

Structure of Some Styrene–Divinylbenzene Copolymers

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SYNOPSIS

Structures of copolymers of styrene and divinylbenzene (50% crosslinking degree) prepared in suspension polymerization in the presence of mixtures of *nonsol* (heptane or decane) and *sol* (toluene or tetralin) diluents were investigated. The studies showed that the diluents enriched with nonsol solvents resulted in an increase of pore volumes and porosities for the prepared copolymers. The sol diluents affected mainly the gel regions of the polymer matrices. Isotropic swelling of the matrices prepared in the presence of toluene is the opposite of the effect observed for tetralin family copolymers. The virtual difference of both kind of matrices was demonstrated in the sorption of phenol. The tetralin family copolymers were characterized by a prolonged time for column breakthrough. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Copolymers of styrene and divinylbenzene (S/DVB) are widely used as sorbents, carriers, and matrices of a great number of ion exchangers. S/DVB copolymers activity began in the 1960s¹ but their properties have not been well recognized so far. The published papers deal with theories of polymerization in the presence of crosslinking agents,^{2,3} effects of solvents on the structure of matrices obtained,^{4–15} and alteration of formed polymer networks during solvent treatment.^{16–20}

Suspension copolymerization in the presence of some diluents has been progressively studied in our lab for the last decade.^{7,17,18,21–26} It was found that different diluents generated formation of uniform polymer networks with an inhomogeneity mostly related to the kind and amount of inerts used. The following factors³ are significant in the creation of inhomogeneities in the polymer gel regions: varied reactivity of the comonomers, solvent-induced phase separation, and growing chain cyclization or permanent entanglement. When one increases the amount of a diluent, an additional factor emerges—the possibility of pore creation is raised. Hence, it is clear that a diluent plays an important (crucial)

contribution to the structure of the copolymer obtained.

The main goal of this study was to show that the structure of copolymers of styrene and divinylbenzene, prepared from the same mixture of reactants, varied with the kind of diluents used. Four diluents were selected for this study: toluene and tetralin, which were considered as highly solvating (*sol* type), and decane and heptane, both poor solvents (*nonsol* type).

EXPERIMENTAL

Preparation of S/DVB Copolymers

Copolymers of styrene and divinylbenzene were obtained by suspension polymerization according to a procedure described elsewhere.¹⁸ Styrene of technical grade (supplied by Oswiecim Chemical Plant, Poland) and divinylbenzene containing 51.8 vol % of *m*- and *p*-isomers (supplied by Merck Ltd, Germany) were used without preliminary purification. The synthesis was carried out under conditions which guaranteed 50% crosslinking. The diluents were changed in each synthesis, but the dilution ratio was set at 0.5 or 0.25 levels. After polymerization, copolymers were extracted with hot benzene in Soxhlets for 8 h. Finally, they were washed with the following solvents: toluene, acetone, methanol, and

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water at the gradient mode of solvent replacement. The copolymers were dried at room temperature. All measurements were performed on the samples prepared in the same way.

Properties of Copolymers

Apparent density (d_0) was measured by a pycnometric method in mercury (dry state) and water (swollen state). Total porosity (P) and specific pore volume (Q) were calculated according to the following equations:

$$P = \frac{d - d_0}{d} \quad (1)$$

$$Q = \frac{d - d_0}{d_0 d} \quad (2)$$

where d_0 is the apparent density and d is the true density of copolymer. The latter value is equal to 1.07 g/cm^3 .

Specific area and pore volume distribution were calculated from the nitrogen desorption data measured at Sorptomatic 1800 (Carlo Erbo, Italy) sorptiographer. Before sorption, samples were degassed at 60°C for 24 h. With the assumption of lognormal distribution of pore radius, the values of $dV/d \log R$ were calculated by means of SorpCalc software (courtesy A. Marczewski, Univ. M. Curie-Skłodowskiej, Lublin).

Water regain (B) was detected gravimetrically by subsequent immersing of a dry sample in toluene, acetone, methanol, and water and then centrifuged (20,000 rpm, rotor diameter 30 cm). The values of volume swelling were calculated according to Beranova et al.²⁷ Direct detection of the diameter of randomly selected beads (50) before and after swelling were performed also to determine the water regain $(D/D_0)^3$. The measurements were performed by means of optical microscopy according to Hintzsche et al.²⁸

Chromatographic porosimetry was performed according to Gorbunov et al.²⁹ The following system was employed for this task: pump LC-6A (Shimadzu, Japan), injector 7255 (Rheodyne, USA) equipped with $20\text{-}\mu\text{L}$ loop, glass column $160 \times 3.2 \text{ mm}$, refractometer RIDK-102 (Ecom, Czech Rep.), integrator IC-100A (Lab Prostroje, Czech Rep.). The mobile phase (water containing 0.1 wt % of sodium dodecylsulphate) was pumped with a rate of $0.1 \text{ cm}^3/\text{min}$. As a molecular standard, a narrow fraction of dextrans (supplied by Pharmacia, Sweden, and Polfa, Poland) were used.

Studies of phenol sorption were performed in a dynamic mode. A glass column of $70 \times 4 \text{ mm}$ was filled with a water-swollen copolymer. Then, the solution of phenol was pumped (Shimadzu LC-6A pump) throughout the column at a rate of $0.6 \text{ cm}^3/\text{min}$. The concentration of feed was set as 0.6 mg/cm^3 ; in some experimental runs the concentration was 0.3 or 1.2 mg/cm^3 . The phenol concentration was monitored by the RIDK-102 (Ecom, Czech Rep.) detector.

DISCUSSION

The kind and amount of diluent used in synthesis of S/DVB copolymers vitally affect the structure of matrices in two regions: in gel and porous structures. To express these changes in numerical ways, one has to use a convenient Hildebrand solubility parameter. When the difference of this parameter for polymer and solvent is large, the conditions for forming a uniform network are very poor. After synthesis of copolymer under such conditions, one gets an inhomogeneous matrix in both gel and porous regions.⁴

The comparison of the Hildebrand parameter for polystyrene and commonly used diluents allows one to classify the latter into two categories: those that well solvate the polymer chain (sol type) and those with poor solvating abilities (nonsol type). In this study, two pairs: toluene (T) or tetralin (Tt), and decane (D) or heptane (H) were selected as representative of the sol and nonsol diluents, respectively. The solubility parameters of diluent mixtures used are juxtaposed in Table I. Analysis of these values leads to the conclusion that the copolymers obtained, in the presence of a mixture enriched with the sol diluents (series 19), should have a different structure than those obtained in a poorly solvating environment (series 11). These former should display lower porosity and higher gel homogeneity than copolymers of series 11 because their supermolecular structure was formed in the well-swollen state. The increase of concentration of the nonsol component should increase the copolymer inhomogeneities. The phase separation processes, chain cycling, and entanglement are mostly responsible for this phenomenon.³ The above speculation was confirmed in investigation of copolymer structure performed by the method of nitrogen sorption-desorption (Table II). Copolymers of series 19 were characterized by lower porosity and pore volume than matrices of series 11. Moreover, the effect of nonsol diluents on the structure of polymer networks of series 19 was marginal

Table I Solubility Parameters of Used Diluents³⁰

| Symbol | Diluents | Vol. Ratio | δ (MPa ^{0.5}) | $(\delta - \delta_p)^2$ ^a (MPa) |
|--------|---------------------|------------|--------------------------------|--|
| HT 19 | Heptane : toluene | 1 : 9 | 17.89 | 0.50 |
| HT 11 | Heptane : toluene | 1 : 1 | 16.65 | 3.80 |
| DT 19 | Decane : toluene | 1 : 9 | 17.73 | 0.76 |
| DT 11 | Decane : toluene | 1 : 1 | 15.85 | 7.65 |
| HTt 19 | Heptane : tetraline | 1 : 9 | 18.97 | 0.14 |
| HTt 11 | Heptane : tetraline | 1 : 1 | 17.25 | 1.82 |

^a δ_p is the solubility parameter of copolymer (18.6 MPa^{0.5}).

(Fig. 1). A slight shift of average pore diameter toward a low value was observed when toluene was replaced by tetralin. For the copolymers of series 11, the effect of diluents on the porous structure of the matrices was markedly evident (Fig. 2). The broadening of pore distribution and the shift of the average pore diameter toward higher values for the case when heptane was replaced with decane were to be expected. But the influence of the sol diluents on the pore distribution, to the best knowledge of the authors, has not been described so far. In Table II, the characteristics of copolymer HT 19 prepared at higher dilution ratio are also presented. The matrix exhibits a very narrow pore diameter distribution (Fig. 3), and is the only one copolymer possessing micropores. The data, once more, confirms the crucial contribution of dilution ratio on the porous structure of the S/DVB copolymer.

The gel and porous structures of copolymer results from two major factors: (1) the conditions of swelling in the copolymerization step. The selection of diluent and dilution ratio governs the copolymer properties.³ (2) the properties of the solvent which

was removed from the swollen matrix. Each solvent induces its own swelling properties which determine the extent of change appearing in the drying process.⁷ The changes of structure in both regions may be detected by solvent uptake. They can appear in two ways: by filling the pores without affecting the gel regions (no volume change) and by chain displacement in the gel regions that causes bead expansion. The latter mode is dependent on gel expandability which, in turn, is the result of the solvation conditions in the copolymerization.

S/DVB copolymers do not swell in water. However, by gradual solvent replacement from toluene, through acetone and methanol, to water, it is possible to fill pores and interchain vacancies with water molecules.¹⁸ In consequence, water regain is observed. The numerical values of this parameter are collected in Table III in the first column. The data suggest that water uptake is affected by the presence of nonsol diluents in the polymerization mixture (series 19 and 11). Its change is congruent to the matrix total porosity (Table III, second column). The fact that the greatest uptake is measured for

Table II Structure Characteristics of the Copolymers in Dry State^a

| Sample | d_0 (g/cm ³) | P | Q (cm ³ /g) | S_{mic} (m ² /g) | S_{BET} (m ² /g) | V_{mic} (cm ³ /g) | V (cm ³ /g) | r (nm) |
|------------|----------------------------|------|--------------------------|-------------------------------|-------------------------------|--------------------------------|--------------------------|----------|
| HT 19 0.25 | 0.558 | 0.48 | 0.86 | 30.00 | 441 | 0.01 | 0.401 | 1.82 |
| HT 19 0.5 | 0.825 | 0.23 | 0.28 | 0.0 | 517 | 0.00 | 0.595 | 2.30 |
| DT 19 0.5 | 0.806 | 0.25 | 0.31 | 0.0 | 515 | 0.00 | 0.592 | 2.30 |
| HTt 19 0.5 | 0.726 | 0.32 | 0.44 | 0.0 | 490 | 0.00 | 0.515 | 2.10 |
| HT 11 0.5 | 0.735 | 0.31 | 0.43 | 0.0 | 503 | 0.00 | 0.758 | 3.01 |
| DT 11 0.5 | 0.667 | 0.38 | 0.56 | 0.0 | 487 | 0.00 | 0.844 | 3.46 |
| HTt 11 0.5 | 0.657 | 0.38 | 0.59 | 0.0 | 516 | 0.00 | 0.692 | 2.68 |

^a The data calculated from the desorption branch of N_2 isotherm. The last number in the sample column means the dilution ratio. d_0 is the apparent density, P is the total porosity, Q is the specific volume of pores, S is the surface of pores, V_{mic} is the volume of micropores, V is the volume of pores, and r is the average pore radius.

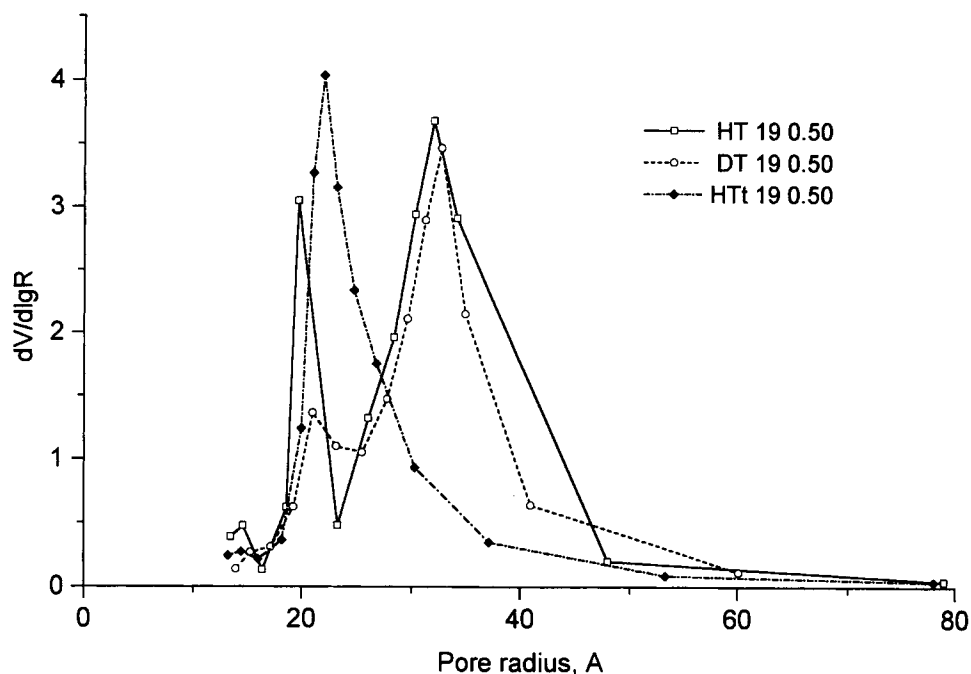


Figure 1 Effect of diluents on the porous structure of copolymers synthesized in the presence of sol type of diluents (series 19).

copolymer obtained at 0.25 dilution ratio is evidently due to the largest porosity and is not discussed here.

All copolymers filled with water exhibit an increase of porosity. Taking into account the contri-

bution of pore porosity, i.e., the copolymer porosity determined by drying the matrix from water, in the total (P_{tot}) porosity one notes its dependence on polymerization conditions (see data in Tables II and

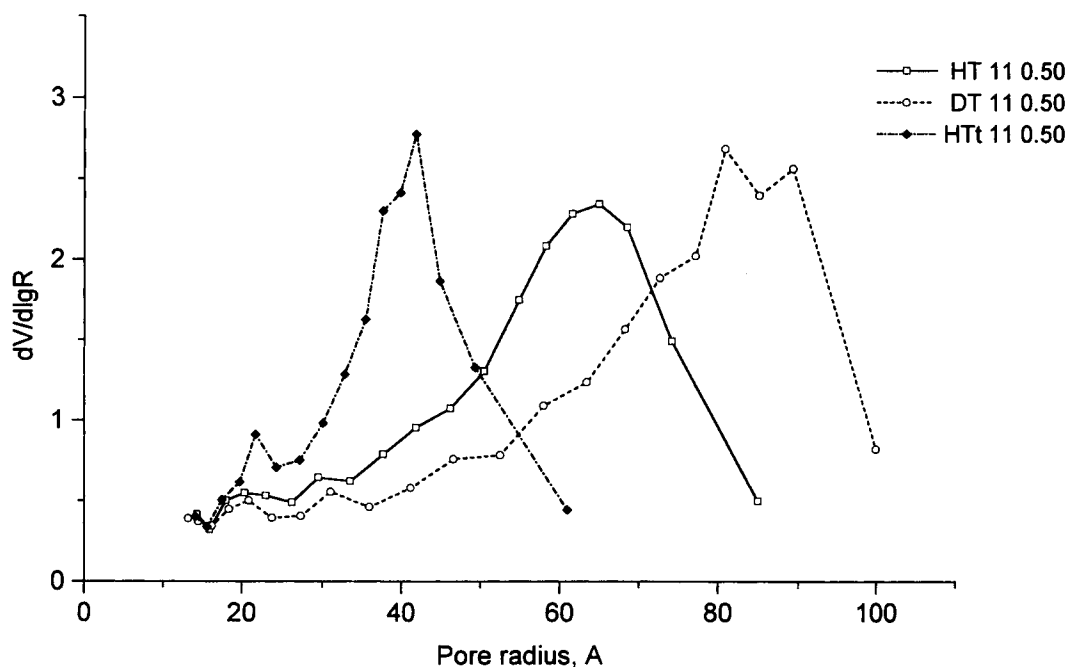


Figure 2 Effect of diluents on the porous structure of copolymers synthesized in the presence of nonsol type of diluents (series 11).

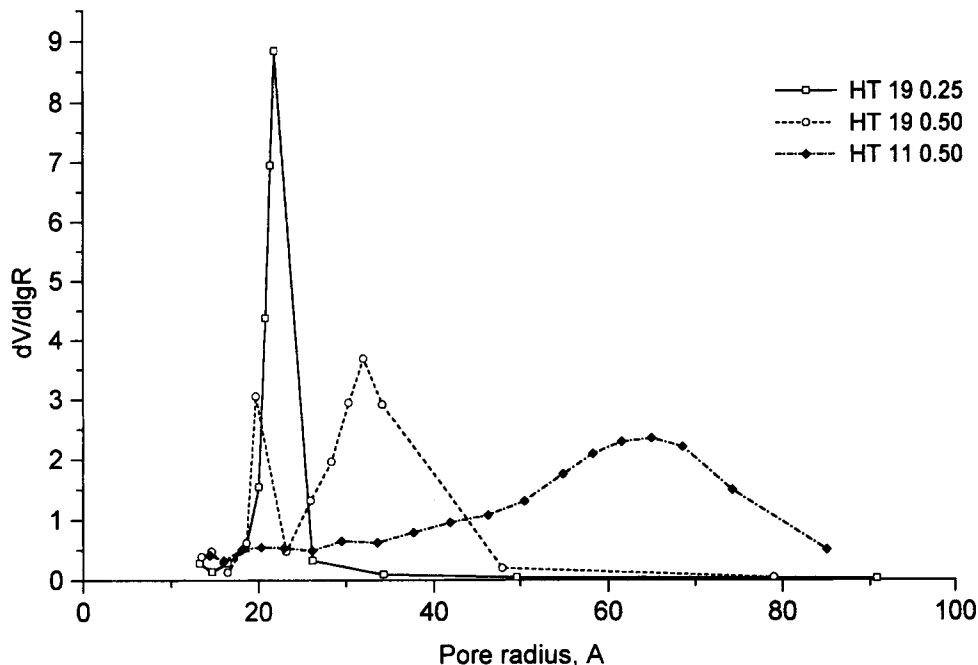


Figure 3 The pore radius distribution of the HT 19 samples.

III). The ratio of pore to total porosity for the toluene series of 19 is smaller than for the toluene series of 11. It implies that the gel fraction of copolymers obtained at high toluene ratio (series 19) has higher reexpansion capability than the gel of series 11. This behavior is not detected for the samples of the tetralin family. Porosity and water regain before and after swelling remain quite similar. This observation allows us to propose the thesis that various structures of gel occur for both sol diluent induced matrices.

Volume swelling (B) determined by gravimetric method, in the light of assumptions of isotropic swelling and porosity exclusion, confirms very well the differences of the gel structures for copolymers

prepared in the presence of tetralin and toluene. In the case of the matrices of the tetralin series, the volume swelling reaches values close to 1. Additionally, swelling determined from comparison of bead diameter before and after swelling $[(D/D_0)^3]$ points to different structures of gel in the toluene and tetralin series. In the case of the toluene series, the $(D/D_0)^3$ value is well correlated to the B parameter. The good correlation confirms the assumption of isotropic swelling of copolymer. In the case of the tetralin series of copolymer, the situation is reversed: There is a lack of dependence. This lack can be elucidated by the change of pore volume partition in the swollen matrices. Hence, the assumption of isotropic swelling of the copolymer entirely fails. The

Table III Structure Characteristics of the Copolymers in the Swollen State^a

| Symbol | Water Regain (g/g) | P_{tot} | Q_{tot} (cm ³ /g) | P/P_{tot} | Q/Q_{tot} | B | $(D/D_0)^3$ |
|------------|--------------------|-----------|--------------------------------|-------------|-------------|------|-------------|
| HT 19 0.25 | 1.91 | 0.71 | 1.78 | 0.68 | 0.48 | 1.59 | 2.25 |
| HT 19 0.5 | 0.57 | 0.37 | 0.57 | 0.62 | 0.49 | 1.24 | 1.26 |
| DT 19 0.5 | 0.57 | 0.39 | 0.52 | 0.64 | 0.60 | 1.16 | 0.97 |
| HTt 19 0.5 | 0.56 | 0.38 | 0.52 | 0.84 | 0.85 | 1.08 | 1.29 |
| HT 11 0.5 | 0.72 | 0.42 | 0.71 | 0.74 | 0.61 | 1.21 | 1.22 |
| DT 11 0.5 | 0.80 | 0.45 | 0.80 | 0.84 | 0.70 | 1.21 | 1.16 |
| HTt 11 0.5 | 0.72 | 0.43 | 0.70 | 0.88 | 0.84 | 1.09 | 1.29 |

^a P and P_{tot} are the pore and total porosities, respectively.

Table IV Chromatographic Porosimetry of the Investigated Copolymers

| Sample | Pore Area (m ² /cm ³) | Average Pore Radius (nm) |
|------------|--|--------------------------|
| HT 19 0.25 | 413 | 2.14 |
| HT 19 0.5 | 678 | 1.31 |
| DT 19 0.5 | 420 | 2.11 |
| HTt 19 0.5 | 437 | 2.03 |
| HT 11 0.5 | 622 | 1.42 |
| DT 11 0.5 | 460 | 1.93 |
| HTt 11 0.5 | 549 | 1.61 |

only way to explain the difference between both copolymer series is to address the different structures of the gel regions.

When one considers the effect of high dilution ratio, one finds similar properties. In this case, however, the reason for such behavior seems to be entirely different. The increase of crosslinking degree,

generated by the chain cyclization, is highly plausible. Finally, one can conclude that both factors, like a kind of sol diluents and the dilution ratio, are mostly involved in creation of the gel regions of the S/DVB copolymers.

The second structure of copolymer which can be affected by diluent is the porous region. Chromatographic porosimetry is a convenient tool in such studies. Dextrans used in this method make visible only the pores with diameter larger than 1 nm (the diameter of the smallest dextran of 1500 Da, which was used in this study, was 1.1 nm). The calculated surface areas and average pore diameter are collected in Table IV. The data support the previous conclusions. The nonsol diluents did not affect significantly the diameter of pores. The pore diameter is influenced more by the presence of the sol diluents. Moreover, tetralin developed larger pores but toluene allowed the structure to have a higher surface. Additionally, any increase of dilution ratio is reflected in the increase of pore diameter. The possi-

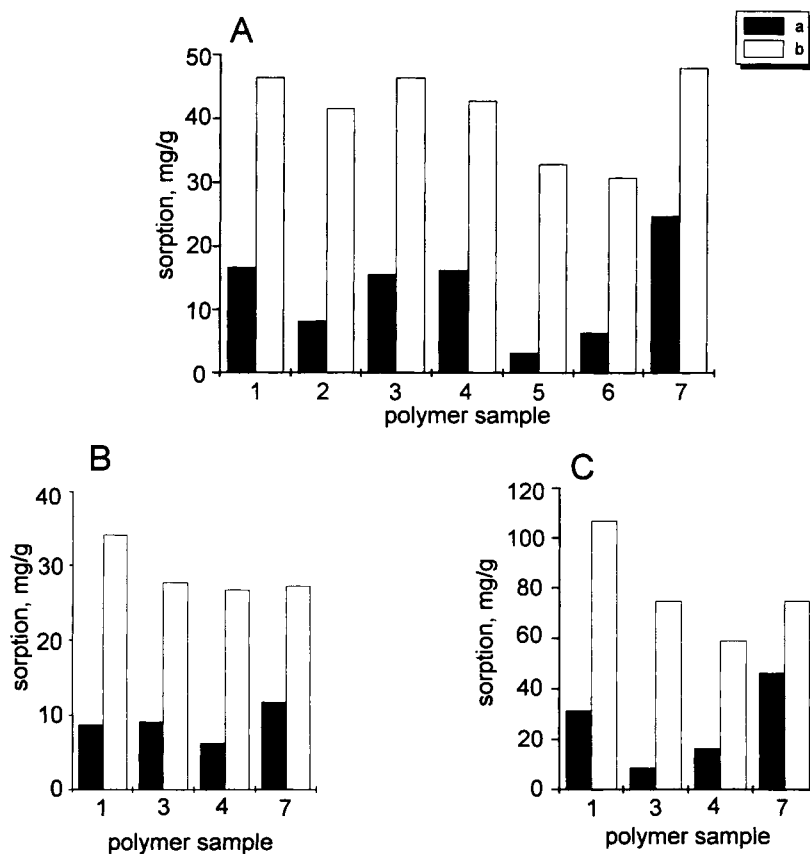


Figure 4 The sorption patterns of toluene and tetraline families. (a) breakthrough capacity, mg/g; (b) total capacity, mg/g. Phenol concentration: (A) 0.6 g/dm³, (B) 0.3 g/dm³, (C) 1.2 g/dm³. Matrices: (1) HT19,0.25; (2) HT19,0.5; (3) DT19,0.5; (4) HTt19,0.5; (5) HT11,0.5; (6) DT11,0.5; (7) HTt11,0.5.

bility of the cauliflower shape of the copolymer bead, which implies the presence of a low permeable dense skin layer, makes the obtained data ambiguous. Therefore the data derived from the chromatographic porosimetry should be skeptically considered. They do not show the real porous structure of the whole copolymer bead but only the structure of the outside skin layer.

The discussed differences of the structures of S/DVB copolymers synthesized in the presence of toluene or tetralin should significantly affect the sorption kinetics of phenol. To demonstrate these differences, a series of sorptions were performed. The results are collected in Figure 4. When the equilibrium sorption was the same for the copolymers investigated, significant differences in kinetics appeared. The copolymers from tetralin were characterized by a prolonged time of column breakthrough. Long-time sorption of phenol showed better access to the polymer surface than for the matrices of the toluene family. There is an additional feature which advocates the use of S/DVB sorbents prepared in the presence of tetralin: They swell very poorly.

CONCLUSIONS

These studies have shown that the structure of S/DVB copolymers depends on the kind of diluent used in the synthesis and the dilution ratio. The nonsol diluents caused an increase of copolymer porosity while the sol diluents affected the gel regions. Various structures of the polymer gel, induced by different sol diluents, defined various properties of the copolymer. The matrices from tetralin do not swell in water as intensively as from toluene family. They are characterized by better properties toward sorption of phenol.

The authors appreciate the Polish Committee of Scientific Research Grant 3 1281 91 01 for the financial support.

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Received May 16, 1994

Accepted July 19, 1994