Water-Swellable Hydrophobic Porous Copolymer Resins Based on Divinylbenzene and Acrylonitrile. I. Water-Swelling Behavior

Xiaoshan Tang, Jia Wei, Jun Yan

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

ABSTRACT: Hydrophobic porous copolymer resins based on divinylbenzene (DVB) and acrylonitrile (AN) could be prepared as directly swellable in water by using purified DVB (98.8%) and technical DVB (79.3%) in the presence of 1,2-dichloroethane as porogen. Compared with the resins based on DVB and methyl acrylate (MA/DVB resins), the AN/DVB resins thus obtained are water-swellable over a wider range of copolymer compositions, and the swelling ability of the AN/DVB resins in water was further confirmed by investigating the water-swelling behavior of the AN/DVB resins undergoing solvent treatment. The copolymer composition (AN and DVB contents) of the resins and the property of the porogen affect the water-swellable behavior of the AN/DVB resins profoundly. The results in this paper provide additional evidence to support the hypothesis that the swelling ability of a hydrophobic porous copolymer in water originates from the existence of the inner stresses in the strained polymer network of the resins and the weak interaction between polymer and water that is negligible in the case of a conventional hydrophobic polymer. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2041–2049, 2004

Key words: divinylbenzene–acrylonitrile; hydrophobicity; water-swelling behavior; structure; crosslinking

INTRODUCTION

Irrespective of the fact that the homopolymer derived from divinylbenzene (DVB) or methyl acrylate (MA) is hydrophobic, the porous copolymer resins prepared under certain conditions by copolymerization of purified DVB (98.8%) and MA were found water-swellable by direct contact with water.[1] Two conditions are necessary for the hydrophobic MA/DVB copolymer resins 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. In other words, at the DVB level below a certain value, the MA/DVB resins are not water-swellable even though a large number of MA units were incorporated to the copolymers. On the other hand, at the MA level below a certain value, the MA/DVB resins do not swell in water, regardless of the DVB content in the copolymer is at a very high level. In contrast to the usual concept of polymer swelling, the swelling behavior of the MA/DVB resins is very striking. On the

basis of the above observations, the nature of the direct swelling of the hydrophobic MA/DVB resins in water was discussed 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 a conventional hydrophobic polymer.[1]

This is the first report that, by simple copolymerization of DVB and a moderately hydrophobic comonomer of alkyl acrylate ester, one can obtain a polymer material even mainly DVB-based, which is hydrophobic in nature, but could be wetted or swelled by direct contact of the material with water. To know more of the water-swelling properties of this kind of hydrophobic copolymer resin, extensive experimental work has been done by preparing the resins using a wider range of monomers. On the basis of the knowledge that the rigidity of a polymer network is of great importance for the hydrophobic porous resins to acquire the water-swelling ability, one of efforts is to synthesize such types of porous resins with a higher degree of crosslinking by copolymerization of two kinds of hydrophobic crosslinkers (DVB and ethylene glycol dimethacrylate or ethylene glycol diacrylate).[2] On the other hand, because the polymer polarity is another important factor, some monomers with different polarities were selected as candidates for further research. Compared with alkyl (meth)acrylate esters,

the monomer acrylonitrile (AN) possesses stronger polarity, although the polymer formed from it is still hydrophobic. It is therefore interesting to know the water-swelling behavior of the hydrophobic copolymer resins based on the DVB and AN (AN/DVB resins). With a replacement of MA by AN, the resulting AN/DVB resins are expected to be water-swellable over a wider range of copolymer compositions, and it is therefore in expectation that the AN/DVB resins may be prepared as water-swellable by using technical DVB. In this case, the new porous materials, which are hydrophobic in nature, but could be wetted or swelled by direct contact with water, will be more valuable from the point of practical application. The aim of this paper is to report the water-swelling behavior of the porous AN/DVB resins prepared by using both the purified and technical DVB. The results obtained afford further understanding of the nature of the swelling of a hydrophobic polymer in water.

EXPERIMENTAL

Materials

Technical DVB (79.3%) and reagent-grade AN were vacuum distilled to remove inhibitor before use. Purified DVB was obtained according to the literature,[3] with a purity of 98.8% (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 had been separated. Reagent-grade 1,2-dichloroethane (DCE), n-heptane, cyclohexane, toluene and most other chemicals were used as received.

Resins synthesis

Copolymer resins were prepared by using purified DVB (98.8%) or technical DVB (79.3%), through a usual suspension copolymerization method.[4,5] DCE and other pure or mixed solvents were used as porogen for the preparation. The monomers AN and DVB 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. The polymerization was allowed to proceed at 70 and 75–78°C for 5 and 3 h, respectively. The resulting polymer 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 resin samples, the contents of DVB and AN in the starting reaction mixture are expressed as the mole percent of the total amount

of monomers. (The purity of the purified DVB and AN was taken as approximately 100% in calculating the contents.) Except for additional illustration, the DCE 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 DCE and n-heptane was used as porogen, the n-heptane content was expressed as a volume percent of the total volume of the mixed porogen, and in this case the dilution degree is 1.4.

Methods

The apparent density (d_a, g/mL) and true density (d_t, g/mL) of the resins were measured according to the methods previously described,[6] from which the pore volume V_p (mL/g) was calculated using the equation

$$V_p = 1/d_a - 1/d_t \qquad (1)$$

The water uptake (V_w, mL/g) was measured by using a centrifuge method, with a relative error of 3% or less for samples where the value of water uptake is above 0.3 mL/g.[6,7] Except for the dynamic swelling experiments, the water uptake was always measured after the swelling equilibrium had been achieved, by direct contact of the resin with water (direct swelling), it usually took about 2 days at room temperature, but for some samples the equilibrium time extended to 2 weeks or more depending on the resin compositions. The volume change of the resins in equilibrium with water was expressed as a volume swelling ratio B of the water-swollen resin beads to the initial dry ones and calculated using the equation[8]

$$B = d_a(V_w + 1/d_t) \qquad (2)$$

RESULTS AND DISCUSSION

AN/DVB resins derived from purified and technical DVB

Water-swelling behavior of the AN/DVB resins was first investigated on the copolymer resins prepared by using purified DVB. Figure 1 shows the dependence of water uptake and pore volume of the AN/DVB resins on the DVB content. The purified DVB with 98.8% purity was utilized for the preparation of the resins. In this case, besides DVB, the other parts of the monomer units in the resins are almost all AN.

As we know, poly(acrylonitrile) (PAN) is not soluble or swellable in water. A slightly crosslinked PAN (1% DVB), even prepared with a great amount of toluene (dilution degree of 2.0) as porogen in our experiment, has a limited ability to absorb water, with a water uptake only 0.396 mL/g. In Figure 1, however, the water uptake at DVB content of 10% reaches a
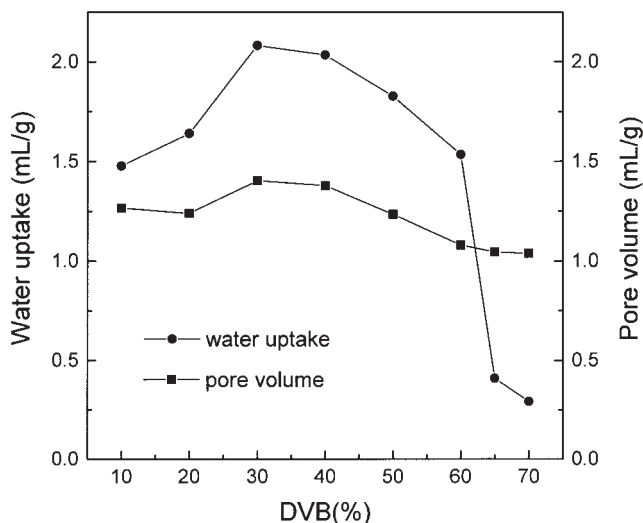
Figure 1 Dependence of water uptake and pore volume of AN/DVB resins on the DVB content. The resins were prepared by using purified DVB (98.8%), and the water uptake in this and other figures of the paper was all measured by direct contact of the resin with water.

value of 1.477 mL/g, which is greater than the pore volume at the same DVB level, indicating that the water not only fills in the already existing air-filled pores, but also penetrates into the gel phase of the resins by direct contact of the resin with water. Although the pore volume of the resins in Figure 1 does not vary significantly in the whole range of DVB contents, the change of the water uptake is great. With an increase in DVB content, the water uptake increases, reaching a maximum around 30% DVB, and then tends to decrease. Beyond 60% DVB, the water uptake declines rapidly and drops to a value far below the corresponding pore volume at 65 or 70% DVB. In parallel with the dramatic change in water uptake, the wetting ability judged by the float–sink test of the dry sample in water[9] also changes greatly. While the resins with DVB content 10–60% sink into water easily, the 65 and 70% DVB resins remain on the surface of water even though being stirred for a long time. With the assumption of isotropic swelling of the AN/DVB resins, the volume swelling ratio for the resins in Figure 1 calculated according to eq. (2) are listed in Table I.

Apparently, the swelling mechanism of the porous AN/DVB resins in water should be different, to a great extent, from the case of a gel-type resin in solvating solvents. It is known that the pore structure of porous copolymers, in many cases, is reversibly collapsible, and the gel portion in the collapsed network may maintain a latent pore structure.[10–13] As a result, the swelling of the porous AN/DVB resins should be a very complex process that must be discussed by considering the expansion of the permanent pores and the "reopen" of the collapsed pores.[10,11] However, any expansion of the permanent or the collapsed pores is not a separate course, it must be accompanied by either the deformation of the gel phase or the relaxation of the crosslinked network chains. This is because the gel phase of the porous copolymers, as we know, is composed of highly crosslinked microgel particles that are closely linked together by less crosslinked networks to form a continuous phase.[14–17] Therefore, there must be some driving forces that cause the hydrophobic porous resins to increase their volume on taking up the water. Generally accepted theories predict the swelling of a polymer network to only depend on the thermodynamic quality of the solvent, the degree of crosslinking, and the functionality of junction points of the network.[18] However, the result in Figure 1 or Table I is contrary to the predictions based on these factors. In a previous paper,[1] on the basis of the facts observed by us,[1,4–6] and reported by other authors,[18–20] the driving forces for the swelling of the MA/DVB resins in water were considered to originate from the inner stresses in the strained polymer network and the weak interaction between polymer and water, which were, respectively, related to the rigidity and the formation history of the polymer network and the polymer polarity of the resins. We think these discussions are applicable to the explanation of the water-swelling behavior of the AN/DVB resins presented in Figure 1 and Table I.

Compared with the MA/DVB polymer resins,[1] the AN/DVB resins, as shown in Figure 1 and Table I, could swell in water over a wider range of DVB contents. Note that the percent used in this paper is by mole. Therefore the AN/DVB resins with DVB contents up to 79% by weight (60% by mole) are water-swellable, in contrast to the MA/DVB resins, which

TABLE I
Volume Swelling Ratio of the AN/DVB Resins Derived from Purified and Technical DVB

DVB (%)	10	20	30	40	50	60	70
B_{pur}	1.097	1.191	1.303	1.300	1.285	1.234	/
B_{tech}	1.095	1.209	1.269	1.178	/	/	/

The AN/DVB resins derived from purified and technical DVB are the same as those in Figures 1 and 2. B_{pur} and B_{tech} represent the volume swelling ratio of the resins derived from purified and technical DVB, respectively.
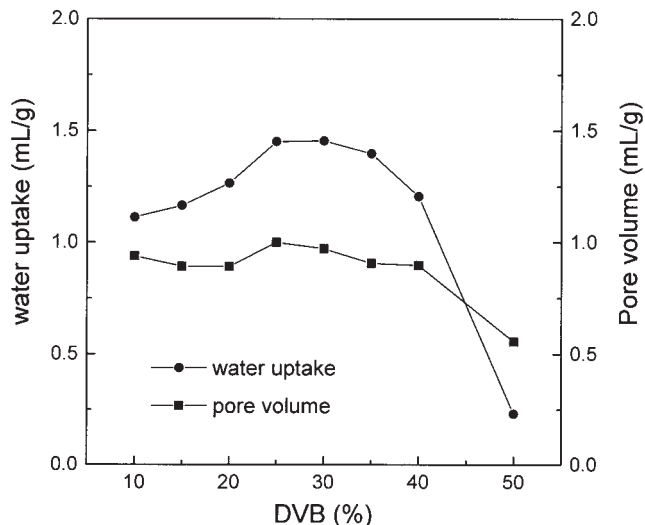
Figure 2 Dependence of water uptake and pore volume of AN/DVB resins on the DVB content. The resins were prepared by using technical DVB (79.3%).

Figure 3 Dependence of water uptake and pore volume of AN/DVB resins on the DVB content, with AN content fixed at 50% and DVB content varied from 20 to 50% by incorporating EVB. The purified DVB (98.8%) was used for the preparation of the resins.

are swellable in water with the DVB contents up to 67% by weight. This is expected since the polarity is stronger for AN than for MA.

For the same reason as has been mentioned before, the AN/DVB resins are expected to be prepared as water-swellable by using technical DVB, while it has been proven impossible for MA/DVB resins, since the portion of EVB in the technical DVB decreases the content of crosslinker or polar monomer component in the copolymer resins, therefore reducing the rigidity of the networks (crosslinking density) or the polymer polarity of the obtained resins.

Figure 2 shows the dependence of water uptake and pore volume of the AN/DVB resins on the DVB content. The resins were prepared by using technical DVB (79.3%). Because the main impurity in technical DVB is EVB, the other part of the monomer unit in the AN/DVB resins, besides the DVB and AN, is EVB.

As can be seen in Figure 2, different from the case of MA/DVB resins derived from technical DVB, which are not water-swellable, the water uptake for technical DVB derived AN/DVB resins is greater than the corresponding pore volume at DVB content of 40% or less, indicating that the resins become water-swellable in a rather wide range of DVB contents. The DVB dependence of water uptake and pore volume in Figure 2 is very similar with that in Figure 1, although in Figure 1 the resins are water-swellable with the DVB contents up to a higher level. The swelling ratio for resins in Figure 2 is also listed in Table I to compare with the ratio for resins in Figure 1. Since the water-swellable AN/DVB resins could also be prepared with high surface area by using commercially available DVB, the result in Figure 2 is very valuable from the point of practical application.
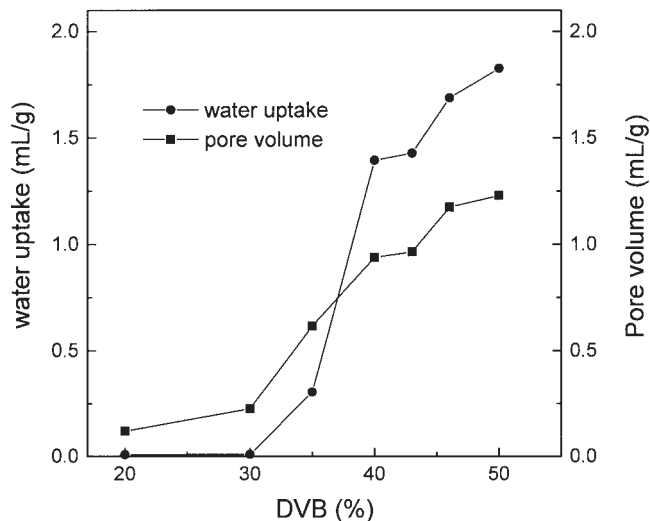
Effect of resin composition

As has been pointed out in a previous paper,[1] two conditions are necessary for a hydrophobic copolymer to swell in water directly. One is that the copolymer should have a rigid network formed in a well-solvating solvent and the other is that the polarity of the copolymer must be enhanced by incorporating enough polar component. The results in Figures 3 and 4 will further confirm the observations described be-
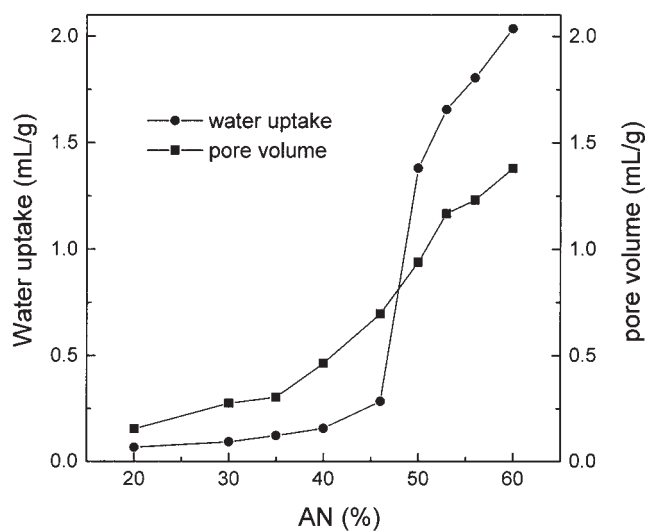

Figure 4 Dependence of water uptake and pore volume of AN/DVB resins on the AN content, with DVB content fixed at 40% and AN content varied from 20 to 60% by incorporating EVB. The purified DVB (98.8%) was used for the preparation of the resins.

fore, by investigating the water-swelling behavior of the AN/DVB resins prepared with different DVB or AN contents.

Figure 3 shows the dependence of water uptake and pore volume of AN/DVB resins on the DVB content, with the AN content fixed at a constant level of 50%, and the DVB content varied from 20 to 50% by incorporating EVB. In this case, the polar/nonpolar composition for all resins in Figure 3 will keep a nearly constant value, while the degree of crosslinking is varied by changing the DVB content. As we can see, the water uptake measured by direct contact of resin with water is negligible at 20 and 30% DVB and is below the value of pore volume at the same DVB levels, indicating that the gel phase of the resins adopts a completely collapsed state in water. Beyond 35% DVB, however, the water uptake increases abruptly and reaches the value much greater than the corresponding pore volume at DVB contents of 40% and more, showing that these resins become water-swellable and, of course, are water-wettable as judged by the simple float–sink test of the dry sample in water.

Just as with the case of MA/DVB resins reported in the previous paper,[1] because the only change in Figure 3 is the DVB content, it is clear that the water-swelling ability of the AN/DVB resins with DVB content of 40% or more should be attributed to the increased crosslinking density of the polymer network, which leads to an increase in inner stresses in the dry resin products.[4,20]

Figure 4 shows the dependence of water uptake and pore volume of AN/DVB resins on the AN content, with the DVB content fixed at 40% and AN content varied from 20 to 60% also by incorporating EVB. As can be seen, at AN content of 20% both water uptake and pore volume are very limited but the latter is greater than the former. With an increase in AN content, while the pore volume increases gradually, the value of water uptake almost remains unchanged up to the AN content of 40%. However, once the AN content is greater than a value of 46%, an abrupt increase in water uptake is also observed as that in Figure 3. With only a 4% AN interval, the water uptake increases from 0.248 mL/g at 46% AN to 1.380 mL/g at 50% AN, and at still higher AN levels the water uptake becomes well above the corresponding pore volume, indicating that the resins become well swellable in water. The water-swelling behavior of AN/DVB resins in this Figure is also similar to that reported for MA/DVB resins with different MA content.[1]

It is known that the glass transition temperature (T_g) would have an effect on the rigidity of a polymer network. Poly(acrylonitrile) (PAN) and poly(methyl acrylate) (PMA) have T_gs of 97 and 10°C, respectively,[21] translating to a glassy state for PAN at room temperature but a rubbery state for PMA at room temperature. It should be then answered whether the T_g plays an important role in governing inner stresses and resultant swelling of the AN/DVB polymer network in water. Here, we can make a comparison between the resins based on MA and DVB and based on methyl methacrylate (MMA) and DVB; the T_g for poly(methyl methacrylate) (PMMA) is 105°C.[21] Regardless of a much higher T_g for PMMA than PMA, the MA/DVB resins are water-swellable but the MMA/DVB resins, prepared under the same conditions in our experiment, are not swellable in water, only because of the extra methyl in MMA, which makes MMA more hydrophobic compared with MA. From this comparison we believe that the effect of T_g is minor and the polarity of AN/DVB resins in Figure 4 is a major factor that leads to the swelling of the resins in water at higher AN levels.

Besides the T_g, the crystallinity, arising from the high polarity of AN units, seems to be another factor that should be taken into account in discussing the water-swelling behavior of the AN/DVB resins in Figure 4. It has been suggested that the copolymers containing AN units have, similar to the case of PAN, a semicrystalline structure in which the ordered regions can act as additional physical crosslinkers.[22] Therefore, the contributions to the increased swelling ability at higher AN levels in Figure 4 probably include, in addition to the increased interaction between the polymer and water, the increased inner stresses resulting from the additional crosslinkers. It is difficult to know the level of the additional crosslinks, but, because the only change in Figure 4 is the AN content, it is clear that an increase in polarity, with increasing the AN content, leads to an increase in swelling ability of the AN/DVB resins in water at higher AN levels. Also, it is believed that, because of the stronger polarity of AN than MA, the AN/DVB resins are in a more favorable water-swelling condition compared with the MA/DVB resins.

In fact, we can really see that, by comparing the results in Figures 3 and 4 with those in the previous report on the MA/DVB resins,[1] the AN/DVB resins could swell in water over a wider range of copolymer compositions compared with the MA/DVB ones. In either case of changing DVB or AN content, the critical value of DVB or AN level, above which the swelling transition occurs and the gel phase of the porous resins turns into a swollen state from a collapsed one, is different for AN/DVB and MA/DVB resins. With the polar monomer of MA or AN fixed at 50%, the critical value of DVB content for MA/DVB resins is 43%, whereas for AN/DVB resins it is 35%. Similarly, with DVB content fixed at 40%, the critical value of MA content for MA/DVB resins is 53% while the critical value of AN content for AN/DVB resins is 46%. Clearly, this difference can be ascribed to the

AN/DVB	AN = 50%				DVB = 40%			
	50/40	50/43	50/46	50/50	50/40	53/40	56/40	60/40
$t_{90\%}$ (min)	90	15	12	1	90	25	10	<1

The resins are the same as those in Figure 3 and 4 with the same compositions. The value of $t_{90\%}$ refers to the time for AN/DVB resins to reach a 90% swelling degree.

stronger polarity of AN units than MA units in the polymer resins.

Just as with the case of MA/DVB resins,[1] the swelling rate of AN/DVB resins is also strongly influenced by the copolymer composition of the resins. Table II shows the time ($t_{90\%}$) for AN/DVB resins to reach 90% swelling degree (Q, %). The resins in Table II are the same as those in Figures 3 and 4 with the same compositions, and the swelling degree Q at different contact times was calculated as $Q = V_{wt}/V_w \times 100$, where V_{wt} was the water uptake at swelling time t and V_w, as denoted under Experimental, was the equilibrium water uptake measured by direct contact of the sample with water. As can be seen, in parallel with the equilibrium water uptake in Figures 3 and 4, the swelling rate increases with an increase in DVB or AN content. For AN/DVB resins with AN content fixed at 50%, the value of $t_{90\%}$ decreases from 90 to 1 min as the DVB content increases from 40 to 50%. Similarly, for AN/DVB resins with DVB content fixed at 40%, the $t_{90\%}$ value decreases from 90 to less than 1 min with raising the AN content from 50 to 60%. Clearly, for AN/DVB resins with both high DVB and AN contents, the swelling is very fast by direct contact with water.

Effect of porogen property

Previously we have mentioned that one of the conditions for a hydrophobic copolymer to directly swell in water is that the copolymer with a rigid network must be prepared in a well-solvating medium. This is consistent with the basic principle of preparing hypercrosslinked polystyrenes, which have the ability to swell in good solvents and in nonsolvents (including water, with the sample first treated by an organic solvent such as methanol.).[18] The basic principle, as discussed in the literature,[23] consists in the formation of a rigid and highly solvated three-dimensional network. This is because the solvating state of the polymer chains during crosslinking reaction is extremely important to the development of the inner stresses in a dry polymer network. In a well-solvated state, the crosslinks fix the stretched polymer chains, and the subsequent deswelling of the formed polymer networks upon removal of porogen is accompanied by a rapid growth of the stresses in the polymer networks, as a result of the retraction and deformation of the

networks. The results in Figure 5 and Table III give a good illustration about the effect of the porogen property on the water-swelling ability of the resulting AN/DVB resins.

Figure 5 shows the dependence of water uptake and pore volume of AN/DVB resins on the n-heptane content in the mixed porogen of DCE and n-heptane. The resins were prepared by using technical DVB (79.3%) with a fixed resin composition of 56% AN and 35% DVB (AN/DVB ratio of 56/35) and with the dilution degree fixed at a constant level of 1.4. As can be seen, at n-heptane content of 33% or less, the water uptake is greater than the value of the corresponding pore volume, indicating that the resins are water swellable. But beyond 33% n-heptane, the water uptake decreases rapidly and becomes far below the corresponding pore volume at 67 and 75% n-heptane. According to the solubility parameter,[21] (δ, cal$^{0.5}$/cm$^{1.5}$), DCE ($\delta = 9.8$) is a good solvent for poly(styrene) (PST, $\delta = 9.1$), whereas for poly(acrylonitrile) (PAN, $\delta = 12.7-15.4$), it is not a good one. However, the δ value for n-heptane (7.45) is still smaller than the δ values for both PST and PAN. Because the only
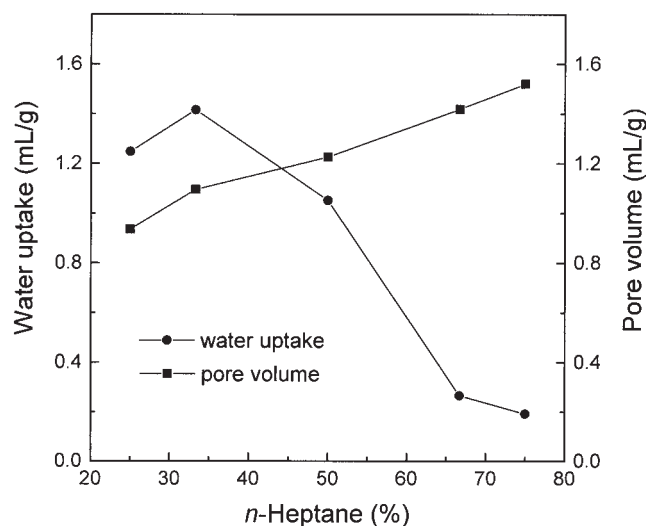

Figure 5 Dependence of water uptake and pore volume of AN/DVB resins on the n-heptane content in the mixed porogen of 1,2-dichloroethane and n-heptane. The resins were prepared by using technical DVB (79.3%) with a fixed resin composition of 56% AN and 35% DVB (AN/DVB ratio of 56/35) and with the dilution degree fixed at 1.4.

TABLE III
The Water-Swelling Ability of the AN/DVB Resins Prepared by Using Pure Solvents with Different Solvating Powers as Porogen

Porogens	V_w (mL/g)	V_p (mL/g)	$V_w - V_p$ (mL/g)	B	δ (cal$^{0.5}$/cm$^{1.5}$)
n-Heptane	0.217	1.193	−0.976	/	7.45
Cyclohexane	0.197	1.122	−0.925	/	8.2
Toluene	1.123	0.906	0.217	1.121	8.9
DCE	0.725	0.428	0.297	1.227	9.8

The resins were prepared by using technical DVB (79.3%) with a fixed composition of 56% AN and 35%DVB, and the dilution degree was fixed at 1.0. V_w, V_p, B, and δ represent water uptake, pore volume, volume swelling ratio, and solubility parameter, respectively. The water uptake in this and other Tables was measured by direct contact of the resin with water.

change in Figure 5 is the variation of the n-heptane content, then the change in water-swelling ability of the AN/DVB resins should be attributed to the variation in the solvating power of the mixed porogen. With an increase in n-heptane content, the polymer chains during copolymrization become less stretched. Consequently, the crosslinking reaction fixes the chains in a less stretched state, resulting in a less strained polymer network of the resins after deswelling; this in turn results in a decreased swelling ability of the AN/DVB resins in water.

Table III presents the water-swelling ability of the AN/DVB resins prepared by using pure solvents with different solvating powers as porogen. Also the technical DVB (79.3%) was used for the preparation of the resins with a fixed resin composition of 56% AN and 35% DVB, and the dilution degree was fixed at 1.0. By comparing the value of water uptake with pore volume in Table III, we can see that the difference between them ($V_w - V_p$) is increased with an increase in the solubility parameter of the porogenic solvent. This result provides additional evidence that the solvating power of the porogen, or the solvating state of the growing polymer chains during crosslinking reaction, is greatly important to the swelling ability of a hydrophobic porous resin in water. Besides, by comparing the swelling ratios of the AN/DVB resins in Table III with different solvents of toluene and DCE as porogen, it is clear that DCE is better as a porogen than toluene to form a water-swellable AN/DVB resin. An additional experiment showed that, when the resins in Figure 2 were prepared using toluene, rather than DCE, as porogen, the resulting AN/DVB resins were water swellable with the DVB contents up to 30%, whereas for AN/DVB resins with DCE as porogen, the DVB content at which the resins were water swellable could reach a higher value of 40%. In other words, the AN/DVB resins could swell in water over a wider range of DVB contents for resins with DCE than with toluene as porogen.

Effect of solvent-treatment of AN/DVB resins

In general, solvent uptake of porous resins can be considered as the result of two processes: filling of pores by solvent and the gel phase swelling.[10] Since no single measurement could distinguish these two processes, in our research, both water uptake and pore volume of the resins in dry state were measured to assess whether the pores were fully filled by water and whether the water could swell the gel phase of the resins. However, because of the complex morphology, crosslinking structure, and the formation process of the porous copolymers, the situation is more complicated. As has been already pointed out, the pore structure of porous copolymers in many cases is not to be fixed. As a result, the pore volume of a given copolymer sample may be considerably larger or smaller than the measured value for a dried sample, depending upon the solvent from which the sample is dried.[10–13] Accordingly, the pore volume of the resins in a dry state is, probably, not a fixed value. For example, for ST/DVB copolymer resin even with a DVB content of 98%, when it is prepared using toluene as porogen (with a dilution of 3.0), the pore volumes for this resin dried from toluene and from water are 1.057 and 1.459 mL/g, respectively,[13] i.e., the pore volume is much smaller for resin dried from toluene than for resin dried from water. For this reason, the volume swelling ratio on the basis of the apparent density (or the pore volume) of a dried sample may be a variable value, and furthermore, one could not even rule out the possibility that, for a given resin sample dried from one solvent, the value of water uptake is greater than the corresponding pore volume, but for the same sample dried from the other solvent, the value of water uptake may be smaller than the corresponding pore volume. The judgement of the swelling on the basis of a comparison between water uptake and pore volume then would be incorrect. To convince us the validity of the results in the previous sections, the same resin samples as those shown in Figures 3 and 4, with AN content fixed at 50% and DVB content varied from 43 to 50%, or with DVB content fixed at 40% and AN content varied from 53 to 60%, were treated before the further measurement of the water uptake and pore volume, with a series of solvents (DCE, acetone, and water) of decreasing solvating power for the AN/DVB copolymer. With first being swollen to equilibrium in DCE, the solvent in the

TABLE IV
Water Uptake and Pore Volume of the AN/DVB Resins Measured after Drying the Samples from Different Solvents

AN/DVB	AN = 50%			DVB = 40%		
	50/43	50/46	50/50	53/40	56/40	60/40
Dried from DCE:						
V_{wd}	1.358	1.645	1.777	1.634	1.760	1.968
V_{pd}	0.808	1.040	1.067	0.896	1.054	1.161
B_d	1.328	1.320	1.370	1.403	1.376	1.410
Dried from Acetone:						
V_{wa}	1.469	1.678	1.780	1.675	1.775	1.950
V_{pa}	0.806	1.002	1.042	0.874	1.019	1.194
B_a	1.396	1.365	1.389	1.443	1.410	1.376
Dried from Water:						
V_{ww}	1.509	1.738	1.826	1.800	1.891	2.200
V_{pw}	0.570	0.706	0.720	0.569	0.678	0.834
B_w	1.653	1.662	1.704	1.819	1.807	1.829

The water uptake (V_w) and pore volume (V_p) measured after drying the samples from DCE, acetone, and water are distinguished by V_{wd}, V_{wa}, and V_{ww}, and by V_{pd}, V_{pa}, and V_{pw}, respectively.

swollen sample was then exchanged with acetone and finally with water. The sample after treatment with water as a final solvent, and part of the sample swollen in DCE or in acetone, were dried *in vacuo* at 80°C. The water uptake and the pore volume, measured after drying the samples from DCE, acetone, or water, are distinguished by V_{wd}, V_{wa}, and V_{ww}, and by V_{pd}, V_{pa}, and V_{pw}, respectively, and are presented in Table IV.

The resins in Table IV, which, as has been mentioned under Experimental, were originally dried from acetone, are all water swellable before retreatment, i.e., the value of water uptake for all these resins is greater than the corresponding pore volume before the additional solvent treatment. As can be seen, after the solvent treatment of the resins with DCE, acetone, and water, the change in pore volume and water uptake really occurs. For all resins with different compositions, the pore volume (V_{pa}) measured after drying the sample from acetone is close to that (V_{pd}) measured after drying from DCE. However, when the pore volume is measured after drying from water (V_{pw}), it becomes much smaller than the pore volume of V_{pa} and V_{pd}. On the contrary, the water uptake in Table IV is greater for samples dried from water (V_{ww}) than dried from acetone (V_{wa}) or DCE (V_{wd}), with a bit greater V_{wa} than V_{wd}. As a result, in any case the water uptake of the resins in Table IV is greater than the corresponding value of pore volume, although the volume swelling ratio for samples dried from water (B_w) is apparently greater than the ratio for samples dried from acetone (B_a) or DCE (B_d), also with a bit greater B_a than B_d. From above results, it is confirmed that, by direct contact of the AN/DVB resins with water, the water not only fills in the already existing air-filled pores, but also penetrates into the gel portion of the network, causing the expansion of the whole copolymer resin.

In contrast to the case of ST/DVB copolymer resins, the variation of the pore volume in Table IV looks strange. For ST/DVB resins, when they are dried from DCE or toluene, collapsing is favored and, when dried from water, collapsing is disfavored. However, for AN/DVB resins, collapsing is favored for the resins dried from water and collapsing is disfavored for resins dried from DCE, as indicated by the smaller pore volume of the resins dried from water than from DCE. At present we have no reasonable explanation for this phenomenon. However, the result in Table IV is reproducible, and a similar phenomenon has also been observed for other copolymer systems such as MA/DVB, methyl methacrylate/DVB, and ethyl methacrylate/DVB copolymers; in each case the copolymer was incorporated with a polar monomer unit. Further investigation in this respect is in progress.

CONCLUSION

The hydrophobic, but water-swellable porous AN/DVB resins can be prepared by copolymerization of DVB and AN in the presence of 1,2-dichloroethane as porogen. By using purified DVB (98.8%), the resulting AN/DVB resins with DVB contents up to 60% (79% by weight) are water swellable by direct contact with water. Additionally, the swelling ability of the AN/DVB resins in water were confirmed by investigating the variation of the pore volume and water uptake of the resin samples treated by a series of solvents with different solvating powers for the AN/DVB copolymers. Because of the stronger polarity of AN than MA, the AN/DVB resins could also be prepared as water-swellable by using technical DVB (79.3%), while the MA/DVB resins derived from the same grade of DVB could not swell in water at almost any DVB level. The effect of DVB and AN contents on the water-swelling behavior of the AN/DVB resins is profound. With AN content fixed at a constant level, a water-swelling transition occurs as the DVB content is increased above a critical value. Similarly, with DVB content fixed at a

constant level, the water-swelling transition occurs as the AN content is increased above a critical value. In addition, the property of the porogens also affects the water-swelling behavior significantly. These results demonstrate that the network rigidity, the polymer polarity of the resins, and the solvating state of the growing polymer chains in the reaction mixture where the structurization process is completed are all extremely important for a hydrophobic copolymer resin to become water swellable by direct contact with water.

References

1. Wei, J.; Bai, X. Y.; Yan, J. Macromolecules 2003, 36, 4960.
2. Zhao, X.; Wang, X. H.; Yan, J. J Appl Polym Sci 2004, 92, 997.
3. Popov, G.; Schwachula, G. Chem Technol 1978, 30, 144.
4. Yan, J.; Wang, X. H.; Chen, J. Q. J Appl Polym Sci 2000, 75, 536.
5. Wang, X. H.; Yan, J.; Zhou, C. C. J Appl Polym Sci 2000, 78, 250.
6. Yan, J.; Wang, X. H.; Cao, Z. N. React Funct Polym 2000, 46, 127.
7. Batich, C. D.; Yan, J.; Bucaria, C.; Elsabee, J. M. Macromolecules 1993, 26, 4675.
8. Kolarz, B. N. Angew Makromol Chem 1980, 90, 183.
9. Dumont, P. J.; Fritz, J. S. J Chromatogr A 1995, 691, 123.
10. Okay, O. Prog Polym Sci 2000, 25, 711.
11. Sherrington, D. C. Chem Commum 1998, 2275.
12. Wieczorek, P. P.; Kolarz, B. N.; Galina, H. Angew Makromol Chem 1984, 126, 39.
13. Yan, J.; Xu, R. N.; Yan, J. T. J Appl Polym Sci 1989, 38, 45.
14. Dusek, K. In Developments in Polymerization; Haward, R. N., Ed.; Applied Science: London, 1982, vol. 3.
15. Negre, M.; Batholin, M.; Guyot, A. Angew Makromol Chem 1982, 106, 67.
16. Shea, K. J.; Stoddard, G. J. Macromolecules 1991, 24, 1207.
17. Albright, R. L. React Polym 1986, 4, 155.
18. Davankov, V. A.; Tsyurupa, M. P. In Synthesis, Characterization and Theory of Polymeric Networks and Gels; Aharoni, S. M., Ed.; Plenum: New York, 1992.
19. Davankov, V. A.; Tsyurupa, M. P. React Polym 1990, 13, 27.
20. Davankov, V. A.; Pastukhov, A. V.; Tsyurupa, M. P. J Polym Sci B: Polym Phys 2000, 38, 1553.
21. Brandrup, J.; Immergut, E. H. Polymer Handbook; Wiley-Interscience: New York, 1975.
22. Wojaczynska, M.; Kolarz, B. N. Makromol Chem 1992, 193, 2259.
23. Tsyurupa, M. P.; Davankov, V. A. React Funct Polym 2002, 53, 193.