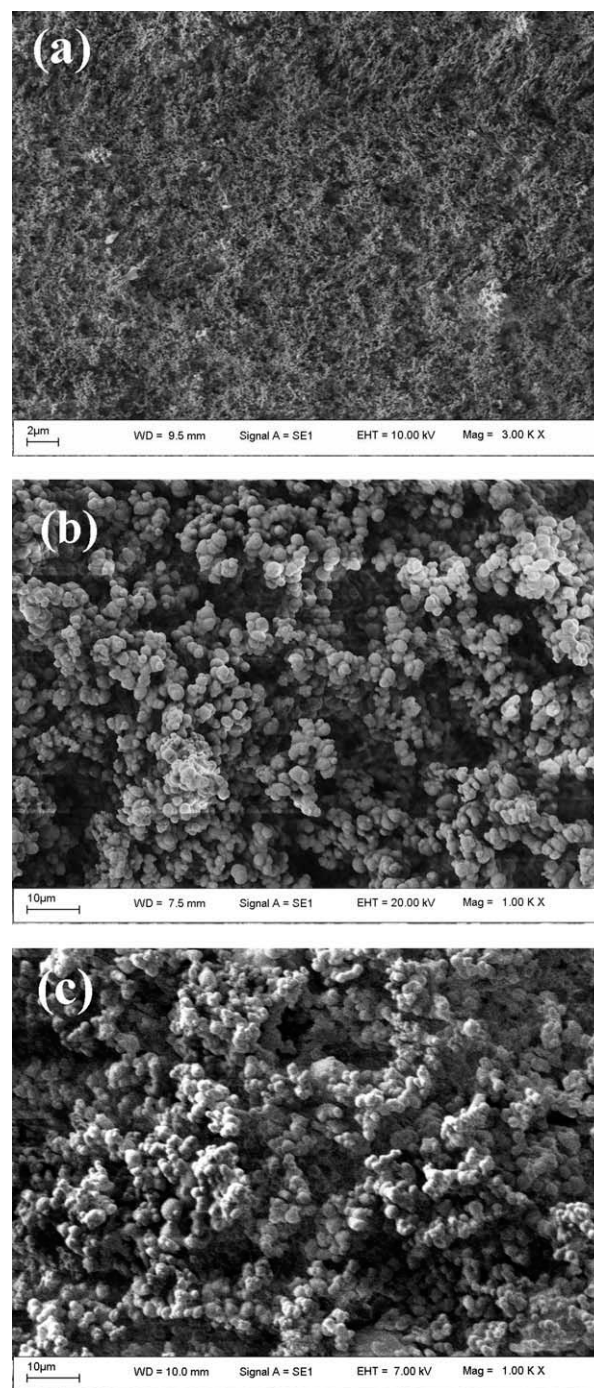

Figure 9. SEM images of the porous polymer with different methanol fractions in the presence of 15% of water (BMA/EDMA = 40/60, initiator fraction = 4%, and UV intensity = 63.57 mW/cm^2): (a) methanol = 45%, (b) methanol = 65%, and (c) methanol = 75%.

solvent, and so the propagation of the molecular chains is disturbed.

Figure 8 shows the pore size distribution of the polymers as a function of methanol fraction with 15% of water as a cosolvent. Table IV tabulates the porous properties determined by mercury porosimetry. Both pore size and porosity of the polymer with 45% of methanol are much smaller than those of polymers with 55% of methanol. Further increase in methanol fraction until about 75%, porosity of the polymers gradually increases, but the pore size does not change very much. At the methanol fraction of 85%, both porosity and pore size decrease due to the disturbance of solvent on the polymerization. Additionally, at lower methanol fraction of 45 and 55%, there is one peak in the pore size distribution. However, with the increase in methanol fraction, there is obviously bimodal pore size distribution, one is in the vicinity of 1–2 μm and the other is around 7 μm. The morphology of the polymers observed by SEM is shown in Figure 9.

CONCLUSIONS

Porous polymers with controlled porous properties have been successfully produced by photoinitiated free-radical polymerization. Both porogen concentration and porogen type have great effects on the porous properties of the polymers. Generally, both porosity and pore size of the polymers increase with the porogen concentration. The addition of water as cosolvent also benefits to obtain the polymers with large pores, but the porosity of the polymers has been slightly decreased. Additionally, the porous properties of the polymers synthesized depend greatly on the properties of porogenic solvents. Polymers with large pores have been obtained with solvents, which are poor solvents for the monomers and have high evaporation rate.

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