Pore Structure of Water-Wettable Hydrophobic Resins Based on Divinylbenzene and Methyl Acrylate

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ABSTRACT: Hydrophobic, but water-wettable porous resins based on divinylbenzene (DVB) and methyl acrylate (MA) were prepared with a wide range of pore structures by suspension copolymerization under different conditions. By using purified DVB (98.8%), the specific surface area for the resulting MA/DVB resins could reach high values at high DVB levels, while these resins are wettable by direct contact with water. An increased content of MA significantly increases the porosity of the resins, whereas the solvating power of the porogen affects both pore structure and water-wettability of the MA/DVB resins profoundly. Treating these MA/DVB resins with ferric chloride in the presence of dichloroethane gives products with larger surface areas and an enhanced water-wettability. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2681–2688, 2004

Key words: water-wettability; divinylbenzene-methyl acrylate resins; macroporous polymers; structure; crosslinking

INTRODUCTION

The applications of hydrophobic porous polymeric resins, especially resins derived from styrene (ST) and divinylbenzene (DVB), are often restricted by problems associated with the hydrophobic surface of the resins. For example, the hydrophobic surface limits their efficiency as a solid-phase extraction sorbent by preventing intimate surface contact with aqueous samples,[1,2] and when they are used for the biochemical separations, such as the purification of the proteins, the hydrophobic surface could result in irreversible adsorption or loss of yield.[3,4]

In recent years, therefore, numerous attempts have been made to increase the hydrophilicity of the hydrophobic resins. The commonly used method is to chemically attach the hydrophilic functional groups, such as carboxy, acetyl, hydroxymethyl, and sulfonic acid groups, to the aromatic rings of the ST/DVB resins.[1,5] The coating of the hydrophobic surface with hydrophilic polymers of poly(vinyl alcohol), poly(oxyethylenes), and so on is also a usual modification procedure.[1,6] The increased hydrophilicity of the DVB based resins can also be achieved by copolymerization of DVB and a hydrophilic monomer, for example, vinylpyridine or *n*-vinylpyrrolidone,[2] or by graft copolymerization of the DVB-based resins with a hydrophilic monomer such as 2-hydroxyethyl methacrylate or *n*-vinylpyrrolidone, via the exposed pendent vinyl

groups on the resin surface.[7] All above attempts are based upon the approaches to introduce a hydrophilic component into the hydrophobic polymeric resins.

We have recently found that, by copolymerization of purified DVB and MA under proper conditions, the resulting porous MA/DVB resins are swellable or wettable by direct contact with water, although both the homopolymers derived from DVB or MA are hydrophobic.[8] The content of MA in the resins is important to the swelling ability of the resins in water, but only when the resins are prepared with DVB content high enough, the direct swelling in water occurs, reflecting the combined effect of the crosslinking density and the weak polymer polarity on the swelling ability of the MA/DVB resins in water. Clearly, this kind of swelling or wetting is different, in nature, to a great extent, from the swelling or wetting of the resins that are obtained by introducing the hydrophilic group or monomer as mentioned above.

In our earlier papers concerning the swelling of some ST/DVB resins in ethanol[9] or in water (assessed by measuring water uptake with the resins pretreated by using a water-miscible solvent),[10,11] we have attributed such ability to the highly strained network of the polymer, in which the strong inner stresses and greatly decreased energy of interaction between polymer chains lead to the swelling of the resins in solvents with very weak solvating power. In other words, under the conditions of the existence of the strong inner stresses, a crosslinking network could swell under a very weak interaction between polymer chains and solvent. Accordingly, the weak polymer–water interaction arisen from the incorporation of the

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MA is believed to be the another factor, which, in conjunction with the inner stresses, enables the direct swelling of the above-mentioned MA/DVB resins in water.[8] Of course, it is impossible for such a weak interaction between the MA/DVB copolymer chains and the water to cause the swelling of a conventional hydrophobic network, such as a gel-type MA/DVB resin, in water.

This is the first time that by simple copolymerization of DVB and a moderately hydrophobic monomer of alkyl acrylate ester, one can obtain a porous copolymer with high DVB content, which is hydrophobic in nature, but could swell in water directly. In a previous paper we have presented the swelling behavior of thus obtained MA/DVB resins in water.[8] It is, however, more valuable that the MA/DVB resins also can be prepared with a wide range of pore structures, while these resins are wettable or swellable in water. The purpose of this paper is to report the pore structure of these water-wettable resins, and the relationship between the pore structure and the synthesis conditions. Great effort has been made to prepare the MA/DVB resins with higher DVB content (higher surface area), which are still water-wettable. On the basis of the obtained results we believe that these new polymer materials with high surface area and characterized by both hydrophobicity and water-wettable property will find their specific applications in the adsorption and separation areas.

EXPERIMENTAL

Materials

Technical DVB (79.3%), methyl acrylate (MA, >98.5%), and ethyl acrylate (EA, 99%) were treated with an anion-exchange resin to remove inhibitors before use. Purified DVB (98.8%, containing 49.3% p-DVB and 49.5% m-DVB) was obtained according to the method of Popov and Schwachula.[12] Ethylvinylbenzene (EVB) containing a small amount of DVB was obtained by fractionating the residue of technical DVB in which the DVB has been separated. Reagent-grade toluene, n-heptane, anhydrous ferric chloride, and most of other chemicals were used as received.

Resin synthesis

Copolymer resins were prepared, unless otherwise described, by usual suspension polymerization in the presence of toluene or the mixtures of toluene and n-heptane as porogen.[10,13] The monomers were first mixed well with the porogen to form an organic phase in which the initiator, 2, 2′-azobis(isobutyronitrile), 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, and the polymerization was allowed to proceed at 70 and 85–90°C for 14 and 4 h, respectively. The resulting MA/DVB resins were washed with hot water and extracted thoroughly with acetone in a Soxhlet apparatus, and the acetone-swollen resins were finally dried *in vacuo* at 80°C. For all resins the contents of DVB, MA, and other monomers are expressed as a weight percentage of the total amount of monomers. (Take the purity of monomers, other than the technical DVB and EVB, approximately as 100% in calculating the contents.). Except for additional illustration, the toluene was used as porogen at a fixed dilution degree (2.0), which was expressed as the volume ratio of porogen to monomers. When a mixture of toluene and n-heptane was used as porogen, the n-heptane content was expressed as a volume percentage of the total volume of the porogen.

For some MA/DVB resins the postcrosslinking was performed.[14] Typically, 5 g of porous resins were first swollen in 30 cm³ of 1.2-dichloroethane. To this mixture, 1.5 g of anhydrous ferric chloride was then added and the reaction with stirring was conducted at 80°C for 8 h. The resins after reaction were washed with HCl-containing aqueous solution and acetone and dried *in vacuo* at 80°C.

Characterization

The apparent density (d_a, g/cm³) of resins in dry state was determined by an improved mercury pycnometric method as described in our previous paper, with a relative error of measurement less than 1%.[10] The true density (d_t, g/cm³) was also measured by pycnometric method but with n-heptane as the confining fluid.[13] From d_a and d_t the porosity (P, vol %) and pore volume (V_p, cm³/g) were calculated using the equations $P = (1 - d_a/d_t) \times 100\%$ and $V_p = 1/d_a - 1/d_t$, respectively. The specific surface area (S, m²/g) was determined by a conventional nitrogen adsorption BET technique using a ST-03 instrument, and the average pore diameter (D, nm) can be calculated by the equation: $D = 4 \times 10^3 V_p/S$ (nm). Pore size distribution was calculated from the nitrogen desorption data obtained on a Micromerities TriStar 3000 analyzer.

Wetting experiments

The water-wettability of the resin or film samples may be quickly checked by the "float-sink" test,[5,15] i.e., by adding a bit of dry sample to water. A water-wettable sample will sink into the water, whereas a nonwettable sample retains air in pores and thereby remains on the surface of the water as long as its skeletal density (true density) is not too high. Additionally, the contact angle measurement was also used to assess the water-wettability of the film samples, by the sessile-
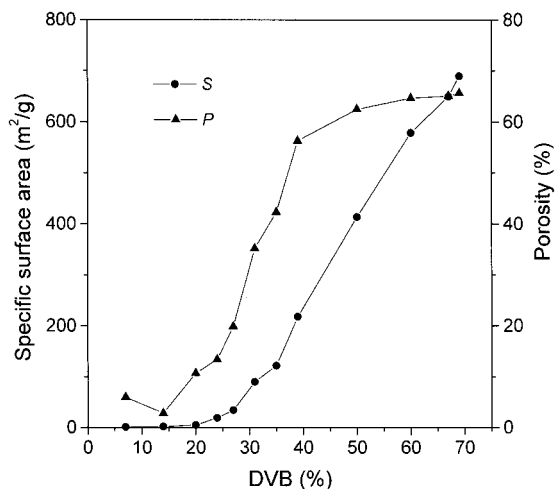
Figure 1 Dependence of the specific surface area (*S*) and porosity (*P*) of the MA/DVB resins on the DVB content. The resins were prepared by using purified DVB (98.8%).

drop method using a JV-82 contact angle meter. The degree of wetting was assessed by measuring water uptake (V_w, cm^3/g) of the samples. For bead samples the water uptake was measured with a centrifuge method, with a relative error of 3% or less for samples where the value of water uptake is above 0.3 cm^3/g,[16] whereas for film samples the water uptake was measured with a gravimetric method as described in literature.[17] In all cases the wetting experiments were carried out by direct contact of polymer with water, i.e., without the pretreatment of the polymers with a water-miscible organic solvent.

RESULTS AND DISCUSSION

Pore structure and water-wettability of the resins with different compositions

In a previous paper we have shown that, by copolymerzation of technical DVB (79.3%) and MA in the presence of toluene as porogen, the resulting porous MA/DVB resins could not be wetted with water directly, but, by using purified DVB and prepared under certain conditions, the porous MA/DVB resins thus obtained with a wide range of DVB contents become water-swellable by direct contact with water.[8] Figure 1 shows the DVB dependence of the specific surface area and porosity of the MA/DVB resins prepared from purified DVB (98.8%) and MA, in a range of DVB contents from 7 to 69%. In Figure 1, the resins with DVB content of 14% or less appear as glassy; in consequence, the surface area and the porosity for these resins are very limited. Beyond 14% DVB, however, the porosity increases rapidly, reaches a value of 56.3% at 39% DVB, and then the increase in porosity slows down with a further increase in DVB content. The DVB dependence of the porosity described here is

similar to that for ST/DVB resins prepared with toluene as porogen. The increase in surface area, on the other hand, is very slow at DVB contents less than 27%, but beyond 27% DVB the surface area increases significantly and almost linearly depends upon the DVB content in the whole range of DVB contents above 27%. In general, the pore size for the resins in Figure 1 decreases with an increase in DVB content. But between the DVB contents of 27 and 39%, because both the porosity and the surface area increase rapidly, the average pore diameter of the resins maintains a nearly constant value of about 20 nm. Above 39% DVB, however, because of a slower increase in porosity than in surface area, the average pore diameter decreases from 20.3 nm at 39% DVB to 9.8 nm at 69% DVB.

Because, even for the gel type resin of PMA (1% DVB as crosslinker), the water uptake is only 0.03 cm^3/g by direct contact with water, the MA/DVB resins that have a MA/DVB matrix should be hydrophobic in nature. In Figure 1, the MA/DVB resins with 7 and 14% DVB really present a hydrophobic character, with water uptakes of only 0 and 0.06 cm^3/g, respectively. Normally, the hydrophobicity of the MA/DVB resins should increase with a further increase in the DVB content. However, as has been reported in a previous paper,[8] the resins are water-swellable, and therefore water-wettable, with higher DVB contents of up to 60%. Even when DVB content is increased up to 67% DVB, the mainly DVB-based resin with surface area of 650 m^2/g can still be wetted by direct contact with water.

Further research on the wettability of the MA/DVB resins with different DVB contents is reported in this paper. To obtain polymer samples with a flat and smooth surface for the contact angle measurement, a series of film samples of the MA/DVB resins was prepared by bulk copolymerization of the purified DVB and MA using the same porogen (toluene) as that in Figure 1, between two glass plates with 0.5 mm space. The results are presented in Table I.

Similar to the bead samples in Figure 1, the film samples in Table I with low DVB contents (14% or less) appear glassy in the dry state, but above 17% DVB the samples become opaque, indicating the appearance of the pore structure. The water uptake for samples with 7 and 14% DVB in Table I is also very limited, but beyond 17% DVB, with an increase in DVB content, the water uptake increases significantly, and the films become easy to wet above 27% DVB, as indicated by the wetting index in Table I. The wetting behavior described here is consistent with the observations on the equilibrium and dynamic swellings in water of the bead samples.[8] For bead samples, as has been reported in the previous paper,[8] the 50% DVB copolymer has the fastest water-swelling rate among the other copolymer samples with different DVB con-

TABLE I
Dependence of the Wetting Properties of the MA/DVB Copolymer Films[a] on the DVB Content

DVB (%)	7	14	17	20	24	27	39	50
Water uptake (cm³/g)	−0.02	0.08	0.15	0.39	0.50	0.73	1.16	1.18
Contact angle[b] (degree)	64.8 ± 3.6	69.2 ± 2.2	66.1 ± 2.9	64.9 ± 3.0	64.8 ± 1.9	68.0 ± 1.3	73.0 ± 1.7	75.4 ± 1.8
Wetting index[c]	D	D	D	C	C	B	B	A

[a] The MA/DVB copolymer films were prepared from purified DVB (98.8%) and MA in the presence of toluene as porogen at a dilution degree of 2.0.

[b] The contact angle was measured by the sessile-drop method using a JV-82 contact angle meter in water; the error limits are standard derivations ($n = 10$).

[c] Judgement of wetting index: (A) sample sinks into water immediately (less than 1 min); (B) sample sinks into water in 15 min or less; (C) sample sinks into water after several hours or overnight with an occasionally agitating; (D) sample sinks into water under the action of gravity.

tents. These results indicate that the wetting or swelling behavior of these MA/DVB copolymers is reproducible when the copolymers are prepared by different polymerization processes.

Usually, the wettability of a material can be assessed by contact angle measurement, which reflects the solid–liquid interaction. Based upon the published results for the wetting of the fiber membranes, the contact angle between 50 and 60°, depending on the pore geometry, was considered assumable for complete wetting of the ST/DVB resins Amberlite XAD-2 and XAD-4.[15] The porous film samples in Table I, which are also the assemblages of the microgel particles as those Amberlite polymeric adsorbents, show the values of water contact angle all above 60° at various DVB levels, and the contact angle tends to increase with increasing the DVB content. An increase in water contact angle reflects an increase in hydrophobicity of a material. Thus, the change in value of contact angle with changing DVB content in Table I seems to be understandable, because PMA is less hydrophobic than PDVB. However, these data of contact angle fail to explain the wettability assessed by the water uptake measurement and the "float–sink" test. The difference in pore sizes for the samples with different DVB contents, in this case, should not be the cause of the change of contact angle. The following arguments can serve to support this opinion: first, as has already been mentioned before, the pore size for the resins in Figure 1 maintains a nearly constant value of about 20 nm, in the range of DVB contents from 27 to 39%, while the contact angle increases apparently in this range; second, the 67% DVB and the 69% DVB resins both possess an average pore diameter of about 10 nm, but the water-wetting ability for them is definitely different. The water uptakes for 67 and 69% DVB resins are 1.61 and 0.41 cm³/g, respectively, while the difference of the pore volumes for them is very small. It would be very interesting to know the cause of this phenomenon, but at present the necessary knowledge is not available and much work remains to be done to make the phenomenon clear.

Figure 2 shows the pore size distribution of the MA/DVB resins with DVB contents of 50 and 60%. The resins in Figure 2 are the same as those in Figure 1 and are easily wettable in water. Comparison between these two resins shows that the pore size distribution tends to shift toward a smaller pore size region as the DVB content is increased. However, both resins contain pores mainly lying in the region of mesopores (2–50 nm) and display the maxima in their pore size distribution at about 31 and 40 nm for the 60 and 50% DVB resins, respectively. The specific surface areas for the 60 and 50% DVB resins determined by using a Micromeritic TriStar 3000 analyzer are 701 and 521m²/g, respectively; both are greater than the values of 579 and 412m²/g shown in Figure 1 obtained on the ST-03 instrument for these two resins.

Tables II and III serve to further illustrate the effect of the DVB and MA contents on the porous properties of the MA/DVB resins, with either the MA or the DVB content fixed at a constant level.

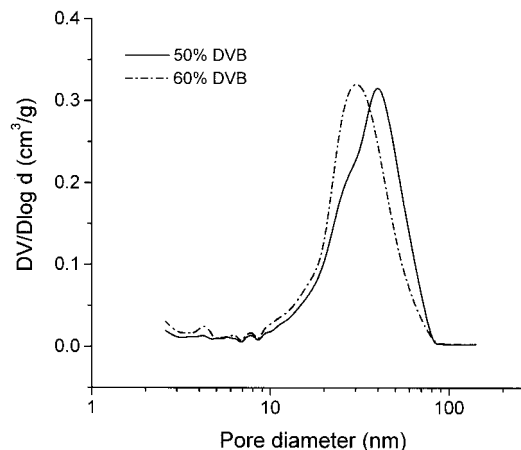Table II presents the effect of DVB content on the porous properties of the MA/DVB resins, with the

Figure 2 Pore size distribution of the MA/DVB resins with DVB contents of 50 and 60%. The resins are the same as those in Figure 1.

TABLE II
Properties[a] of the MA/DVB Resins with the MA Content Fixed at 40% and the DVB Content Varied from 36 to 60%

DVB (%)	S (m^2/g)	d_a (g/cm^3)	P (%)	V_P (cm^3/g)	D (nm)	Wettability[b]
36	167	0.830	27.8	0.334	8.0	F
48	421	0.472	59.1	1.253	11.9	F
52	421	0.453	61.3	1.352	12.8	F
55	534	0.462	61.0	1.318	9.9	S
60	579	0.408	64.7	1.586	11.0	S

[a] S, specific surface area; d_{ra} apparent density; P, porosity; V_P, pore volume; D, average pore diameter.
[b] Judged by the float–sink tests of the dry resin samples. F and S represent float and sink, respectively.

MA content fixed at 40% and the DVB contents varied from 36 to 60% by incorporating the third comonomer of EVB. It is seen that both the specific surface area and the porosity or pore volume increase rapidly with increasing the DVB content at relatively low DVB levels, but the increases slow down with a further increase in DVB content. Because the increase of surface area is essentially in parallel with the porosity, the variation of the average pore diameter for MA/DVB resins in Table II is not significant. The DVB dependence of surface area and porosity for MA/DVB resins presented in Table II is similar to that for ST/DVB resins synthesized under similar conditions,[14] regardless of the difference in polarity existing between the monomers of MA and ST. But this relationship is different from that for methacrylic acid (MAA)/DVB copolymer resins; in the case of the MAA/DVB resins, an increase in DVB content causes a decrease in the porosity of the resulting resins.[18] This fact suggests that the effect of the polarity of MA is much less than that of MAA.

It is worth noting that at high DVB levels in Table II the MA/DVB resins become water-wettable, as simply judged by the float–sink test of the dry sample in water.[5,7,15] Since the large surface area can be achieved usually at a high crosslinker level, it is therefore possible to prepare the MA/DVB resins with large surface areas while these resins are water-wettable.

Table III presents the effect of MA content on the porous properties of the MA/DVB resins, with the DVB content fixed at 50% and the MA content varied from 30 to 50% also by incorporating EVB. As can be seen in Table 3, while the surface area almost remains unchanged with the change in MA content, the apparent density decreases gradually and the porosity or the pore volume increases apparently. As a result, the average pore diameter of the MA/DVB resins increases from 10.2 to 14.1 nm as the MA content is increased from 30 to 50%. Making a comparison of the solubility parameters between the polymers PMA and PDVB may help to explain the MA dependence of the porosity of the MA/DVB resins in Table III. The solubility parameters, δ (cal$^{0.5}$/cm$^{1.5}$), for PMA and PST (an analogue of PDVB) are 9.8–10.1 and 9.1, respectively.[19] On the other hand, the δ values for both toluene (porogen) and MA are 8.9 and for ST is a bit greater than 8.9.[19] Therefore, all these δ values of the porogen and monomers are close to that of PST, but much smaller than that of PMA. Accordingly, with increasing the fraction of MA in the monomer system, the δ value for the monomers mixture doesn't change too much, whereas the δ value for the MA/DVB polymers formed at various stages of the copolymerization increases profoundly. As a result, the earlier phase separation of the growing polymer chains occurs in the case of the resins prepared with the higher MA content, leading to the increased porosity of the resulting MA/DVB resins.

With the MA content increased to a level of 46% or higher, the resins become water-wettable as presented in Table III. Because the PMA itself is a hydrophobic polymer as has mentioned before, the effect of the MA content on the water-wettability of the MA/DVB resins presented in Table III is very striking. The similar observation on the swelling of the MA/DVB resins in water has been explained by considering the com-

TABLE III
Properties of the MA/DVB Resins with the DVB Content Fixed at 50% and the MA Content Varied from 30 to 50%

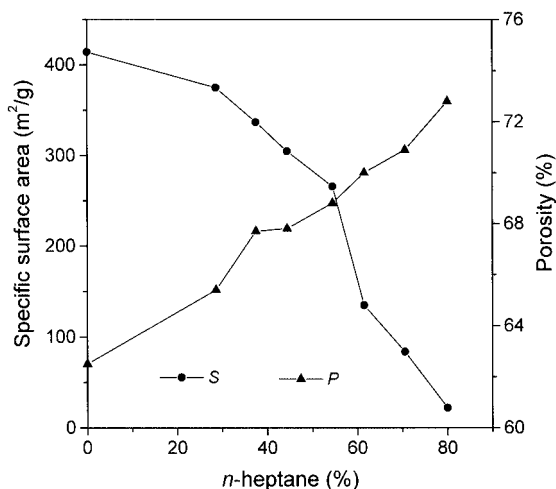| MA (%)	S (m^2/g)	d_a (g/cm^3)	P (%)	V_P (cm^3/g)	D (nm)	Wettability
30	413	0.510	53.6	1.052	10.2	F
40	424	0.470	58.8	1.250	11.8	F
43	436	0.453	60.6	1.338	12.3	F
46	412	0.452	62.1	1.375	13.3	S
50	414	0.428	62.5	1.459	14.1	S

See Table 2 footnotes.

Figure 3 Dependence of the specific surface area (S) and porosity (P) of the MA/DVB resins on the n-heptane content in the mixed porogen of toluene and n-heptane. The resins were prepared with a fixed MA/DVB ratio of 50/50 and a dilution degree of 2.0.

bined effect of the weak interaction between the polymer and water and the release of inner stresses existing in the dry resin network.[8]

Effect of the porogen

Figure 3 shows the dependence of the specific surface area and porosity of the MA/DVB resins on the n-heptane content in the mixed porogen of toluene and n-heptane. The resins were prepared with a fixed MA/DVB ratio of 50/50 and a dilution degree of 2.0. As it is known, the solvating power of the porogen has a critical effect on the porous structure of the porous resins.[20,21] In Figure 3, with an increase in the n-heptane content, the porosity increases monotonously, whereas the surface area decreases significantly. Comparing the porous properties of the MA/DVB resins with those of the ST/DVB based resins,[14] it is seen that the former is more strongly influenced by the n-heptane content than the latter under similar conditions. For ST/DVB resins, while the porosity also shows an apparent increase, the surface area only shows a weak tendency to decrease, with an increase in the n-heptane content.[14] This means that larger pores form for MA/DVB resins than for ST/DVB resins as the n-heptane content increases. Consequently, the average pore diameter for MA/DVB resins increases from 14.1 to 101 nm, with an increase in the n-heptane content from 0 to 70.6%; whereas the average pore diameter for ST/DVB resins increases from 6.1 to 13.3 nm only, with an increase in n-heptane content from 16.7 to 66.7%. The stronger effect of the n-heptane content on MA/DVB than on ST/DVB copolymer resins may be attributed to the different thermodynamic properties

of MA/DVB and ST/DVB copolymers, which results in a greater difference in solubility parameters between n-heptane (δ = 7.45) and MA/DVB copolymer (PMA, δ = 9.8–10.1) than between n-heptane and ST/DVB copolymer (PST, δ = 9.1).

As reported in our previous paper, the solvating power of the porogen also has an important effect on the water-swelling ability of the resulting MA/DVB resins in water.[8] This was explained by the change of the inner stresses in MA/DVB copolymer networks, resulting from the change of the solvating state of the growing polymer chains in porogens with different solvating powers.[8] Differing only in the content of n-heptane, the resins in Figure 3 of this paper are water-wettable up to the n-heptane content of 61.5%, but beyond that the resin samples keep floating on the surface of water even with stirring.

Figure 4 shows the dependence of the specific surface area and porosity of the MA/DVB resins on the dilution degree of the monomers. The resins were prepared using toluene as porogen, with the MA/DVB ratio fixed at 50/50. Instead of a monotonous decrease or increase in the surface area or porosity in Figure 3, both the surface area and porosity, as exhibited in Figure 4, increase initially, and approach their maxima of 452 m^2/g and 62.5% at the dilution degrees of 3.0 and 2.0, respectively. A further increase in dilution degree, however, results in a decrease in surface area and in porosity. This phenomenon is similar to our previous observation of the ST/DVB resins.[14] For ST/DVB resins, with DVB content fixed at a constant level, their crosslinking density is known to be very much dependent on the amount of the solvating dilution (porogen).[9,14] At a too high degree of monomer dilution, the network structure between the phase-
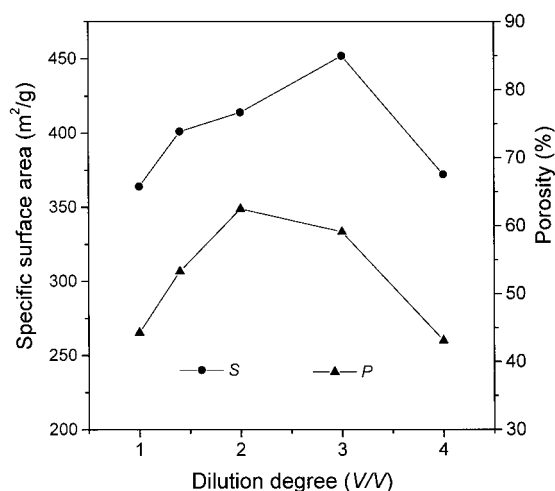

Figure 4 Dependence of the specific surface area (S) and porosity (P) of the MA/DVB resins on the dilution degree of the monomers. The resins were prepared using toluene as porogen, with the MA/DVB ratio fixed at 50/50.

TABLE IV
Specific Surface Area, Pore Volume, and Water Uptake for MA/DVB and EA/DVB Resins[a] Before and After Postcrosslinking Reaction

Resins		S (m²/g)		V_p (cm³/g)		V_w (cm³/g)		$V_w - V_p$ (cm³/g)	
No.	Compositions	Before[b]	After[b]	Before[b]	After[b]	Before[b]	After[b]	Before[b]	After[b]
	MA/DVB[c]								
1	41/48	381	378	0.880	1.097	0.201	0.438	−0.679	−0.658
2	29/57	517	559	0.982	1.409	0.080	0.189	−0.902	−1.220
3	18/65	576	659	1.176	1.609	0.035	0.100	−1.140	−1.509
	MA/DVB[d]								
4	40/60	579	579	1.586	1.658	1.908	1.883	0.322	0.225
5	33/67	650	710	1.557	1.692	1.611	1.766	0.054	0.074
6	31/69	690	773	1.689	1.775	0.407	1.930	−1.282	0.155
	EA/DVB[d]								
7	54/46	366	380	1.051	1.062	0.204	1.506	−0.847	0.444
8	44/56	539	597	1.397	1.450	0.204	1.850	−1.193	0.400
9	34/66	729	751	1.553	1.590	0.123	1.636	−1.43	0.046

[a] The EA/DVB resins were prepared from ethyl acrylate (EA) and DVB under the same conditions as those for MA/DVB resins.
[b] Before and after represent before and after postcrosslinking reaction, respectively.
[c] Technical DVB (79.3%) was used for the preparation of MA/DVB resins 1–3.
[d] Purified DVB (98.8%, containing 49.5% m-DVB and 49.3% p-DVB) was used for the preparation of MA/DVB and EA/DVB resins 4–9.

separated microgel particles becomes very loose; this reduces the ability of the resulting porous copolymers to keep from shrinking when the porogen is removed. We believe the same explanation can be applied to interpret the decrease of surface area and porosity in Figure 4 at a high degree of dilution.

All resin samples in Figure 4 are water-wettable, regardless of the amount of the solvating porogen used in the copolymerization.

Effect of the postcrosslinking

In Table II of this paper we have seen that, with MA content fixed at a constant level, the specific surface area and porosity increase as the DVB content is increased, and at high DVB levels the resins become wettable in water. Undoubtedly, the water-wettable property in combination with the high surface area should be particularly valuable for a mainly DVB-based porous resin to be used as an adsorbent. However, even using purified DVB, the fraction of DVB in the MA/DVB resins is restricted by the portion of MA, and therefore the surface area of the resins, as shown in Table II, can't reach a higher value.

In recent years, the postcrosslinking of the ST/DVB resins via the pendant vinyl groups in the copolymers has been reported.[14,22] Without an externally added crosslinking agent, the surface area of the resins increases significantly by simply heating the solvating solvent-swollen resins in the presence of anhydrous ferric chloride.[14] IR spectra of the MA/DVB resins show that an appreciable amount of pendant vinyl group also exists in the MA/DVB resins with rela-

tively high DVB content. The investigation of the postcrosslinking therefore has been done on the MA/DVB resins with different monomer compositions. Parts of the data are listed in Table IV.

In Table IV, resins 1–3 were prepared by using technical DVB (79.3%). It is seen that in most cases the surface area and pore volume increase after postcrosslinking reaction, but the increase is more significant for resins with higher DVB content than with lower DVB content. This is because the vinyl group content of the resins increases with an increase in the DVB content, which leads to more new crosslinking bonds created by the alkylation reaction. By comparing water uptake with the value of corresponding pore volume of these resins, we can see that the pores of all three resins before and after postcrosslinking can't be fully filled with water, therefore these resins are not water-wettable.

Resins 4–6 were prepared by using purified DVB (98.8%), in this case the MA amounts in the MA/DVB resins with the same DVB content are increased compared with the resins prepared using technical DVB. For these three resins the surface area and pore volume also increase apparently after postcrosslinking. It is worth noting that, before the postcrosslinking reaction, resin 6 is not water-wettable, but after the reaction the resin becomes water-wettable, as indicated by the difference between the corresponding values of water uptake and pore volume ($V_w - V_p$). This result is reproducible and is consistent with the observation in Table II, where an increased crosslinking degree at a fixed MA level is in favor of the increase in the wetting ability of the resin in water.

Instead of MA, resins 7–9 were prepared by the copolymerization of EA and purified DVB. Similarly, both the surface area and the pore volume for these three resins increase after postcrosslinking. But more interestingly, all three resins are water-wettable after postcrosslinking, while they originally were not water-wettable because of the presence of an extra methyl group in EA compared with MA. This fact indicates that more kinds of hydrophobic alkyl (meth)acrylate esters could be used to synthesize the mainly DVB-based porous resins that are wettable in water.

From the results presented in Table IV we have seen that the water-wettable, mainly DVB-based resins could be obtained with specific surface areas up to 773 m^2/g for MA/DVB resins and with specific surface areas up to 751 m^2/g for EA/DVB resins, after post-crosslinking. We believe that, through further research, the mainly DVB-based resins could be prepared with a wider range of porous structures, while these resins are water-wettable.

CONCLUSION

The hydrophobic porous MA/DVB resins can be prepared with a wide range of pore structures while these resins are water-wettable. The DVB and MA contents affect the pore structure of the MA/DVB resins profoundly. With the MA content fixed at a constant level, both the specific surface area and the porosity increase with an increase in DVB content, but just at high DVB levels, the resins are water-wettable. On the other hand, with the DVB content fixed at a constant level and the MA content increased, the porosity increases significantly, whereas the surface area almost remains unchanged. A decrease of the solvating power of the porogen causes a rapid decrease in specific surface area and an increase in porosity and, at the same time,

leads to a decrease in the wetting ability of the resulting resins in water. A further increase in the degree of crosslinking of the MA/DVB resins by postcrosslinking leads to an increase, not only in surface area and porosity, but also in water-wetting ability. Even MA/DVB resin with the MA/DVB ratio of 31/69 is also water-wettable after postcrosslinking, having a specific surface area of 773 m^2/g. It is believed that these new polymer materials will find their specific applications in the adsorption and separation areas.

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