

# Water-Swelling Behavior of Hydrophobic Porous Copolymer Resins Composed of Two Kinds of Crosslinkers

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**ABSTRACT:** Hydrophobic, but water-swella-ble, porous copolymer resins composed of divinylbenzene (DVB) and ethylene glycol dimethacrylate (EGDM) or ethylene glycol diacrylate (EGDA) were prepared by using purified DVB (98.8%) in the presence of toluene as porogen. The EGDM/DVB resins thus obtained, whose polarity was nearly identical to that of the resins based on DVB and methyl methacrylate (MMA) at the same DVB levels, were water-swella-ble by direct contact with water up to a DVB content of 64%, whereas the latter did not swell in water at any DVB levels. EGDA is also hydrophobic, but with a polarity greater than that of EGDM. As a result, the EGDA/DVB resins were

more water swella-ble than EGDM/DVB resins, and could also be prepared as water-swella-ble materials by using technical DVB (79.3%), besides the use of the purified DVB. All these results were explained on the basis of the network rigidity (crosslinking density) and the polymer polarity of the resins that were formed in the presence of a well-solvating porogenic solvent. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 997–1004, 2004

**Key words:** water-swella-ble copolymers; divinylbenzene; copolymerization; swelling; resins

## INTRODUCTION

We recently found that by copolymerization of purified DVB (98.8%) and methyl acrylate (MA) in the presence of a solvating porogenic solvent, the resulting porous MA/DVB resins are wettable or swella-ble in water, regardless of the hydrophobic character of homopolymer derived from DVB or MA.<sup>1</sup> This is the first report that one can obtain a polymer material that is hydrophobic in nature, but could be wetted or swell by direct contact of the resin with water. The result is striking because it is well known that hydrophobic polymers present a water-repellent surface, so that the pores of the hydrophobic porous copolymers cannot be filled with water spontaneously, and the gel phase of these copolymers cannot swell in water. Generally accepted theories predict the swelling of a polymer network to depend only on the thermodynamic quality of the solvent, the degree of crosslinking, and the functionality of junction points of the network.<sup>2</sup> The swelling ability of the hydrophobic MA/DVB resins in water was therefore attributed to the existence of the inner stresses in the strained polymer network of the MA/DVB resins, and at the same time, the interaction between polymer and water was also considered a critical factor for the swelling of the resins in water

directly, although such a weak interaction is usually negligible in the case of conventional hydrophobic polymers.

A porous copolymer that is hydrophobic in nature, but has the ability to swell in water directly, should also be very valuable from the standpoint of practical application. For example, instead of the usual method to increase the hydrophilicity of the ST/DVB copolymer by introducing a hydrophilic component,<sup>3</sup> such as carboxylic and sulfonic acid groups, or a hydroxyl-containing monomer, our findings provide a new, unique approach to obtain a water-wettable or -swella-ble polymer adsorbent.

To ascertain more of the water-swelling properties of this kind of hydrophobic copolymer resin, extensive experimental work has been done by preparing the resins using a wider range of monomers with different hydrophobicities. On the basis of the knowledge that the crosslinking density is of great importance for hydrophobic porous resins to acquire the water-swelling ability,<sup>1</sup> one of the efforts was to synthesize the porous resins with a higher degree of crosslinking by copolymerization of two kinds of crosslinkers. One of the crosslinkers is DVB, either the purified (98.8%) or commercially available variety (79.3%); the other is ethylene glycol dimethacrylate (EGDM) or ethylene glycol diacrylate (EGDA) with different polarities, whereas either of them is hydrophobic. The research on the water-swelling behavior of the resins thus obtained provided additional evidences to support the

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hypothesis that the inner stresses in the strained polymer network, and the weak interaction between polymer and water, are the driving forces that induce the direct swelling of the hydrophobic copolymer resins in water. This article reports the results.

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA), ethyl methacrylate (EMA), *n*-butyl methacrylate (BMA; Shanghai General Factory of Reagents), ethylene glycol dimethacrylate (EGDM) (Su Zhou An Li Chemical Factory), and technical divinylbenzene (DVB, 79.3%) were vacuum distilled to remove inhibitors before use. Purified DVB was obtained according to the method of Popov and Schwachula,<sup>4</sup> in most cases with the purity of 98.8% (49.3% *p*-DVB and 49.5% *m*-DVB). Ethylene glycol diacrylate (EGDA, 96%) was prepared according to the method reported by Xie et al.,<sup>5</sup> with a further fractional distillation. Ethylvinylbenzene (EVB) containing a small amount of DVB was obtained by fractionating the residue of technical DVB in which DVB was previously separated. Most other chemicals were used as received.

### Synthesis of resins

Copolymer resins were prepared by the usual suspension polymerization in the presence of toluene or its mixture with *n*-heptane as porogen.<sup>6,7</sup> The monomers were first mixed well with the porogen to form an organic phase in which the initiator, 2,2'-azobisisobutyronitrile, was added in the amount of 1 wt % of monomers. The organic phase mixture was then added, at a 1 : 3 volume ratio, to the aqueous phase containing 0.2% hydroxyethyl cellulose and 20% NaCl. The polymerization was allowed to proceed at 80°C for the EGDM/DVB monomer system or at 70°C for the other monomer systems for 14 h, and after a further reaction at 90°C for 4 h, the resulting polymer resins were washed with hot water and extracted thoroughly with acetone in a Soxhlet apparatus; the acetone-swollen resins were finally dried *in vacuo* at 70°C. For all resin samples, the contents of DVB, EGDM, EGDA, and other monomers in the starting reaction mixture are expressed as mole percentage of the total amount of monomers. (The purity of monomers, other than the technical DVB and EVB, were taken as approximately 100% in calculating the contents.) Except for additional illustration, the toluene was used as porogen at a 2 : 1 ratio (vol/vol) to the monomers. When a mixture of toluene and *n*-heptane was used as porogen, the *n*-heptane content was expressed as volume percentage of the total volume of the mixed po-

rogen, and in this case the ratio of porogen to monomers was 1.4 : 1.

### Methods

The apparent density ( $d_a$ , g/mL) and true density ( $d_t$ , g/mL) of the resins were measured according to the methods previously described,<sup>6,8</sup> from which the pore volume  $V_p$  (mL/g) was calculated using the following equation:

$$V_p = 1/d_a - 1/d_t$$

The solvent (toluene or water) uptake (mL/g) was measured by a centrifuge method, with a relative error of 3% or less for samples where the value of solvent uptake was above 0.3 mL/g.<sup>6,9</sup> For the swelling experiments in water, all the values of water uptake  $V_w$  were measured by direct contact of the resin sample with water (direct swelling). Except for the dynamic swelling experiments, the water uptake was always measured after the swelling equilibrium was achieved; this usually took about 2 days at room temperature, but for some samples the equilibrium time extended to 2 weeks or more depending on the resin compositions. In the dynamic swelling experiments, the degree of swelling  $Q$  (%) at different contact times was calculated as  $Q = V_{wt}/V_w \times 100\%$ , where  $V_{wt}$  is the water uptake at swelling time  $t$  and  $V_w$ , as just denoted, is the equilibrium water uptake measured by direct contact of the sample with water.

## RESULTS AND DISCUSSION

### EGDM/DVB resins

First, the three kinds of alkyl methacrylate esters (AMA), MMA, EMA, and BMA, were used to synthesize porous resins with purified DVB as crosslinker and the toluene as porogen. Table I presents the water uptake and pore volume of the resulting AMA/DVB resins with different compositions. The water uptake was measured by direct contact of resin with water. In general, the solvent uptake of porous resins can be considered as the result of two processes: (1) filling of pores by solvent and (2) the gel phase swelling.<sup>10</sup> Because no single measurement could distinguish these two processes, both water uptake and pore volume in the dry state were measured to assess whether the pores were fully filled by water, and whether the water could swell the gel phase of the resins. By comparing water uptake with pore volume in Table I, it is seen that for all AMA/DVB resins with different DVB contents, the value of water uptake is much less than the corresponding pore volume, which indicates that only a small part of the resins' pores were filled

**TABLE I**  
**Water Uptake and Pore Volume of AMA/DVB Resins with Different Compositions<sup>a</sup>**

Copolymer resin	AMA/DVB				
	90/10	80/20	70/30	60/40	50/50
MMA/DVB					
$V_w$ (mL/g)	0.016	0.166	0.373	0.413	0.304
$V_p$ (mL/g)	0.028	0.541	1.227	1.449	1.475
EMA/DVB					
$V_w$ (mL/g)	0.021	0.040	0.084	0.129	0.126
$V_p$ (mL/g)	0.040	0.132	0.899	1.081	1.231
BMA/DVB					
$V_w$ (mL/g)	0.028	0.030	0.027	0.036	0.062
$V_p$ (mL/g)	0.051	0.067	0.178	0.436	0.721

<sup>a</sup> AMA/DVB resins were prepared by copolymerization of purified DVB with methyl methacrylate (MMA/DVB), ethyl methacrylate (EMA/DVB), or *n*-butyl methacrylate (BMA/DVB);  $V_w$  is water uptake measured by direct contact of resin with water and  $V_p$  is pore volume.

with water, and the water cannot directly wet or swell any of these AMA/DVB resins.

We previously showed that two conditions are necessary for a hydrophobic porous copolymer to swell in water directly.<sup>1</sup> First, the copolymer should have a rigid network (high crosslinker content) that was formed in a well-solvating medium. Second, the polarity of the copolymer must be enhanced by incorporating a sufficient amount of polar hydrophobic monomer unit to reach a critical value. In Table I, although all the resins are not directly water-swelling, the water uptake is different for each individual resin. If we make a comparison between the AMA/DVB resins derived from different AMA monomers of BMA, EMA, and MMA, we can find that water uptake increases with a decrease in alkyl side-chain lengths from C<sub>4</sub> to C<sub>1</sub>. This reflects the effect of polymer polarity on the water uptake of these AMA/DVB resins based on different AMA monomers, and implies that a further decrease of the number of methyl may result in a water-wettable or water-swelling resin, as is the case with MA/DVB resins reported in the previous study.<sup>1</sup>

On the other hand, if we make a comparison between the AMA/DVB resins with different DVB contents, we can find that in a wide range of DVB levels, the water uptake of all three kinds of AMA/DVB resins increases with increasing the amount of DVB in resins, indicating that an increase in rigidity of polymer network leads to the enhancement of the water-wetting ability of the AMA/DVB resins. For MMA/DVB resins, it is predictable that the resins may become water-wettable or water-swelling, if the polymer network of the resins becomes more rigid and the MMA content is above a certain level. However, the problem is that, even using purified DVB, the fraction of DVB in the MMA/DVB resins is restricted

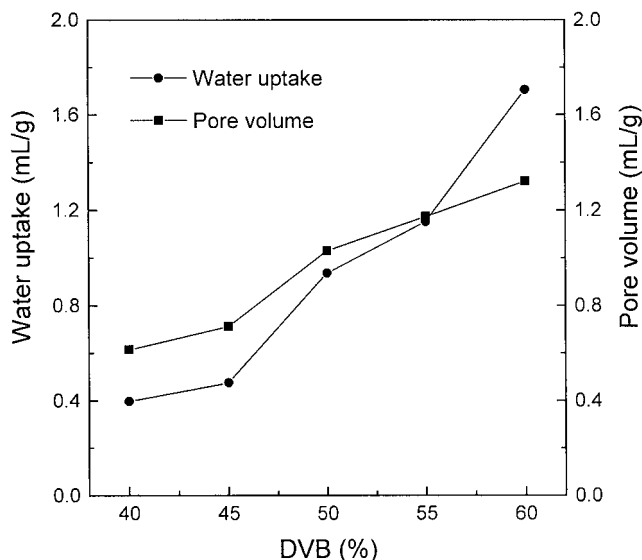
by the portion of MMA, which is necessary for maintaining the polymer polarity above a critical value. Accordingly, the crosslinking density of the MMA/DVB resins cannot reach a higher level. We therefore attempted to replace MMA with a bifunctional methacrylate monomer of EGDM, in the synthesis of the resins. EGDM, with the component nearly the same as that of MMA, is less hydrophobic than DVB, but it still forms a hydrophobic polymer and its polarity should be very close to that of MMA. Table II presents the water uptake and pore volume of the EGDM/DVB resins thus obtained with different DVB contents.

As can be seen, in a wide range of DVB contents (64% or less), the value of water uptake is greater than the corresponding pore volume in all cases, showing that the water not only fills in the existing air-filled (permanent) pores, but also penetrates into the gel phase of the resins (i.e., the spontaneous wetting and swelling of the resins occurs). The spontaneous wetting could also be judged by the float-sink test of the dry sample in water.<sup>11</sup> Whereas the resins with DVB content above 64% remain on the surface of the water, the resins with DVB content less than 64% easily sink into the water. Of course, the swelling of this kind of resin is different, to a great extent, from the swelling of a gel-type resin in solvating solvents. As a porous copolymer, the swelling of the EGDM/DVB resins is a very complex process that must be discussed by considering the expansion of the permanent pores, and the "reopening" of the collapsed pores.<sup>12-14</sup> However, the gel phase of the porous copolymers, as we know, is composed of highly crosslinked microgel particles that are closely linked together by fewer crosslinked networks to form a continuous phase.<sup>15-18</sup> In this case, any expansion of the permanent or the collapsed pores is not a separate course, and it must be accompanied by either the deformation of the gel phase or the relaxation of the crosslinked network chains. Therefore, there must be some driving forces that cause the hydrophobic porous resins to increase their volume on absorbing water. In our previous article,<sup>1</sup> the driving forces were considered from the inner stresses in the strained polymer network, and the weak interaction

**TABLE II**  
**Water Uptake and Pore Volume of EGDM/DVB Resins<sup>a</sup> with Different Compositions**

Parameter	EGDM/DVB					
	60/40	50/50	44/56	36/64	31/69	26/74
$V_w$ (mL/g)	1.78	1.74	1.52	1.25	0.52	0.29
$V_p$ (mL/g)	1.26	1.37	1.24	1.12	1.25	1.03

<sup>a</sup> EGDM/DVB resins were prepared by copolymerization of purified DVB with EGDM;  $V_w$  is water uptake measured by direct contact of resin with water and  $V_p$  is pore volume.



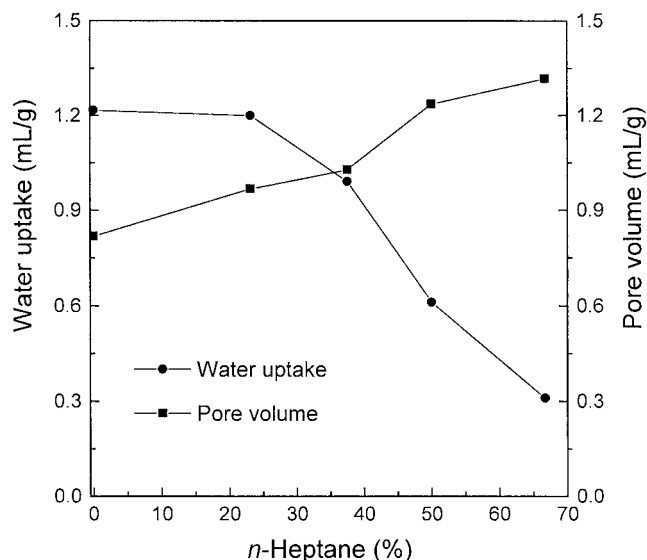
**Figure 1** Dependency of water uptake and pore volume of EGDM/DVB resins on the DVB content. The resins were prepared with EGDM content fixed at 40%.

between polymer and water, which were closely related to the rigidity and the formation history of the polymer network, and the polymer polarity of the resins.

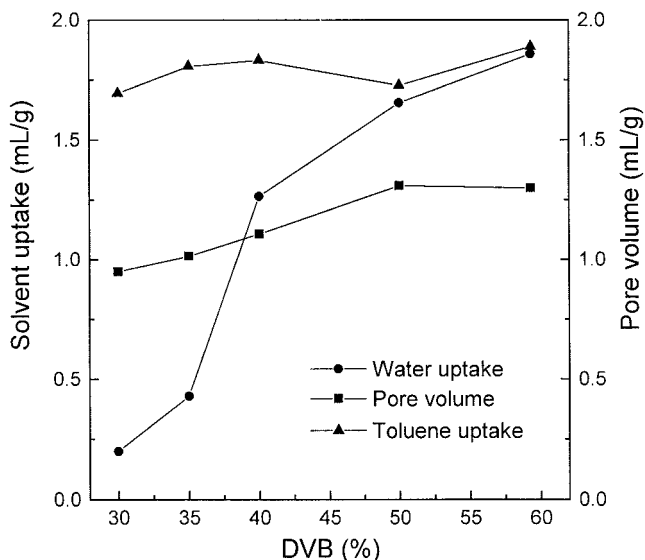
Because the polarity of EGDM/DVB and MMA/DVB resins is nearly the same at the same DVB levels, the striking difference in water-swelling ability between these two kinds of resins may be considered to result from only the change in crosslinking density or rigidity of the polymer network, which leads to the greater inner stresses in EGDM/DVB than those in MMA/DVB resins. Figures 1 and 2 provide strong evidences of the effect of the rigidity and formation history of the EGDM/DVB resins on their swelling ability in water.

Figure 1 shows the dependency of water uptake and pore volume of the EGDM/DVB resins on the DVB content. The resins were prepared with EGDM content fixed at 40%, and DVB content varied from 40 to 60% by incorporating the third comonomer of EVB. In this way, the polar/nonpolar composition for these resins will keep a nearly constant value, whereas the degree of crosslinking is varied with a change in DVB content. As can be seen, at lower DVB levels the value of water uptake is less than the corresponding pore volume, but with an increase in DVB content the difference between them decreases. At 60% DVB, the resin becomes water-swallowable, as judged by the value of water uptake, which is much greater than the pore volume. Because the only change in Figure 1 is the DVB content, it is clear that the water-swelling ability of the 60% DVB resins should be attributed to the increased crosslinking density (rigidity) of the polymer network, which leads to an increase in inner stresses in the dry resin products.<sup>1,19–21</sup>

Figure 2 shows the dependency of water uptake and pore volume of the EGDM/DVB resins on the *n*-heptane content in the mixed porogen of toluene and *n*-heptane. The resins were prepared with EGDM and DVB contents fixed at constant levels of 40 and 60%, respectively, and with the *n*-heptane content varied from 0 to 67%. It is known that the solvating state of the growing polymer chains during the crosslinking reaction is important to the development of the inner stresses.<sup>6,19</sup> In a well-solvated state, the crosslinks fix the stretched polymer chains, and the subsequent deswelling of the formed polymer networks upon removal of porogen is accompanied by a rapid growth of the stresses in the polymer networks, as a result of the retraction and deformation of the networks. In Figure 2, at *n*-heptane content of 23% or less, the water uptake is much greater than the value of the corresponding pore volume, indicating that the resins can swell in water directly. However, with an increase in *n*-heptane content above 23% *n*-heptane, the value of water uptake decreases abruptly and becomes far below the corresponding pore volume at 50 or 67% *n*-heptane. Because the only change for the synthesis of the resins in Figure 2 is the variation of the *n*-heptane content in the mixed porogen, the change in the swelling ability of the EGDM/DVB resins in water must be ascribed to the variation in the solvating power of the mixed porogen. With an increase in the content of *n*-heptane, a nonsolvent for EGDM/DVB copolymer chains, the polymer chains during copolymerization must become less stretched. Consequently, the crosslinking reaction fixes the chains in a less-



**Figure 2** Dependency of water uptake and pore volume of EGDM/DVB resins on the *n*-heptane content in the mixed porogen of toluene and *n*-heptane. The resins were prepared with EGDM and DVB contents fixed at 40 and 60%, respectively, and with the ratio of porogen to monomers of 1.4 : 1.



**Figure 3** Dependency of solvent (toluene and water) uptake and pore volume of EGDA/DVB resins on the DVB content. The resins were prepared with EGDA content fixed at 40%.

stretched state, which results in a less-strained polymer network of the resins, because the deswelling causes a less-compacted network of the resins compared with the case of the network formed in a better-solvating state. The result in Figure 2 therefore provides additional evidence that the solvating state of the growing polymer chains, or the formation history of the polymer networks, is extremely important to the swelling ability of the hydrophobic porous resins in water.

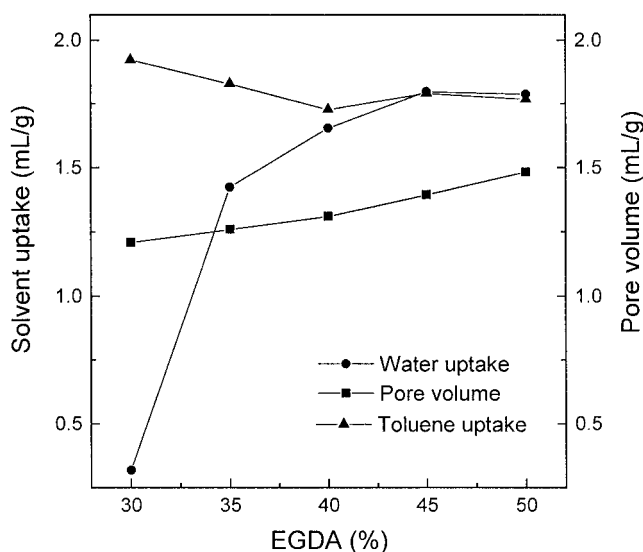
#### EGDA/DVB resins

MMA is more hydrophobic than MA because of the presence of an extra methyl group in MMA. Such a difference in hydrophobicity has a dramatic effect on the water-swelling ability of their copolymers with DVB; the copolymers obtained from MA and purified DVB in many cases are water-swellingable,<sup>1</sup> whereas copolymers obtained from MMA and purified DVB are not water-swellingable, as presented in Table I. Just as with the case of MA and MMA, EGDA is similar to EGDM in chemical structure, and is less hydrophobic than EGDM. Therefore, it was of interest to know the swelling behavior of the EGDA/DVB resins in water.

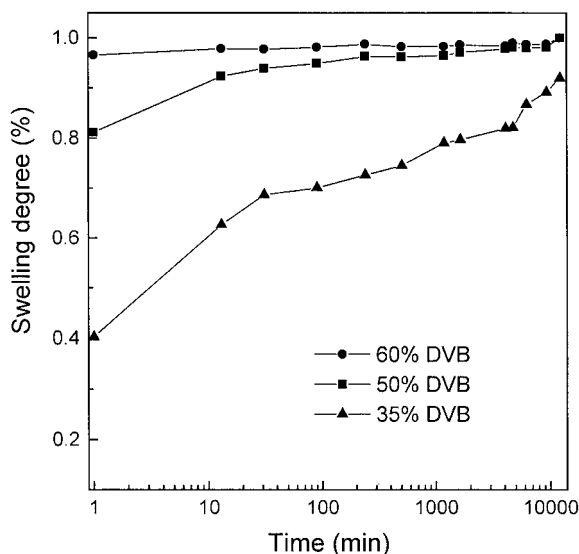
Figure 3 shows the dependency of water uptake and pore volume of the EGDA/DVB resins on the DVB content, and the toluene uptake is also plotted against the DVB content for comparison. Similar to the case in Figure 1, the resins in Figure 3 were prepared with EGDA content fixed at a constant level of 40%, and the DVB content varied from 40 to 60% by incorporating EVB. It may be seen that the value of water uptake is

also much less than the pore volume at lower DVB levels, and becomes greater than the corresponding pore volume at higher DVB contents. However, a comparison of Figure 3 with Figure 1 reveals a great difference in water-swelling ability between the EGDA/DVB and EGDM/DVB resins. In Figure 1, the resin becomes water-swellingable at a DVB content of 60%, but in Figure 3, the water uptake is greater than the pore volume at 40% DVB; that is, the EGDA/DVB resins could swell in water at a much lower DVB level than EGDM/DVB resins, if the EGDA and EGDM contents are fixed at the same level. In the previous study we observed the combined effect of the crosslinking density and the polymer polarity on the swelling ability of the hydrophobic resins in water.<sup>1</sup> In this way, an enhanced polarity of the copolymer may lower the critical value of the crosslinking degree at which the swelling in water occurs, and vice versa. Clearly, a stronger polarity for EGDA than for EGDM induces the resins in Figure 3 to become water-swellingable at much lower DVB levels compared with the resins in Figure 1. This is because, with a stronger polymer polarity of the EGDA/DVB resins, the interaction between polymer and water increases. As a result, less driving force from the inner stresses, or the lower crosslinking density of the networks, is needed for EGDA/DVB than for EGDM/DVB resins to swell in water.

The effect of the polymer polarity, or the interaction between polymer and water, on the water-swelling ability of the resins could be further demonstrated by the result in Figure 4. In this figure, the resins were prepared with a fixed DVB content of 50%, and the



**Figure 4** Dependency of solvent (toluene and water) uptake and pore volume of EGDA/DVB resins on the EGDA content. The resins were prepared with DVB content fixed at 50%.



**Figure 5** Dynamic swelling behavior of EGDA/DVB resins with the EGDA content fixed at 40% and the DVB content varied from 35 to 60%. The swelling degree (%) was plotted against the logarithmic contact time of the resin with water, and the resins are the same as those in Figure 3.

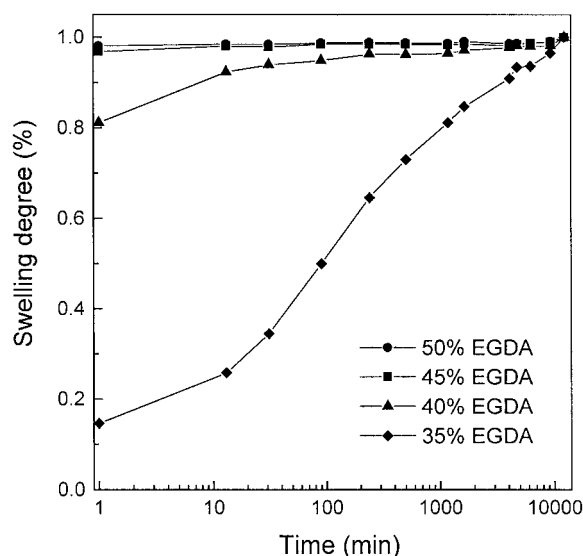
EGDA content was varied from 30 to 50% by incorporating EVB. In this case, the crosslinking density, as well as the polymer polarity, will increase simultaneously with an increase in EGDA content. Then, we can see that, as the EGDA content is increased to a value of only 35%, the water uptake for EGDA/DVB resin becomes greater than the value of the pore volume, and in a wider range of crosslinker levels, the resins are water-swellable compared with the resins in Figure 3. Because EGDA is a less-efficient crosslinker than DVB, the increased water-swellability in Figure 4 should, to a great extent, also be attributed to the increase of the polymer polarity with increasing the EGDA content.

In addition to the above discussions, it is also noteworthy that, in both Figures 3 and 4, the water uptake approaches close to the value of toluene uptake with raising the degree of crosslinking, and at 60% DVB in Figure 3 and at 45 and 50% EGDA in Figure 4, the water uptake reaches an almost identical value to that of the corresponding toluene uptake, regardless of the great difference in solvating power between toluene and water for the polymer chains. This fact suggests that, besides the polymer-solvent interaction, there is really an additional swelling-driving force in the rigid networks of the highly crosslinked resins, and such a driving force increases with an increase in crosslinking density to some extent. Because the rigid networks of the EGDA/DVB resins are also formed in a well-solvating porogenic solvent, the removal of the porogen after copolymerization, as discussed earlier, unavoidably results in a strongly strained network in the

dried state. Accordingly, it is reasonable to regard the inner stresses as an additional swelling-driving force for this kind of resin to swell in water, because in this case the volume increase of the resins is in favor of the release of the inner stresses.

Both the equilibrium water uptake and the swelling rate of the EGDA/DVB resins in water are strongly influenced by the composition of the resins. Figures 5 and 6 show the dynamic swelling behavior of the same resins as those in Figures 3 and 4, respectively. The swelling degree of the resins was assessed by measuring water uptake directly, and was plotted against the logarithmic contact time. In parallel with the equilibrium water uptake at 60% DVB in Figure 3 and at 45 and 50% EGDA in Figure 4, which reach nearly the same value as that of the corresponding toluene uptake, the swelling of the resins at the same DVB level in Figure 5 and at the same EGDA levels in Figure 6 is very fast: the swelling equilibrium is achieved almost immediately after the contact of these resins with water. On the contrary, at the low levels of the DVB or EGDA content, the swelling (or the uptake of water) is extremely slow. At 35% EGDA in Figure 6, although the resin is still water-swellable, it takes a swelling time of more than 9335 min (about 6.5 days) to achieve the swelling equilibrium. At 35% DVB in Figure 5, the resin does not swell in water as shown in Figure 3; rather, it takes as long as 12,215 min (about 8.5 days) for this resin to reach a water uptake value of only 0.40 mL/g, which is still less than the equilibrium water uptake of 0.43 mL/g.

Just as in the case of equilibrium swelling, the dynamic swelling behavior of EGDA/DVB resins pre-



**Figure 6** Dynamic swelling behavior of EGDA/DVB resins with the DVB content fixed at 50% and the EGDA content varied from 35 to 50%. The swelling degree (%) was plotted against the logarithmic contact time of the resin with water, and the resins are the same as those in Figure 4.

**TABLE III**  
**Water Uptake and Pore Volume of EGDA/DVB**  
**Resins Prepared<sup>a</sup> by Using Technical DVB**

Parameter	EGDA/DVB			
	48/42	43/46	35/52	30/56
$V_w$ (mL/g)	1.76	1.76	1.66	1.02
$V_p$ (mL/g)	1.15	1.31	1.22	1.08

<sup>a</sup> Besides EGDA and DVB, the third comonomer unit in the EGDA/DVB resins of this table is EVB from the tech. DVB (79.3%);  $V_w$  is water uptake measured by direct contact of resin with water and  $V_p$  is pore volume.

sented in Figures 5 and 6 could not be explained on the basis of the generally accepted swelling theories. However, we believe the same factors cause the resins to swell more at the higher crosslinker levels, as shown in Figures 3 and 4, and to swell faster at the higher crosslinker levels, as shown in Figures 5 and 6. The factors, as discussed earlier, are the existence of the inner stresses in the strained polymer network of the resins and the weak interaction between polymer and water. The magnitude of the inner stresses or the interaction is known to increase with an increase in crosslinking density or in polymer polarity of the resins.<sup>1</sup>

#### EGDA/DVB resins prepared by using technical DVB

We successfully prepared water-swallowable porous resins by copolymerization of purified DVB (98.8%) with MA, and have also shown that by using technical DVB (79.3%), the resulting MA/DVB resins are not swallowable in water directly.<sup>1</sup> This is because the portion of EVB in the technical DVB decreases the content of DVB or MA in the copolymers, therefore reducing the crosslinking density (rigidity of the network) or the polymer polarity of the resulting resins, which are necessary for the hydrophobic porous resins to swell in water directly. EGDA, with the component or polarity nearly identical to that of MA, is a bifunctional acrylate monomer, and therefore should act as a crosslinker as described in the previous section. As a result, the crosslinking density for EGDA/DVB resins should be higher than that for MA/DVB resins, if their DVB content is at the same level. It should then be possible to prepare the water-swallowable porous resins by copolymerization of EGDA with technical DVB (79.3%), besides the use of the purified DVB.

Table III presents the water uptake and pore volume of the EGDA/DVB resins with different EGDA/DVB ratios prepared by using technical DVB (79.3%); the water uptake was measured by direct contact of the resins with water. It may be seen that the technical DVB-derived resins with EGDA content from 48 to 35% are water-swallowable, as judged by a comparison of

water uptake with pore volume. With a further decrease of the EGDA content to 30% (EGDA/DVB ratio of 30/56), however, the water uptake becomes less than the pore volume value, and the resin will remain on the surface of the water even if stirred for a long time.

The above result is important because it points out that one can use commercially available DVB (about 80%) and a moderately hydrophobic monomer to synthesize porous resins that are hydrophobic, but could swell in water by direct contact with water. Because the water-swallowable porous resins derived from technical DVB could also be prepared with adjustable pore structures and high surface area, for example, a specific surface area of about 550 m<sup>2</sup>/g for 43/46 EGDA/DVB resin in Table III, we believe these new porous materials will find their specific applications in such areas as adsorption and separation.

#### CONCLUSIONS

EGDM/DVB resins, whose polarity is nearly the same as that of resins based on DVB and MMA at the same DVB levels, could be prepared as water-swallowable materials in a wide range of DVB contents by using purified DVB (98.8%), whereas the latter do not swell in water at any DVB levels. As a bifunctional methacrylate monomer, the EGDM must act as a crosslinker during copolymerization, and thus the enhanced water-swallowing ability could be attributed to the increase of the crosslinking density (network rigidity), which is considered to result in an increase in inner stresses in the dry polymer resins if the resins are synthesized in the presence of a well-solvating solvent such as porogen.

As a bifunctional acrylate monomer, EGDA could also act as a crosslinker, with a chemical structure similar to that of EGDM, but is less hydrophobic than EGDM. Compared with EGDM/DVB resins, the porous resins derived from EGDA and DVB are more water swallowable. Clearly, this can be attributed to the stronger polarity of the EGDA/DVB than that of EGDM/DVB resins, which is believed to lead to an increase in polymer-water interaction of the EGDA/DVB resins. Both the equilibrium water uptake and the swelling rate of the EGDA/DVB resins in water are strongly influenced by the crosslinking density and polymer polarity of the resins.

EGDA has a polarity almost identical to that of MA, although because EGDA itself acts as a crosslinker, the EGDA/DVB resins are more densely crosslinked than MA/DVB resins at the same DVB levels. As a result, the EGDA/DVB resins could also be prepared directly as water-swallowable materials by using technical DVB (79.3%). Because the water-swallowable porous resins derived from the commercially available DVB could also be prepared with a high surface area, this result is

important for these new porous materials to find their specific applications in such areas as adsorption and separation.

### References

1. Wei, J.; Bai, X. Y.; Yan, J. *Macromolecules* 2003, 36, 4960.
2. Davankov, V. A.; Tsyurupa, M. P. In *Synthesis, Characterization and Theory of Polymeric Networks and Gels*; Aharoni, S. M., Ed.; Plenum Press: New York, 1992; p 179.
3. Huck, C. W.; Bonn, G. K. *J Chromatogr A* 2000, 885, 51.
4. Popov, G.; Schwachula, G. *Chem Technol* 1978, 30, 144.
5. Xie, C. X.; Sun, Z. L. *Chem World* 1999, 40, 136.
6. Yan, J.; Wang, X. H.; Chen, J. Q. *J Appl Polym Sci* 2000, 75, 536.
7. Yan, J.; Wang, X. H.; Cao, Z. N. *React Funct Polym* 2000, 46, 127.
8. Wang, X. H.; Yan, J.; Zhou, C. C. *J Appl Polym Sci* 2000, 78, 250.
9. Batich, C. D.; Yan, J.; Bucaria, C.; Elsabee, J. M. *Macromolecules* 1993, 26, 4675.
10. Okay, O. *Prog Polym Sci* 2000, 25, 711.
11. Dumont, P. J.; Fritz, J. S. *J Chromatogr A* 1995, 691, 123.
12. Howdle, S. M.; Jerabek, K.; Leocorbo, V.; Marr, P. C.; Sherrington, D. C. *Polymer* 2000, 41, 7273.
13. Wieczorek, P. P.; Kolarz, B. N.; Galina, H. *Angew Makromol Chem* 1984, 126, 39.
14. Yan, J.; Xu, R. N.; Yan, J. T. *J Appl Polym Sci* 1989, 38, 45.
15. Dusek, K. In: *Developments in Polymerization*; Haward, R. N., Ed.; Applied Science: London, 1982; Vol. 3, p 143.
16. Negre, M.; Batholin, M.; Guyot, A. *Angew Makromol Chem* 1982, 106, 67.
17. Shea, K. J.; Stoddard, G. J. *Macromolecules* 1991, 24, 1207.
18. Albright, R. L. *React Polym* 1986, 4, 155.
19. Davankov, V. A.; Tsyurupa, M. P. *React Polym* 1990, 13, 27.
20. Davankov, V. A.; Pastukhov, A. V.; Tsyurupa, M. P. *J Polym Sci Part B: Polym Phys* 2000, 38, 1553.
21. Tsyurupa, M. P.; Davankov, V. A. *React Funct Polym* 2002, 53, 193.