

Styrene–Divinylbenzene Copolymers: Influence of the Diluent on Network Porosity

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Synopsis

The formation of the permanent porosity in the classical matrix, styrene–divinylbenzene copolymers, using cyclohexane, cyclohexanol, or cyclohexanone as diluent was studied. The data concerning porous networks were corroborated with the solvent–polymer interaction factor and the cohesive energy density which are important in the prediction of copolymer porosity. Between diluents there are noticeable differences, though the diluent volume and the divinylbenzene percent strongly influence the porous structure of the network. Cyclohexanol was the most efficient diluent for building up the highest porosity even at low percents of divinylbenzene.

INTRODUCTION

Kunin and his co-workers^{1,2} developed the macroreticular network synthesis based on the styrene–divinylbenzene copolymers (St–DVB). There has been an increasing interest in using such materials as chromatographic packing supports or porous starting structure for the ion exchangers. This was a great advance in the syntheses of ion exchangers for the removal of organic substances.

Styrene copolymerized with a small amount of divinylbenzene (DVB) results in gel-type copolymers, which are characterized by a swollen state porosity. The pore size only depends on the percent of DVB.

The principle of the crosslinked heterogeneous network synthesis lies in monomer copolymerization in the presence of an inert compound termed "diluent."^{3–6}

The most important factors governing the heterogeneity of the networks are technical-grade divinylbenzene and the percent of DVB. But, the diluent and its volume used for monomer dilution also influence the porosity structure. Large volumes of diluent and high percents of DVB result in brittle networks, which may have low mechanical resistance. Any macroreticular network has, besides a permanent porosity, an amount of swelling porosity which exists only in the swollen state.

Lloyd and Alfrey,^{7–9} have shown that the equilibrium swelling occurs when the overall free energy is at minimum:

$$\delta\Delta F/\delta V = 0 \quad (1)$$

At equilibrium, we might have

$$\delta\Delta F_{\text{mix}}/\delta V = -\delta\Delta F_{\text{net}}/\delta V \quad (2)$$

where ΔF_{mix} and ΔF_{net} are the free energies of polymer solvent mixing and of network stretching, respectively.

Solvent-polymer interactions (δ) for different solvents (inert media) have much more importance in porosity formation than other parameters.

Usually, the free energy equation might be used in the process of mixing or dissolving a polymer in solvent:

$$\Delta F = \Delta H - T\Delta S \quad (3)$$

The value of the free energy equation allows us to know whether or not a given process will operate.

The copolymerization process (styrene and DVB) develops inside of organic droplets, where there is a large diluent volume (good or poor solvent for the polymeric chains). The monomer/diluent volume ratio, inside of the droplets, is changing during the copolymerization process, yielding a swollen or collapsed network.

In this case, the magnitude of the term ΔF is the deciding factor in the sign of the free energy change and, in consequence, the solubility of the polymer.

But, the overall heat of mixing (calories) may be written¹⁰

$$\Delta H_m = V_m \left[\left(\frac{\Delta E_1}{V_1} \right)^{1/2} - \left(\frac{\Delta E_2}{V_2} \right)^{1/2} \right]^2 \phi_1 \phi_2 \quad (4)$$

where V_m = total volume of mixture (mL), ΔE = energy of vaporization of component 1 or 2 (cal), V = molar volume of component 1 or 2 (mL), ϕ = volume fraction of component 1 or 2 in the mixture (dimensionless).

The expression $(\Delta E/V)$ is termed energy of vaporization/mL or "cohesive energy density (CED), and it measures the concentration of forces which causes the molecules to cohere.

Equation (4) can be written

$$\frac{\Delta H_m}{V_m \phi_1 \phi_2} = \left[\left(\frac{\Delta E_1}{V_1} \right)^{1/2} - \left(\frac{\Delta E_2}{V_2} \right)^{1/2} \right]^2 \quad (5)$$

Hildebrand and Scott¹⁰ defined solubility parameter (δ) as

$$\delta = (\Delta E/V)^{1/2} \quad (6)$$

In this case, the right-hand expression becomes $(\delta_1 - \delta_2)^2$. The heat of mixing for the two substances is dependent on the square of the difference of the solubility parameters for the two components; when $(\delta_1 - \delta_2)^2 = 0$, i.e., $\delta_1^2 = \delta_2^2$, the two substances will be miscible.

In the case of copolymer swelling, δ_1 was assigned to the solubility parameter for the solvent system and δ_2 = the solubility parameter for the polymer.⁹

Alfrey and Lloyd⁹ found that $\delta_1 = \delta_2 \pm 0.8$ when a suitable solvent or mixtures are used as diluent medium to generate porous copolymers. In practice, the solvent or diluent mixture has a cohesive energy density (CED) of about 65–85 cal/mL.

Cohesive energy density can be calculated using the equation¹⁰

$$\text{CED} = (\Delta H - RT)/V = \delta^2 \quad (7)$$

where ΔH is the latent heat of vaporization, R the gas constant, T the absolute temperature, and V the molar volume.

The solvent-polymer interaction factor determines decisively the porous structure (pore internal distribution) of the networks.

The structure formation of the porous copolymers must be explained as the difference between the solvent-polymer interaction parameter values.⁷⁻⁹

In the last decade a large variety of porous networks were made for use as materials for ion exchangers, polymeric reagents, etc.¹¹

The paper deals with the study of the porous styrene-ethylstyrene-divinylbenzene copolymers, using cyclohexane, cyclohexanol, or cyclohexanone as diluent.

The parameter influence, as, for instance, the percent of DVB and the diluent volume, as well as the diluent kind in connection with the solvent-polymer interaction on the network porous structure is also studied and emphasized.

EXPERIMENTAL

Preparation of Porous Networks

Styrene and divinylbenzene were washed with a 5.0% NaOH aqueous solution, water, and vacuum distilled. Technical-grade DVB had the following chemical composition (by gas chromatography): 51.41% DVB, 45.00% ethylstyrene, and 3.59% nonpolymerizable compounds.

Because, ethylstyrene, which accompanies technical-grade DVB takes place in the copolymerization process yielding a ternary copolymer, which can be termed styrene-ethylstyrene-divinylbenzene copolymer. The second component (ethylstyrene) becomes dominant when high percents of the crosslinking agent are used.

The suspension copolymerization technique of the monomer mixture is used most frequently to obtain pearl-shaped networks.

The organic/water phase ratio throughout the experiments was 1:3 v/v.

The copolymerization process was run in a 1-L capacity flask, three necked, cylindrical shape, fitted with a variable mechanical stirrer, thermometer, and reflux condenser. A solution of styrene, DVB, and variable volumes of diluent (cyclohexane, cyclohexanol, or cyclohexanone) was poured into the flask which contained an aqueous solution of styrene-maleic anhydride copolymer ammonium salt (0.25-0.50%) and gelatin (0.0-0.15%).

The mixture of monomers and diluent was dispersed as fine droplets, and the copolymerization process was performed at 80°C, for about 20 h in a thermostated water bath. The copolymer beads were washed, sieved, dried, and then extracted with methanol in a Soxhlet apparatus.

Characterization of Copolymers

Porous networks were characterized from the physical point of view obtaining information concerning the influence of the diluent kind on the network structure. The copolymer beads were vacuum-dried at 50°C, for about 24 h, and the apparent densities (ρ_{ap}), solvent uptake coefficients, and surface area (S) were measured. Some magnitudes as the porosity (% P), pore volume (PV), volume swelling coefficients (B), and pore average diameter (\bar{D}), were calculated from the experimental measured data.

The apparent density (ρ_{ap}) was picnometrically measured,¹² and the surface area (S) was determined by the nitrogen-adsorption method¹³ on a Ströhlein AREA meter.

The solvent uptake coefficients (toluene, cyclohexane, and methanol) were determined using the centrifugation method of the swollen networks.¹⁴ The dried network samples were placed in metal tubes equipped with fritted bottom, which were sunk in the solvent for 48 h and then centrifuged.

The pore volume (PV) or the macroporosity of the copolymers was calculated using the equation^{12,15}

$$PV = \frac{1}{\rho_{ap}} - \frac{1}{\rho} \quad (\text{mL/g}) \quad (8)$$

where ρ_{ap} is the apparent density (g/mL) and ρ is the skeletal density (g/mL), determined by the picnometric technique in *n*-heptane.

The copolymer porosity (% P) was calculated according to the equation¹⁵

$$\% P = 100 \times (1 - \rho_{ap}/\rho) \quad (9)$$

and reflects the pore percent in the porous network.

The volume swelling coefficient (B) was calculated using Dusek's equation,¹⁶

$$B = \frac{\rho_{ap}}{\rho} + (W - 1) \times \frac{\rho_{ap}}{\rho_{solv}} \quad (\text{mL/mL}) \quad (10)$$

where ρ_{solv} is the solvent density ($\rho_{\text{toluene}} = 0.8669$ g/mL), W is the swollen copolymer weight/dried copolymer weight, and $W-1$ has the same meaning and value as the solvent uptake coefficient measured in toluene or another good solvent.

The pore average diameter size was calculated according to the equation

$$\bar{D} = \frac{4 \times PV}{S_{BET}} \times 10^4 \quad (\text{\AA}) \quad (11)$$

(the cylindrical model was assumed for the pore shape).

RESULTS AND DISCUSSION

Seidl et al.³ and Millar et al.¹⁷ have shown that porous networks are obtained when the percent of DVB and the diluent volume pass a critical value. The presence of an inert compound in the polymerizing system (for example, styrene and divinylbenzene) favors the formation of porosity. The volume as well as the diluent kind are the most important factors that influence the porosity and the heterogeneity of the networks, due to the solvent-polymer interaction, whose values are given in Table I.

Sederel and DeJong⁴ and Alfrey and Lloyd⁹ showed that proper pore size can be achieved using a mixture of two diluents. The mixture is usually composed of a good solvent for polymeric chains, leading to the small pores, while the second one is a poor solvent (precipitating agent) which contributes to larger pore formation.

The results concerning the influence of cyclohexane, cyclohexanol, or cyclohexanone on the porosity depending on DVB for the styrene-ethylstyrene-divinylbenzene copolymers are plotted in Figures 1-8.

TABLE I
Values of the Solvent-Polymer Interaction Parameters

Compound	δ_1	δ_2	CED ^a
Cyclohexane	7.81	—	61.00
Cyclohexanol	9.94	—	98.90
Cyclohexanone	9.90	—	98.01
Toluene ^b	8.90	—	79.21
Polystyrene	—	9.10	82.81
Polyvinylbenzene	—	8.80	77.44

^a Cohesive Energy Density.

^b Toluene was given as an example of good solvating diluent.

The diluents are characterized by differences in polarity, chemical structure (i.e., functional behavior) and solvent-polymer interaction values (see Table I) that will lead to networks with a large variety in porosity structure.

Cyclohexane and cyclohexanol are precipitating agents having CED quite different, while cyclohexanone is a good solvent for polystyrene. The influence of these compounds will be reflected in the network porous structure. δ and CED values of cyclohexanol and cyclohexanone are very close, though the diluents belong to two different kinds of solvents.

The diluent solubility in water phase is given in Table II.¹⁸ The solvents used by comparison with toluene are slightly soluble in water. Some of them give azeotropes with water, but it should be emphasized that the diluents were used together with large volumes of styrene and DVB, which were not miscible with water. In this case the distribution coefficients of the diluents between water and monomer phase are altered, and almost all quantity of diluent is dissolved in the monomer phase.

Because we deal with two kinds of diluents, it is imperative to mention that a perfectly nonsolvating system is not realizable, since the monomer mixture itself can solvate the chains of the macromolecules. During the polymerization process there is a mixture consisting of precipitating diluent and monomers that are solvating compounds of the polystyrene chains. The ratio between the precipitating and solvating compounds is changing during the copolymerization reaction. The system becomes richer in the precipitating diluent, and the separation phases occur. As the network chains form, they are no longer extended, as in the case where the diluent shows a high interaction with the copolymer;

TABLE II
Solubility of the Diluents in the Water Phase at 20°C

Diluent ¹⁸	Diluent % (w/w)	Water % (w/w)	Boiling point (°C)
Cyclohexane	91.60	8.40	68.95
Cyclohexanone	95.00	5.00	—
Cyclohexanol	94.00	6.00	—
	20.00	80.00	97.80
			(azeotrope)
Toluene		0.047	—
	80.40	19.60	84.10
			(azeotrope)

there is an increasing tendency for growing chains to entangle inside the virtually unswollen nuclei. The obtained structure, therefore, is one in which large entangled nuclei are connected by a relatively small number of coiled and crumpled intermolecular chains, and the polymer and diluent phases are segregated. The diluent-filled network can no longer be regarded as a swollen gel. This is the case when cyclohexane or cyclohexanol are used as diluents.

When the process develops in the presence of a good solvent (cyclohexanone), but otherwise inert diluent, the chains are at all times fully solvated, and thus, during the copolymerization reaction, less shrinkage occurs than in corresponding systems in the absence of a solvating agent. Therefore, the nuclei are less entangled, and with the increasing dilution the growing chains attain greater length.

The removal of diluent results in collapse of the expanded network to an extent depending on both the size of the nuclei and their separation. If the percents of DVB and the dilution (volume of cyclohexanone) are sufficiently high, the collapse phenomenon of the polystyrene chains in contact with the nuclei before all cyclohexanone has been removed yields a porous network.

The expanded network of macroporous materials, before the removal of cyclohexanone, may be regarded as solvent-swollen gels.

We must regard the influence of cyclohexanol, cyclohexane, or cyclohexanone together with the percent of DVB on the porosity formation of the styrene-ethylstyrene-divinylbenzene network.

Both the diluent and the percent of divinylbenzene influence the main characteristics of the networks.

Figures 1 and 2 show the diluent influence on the apparent densities of copolymers, for the different percents of DVB (10.0–50.0%).

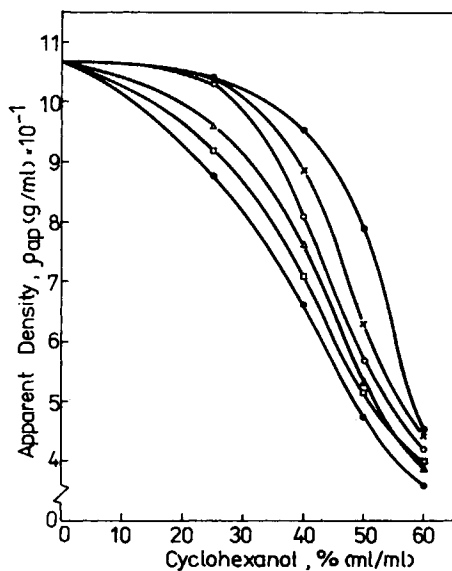


Fig. 1. The apparent density (ρ_{ap}) vs. cyclohexanol (%; v/v), for the styrene-divinylbenzene copolymers which contain different percentages of the crosslinking agent (DVB): (●) 10%; (×) 15%; (○) 20%; (Δ) 30%; (□) 40%; (⊙) 50%.

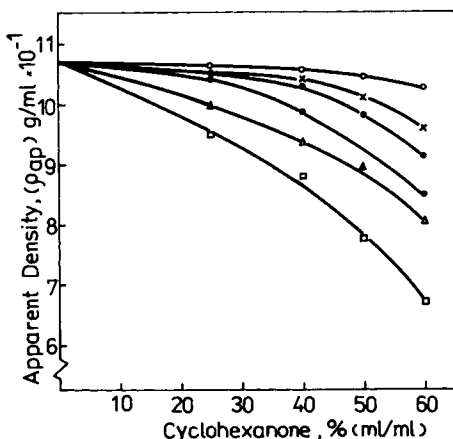


Fig. 2. The apparent density (ρ_{ap}) vs. cyclohexanone (%; v/v), for the styrene-divinylbenzene copolymers which contain different percentages of the crosslinking agent (DVB): (●) 10%; (×) 15%; (○) 20%; (◐) 30%; (△) 40%; (◻) 50%.

Cyclohexanol is a stronger precipitating diluent than cyclohexanone. For instance, the matrices prepared in the presence of cyclohexanol are more spongy than the one obtained using cyclohexanone, though the δ values are very close. The curve shapes are distinctly different, emphasizing the influence of the diluent because cyclohexanol behaves differently against the polystyrene segments when compared with cyclohexanone. Cyclohexanone is a good solvent for polymer chain solvation (polystyrene, $\bar{M}_w = 95,000$, is soluble in cyclohexanone).

The authors also carried out experiments in order to compare cyclohexanol and cyclohexanone with cyclohexane in network pore formation. We plotted the apparent densities vs. the percent of DVB together with the measured values for cyclohexanol and cyclohexanone (Fig. 3).

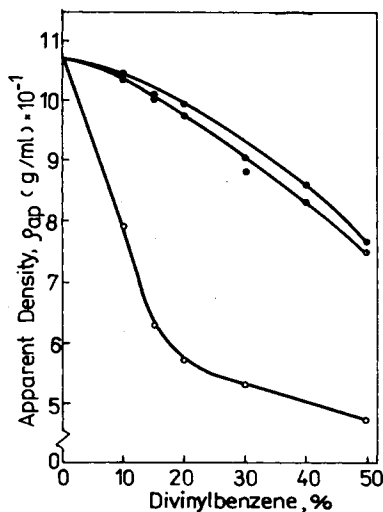


Fig. 3. The apparent density (ρ_{ap}) vs. divinylbenzene content (w/w) for the macroporous styrene-divinylbenzene copolymers prepared in the presence of 50% cyclohexane (●), cyclohexanol (○), or cyclohexanone (◐).

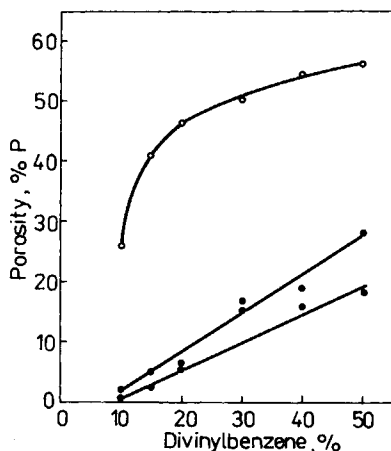


Fig. 4. The porosity (% P) vs. divinylbenzene content (w/w) for the macroporous styrene-divinylbenzene copolymers prepared in the presence of 50% cyclohexane (●), cyclohexanol (O), or cyclohexanone (⊙).

The use of cyclohexanol results in higher porous networks than those obtained in the presence of cyclohexane or cyclohexanone.

The apparent densities when cyclohexane or cyclohexanone are used are very close, though the CED values are quite different (see Table I). It is obvious that cyclohexanol is the most powerful precipitant diluent, allowing preparation of macroporous networks with a lower divinylbenzene percent (for instance, a 15% DVB network, $\rho_{ap} = 0.6300$ g/mL, and 10% DVB one, $\rho_{ap} = 0.7900$ g/mL).

The network porosity (% P), for the porous copolymers prepared in the presence of the above diluents and the data, were plotted vs. the percent of DVB (Fig. 4).

Cyclohexanol proved to be a strong precipitant diluent by comparison with cyclohexane or cyclohexanone (Fig. 4). In this case, there is also a small difference between the last two diluents. The porosity of the networks, carried out in the presence of cyclohexane, varies according to a straight line. Based on these results related to the network porosity, we researched the copolymer porosity development in the case of cyclohexanol. The degree of monomer dilution has a positive influence (Fig. 5) on the porosity. The diluent volume was kept constant throughout the experiments while the percent of DVB was changed (Fig. 5). In view of the cyclohexanol volume of 25.0% and 60.0%, the porosity variation develops according to a straight line (Fig. 5). The macroporous copolymer porosity for the rest of the experiments evolves beginning with 20.0% DVB.

It is, therefore, possible to predict the porosity of the network, choosing the best percent of DVB and the diluent volume of cyclohexanol, resulting in a network with good physical stability and high porosity. It is possible to prepare low crosslinked copolymers with high porosity (Fig. 5).

The styrene-DVB copolymers swell in good solvents (swelling diluents), and the degree of swelling depends on the crosslinking percent. The macroporous networks have, besides the permanent porosity (in the dry state), a swelling porosity whose magnitude depends on the diluent kind used for monomer dilution. Therefore, the macroporous copolymers employed as packing chromato-

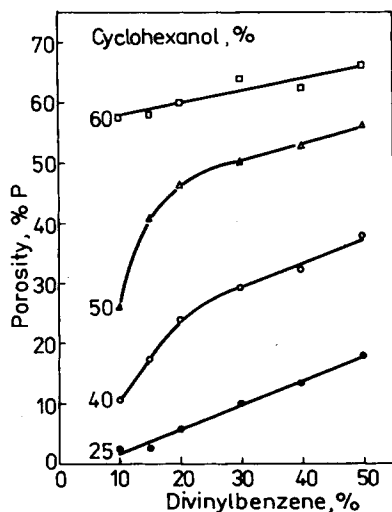


Fig. 5. The porosity (% P) vs. divinylbenzene content (%) for the styrene-divinylbenzene copolymers prepared in the presence of the variable amount of cyclohexanol.

graphic materials will swell in good solvents working with a higher porosity. The swelling porosity could be avoided (minimized) if a large divinylbenzene percent (DVB > 40.0%) had been used in the copolymerization process. But the experimental results did not prove that assumption (Fig. 6).

The network with 50.0% DVB has a significant volume swelling coefficient (*B*), which depends on the kind and volume of diluent as well as the percent of DVB. The percent of DVB influences the volume swelling coefficient up to 20.0% DVB for cyclohexane and cyclohexanol, while it is almost constant for cyclohexanone (Fig. 6).

The macroporous highly crosslinked copolymer still swells in good solvents (toluene, etc.), due to the behavior of DVB.¹⁹ When a mixture of styrene and

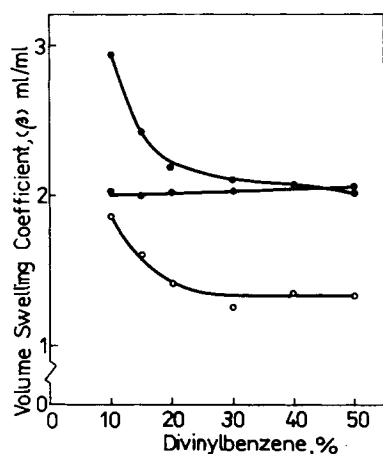


Fig. 6. The volume swelling coefficient (*B*) vs. divinylbenzene (%) for the macroporous styrene-divinylbenzene copolymers prepared in the presence of 50% cyclohexane (●), cyclohexanol (○), or cyclohexanone (⊙).

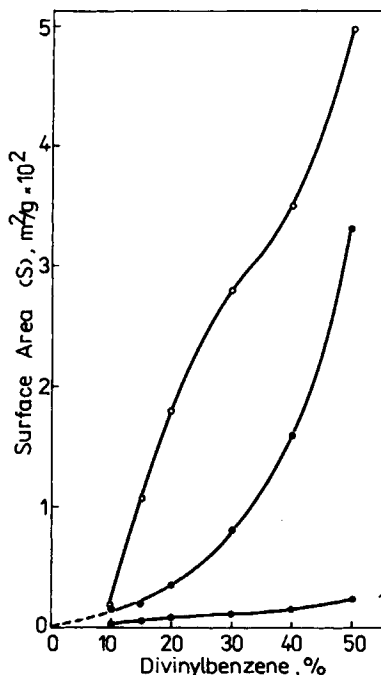


Fig. 7. The surface area (S) as a function of the divinylbenzene percentage for the macroporous networks prepared in the presence of 50% cyclohexane (●), cyclohexanol (○), or cyclohexanone (⊙).

DVB is too low, conversions in the matrix will be richer in crosslinking agent than the monomer mixture. But, in the case of the last part of the copolymerization process, this monomer mixture is always richer in styrene, and the densely crosslinked microparticles are covered and there is less crosslinking.

The styrene-divinylbenzene copolymers, spongy networks, are implicitly characterized by the surface area (S) and the average pore diameter (\bar{D}) (Fig. 7). The average diameter was calculated according to eq. (4).

Seidl et al.³ have shown that the magnitude of the surface area depends on the diluent kind, i.e., its solvent-polymer interaction parameter (δ). The curves clearly show how the differences between the three diluents influence the surface area magnitude (Fig. 7) and, consequently, the average pore diameter (\bar{D}) of the networks.

The above diluents belong to the precipitant and solvating compounds. Cyclohexane and cyclohexanol give networks with higher surface area than cyclohexanone, but between them there is a difference as a consequence of the CED values, or δ parameter, respectively (see Table I).

Cyclohexanone, which is a solvating diluent, behaves entirely differently by comparison with toluene. This difference consists of the fact that the highly crosslinked macroporous copolymers performed in the presence of toluene are characterized by high values of the surface area (small average pore diameter) while the networks prepared in the presence of cyclohexanone have low values of the surface area (large average pore diameter) (Figs. 7 and 8).

We assume that this peculiar behavior causes the CED value differences. For

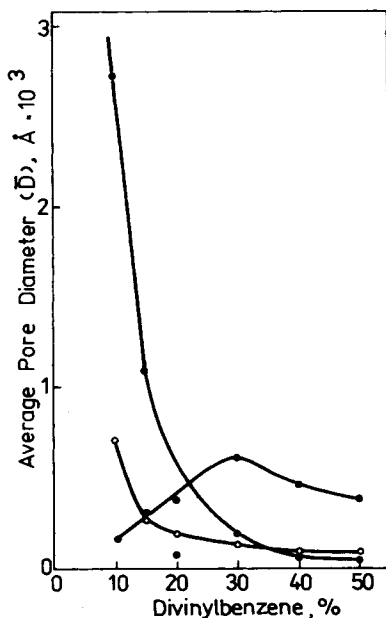


Fig. 8. The average pore diameter (\bar{D}) as a function of the divinylbenzene percentage for the macroporous networks prepared in the presence of 50% cyclohexane (●), cyclohexanol (○), or cyclohexanone (⊙).

instance, in the 50.0% DVB and 50.0% monomer mixture dilution, the measured surface area values of the performed networks are 490.0 m²/g (cyclohexanol), 332.0 m²/g (cyclohexane), and 280.0 m²/g (cyclohexanone), respectively (Fig. 7).

The average pore diameters show large differences for low percents of DVB, while the copolymers are more homogeneous when cyclohexane and cyclohexanol are used as diluents (Fig. 8).

Also, the networks performed in the presence of cyclohexanone and whose percents of DVB vary from 10.0% to 50.0% DVB do not show significant modifications in the surface area values (Fig. 8). The average pore diameter shows a maximum at about 30.0% DVB (609 Å), and then it decreases to 387 Å for 50.0% DVB (Fig. 8).

The average pore diameter variation curves for cyclohexane have the same shape, but they differ in size. The largest average pore diameter measured for cyclohexane was about 2700 Å (10.0% DVB and 50.0% diluent) (Fig. 8).

CONCLUSIONS

The best diluent was cyclohexanol, because it favored the highest porosity formation. It was also possible to perform porous networks at low percents of DVB using cyclohexanol.

Cyclohexanone, although it is a solvating diluent, differs from toluene. The networks were characterized by low surface area values. The differences in behavior of cyclohexanone and toluene might result in the δ factor and CED values. The same explanation is also valid for cyclohexane and cyclohexanol.

The percent of DVB and the volume of the diluent also strongly influence the network porosity.

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