Cosolvency effects of benzyl alcohol and heptane on the formation of macroporous styrene-divinylbenzene copolymers

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SUMMARY

Styrene-divinylbenzene copolymers were synthesized by suspension polymerization in the presence of benzyl alcohol (BA) and heptane (Hep). The influence of BA/Hep ratio, dilution degree and DVB content on the formation of porous structure and swelling of the copolymers were investigated. The results were interpreted according to the solubility parameter theory.

INTRODUCTION

Preparation of porous styrene–divinylbenzene (Sty-DVB) copolymer beads has received considerable attention in the last 30 years [1,2]. Porous Sty-DVB copolymers have been synthesized by suspension polymerization of the monomers in the presence of an inert (non-polymerizable) diluent. The inert diluent may remain in the network (gel) phase throughout the copolymerization producing expanded networks, or may separate out of the network phase resulting in the formation of porous copolymers. The distribution of the diluent between network and diluent phases at the end of the copolymerization depends on the nature and amount of diluent as well as on the crosslinking degree [3]. In previous papers [4-6], it had been found that a diluent which is a good solvent for the polystyrene chains produces expanded networks, micropores which collapse upon diluent removal, or small fixed pores, depending on the dilution degree and DVB content. By contrast, poor solvents produce rather larger fixed pores and polymeric nuclei with smaller swelling capacity than a good solvent [6]. The proper pore size can be achieved by using mixtures of good and bad solvents. The increasing of the good solvent proportion in the diluent mixture reduces the pore size and the total porosity. The porous characteristics of the copolymers are controlled by the polymer-solvent interactions which determine the distribution of the diluent between the network and diluent phases as well as the size and distribution of the two phases inside the copolymer beads [3-8].

The thermodynamic description of polymer-solvent mixing is given by the equation I [9]:

$$\Delta G = \Delta H - T\Delta S \qquad (I)$$

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where ΔG is the change in free energy of mixing, ΔH is the change in enthalpy of mixing, T is the absolute temperature and ΔS is the change in entropy of mixing. A negative ΔG predicts that the solution process will occur spontaneously. Since the value of ΔS in a solution process is always positive, the magnitude of the enthalpy term is the deciding factor in determining the sign of the free energy change. The ΔH term can be written as [9]:

$$\Delta H = V_m \, (\delta_1 - \delta_2)^2 \, \phi_1 \, \phi_2 \qquad (II)$$

where, V_m is the molar volume of the solvent (cm^3), ϕ_1 and ϕ_2 are the volume fractions, δ_1 and δ_2 are the solubility parameters of solvent and polymer $(cal/cm^3)^{1/2}$, respectively. The solubility of a polymer in a given solvent is favored when the ΔH term is minimized, i.e., the best solvent for a polymer is one whose solubility parameter is equal or close to the solubility parameter of the polymer $(\delta_1 \simeq \delta_2)$. In a general way, when $\delta_1 - \delta_2 > 1.7$, the miscibility between the polymer and the solvent does not occur. The solubility parameters are useful to predict the formation of porous structures of Sty-DVB copolymers synthesized in the presence of different pure diluents or their mixtures [10-12]. In the case of diluent mixtures, the solubility parameter (δ_{mix}) can be considered as an average value of the δ parameters of the pure diluents. δ_{mix} is given by equation III [9, 11]:

$$\delta_{mix} = \frac{x_1 \, V_1 \, \delta_1 + x_2 \, V_2 \, \delta_2}{x_1 \, V_1 + x_2 \, V_2} \qquad (III)$$

where x_1 and x_2 are molar fractions of the components 1 and 2, V_1 and V_2 are molar volumes of components 1 and 2, and δ_1 and δ_2 are solubility parameters of components 1 and 2. Therefore, a poor solvent can be mixed with a good one yielding a mixture with a δ value suitable to obtain a Sty-DVB copolymer with a more uniform porosity.

This paper deals with the influence of a non-solvating diluent, the δ value of which is higher than that of the copolymer, in mixture with a non-solvating one, the δ value of which is smaller than that of the copolymer, on the formation of copolymer porous structure. The influence of the dilution degree and DVB content was also investigated for different diluent mixtures.

EXPERIMENTAL

Sty-DVB copolymers were synthesized by suspension polymerization in the presence of benzyl alcohol (BA) and heptane (Hep) and purified as previously described [4]. The dilution degrees were expressed as volume percent in relation to the total volume of the monomers. The DVB contents were expressed as molar percents in relation to 0.3 mol of styrene.

The copolymer samples were characterized by the apparent densities (d_{ap}), the fixed pore volumes (V_p), the toluene (Tol) and heptane (Hep) uptake coefficients, the surface area (S), the integral pore size distributions, and the average pore diameter $(\bar{D})$ according to methods previously presented [6,13].

RESULTS AND DISCUSSION

The solubility parameters of BA, Hep and Sty–DVB copolymers are 12.1, 7.4 and 9.1 $(cal/cm^3)^{1/2}$, respectively [14]. Table 1 presents the properties of the Sty–DVB copolymers prepared in presence of pure BA, pure Hep and their mixtures.

Influence of diluent composition

As expected, the pure diluents, BA and Hep, produced macroporous copolymers with rather high porosities ($V_p > 0.20$ cm^3/g). Mixtures of BA with Hep produced copolymers with smaller porosity than those with pure diluents. When the diluent composition was changed by a gradual replacing of BA for Hep, the copolymer porosity decreased until a minimum and after that it began to increase. The apparent density (d_{ap}) value was maximum and the V_p was minimum at BA/Hep = 45/55 (Table 1). This behavior can be explained by the solubility parameter theory.

Hep has a smaller δ (7.4) and BA has a higher δ (12.1) than the δ of Sty–DVB (9.1). In this case, the average δ of a given diluent mixture is closer to the δ of the copolymer than that of the pure diluents. When the δ of the diluent is closer to the δ of the copolymer, miscibility improves, i.e., during the copolymerization the diluent remains in the network phase. Thus, the best solvent system was the mixture with BA/Hep = 45/55 whose δ (9.5) is the closest to the δ of the copolymer (Figure 1).
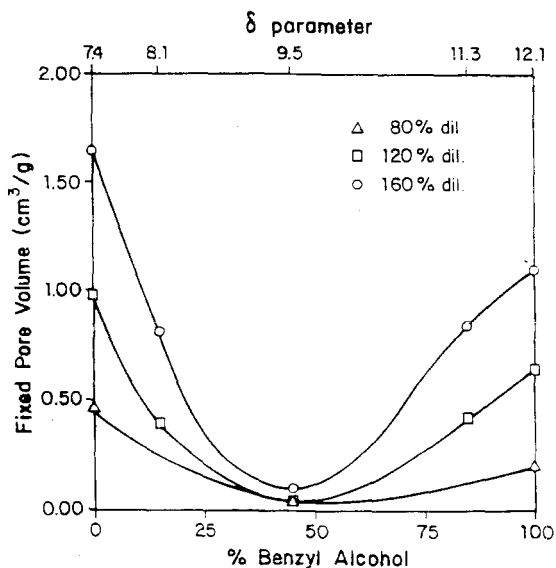

Figure 1 – Influence of composition and solubility parameter of the BA/Hep mixtures on the fixed pore volumes of Sty–DVB copolymers

Table 1 – Characteristics of the Sty-DVB copolymers prepared with Benzyl
Alcohol (BA) and Heptane (Hep) as diluents

DVB (%)	Dilution (%)	BA/Hep ratio V/V (%)	d_{ap} (g/cm^3)	S (m^2/g)	$\overline{D}$ (Å)	Solvent Uptake (cm^3/g)		
						Tol	Hep	Water
15	120	100/0	0.53	nd	nd	1.46	0.64	0.21
15	120	45/55	0.59	0	nd	1.36	0.03	0.01
15	120	0/100	0.40	43	540	2.04	1.21	0.58
30	80	100/0	0.50	nd	nd	0.91	0.60	0.21
30	80	45/55	0.63	nd	nd	0.80	0.26	0.06
30	80	15/85	0.60	nd	nd	0.98	0.54	nd
30	80	0/100	0.42	nd	nd	1.11	0.88	0.47
30	120	100/0	0.35	110	236	1.48	1.10	0.65
30	120	85/15	0.42	132	130	1.28	0.91	0.43
30	120	45/55	0.59	0	nd	1.19	0.67	0.07
30	120	15/85	0.44	147	109	1.35	1.01	0.40
30	120	0/100	0.32	68	582	1.91	1.57	0.99
30	160	100/0	0.25	106	419	1.93	1.64	1.11
30	160	85/15	0.29	nd	nd	1.89	1.59	0.85
30	160	45/55	0.48	0	nd	1.55	0.88	0.10
30	160	15/85	0.33	82	400	1.93	1.49	0.82
30	160	0/100	0.22	92	713	3.06	2.70	1.64
40	120	100/0	0.33	104	273	1.45	1.23	0.71
40	120	45/55	1.57	0	nd	0.98	0.72	0.06
40	120	0/100	0.31	107	366	2.02	1.75	0.98

(*) water uptake = fixed pore volume
    nd = not determined

An increase in the solvating power of the diluent reduces the sizes of
the diluent and network phases, and yields a more regular porous
structure (4). In a general way, the average pore diameter ($\overline{D}$) of the
copolymers decreased when δ of the diluent mixture was closer to the δ
of the copolymer. The mixture BA/Hep = 45/55 produced very small pores
which probably collapsed upon diluent removal (surface area S $\simeq$ 0 and V_p
< 0.10 cm^3/g). The addition of small amounts of BA to Hep or vice-versa
enhanced the surface area and diminished $\overline{D}$ in relation to the pure
diluents (Table 1). That effect on the pore size distribution determined
by mercury porosimetry is also shown in Figure 2.

When the copolymer is synthesized in the presence of a good solvent the
polymer chains are more expanded and less entangled than when the
copolymer is obtained in the presence of a bad solvent (1,6). Thus, the
increase of the solvating power of the diluent enhances the swelling
capacity of the network structure. The toluene (Tol) uptake of

copolymers decreased as the V_p diminished, i.e., the solvating power of the diluent increased. Tol uptake may be considered as a result of three contributions: filling of fixed pores, expansion of fixed pores, and swelling of polymer nuclei (1,6). Therefore the copolymer prepared with poor solvents presented higher Tol uptakes due to a greater contribution of the filling of the fixed pores. As expected, the heptane (Hep) uptakes also diminished as the pore volumes decreased. However, Hep cannot swell the network like toluene so that Hep uptake is a result of only two contributions: filling of fixed pores and expansion of fixed pores. The latter contribution is shown in Table 1 where the Hep uptakes for practically all obtained copolymers is greater than the fixed pore volumes. The difference between Tol and Hep uptake may be a measure of nuclei swelling. Figure 3 shows the influence of diluent composition on network swelling. When δ of the diluent became closer to the δ of the copolymer, network swelling increased, what shows that the polymer chains were more expanded when the solvating power of the diluent increased.
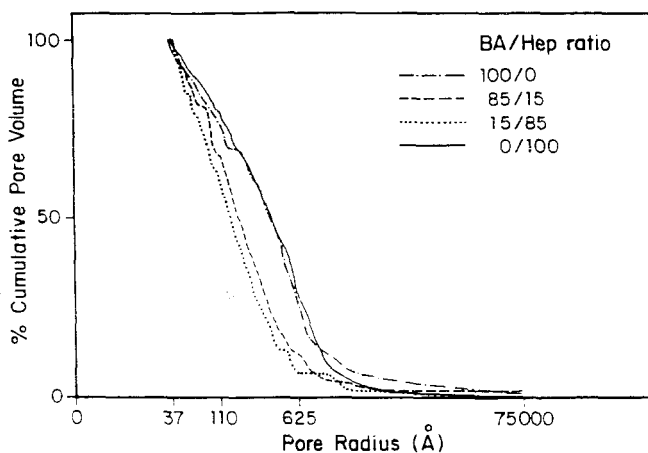

Figure 2 - Integral pore size distribution of Sty-DVB copolymers prepared in presence of diluent with different BA/Hep ratios

Influence of dilution degree

The increase of the dilution degree of the monomers enhanced V_p for all BA/Hep ratios, except for the 45/55 which practically did not change with the dilution (Figure 1). In general the effect of dilution on the formation of macropores for a good solvent is smaller than the effect of dilution for a bad solvent (4-6). The diluent mixture with the closest δ to the δ of the copolymer presented the smallest dilution effect on the

fixed pore volume (Figure 1). At BA/Hep = 45/55, the increase of dilution produced copolymers with increasing Hep uptakes, although V_P remained almost constant (Table 1). Therefore, the increase of dilution also favors phase separation, however, when the diluent is a good solvent, collapsed micropores are formed.
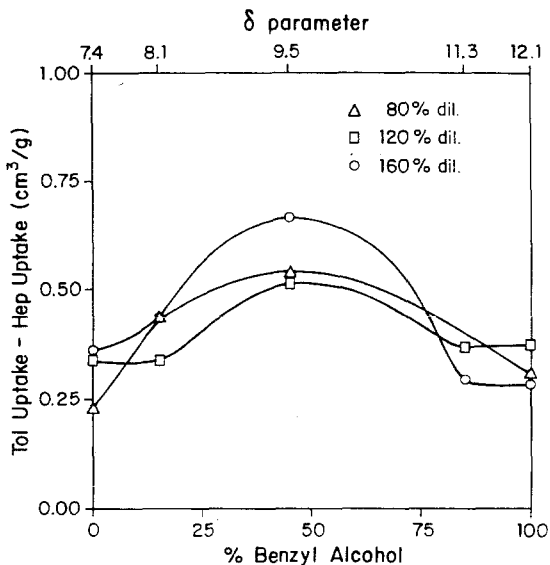

Figure 3 - Influence of composition and solubility parameter of the BA/Hep mixtures on the polymeric nuclei swelling of Sty-DVB copolymer

For a solvating diluent, the higher the dilution the more expanded the network, whereas for a poor solvent the increase of dilution enhances the precipitation so that the swelling of nuclei diminish or do not change (6). In a general way, the increase of dilution by the BA/Hep systems did not produce large modifications of swelling of the network. The solvating diluent mixture of BA/Hep = 45/55 presented a small increase of the nuclei swelling with enhanced dilution. In comparison with a good solvent such as Tol, the cosolvent mixture of BA and Hep presents a lower affinity to the polystyrene chains, although both diluent systems have produced small fixed pore volumes. According to ref. (6), as dilution with pure Tol increased from 60 to 200%, swelling increased 2.4 times. In contrast, as dilution with the BA/Hep mixture increased from 80 to 160%, the swelling increased only 1.2 times. Under the same conditions of dilution and degree of crosslinking Tol produced more expanded networks than the BA/Hep mixture.

Influence of DVB content

The increase of DVB content either enhanced the fixed pore volume or did not affect total porosity. The pure diluents, BA or Hep, produced macroporous structures even at 15% of DVB. By contrast, the mixture BA/Hep = 45/55, at the same crosslinking degree, produced expanded networks. Hep uptakes of the copolymers prepared in the presence of the cosolvent mixture increased with DVB content, although the fixed pore volume practically did not change. As the effect of dilution increased, the higher crosslinking degrees promoted phase separation. However, the solvating diluent mixture produced rather collapsed micropores.

The increase of the DVB content diminished swelling of networks prepared in the presence of all diluent systems. At a high crosslinking degree the nuclei swelling tends to be independent of the solvating power of the diluent used in copolymer synthesis (Figure 4). The effect of DVB content on swelling was also observed with mixed diluents of Tol and Hep [6].
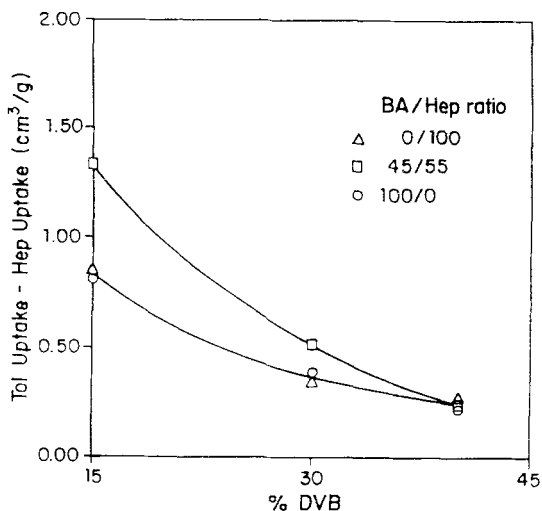
Figure 4 - Influence of DVB content on the polymeric nuclei swelling of Sty-DVB copolymers

REFERENCES

1. Millar, J.R.; Smith, D.G.; Marr, W.E.; Kressman, T.R.E.; J. Chem. Soc., 218(1963).

2. Okay, O.; Angew. Makromol. Chem., 157, 1(1988).

3. Sederel, W.L.; De Jong, G.J.; J. Appl. Polym. Sci., 17, 2835(1973).

4. Coutinho, F.M.B.; Rabelo, D.; Eur. Polym. J., 28, 1553(1992).

5. Coutinho, F.M.B.; Rabelo, D.; Polímeros Ciência e Tecnologia, II(4), 34(1992).

6. Rabelo, D.; Coutinho, F.M.B.; Eur. Polym. J., submitted.

7. Coutinho, F.M.B.; Cid, R.C.A.; Eur. Polym. J., 26, 1185(1990).

8. Coutinho, F.M.B.; Siqueira, M.I.N., Barbosa, C.R.; Eur. Polym. J., 26, 1189(1990).

9. Rabec, J.F.; "Experimental Methods in Polymer Chemistry", John Wiley & Sons, New York (1980).

10. Poinescu, Ig. C.; Beldie, C.; Vlad, C.; J. Appl. Polym. sci., 29, 23(1984).

11. Poinescu, Ig. C.; Beldie, C.; Angew., Makromol. Chem. 164, 45(1988).

12. Coutinho, F.M.B.; Rabelo, D.; Revista Iberoamericana de Polímeros, in press.

13. Rabelo, D.; Coutinho. F.M.B.; Polym. Bull., in press.

14. Brandrup, J., Immergut, E.H., Eds.; Polymer Handbook, 2nd. ed., Wiley, New York, 1975.