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# Porosity Variation and Swelling of Styrene-Divinylbenzene Copolymers

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## Summary

The porosity measured for two series of diluent-modified styrene (S) - divinylbenzene (DVB) copolymers (10 and 20 wt.-% of DVB) was found to depend on sample pretreatment. A correlation between the volume fraction of the polymer in the swollen gel and the volume fraction of octane used as diluent has been established assuming the isotropic swelling of the sample pretreated with water before porosity determination.

## Introduction

The mechanism of the porous structure formation in the copolymerization of styrene and divinylbenzene performed with inert diluents of the monomers is well known (DUŠEK 1967). Although DUŠEK's theory predicts a single porosity value (volume fraction of pores in the copolymer beads), HÄUPKE and PIENTKA (1974) found that in some cases the pretreatment of the S-DVB copolymer with methanol led to a porosity considerably differing from that measured after swelling the sample in toluene. The changes of porosity were found to be reversible. Since porous S-DVB copolymers are also used in various solvents (for example, as GPC stationary phases), the porosity variations induced by solvent exchange called our attention.

## Experimental

The S-DVB copolymers were prepared in aqueous suspension. After extraction with hot benzene, the polymer beads were washed in a column with a series of solvents of increasing polarity; a small sample of polymer was removed after passing through each solvent. The samples were dried at 298±0.5 K (25°C).
The composition of the copolymers was coded as in the following example. The copolymer OT 21 0.5/20 was prepared with a diluent consisting of 2 and 1 parts by volume of octane and toluene, respectively. The monomer +diluent mixture contained a 0.5 volume fraction of mo-

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nomers, and the content of m- and p-DVB in the monomers was 20 wt.-%.

The apparent density was determined using a mercury pycnometr. The density of swollen copolymer was determined pycnometrically assuming the deviation from the additivity of volumes as an increase of the copolymer density. The true density was assumed to be 1.029 and 1.040 g/cm$^3$ for copolymers, prepared with 10 and 20 wt.-% of DVB, respectively, which are apparent densities of the copolymers prepared without any diluent.

The amount of the solvent in equilibrium with a swollen sample was determined by centrifugation.

## Results and Discussion

According to DUŠEK (1967), the condition for phase separation in vinyl-divinyl copolymerization occurs when a gel being formed reaches its maximum degree of swelling. This condition holds from the point of critical conversion at which phase separation occurs until all monomers have reacted. One may expect that the volume fraction of the polymer, $v_2$, in a gel of the porous copolymer depends on the location of the critical conversion, i.e. on the fraction of the poorly solvating agent in the diluent mixture, if other parameters of the reaction are kept constant. Therefore, when the sequence of porous S-DVB copolymers prepared using increasing fractions of octane in the mixture with toluene as diluent is swollen in any solvent, an increase or at least constancy of $v_2$ should be observed.

The determination of $v_2$ of the swollen porous gel requires information on the distribution of the solvent between pores and gel. This information is available, so far, only from indirect measurements (such as GPC or SAXS). These methods, however, give results highly affected by the sensitivity of detection of phase boundaries within the heterogeneous material. On the other hand, the porosity is easy to determine for dry samples using a simple mercury pycnometer. Then, adopting the BERANOVÁ and DUŠEK (1969) assumption on the isotropy of swelling, $v_2$ of the swollen gel may be calculated. According to this assumption, the volume fraction of pores remains constant upon swelling the S-DVB copolymer in a solvent. Thus, Eg. (1) results

$$v_2 = \frac{d_s d_{op}}{d_o(Bd_p + d_s)}, \quad (1)$$

where $d_s$,$d_o$,$d_{op}$,and $d_p$ are density of solvent,apparent density of solvent, apparent density of dry copolymer, true copolymer density, and density of copolymer swollen in the solvent, respectively, and B is the total amount of solvent in the copolymer bead.

In Table 1 the calculated values of $v_2$ are listed for porous S-DVB copolymers swollen in toluene, acetone and cyclohexane. As can be seen, the values of $v_2$ do not

Table 1

Pycnometrically determined apparent, $d_o$, and skeletal, $d_p$, densities and swelling agent regain, B, for S–DVB copolymers, and calculated volume fractions of polymer in the gel, $v_2$

| Sample | TOLUENE |  |  |  | ACETONE |  |  |  | CYCLOHEXANE |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | $d_o$ | B | $d_p$ | $v_2$ | $d_o$ | B | $d_p$ | $v_2$ | $d_o$ | B | $d_p$ | $v_2$ |
|  | g/cm$^3$ | g/g | g/cm$^3$ |  | g/cm$^3$ | g/g | g/cm$^3$ |  | g/cm$^3$ | g/g | g/cm$^3$ |  |
| 0 0.5/20 | 0.527 | 1.590 | 1.101 | .657 | 0.487 | 1.249 | 1.107 | .781 | 0.491 | 1.293 | 1.068 | .768 |
| OT 21 0.5/20 | 0.922 | 1.319 | 1.102 | .439 | 0.760 | 1.042 | 1.107 | .560 | 0.705 | 1.072 | 1.070 | .600 |
| OT 11 0.5/20 | 1.022 | 1.175 | 1.098 | .411 | 0.974 | 0.894 | 1.113 | .476 | 0.976 | 0.852 | 1.082 | .491 |
| OT 12 0.5/20 | 1.034 | 1.097 | 1.103 | .422 | 1.014 | 0.787 | 1.105 | .494 | 1.024 | 0.774 | 1.094 | .490 |
| T 0.5/20 | 1.039 | 1.032 | 1.107 | .435 | 1.027 | 0.672 | 1.110 | .525 | 1.031 | 0.674 | 1.080 | .525 |
| T 0.33/20 | 1.057 | 1.900 | 1.110 | .291 | 0.965 | 1.337 | 1.120 | .378 | 1.031 | 1.489 | 1.077 | .334 |
| O 0.5/10 | 1.005 | 1.615 | 1.097 | .336 | 0.636 | 1.117 | 1.105 | .630 | 0.578 | 1.238 | 1.061 | .661 |
| OT 11 0.5/10 | 1.029 | 1.251 | 1.093 | .387 | 1.032 | 0.507 | 1.092 | .586 | 1.027 | 0.594 | 1.068 | .551 |
| OT 12 0.5/10 | 1.044 | 1.326 | 1.098 | .424 | 1.038 | 0.461 | 1.105 | .610 | 1.032 | 0.563 | 1.072 | .568 |
| T 0.5/10 | 1.044 | 1.367 | 1.091 | .362 | 1.043 | 0.430 | 1.088 | .628 | 1.031 | 0.533 | 1.055 | .586 |
| T 0.33/10 | 1.047 | 2.373 | 1.091 | .246 | 1.044 | 0.504 | 1.094 | .589 | 1.037 | 0.425 | 1.054 | .640 |

correlate with the fraction of octane used in the polymerization, although $d_0$ values were determined using samples pretreated with their appropriate swelling agents before drying.
The apparent density of the S-DVB copolymers studied strongly depends on sample pretreatment, as shown schematically in Fig. 1.

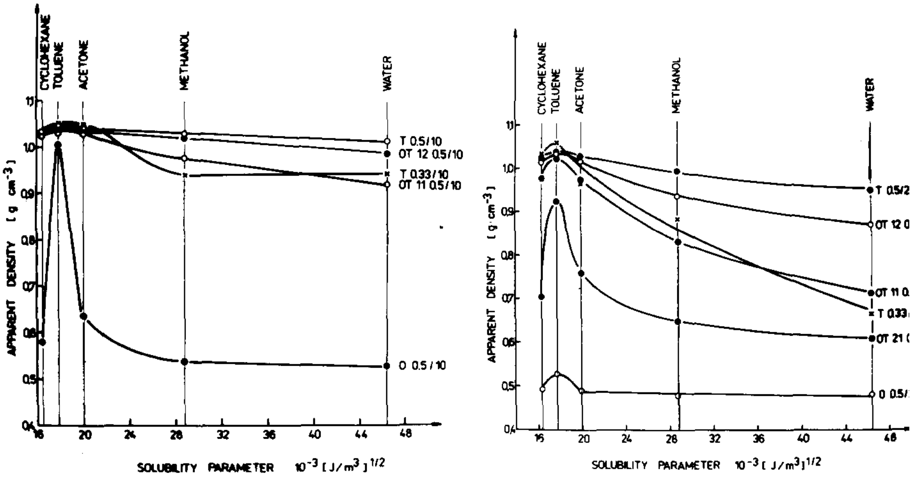

Fig. 1. Apparent density of copolymers vs. solubility parameter of the solvent used in the pretreatment of copolymers.

As we have suggested recently (BALDRIAN et al. 1979), the point during the drying process at which $T_g$ of the solvated copolymer approaches the temperature of drying determines the final porosity. After this point is passed, the porous structure of the copolymer is fixed.The differences among copolymers with a range of porosity changes are probably related to their morphologies.
Using the SAXS method we have also found that the 'porosity' of a swollen copolymer seems to be constant, i.e. independent of the solvent used, and is close to the maximum porosity of the dry copolymer (pretreated with water). Now, using the highest value of $d_0$ for each copolymer, the expected relation between $v_2$ (Eq.1) and the fraction of octane in the monomer phase may be obtained with toluene, acetone and cyclohexane used as swelling agents (see Fig. 2).
As can be seen in Fig. 2, $v_2$ of the swollen copolymer approaches a value of 1 in the limit of the fraction of octane in the monomer mixture being unity. This result, although not verifiable experimentally, seems reasonable as it corresponds to the formation of a gel with vanishing volume (the porosity approaches 1) thus causing an increase of the concentration of elastically

active network chains without limit.

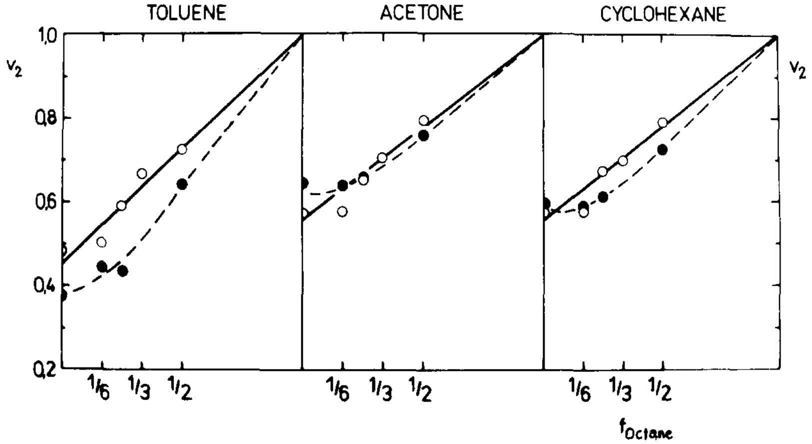

Fig. 2. Volume fraction of polymer in swollen copolymers vs. fraction of octane used as diluent. Volume fraction of monomers in the polymerizing mixture: 0.5 —— Copolymers with 20% DVB; --- copolymers with 10% DVB.

## References

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