# Heterogeneous Styrene–Divinylbenzene Copolymers in Collapsed and Reexpanded States

O. OKAY and T. I. BALKAŞ, *Tubitak, Marmara Scientific and Industrial Research Institute, Department of Chemical Engineering, P. O. Box 21, Gebze, Kocaeli, Turkey*

## Synopsis

The pore structure of styrene–divinylbenzene (DVB) copolymers formed by phase separation before or after gelation was compared using apparent densities and mercury porosimetry. The copolymers were prepared with di-2-ethylhexyl phthalate (DOP) as diluent. The pore structure of copolymers formed in homogeneous gelation can collapse upon drying in the rubbery state. The collapsed pores have a mean diameter of about 100–200 Å corresponding to the interstices between the microspheres. The collapsed microspheres reexpand again during the sulfonation or chloromethylation reactions, or during the solvent exchange. The pore structure of styrene–DVB networks formed in heterogeneous gelation do not collapse on drying in the swollen state, this being a stable and permanent porosity. The critical crosslink density for transition from homogeneous to the heterogeneous gelation represents a borderline between stable and unstable porosity. The drastical change of swelling and porosity values at the critical crosslink density is due to the collapse of unstable pores.

## INTRODUCTION

Phase separation during the styrene–divinylbenzene (DVB) copolymerization can result in the formation of heterogeneous (porous) networks.[1] Incipient phase separation during the polymerization can occur above or below the gel point, depending on the degree of crosslinking and the polymer–solvent interaction parameter $\chi$.[1-3] Due to the continuous change of the concentration of the polymer and the diluent, and change in the crosslinking degree as a function of conversion, the separation of a pure solvent phase outside the gel phase takes place gradually. The study of the pore structure of styrene–DVB copolymers has been reported in many papers.[4-9]

It is also well known fact that the pores in these networks can collapse during the synthesis, particularly during the removal of the diluent or during drying.[4,10,11] The collapsed network can reexpand again if, before drying, the interactions between polymer chains and the solvent is decreased.[11] This can be attained by removal of the diluent (or solvent) with another nonsolvating one (solvent exchange method). The introduction of functional groups like —$SO_3H$, —$CH_2Cl$, etc. into the styrene–DVB matrices also changes the morphology of the network.[12,13]

In our previous work,[9] the formation of porous styrene–DVB copolymers with di-2-ethylhexyl phthalate (DOP) as diluent was studied. It was found that the transition from homogeneous to the heterogeneous gelation occurs at $\nu_2^\infty = 0.52$ between 18 and 22% DVB. ($\nu_2^\infty$ is the initial volume fraction

Journal of Applied Polymer Science, Vol. 31, 1785–1795 (1986)
CCC 0021-8995/86/061785-11$04.00

of the monomers in the organic phase.) Moreover, the phase separation after gelation was also the cause of formation of a porous structure, even in the absence of the diluent.

In this study, a comparison of the pores in styrene–DVB networks formed in homogeneous and heterogeneous gelation is presented. For this purpose, the sulfonation and chloromethylation reactions, and a slow solvent exchange method, induced by decreasing the solvent power of the swelling agent, were used. The morphological changes during these reactions were observed using mercury porosimetry and apparent densities of samples in the dried state.

## EXPERIMENTAL

### Materials

All monomers and reagents were purified and distilled prior to use. The styrene–DVB copolymer matrices were obtained by the suspension polymerization method. DOP was used as the diluent. The experimental conditions used for the copolymerization are given in Ref. 9.

### Sulfonation

The sulfonated products were prepared by adding concd sulfuric acid (97–98%, from MKEK, Ankara, Turkey) to copolymer matrices swollen in 1,2-dichloroethane, and heating it in a water bath at 80°C for 4 h (copolymer: $H_2SO_4$ molar ratio 1:16). The reaction mixture was then cooled, washed with different concentrations of sulfuric acid (80, 60, 40, 20, and 10%), and finally with distilled water to remove the excess acid. The resin was then filtered and dried *in vacuo* at 60°C.

### Chloromethylation

The chloromethylated products were obtained by the reaction of the matrices with chloromethyl methyl ether (CMME) in 1,2-dichloroethane in the presence of anhydrous $AlCl_3$ (copolymer:CMME:$AlCl_3$ molar ratio 1:1.5:0.4) at 40°C for 6 h. At the end of the reaction time, the products were washed with excess water and dried *in vacuo* at 60°C.

### Solvent Exchange

The copolymer matrices were swollen to equilibrium in toluene at room temperature. The swollen copolymers were then filtered and washed thoroughly, first with acetone, then with methanol and finally with water; they were then dried *in vacuo* at 60°C. For comparison, part of the samples swollen in toluene were dried without solvent exchange.

## METHODS

The apparent density of the copolymers $d_0$ was determined by the mercury pycnometric method.[14] The graduated density $d_{grad}$ was measured in a calibrated tube. Pore size distribution of the copolymers was determined by mercury porosimetry with an Aminco Porosimeter.[9] The weight swelling ratio in toluene or in water, $q_w$, was determined by the centrifugation method.[15] The volume swelling ratio $q_v$ was calculated from $q_w$ using the equation[16]

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

where $d_1$ and $d_{2,r}$ are the densities of the solvent and the copolymer in the rubbery state, respectively ($d_{2,r} \cong 1090$ kg/m$^3$).

The volume fraction of copolymer in the swollen gel, $\nu_2$, was calculated using the equation[16]

$$\nu_2 = \frac{d_2}{d_{2,r}q_v} \tag{2}$$

where $d_2$ is the polymer density taken as 1050 kg/m$^3$.

## RESULTS AND DISCUSSION

### Homogeneous Gelation

Samples 1–4 represent the networks where phase separation after the gel point was observed.[9] Table I indicates that the porosity increases during the chemical modification of these samples, with the exception of sample 2. The strongest morphological changes were observed in samples 3 and 4. The pore size distribution of these samples before and after the sulfonation or chloromethylation reactions is given in Figures 1 and 2. During these reactions, while the amount of pores larger than 1000 Å in diameter decreases, those between 100 and 200 Å increases significantly. This causes an increase in the porosity and a decrease in the randomness of the pore size distribution. Similar results were obtained for sample 1 prepared without using DOP (Table I and Fig. 3).

The polymer chains separated after the gel point are relatively swollen and, therefore, less entangled compared to those separated prior to the gel

TABLE I
Composition and Properties of Copolymers[a]

| Sample no. | DBV (wt %) | $\nu_2^{00}$ | $d_0 \times 10^{-3}$ (kg/m$^3$) (1) | (2) | (3) | $P$ (%) (1) | (2) | (3) |
|---|---|---|---|---|---|---|---|---|
| 1 | 15 | 1.00 | 1.06 | 1.01 | — | 3.6 | 6.4 | — |
| 2 | 8 | 0.52 | 1.07 | 1.49 | — | 5.7 | 0.6 | — |
| 3 | 15 | 0.52 | 1.02 | 0.79 | 0.85 | 7.1 | 28.3 | 25.6 |
| 4 | 18 | 0.52 | 0.98 | 0.85 | 0.81 | 13.3 | 26.3 | 26.5 |
| 5 | 22 | 0.52 | 0.61 | 0.65 | 0.64 | 47.6 | 41.5 | 42.0 |
| 6 | 32 | 0.52 | 0.59 | 0.59 | — | 44.9 | 43.6 | — |

[a] $\nu_2^{00}$ = initial volume fraction of the monomers in the organic phase; $d_0$ = apparent density and $P$ % = total porosity[9] of copolymer matrices (1), their sulfonated (2) and chloromethylated derivates (3).

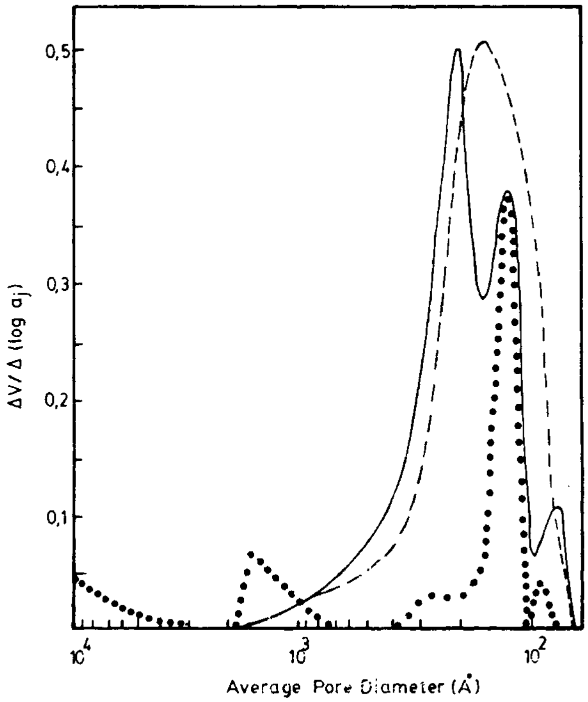

Fig. 1. Pore size distribution of sample 3 before (· · ·) and after sulfonation (- - -) or chloromethylation reactions (- - -) in differential mode.

point. The loose pore structure formed in this way can collapse on drying. From the experimental data, we conclude that the collapsed network reexpands during its chemical modification.

In all samples, the collapse or reexpansion phenomena is exhibited by the pores of about 100–200 Å in diameter. These pore radii correspond to the interstices between the microspheres.[9] The microspheres in these networks, formed in the second stage of the pore structure formation, are mostly unstable. However, a certain amount of stable microspheres exists in collapsed networks, and their amount increases with increasing amounts of DVB. The existence of stable pores in collapsed networks may be related to the inhomogeneity in crosslink distribution. During the polymerization, the more reactive monomer, DVB, is exhausted more rapidly than the less reactive monomer styrene.[17] The inhomogeneous crosslinking results in the formation of short chains in the beginning of the polymerization and long chains in the end. Thus, the earlier phase separated portions of the network, where the crosslink density is locally high, do not collapse on drying and illustrate the stable part of the porosity of samples in the dried state.

## Solvent Exchange

The graduated density of the samples dried after the solvent exchange, and after solvatation in toluene is given in Table II. As with previous results, with the exception of sample 2, the graduated density of samples decreases (i.e., the porosity increases) or does not change (in sample 6) during the

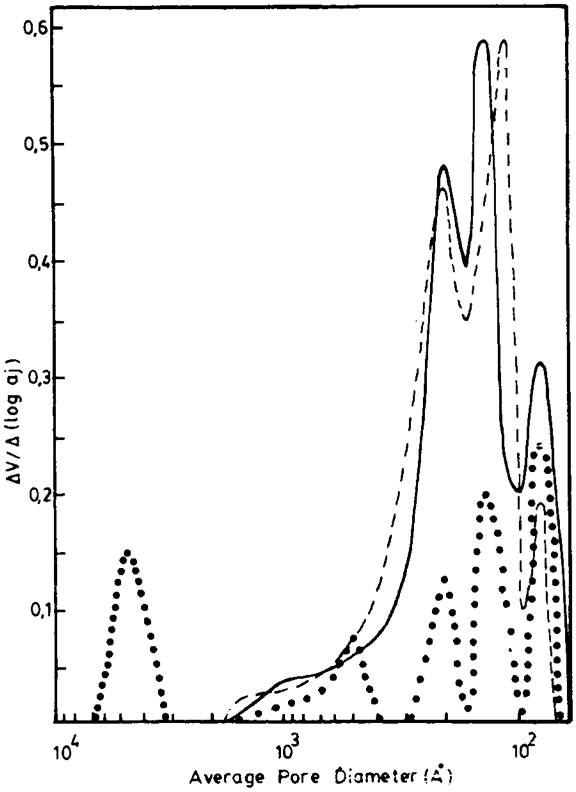

Fig. 2. Pore size distribution of sample 4 (see Fig. 1 caption)

solvent exchange. For example, samples 3 and 4 dried in the swollen state are optically clear. But, the same samples dried in the glassy state exhibited milky turbidity showing the presence of scattering centers due to reexpanded pores.

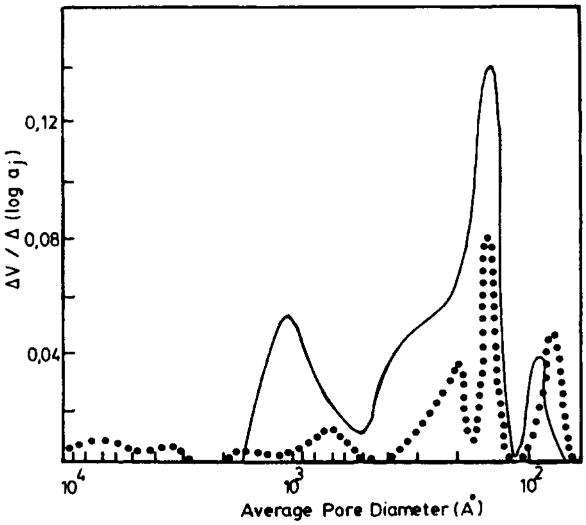

Fig. 3. Pore size distribution of sample 1 (see Fig. 1 caption)

To calculate the glass transition temperature of samples swollen in toluene, $T_{g12}$, the modified Couchman–Karasz equation was used[18]:

$$T_{g12} = \frac{x_1 \Delta C_{p1}^{\mathrm{act}}(X)\, T_{g1}(X) + x_2 \Delta C_{p2} T_{g2}}{x_1 \Delta C_{p1}^{\mathrm{act}}(X) + x_2 \Delta C_{p2}} \tag{3}$$

where $x$ is the mole fraction and $\Delta C_p$ is the incremental change in heat capacity at $T_g$. Subindex 1 relates to the network, whereas subindex 2 is related to the solvating diluent. $\Delta C_{p1}^{\mathrm{act}}$ $(X)$ is $\Delta C_{p1}$ of the network portions capable of being activated, given as [18]

$$\Delta C_{p1}^{\mathrm{act}}\ (X) = \frac{\Delta C_{p1}(X=0) T_{g1}(X=0)}{T_{g1}(X)} \tag{4}$$

where $X$ refers to the crosslink density of the network, such that $X=0$ represents polystyrene.

The thermal properties of the samples and toluene together with the calculated glass transition temperatures of the samples swollen in toluene, $T_{g12}$, are given in Table III. As can be seen, at room temperature, samples 1–5 swollen in toluene are in the rubbery state, whereas sample 6 swollen in toluene is in the glassy state. The theoretical prediction of eq. (3) is in good agreement with experimental results in Table II. On transition from rubbery into the glassy state, the reexpanded pore structure of copolymer matrices remains preserved, resulting in an increase of the porosity (or decrease of $d_{\mathrm{grad}}$). Since sample 6 in equilibrium with toluene is in the glassy state, the porosity of this sample does not change during the solvent exchange.

It is interesting to note the decrease of the porosity in sample 2 with the lowest DVB content, both during the sulfonation reaction and during solvent exchange. In Table IV, the equilibrium swelling values of copolymer matrices and their sulfonated and chloromethylated derivates are given in terms of $\nu_2$. As can be seen from this table, sample 2 swells significantly both in hydrophobic and hydrophilic forms. It is known that at such low

TABLE II

Graduated Density $d_{\mathrm{grad}}$ of Copolymer Matrices Dried after Solvatation (1) and after Solvent Exchange (2)

| Sample no. | $d_{\mathrm{grad}} \times 10^{-3}$ (kg/m$^3$) (1) | (2) |
|---|---|---|
| 1 | 0.67 | 0.62 |
| 2 | 0.63 | 0.83 |
| 3 | 0.65 | 0.42 |
| 4 | 0.50 | 0.36 |
| 5 | 0.47 | 0.34 |
| 6 | 0.39 | 0.39 |

TABLE III
Thermal Properties of Samples 1–6, Toluene and Samples Swollen in Toluene

| Sample no. | $T_{g1}$[a] (°C) | $\Delta C_{p1}^{act}$ (J/g K) | $\chi_1$[e] | $T_{g12}$ (°C) |
|---|---|---|---|---|
| Polystyrene | 112 | 0.283[c] | | |
| 1 | 132 | 0.269 | 0.77 | + 4 |
| 2 | 121 | 0.277 | 0.35 | -110 |
| 3 | 132 | 0.269 | 0.50 | - 79 |
| | | | 0.53 | - 72 |
| 4 | 136 | 0.266 | 0.52 | - 74 |
| | | | 0.55 | - 66 |
| 5 | 144 | 0.261 | 0.70 | - 20 |
| 6 | 162 | 0.251 | 0.81 | + 35 |
| Toluene | $T_{g2} = -160$[b] | | $\Delta C_{p2} = 0.70$[d] | |

[a] Obtained as an approximation from $T_{g1}$ vs. DBV% dependence according to Ref. 18.
[b] Reference 19.
[c] Reference 18.
[d] $\Delta C_{p2}$ value of ethylbenzene in Ref. 18.
[e] Mole fraction of the network in the swollen gel, calculated from $\nu_2$ values of the copolymers (for samples 3 and 4, $\nu_2$ values of reexpanded networks in Table IV was used).

DVB content and in the presence of a diluent the pore structure formed is loose, consisting of rather weakly joined microgel particles.[16] Most probably, the destruction of this weak matrix of sample 2 takes place by solvent exchange or during the sulfonation reaction, resulting in the disappearance of the pores in this network. Table IV also shows that the chemical modification of the matrices causes, like the solvent exchange method, a decrease of the interactions between polymer network and the solvent. Thus, the reexpanded pore structure in the rubbery state is stabilized during sulfonation or chloromethylation of copolymer matrices formed in homogeneous gelation.

TABLE IV
Comparison of $\nu_2$ Values of Copolymer Matrices (1) with That of Their Sulfonated (2) and Chloromethylated Derivates (3)

| | $\nu_2$ | | |
|---|---|---|---|
| Sample no. | (1) In toluene | (2) In water | (3) In toluene |
| 1 | 0.73 | 0.87 | — |
| 2 | 0.33 | 0.15 | — |
| 3 | 0.39 (0.47)[a]<br>(0.50)[a] | 0.50 | 0.62 |
| 4 | 0.43 (0.50)[a]<br>(0.52)[a] | 0.59 | 0.65 |
| 5 | 0.67 | 0.78 | 0.68 |
| 6 | 0.78 | 1.02 | — |

[a] Calculated for reexpanded networks using eq. (1) from the $d_0$ values of sulfonated or chloromethylated networks and from the same weight swelling data as their matrices.

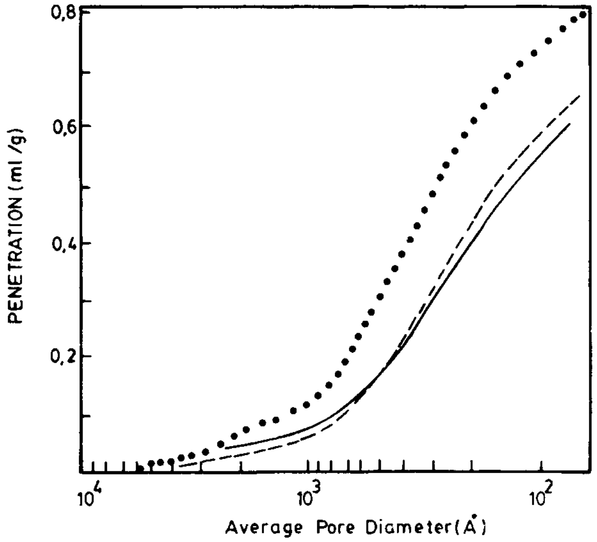

Fig. 4. Pore size distribution of sample 5 in integral mode (see Fig. 1 caption)

## Heterogeneous Gelation

The total porosity of heterogeneous samples 5 and 6 does not undergo any significant change with chemical modification (Table I and Figs. 4 and 5). The slight decrease in the porosity may be attributed to the partial destruction of the rigid pore structure during reactions or during measurements. It seems that the phase separation prior to the gel point leads to the formation of stable pores, and these pores do not collapse upon drying in the swollen state.

In Figure 6, the total porosities of samples 2–6 were plotted as a function of DVB content. For copolymer matrices (dried after solvation in acetone[9]),

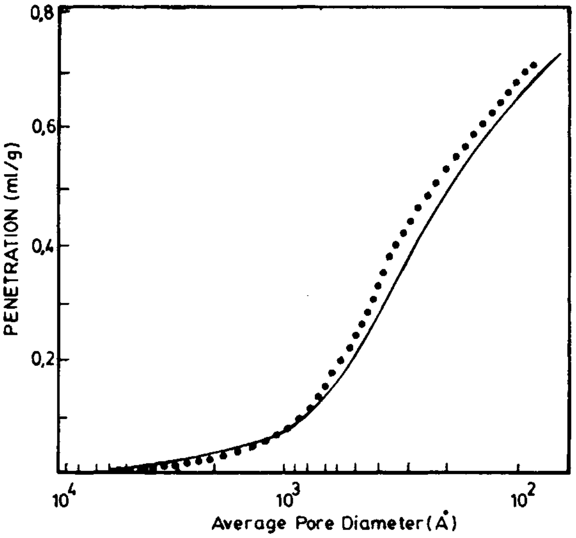

Fig. 5. Pore size distribution of sample 6 in integral mode (see Fig. 1 caption)

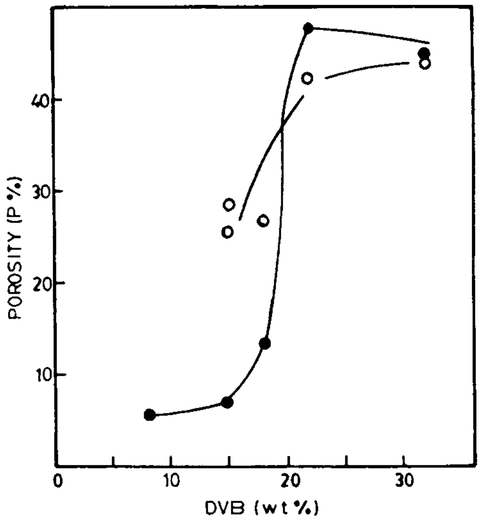

Fig. 6. dependence of the porosity on the DVB concentration for collapsed (●) and reexpanded (○) networks.

the curve shows an inflection point between 18 and 22% DVB corresponding to the critical crosslink density for transition from homogeneous to the heterogeneous gelation. For the reexpanded (sulfonated or chloromethylated) copolymers, however, it shows a continuous increase in the porosity with an increase in the DVB concentration until it reaches 22% DVB. It is evident that, at a constant dilution, the porosity of copolymers in the swollen state increases continuously with increasing crosslink density up to its critical value and then remains constant. This critical value represents a borderline between unstable and stable porosity.

A similar transition was observed in Figure 7, which shows DVB concentration plotted against swelling ratio, $\nu_2/\nu_2^\infty$, for collapsed and reexpanded networks. The swelling data of reexpanded networks in toluene were calculated using eq. (1) from the $d_0$ values of sulfonated or chloromethylated networks and from the same weight swelling data as their matrices (Table IV). Assuming a homogeneous distribution of crosslinks, at $\nu_2/\nu_2^\infty = 1$, the critical value of crosslink density is exceeded,[9] and the phase separation takes place at the gel point. $\nu_2/\nu_2^\infty < 1$ indicates that it swells.

Figure 7 indicates that the increase of $d_0$ on drying (pores collapse) of copolymer matrices leads to the lower $\nu_2$ values, and induces a more marked transition at the critical crosslink density. Thus, the condition of isotropic swelling is not valid for styrene–DVB networks. The mixing of a good solvent with the dry network results in an appreciable change in the total volume of the system, depending on the synthesis conditions of the network.

## CONCLUSIONS

Phase separation above the gel point in styrene–DVB copolymerization induces a loose pore structure which can collapse upon drying in the rubbery state. The collapsed pores have a mean diameter of about 100–200 Å cor-

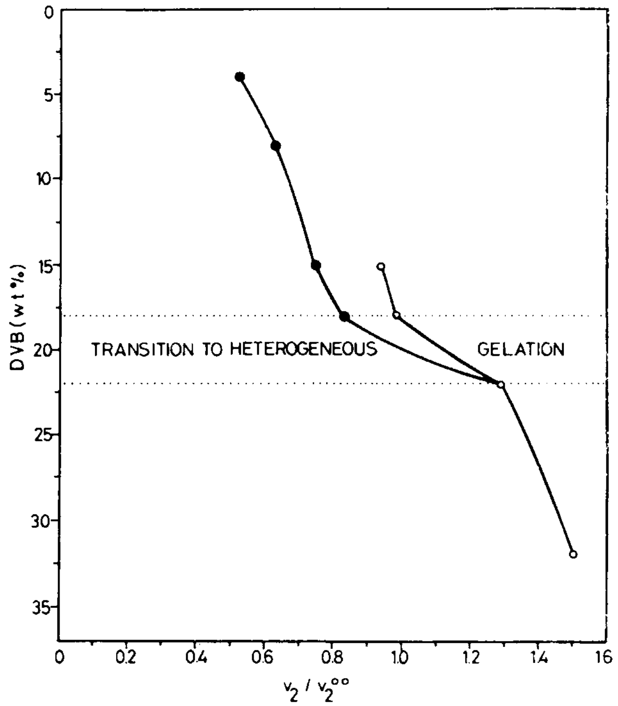

Fig. 7. Dependence of the swelling ratio, $\nu_2/\nu_2^{\infty}$, on the DVB concentration for collapsed (●) and reexpanded (○) networks.

responding to the interstices between the microspheres. The collapsed microspheres reexpand again during the sulfonation or chloromethylation reactions, or during the solvent exchange. However, a small portion of microspheres do not collapse on drying due to the inhomogeneous crosslinking. The pore structure of the styrene–DVB networks formed by phase separation before gelation do not collapse on drying in the swollen state. It is a stable and permanent porosity. At a constant dilution, the porosity of the network in the swollen state increases continuously with increasing DVB content up to the critical crosslink density corresponding to the phase separation at the gel point. This critical point represents a borderline between stable and unstable porosity.

The authors wish to thank Dr. Aral I. Okay from the Istanbul Technical University for critically reading the manuscript, and Mr. Ramazan Garip for technical assistance. This work was supported by the NATO Scientific Affairs Division within the program of Science for Stability.

## References

1. J. Seidl, J. Malinsky, K. Dusek, and W. Heitz, *Adv. Polym. Sci.,* **5**, 113 (1967).
2. K. Dusek, *J. Polym. Sci., C,* **16**, 1289 (1967).
3. K. Dusek and W. Prins, *Adv. Polym. Sci.,* **6**, 1 (1969).
4. K. A. Kun and R. Kunin, *J. Polym. Sci., A-1,* **6**, 2689 (1968).
5. W. L. Sederel and G. J. DeJong, *J. Appl. Polym. Sci.,* **17**, 2835 (1973).
6. H. Jacobelli, M. Bartholin, and A. Guyot, *J. Appl. Polym. Sci.,* **23**, 927 (1979).
7. A. Warshawsky and R. Kalir, *J. Appl. Polym. Sci.,* **24**, 1125 (1979).

8. G. J. Howard and C. A. Midgley, *J. Appl. Polym. Sci.*, **26**, 3845 (1981).
9. O. Okay, E. Soner, A. Güngör, and T. I. Balkaş, *J. Appl. Polym. Sci.*, to appear.
10. K. Haeupke and V. Pientka, *J. Chromatogr.*, **102**, 117 (1974).
11. H. Hilgen, G. J. DeJong, and W. L. Sederel, *J. Appl. Polym. Sci.*, **19**, 2647 (1975).
12. F. Krska, J. Stamberg, and Z. Pelzbauer, *Angew. Makromol. Chem.*, **3**, 149 (1968).
13. C. Luca, Ig. Poinescu, E. Avram, A. Ioanid, I. Petrariu, and A. Carpov, *J. Appl. Polym. Sci.*, **28**, 3701 (1983).
14. J. Seidl and J. Malinsky, *Chem. Prumysl*, **13**, 100 (1963).
15. K. W. Pepper, *J. Appl. Chem.*, **1**, 124 (1951).
16. H. Beranova and K. Dusek, *Coll. Czech. Chem. Commun.*, **34**, 2932 (1969); P. P. Wieczorek, M. Ilavsky, B. N. Kolarz, and K. Dusek, *J. Appl. Polym. Sci.*, **27**, 277 (1982).
17. G. Schwachula, *J. Polym. Sci., Polym Symp. Ed.*, **53**, 107 (1975).
18. T. S. Ellis, F. E. Karasz and G. Ten Brinke, *J. Appl. Polym. Sci.*, **28**, 23 (1983).
19. M. R. Carpenter, D. B. Davies and A. J. Matheson, *J. Chem. Phys.*, **46**, 2451 (1967); see also C. A. Angell, J. M. Sare, and E. J. Sare, *J. Phys. Chem.*, **82**, 2622 (1978).

Received December 5, 1984
Accepted June 11, 1985