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Structure and properties of styrene-divinylbenzene copolymers

III. Mixtures of different diluents with alcohols as pore forming agents

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ABSTRACT

The influence of binary mixtures of alcohols with different diluents on the porous structure of styrene-divinylbenzene (Sty-DVB) copolymers was investigated. Two series of binary mixtures were tested: one with isoamyl alcohol (i-AmA) and another with benzyl alcohol (BA). For systems containing i-AmA, the hydrogen bonds between alcohol and polar solvent molecules exert strong precipitating effects. Copolymers prepared with polar solvent/i-AmA presented higher porosities than copolymers obtained in presence of nonpolar solvent/i-AmA. Binary mixtures with i-AmA produced more porous and rigid networks than with BA.

INTRODUCTION

In the previous papers of this series, we have presented the effects of pure diluents and binary mixtures of heptane with different diluents on the porous structure and swelling properties of Sty-DVB copolymers (1,2). For the pure diluents, the copolymer porosities can be reasonably predicted by three-dimensional solubility parameters when molar volume effects are not important. In the case of diluent mixtures, we have suggested that the porous structure depends not only on the affinity of each diluent for the copolymer but also on the interaction of the diluents with themselves. Specific interactions between the diluents besides of molecular orientation can explain the cosolvency effects observed with polar aromatic solvent/heptane systems and the weaker precipitating effect of heptane in presence of polar solvents. These results show that weak and moderate interactions (dispersion forces and dipole-dipole interactions) between the diluents affect the solvating power of binary diluent mixtures. Therefore, we expect that strong interactions like hydrogen bonding will exert an important role on the solvating power of binary diluent mixtures.

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In this work, we have investigated the effect of the solvating power of binary mixtures of alcohols with different diluents on the porosity and swelling of Sty-DVB copolymers.

EXPERIMENTAL

Two series of binary mixtures were tested as pore forming agents: one with isoamyl alcohol (i-AmA) and another one with benzyl alcohol (BA). The diluents combined with the alcohols were: acetophenone (ACP), decalin (Dec), toluene (Tol), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), di-2-ethylhexyl phthalate (DOP), heptane (Hep), ethyl acetate (EtAc), butyl acetate (BuAc), isoamyl acetate (i-AmAc) and methylisobutylketone (MIBK).

The Sty-DVB copolymers were prepared by suspension polymerization and purified as described **(3)**. The copolymers were characterized by apparent density (d_{ap}), fixed pore volume (V_{fp}), toluene uptake (U_{Tol}) and heptane uptake (U_{Hep}) according to methods previously described **(4,5)**.

RESULTS AND DISCUSSION

The polymer-diluent distances (D_o) in the three-dimensional solubility parameter diagram for the diluent mixtures were calculated as shown in references 1 and 2. Table 1 shows the characteristics of Sty-DVB copolymers prepared in presence of the binary mixtures of i-AmA with different diluents. For these mixtures, the porosity cannot be predicted by D_o values. Hydrogen bonding between the diluent molecules seems to determine the degree of phase separation during polymerization.

Hep is a worse solvent than acetates and phthalates **(1)**. However, Hep/i-AmA was a better solvent mixture than acetate/i-AmA and phthalate/i-AmA mixtures. In general, the nonpolar solvents (Dec, Tol, Hep) mixed with i-AmA produced smaller fixed pore volumes (V_{fp}) than polar solvents (acetates, ketones and phthalates). Probably, the hydrogen bonds between i-AmA and polar solvents were responsible for the phase separation. That also explains why polar solvent/i-AmA mixtures produced much higher V_{fp} than polar solvent/Hep mixtures (ACP/i-AmA - V_{fp} = 0.61 and ACP/Hep - V_{fp} = 0.04; EtAc/i-AmA - V_{fp} = = 0.77 and EtAc/Hep - V_{fp} = 0.32; DEP/i-AmA - V_{fp} = 0.92 and DEP/Hep - V_{fp} = 0.16) **(2)**.

Table 2 shows the characteristics of Sty-DVB copolymers prepared in the presence of binary mixtures of BA with different diluents. BA mixed with nonpolar solvents (Tol, Dec), also produced smaller V_{fp} than BA mixed with polar solvents (acetates, DEP). Hydrogen bonding between BA and polar solvents probably promoted phase separation. In contrast to systems containing i-AmA, hydrogen bonding in systems containing BA does not cause significant precipitations. Acetate/BA mixtures produced smaller V_{fp} than acetate/Hep mixtures (EtAc/BA = V_{fp} = 0.23 and EtAc/Hep - V_{fp} = 0.32; i-AmAc/BA - V_{fp} = 0.32 and i-AmAc/Hep - V_{fp} = 0.43). In general, binary mixtures with BA were better solvents than those with i-AmA.

TABLE 1 - Characteristics of Sty-DVB copolymers synthesized in presence of mixtures of different diluents with isoamyl alcohol - 120% dil. and 15% DVB

Diluent mixtures	D_o ($MPA^{1/2}$)	d_a (g/cm^3)	V_{fp} (cm^3/g)	U_{Tol} (cm^3/g)	U_{Hep} (cm^3/g)	$U_{Tol}-U_{Hep}$ (cm^3/g)	V_{ap}^*/V_f
ACP/i-AmA	10.8	0.38	0.61	1.41	1.11	0.30	1.8
Dec/i-AmA	11.2	0.43	0.37	1.30	0.91	0.39	2.5
Tol/i-AmA	11.7	0.48	0.26	1.18	0.92	0.26	3.5
DIBP/i-AmA	12.3	0.36	0.57	1.38	1.05	0.33	1.6
DEP/i-AmA	12.7	0.32	0.92	1.74	1.33	0.41	1.4
DOP/i-AmA	12.8	0.27	0.95	1.70	1.40	0.30	1.5
Hep/i-AmA	13.9	0.36	0.58	1.48	1.15	0.33	2.0
BA/i-AmA	14.0	0.32	0.77	1.48	1.18	0.30	1.5
BuAc/i-AmA	14.1	0.33	0.78	1.47	1.20	0.27	1.5
EtAc/i-AmA	14.5	0.33	0.72	1.46	1.15	0.31	1.6
i-AmAc/i-AmA	14.7	0.34	0.77	1.57	1.27	0.30	1.6
MIBK/i-AmA	15.0	0.32	0.90	1.57	1.30	0.27	1.4

(*) V_{ap} = accessible pore volume = U_{Hep} .

TABLE 2 - Characteristics of Sty-DVB copolymers synthesized in presence of mixtures of different diluents with benzyl alcohol - 120% dil. and 15% DVB

Diluent mixtures	D_o ($MPA^{1/2}$)	d_a (g/cm^3)	V_{fp} (cm^3/g)	U_{Tol} (cm^3/g)	U_{Hep} (cm^3/g)	$U_{Tol}-U_{Hep}$ (cm^3/g)	V_{ap}^*/V_f
Dec/BA	7.0	0.60	0.09	1.05	0.69	0.36	7.7
Tol/BA	7.6	0.52	0.08	1.19	1.18	1.01	2.3
DEP/BA	8.7	0.35	0.66	1.56	1.13	0.43	1.7
BuAc/BA	10.2	0.48	0.32	1.25	0.88	0.37	2.8
EtAc/BA	10.5	0.49	0.23	1.21	1.72	0.49	3.1
i-AmAc/BA	10.8	0.48	0.32	1.37	1.85	0.52	2.7

(*) V_{ap} = accessible pore volume = U_{Hep} .

The copolymers prepared with binary mixtures containing i-AmA presented small $U_{Tol}-U_{Hep}$ differences, i.e., low nuclei swelling. Due to the low solvating power of these diluent mixtures, the nuclear chains showed a tendency to coil and entangle during the polymerization (6).

The elasticity of internuclear chains can be measured by the V_{ap}/V_{fp} ratios. The higher the V_{ap}/V_{fp} ratio, the more elastic are the chains. Copolymers prepared with nonpolar solvent/i-AmA mixtures led to more elastic chains than copolymers prepared with polar solvent/i-AmA mixtures. The hydrogen bonding between i-AmA and polar solvents promoted the formation of more rigid structures (Table 1).

Copolymers prepared with binary mixtures containing BA showded more swelling and more elastic internuclear chains than copolymers prepared with binary mixtures containing i-AmA.

Our results show that the diluent-copolymer affinity determines the total porosity, the pore size distribution and rigidity of macroporous Sty-DVB copolymers. The solvating power of diluent mixtures depends not only on the affinity of each diluent for the copolymers but also on the interaction of the diluent molecules with themselves. Hydrogen bonding between diluent molecules leads to precipitation during polymerization.

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