

# Swelling of Porous Styrene–Divinylbenzene Copolymers in Water

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**ABSTRACT:** The swelling capacity of porous styrene–divinylbenzene (DVB) copolymers in water was studied by displacing methanol from the swollen polymer. The copolymers with different amounts of DVB were prepared in the presence of solvents with different solvating powers as inert diluents. Using a solvating solvent or its mixture with a nonsolvent as diluent, most of the obtained copolymers increase their volume in water, and the increase in volume becomes more significant with increasing the degree of crosslinking in some range of the DVB contents. The swelling capacity in water for the same copolymers with a high degree of crosslinking is linearly dependent on the dilution degree in the initial reaction mixture, to some extent. The unusual swelling behaviors in water were explained by the inner strain, which existed mainly in the less crosslinked domains between the highly crosslinked microgel particles, which are released in the course of swelling of the copolymers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 536–544, 2000

**Key words:** styrene–divinylbenzene copolymers; inert diluent; swelling; water uptake; pore volume

## INTRODUCTION

Many papers have been devoted to the study of the swelling of conventional styrene–divinylbenzene (St–DVB) copolymers in organic solvents, such as benzene and toluene.<sup>1–4</sup> The purpose of these studies was usually to characterize the structure and primarily to determine the degree of cross-linking of the copolymers.

During the latter part of the 1950s and through the decade of 1960s special polymerization techniques for manufacturing the precursors of new type ion exchangers, mainly the porous St–DVB copolymers, were largely developed. Instead of simple polymerization of St with DVB, the reaction was carried out in the presence of inert organic substances, referred to as diluents, which

are miscible with monomers but essentially insoluble in water.<sup>5</sup> The St–DVB copolymer products thus obtained were nontransparent with porous structure even after removal of the diluent. There are three classes of diluents used to prepare the porous copolymers<sup>5,6</sup>: solvating solvent (SOL), nonsolvating solvent (NONSOL), and linear polymer. The relationship between the synthesis variables, including the nature of diluents and the structure of the resulting St–DVB copolymer products, has been thoroughly studied,<sup>5–8</sup> and at the same time, some unusual swelling properties of the copolymers in thermodynamically poor solvents were observed.<sup>9–12</sup> As early as 1963, Millar et al.<sup>9</sup> have discovered that in contrast to the conventional ones prepared in the absence of the diluent, the St–DVB copolymers prepared with toluene as diluent are capable of swelling not only in solvating solvents such as toluene, but also in solvents that solvate poorly, polystyrenes, e.g., *n*-heptane and nitromethane. However, the ab-

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sorption of water, according to Millar et al., is due to the filling of the already existing air-filled pores and is not accompanied by an increase in the polymer volume. This viewpoint was generally accepted later,<sup>13</sup> and on the basis of this knowledge, a method of pore volume determination using water for porous St-DVB copolymers was developed.<sup>14</sup>

In our previous studies<sup>11</sup> the unusual swelling properties of porous St-DVB copolymers were correlated to the stability of their pore structures, and the copolymers were found to be able to swell, even in an aqueous solution of ethanol. As a continuation of the earlier studies, we further investigated the water uptake of porous St-DVB copolymers prepared in the presence of the diluents with different solvating powers. Some results related to the swelling of the hydrophobic copolymers in water are reported in this paper.

## EXPERIMENTAL

### Synthesis of Copolymers

The technical styrene (St) and divinylbenzene (DVB) were treated with anion exchange resin to remove inhibitors. The gas chromatography analysis of DVB gave the following results: 17.4% *p*-DVB, 42.0% *m*-DVB, 9.2% *p*-ethylvinylbenzene, and 24.5% of *m*-ethylvinylbenzene. Reagent-grade toluene and *n*-heptane were used as received.

The St-DVB copolymers were prepared by the general suspension polymerization method with toluene, *n*-heptane, or their mixture as diluent. The monomers St and DVB were first mixed well with diluent to form an organic phase, in which the initiator, benzoyl peroxide, was added in the amount of 1 wt % of monomers used. The organic phase mixture was then added in a 1 : 1.6 volume ratio to the aqueous phase of a 0.2 wt % hydroxyethyl cellulose solution in a three-neck flask at 60°C. The polymerization was allowed to proceed at 80°C and at reflux temperature for 14 and 4 h, respectively. The copolymers obtained in the shape of beads were washed with water and then acetone. After final washing with water, the beads were dried at 80°C and those with 28–40 mesh size were used for further treatment and characterization. For the convenience of description, the terms of “SOL copolymer” and “NON-SOL copolymer” are used to distinguish the copolymers synthesized in the presence of solvating

solvent (SOL) or nonsolvating solvent (NONSOL) as diluent.

In any case, the DVB content was expressed as weight percent of the total weight of the monomers and the dilution degree as volume ratio of diluent to monomers. When the mixed diluent of toluene and *n*-heptane was used, the *n*-heptane content was expressed as volume percent of the total volume of the mixed diluent.

### Pretreatment

The copolymer beads with the 28–40 mesh size were soaked in toluene for 24 h and then extracted with acetone in a Soxhlet apparatus. After that the acetone-swollen beads were washed thoroughly with water, and finally water was evaporated at 80°C. Part of the dried beads were soaked again in toluene, and the beads in equilibrium with toluene were dried directly at the same temperature. The copolymer beads dried from water and from toluene are distinguished by letters W (W-type) and T (T-type), respectively.

### Characterization

The apparent density  $d_a$  of the copolymers in dry state was determined by an improved mercury pycnometric method.<sup>15</sup> Good reproducibility in the values of  $d_a$  was obtained for each set of duplicate samples, with a relative error less than 1%. The true density  $d_t$  was assumed to be equal to the homogeneous St-DVB copolymers prepared beforehand from monomers containing various amounts of DVB. The pore volume  $V_p$  was calculated using the equation:

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

### Swelling Experiments

Swelling experiments were carried out in the solvent of toluene, methanol, or water. The solvent uptakes (mL/g) were measured with a centrifuge method, essentially as described by Pepper et al.<sup>16</sup> (with appropriate correction for solvent retained between sample beads and in the sinter). However, for water uptake measurement,<sup>9,13</sup> the copolymer sample was first immersed in methanol for 24 h and subsequently was washed with water thoroughly to remove methanol. Two or more measurements were taken for each number reported, with a relative error of 3% or less for samples with the value of water uptake greater than 0.3 mL/g. The volume change of the copoly-

**Table I** Pore Volume, Water Uptake, and the Related Data of St-DVB Copolymers (W-type)

DVB (wt %)	$d_a$ (g/cm <sup>3</sup> )	$V_p$ (mL/g)	$V_w$ (mL/g)	$\Delta V$ (mL/g)	$B_w$ (v/v)
5	0.675	0.508	0.445	-0.063	0.959
10	0.629	0.618	0.566	-0.052	0.967
15	0.537	0.893	0.830	-0.063	0.965
20	0.504	1.019	0.945	-0.074	0.963
40	0.489	1.091	1.054	-0.037	0.984
60	0.460	1.234	1.181	-0.053	0.982

Various DVB contents were prepared in the presence of *n*-heptane as diluent at a fixed dilution degree of 1.0.  $d_a$ , apparent density;  $V_p$ , pore volume;  $V_w$ , water uptake;  $\Delta V = V_w - V_p$ ;  $B_w$ , swelling ratio (v/v) in water.

mers in equilibrium with solvent was then expressed as a swelling ratio  $B$  of the swollen polymer to the initial dry one (v/v) and calculated using the equation<sup>17</sup>:

$$B = d_a(V_s + 1/d_t)$$

where  $V_s$  is the solvent uptake.

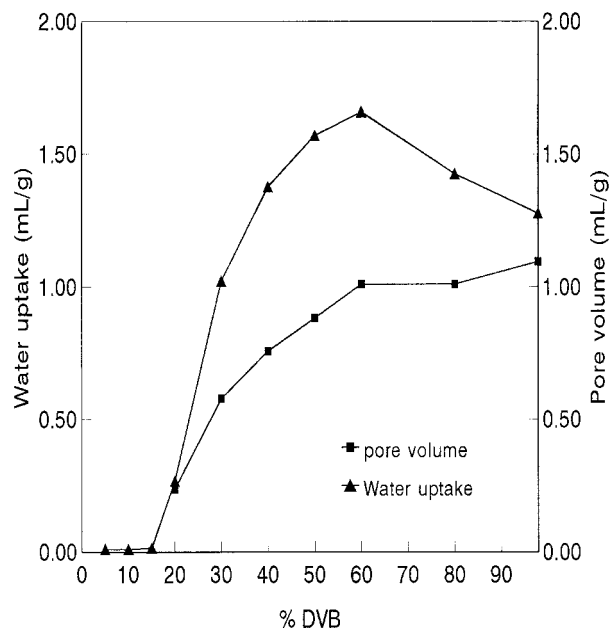
## RESULTS AND DISCUSSION

First, a series of St-DVB copolymers (W-type) with different degrees of crosslinking were prepared in the presence of a NONSOL-type diluent, *n*-heptane, and their pore volume and water uptake were investigated. The related data of the investigation are presented in Table I.

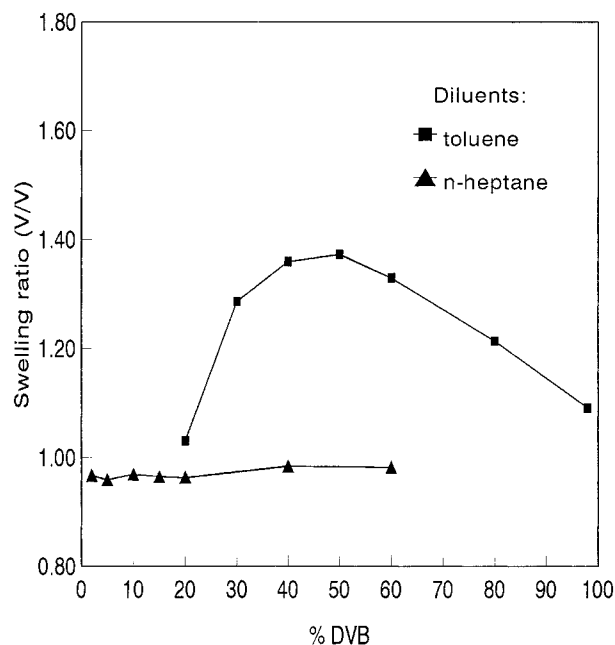
By comparing water uptake with pore volume of the copolymers at various DVB contents, we can see that they are very close, with a little less of the former than the latter. As a result, the difference between water uptake and pore volume ( $V_w - V_p$ ), denoted by  $\Delta V$  for all copolymers in this table, is a minus value, and the swelling ratio is less than one. The minus value here perhaps results from the different method of measurement, but from these results it is clear that the water absorbed by these copolymers is just accommodated in the already existing air-filled pores and does not cause an increase in the polymer volume.

But, when a SOL-type diluent was used in the polymerization of St with DVB, the result was different. Figure 1 shows the dependence of water uptake and pore volume of St-DVB copolymers (W-type) on the DVB content. The copolymers were prepared in the presence of toluene as diluent at a fixed dilution degree of 2.0 (for 82% and 98% DVB copolymers in Fig. 1, the purified DVB

with 48.2% *p*-DVB and 50.2% *m*-DVB was used for the preparation of these two copolymers). In most cases, the value of water uptake is significantly greater than the corresponding pore volume of the copolymers. The difference between water uptake and pore volume, perceptible at about 20% DVB, increases rapidly with an increase in the degree of crosslinking and passes through a maximum at about 50% DVB. The dependence of the corresponding swelling ratio in water on the DVB content is shown in Figure 2, and as a comparison, the swelling ratios for NON-SOL copolymers in Table I at various DVB contents are also shown.



**Figure 1** Dependence of water uptake and pore volume of St-DVB copolymers (W-type) on the DVB content. The copolymers were prepared in the presence of toluene as diluent at a fixed dilution degree of 2.0.



**Figure 2** Dependence of swelling ratio in water on the DVB content for St-DVB copolymers (W-type) prepared in the presence of *n*-heptane or toluene at a fixed dilution degree of 1.0 or 2.0.

Here, presenting to us is the fact that the hydrophobic aromatic SOL copolymers, which are devoid of any polar constituent, increase their volume in water, and the increase in volume becomes more significant with increasing the degree of crosslinking in some range of the DVB contents.

We do not clearly understand the nature of the swelling of St-DVB copolymers in water, but we think that the explanation of the unusual swelling behaviors in water needs to be sought in the structure peculiarities and the formation history of the porous copolymers.

It is known that the polymerization to form a porous copolymer, whether a SOL- or a NONSOL-type diluent is used, is accompanied by continuous phase separation.<sup>18-20</sup> Once the phase separation occurs for the first time, the monomers will react further in gel phase and in dilute phase under different conditions, and the gel portions formed in dilute phase are expected to have much less degree of crosslinking as compared with those that have the earlier phase separated. Consequently, the copolymer matrix finally formed is composed of highly crosslinked microgel-like particles (nuclei) or small nodules linked together by less crosslinked networks.<sup>10,19</sup> With the removal of the inert diluent after polymerization, the highly crosslinked regions in the copolymer do not

collapse entirely, and part of the volume, which primarily contained the diluent, appears as pores in the dry state. As a result, both the SOL and NONSOL copolymers are similar in their morphology and crosslinking structure.

In general, the densely crosslinked and entangled networks of microgel particles, especially for copolymers with high content of DVB, have entirely or partially finished the course of deswelling under the strong elastic retraction during the copolymerization. These rigid microgel particles do not swell much, even in solvating solvents such as toluene. On the other hand, the networks between the microgel particles are relatively loose, capable of swelling in solvents and shrinking on removal of the solvents, the volume variation of the swelling copolymers could be considered mainly to result from the expansion of these less crosslinked domains.<sup>10</sup>

Although it is true that the SOL copolymers are similar to the NONSOL ones in their morphology and crosslinking structure, the differences in some respects of the formation history of their networks should be definitely important to cause their different swelling behaviors in water.

When a copolymer is prepared in NONSOL-type diluent, its crosslinking structure is formed in a nonsolvating state and the crosslinking reaction fixed is the retracted chains. In this case, if the formed copolymer is brought into contact with a solvent and if swelling occurs, the inner strain in the copolymer, mainly in the networks between the microgel particles, arises and grows, with an increase in volume of the copolymers, and the increasing strain prevents further swelling of the copolymer. As a result, the high energy of interchain interactions greatly diminishes the ability of copolymers to swell in nonsolvents, although the crosslinked networks between the microgel particles are relatively loose. On the contrary, when a copolymer with a great amount of DVB is prepared in SOL-type diluent, the crosslinking structures are formed in a solvating state, and the crosslinking reaction fixes the stretched chains. In this case, the deswelling of the copolymer upon removal of diluent must be accompanied by a rapid growth of strain in the copolymers as a result of the retraction and deformation of the networks, mainly in the less crosslinked domains. The strain ultimately stops the collapse of the networks, resulting in the porous copolymer. Since an increase in volume during swelling is favorable to the release of the strain, the strained networks increase drastically the ability of the

**Table II Swelling Ratios in Methanol and in Toluene for St-DVB Copolymers (W-Type)**

DVB (wt %)	NONSOL Copolymers		SOL Copolymers	
	$B_m$	$B_t$	$B_m$	$B_t$
2	1.039	4.325	/	/
5	1.029	2.028	/	/
10	1.030	1.644	1.053	3.684
15	1.068	1.429	1.093	3.034
20	1.059	1.254	1.374	2.582
30	/	/	1.740	2.039
40	1.048	1.092	1.878	1.997
50	/	/	1.842	1.905
60	1.078	1.100	1.676	1.719
82	/	/	1.413	1.461
98	/	/	1.272	1.280

Various DVB contents were prepared in the presence of *n*-heptane (NONSOL copolymers) or toluene (SOL copolymers) as diluent at a fixed dilution degree of 1.0 or 2.0.  $B_m$ , swelling ratio (v/v) in methanol;  $B_t$ , swelling ratio (v/v) in toluene.

obtained copolymers to swell in solvents, especially those poorly solvating the polymer chains.

The opposite effects of the strain in SOL and in NONSOL copolymers on the swelling ability probably provides a clue for explaining the swelling behaviors of the SOL copolymers in water. In fact, the inner strain has been used to interpret the unusual swelling behaviors of SOL copolymers in nonsolvents,<sup>11</sup> and the converse is also true, that the ability of SOL copolymers to swell in nonsolvents proves the existence of the inner strain in deswelled state. The swelling ratios in methanol and in toluene for the same copolymers as those in Table I and Figures 1 or 2 are presented in Table II.

As shown, once the DVB content for SOL copolymers (toluene as diluent) reaches a value of about 20%, at which the pore structure arises in the SOL copolymers (see Fig. 1), the copolymers become apparently swellable in methanol, and the swelling ratio rapidly increases and approaches that in toluene. However, although the swelling ratio in toluene for NONSOL copolymers (*n*-heptane as diluent) increases significantly with decreasing the degree of crosslinking, the swelling ratio in methanol for the same copolymers with various DVB contents is very limited, regardless of the fact that the copolymers (W-type) have become porous as early as at 5% DVB (refer to Table I).

For the swelling of a network to occur, it is necessary that the energy of the interaction of polymer chains with the solvent should be higher

than the energy of interchain interactions, the swelling of SOL copolymers in methanol reflects the low energy of interchain interactions in the strained networks between the microgel particles. In fact, in our previous paper,<sup>11</sup> we observed that the St-DVB copolymers prepared in toluene could swell even in aqueous solutions of ethanol, and the swelling ratios maintained a nearly constant value within a broad range of concentrations of ethanol in water. These observations indicate that the interaction of the polymer chains in the strained networks is so weak that the influence of the affinity of polymer to solvent on the swelling capacity of this type of copolymers is very limited.

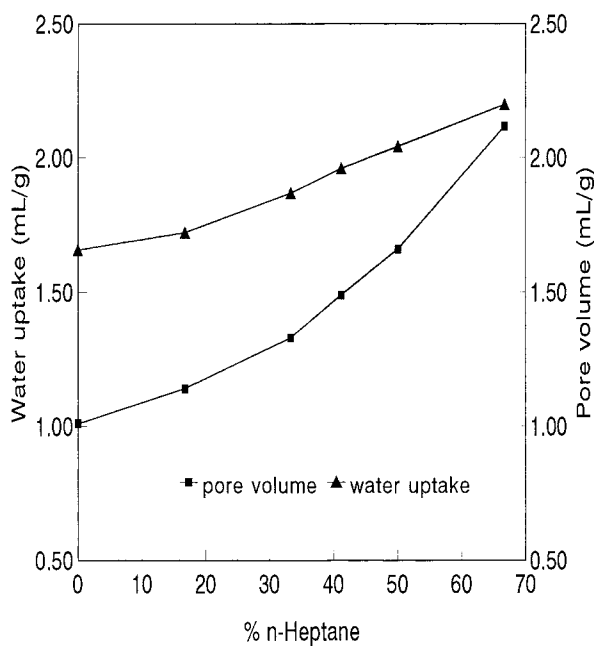
By comparing the swelling data in Table II with those in Figure 2, it is reasonable for us to believe that the swelling behaviors in water and in methanol are similar in nature for SOL copolymers. Because the affinity of polymer to solvent has only a limited influence on the swelling capacity of this class of copolymers, it could be assumed that a very weak polymer–water interaction in the equilibrium of polymer with water is enough to partially relax the strained networks and thus to increase the interparticle spaces and reopen the collapsed pores. With an increase in the degree of crosslinking, the strain increases in the domains between the microgel particles, resulting in an increase in the swelling capacity of the copolymers in water in some range of the DVB content.

Since the swelling properties of the SOL and NONSOL copolymers in water are different, it is

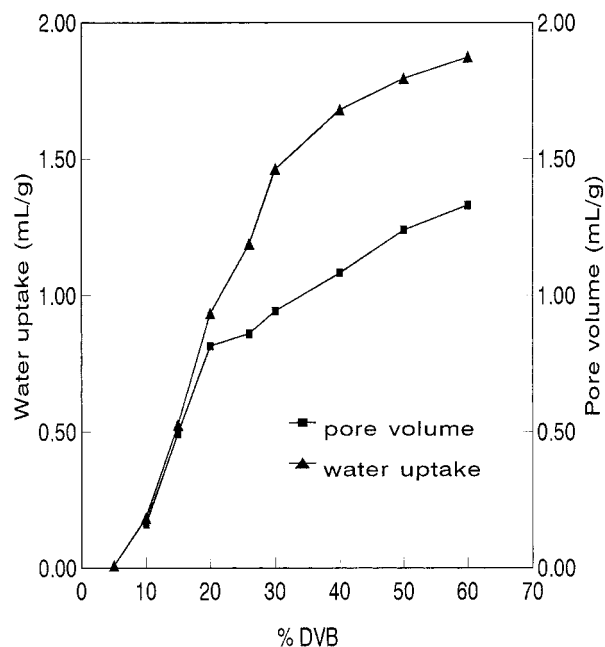
expected that if we use a mixture of SOL and NONSOL as diluent, the swelling properties in water for the obtained copolymers will change with changing the composition of the mixed diluent. In Figure 3, the water uptake and pore volume of the copolymers (W-type) prepared in a mixed diluent of toluene and *n*-heptane were plotted against the *n*-heptane content in the mixed diluents. As shown, the swelling capacity in water changes as a function of the *n*-heptane content, and with an increase of *n*-heptane content from 0 to 66.7%, the difference  $\Delta V$  between water uptake and pore volume decreases gradually from 0.648 to 0.081 mL/g, corresponding to a decrease in swelling ratio from 1.33 to 1.027.

A further study of the St-DVB copolymers prepared using mixed diluent was done, and Figure 4 shows the dependence of water uptake and pore volume of copolymers dried from water (W-type) on the DVB content. It is seen that the dependence of the water uptake and the pore volume on the DVB content in Figure 4 is similar to that in Figure 1, but the DVB percentage at which the water uptake and the pore volume abruptly grow in Figure 4 shifts to a lower value compared to that in Figure 1, due to the earlier phase separation for copolymers in Figure 4.

The porous structure of St-DVB copolymers has been found in many cases not to be



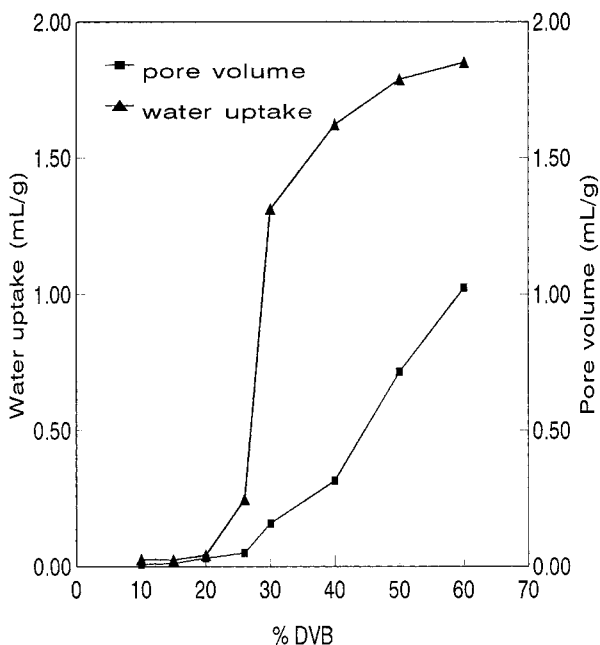
**Figure 3** Effect of *n*-heptane content on water uptake and pore volume of St-DVB copolymers (W-type). The copolymers were prepared in the presence of a mixed diluent of toluene and *n*-heptane at a fixed DVB content of 60% and a dilution degree of 2.0.



**Figure 4** Dependence of water uptake and pore volume of St-DVB copolymers (W-type) on the DVB content. The copolymers were prepared in the presence of a mixed diluent with 33% *n*-heptane at a fixed dilution degree of 2.0.

fixed.<sup>11,19,20</sup> It changes reversibly, sometimes in quite broad ranges even at a high degree of crosslinking. For example, a St-DVB copolymer with even 98% DVB prepared in toluene at a dilution degree of 4.0 has pore volumes of 1.526 and 1.004 mL/g when dried from water and from toluene, respectively.<sup>11</sup> Consequently, the volume increase from dried-to-swollen state during swelling for copolymers pretreated with different solvents will be different.

In Figure 5 the same copolymers as those in Figure 4 were dried from toluene (T-type). The DVB percentage at which the transitions of water uptake and pore volume occur shifts to a higher value compared to that in Figure 4. While the pore volume in Figure 5 is significantly lower than that in Figure 4 at various DVB contents, the water uptakes in these two figures are very close in the range of relatively high DVB content. As a result, the difference  $\Delta V$  between water uptake and pore volume in Figures 4 and 5 are different. The dependence of the swelling ratio, corresponding to the water uptake in Figures 4 and 5, on the DVB content is shown in Figure 6. On the basis of the results in Figures 4, 5, and 6 we can see that the swelling capacity in water for porous St-DVB copolymers is also changeable.



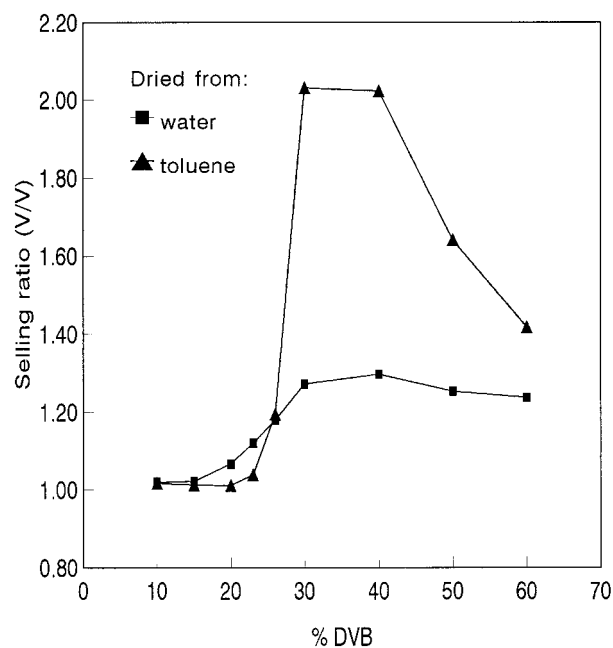
**Figure 5** Dependence of water uptake and pore volume of St-DVB copolymers (T-type) on the DVB content. The copolymers were prepared in the presence of a mixed diluent with 33% *n*-heptane at a fixed dilution degree of 2.0.

Figure 7 shows the dependence of water uptake and the pore volume of porous St-DVB copolymers (W-type) on the degree of dilution. The copolymers with 60% DVB were prepared in the presence of a mixed diluent of toluene and *n*-heptane at a fixed *n*-heptane content of 33.3%. It is seen that the pore volume in Figure 7 increases with an increase in dilution degree up to about 3.0 and then decreases, but the water uptake increases more rapidly with increasing the dilution degree up to 4.0. As a result, the difference  $\Delta V$  between water uptake and pore volume rapidly increases with an increase in dilution degree. The difference  $\Delta V$  at various dilution degrees and the corresponding swelling ratio  $B_w$  are listed in Table III; for comparison, the  $\Delta V$  and  $B_w$  of copolymers dried from toluene (T-type) are also listed. While the swelling in water at the low dilution degree of 0.75 is very limited for copolymers dried from either water or toluene, the swelling at higher dilution degrees is significant in both the cases, with higher values of  $\Delta V$  and  $B_w$  for copolymers dried from toluene. At a dilution degree of 4.0, the swelling ratio reaches a value up to 2.479 for copolymer dried from toluene, i.e., the volume of the hydrophobic St-DVB copolymer (T-type) in water increases about 1.5 times as compared with that in dry state.

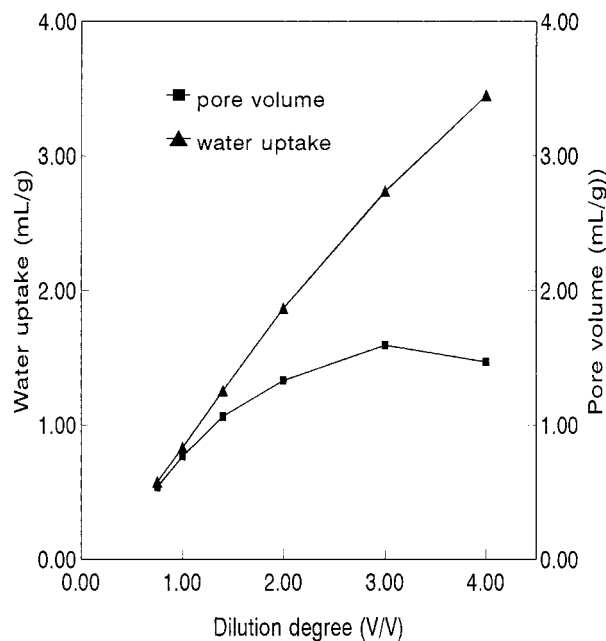
The following equation describes the swelling capacity in toluene for St-DVB copolymers prepared in the presence of toluene<sup>9</sup>:

$$V_s = V_n + S$$

where  $V_s$  and  $V_n$  are solvent (toluene) uptakes (mL/g) for copolymers prepared with and without toluene as diluent, and  $S$  is the volume of toluene used as diluent per unit weight of monomers (mL/g). From this equation, it follows that the swelling capacity of St-DVB copolymers in solvating solvent linearly depends on the dilution degree in the initial reaction mixture. In Figure 8, the observed water (solvent) uptake of the copolymers (W-type) are plotted against those calculated from the above equation, and the line is drawn with a unit slope. For comparison, the plots of the observed methanol and toluene (solvent) uptakes against the corresponding calculated value of  $V_s$  are shown (Fig. 8). For all calculations of  $V_s$ , the term  $V_n$  was assumed to be zero, which should be true for St-DVB copolymers with 60% DVB prepared in the absence of diluent, and therefore, the calculated values of  $V_s$  for copolymers swelling in toluene, methanol, and water are the same. As can be seen in Figure 8, the plots for both meth-



**Figure 6** Dependence of swelling ratio in water on the DVB content for St-DVB copolymers dried from water (W-type) and from toluene (T-type). The copolymers were prepared in the presence of a mixed diluent with 33% *n*-heptane at a fixed dilution degree of 2.0.



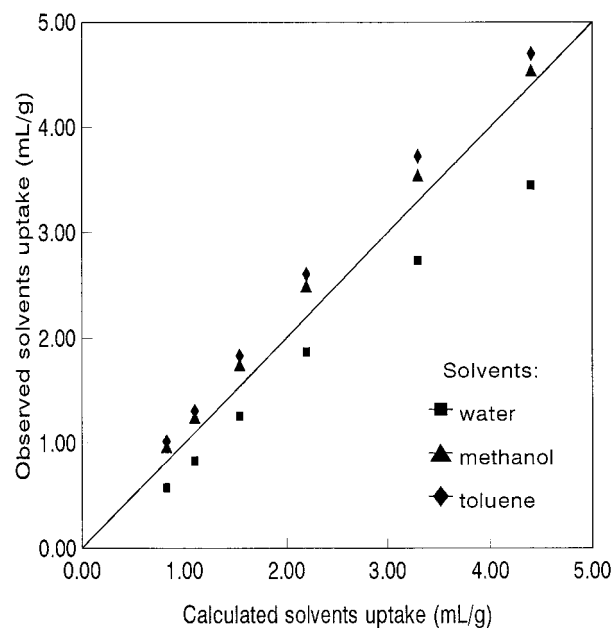
**Figure 7** Dependence of water uptake and pore volume of St-DVB copolymers (W-type) on the dilution degree. The copolymers with 60% DVB were prepared in the presence of a mixed diluent at a fixed *n*-heptane content of 33%.

anol and toluene uptakes are very close to the line, with slopes of 1.11 and 1.12, respectively. A more unexpected result is that a relation similar to that described by above equation is obeyed to some extent by the swelling of St-DVB copolymers in water. Up to a calculated solvent uptake of 3.3 mL/g (dilution degree of 3.0), the plot for swelling in water does not deviate very much from the line, with a slope just less than one (0.84). Thus, not only in solvating solvent, but in

**Table III** Difference and Swelling Ratio at Various Dilution Degrees

Dilution Degree (v/v)	$\Delta V$ (mL/g)		$B_w$ (v/v)	
	W-type	T-type	W-type	T-type
0.75	0.038	0.018	1.025	0.985
1.0	0.065	0.204	1.038	1.129
1.4	0.190	0.377	1.094	1.209
2.0	0.538	0.826	1.236	1.418
3.0	1.143	1.469	1.449	1.676
4.0	1.979	2.457	1.817	2.479

The St-DVB copolymers with 60% DVB were prepared in the presence of a mixed diluent of toluene and *n*-heptane at a fixed *n*-heptane content of 33.3% and were dried from water (W-type) and from toluene (T-type), respectively.



**Figure 8** Plots of observed solvent (water, methanol, or toluene) uptakes of St-DVB copolymers (W-type) against those calculated values. The line in the figure is drawn with unit slope, and the copolymers were prepared in the presence of different amounts of mixed diluent with 33% *n*-heptane at a fixed DVB content of 60%.

nonsolvent including water, the swelling capacity of St-DVB copolymers prepared in diluent with relatively high solvating power is strongly dependent on the degree of dilution, with a linear relation between the swelling capacity and the dilution degree to some extent. In addition, because the swelling capacities in toluene and in methanol are essentially identical, and even in water, the swelling capacity does not deviate much from that in these two organic solvents. The results presented in Figure 8 provide evidence in favor of the previous understanding that the swelling capacity of St-DVB copolymers prepared in the presence of diluent with relatively high solvating power is dependent only to a limited extent on the solvating power of the swelling media, including water.

Finally, it is interesting to correlate the unusual swelling properties of porous St-DVB copolymers with those of hypercrosslinked polymer of styrene.<sup>13,21,22</sup> Such hypercrosslinked polystyrene are prepared by crosslinking the polymer chains in solution or in the swollen state via a Friedel-Grafts reaction, and the polymers thus obtained are fundamentally different in structure from the porous St-DVB copolymers.<sup>22</sup> The swell-



ing capacity of the hypercrosslinked polymer of styrene in water previously has been considered as an important feature to distinguish from porous St-DVB copolymers, although the swelling behaviors in organic nonsolvents for them are somewhat similar. However, it is not true now; the fact that the porous St-DVB copolymers prepared in some conditions are able to swell in water provides additional strong evidence for the viewpoint that the unusual swelling properties in nonsolvating media are inherent, to some extent, in all densely crosslinked polymers prepared in the presence of a large amount of diluent with relatively high solvating power.<sup>10,21</sup>

## CONCLUSIONS

By using SOL or its mixture with NONSOL as diluent, the obtained porous St-DVB copolymers have been found to be able to swell in water.

The swelling of SOL copolymers in water, undetectable up to about 20% DVB, increases rapidly with a further increase in the degree of crosslinking and increases to a maximum at about 50% DVB; even at a very high degree of crosslinking, the volume increase of copolymers in water is still observed. NONSOL copolymers with various DVB contents show no volume increase in water, but with a mixture of SOL and NONSOL as diluent, the copolymers thus obtained could swell in water, and the swelling capacity decreases with increasing NONSOL content in the mixed diluent. The dependence of the swelling capacity in water for copolymers prepared in mixed diluent on the DVB content is very similar to that for SOL copolymers, with a shift of % DVB at which the swelling transition occurs to a lower value. Not only in solvating solvent, but in nonsolvent including water, the swelling capacity of highly crosslinked St-DVB copolymers prepared in a mixed diluent with relatively high solvating power is linearly dependent on the dilution degree in the initial reaction mixture to some extent.

The unusual swelling behaviors in water have been ascribed to the same factor as St-DVB copolymers that swell in methanol or other organic nonsolvents of polystyrene: the inner strain, which mainly exists between the highly crosslinked microgel particles in the copolymers, and is

released in the course of the swelling. The ability of the porous St-DVB copolymers to swell in water provides additional strong evidence that the unusual swelling properties in nonsolvating media are inherent, to some extent, in all densely crosslinked polymers prepared in the presence of a great amount of diluent with relatively high solvating power.

## REFERENCES

1. Boyer, R. F.; Spencer, R. S. *J Polym Sci* 1948, 3, 97.
2. Errede, L. A. *J Appl Polym Sci* 1986, 31, 1749.
3. Errede, L. A. *Macromolecules* 1986, 19, 1522.
4. Barr-Howell, B. D.; Peppas, N. A. *J Appl Polym Sci* 1985, 30, 4583.
5. Abrams, I. M.; Millar, J. R. *React Polym* 1997, 35, 7.
6. Sederel, W. L.; Dejong, G. J. *J Appl Polym Sci* 1973, 17, 2835.
7. Seidl, J.; Malinsky, J.; Dusek, K.; Heitz, W. *Adv Polym Sci* 1967, 5, 113.
8. Kun, K. A.; Kunin, R. *J Polym Sci* 1968, A-1, 6, 2689.
9. Millar, J. R.; Smith, D. G.; Marr, W. E.; Kressman, T. R. E. *J Chem Soc* 1963, 218.
10. Negre, M.; Batholin, M.; Guyot, A. *Angew Makromol Chem* 1982, 106, 67.
11. Yan, J.; Xu, R. N.; Yan, J. T. *J Appl Polym Sci* 1989, 38, 45.
12. Coutinho, F. M. B.; Neves, M. A. F. S.; Dias, M. L. *J Appl Polym Sci* 1997, 65, 1257.
13. Davankov, V. A.; Rogozhin, S. V.; Tsyurupa, M. P. in *Ion Exchange and Solvent Extraction*; Marinsky, J. A.; Marcus, Y. Eds.; Marcel Dekker: New York and Basel, 1977, Vol. 7, Chapter 2.
14. Rabelo, D.; Coutinho, F. M. B. *Polym Bull* 1993, 30, 725.
15. Yan, J.; Wan, J. *Lizi Jiaohuan Yu Xifu* 1988, 4, 216. CA 110; 174324p.
16. Pepper, K. W.; Reichenberg, D.; Hale, D. K. *J Chem Soc* 1952, 3129.
17. Kolarz, B. N. *Angew Makromol Chem* 1980, 90, 183.
18. Dusek, K. *J Polym Sci* 1967, C16, 1289.
19. Dusek, K. in *Development in Polymerization*, Howard, R. N., Ed.; Applied Science: London, 1982, Vol. 3, Chapter 4.
20. Wieczorek, P. P.; Kolarz, B. N.; Galina, H. *Angew Makromol Chem* 1984, 126, 39.
21. Davankov, V. A.; Tsyurupa, M. P. *Angew Makromol Chem* 1980, 91, 127.
22. Davankov, V. A.; Tsyurupa, M. P. *React Polym* 1990, 13, 27.