Pore Memory of Macroporous Styrene–Divinylbenzene Copolymers

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ABSTRACT: The variation of the pore structure of styrene–divinylbenzene (S–DVB) copolymer beads with the drying conditions was investigated. Macroporous S–DVB copolymer beads with various DVB contents were prepared in the presence of toluene-cyclohexanol mixtures as a diluent. It was found that the pores of 10^1-nm radius, corresponding to the interstices between the microspheres, collapse upon drying of the copolymers from toluene. The collapsed pores reexpand if the copolymers were dried from methanol. The collapse–reexpansion process of the pores was found to be reversible, indicating that the actual pore structure formed during the crosslinking copolymerization is memorized by the copolymer network. The magnitude of the pore structure variation increased on worsening the polymer–diluent interactions during the gel formation process due to the simultaneous increase in crosslink density distribution. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1055–1062, 1999

Key words: macroporous styrene–divinylbenzene copolymers; pore structure; pore memory; pore structure variation; crosslink density distribution

INTRODUCTION

Macroporous (heterogeneous) styrene–divinylbenzene (S–DVB) copolymer networks are widely used as starting materials for ion exchangers and as specific sorbents; therefore, they have been the subject of a large number of studies.[1–5] These materials are mainly prepared by free-radical crosslinking copolymerization of S and DVB monomers in the presence of an inert diluent. The diluent (a solvent, a nonsolvent, or a linear polymer) is included in the reaction system as a pore forming agent and plays an important role in the design of the pore structure of these crosslinked materials.[2]

If the diluent remains in the gel throughout the copolymerization, an expanded network structure is obtained. The expanded networks thus formed shrink during the removal of the diluent after their synthesis and therefore they are nonporous in the glassy state. Heterogeneities in the network structure appear if the diluent separates out of the gel phase during the polymerization reactions.[2,6–10] The incipient phase separation during the crosslinking copolymerization may occur before the onset of macrogelation; this results in the formation of a polymer dispersion in the liquid

phase. Otherwise, if the system phase separates beyond the gel point, the gel shrinks and results in a dispersion of the expelled liquid droplets in the network phase. In both cases, after complete conversion of the monomers a heterogeneous S–DVB network consisting of network and diluent phases is obtained. Removing the diluent from the network creates voids (pores) 1–1000 nm in size in the glassy state.

Relationships between the synthesis conditions and the structure of macroporous S–DVB networks have been the subject of intensive studies during the last four decades.[2,4,11–20] Experiments showed that a phase separation during the gel formation process is promoted; i.e., the volume of the diluent phase (pore volume) in the network increases as the concentration of the crosslinker (DVB) or that of the diluent increases, or as the solvating power of the diluent decreases. It was also shown that good solvents as a diluent create small pores and therefore a large specific surface area, whereas bad solvents or linear polymers produce materials with irregularly shaped large pores.

Although the final pore structure of a S–DVB network is fixed during the gel formation process when the network is in a rubbery state, its structural characterization is performed with the polymer sample in the glassy state. Krska et al. were the first to show the difference in the pore structure of S–DVB copolymers between the swollen and the dried states.[21] It was also found that the pore structure of these copolymers varies with the type of the solvent used to treat the network.[22–38] For instance, the copolymers dried from nonsolvents show a "maximum porosity," which is close to the porosity in the swollen state.[31] The drying process of the copolymers swollen in good solvents may lead to a partial or total collapse of the pores.[35,36] These experimental findings indicate that the swollen state porosity can be preserved in the dried state if the interactions between the polymer and the solvent are decreased before the drying process. It seems that the pore structure variation of S–DVB copolymers is closely related to the degree of inhomogeneity in crosslink distribution[29,31,35]; the pores in the loosely crosslinked (rubbery) regions of the material collapse during the drying process, whereas those in the highly crosslinked (glassy) regions remain unchanged.

This study seeks to obtain further insight into the pore structure variation in S–DVB copolymers, depending on the drying conditions. The reversibility of the pore structure variation and the size of the variable pores, as well as the magnitude of this variation, depending on the synthesis conditions, were investigated. Our primary aim was to determine the synthesis condition of macroporous S–DVB copolymers exhibiting a maximum memory of pores. For this purpose, a number of S–DVB copolymer beads with various DVB contents were prepared by the suspension polymerization technique. Cyclohexanol, toluene, and their mixture were used as a diluent. Toluene is a good solvent for polystyrene and its thermodynamic properties are the same as the monomers used in the polymerization. However, cyclohexanol has the solubility parameter value of 23.3 $(MPa)^{0.5}$ in contrast to the value of 15.6–21.1 $(MPa)^{0.5}$ for S–DVB copolymer,[39] which indicates that cyclohexanol is a nonsolvating diluent for the S–DVB copolymerization system. The changes in the pore structure of S–DVB copolymer beads were investigated by mercury porosimetry using copolymer samples dried from methanol and toluene.

EXPERIMENTAL

Materials

The S (Sabic), DVB (Riedel-de Haen), dibenzoyl peroxide (DBP, Elf Atochem), *tert*-butyl perbenzoate (TBP, Interchem), cyclohexanol (Merck), toluene (Merck), tricalcium phosphate (TCP, Budenheim), calcium chloride (Kemira Kemi), and dodecylbenzene sodiumsulfonate (DBS, Henkel) were used as received. Commercial DVB consisted of 62% DVB isomers with the rest being mostly ethylvinyl benzenes (35%). Fresh distilled water was used in the synthesis of the copolymers.

The S–DVB copolymer beads were obtained by the suspension polymerization technique.[40,41] Mixtures of cyclohexanol and toluene were used as the diluent of the organic phase. The volume fraction of the monomers in the organic phase (monomer–diluent mixture), ν_2^{00}, was taken to be constant at 0.5 throughout the study, whereas the DVB concentration and the composition of the diluent were varied. The DVB concentrations were expressed in terms of the mole percent of the DVB isomers in the monomer mixture. DBP and TBP were used as the initiator of the low and high temperature period of the free-radical copolymerization, respectively. Suspension polymerization
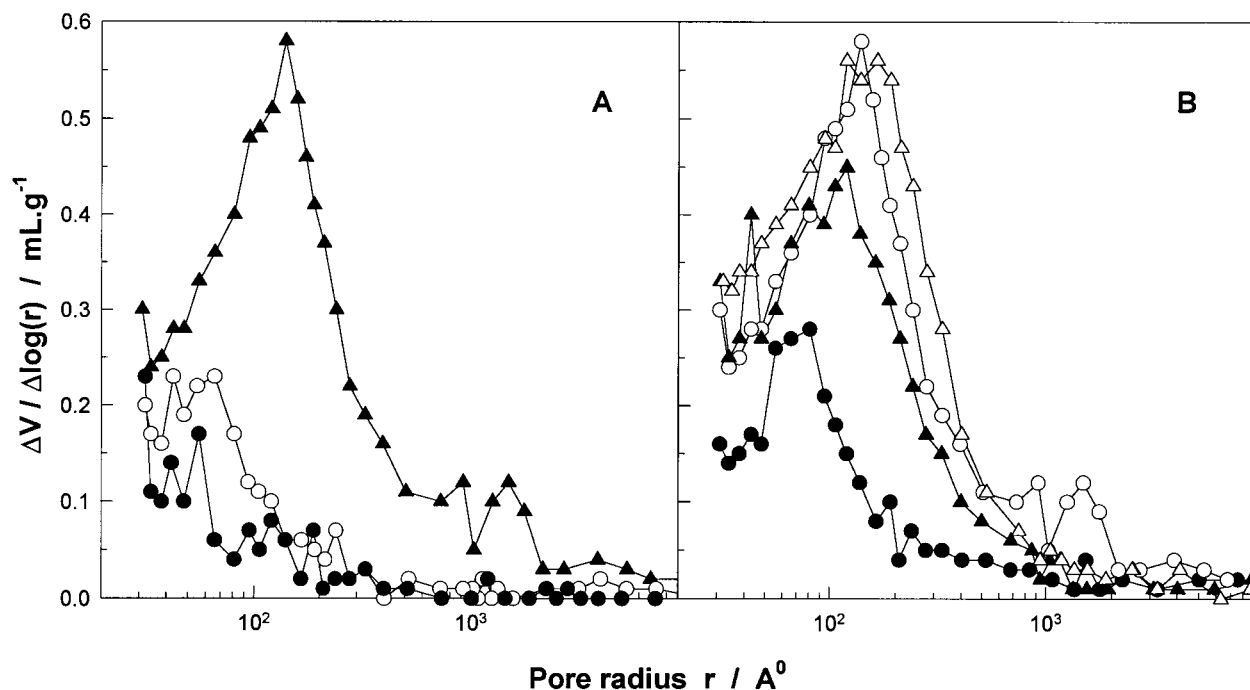
Figure 1   Effects of (A) the solvating power of the diluent and (B) the DVB concentration on the pore size distribution of macroporous S–DVB copolymers. $v_2^{00} = 0.5$. (A) DVB = 10%. Diluents: (●) toluene, (○) cyclohexanol/toluene [75/25 (v/v)], and (▲) cyclohexanol. (B) Diluent: cyclohexanol. DVB = (●) 5, (○) 10, (▲) 17.5, and (△) 24%.

was conducted in a 1-L Buchi jacketed glass reactor fitted with a mechanical stirrer, nitrogen inlet, condenser, and temperature and pressure indicators. A 3% aqueous NaCl solution (500 mL), the diluent (100 mL), and the S–DVB monomer mixture (100 mL) were first introduced into the reactor, heated to 70°C, and 100 mL of an aqueous suspension agent containing CaCl$_2$ (0.095 g), TCP (7.43 g), and DBS (0.017 g) were then added to the reactor under a nitrogen atmosphere at 300 rpm. The reaction mixture was heated to 90°C and the initiators DBP (0.50 g) and TBP (0.035 g) were fed to the mixture to initiate the polymerization reactions. The reaction was allowed to proceed at 90°C for 5.5 h and at 120°C for 1.5 h under a nitrogen atmosphere and at 300 rpm. After polymerization, a dilute HCl solution was added to the reactor to dissolve the TCP surrounding the beads. After filtration of the copolymer beads of 0.5–1.4 mm size, they were first washed with water and then extracted with acetone for 6 h in a Soxhlet apparatus.

Solvent Treatment

The copolymer beads thus obtained were swollen to equilibrium in toluene for at least 1 week. Then they were washed first with acetone and finally with pure methanol. Using this solvent exchange procedure, the good solvent toluene in the swollen gel was replaced with the nonsolvent methanol; thus, the gel was transferred from the rubbery to the glassy state before the drying process.[31] The copolymer beads after treatment with methanol as a final solvent were dried *in vacuo* at room temperature for 15 h. For comparison, part of the copolymer beads swollen in toluene were dried without the solvent exchange for 30 h at 80°C.

Methods

The pore volume and the pore size distribution of the copolymer beads were determined by mercury intrusion porosimetry on a Micromeritics 9305 model porosimeter. Cumulative pore volumes and the distribution function $\Delta V/\Delta \log(r)$ was used to express the pore size distribution, where ΔV is the pore volume change when the radius of a cylindrical pore was changed from r to $r - \Delta r$. The pore volume, V_p, and the total porosity, $P\%$, were calculated as

$$V_p = \frac{1}{d_0} - \frac{1}{d_2} \tag{1}$$

$$P\% = \left(1 - \frac{d_0}{d_2}\right) \times 100 \qquad (2)$$

where d_0 is the apparent density of the copolymers and d_2 is the density of homogeneous S–DVB copolymers, taken as 1.06 g/mL.

To check the repeatability of the porosity measurements by the mercury porosimetry, three measurements were carried out on copolymer beads obtained at 44% DVB concentration and in the presence of toluene as a diluent. An average value of 0.355 mL/g for the pore volume with a standard deviation of 0.018 was obtained, indicating that the porosimeter gives reproducible results and the copolymer beads withstand the measurements of their pore structure.

RESULTS AND DISCUSSION

Macroporous S–DVB copolymer beads were prepared at a fixed monomer concentration (ν_2^{00} = 0.5). The synthesis parameters varied were the DVB concentration and the composition of the cyclohexanol–toluene diluent mixture (i.e., the solvating power of the diluent). Figure 1(A,B) illustrates the variation of the differential pore size distributions of S–DVB copolymers, depending on the quality of the diluent and the DVB concentration, respectively. Figure 1(A) shows that in copolymers with 10% DVB content the amount of pores of 10^1–10^2 nm in radius increases as the cyclohexanol content of the diluent increases (i.e., as the solvating power of the diluent decreases: (χ-induced syneresis[4]). Also, the average pore size becomes larger and the pore size distribution shifts toward the larger pores on worsening of polymer–diluent interactions as seen in Figure 1(A). From Figure 1(B) it is seen that with cyclohexanol as a diluent the porosity increases on raising the DVB concentration to 10% (ν-induced syneresis[4]) and then remains constant. Increasing the DVB content also shifts the pore size distribution toward the smaller pores. These results are expected and are in accord with previous reports.[2,4,31]

The pore size distributions of the copolymers shown in Figure 1 were measured using samples dried from methanol. Thus, Figure 1 represents the swollen state porosities, which are, the maximum porosities of the samples because the swelling agent toluene was replaced with the nonsol-
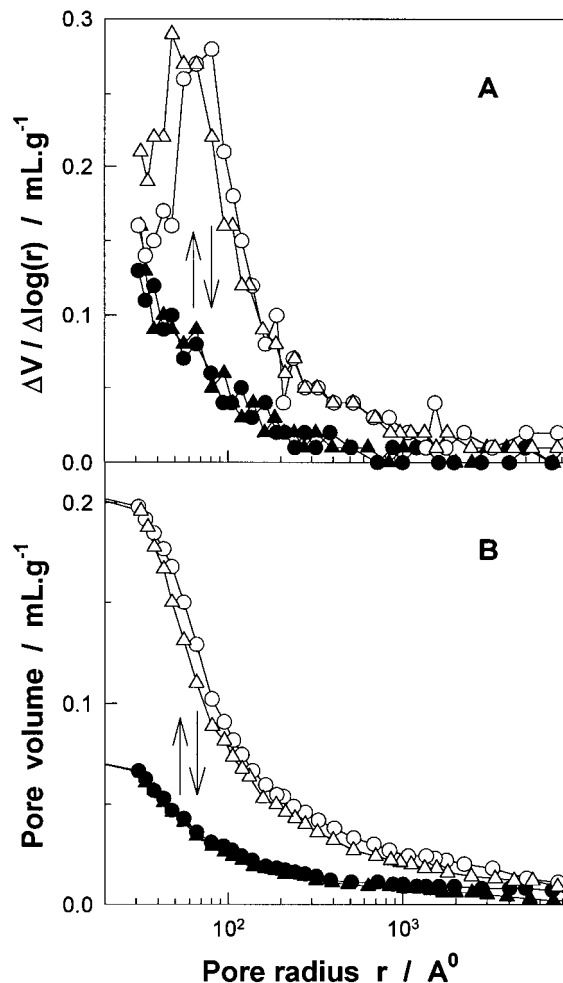

Figure 2 Pore size distribution of a macroporous S–DVB copolymer dried from toluene (filled symbols) and methanol (open symbols) in (A) differential and (B) integral modes. The copolymer samples dried from (●) toluene and (○) methanol. The sample dried from toluene was swollen again in toluene and thereafter dried from (△) methanol and (▲) vice versa. ν_2^{00} = 0.5. DVB = 10%. Diluent: cyclohexanol.

vent methanol before the drying process. Figure 2 compares the pore size distributions of copolymers with 10% DVB dried from methanol and from toluene. Cyclohexanol was used as the diluent during the synthesis. The pore sizes of 10^1-nm radius largely disappeared if the copolymers were swollen in toluene before the drying process (i.e., if they were dried in the rubbery state). To check the reversibility of the pore structure variation, the copolymers dried from toluene were swollen in toluene and then dried again from methanol and vice versa. The results of the
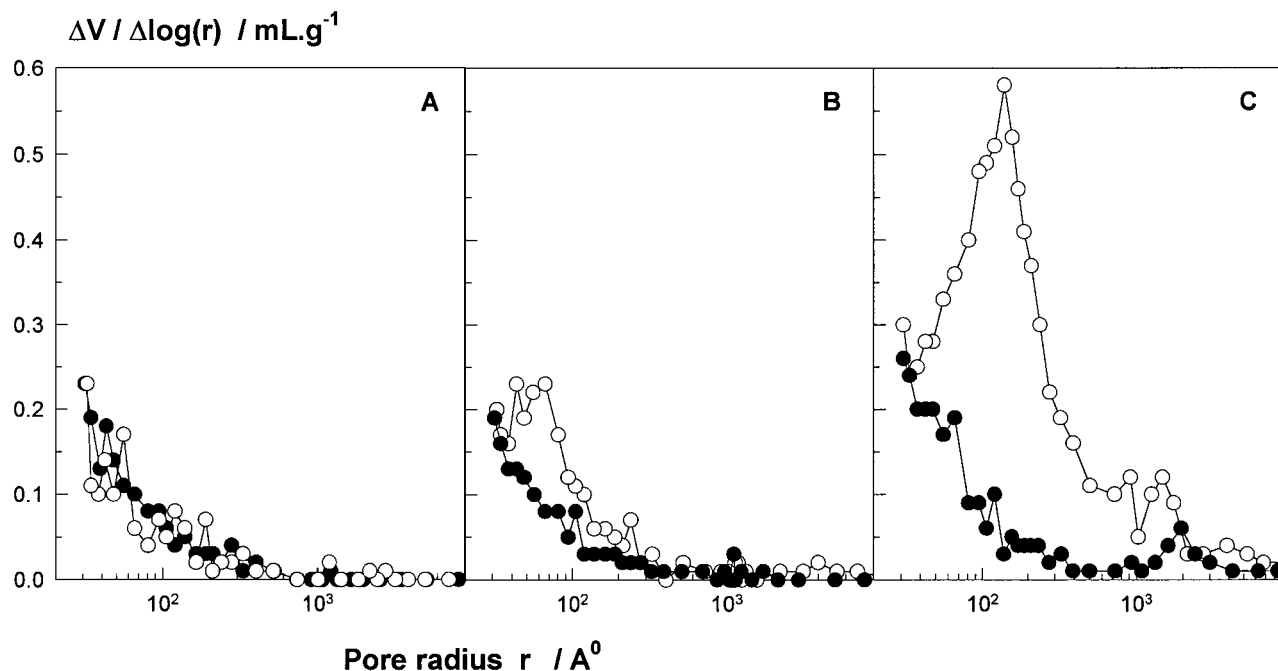
Figure 3 Effect of the solvating power of the diluent on the pore size distribution of macroporous S–DVB copolymers dried from (●) toluene and (○) methanol. ν_2^{00} = 0.5. DVB = 10%. Diluents: (A) toluene, (B) cyclohexanol/toluene [75/25 (v/v)], and (C) cyclohexanol.

porosity measurements are also shown in Figure 2. It is seen that the collapse–reexpansion process of the pores of 10^1-nm radius is reversible. This indicates that the pore structure of S–DVB copolymers created during the crosslinking copolymerization is memorized by the copolymer network.

The structure of macroporous S–DVB copolymers is known to consist of globules[11]; the smallest, rather spherical particles of about 10–20 nm in diameter are the "nuclei," and the aggregation of these nuclei results in microspheres with diameters of 50–100 nm; the microspheres are aggregated again in particles of about 250–1000 nm in diameter. The pores are defined as the spaces between the nuclei and the particles and the microspheres and the particles. According to this picture, the variable pores of 10^1-nm radius shown in Figure 2 correspond to the interstices of the microspheres formed from the nuclei. This variation of the pore structure is mainly due to the higher reactivity of DVB compared to S in free-radical crosslinking copolymerization.[8] Because DVB monomer is incorporated into the polymer more rapidly than S, the parts of the network formed earlier (the nuclei and the inner part of the microspheres) are more highly crosslinked than those formed later. Therefore, the surface and the interstices of the microspheres formed at a later stage of the copolymerization (at which the reaction mixture is reached on the unreacted S monomer) are loosely crosslinked. The pores in these regions collapse during drying from toluene due to the cohesional forces between the solvated network chains. Thus, the reversibility of the pore structure variation originates from the crosslink density distribution, which is fixed for a given copolymer sample.

In Figures 3 and 4 the pore size distributions of S–DVB copolymers dried from toluene and methanol are shown as a function of the solvating power of the diluent and the DVB concentration, respectively. For a fixed amount of DVB, decreasing the solvating power of the diluent increases the magnitude of the pore structure variation (Fig. 3). As the diluent becomes poorer for the copolymer chains, pores of 10^1–10^2 nm radius start to appear. However, these pores are largely unstable and they collapse during the drying process. On the other hand, increasing DVB content to 10% increases the total porosity, as well as the amount of unstable pores (A and B in Fig. 4). A further increase in
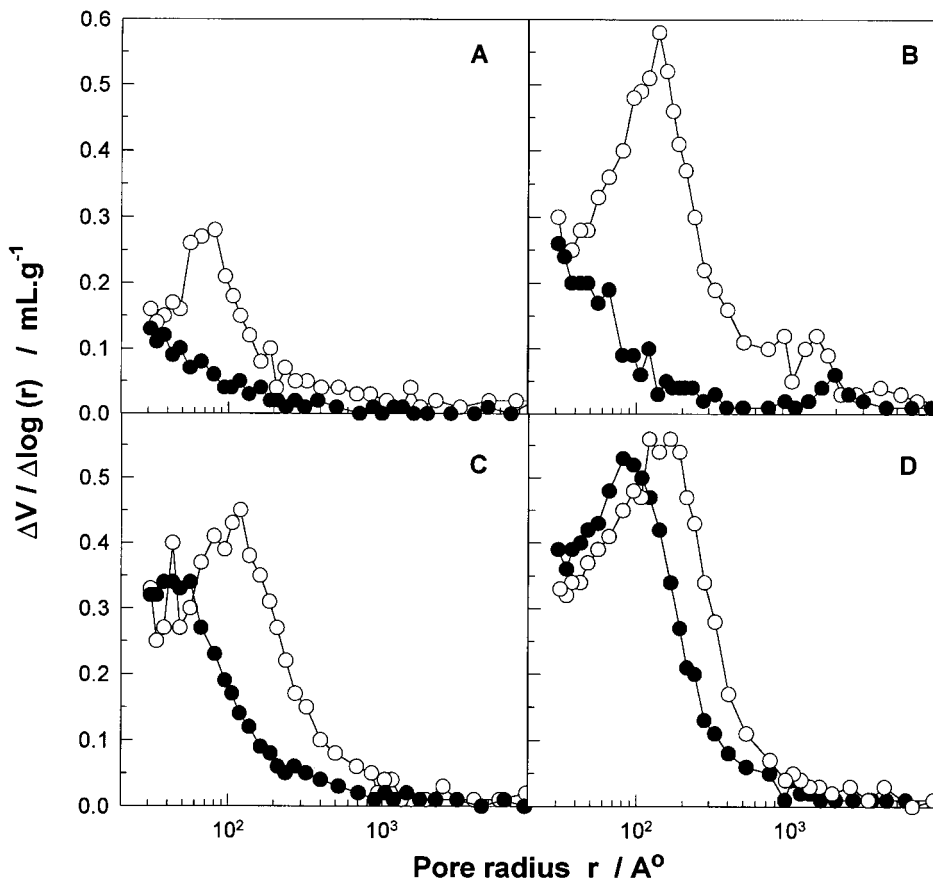
Figure 4   Effect of the DVB concentration on the pore size distribution of macroporous S–DVB copolymers dried from (●) toluene and (○) methanol. $v_2^{00} = 0.5$. Diluent: cyclohexanol. DVB = (A) 5, (B) 10, (C) 17.5, and (D) 24%.

the DVB concentration up to 24% does not change the total porosity much but increases the stability of the pores. These results can be explained as follows: a decrease in the solvating power of the diluent causes the process of phase separation to take place prior to gelation. This leads to an increase in the inhomogeneity in the final material (i.e., to an increase in the graduation of the crosslink distribution through the microspheres). As a result, the extent of the collapse–reexpansion process of the pores increases on decreasing the solvating power of the diluent. On the other hand, for a given type of diluent, increasing the DVB content promotes phase separation of the copolymers during the gel formation process and thus increases the inhomogeneity in the final copolymers. However, at high DVB contents even the less crosslinked regions of the network remain in the glassy state during drying due to the high

overall crosslink density of the material. Thus, if the DVB concentration is sufficiently high [Fig. 4(D)], the pores remain almost stable and do not collapse on drying.

Defining $P_s\%$ as the fraction of stable pores,

$$P_s\% = \frac{P\%}{P_{max}\%} \times 100 \qquad (3)$$

where $P\%$ and $P_{max}\%$ are the total porosities of the copolymer samples dried from toluene and methanol, respectively, one may calculate the pore stability of S–DVB copolymer beads as a function of the synthesis conditions. Figure 5 shows the fraction of stable pores plotted as a function of the DVB concentration and the solvating power of the diluent. The solvating power of the diluent was estimated from $(\delta_1 - \delta_2)$, where δ_1 and δ_2 are the solubility parameters of the diluent
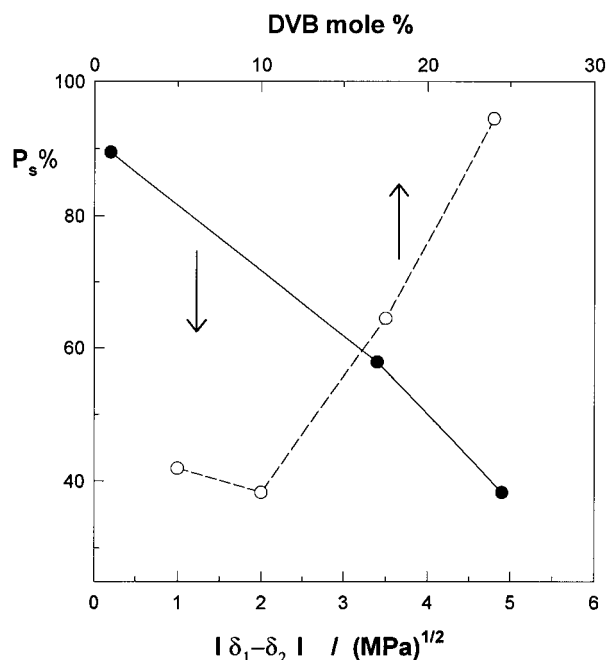
Figure 5 Fraction of stable pores in S–DVB copolymers, $P_s\%$, shown as a function of the solvating power of the diluent $(\delta_1 - \delta_2)$ and the DVB concentration. $v_2^{00} = 0.5$. DVB = (●) 10%. Diluent: (○) cyclohexanol.

and the polymer, respectively. The solubility parameter of the diluent mixture was calculated from the solubility parameters of cyclohexanol and toluene as given previously.[17] Macroporous S–DVB copolymers with a stable pore structure form at high crosslinker concentrations or in the presence of good solvents as a diluent. Copolymers with a high number of variable pores are obtained in the presence of nonsolvating diluents and at medium DVB concentrations.

In summary, the present work shows the synthesis conditions of macroporous S–DVB copolymers that exhibit a reversible change in their pore structure. The reversible collapse–reexpansion phenomenon of pores of 10^1-nm radius occurs using copolymer beads with the methanol-toluene solvent pair as the posttreatment agent. The observed pore memory of S–DVB copolymers seems to widen their application area in size-selective separation of materials.

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