

Swelling of Porous Ethylvinylbenzene–Divinylbenzene Copolymers and the Stability of the Pore Structure*

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Synopsis

A series of porous ethylvinylbenzene–divinylbenzene (EVB–DVB) copolymers with DVB contents ranging from 22.0 to 98.4% were prepared using various amounts of toluene as the inert diluent, and studies were made on the copolymers as to their swelling properties, the stability of their pore structure, and the relationship between swelling in nonsolvents and variations in their pore structure. The swelling experiments showed that the ethanol regains of the copolymers were closely related to the course of phase separation, and the increases in both the DVB content and the volume fraction of monomers in the organic phase resulted in enhanced capacity of the highly crosslinked copolymers to keep swelling in solvents having extremely small affinity for these copolymers. The variations in pore structure, sometimes quite considerable, for copolymers pretreated with different solvents were observed even at DVB content up to 98.4%, and further studies showed that a consistent relationship existed between pore volume variation and volume swelling ratio in ethanol for toluene modified copolymers.

INTRODUCTION

The polymerization that leads to a porous copolymer must be accompanied by a phase separation.^{1,2} After phase separation in the copolymerization system monomers will react further in gel and dilute phases under different conditions.^{3–5} As a result, the copolymer finally obtained is porous and its skeleton consists of highly crosslinked microgel-like particles linked together by loosely crosslinked chains² (or network), and the copolymer is thus heterogeneous not only in morphology, but also in the crosslinked structure of the skeleton.⁶ In this article, a series of porous ethylvinylbenzene–divinylbenzene (EVB–DVB) copolymers with DVB contents ranging from 22.0 to 98.4% were prepared using various amounts of toluene as the diluent, and, on the basis of the heterogeneity of the copolymers structure, we studied the swelling features, the pore structure variation induced by solvent treatment, and the relationship between swelling in ethanol and pore structure variation of these copolymers.

*Project supported by the Science Fund of the Chinese Academy of Sciences.

EXPERIMENTAL

Synthesis of Copolymers

The technical DVB was purified according to the method of Popov and Schwachula,⁷ and the GC analysis of the purified DVB gave the following results: 48.2% *p*-DVB, 50.2% *m*-DVB, 1.2% *p*-EVB, and 0.4% *m*-EVB. Ethylvinylbenzene (EVB) containing a little DVB was obtained by fractionating the residue of technical DVB in which the DVB has been separated. The purified DVB was mixed with EVB to give the various batches of monomer mixtures (22.0–98.4 wt % of DVB), and in each batch the ratio of DVB isomers (*m*:*p*) was close to 1:1. Reagent-grade toluene was used as the diluent.

The EVB–DVB copolymers were prepared by the general suspension polymerization method with the volume fraction F_m of the monomers in the organic phase (monomers + diluent) ranging from 0.11 to 1.0. Dibenzoyl peroxide was used as the initiator (1 wt % of the monomers), and the suspension was stabilized by using 0.2% aqueous hydroxyethyl cellulose. The polymerization was allowed to proceed at 80 and 88°C for 14 and 4–10 h, respectively. The copolymer beads obtained were washed with hot water, extracted with methanol, and then dried *in vacuo* at 40°C. The beads of 24–60 mesh were taken for the pretreatment before measurement.

Pretreatment of Copolymers

The copolymer beads were swollen to equilibrium in toluene at 60°C, part of the swollen beads was directly dried from toluene (*t*) *in vacuo* at 40°C, and the other part was washed thoroughly with acetone and water in turn, then dried from water (*w*) under the condition mentioned above.

Measurements of Copolymers

The apparent density d_a of the copolymers was determined by the improved mercury pycnometric method. The true densities d_p were assumed to be 1.034, 1.043, 1.051, 1.076, and 1.109 g/mL for the homogeneous EVB–DVB copolymers prepared beforehand from monomers containing 22.0, 43.3, 63.9, 81.1, and 98.4 wt % of DVB, respectively. The pore volume v was calculated using the equation

$$v = 1/d_a - 1/d_p \text{ (mL/g)} \quad (1)$$

and the porosity $p\%$ was calculated as

$$p\% = (1 - d_a/d_p) \times 100\% \quad (2)$$

The specific surface areas s was obtained from nitrogen adsorption measurements following the BET method and the pore average diameter size \bar{D} was

calculated according to the equation

$$\bar{D} = \frac{4 \times v}{s} \times 10^4 \text{ (\AA)} \quad (3)$$

The solvent regain v_s (mL solvent/g dry copolymer) was determined by centrifugation.⁸ The volume swelling ratio B_1 in pure solvents was calculated using the equation⁹

$$B_1 = d_a \cdot \bar{V} \quad (4)$$

where \bar{V} is the total volume of 1 g of dry copolymer after swelling, i.e., $\bar{V} = v_s + 1/d_p$. The volume swelling ratio B_2 in ethanol-water-mixed solvents was calculated using the equation

$$B_2 = \frac{d_{\text{grad}}^*}{d_{\text{grad}}} \quad (5)$$

where d_{grad} and d_{grad}^* are the graduated density measured in calibrated tubes for dry and swelled copolymers, respectively. The samples used for measurements of v_s , B_1 , and B_2 are all copolymers dried from toluene.

RESULTS AND DISCUSSION

Swelling Features

Porous DVB copolymers with other vinyl compounds prepared under certain conditions can swell both in solvating solvents and nonsolvents.^{10,11} We investigated in a broad range of degree of crosslinking the swelling features of toluene modified EVB-DVB copolymers in toluene (a solvating solvent) and, mainly, in ethanol (a nonsolvent).

Figure 1 shows the dependence of the toluene or ethanol regains and the pore volume of the copolymers prepared at a fixed volume fraction of monomers, $F_m = 0.33$, on the DVB content. As seen from this figure, the

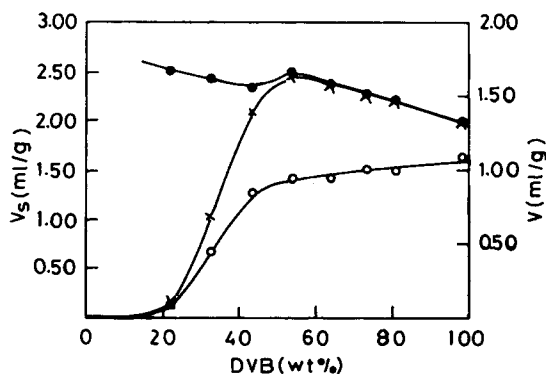


Fig. 1. Dependence of the toluene regain v_s (●), ethanol regain v (×), and pore volume v (○) of the copolymers on the DVB content; $F_m = 0.33$.

ethanol regain of the copolymers prepared from 22.0% DVB is much less than its toluene regain, but they approach each other with the increase of DVB content. The ethanol regains increase rapidly with the increase of DVB content, reaching a maximum value at about 50% DVB, and then become nearly equal to the toluene regains at higher DVB content. By comparing the ethanol regains with the pore volumes for the copolymers in Figure 1, we can see that the volume of the ethanol sorbed per g of dry copolymer is much larger than its pore volume, showing that the ethanol sorbed not only fills in the pores of the porous copolymers, but also causes the skeleton of these copolymers to swell. Obviously, it is impossible to explain such a capacity of the copolymers to swell in ethanol, a nonsolvent for polystyrene, on the basis of the classical concepts of network structure and behavior. But, if we compare further the ethanol regains with the pore volumes presented in Figure 1, we can find that the curve shapes, namely, the relationships between both of them and the DVB contents, are very similar at least up to 50% DVB. Since the formation of pore structure is closely related to the phase separation during copolymerization, which is characterized by the drastic increase of pore volume (or drastic decrease of apparent density), both of these drastic increases in the same region of DVB contents illustrate that the swelling of the copolymers in ethanol is also related to phase separation, and the increase of the ethanol regains indicates the increase of the extent of phase separation and, consequently, the heterogeneity of the copolymers.

In order to understand further the swelling feature of highly crosslinked EVB-DVB copolymers in nonsolvents, we prepared a set of mixed solvents of ethanol-water with the ethanol percentage ranging between 10 and 100 vol %, and the swelling behaviors of the copolymers in these mixed solvents were investigated. The solubility parameters δ_{sm} of mixed solvents were estimated using the equation

$$\delta_{sm} = \delta_1\phi_1 + \delta_2\phi_2 \quad (\text{cal/cm}^3)^{0.5} \quad (6)$$

where δ_1 and δ_2 are the solubility parameters of ethanol and water, and ϕ_1 and ϕ_2 are the volume fractions of ethanol and water in the mixed solvent, respectively.

In Figure 2, the volume swelling ratios B_2 for copolymers ($F_m = 0.25$) with different DVB contents are plotted against the δ_{sm} parameters of mixed solvents. It may be seen that in the wide region up to $\delta_{sm} = 19.1$ (40% of ethanol) the swelling ratios B_2 for copolymer with DVB content of 98.4% remains practically unchanged at a medium value, even at $\delta_{sm} = 22.3$ (10% of ethanol). However, with the decrease of DVB content, there is an increasing tendency for the B_2 values to drop starting from rather high values, with the increase of δ_{sm} parameters, and the swelling ratios are very low at $\delta_{sm} = 22.3$.

Denoting the highest and lowest values of B_2 in Figure 2 for each curve by B_{2h} and B_{2l} , respectively, then $(B_{2h} - B_{2l})/2$ is equal to the one half of the drop of the B_2 value for each copolymer, and we can find that the δ_{sm}^* parameters corresponding to $(B_{2h} - B_{2l})/2$ for the above-mentioned copolymers with DVB content of 98.4, 81.1, and 63.9% are 21.4, 20.4, and 18.7, respectively. If we plot $\delta_{sm}^* - \delta_m$, in which δ_m is the solubility parameter of

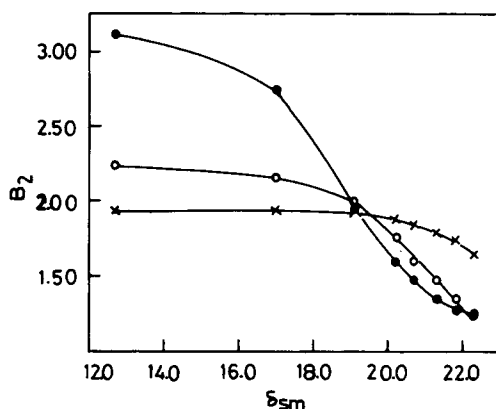


Fig. 2. Dependence of volume swelling ratio B_2 on the solubility parameter δ_{sm} of mixed solvents for copolymers ($F_m = 0.25$) with DVB contents of 98.4% (×), 81.1% (○), and 63.9% (●).

the copolymer and is assumed to be 9.1 for polystyrene, as a function of DVB contents, the curve B in Figure 3 may be obtained. In the same way, curve A in Figure 3 is obtained for copolymers prepared at $F_m = 0.33$, and both curves show clearly that, with increase of DVB content, the copolymers can keep swelling in a solvent with lower solvating power.

In Figure 4, the swelling ratios B_2 for copolymers (DVB = 98.4%) prepared at different F_m are plotted against the δ_{sm} parameters of mixed solvents. It is plain here that, with the decrease of volume fraction F_m , the drop in the values of B_2 also increases with increase of the δ_{sm} parameters. Using the method mentioned above, the δ_{sm}^* parameters corresponding to $(B_{2h} - B_{2l})/2$ for copolymers with $F_m = 0.25$, 0.14, and 0.11 are obtained, being 21.4, 21.1, and 20.1, respectively.

It is known that, at a fixed DVB content, the crosslinking density of the copolymer is very much dependent on the amount of solvating diluent, and with an increase of the amount of the diluent the crosslinking density decreases due to the enhanced intramolecular reactions and the same is true the other way round.¹² Thus, increase of both the volume fraction F_m in

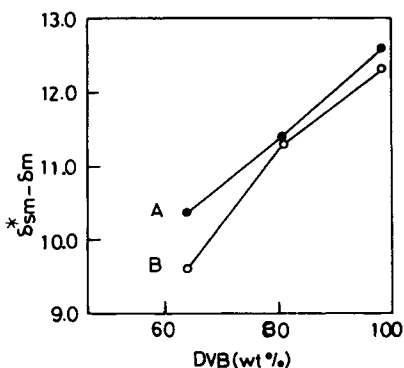


Fig. 3. Relationship between $\delta_{sm}^* - \delta_m$ and DVB content for copolymers prepared at $F_m = 0.25$ (○) and 0.33 (●).

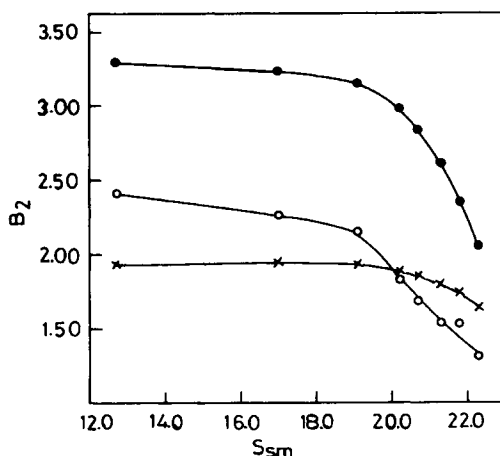


Fig. 4. Dependence of volume swelling ratio B_2 on the solubility parameter δ_{sm} of mixed solvents for copolymers (DVB = 98.4%) prepared at $F_m = 0.25$ (\times), 0.14 (\circ), and 0.11 (\bullet).

Figure 4 and DVB content in Figure 2 show the same result, namely, an enhanced capacity of the copolymers to keep swelling in a less solvating solvent from an increase in crosslinking density. It is a rather puzzling phenomenon. To explain such swelling behavior of the highly crosslinked copolymers, we shall return to the heterogeneity in the crosslinking structure of the copolymers.

As mentioned in the Introduction, the skeleton of porous copolymers consists of highly crosslinked microgel particles linked by loosely crosslinked network. In general, the highly crosslinked and entangled network of microgel particles has entirely or partially finished the course of deswelling under the strong elastic retraction during the copolymerization. Therefore, these particles rarely swell even in solvating solvents. On the contrary, the network between the microgel particles is quite loose, capable of swelling in solvents and shrinking on removal of the solvents, the volume variation of the swelling copolymer can be considered as resulting mainly from the expansion of the loose network. Then, since the elastic free energy resulting from the loose network is weak, only small free energy of mixing for polymer-solvent is needed to cause the copolymers to swell.

But, since an increase of the crosslinker content or volume fraction F_m results in not lower, but higher, crosslinking density of the loose network between microgel particles, the above description seems fail to explain the results presented in Figures 2, 3, and 4. The most likely explanation of these observed behaviors is thus the existence of strain in the loosely crosslinked network between the microgel particles. The strain that has been used to explain the unusual structure and properties of macronet isoporous styrene copolymers¹³ can be supposed to appear and grow in the course of removal of solvents as a result of the retraction and deformation of the loose network. The higher the crosslinking density, the more rigid the loose network, thus resulting in a greater strain in the deswelled copolymers. Because the swelling of the copolymers is accompanied by an increase of their volume, which is favorable to the release of strain, the existence of strain in turn means that

only a weak polymer-solvent interaction is needed to cause the copolymers to swell. Greater strain facilitates the copolymers to swell in a solvent with lower solvating power. Consequently, both the increase of DVB content and volume fraction F_m enhance the capacity of the copolymers to keep swelling in solvents having extremely small affinity for this copolymer.

Pore Structure Variation and Swelling

Many articles have reported that the pore structure of porous copolymers is not fixed; it varies with the type of solvents used to treat the copolymers.^{5,14-21} But in these studies copolymers with only up to 60% DVB were dealt with. Our works deal with porous EVB-DVB copolymers with higher DVB contents prepared with toluene as the inert diluent. It was found that even at such a high DVB content as 98.4% the pore structure variation for copolymers pretreated with different solvents could still be observed over quite a broad range. The experimental results for copolymers (98.4% DVB) prepared at various volume fractions F_m are shown in Table I.

As is seen in Table I, the differences in the pore volume and surface areas measured for the same sample dried from toluene and from water are both related to F_m , i.e., the amount of diluent used in polymerization. They are considerable at $F_m = 0.20$ or 0.14 . Thus it is clear that, though the pore structure of highly crosslinked copolymers have higher stability in comparison with those low crosslinked, the stability is relative and can still vary with change in conditions for their preparation.

It is plain that such a structural feature of porous copolymers is also related to the heterogeneity in crosslinking structure of the copolymers, and it has been well discussed in literature.^{2,5} But Figure 5 shows the relationship more clearly. The pore volume v_t for copolymers dried from toluene, which is considered as resulting from stable pores, is found to be linearly dependent on

TABLE I
The Pore Structure of Highly Crosslinked EVB-DVB Copolymers (DVB = 98.4%)
Dried from Toluene (T) and from Water (W)^a

F_m		d_a (g/mL)	v (mL/g)	p (%)	s (m ² /g)	\bar{D} (Å)
0.50	T	0.726	0.476	0.345	677	28.1
	W	0.689	0.550	0.379	755	29.1
0.33	T	0.547	0.926	0.507	758	48.9
	W	0.501	1.095	0.549	819	53.5
0.25	T	0.511	1.057	0.540	844	50.1
	W	0.424	1.459	0.618	986	59.2
0.20	T	0.525	1.004	0.527	949	42.3
	W	0.412	1.526	0.629	1101	55.5
0.14	T	0.560	0.885	0.496	924	38.3
	W	0.424	1.455	0.617	1012	57.5
0.11	T	0.638	0.665	0.425	903	29.5
	W	0.487	1.154	0.561	942	49.0

^a F_m = volume fraction of monomers in the organic phase, d_a = apparent density, v = pore volume, $p\%$ = porosity, s = specific surface area, and \bar{D} = pore average diameter size.

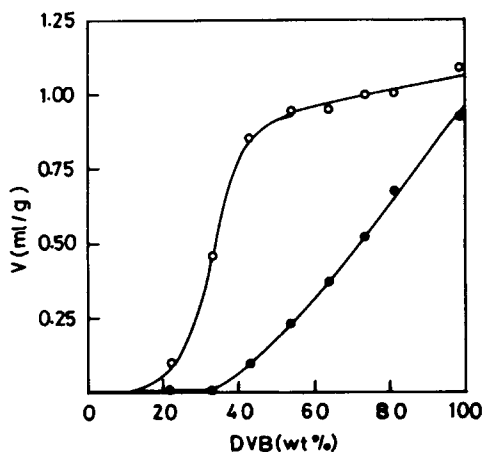


Fig. 5. Dependence of the pore volume v on DVB content for copolymers ($F_m = 0.33$) dried from toluene (●) and from water (○).

the DVB contents above 40%. In contrast to this, the pore volume v_w for copolymers dried from water appears abruptly at DVB content between 20 and 30%, and increases rapidly with the increase of the extent of the phase separation as mentioned above. By comparing the pore volumes v_t and v_w measured for the same sample from Figure 5, we can see that the pore volume v_w consists mainly of unstable pores up to about 50% DVB. This shows that the unstable pores, or the pore volume variations for copolymers dried from toluene and water, are also related to the course of phase separation, or heterogeneity in the crosslinking structure of the copolymers.

It seems of interest to correlate the pore volume variation in Figure 5 with the ethanol regain in Figure 1, for both of them are closely related to the heterogeneity in crosslinking structure of the copolymers, and further study on the relationship between pore volume variation and swelling capacity in ethanol has been done. Figure 6 shows the dependences of pore volume

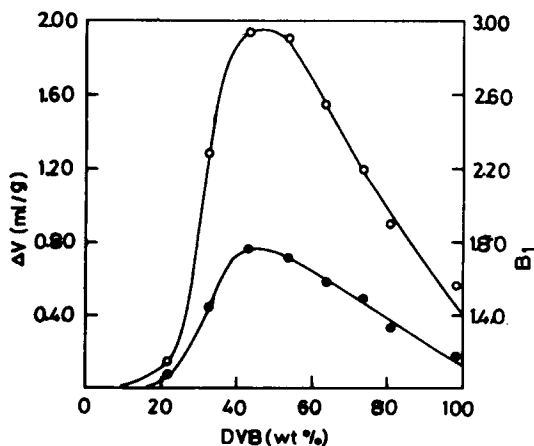


Fig. 6. Dependence of pore volume variation Δv (●) or volume swelling ratio B_1 in ethanol (○) on DVB content for copolymers prepared at $F_m = 0.33$.

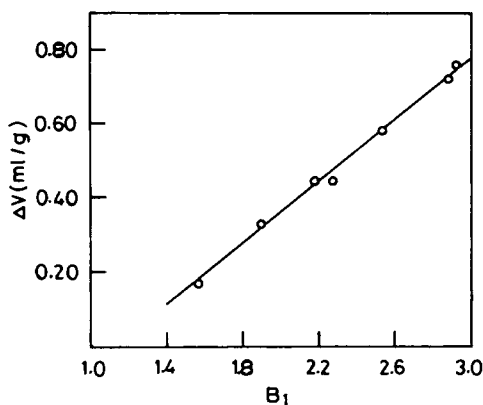


Fig. 7. Relationship between the pore volume variation Δv and the volume swelling ratio B_1 in ethanol for copolymers prepared at $F_m = 0.33$.

variation Δv or volume swelling ratio B_1 in ethanol on DVB content for copolymers prepared at $F_m = 0.33$. The pore volume variation Δv is calculated as $\Delta v = v_w - v_t$. From Figure 6 it can be found that both the pore volume variation Δv and the volume swelling ratio B_1 show the same trends of change with increase in DVB contents. If the pore volume variation Δv is plotted against the swelling ratio B_1 , Figure 7 is obtained, and shows that the pore volume variation seems to increase according to a straight line with the increase of swelling ratio for copolymers prepared at $F_m = 0.33$.

The relationship between the pore volume variation Δv and swelling ratio B_1 for copolymers with the same DVB content prepared in the presence of various amount of toluene is shown in Table II, the similar trend is observed for the variation of Δv and B_1 with volume fraction F_m , and both Δv and B_1 have maximum value at $F_m = 0.14$.

From the results above it can be seen that, regardless of DVB content of monomers and the amount of diluent used in copolymerization, certain consistent relationships should always exist between the solvent induced variation in pore structure and swelling capacity in nonsolvents. Though much remains to be understood in this respect, we can conclude for the time being that the stronger the swelling capacity in ethanol, the more evident the variation in pore volume is, and the volume swelling ratio in ethanol can be regarded as an indication of the extent to which the pore volume changes upon solvent treatment for the toluene modified copolymers.

TABLE II
Pore Volume Variation Δv and Volume Swelling Ratio B_1 in Ethanol
for Copolymers (DVB = 98.4%) Prepared at Various Volume Fraction
 F_m of Monomers in Organic Phase

F_m	0.50	0.33	0.25	0.20	0.14	0.11
Δv (mL/g)	0.074	0.166	0.402	0.523	0.569	0.488
B_1	1.33	1.57	1.84	2.39	2.82	2.39

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Received September 10, 1987

Accepted July 13, 1988