

# Pore Structure and Water-Swelling Behavior of Porous Resins Based on Methyl Acrylate and Different Divinylbenzene Isomers

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**ABSTRACT:** Porous resins based on divinylbenzene (DVB) and methyl acrylate (MA) were prepared with *m*-DVB (98.3%) or *p*-DVB (99.1%) in the presence of toluene as a porogen. The MA/DVB resins thus obtained with a wide range of pore structures were hydrophobic in nature and were swellable by direct contact with water. The behavior of *m*-DVB and *p*-DVB as a crosslinker in the MA/DVB monomer system was different from that in the styrene (ST)/DVB system and was influenced by the amount of MA in the MA/DVB monomer system. As a result, a larger specific surface area and pore volume were observed for MA/DVB resins derived from *p*-DVB than for those derived from *m*-DVB, which was opposite to that observed for resins

based on DVB and ST. The different behaviors of *m*-DVB and *p*-DVB in the MA/DVB monomer system also resulted in different swelling abilities of the resins in water. Compared with the MA/DVB resins derived from *m*-DVB, the *p*-DVB derived resins swelled faster in water and were water-swellable when the resins had a higher DVB content and, therefore, a stronger hydrophobicity and a larger specific surface area. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2071–2078, 2005

**Key words:** isomer/isomerization; resins; structure; swelling

## INTRODUCTION

Divinylbenzene (DVB) as a crosslinker has been used extensively for the preparation of porous copolymers, typically, porous styrene (ST)/DVB resins, which are applied as starting materials for ion-exchange resins and as polymer adsorbents.<sup>1–3</sup> Commercially available DVB used in these preparations contains the *m*-DVB and *p*-DVB isomers and a substantial amount of ethylvinylbenzene. *m*-DVB and *p*-DVB as crosslinkers behave differently during copolymerization, which leads to porous resins with different crosslinking structures and pore structures. The effect of the DVB isomers on the crosslinking copolymerization has been well reported in the literature.<sup>2–4</sup>

We recently found that by the copolymerization of purified DVB (98.8%, containing 49.5% *m*-DVB and 49.3% *p*-DVB) and methyl acrylate (MA) in the presence of a solvating porogen, the resulting porous MA/DVB resins could swell or be wetted by direct contact with water, regardless of the hydrophobic character of

the homopolymer derived from DVB or MA.<sup>5,6</sup> In contrast to the usual concept of polymer swelling, this phenomenon was very striking. The nature of the direct swelling of these hydrophobic resins in water was discussed by consideration of two factors: the existence of inner stresses in the strained polymer network<sup>7–10</sup> and the effect of the weak polymer–water interaction, which is usually negligible in hydrophobic polymers.

We studied the pore structure and the water-swelling behavior of the MA/DVB resins thus obtained. To avoid the complexity of the copolymerization of the mixture of DVB isomers with MA, these studies were done with pure *m*-DVB and *p*-DVB. To our surprise, exactly different effects of *m*-DVB and *p*-DVB on the pore structure of the porous MA/DVB resins, compared to porous resins based on ST and DVB, were observed. This reflected the different behaviors of *m*-DVB and *p*-DVB as crosslinkers in these two copolymerization systems. On the other hand, an unexpected phenomenon was also observed for the direct swelling of the MA/DVB resins in water: despite the equal hydrophobicity for *m*-DVB and *p*-DVB, the MA/DVB resins derived from *m*-DVB and *p*-DVB exhibited different swelling abilities in water. This article reports the results of these studies.

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## EXPERIMENTAL

### Resins synthesis

MA (>98.5%) and methyl methacrylate (MMA; >98%) were treated with an anion-exchange resin to remove inhibitors before use. *p*-DVB (99.1%) and *m*-DVB (98.3%) were obtained according to the method of Popov and Schwachula.<sup>11</sup> Reagent-grade toluene, anhydrous ferric chloride, and most of the other chemicals were used as received.

The copolymer resins were prepared by the usual suspension polymerization in the presence of toluene as a porogen<sup>5</sup> at a fixed dilution degree (2.0), which was expressed as the volume ratio of porogen to the monomers. For all resins, the contents of DVB, MA, and MMA were expressed as weight percentages of the total amount of monomers (the purity of monomers was taken as approximately 100% in the calculation of the content).

For some MA/DVB resins, postcrosslinking was performed.<sup>12</sup> Typically, 5 g of porous resins were first swollen in 30 mL of 1,2-dichloroethane. To this mixture, then, 1.5 g of anhydrous ferric chloride was added, and the reaction with stirring was conducted at 80°C for 8 h. After the reaction, the resins were washed with a HCl-containing aqueous solution and acetone and were dried *in vacuo* at 80°C.

### Characterization

The apparent density [ $d_a$  (g/mL)] of copolymers in the dry state was determined by an improved mercury pycnometric method as described in our previous article,<sup>13</sup> with a relative error of measurement less than 1%. The true density [ $d_t$  (g/mL)] was also measured by a pycnometric method but with *n*-heptane as the confining fluid.<sup>14</sup> From  $d_a$  and  $d_t$ , the porosity ( $P$ ; vol %) was calculated with the equation

$$P = (1 - d_a/d_t) \times 100\% \quad (1)$$

and the pore volume [ $V_p$  (mL/g)] was calculated with the equation

$$V_p = 1/d_a - 1/d_t \quad (2)$$

The specific surface area [ $S$  (m<sup>2</sup>/g)], unless indicated otherwise, was determined by a conventional nitrogen adsorption BET technique with a ST-03 instrument (Beijing Analytical Instrument Factory, Beijing, China), and the average pore diameter [ $D$  (nm)] can be calculated by the equation

$$D = 4 \times 10^3 V_p/S \text{ (nm)} \quad (3)$$

Pore size distribution was calculated from the nitrogen desorption data obtained on a Micromeritics TriStar 3000 analyzer (Norcross, Georgia).

Fourier transform infrared (FTIR) spectra were used to quantify the relative amount of pendant vinyl groups in the MA/DVB resins on the basis of a technique developed by Bartholin et al.,<sup>15</sup> and with referral to the method of Hubbard et al.,<sup>16</sup> the content of pendant vinyl groups [ $X_{vb}$  (mol % of double bonds)] was calculated by

$$X_{vb} = [(A + B)/2(C + D)] \times \text{DVB (mol \%)} \quad (4)$$

where  $A$ ,  $B$ ,  $C$ , and  $D$  were obtained by multiplying the peak heights at various bands and their extinction coefficients given by Bartholin et al.<sup>15</sup> The bands at 1630 cm<sup>-1</sup> ( $A$ ) and 990 cm<sup>-1</sup> ( $B$ ) were the vinyl peaks, and the bands at 1510 cm<sup>-1</sup> ( $C$ ) and 795 cm<sup>-1</sup> ( $D$ ) were the *p*-DVB and *m*-DVB disubstituted phenyl ring peaks, respectively.  $C$  and  $D$  accounted for all of the repeat units in the DVB portion of the MA/DVB copolymer. DVB (mol %) is the molar percentage of DVB in feed, and it was assumed that the monomer content of the copolymer was similar to that of the starting monomer mixture.

### Swelling experiments

The solvent (toluene or water) uptake (mL/g) was measured as described in a previous article by a centrifuge method,<sup>5</sup> with a relative error of 3% or less for samples where the value of solvent uptake was above 0.3 mL/g.<sup>5,17</sup> For the swelling experiment in water, the water uptake [ $V_w$  (mL/g)] was measured by direct contact of the resin with water, that is, without prior wetting of the resin with a water-miscible organic solvent. The swelling equilibrium at room temperature in water was usually achieved within 2 days; but for some samples, the equilibrium time extended to 2 weeks or more depending on the copolymer compositions. In the dynamic swelling experiments in water, 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 contact time  $t$  and  $V_w$ , as just denoted, is the equilibrium water uptake measured by direct contact with water. The volume change of the copolymers in equilibrium with water was expressed as the volume swelling ratio ( $B$ ) of the swollen copolymer beads to the initial dry ones and was calculated with the equation<sup>18</sup>

$$B = d_a(V_w + 1/d_t) \quad (5)$$

## RESULTS AND DISCUSSION

### Porous properties of MA/DVB resins derived from *m*-DVB and *p*-DVB

Although the aliphatic adsorbent based on MA and multifunctional methacrylate, known as Amberlite

TABLE I  
Porous Properties of the MA/DVB Resins Prepared from MA and *m*-DVB or *p*-DVB<sup>a</sup>

MA/DVB	DVB isomer	<i>S</i> (m <sup>2</sup> /g)	<i>d<sub>a</sub></i> (g/mL)	<i>P</i> (%)	<i>D</i> (nm)
50/50	<i>m</i> -DVB	394	0.503	57.7	11.6
	<i>p</i> -DVB	449	0.414	63.7	13.7
40/60	<i>m</i> -DVB	566	0.459	61.3	9.4
	<i>p</i> -DVB	577	0.403	64.0	11.0
31/69	<i>m</i> -DVB	656	0.476	58.3	7.5
	<i>p</i> -DVB	716	0.396	65.9	9.3

*D*, average pore diameter.

<sup>a</sup> The purities of the *m*-DVB and *p*-DVB were 98.3 and 99.1%, respectively.

XAD-6 (with surface area of 63 m<sup>2</sup>/g), was reported many years ago,<sup>19</sup> the highly crosslinked porous MA/DVB copolymer resins, to our knowledge, have not been well described in literature. Table I presents the porous properties of the MA/DVB resins prepared by the copolymerization of MA and *m*-DVB (98.3%) or *p*-DVB (99.1%) in the presence of toluene as a porogen. As shown, with increasing DVB content from 50 to 69%, *S* for both the *m*-DVB and *p*-DVB derived resins increased apparently and reached rather large values for resins with DVB contents of 60% or more. Because the increase in *P* was not as great as that of the surface area with increasing DVB content, the average diameter in Table I for both the *m*-DVB and *p*-DVB derived resins decreased with an increase in DVB content. From these results, we could see that both the *m*-DVB and *p*-DVB derived MA/DVB resins could also be prepared with a wide range of pore structures, and a large surface area could be achieved if the DVB content was increased to a high level.

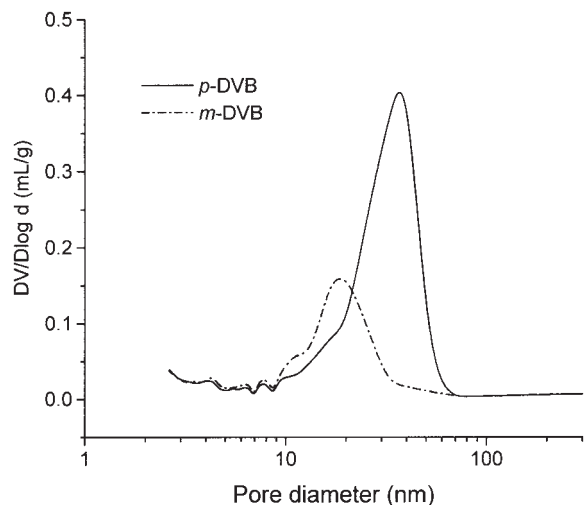
The DVB dependence of *S* and *P* for the MA/DVB resins presented in Table I was similar to that for ST/DVB resins prepared under similar conditions.<sup>12</sup> However, for both of the resins derived from *m*-DVB and *p*-DVB, *P* of the MA/DVB resins was much higher than that of the corresponding ST/DVB resins with the same DVB content. For example, the *P*'s (or *V<sub>p</sub>*'s) for *m*-DVB and *p*-DVB derived MA/DVB resins with 60% DVB, as shown in Table I, were 61.3% (1.336 mL/g) and 64.0% (1.587 mL/g), whereas the *P*'s (or *V<sub>p</sub>*'s) for ST/DVB resins derived from *m*-DVB and *p*-DVB at the same DVB level were only 47.3% (0.856 mL/g) and 39.3% (0.616 mL/g), respectively. This fact can be explained on the basis of the thermodynamic properties of the polymers, monomers, and porogen existing in the MA/DVB copolymerization system. The solubility parameters [ $\delta$ 's (cal<sup>0.5</sup>/cm<sup>1.5</sup>)] for poly(methyl acrylate) and polydivinylbenzene are rather different, with values of 9.8–10.1 for poly(methyl acrylate) and 9.1 for polystyrene (an analogue of polydivinylbenzene). The  $\delta$  values for both toluene (porogen) and MA were 8.9, and for ST (an analogue of DVB), the value was a bit greater than 8.9.<sup>20</sup> Therefore, the thermodynamic properties of monomers and po-

rogen in the ST/DVB copolymerization system were very close to that of the growing ST/DVB copolymer chains, but in the MA/DVB monomer system, they were different, to a great extent, from that of the growing MA/DVB copolymer chains during copolymerization. Accordingly, due to the reduced polymer-solvent interactions in the case of MA/DVB copolymerization system, the phase separation and structural heterogeneity were enhanced, which led to a higher *P* in the MA/DVB resins than in the ST/DVB ones.

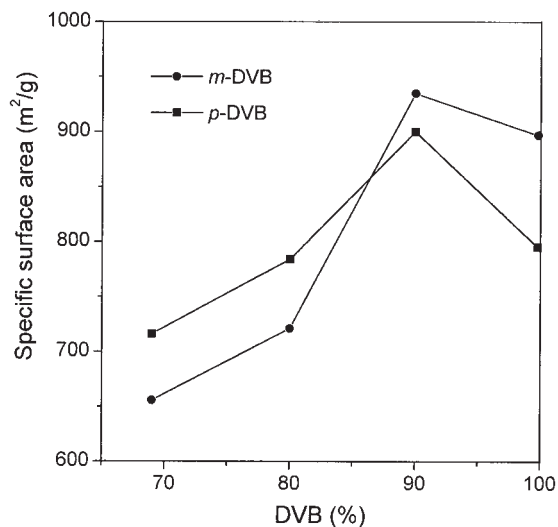
As we know, *m*-DVB and *p*-DVB as crosslinkers behave differently during copolymerization, which results in different pore structures in *m*-DVB and *p*-DVB derived resins.<sup>2–4</sup> For example, the ST/DVB resin with 60% DVB, as just mentioned, had a *P* value of 47.3% for the *m*-DVB derived resin, which was much larger than the value of 39.3% for the *p*-DVB derived one.

From the data in Table I, we also made a comparison of the *S* and *P* values between the *m*-DVB and *p*-DVB derived MA/DVB resins. To our surprise, exactly opposite to that observed for resins based on ST and DVB, both the *S* and the *P*, as shown in Table I, were larger for the *p*-DVB derived MA/DVB resins than for the *m*-DVB derived resins at various DVB levels. In addition, because the difference in *P* was greater than the difference in surface area; the average pore diameter, as shown in Table I, was also greater for the *p*-DVB resins than for the *m*-DVB resins.

Figure 1 shows the pore size distribution of the 31/69 MA/DVB resins derived from *m*-DVB and *p*-DVB. The resins in this figure are the same as those in Table I. As shown, the pore size distribution of the *p*-DVB resin was sharper and shifted toward a larger pore size region compared with that of the *m*-DVB resins. The pore size distributions for both the *m*-DVB and *p*-DVB resins were mainly in the range of mesopores, with the maxima localized at about 20 and 34 nm, respectively. The *S* and *V<sub>p</sub>* values determined with the Micromeritics TriStar 3000 analyzer were 762 m<sup>2</sup>/g and 1.23 mL/g, respectively, for the *m*-DVB resin and 836 m<sup>2</sup>/g and 1.82 mL/g, respectively, for the *p*-DVB resin. These results further confirmed the different behaviors between *m*-DVB and *p*-DVB in the



**Figure 1** Pore size distribution of the 31/69 MA/DVB resins derived from *m*-DVB and *p*-DVB; the resins in this figure are the same as those in Table I.



**Figure 2** Dependence of  $S$  of the *m*-DVB and *p*-DVB derived MA/DVB resins on the DVB content. The resins were prepared under the same conditions as the resins in Table I.

copolymerization of MA and DVB, which was opposite to those in the ST/DVB monomer system.

For ST/DVB copolymer resins, the greater surface area and  $V_p$  of *m*-DVB resins than *p*-DVB resins have been mainly ascribed to the higher conversion of the second vinyl group in *m*-DVB than in *p*-DVB during copolymerization.<sup>12,21</sup> The conversion level of the second vinyl groups was assessed, in our study and other studies,<sup>12,21,22</sup> by the pendant (residue) vinyl group content in the resulting ST/DVB resins. Because of the lower reactivity of the second vinyl groups for *p*-DVB than for *m*-DVB,<sup>21,22</sup> the pendant vinyl group content is much higher in *p*-DVB resins than in *m*-DVB resins.<sup>12,21</sup>

We, therefore, measured the pendant vinyl group content of the *m*-DVB and *p*-DVB derived MA/DVB resins, with a DVB content ranging from 50 to 100% (the purity of MA, *m*-DVB, and *p*-DVB was taken as approximately 100% in the calculation of the content). As shown in Table II, for all of the *p*-DVB derived resins, the vinyl group content was also higher than that for *m*-DVB derived resins. In other words, no reversal was observed for the MA/DVB resins in the relationship between the vinyl group content and the type of DVB isomer compared with that observed for ST/DVB resins.

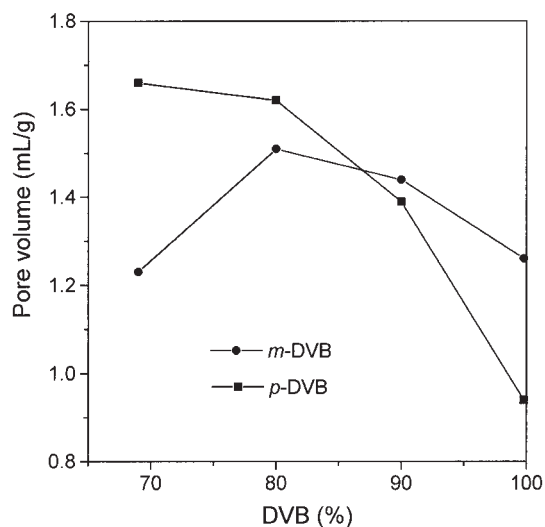
As we failed to explain the cause of the difference in pore structures between the *m*-DVB and *p*-DVB derived MA/DVB resins by the measurement of the content of pendant vinyl groups, an attempt was made to study this phenomenon on the basis of the different reactivities of *m*-DVB and *p*-DVB and of the different thermodynamic properties of the monomers, porogen, and growing polymer chains. However, in reality, the manner in which the pore structure developed for the *m*-DVB and *p*-DVB derived MA/DVB resins was very complex; it is difficult at our present level of the understanding to explain the differences presented previously.

Nevertheless, a further investigation was still done on the pore structure of *m*-DVB and *p*-DVB derived MA/DVB resins, to learn more about the behavior of *m*-DVB and *p*-DVB as crosslinkers in the MA/DVB system. Figures 2 and 3 show, respectively, the dependence of  $S$  and  $V_p$  of the MA/DVB resins on the DVB content, with the DVB content increased to a level of about 100%. It was very interesting to see that a reversal occurred in the relationship between the porous properties and the type of DVB isomer in Figures 2 and 3.  $S$  and the  $V_p$  were larger for the *p*-DVB resins than for *m*-DVB resins at DVB contents of about 80%

**TABLE II**  
 $X_{vb}$  (%) of *m*-DVB and *p*-DVB Derived MA/DVB Resins<sup>a</sup> with DVB Contents Ranging from 50 to 100%

	MA/DVB					
	50/50	40/60	31/69	20/80	10/90	100
<i>m</i> -DVB	13.9	19.0	26.3	27.2	32.2	38.6
<i>p</i> -DVB	16.8	25.5	27.9	34.5	47.2	59.0

<sup>a</sup> The MA/DVB resins were prepared under the same conditions as those for the resins in Table I.



**Figure 3** Dependence of  $V_p$  of the *m*-DVB and *p*-DVB derived MA/DVB resins on the DVB content. The resins were prepared under the same conditions as the resins in Table I.

or less, which was consistent with the results shown in Table I and Figure 1. However, at DVB contents of 90% or more, the opposite phenomenon was observed. Both  $S$  and  $V_p$  became smaller, as shown in Figures 2 and 3 for the *p*-DVB resins than for the *m*-DVB resins. At 100% DVB, that is, when the resins were free from MA, the  $S$  values for the *m*-DVB and *p*-DVB resins were 897 and 795  $\text{m}^2/\text{g}$ , respectively. The difference between the  $V_p$  values for the *m*-DVB and *p*-DVB derived resins at 100% DVB was greater, with  $V_p$ 's of 1.261 and 0.936 mL/g for the *m*-DVB and *p*-DVB derived resins, respectively. As shown by the results in Figures 2 and 3, it was clear that the behavior of *m*-DVB and *p*-DVB as crosslinkers was influenced by the amount of MA in the MA/DVB monomer system.

Although we are not able to explain the difference in the behaviors of *m*-DVB and *p*-DVB in the MA/DVB copolymerization system at this stage, the similar behaviors of the *m*-DVB and *p*-DVB as crosslinkers were also observed in the MMA/DVB monomer system, which were different from the observations in the ST/DVB system. For *m*-DVB and *p*-DVB derived resins with a MMA/DVB ratio of, for example, 54/46, the corresponding porous properties are shown in Table III. Clearly, both  $S$ ,  $V_p$ , and the average pore diameter

were greater for *p*-DVB derived MMA/DVB resins than for *m*-DVB derived ones. The vinyl group content for the *p*-DVB resin was also higher than that for the *m*-DVB resin, as indicated by the FTIR spectra of the resins. This result may help us to understand the different behaviors of *m*-DVB and *p*-DVB in the copolymerization of DVB and an alkyl (meth)acrylate ester.

#### Water-swelling behavior of the MA/DVB resins derived from *m*-DVB and *p*-DVB

Table IV presents the water uptake and  $V_p$  values of the *m*-DVB and *p*-DVB derived MA/DVB resins. The resins are the same as those in Table I, and the water uptake was measured by direct contact of the resin with water. For comparison, the toluene uptake was also measured and is listed in Table IV. In general, the solvent uptake of porous resins can be considered the result of two separate processes: the filling of pores by the solvent and gel phase swelling, which depends on polymer-solvent interaction.<sup>3</sup> Because no single measurement can distinguish these two processes, both solvent uptake and  $V_p$  in a dry state were measured to assess whether the solvent could penetrate into the gel phase of the copolymers.

By comparing of the water uptake with  $V_p$ , as shown in Table IV, we could see that except for the 31/69 MA/DVB resin derived from *m*-DVB, the water uptake for all of the resins in Table IV was greater than the corresponding  $V_p$ . This indicated that not only were the pores of these resins fully filled with water, but also part of the water absorbed by the porous resins penetrated into the gel phase. With the assumption of isotropic swelling of the porous resins synthesized with solvating solvent as a porogen, the expansion of the resins could be expressed by the volume swelling ratio, which was calculated according to eq. (5) and is also listed in Table IV. Just as with the case of the MA/DVB copolymers prepared with mixed DVB (49.5% *m*-DVB and 49.3% *p*-DVB),<sup>5</sup> the nature of the water-swelling of the porous MA/DVB resins, derived from the pure DVB isomers in Table IV, can also be discussed by consideration of two factors: the existence of the inner stresses in the strained polymer network and the effect of weak interactions between the polymer and water.

A further observation from Table IV is that the water uptake for both the *m*-DVB and *p*-DVB derived

**TABLE III**  
Properties of the MMA/DVB Resins<sup>a</sup> Prepared from MMA and *m*-DVB or *p*-DVB with a MMA/DVB Ratio of 54/46

DVB isomer	$S$ ( $\text{m}^2/\text{g}$ )	$V_p$ (mL/g)	$D$ (nm)	$V_w$ (mL/g)	$V_w - V_p$ (mL/g)
<i>m</i> -DVB	350	0.744	8.5	0.390	-0.354
<i>p</i> -DVB	416	1.122	10.8	1.597	0.475

$D$ , average pore diameter.

<sup>a</sup> The MMA/DVB resins were prepared under the same conditions as those for the MA/DVB resins in Table I.

TABLE IV  
Swelling Properties of the MA/DVB Resins Prepared from MA and *m*-DVB or *p*-DVB

MA/DVB	DVB isomer	$V_t$ (mL/g)	$V_w$ (mL/g)	$V_p$ (mL/g)	$V_w - V_p$ (mL/g)	$B_w$
50/50	<i>m</i> -DVB	1.974	1.545	1.147	0.398	1.200
	<i>p</i> -DVB	2.061	2.001	1.540	0.461	1.192
40/60	<i>m</i> -DVB	2.066	1.732	1.336	0.396	1.181
	<i>p</i> -DVB	2.058	1.914	1.587	0.327	1.131
31/69	<i>m</i> -DVB	1.839	0.400	1.231	-0.831	—
	<i>p</i> -DVB	2.143	1.979	1.664	0.315	1.125

$V_t$ , toluene uptake;  $B_w$ , volume swelling ratio in water.

resins, except for the 31/69 MA/DVB resin derived from *m*-DVB, reached rather high values. For the *p*-DVB derived resins, the water uptake reached a value nearly the same as the toluene uptake, regardless of the great difference in solvating power between toluene and water for the polymer chains. This fact indicated that besides the polymer-solvent interaction, there really was an additional swelling-driving force in the rigid networks of the highly crosslinked MA/DVB resins. Because the rigid polymer networks formed in a well-solvating porogenic solvent, the removal of the solvent after copolymerization unavoidably resulted in a strongly strained network of resins in a dried state.<sup>7-10</sup> In this case, it was reasonable that the inner stresses acted as the swelling-driving force for the resins to swell in water because the volume increase of the polymer was in favor of the release of the inner stresses.

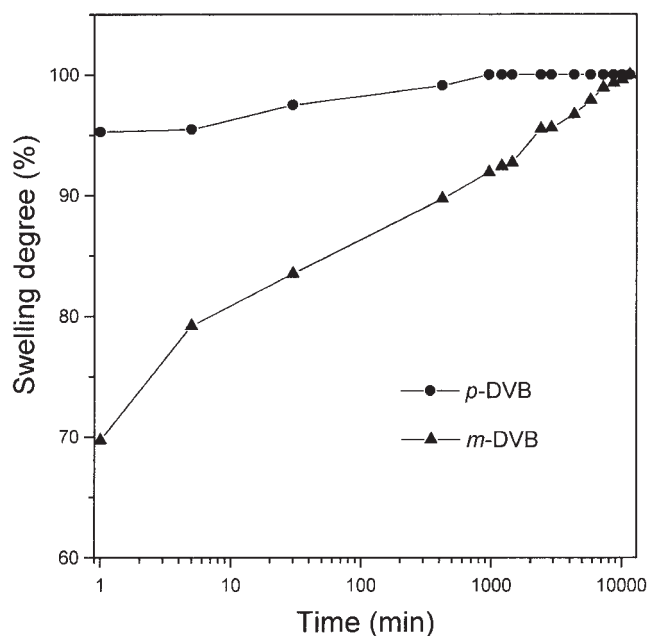
Compared with the water uptake for the *m*-DVB resins, as shown in Table IV, the water uptake for the *p*-DVB resins was much greater. More strikingly, with the same ratio of MA to DVB, the 31/69 MA/DVB resin derived from *m*-DVB was not water-swellable (judged by the value of  $V_w - V_p$ ), whereas the resin derived from *p*-DVB was swellable by direct contact with water. This result was reproducible for the 33/67 MA/DVB resin (see Table V), and the same phenomenon was also observed for MMA/DVB resins, as shown in Table III. This finding is quite valuable because it means that we can obtain water-swellable hydrophobic resins with higher DVB contents and, in turn, with higher  $S$  values.

Not only in equilibrium swelling but also in dynamic swelling in water, the *m*-DVB and *p*-DVB derived MA/DVB resins showed greatly different behaviors. In Figure 4,  $Q$  of the 50/50 MA/DVB resins derived from *m*-DVB and *p*-DVB was plotted against the logarithmic contact time of the resin with water. As shown, at a contact time of 1 min,  $Q$  for the *p*-DVB resin reached a value of 95.3%, showing a very fast swelling rate. For the *m*-DVB resin, however, it was only 69.7% at the same contact time, and after that, the swelling became slower and took 1 day to reach a value of about 95%. Clearly, the swelling rate was much greater for *p*-DVB resins than for *m*-DVB resins.

The different water-swelling behaviors of the *m*-DVB and *p*-DVB derived resins presented in Tables III and IV and Figure 4 could probably be ascribed to the different reactivities of the different DVB isomers. Because the values of the reactivity ratio ( $r$ ) for the MA/DVB monomer system are not available from the literature, we explain the previous phenomena on the basis of the reactivity ratios for the MMA/DVB monomer system. For this system, the reactivity ratios  $r_{12}$  and  $r_{21}$  for MMA ( $M_1$ ) and *m*-DVB ( $M_2$ ), respectively, were 0.41 and 0.61 and, for MMA ( $M_1$ ) and *p*-DVB ( $M_2$ ), were 0.62 and 1.3, respectively.<sup>20</sup> These values served to predict the MMA/DVB copolymer composition at various degrees of monomer conversion during the copolymerization. Because *m*-DVB and *p*-DVB are more reactive than MMA in the copolymerization of DVB and MMA, the polymers formed at the initial stages of copolymerization contained more DVB units than in the monomer mixture. In the meantime, how-

TABLE V  
 $S$ ,  $V_p$ , and  $V_w$  for *m*-DVB and *p*-DVB Derived MA/DVB Resins Before and After the Postcrosslinking Reaction

Resin and composition	$S$ (m <sup>2</sup> /g)		$V_p$ (mL/g)		$V_w$ (mL/g)		$V_w - V_p$ (mL/g)	
	Before	After	Before	After	Before	After	Before	After
MA/ <i>m</i> -DVB								
33/67	686	747	1.265	1.350	0.734	1.620	-0.531	0.270
31/69	656	754	1.231	1.385	0.400	1.615	-0.831	0.230
MA/ <i>p</i> -DVB								
33/67	672	736	1.580	1.719	1.834	1.805	0.254	0.086
31/69	716	716	1.664	1.826	1.979	1.942	0.315	0.116
26/74	806	823	1.518	1.721	1.345	1.868	-0.173	0.147



**Figure 4** Dynamic swelling behavior of *m*-DVB and *p*-DVB derived MA/DVB resins in water. The swelling degree (%), which was assessed by direct measurement of water uptake, is plotted against the logarithmic contact time. The resin samples were the same as those in Table IV with a MA/DVB ratio of 50/50.

ever, because the relative consumption of DVB over MMA in the MMA/*p*-DVB system, as can be predicted by the values of  $r$ , was much more rapid than in the MMA/*m*-DVB system, the fraction of MMA in the monomer mixture must have been much greater for MMA/*p*-DVB than for the MMA/*m*-DVB system at the same conversion degree. Therefore, it was evident that more MMA units were incorporated into the copolymers at the later stages for MMA/*p*-DVB than for the MMA/*m*-DVB monomer system.

The early formed copolymer portions, rich in crosslinker DVB, were highly crosslinked and led to the formation of microgel particles. These microgel particles, according to the monomer reactivity just described, were, therefore, surrounded and linked together by the less crosslinked MMA-rich copolymer portions. Because the densely crosslinked networks of the microgels had entirely or partially finished the course of deswelling under the strong elastic retraction during the copolymerization, these rigid microgel particles were hardly penetrated even with solvating solvents. On the contrary, the networks between the microgel particles were capable of swelling in solvents and shrinking on the removal of the solvents. Therefore, the volume variation of the resins during swelling could be considered a result mainly arising from the expansion of the less crosslinked MMA-rich polymer networks. Accordingly, because more MMA units in the MMA/*p*-DVB resins were incorporated in the

networks between the microgel particles, as compared the MMA/*m*-DVB resins, it was understandable that the MMA/DVB resins derived from *p*-DVB were more water-swellaible than the resins derived from *m*-DVB.

As an analogue of the MMA, the MA in the MA/DVB monomer system should have behaved similarly to the MMA in the MMA/DVB system during copolymerization. We believe the previous explanation for the MMA/DVB system is applicable to the MA/DVB monomer system.

#### Postcrosslinking of MA/DVB resins derived from *m*-DVB and *p*-DVB

In a previous study,<sup>5</sup> we showed that by the copolymerization of technical DVB (79.3%) and MA in the presence of toluene as a porogen, the resulting porous MA/DVB resins could not swell in water directly, but with purified DVB prepared under certain conditions, the resultant porous MA/DVB resins with a wide range of DVB contents became swellaible by direct contact with water. However, to obtain water-swellaible MA/DVB resins with a high as possible surface area, the increase in the fraction of DVB in the MA/DVB resins, even with purified DVB, was restricted by the portion of MA.

In addition to increasing the amount of DVB, increasing the degree of crosslinking, and therefore the surface area, has also been reported for ST/DVB resins by postcrosslinking through the pendant vinyl groups in resins.<sup>12,21</sup> Without an externally added crosslinking agent, the crosslinking reaction occurs between the pendant vinyl groups and the neighboring vinyl groups or aromatic rings, in the presence of a Friedel-Crafts catalyst, to form alkylene-type bridge structures between the aromatic rings.<sup>12</sup> IR spectra of the MA/DVB resins showed that an appreciable amount of pendant vinyl groups also existed in the MA/DVB resins with high DVB contents (see Table II). Accordingly, the postcrosslinking of the *m*-DVB and *p*-DVB derived MA/DVB resins was done, and the results are shown in Table V.

As shown, the surface area for the *m*-DVB derived resins after postcrosslinking increased apparently, reached values of 747 m<sup>2</sup>/g for the 67% DVB resin and 754 m<sup>2</sup>/g for the 69% DVB resin, respectively. For *p*-DVB derived resins, on the other hand, the surface area did not increase as apparently as that for *m*-DVB but still reached high values, for example, 823 m<sup>2</sup>/g for the 74% DVB resin. The increase in  $V_p$  after postcrosslinking, however, was more significant for the *p*-DVB resins than for the *m*-DVB resins. This indicated that more small-size pores were formed after postcrosslinking for the *m*-DVB resins than for the *p*-DVB resins. As shown in Figure 1, the pore size distribution for *m*-DVB was localized in a smaller pore size region for the *p*-DVB resin. If we assumed that

more small-size pores also existed in the swollen *m*-DVB resins, because the newly created crosslinks during postcrosslinking fixed the swollen structure in place,<sup>12</sup> more small-size pores should have formed after postcrosslinking for the *m*-DVB resins than for the *p*-DVB resins. Therefore, the observed phenomenon was understandable.

More interesting is that the *m*-DVB derived MA/DVB resins, as shown in Table V, which were originally not water-swellaible, became water-swellaible after the postcrosslinking reaction, as indicated by the difference between the corresponding values of water uptake and  $V_p$  ( $V_w - V_p$ ). The *p*-DVB resin, even with a MA/DVB ratio of 26/74 in which the fraction of the strongly hydrophobic DVB was almost three times as great as that of MA, also turned into a water-swellaible one after postcrosslinking. The change of the swelling ability could also have been attributed to an increase in crosslinking degree after postcrosslinking, which resulted in more rigid and strained copolymer networks and, therefore, an increased swelling ability in water. From these results, it is clear that the porous MA/DVB resins could be prepared with high *S*, whereas these resins were water-swellaible by direct contact with water.

### CONCLUSIONS

Hydrophobic, but water-swellaible porous MA/DVB resins were prepared by the copolymerization of MA and *m*-DVB or *p*-DVB in the presence of toluene as a porogen. The behavior of *m*-DVB and *p*-DVB as crosslinkers in the MA/DVB monomer system was different from that in the ST/DVB system and was influenced by the amount of MA in the MA/DVB monomer system. As a result, *S* and the  $V_p$  were greater for the *p*-DVB derived MA/DVB resins than for the *m*-DVB derived MA/DVB resins at DVB content levels of 80% or less. However, at DVB contents of 90% or more, a reversal occurred in the relationship

between the porous properties and the type of DVB isomer, resulting in smaller *S* and  $V_p$  values for the *p*-DVB resins than for the *m*-DVB resins. In addition, the *p*-DVB derived resins could be prepared as water-swellaible at higher DVB levels, and therefore with larger *S* values, than the *m*-DVB derived resins. Consequently, the *p*-DVB resins were water-swellaible with DVB contents of up to 69% (*S*: 716 m<sup>2</sup>/g), whereas the *m*-DVB resins with DVB contents of up to 60% (*S*: 577 m<sup>2</sup>/g) were water-swellaible. After postcrosslinking, even with a DVB content of 74%, the MA/DVB resin derived from *p*-DVB could swell by direct contact with water.

### References

1. Abrams, I. M.; Millar, J. R. *React Funct Polym* 1997, 35, 7.
2. Sherrington, D. C. *Chem Commun* 1998, 2275.
3. Okay, O. *Prog Polym Sci* 2000, 25, 711.
4. Schwachula, G. *J Polym Sci Polym Symp* 1975, 53, 107.
5. Wei, J.; Bai, X. Y.; Yan, J. *Macromolecules* 2003, 36, 4960.
6. Wei, J.; Zhao, X.; Yan, J. *J Appl Polym Sci* 2004, 92, 2681.
7. Yan, J.; Wang, X. H.; Chan, J. Q. *J Appl Polym Sci* 2000, 75, 536.
8. Wang, X. H.; Yan, J.; Zhou, C. C. *J Appl Polym Sci* 2000, 78, 250.
9. Davankov, V. A.; Tsyurupa, M. P. *React Polym* 1990, 13, 27.
10. Tsyurupa, M. P.; Davankov, V. A. *React Funct Polym* 2002, 53, 193.
11. Popov, G.; Schwachula, G. *Chem Technol* 1978, 30, 144.
12. Zhou, C. C.; Yan, J.; Cao, Z. N. *J Appl Polym Sci* 2002, 83, 1668.
13. Yan, J.; Wan, J. *Lizi Jiaohuan Yu Xifu* 1988, 4, 216; *Chem Abstr* 1988, 110, 174324p.
14. Yan, J.; Wang, X. H.; Cao, Z. N. *React Funct Polym* 2000, 46, 127.
15. Bartholin, M.; Boissier, G.; Dubois, J. *Makromol Chem* 1981, 182, 2075.
16. Hubbard, K. L.; Finch, J. A.; Darling, G. D. *React Funct Polym* 1998, 36, 17.
17. Batich, C. D.; Yan, J.; Bucaria, C.; Elsabee, J. M. *Macromolecules* 1993, 26, 4675.
18. Kolarz, B. N. *Angew Macromol Chem* 1980, 90, 183.
19. Paleos, J. *J Colloid Interface Sci* 1969, 31, 7.
20. Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 2nd ed.; New York: Wiley, 1975.
21. Nyhus, A. K.; Hagen, S.; Berge, A. *J Polym Sci Part A: Polym Chem* 2000, 38, 1366.
22. Jiang, L. U.; Wang, S. T.; He, B. L. *React Polym* 1990, 12, 269.