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Water-Swellable Hydrophobic Porous Copolymers Based on Divinylbenzene and Methyl Acrylate: Preparation and Water-Swelling Behavior

J. Wei, X. Y. Bai, and J. Yan*

Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, People's Republic of China

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ABSTRACT: Porous copolymers based on divinylbenzene (DVB) and methyl acrylate (MA) were prepared by suspension polymerization in the presence of toluene as porogen. By using purified DVB (98.8%), the resulting MA/DVB copolymers with a wide range of DVB contents were found to be able to swell in water directly, although both the homopolymers derived from DVB and MA are hydrophobic. The amounts of DVB and MA in the copolymers affect the water-swelling behavior profoundly. However, the direct swelling in water occurs only after the DVB or MA content reaches a critical value, and the effect of the MA content will be significant only when the DVB content is at a high level. The latter observation reflects the combined effect of the cross-linking density and the polymer polarity on the swelling ability of the MA/DVB copolymers in water. The nature of the direct swelling of these hydrophobic porous copolymers in water was discussed by considering both factors: the existence of the inner stresses in the strained polymer network and the weak interaction between polymer and water that is negligible in the case of the conventional hydrophobic polymers.

Introduction

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. As early as 1963, Millar et al. discovered that, for styrene/divinylbenzene (ST/DVB) copolymers prepared with toluene as porogen, the pores of these copolymers could be filled with water, after first treating these copolymers with methanol.[1] But the volume increase of the copolymers on taking up water was thought to be zero; i.e., the water was just accommodated in the already existing air-filled pores and could not swell the copolymers.[1] Because of the strong hydrophobic character of the ST/DVB copolymers, this viewpoint was generally accepted later, and on the basis of this knowledge, a method of pore volume determination using water for ST/DVB copolymers was developed.[2] In this method, the water uptake of a copolymer sample was measured after treatment with methanol and was taken as the pore volume of the sample in dry state.[2]

We have recently shown that when a solvent with strong solvating power is used as a porogen for preparing the porous ST/DVB copolymers, the resulting products could increase their volume in water, which is assessed by measuring water uptake of the copolymers after treatment with methanol.[3] We therefore pointed out that the use of water to measure the pore volume of porous ST/DVB copolymers did not always give a true value of the pore volume in dry state.[3] At the same time, a systematic work has been done on the swelling behavior of the ST/DVB copolymers in water, with the copolymers first treated by methanol.[4]

While the water-swelling behavior of the general hydrophobic porous copolymers, especially the porous ST/DVB copolymers, has not received deserved attention, the swelling ability in water of a class of polymers called "hyper-cross-linked polystyrene", developed by Davankov and Tsyurupa et al., was well reported for many years.[5,6] As hydrophobic polymers, however, it is also necessary to measure the water-swelling capacity by first treating the sample with a water-miscible solvent.[7] The hyper-cross-linked polystyrene was prepared by post-cross-linking the polymer chains in solution or in swollen state via a Friedel−Crafts reaction; the products thus obtained are different in structure from the porous ST/DVB copolymers.[5,6] However, because in our case the ST/DVB copolymers were also prepared in the presence of a solvating solvent, in the same way of thinking as Davankov et al., the indirect swelling ability of the porous ST/DVB copolymers in water was ascribed to the existence of inner stresses in the dry polymer network, which arises during the removal of the porogen after polymerization.[4] Since an increase in volume of the copolymers during swelling is in favor of the release of the stresses, the strained network drastically increases the ability of the copolymer to swell in solvents with weak solvating power for the copolymer.

Then, an interesting question arises whether the hydrophobic copolymers could swell by direct contact with water. In the previous study we observed that the ST/DVB copolymers prepared with toluene as porogen could directly swell in an aqueous solution of ethanol with different concentrations, depending upon the degree of cross-linking. When the amount of DVB in the copolymer increased up to 98%, this copolymer could swell in the solution of ethanol with a concentration as low as 10% (v/v), but it still did not swell directly in

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* To whom correspondence should be addressed.

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water.[8] Recently, we prepared the porous copolymers based on alkyl methacrylate ester and ethylene glycol dimethacrylate with toluene as porogen. These copolymers do not interact favorably with water, but when prepared with high degrees of cross-linking they were found directly swellable in water.[9]

Following the thinking of the effect of the inner stresses on the swelling ability of the polymers in solvents with weak solvating power, and on the basis of the findings described above, further research has been done. Several series of porous copolymers based on DVB and a moderately hydrophobic comonomer MA were synthesized, with the copolymer compositions as well as the type and amount of the porogens varied, for the investigation of the swelling properties of this kind of copolymer. Finally, the hydrophobic, in some cases mainly DVB based, porous MA/DVB copolymers were prepared, which are water-wettable and capable of swelling in water directly.

To our knowledge, this is the first time that, with the incorporation of a moderately hydrophobic monomer of alkyl acrylate ester, the resulting copolymers, even mainly DVB based, could directly swell in water. This paper reports the preparation and the water-swelling behavior of these DVB- and MA-based copolymers.

Experimental Section

Materials. Technical divinylbenzene (DVB, 79.3%) and methyl acrylate (MA, >98.5%) were treated with an anion-exchange resin to remove inhibitors before use. Purified DVB (98.8%) was obtained according to the method of Popov and Schwachula,[10] with 49.3% *p*-DVB and 49.5% *m*-DVB. Ethylvinylbenzene (EVB) containing a small amount of DVB was obtained by fractionating the residue of technical DVB in which the DVB has been separated. Most other chemicals were used as received.

Copolymer Synthesis. Copolymers were prepared by the usual suspension polymerization in the presence of toluene or its mixture with *n*-heptane as porogen.[4] 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 ratio (v/v), 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 copolymer beads were washed with hot water and extracted thoroughly with acetone in a Soxhlet apparatus, and the acetone-swollen beads were finally dried in vacuo at 80 °C. For all copolymer samples the DVB and MA contents are expressed as weight percent of the total amount of monomers. (Take the purity of MA and purified DVB, approximately, as 100% in calculating the MA and DVB contents.) Except for additional illustration, the toluene was used as porogen at a 2:1 ratio (v/v) to the monomers. When a mixture of toluene and *n*-heptane was used as porogen, the *n*-heptane content was expressed as volume percent of the total volume of the porogen.

Methods. The apparent density d_a and true density d_t of the copolymer samples were measured according to the methods previously described,[4,11] from which the pore volume V_p (mL/g) was calculated using the equation

$$V_p = 1/d_a - 1/d_t \tag{1}$$

The solvent (toluene or water) uptake (mL/g) was measured with a centrifuge method, with a relative error of 3% or less for samples where the value of solvent uptake is above 0.3 mL/g.[4,12] For the swelling experiments in water, the water uptake V_w was measured by direct contact of the copolymer sample with water (direct swelling) or by first immersing the sample in methanol for 24 h or more and subsequently washing it with water to remove the methanol (indirect swelling). The swelling equilibrium for the direct swelling in water at room temperature was usually achieved within 2 days, but for some samples the equilibrium time extended to 2 weeks or more depending on the copolymer compositions. The water uptakes measured directly and indirectly were denoted by V_{dw} and V_{iw}, respectively. In the dynamic swelling experiments, the degree of swelling Q (%) at different times was calculated as $Q = V_{wt}/V_{dw} \times 100\%$, where V_{wt} was the water uptake at swelling time t and V_{dw}, as just denoted, was the equilibrium water uptake measured by direct contact of the sample with water. The volume change of the copolymers in equilibrium with water was expressed as a volume swelling ratio B of the swollen copolymer beads to the initial dry ones and calculated using the equation[13]

$$B = d_a(V_w + 1/d_t) \tag{2}$$

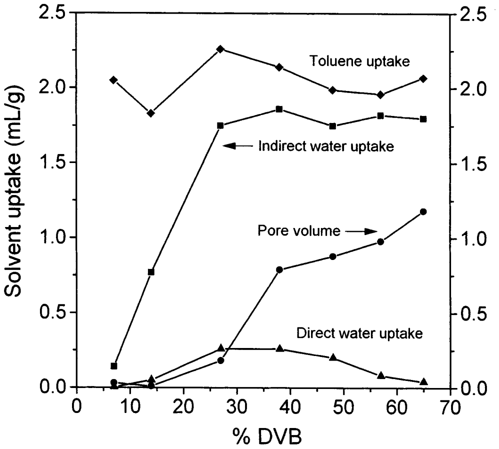

Figure 1. Dependence of the solvent (toluene or water) uptake and pore volume of MA/DVB copolymers on the DVB content. The copolymers were prepared from technical DVB (79.3% DVB). The water uptake was measured after treatment with methanol (indirect water uptake) or by direct contact of polymer with water (direct water uptake).

Results and Discussion

Preparation and Water-Swelling Behavior. First, the technical DVB (79.3%) was used to synthesize MA/DVB copolymers in the presence of toluene as porogen. Figure 1 presents the dependence of water uptakes (measured directly and indirectly) and pore volume of the MA/DVB copolymers on the DVB content. For comparison, the toluene uptake is also plotted against the DVB content in the same figure. As shown, the water uptake measured indirectly (indirect water uptake, V_{iw}) is very limited at DVB content of 7%, in contrast to the toluene uptake which reaches a high value at the same DVB level. Beyond 7% DVB, however, the indirect water uptake rapidly increases with increasing the DVB content and is getting close to the value of toluene uptake at higher degrees of cross-linking above 38% DVB. The DVB dependence of the indirect water uptake for the MA/DVB copolymers described here is very similar to that for ST/DVB copolymers reported in our previous paper.[4]

In general, the solvent uptake of porous copolymers can be considered as the result of two separate processes: filling of pores by solvent and the gel phase swelling which depends on the polymer−solvent interaction.[14] However, no single measurement could distinguish these two processes. Accordingly, both water uptake and pore volume in dry state were measured to

Table 1. Solvent Uptake and Pore Volume of MA/DVB Copolymers[a] with Different DVB Contents

DVB (%)	14	20	27	39	50	60	67	69
toluene uptake (mL/g)	1.56	2.21	2.27	2.01	2.08	2.09	1.94	2.08
water uptake[b] (V_{dw}, mL/g)	0.06	0.19	0.51	1.63	1.92	1.91	1.61	0.41
pore volume[c] (mL/g)	0.03	0.10	0.21	1.11	1.46	1.59	1.56	1.69
swelling ratio in water	1.04	1.09	1.28	1.27	1.20	1.13	1.02	/

[a] The MA/DVB copolymers were prepared from purified DVB (98.8%) with toluene as porogen. [b] The water uptake (V_{dw}) was measured by direct contact of the copolymer with water. [c] The data of pore volume listed in this table were measured, as described in the Experimental Section, after drying the acetone-swollen copolymer beads. However, to estimate the dependence of the value of pore volume on the solvent treatment process of the sample before the measurement,[8,14] the pore volume for samples with DVB contents from 39% to 69% in this table has been additionally measured by first treating these samples with a series of solvents of increasing polarity (toluene, acetone, and water). The values of pore volume for samples dried from toluene and acetone are almost the same as those listed in this table, and the values for samples dried from water are smaller than all those for samples dried from toluene and acetone. This result looks strange in contrast to the case of the porous ST/DVB copolymers,[8,14] but it is reproducible. Therefore, it is confirmed that, for samples with DVB contents of 39−67% in this table, the value of water uptake should be always greater than the corresponding pore volume.

assess whether the water could penetrate into the gel phase of the copolymers.

Then, if we make a comparison between indirect water uptake and pore volume in Figure 1, we can see that beyond 7% DVB the values of indirect water uptake are all greater than the corresponding pore volumes of the MA/DVB copolymers. This indicates that part of the water absorbed by the porous copolymers penetrates into the gel phase. With the assumption of isotropic swelling of the MA/DVB copolymers, the volume swelling ratios for 38%, 48%, 57%, and 65% DVB copolymers in Figure 1 calculated according to eq 2 are 1.65, 1.50, 1.45, and 1.31, respectively.

As compared with the indirect water uptake, the water uptake measured by direct contact of polymer with water (direct water uptake, V_{dw}) is less significant in Figure 1. Beyond 27% DVB, the value of direct water uptake is much less than the corresponding pore volume, indicating that the pores cannot be filled with water and the gel phase cannot swell in water directly. Considering the hydrophobic character of both the homopolymers derived from DVB and MA, this result is expected. We have prepared gel-type resins of PST (an analogue of PDVB) and PMA both with 1% DVB as cross-linker; the direct water uptakes for them are 0 and 0.03 mL/g, respectively.

Quite surprisingly, however, once we use the purified DVB (98.8%), instead of the technical one, to synthesize the MA/DVB copolymers, a dramatic change occurs. The hydrophobic MA/DVB copolymers with a wide range of DVB levels turn into the water-wettable ones, as judged simply by the float-sink test of the dry copolymer samples in water.[15] Although the water uptake (measured directly, V_{dw}) is very limited at DVB content less than 27%, as shown in Table 1, it increases rapidly beyond 27% DVB and reaches a maximum at about 50% DVB, which is very close to the corresponding toluene uptake. For 39%, 50%, and 60% DVB copolymers, the values of water uptake (V_{dw}) are apparently above the corresponding pore volume, with the volume swelling ratios of 1.27, 1.20, and 1.13, respectively. It should be noted that even for 67% DVB copolymers, the weight fraction of the strongly hydrophobic DVB is twice as great as that of MA, the spontaneous wetting, i.e., the spontaneous displacement of air in pores by water, occurs. To our knowledge, it is the first time that, by simple polymerization of DVB and a moderately hydrophobic comonomer of alkyl acrylate ester, one can obtain a mainly DVB-based copolymer, which is hydrophobic in nature but could be wetted and even swell in water directly. Moreover, the water-swellable copolymers reported here could also be prepared with a wide range of porous structures. For example, the specific surface area for above 67% DVB copolymer may reach a value of 650 m^2/g. By post-cross-linking, the water-swellable MA/DVB copolymers with higher DVB contents, and therefore with stronger hydrophobicity and higher surface area, can be obtained which will be reported elsewhere.

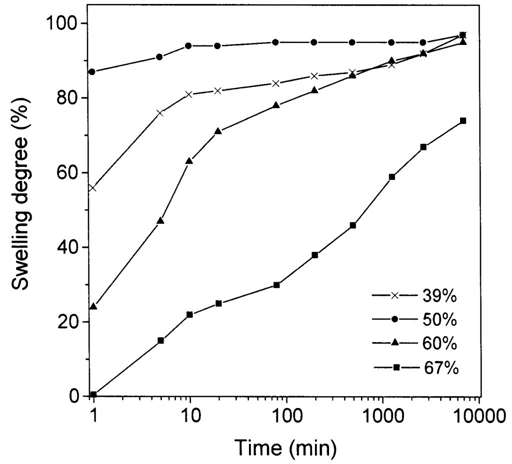

Figure 2. Dynamic swelling behavior of MA/DVB copolymers with different DVB contents in water. The swelling degree (%), which was assessed by measuring water uptake directly, was plotted against the logarithmic contact time. The copolymer samples are the same as those in Table 1 with the DVB contents from 39% to 67%.

Figure 2 shows the dynamic swelling behavior of the same copolymer samples as those in Table 1 with the DVB content from 39% to 67%. The degree of swelling was assessed by measuring water uptake directly and was plotted against the logarithmic contact time. As can be seen, with increasing the DVB content from 39% to 50% the swelling rate apparently increase; the time for 39% DVB copolymer to reach a 80% degree of swelling is about 8 min, whereas for 50% DVB sample it is less than 1 min. On the contrary, beyond 50% DVB the swelling rate reduces rapidly with a further increase in DVB content; for 60% and 67% DVB copolymers the time to reach 80% swelling degree are 130 and 16 000 min (11.1 days), respectively. The swelling rate was found to be able to greatly increase by post-cross-linking or by using different DVB isomers. In the latter case for the 67% DVB copolymer, the time to reach 80% swelling degree would decrease from 11.1 days to 8 min if the purified DVB (a mixture of 49.3% *p*-DVB and 49.5% *m*-DVB) was replaced by *p*-DVB (99.1%).

The results presented in Table 1 and Figure 2 are very striking. In general, a copolymer derived from strongly hydrophobic monomers, even with a fair amount of hydrophilic component incorporated, will remain adopting a collapsed state in water, only if the content of the hydrophilic component is below a certain value.[11,12] For example, a copolymer prepared by copolymerization of 65% *n*-butyl methacrylate, 5% ethylene glycol dimethacrylate, and 30% hydrophilic monomer of methacrylic acid, in the presence of butyl acetate as porogen, still displays a hydrophobic characteristic, with the water uptake of only 0.05 mL/g.[11] Therefore, the direct swelling in water for MA/DVB copolymers, in which both DVB and MA are hydrophobic, is a phenomenon difficult to be understood in contrast to the usual concept of polymer swelling. Generally accepted theories predict the swelling of a polymer network to only depend on the thermodynamic quality of the solvent, the degree of cross-linking, and the functionality of junction points,[7] while the results in Table 1 and Figure 2 are contrary to the predictions based upon these factors. Not much of the necessary knowledge, at this stage, is available to obtain a clear picture of how the swelling in water occurs. However, on the basis of the facts presented in this report and other papers,[3−9] we believe that it is possible to make some explanations about the unusual water-swelling behavior of the MA/DVB copolymers we found.

The MA/DVB copolymer with 14% DVB in Table 1 or Figure 1 appears as glassy, but beyond 27% DVB the copolymers become strongly opaque,[16] indicating the appearance of heterogeneity or (macro)porosity. When a solvating solvent was used as a porogen, the driving force for pore formation is cross-linking-induced phase separation.[14,17−19] In the phase-separated system, because of the different reactivities[20] of MA and DVB in copolymerization system, the gel phase of the porous MA/DVB copolymers finally formed, as is the case with ST/DVB copolymers,[21−23] should be also composed of highly cross-linked microgel particles (rich in cross-linker DVB) or their aggregater, which are closely linked together by the less cross-linked network (rich in MA), to form a continuous phase.

From above discussion it should be acceptable that the porous MA/DVB copolymers thus obtained are different, in both the cross-linking structure and the pore structure, from the hyper-cross-linked polystyrene.[5,6] However, just as with ST/DVB copolymers described in previous paper,[4] the MA/DVB copolymers in Table 1 or Figure 1 are also prepared in the presence of a solvating solvent (toluene) as porogen. In this case, the rigid networks for these MA/DVB copolymers are also formed in a well-solvated state, and the cross-linking reaction fixes the chains in a stretched state. Accordingly, the subsequent deswelling of the copolymers on removing porogen is, undoubtedly, accompanied by a rapid growth of the inner stresses in the copolymers, from the retraction and deformation of the network. Finally, the MA/DVB copolymers with a strained network in dry state are formed. The inner stresses, according to Davankov and et al., represent an additional strong driving force for the network to swell.[6,7] On the basis of this understanding, we believe that in Figure 1 the indirect swelling of the MA/DVB copolymers in water should be mainly attributed to the existence of the inner stresses in the polymer networks prepared by using technical DVB (79.3%).

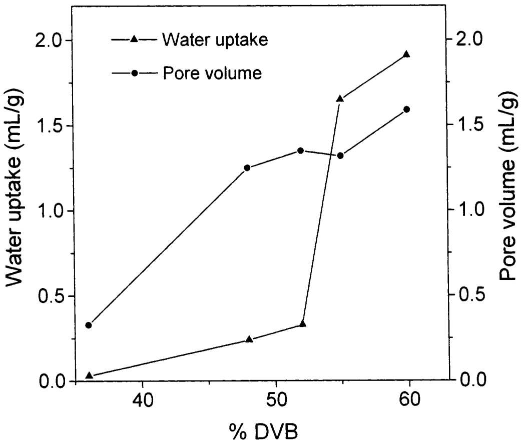

Figure 3. Effect of DVB content on the water uptake (V_{dw}) and pore volume of MA/DVB copolymers with MA content fixed at 40%. The water uptake was measured by direct contact of polymer with water.

Comparison of the result in Table 1 with that in Figure 1 shows that the striking change in water-swelling behavior for MA/DVB copolymers results from the only change in DVB purity. Because the use of the purified DVB (98.8%) makes the amount of EVB in copolymers reduce to a very low value, the amount of MA increases for the MA/DVB copolymers with the same DVB content. It is evident that an increased amount of MA results in the direct swelling in water for MA/DVB copolymers derived from purified DVB. This fact suggests that the polymer polarity plays an important role in the swelling of the hydrophobic MA/DVB copolymers in water, and there must be a relationship between the water-swelling ability of the MA/DVB copolymers and the polymer−water interaction. Since such an interaction would be extremely weak in view of the fact that the PMA itself is not water-swellable, we must find other factors that affect the water-swelling ability of the MA/DVB copolymers. Reasonably, the existence of the inner stresses is considered as another decisive factor that in conjunction with the weak interaction between the polymer and the water enables the direct swelling of the MA/DVB copolymers in water. The experiments in the next section will serve to further illustrate the effect of the cross-linking density and the polymer polarity on the swelling ability of the MA/DVB copolymers in water.

Effect of Copolymer Composition. From the results in above section we have seen that two conditions are necessary for the hydrophobic MA/DVB copolymers to swell in water directly. First, the copolymers should have a rigid network (high cross-linking density) that was formed in a well-solvating medium. Second, the polarity of the copolymers must be enhanced by incorporating enough amount of MA. To know more of the effect of cross-linking density and polymer polarity, more detailed works have been done on the MA/DVB copolymer samples with a fixed MA content but different amount of DVB or with a fixed DVB content but different amount of MA; Figures 3 and 4 present the results. All the data of water uptake in these two figures were measured by direct contact of the copolymer with water.

In Figure 3, the MA content is fixed at 40%, with the amount of DVB varied from 36% to 60% by incorporating the third comonomer of EVB; in this way the polar/nonpolar composition for all samples in Figure 3 will

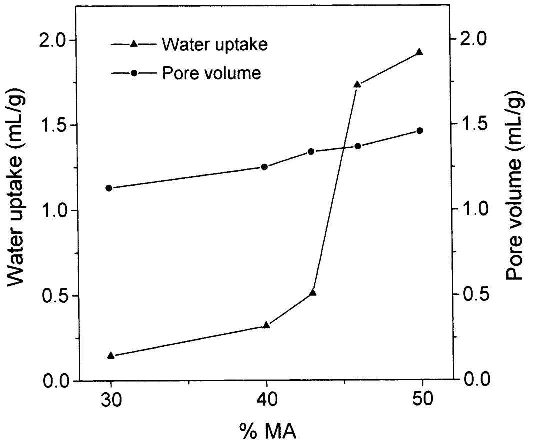

Figure 4. Effect of MA content on the water uptake (V_{dw}) and pore volume of MA/DVB copolymers with DVB content fixed at 50%. The water uptake was measured by direct contact of polymer with water.

keep a nearly constant value, while the degree of cross-linking is varied. As can be seen, the water uptake (V_{dw}) measured directly increases slightly with an increase in degree of cross-linking at DVB content less than 52% and is far below the corresponding value of pore volume. But beyond 52% DVB, the water uptake abruptly increases and reaches a high value above the corresponding pore volume at 55% DVB, with only 3% DVB interval. Since the only change in Figure 3 is the content of DVB, the increase of the cross-linking density, or the rigidity of the network, should be responsible for the increase of the direct swelling ability of the copolymers in water.

As has discussed in above section, because the networks of the MA/DVB copolymers are formed in a well-solvating solvent of toluene, inner stresses build up when the solvent is removed from the swollen networks. The inner stresses originate from two opposite tendencies.[5,6] On one hand, the polymer chains tend to reach dense packing on removing the solvent. On the other hand, the compaction process is hindered by the rigid cross-linking bridges. Then, with an increase in DVB content, larger amounts of rigid spacers are created which more strongly prevent polymer chains from approaching each other. As a result, the contracting polymer network finally attains a new equilibrium state characterized by a more strained network of copolymers which increases the direct swelling ability of the copolymers in water.

In Figure 4, the DVB content is fixed at 50%, with the amount of MA varied from 30% to 50% also by incorporating EVB. Very similar to the case of varying DVB content in Figure 3, the water uptake of the copolymers is much less than the corresponding pore volume at lower MA levels, but beyond 43% MA the swelling transition occurs. Only a 3% MA interval, the water uptake increases from 0.510 mL/g at 43% MA to 1.73 mL/g at 46% MA, which is well above the pore volume of 1.37 mL/g at the same MA level. In contrast to the water uptake, a gradual increase in pore volume is also observed. From this result we can see that the swelling ability of the copolymers in water is remarkably sensitive to the polarity variation of the MA/DVB copolymers in some range of the MA levels, and there is a critical value of the MA content only above which the swelling transition occurs.

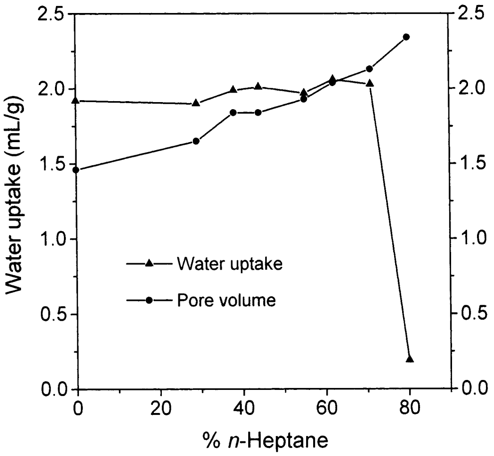

Figure 5. Effect of *n*-heptane content on the water uptake (V_{dw}) and pore volume of MA/DVB copolymers, which were prepared in the presence of the mixture of toluene and *n*-heptane as porogen at a 2:1 ratio (V/V) to the monomers. For all copolymers samples the MA and DVB contents were fixed at 50% and 50%, respectively. The water uptake was measured by direct contact of polymer with water.

For a conventional hydrophilic polymer network there is no doubt that the swelling of the network in water arises from the polymer−water interaction. For the swelling of these hydrophobic MA/DVB copolymers, the hydrophilic interaction is so weak that usually it should be negligible. However, since the variation of the MA content alone in Figure 4 is responsible for the water-swelling transition, the strong dependence of the water-swelling behavior on the MA content, or polymer polarity, demonstrates well the effect of polymer−water interaction on the swelling of the MA/DVB copolymers. Accordingly, the result presented in Figure 4 is of great importance, which, to some extent, affords insight into the nature of the swelling of the MA/DVB copolymers in water.

Effect of Porogen. It is known that the type and amount of the porogen affect not only the pore structure but also the swelling properties of the resulting porous copolymers.[14] In Figure 5, the work has been done on the copolymer samples prepared with a fixed copolymer composition (50% MA and 50% DVB, respectively), but using the mixed porogen[14,24] of toluene and *n*-heptane with different *n*-heptane contents. As shown, at 0% *n*-heptane (i.e., pure toluene as porogen) the value of water uptake measured by direct contact with water is 1.92 mL/g, well above the corresponding pore volume. However, with an increase in *n*-heptane content, the difference between the values of water uptake and pore volume becomes smaller. Beyond 71% *n*-heptane, the water uptake of the copolymer declines sharply and drops to a value of only 0.19 mL/g at 80% *n*-heptane, greatly smaller than the pore volume at the same *n*-heptane level, irrespective of the fact that for all these copolymers both the DVB and the MA contents are the same.

Differing only in the content of *n*-heptane, a nonsolvent for the MA/DVB copolymers, the result in Figure 5 shows a profound effect of the solvating power of the porogenic solvent on the direct swelling ability of the MA/DVB copolymers in water. From Figure 3 in the above section we have seen that the cross-linking density or the rigidity of network plays an important role in the direct swelling of the MA/DVB copolymers in water, which are attributed to the existence of the

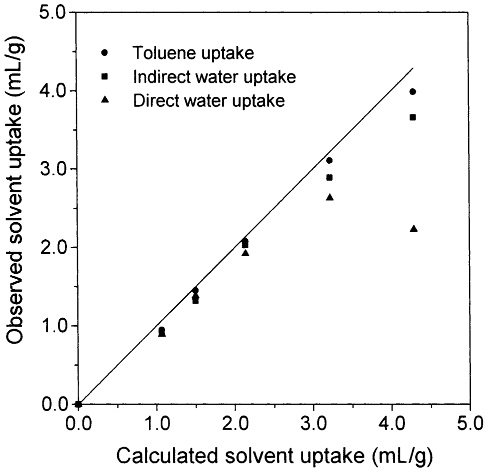

Figure 6. Plots of observed solvent (toluene or water) uptake of MA/DVB copolymers against those calculated values (V_s). The line in this figure is drawn with unit slope. The copolymers were prepared in the presence of different amounts of toluene as porogen at the fixed MA and DVB contents of 50% and 50%, respectively. The water uptakes (V_{dw} and V_{iw}) were measured directly (direct water uptake) and indirectly (indirect water uptake).

inner stresses in the dry copolymers. Then, the result presented in Figure 5 demonstrates that the formation history of the polymer networks, or the solvating state of the growing polymer chains in the reaction mixture where the structurization process is completed, is extremely important to the development of the inner stresses. With an increase in *n*-heptane content the cross-linking networks will form in a less stretched state, which leads to the copolymer products with less strained network and therefore decreases the swelling ability of the copolymers in water.

In Figure 6, the direct swelling behavior in water is investigated on the MA/DVB copolymer samples with a fixed copolymer composition (50% MA and 50% DVB, respectively), but using different amount of toluene as porogen. The solvent uptake of the porous copolymers, as we know, is influenced by the amount of porogen utilized in the copolymerization. The following equation describes the toluene uptake for ST/DVB copolymers prepared in the presence of toluene as porogen:

$$V_s = V_n + S_p \qquad (3)$$

where V_s and V_n are solvent (toluene) uptake (mL/g) for copolymers prepared with and without toluene as porogen, respectively, and S_p is the volume of toluene used as porogen per unit weight of monomers (mL/g).[1] For copolymers with high degree of cross-linking, the term V_n should be zero, and then $V_s = S_p$ according to eq 3.

In our previous paper we found that for ST/DVB copolymers with solvating solvent as porogen the water uptake (V_{iw}) measured indirectly could also be described, to a great extent, by this equation.[4] In Figure 6, the observed value of water uptake (V_{dw}) measured directly, together with the toluene uptake and the indirect water uptake (V_{iw}) (solvent uptake), is plotted against those calculated from the above equation, and for comparison the line in Figure 6 is drawn with a unit slope. As shown, up to a calculated solvent uptake (V_s) of 3.2 mL/g (porogen:monomers ratio of 3:1, v/v), the plots for both toluene uptake and indirect water uptake are very close to the line, with a little departure from the linearity for the latter at V_s value of 3.2 mL/g. Even for direct water uptake (V_{dw}), the deviation of the plot from the line is not too big at the same V_s value, and this plot is almost coincides with the other two plots at the V_s values below 2.1 mL/g.

From Figure 6 we can see that regardless of the great difference in solvating powers between toluene and water, the toluene and water uptakes for MA/DVB copolymers prepared under certain conditions are almost of no difference in a wide range of the ratios of porogen to monomers. This result also gives information that really there is an additional strong swelling-driving force, besides the polymer–solvent interaction, and reasonably it should be the inner stresses existing in these rigid MA/DVB copolymer networks prepared by using well-solvating solvent as porogen.

Conclusions

Regardless of the hydrophobic character of the homopolymer derived from DVB or MA, the copolymers prepared under certain conditions by copolymerization of purified DVB (98.8%) and MA were found to be able to swell in water directly. Even for 67% DVB copolymer, in which the weight fraction of the strongly hydrophobic DVB is twice as great as that of MA, the spontaneous wetting and slight swelling occur by direct contact of the copolymer with water. Two conditions are necessary for the hydrophobic MA/DVB copolymers to swell in water directly. First, the copolymers should have a rigid network (high DVB content) that was formed in a well-solvating medium. Second, the polarity of the copolymers must be enhanced by incorporating enough MA to reach a critical value. On the basis of these observations, we can explain the direct water-swelling behavior by considering both factors: the existence of the inner stresses in the strained polymer networks and the weak interaction between polymer and water that is negligible in the case of the conventional hydrophobic polymers.

References and Notes

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