

Styrene-Divinylbenzene Copolymers, V*

Inhomogeneity in the Structure and the Average Degree of Swelling

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SUMMARY:

The compositional inhomogeneity and the average degree of swelling of heterogeneous styrene-divinylbenzene (S-DVB) copolymers were investigated using two morphological features of porous copolymers. At a fixed volume fraction of a non-solvating diluent, the extent of inhomogeneous crosslinking increases with increasing DVB concentration. In addition, the crosslinking density of less crosslinked regions of the network decreases as the DVB concentration increases. The experimental results can be explained by the microgel-model of the network formation. The average degree of volume swelling can be predicted from the composition of the starting monomer mixture and from the porosity of the final copolymer dried from water. Depending on these parameters, the changes in the value of v_2 , the volume fraction of copolymer in the swollen gel, and the conditions for the pore stability are discussed.

ZUSAMMENFASSUNG:

Die Inhomogenität in der Zusammensetzung und der mittlere Quellungsgrad von heterogenen Styrol-Divinylbenzol-Copolymeren (S-DVB) wurden mit Hilfe von zwei morphologischen Eigenschaften der porösen Copolymeren untersucht. Für einen bestimmten Volumenbruch eines nicht-solvatisierenden Verdünnungsmittels steigt die Inhomogenität mit zunehmender DVB-Konzentration an. Außerdem nimmt die Vernetzungsdichte der schwach vernetzten Bereiche des Netzwerkes mit zunehmender DVB-Konzentration ab. Die experimentellen Ergebnisse werden durch das Mikrogel-Modell für die Netzwerk-Bildung erklärt. Der mittlere Volumenquellungsgrad kann aus der Zusammensetzung des anfänglichen Monomergemisches und aus der Porosität des getrockneten Copolymeren vorhergesagt werden. Die Änderungen in v_2 , dem Volumenbruch des Polymeren im gequollenen Gel, und die Bedingungen für die Poren-Stabilität werden in Abhängigkeit von diesen Parametern diskutiert.

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Introduction

Heterogeneous (porous) styrene-divinylbenzene (S-DVB) copolymers are widely used as starting materials for ion exchangers and as specific sorbents, and, therefore, have been the subject of a large number of studies¹. Heterogeneous structures are formed as a result of phase separation during copolymerization of styrene with divinylbenzene (DVB) in the presence of inert diluents^{2,3}. The degree of phase separation is dependent on the concentration of the crosslinking agent, concentration and type of the diluent, and the reaction temperature. Relationships between the synthesis conditions and the structure of S-DVB copolymers have been studied for many years^{1,4-7}.

Moreover, due to the flexibility of the network chains, the porous structure of S-DVB copolymers varies with the type of solvent in which the copolymer is swollen before drying⁸⁻¹³. For instance, the copolymers dried from bad solvents show a maximum porosity⁹, which is close to the porosity in the swollen state¹¹. The drying process of the copolymers swollen in good solvents may lead to a partial or total collapse of the pores. Recently, we have shown that during the drying process the pores collapse in the rubbery rather than in the glassy state^{14,15}. Thus, the stability of the porous structures is determined primarily by the volume fraction of copolymer in the swollen gel (v_2). An increase in v_2 results in an increase in the glass transition temperature of the polymer-solvent system, so that the system may remain in the glassy state during the swelling, thus resulting in an increase in the stability of the pores.

Conversely, the stability of the porous structures decreases with a decrease in v_2 . The inhomogeneity in crosslink distribution also plays an important role in the pore stability¹⁵. In S-DVB copolymers there are regions that swell either less or more than the average degree of swelling due to the preferential reaction between the DVB monomers and the mechanism of network formation. Thus, the pores in network portions in the rubbery state can collapse, whereas those in the glassy state do not collapse on drying.

The present article deals with the investigation of the compositional inhomogeneity and the average degree of swelling of heterogeneous S-DVB copolymers. This is done, by using the two following important features observed in porous S-DVB copolymers:

- (1) The extent of change in the porosity during the treatment of swollen copolymers with solvents with decreasing solvating power is an indication of the inhomogeneity in the structure¹³.

(2) The porosity of the copolymers dried from bad solvents such as water can be regarded as the swollen state porosity¹¹.

Experiments are presented that indicate the extent of inhomogeneous crosslinking as a function of the DVB concentration. For this purpose, a number of S-DVB copolymers with various DVB concentrations was prepared. Cyclohexanol was used as a nonsolvating diluent at a fixed volume fraction of the organic phase (0.50).

The changes in the porosity were observed using apparent densities of samples dried from various solvents. The swelling properties of heterogeneous S-DVB copolymers were also studied, and an equation was derived that predicts the value v_2 from the composition of the starting monomer mixture and from the apparent density of the final network dried from water.

Experimental

All monomers and reagents were purified and distilled prior to use. The S-DVB copolymer beads were obtained by the suspension polymerization method as described previously⁷. Cyclohexanol was used as diluent at a fixed volume fraction of the organic phase (0.50). After polymerization, the copolymer beads of 0.35 to 1.00 mm in diameter were extracted with acetone for 16 h and then they were swollen to equilibrium in toluene at room temperature. The swollen copolymers were then successively washed with a series of solvents of increasing polarity, namely toluene, methyl ethylketone, acetone, isobutyl alcohol, isopropyl alcohol, methanol, and water. After treatment with each solvent, a part of the copolymers was dried in vacuo at room temperature.

The apparent density of the copolymers (d_0) was determined by the mercury pycnometric method¹⁶. Porosity ($P\%$) was calculated from d_0 as follows:

$$P\% = (1 - d_0/d_2) \cdot 100\% \quad (1)$$

where d_2 is the density of homogeneous S-DVB copolymers taken as 1.08 g/cm³.

Results and Discussion

Inhomogeneity in the Structure

The composition of the copolymers and their apparent densities for various solvents are given in Tab. 1. As expected, the apparent density of the networks decreases, i. e., the porosity increases with increasing polarity of

Tab. 1. Composition and apparent densities of copolymers.

Sample DVB number (wt.-%)		Apparent density (g/cm ³)						
		Toluene	Methyl ethyl- ketone	Acetone	i-Buta- nol	i-Pro- panol	Metha- nol	Water
1	5	1.03	0.99	0.93	0.93	0.94	0.93	0.93
2	10	1.03	0.955	0.77	0.59	0.59	0.60	—
3	15	0.91	0.70	0.65	0.565	0.55	0.55	0.55
4	20	0.66	0.65	0.63	0.60	0.58	—	0.57
5	25	0.57	0.565	0.555	0.545	0.555	0.53	0.54

the solvents. At a critical value of the polarity, the apparent density reaches to its minimum value and then remains constant. This critical value corresponds to the transition of the whole network regions from the rubbery to the glassy state.

In Fig. 1 the change in the apparent density is plotted against the solubility parameter of the solvents used in the network treatment. With increasing concentration of DVB, the porosity changes occur in a wide range of the solubility parameter values. This indicates that the inhomogeneity in porous S-DVB copolymers increases with increasing DVB concentration. The fraction of the stable porosity is given in Fig. 2 as a function of the solubility parameter of the solvents. It is interesting to note that the networks with lower DVB concentration pass into the glassy state earlier, i. e., in less polar solvents, than those with higher DVB concentration. For instance, sample 1 with 5% DVB passes into the glassy state at $\delta = 9.9$ (cal/cm³)^{0.5}, whereas sample 2 with 10% DVB at $\delta = 10.5$ (cal/cm³)^{0.5}, and sample 3 with 15% DVB at $\delta = 11.5$ (cal/cm³)^{0.5}. It seems that the crosslinking density of the less crosslinked regions of the network decreases with increasing DVB concentration.

The experimental data can be explained with the mechanism of the network formation corresponding to the microgel-model¹⁷. Experimental results in recent years show the existence of microgel particles in the pregel stage of the chain crosslinking polymerization. In S-DVB copolymerization, the growing chains formed in the pregel stage are rich in DVB units due to the higher reactivity of the DVB monomer. At the beginning of the polymerization, most of these units are double reacted due to the high ratio of

Styrene-Divinylbenzene Copolymers, V

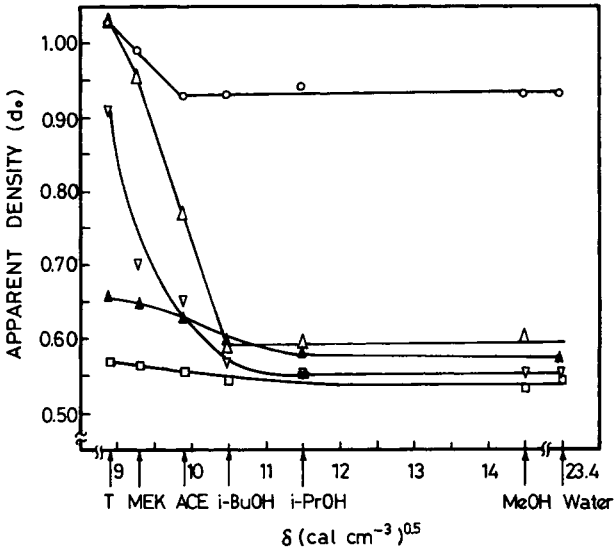


Fig. 1. Dependence of the apparent density, d_0 , on the solubility parameter of the solvents used in the network treatment; DVB: 5 wt.-% (\circ), 10 wt.-% (Δ), 15 wt.-% (∇), 20 wt.-% (\blacktriangle), and 25 wt.-% (\square). Volume fraction of cyclohexanol in the monomer mixture: 0.50.

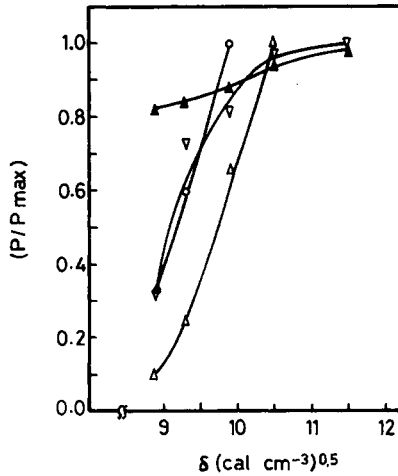


Fig. 2. Dependence of the fraction of the stable porosity, P/P_{max} , on the solubility parameter of the solvents used in the network treatment; DVB: 5 wt.-% (\circ), 10 wt.-% (Δ), 15 wt.-% (∇), 20 wt.-% (\blacktriangle), and 25 wt.-% (\blacksquare).

cyclization. As a consequence, the growing chain becomes internally cross-linked and its structure resembles to a microgel particle¹⁸.

It is expected that in the presence of a poor solvent as the diluent and at a higher content of the DVB, compact microgel particles are formed. In such systems, the pendant double bonds in the particles are sterically prevented from reaction with further monomer molecules and vitrification inside microgels can occur before overall vitrification. This results in the less reactivity of the pendant vinyls inside microgel particles. Thus, the microgel particles are linked together through their peripheric double bonds to yield a gel. With increasing DVB concentration, the microgel particles will be more compact and the linkage of these particles will be weaker, i.e., the crosslink density of the later formed portions of the network will be lower, as found experimentally with the apparent density measurements.

Swelling

The swelling agent regain of heterogeneous S-DVB copolymers increases linearly with increasing dilution of the monomers in the polymerization system. The relationship between the swelling agent regain and the dilution is given by¹⁹

$$U = U_0 + D \quad (2)$$

where U is the equilibrium volume of the swelling agent per unit mass of dry heterogeneous copolymer, U_0 is the corresponding value for a copolymer prepared without diluent, i.e., for a homogeneous (standard) copolymer, and D is the volume of the diluent per unit mass of monomers.

Previous studies show that this equation holds at least up to a dilution $D = 3$ for solvating diluents, and $D = 1$ for nonsolvating diluents^{1,6,19}. Eq. (2) was also confirmed by us using 16 copolymer samples prepared in an earlier study at $D = 1.10$ and in the presence of toluene and cyclohexanol as the diluents¹⁵. Eq. (2) can also be given in terms of the weight swelling ratio as,

$$\frac{(q_w - 1)}{d_1} = \frac{(q_{w,st} - 1)}{d_1} + \frac{r}{d_M} \quad (2')$$

where q_w and $q_{w,st}$ are the weight swelling ratio of heterogeneous and homogeneous (standard) copolymers, respectively, r is the volume ratio of diluent/monomers in the starting monomer mixture, d_1 and d_M are the

densities of the swelling agent and the monomers, respectively. The volume swelling ratio, q_v , can be calculated from q_w using the equation²⁰

$$q_v = \frac{d_0}{d_{2,r}} + \frac{(q_w - 1)d_0}{d_1} \quad (3)$$

where $d_{2,r}$ is the density of the copolymer in the rubbery state. Assuming isotropic swelling, the volume fraction of copolymer in the swollen gel, v_2 , is given by²⁰

$$v_2 = \frac{d_2}{d_{2,r} q_v} \quad (4)$$

$$= \frac{d_2/d_0}{1 + d_{2,r}(q_w - 1)/d_1} \quad (5)$$

From Eq. (2) – (5), we have

$$v_2 = \frac{d_2/d_0}{1/v_{2,st} + r d_{2,r}/d_M} \quad (6)$$

where $v_{2,st}$ is the value of v_2 for the corresponding standard copolymers. Eq. (6) indicates that v_2 of heterogeneous copolymers depends on three parameters, namely,

- (1) the standard value of v_2 which is determined by the DVB concentration,
- (2) the volume ratio diluent/monomers in the starting monomer mixture,
- (3) the apparent density of the final copolymer dried from bad solvents.

The parameters (1) and (2), i.e., the composition of the starting monomer mixture, determine the weight swelling ratio of the copolymers, according to Eq. (2). The third parameter determines the distribution of the swelling agent between gel and pore portions of the network. Fig. 3 shows how the value v_2 varies according to these parameters. During the calculations, the used values were $d_2 = 1.08 \text{ g/cm}^3$, $d_{2,r} = 1.09 \text{ g/cm}^3$ and $d_M = 0.91 \text{ g/cm}^3$.

It seems that for a given composition of the starting monomer mixture ($v_{2,st}$ and r are taken to be constant) v_2 varies between two limiting values depending on the apparent density of the copolymers, i.e., between A and A' or B and B' (Fig. 3). At point A or B, all the diluent present during the network formation separates out of the network phase, and acts only as a pore-forming agent. Thus, the v_2 value of heterogeneous copolymers corresponds to that of homogeneous copolymers prepared at the same DVB concentration. On the other hand, minimum value for v_2 can be achieved if $d_0 = d_2$, i.e., if the copolymer is nonporous (at point A' or B'). In this case, all the

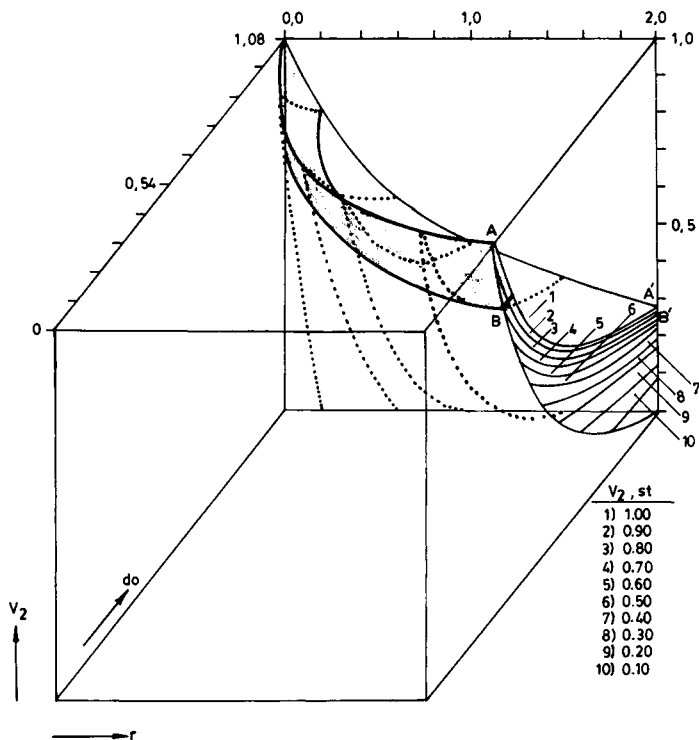


Fig. 3. Dependence of v_2 on $v_{2, st}$, d_0 , and r according to Eq. (6). The heavy line represents the critical v_2 values for glassy transition of copolymers swollen in toluene at room temperature. The copolymer gels in toluene are in the glassy state above this line in darker regions.

diluent remains in the network phase and the final networks are obtained in an expanded state.

The location of v_2 between these two limiting values is dependent on the quality of the diluent present during the network formation. As seen from Fig. 3, v_2 varies in a much broader range as the dilution increases. Fig. 4 shows the volume fraction of the diluent separated out of the network phase, v_D , as a function of the DVB concentration for two different diluents, namely for toluene and cyclohexanol. v_D was calculated as

$$v_D = \frac{v_2 - v_{2, \min}}{v_{2, st} - v_{2, \min}} \quad (7)$$

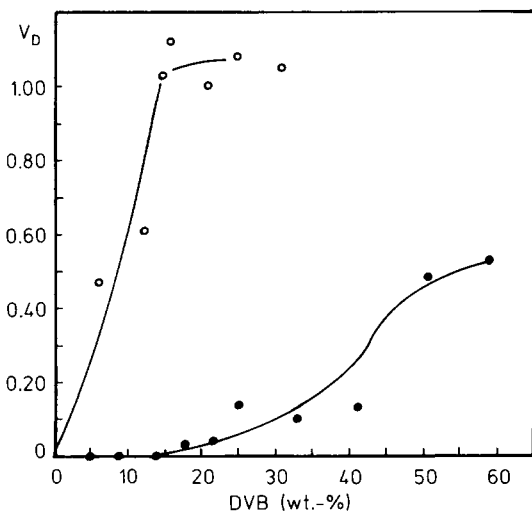


Fig. 4. Dependence of the volume fraction of the diluent separated out of the network phase, v_D , on the DVB concentration; Diluent: toluene (●), cyclohexanol (○); $r = 1.00$.

where $v_{2, st}$ and $v_{2, min}$ are the calculated maximum (standard) and minimum values of v_2 , and v_2 is the experimentally determined value given in¹⁵.

During the copolymerization, toluene remains as a solvating diluent in the network phase up to 15% DVB. With a further increase in the DVB concentration, the network phase deswells slightly and, at 50–60% DVB, v_D reaches to 0.50. In contrast to toluene, cyclohexanol as a nonsolvating diluent separates out totally of the network phase at 15% DVB ($v_2 = v_{2, st}$). At higher DVB concentrations, v_2 is higher than $v_{2, st}$ (or $v_D > 1$) due to the inverse synerese^{1,2} in the polymerization system.

The heavy line in Fig. 3 represents the critical v_2 values for glassy transition of copolymers swollen in toluene at room temperature calculated as in¹⁴. Assuming a homogeneous distribution of crosslinks, the copolymer gels in toluene are in the glassy state above this line (in darker regions), i. e., the porous structures are stable. It seems that the area for obtaining copolymers with stable porous structures becomes smaller as the dilution increases. For instance, a minimum of 29% of the diluent must separate out of the network phase at $r = 0.33$ to obtain a stable structure, whereas this value increases to 63% at $r = 1.00$, and to 74% at $r = 3.00$. The results show that at a higher dilution only nonsolvating diluents may induce stable porous structures.

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