Structure and properties of styrene-divinylbenzene copolymers

I. Pure solvents as pore forming agents

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ABSTRACT

The effects of the solvating power of pure diluents on the porous
structure and swelling properties of styrene-divinylbenzene
(Sty-DVB) copolymers were investigated. The Hildebrand solubility
parameter (δ) and the three-dimensional solubility parameter (δ_T) were
used to predict the diluent-polymer affinity. In a general way, δ_T was a
better predictor than δ. It was found that the accessibility of polymer
surfaces depends not only on the fixed pore volume but also on the
elasticity of internuclear chains.

INTRODUCTION

The most important factors which control the heterogeneity of the
macroporous network polymers are the type and amount of diluent as well
as the crosslinking density (1). Solvating diluents, generally, produce
small pore while nonsolvating ones produce large pores. Therefore, the
polymer-solvent interaction is the main factor in determining the pore
size distribution (2). The thermodynamic affinity of the diluent for the
copolymer can be predicted by the knowledge of their solubility
parameters. The solubility parameter theory has been applied in many
papers to explain the porous structure patterns and the swelling
properties of macroporous network polymers synthesized in the presence
of different diluent systems (2-6).

Let δ_1 and δ_2 be the solubility parameters of the diluent and polymer,
respectively. When $|\delta_1-\delta_2| \simeq 0$, miscibility is favoured, i.e., the
diluent is a good solvent which produces expanded network gels or small
pores. In general, when $|\delta_1-\delta_2| > 3.0$ $(MPa)^{1/2}$, miscibility does not
occur spontaneously so that the diluent separates out the polymer phase
producing rather large pores (7).

The solubility parameter theory has been developed for mixtures of
nonpolar substances. Some deviations in its predictions should be
expected when the diluent and polymer are polar, i.e., have dipole

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moments and/or capabilities for hydrogen bonding. Hansen (8) proposed an extension of the Hildebrand theory dividing the solubility parameter into contributions from dispersive (δ_d), dipolar (δ_p) and hydrogen-bond (δ_h) interactions and represented δ as:

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (I)$$

which may be taken as a vector sum. In a three-dimensional diagram with δ_d, δ_p and δ_h as coordinates, a given liquid or polymer is represented by a point. Around the polymer point (δ_{2d}, δ_{2p}, δ_{2h}), a sphere can be constructed so that any liquid characterized by a point lying within the sphere is a solvent for the polymer, while one lying outside the sphere is a nonsolvent. In the diagrams, the unit length on the axis represented by δ_d is twice the unit length used for δ_p and δ_h. Thus, polymer-diluent distances (D_o) which predict the solvent power are given by (9):

$$D_o = \left[4 \, (\delta_{1d} - \delta_{2d})^2 + (\delta_{1p} - \delta_{2p})^2 + \delta_{1h} - \delta_{2h})^2 \right]^{1/2} \qquad (II)$$

where δ_{1i} and δ_{2i} (i = d, p, h) represent the coordinates of diluent and polymer, respectively. The radius of the sphere, R_o, has to be determined experimentally.

In this work, the influence of diluent-polymer affinity on pore structure formation and swelling properties of Sty-DVB copolymers was investigated. The predictions of the solvating power of different pure diluents using Hildebrand and three-dimensional solubility parameters were compared with the experimental results.

EXPERIMENTAL

Sty-DVB copolymers were synthesized by suspension polymerization in the presence of different diluent systems and purified as previously described (10). The degrees of dilution employed were 120 and 200% in relation to the total volume of monomers. The DVB content was approximatively 15% in relation to the monomer weight. The crosslinking degree was chosen such that a diluent with a medium solvating power at 120 and 200% dilution produces a macroporous network.

The copolymer samples were characterized by apparent densities (d_a), fixed pore volumes (V_{fp}), surface areas (S), average pore diameters ($\overline{D}$), toluene uptakes (U_{Tol}), and heptane uptakes (U_{Hep}) according to methods previously described (11, 12).

RESULTS AND DISCUSSION

Table 1 shows the Hildebrand solubility parameters, the coordinates of three-dimensional solubility parameters and the molar volumes of the diluents used in copolymer synthesis. In order to simplify the relation between the solvating power of the diluent and characteristics of Sty-DVB copolymers, the predictions using Hildebrand and three-dimensional solubility parameters will be discussed separately.

TABLE 1 - Hildebrand solubility parameters (δ), coordinates of three-dimensional solubility parameters δ_T $(\delta_d, \delta_p, \delta_h)$ and molar volumes of the diluents used in the synthesis of Sty-DVB copolymers **(8,9,13)**

D I L U E N T	δ(MPA)$^{1/2}$	δ_T (MPA)$^{1/2}$			V (cm^3/mole)
		δ_d	δ_p	δ_h	
Acetophenone (ACP)	21.7	19.6	8.6	3.7	117
Benzyl alcohol (BA)	24.7	18.4	6.3	13.7	104
Butyl acetate (BuAc)	17.4	15.8	3.7	6.3	132
Decaline (Dec)	18.0	18.4	0.0	0.0	154
Diethyl phthalate (DEP)	20.5	17.6	9.6	4.5	199
Diisobutyl phthalate (DIBP)	19.0	17.8	8.6	4.1	265
Dioctyl phthalate (DOP)	16.2	16.6	7.0	3.1	377
Ethyl acetate (EtAc)	18.6	15.8	5.3	7.2	98
Heptane (Hep)	15.1	15.3	0.0	0.0	147
Isoamyl acetate (i-AmAc)	16.0	15.3	3.1	7.0	150
Isoamyl alcohol (i-AmA)	20.5	16.0	4.5	13.9	109
Methyl-isobutyl ketone (MIBK)	17.2	15.3	6.1	4.1	126
Toluene (Tol)	18.2	18.0	1.4	2.0	106

Hildebrand solubility parameter predictions

The solubility parameter of Sty-DVB copolymer (δ_2) is 18.6 (MPa)$^{1/2}$. According to Hildebrand's theory a given diluent will be a good solvent for the polymer when $|\delta_1-\delta_2| \simeq 0$. Toluene is a good solvent for polystyrene chains with $|\delta_1-\delta_2| = 0.4$ (MPa)$^{1/2}$. Thus we have classified the diluents as good solvents when $|\delta_1-\delta_2| < 1.0$ (MPa)$^{1/2}$. In general, when $|\delta_1-\delta_2| > 3.0$ (MPa)$^{1/2}$, the diluent is a poor solvent. Therefore, we can expect that heptane and benzyl alcohol will produce the largest pore volumes. The borderline between solvating and nonsolvating diluents is not well defined. Thus, we have classified the diluents for which $|\delta_1-\delta_2|$ is between 1.0 and 3.0 (MPa)$^{1/2}$ as intermediary solvents, taking also into account their chemical structure. Near the lower limit, butyl acetate was considered an intermediary solvent due to the similarity of its chemical structure to isoamyl acetate. Near the upper limit, acetophenone was classified as intermediary solvent due to its aromatic structure (Table 2).

Three-dimensional solubility parameter predictions

For polystyrene, the center point coordinates and radius of the solubility sphere in the three-dimensional $\delta_d, \delta_p, \delta_h$ space is 21.3, 5.8, 4.3 and 12.7 (MPa)$^{1/2}$, respectively. The diluent-polymer distances (D_o) were calculated using equation II. According to Hansen's scheme if $D_o < 12.7$ the diluent will be a good solvent for polystyrene, while if $D_o > 12.7$, the diluent will be a nonsolvent. However, the

boundary of the solubility sphere is not clear-cut between solvents and nonsolvents **(9)**. As toluene, a known good solvent for polystyrene, has $D_0 = 8.3$ $(MPa)^{1/2}$, we think that it is reasonable to expect that a diluent which $D_0 < 10.0$ $(MPa)^{1/2}$ will be a good solvent. The diluents whose D_0 is between 10.0 and 12.7 $(MPa)^{1/2}$ were considered intermediary solvents, while the diluents with $D_0 > 12.7$ $(MPa)^{1/2}$ were classified as poor solvents (Table 3).

TABLE 2 - Classification of the solvating power of the diluents according to their solubility parameters

DILUENT	$\lvert \delta_1 - \delta_2 \rvert$ $(MPa)^{1/2}$	PREVISION
EtAc	0.2	Good Solvents
Tol	0.4	$\lvert \delta_1 - \delta_2 \rvert < 1.0$
DIBP	0.4	
Decal	0.6	
BuAc	1.2	
MIBK	1.4	Intermediary Solvents
DEP	1.8	
i-AmA	1.9	$1.0 \; \lvert \delta_1 - \delta_2 \rvert < 3.0$
DOP	2.4	
i-AmAc	2.6	
ACP	3.1	
Hep	3.5	Poor Solvents
BA	6.1	$\lvert \delta_1 - \delta_2 \rvert > 3.0$

Influence of diluent-copolymer affinity on porous structure

Table 4 shows the characteristics of Sty-DVB copolymers synthesized in the presence of different diluents at 120 and 200% dilution. The copolymers prepared with Tol, Dec and ACP presented the lowest fixed pore volumes (V_{fp}) and the highest apparent densities (d_a) at both dilutions. That means these diluents have good affinities for the polymer. By the values of $\lvert \delta_1 - \delta_2 \rvert$ and D_0, Tol and Dec were classified as good solvents but only D_0 predicted that ACP would behave as a good solvent (Tables 2 and 3).

TABLE 3 – Classification of the solvating power of the diluents according to diluent-polymer distances (D_o) in a three-dimensional δ_d, δ_p and δ_h space

DILUENT	D_o $(MPa)^{1/2}$	PREVISION
ACP	3.5	
DIBP	7.5	Good Solvents
Tol	8.3	
DEP	8.3	$D_o < 10.0$
Dec.	9.3	
DOP	9.5	
BA	11.1	
EtAc	11.4	Intermediary
BuAc	11.4	
MIBK	12.0	$10.0 < D_o < 12.7$
i-AmAc	12.4	
Hep	14.0	Poor Solvents
i-AmA	14.4	$D_o > 12.7$

The phthalates DEP, DIBP and DOP produced higher porosities than on the basis of expected by $|\delta_1-\delta_2|$ and D_o predictions. The copolymer synthesized with these diluents presented higher V_{fp} and lower d_a than the copolymers prepared with acetates or ketones (Table 4). These unexpected results can be explained by the effect of molar volume (V_m). The enthalpy of mixing (ΔH) is proportional to the diluent molar volume (V_m). Therefore, when V_m increases from common solvents like acetates and ketones to plasticizers like phthalates, ΔH tends to increase and the miscibility diminishes **(14)**. For the phthalate (DEP, DIBP and DOP) the increase of V_m also prevails over the solubility parameter on the porosity.

The copolymer prepared with BA, H_{ep} and i-AmA presented rather high V_{fp} and low d_a. The degree of phase separation increased in the order: BA, H_{ep} and i-AmA. The D_o distances predict for these diluents the same order of solvating power decrease, but for $|\delta_1-\delta_2|$ the prediction is in a reverse order.

The acetate series and MIBK produced intermediary porosities. That was the prediction of $|\delta_1-\delta_2|$ for all these diluents, except EtAc which was classified as good solvent. The predictions of the solvating power of acetates and MIBK by D_o values are in accord with experimental results.

TABLE 4 – Characteristics of Sty-DVB copolymers synthesized in the presence of different diluents – 15% of DVB

Dilution	Diluent (%)	da (g/cm^3)	V_{fp} (cm^3/g)	S (m^2/g)	$\overline{D}$ (Å)	U_{Tol} (cm^3/g)	U_{Hep} (cm^3/g)	$U_{Tol} - U_{Hep}$ (cm^3/g)	V_{ap}^*/V_f
Tol	120	0.65	0.01	0	–	1.41	0.28	1.13	28.0
ACP	120	0.59	0.06	0	–	1.49	0.47	1.02	7.8
MIBK	120	0.58	0.06	0	–	1.17	0.23	0.94	3.8
Dec	120	0.58	0.12	0	–	1.49	0.70	0.79	5.8
EtAc	120	0.55	0.13	–	–	0.93	0.61	0.32	4.7
i-AmAc	120	0.50	0.34	30	453	1.40	1.02	0.38	3.0
BuAc	120	0.45	0.41	–	–	1.61	1.11	0.50	2.7
DEP	120	0.40	0.47	149	126	1.65	1.18	0.47	2.5
DIBP	120	0.41	0.57	83	275	1.79	1.36	0.43	2.4
BA	120	0.35	0.65	110	236	1.48	1.10	0.38	1.7
DOP	120	0.33	0.88	75	469	1.85	1.48	0.37	1.7
Hep	120	0.32	0.99	68	582	1.91	1.59	0.32	1.6
i-AmA	120	0.24	1.00	7	1429	1.20	1.07	0.13	1.1
Tol	200	0.62	0.05	0	–	2.20	0.67	1.53	13.4
Dec	200	0.58	0.04	0	–	1.97	0.96	1.01	24.0
ACP	200	0.46	0.26	44	236	2.03	1.02	1.01	3.9
i-AmAc	200	0.44	0.50	–	–	2.40	1.31	1.09	2.6
MIBK	200	0.40	0.55	–	–	1.74	1.29	0.45	2.3
EtAc	200	0.38	0.53	–	–	1.46	1.14	0.32	2.2
DEP	200	0.27	1.26	130	388	2.49	2.08	0.41	1.7
BA	200	0.27	1.30	96	542	2.08	1.84	0.24	1.4
Hep	200	0.20	2.06	63	1308	3.11	2.95	0.16	1.4

*V_{ap} = accessible pore volume = U_{Hep}

In general, D_o was a better predictor of diluent solvating power than $|\delta_1-\delta_2|$. As expected, the average pore diameter ($\overline{D}$) decreased when the solvating power increased.

Influence of diluent-copolymer affinity on swelling properties

It is well known that copolymers synthesized in presence of good solvents have more expanded and less entangled chains than copolymers prepared with bad solvents (15). Due to the higher reactivity of DVB in comparison to styrene, the network structure is formed by highly

crosslinked nuclei interconnected by more linear chains (15). In a previous paper (11), we have considered that the toluene uptake (U_{Tol}) of a macroporous copolymer is a result of three contributions: filling of fixed pores, pore expansion due to uncoiling of internuclear chains and swelling of highly crosslinked nuclei. On the other hand, for a poor solvent like heptane (H_{ep}), the uptake can be a result of filling and expansion of the porous structure but Hep cannot swell the highly crosslinked nuclei. Then the difference between U_{Tol} and U_{Hep} can be taken as a measure of nuclei swelling.

The comparison of the predictions by $|\delta_1 - \delta_2|$ and D_0 with the experimental results show that nuclei swelling can be predicted as the copolymer porosity. In general, the higher the diluent solvating power, the lower the porosity and the higher the nuclei swelling. That shows that the nuclear chains were synthesized in a more expanded and less entangled state when the solvating power increased.

The diluent-copolymer affinity modifies not only the nuclear chains but also the internuclear ones. When the diluent solvating power increases, the formation of more expanded and less entangled internuclear chains is also expected, i.e., the porous structure becomes more elastic. We have supposed that the ratio between heptane uptake and water uptake represents how many times the accessible pore volume (V_{ap}) is greater than the fixed pore volume (V_{fp}). That ratio depends more on the elasticity of the internuclear chains than on the total porosity. However, when $V_{ap}/V_{fp} = 1$ the result should be interpreted according to the total porosity by two possibilities. If $V_{ap} = V_{fp} \simeq 0$, phase separation does not occcur during the polymerization so that the final copolymer presents a gel. If $V_{ap} = V_{fp} \gg 0$ the copolymer is rather rigid and macroporous with internuclear chains entangled to the extent that the nuclei cannot be separated. Table 4 shows experimental V_{ap}/V_{fp} ratios. The copolymers synthesized with good solvents (Tol, Dec and ACP) presented the highest V_{ap}/V_{fp} ratios, while the copolymers prepared with bad solvents (i-AmA, Hep, DOP, BA) presented the lowest V_{ap}/V_{fp} ratios. The intermediary solvents (acetates, MIBK) produced porous structures with V_{ap}/V_{fp} ratios between those produced by good and bad solvents. These results indicate that the V_{ap}/V_{fp} ratio can be considered a measure of internuclear chain elasticity of macroporous copolymers. The lower the diluent-copolymer affinity the lower is the internuclear chain elasticity.

Mechanism of porous structure formation

When the diluent solvating power changes, the main differences on the porous structure formation are the critical concentrations for polymer precipitation during the early stages of polymerization, the tendency of precipitated polymer to agglomerate in microspheres and the entanglement degree of nuclear and internuclear chains. Polymer precipitation occurs earlier as the diluent solvating power decreases. In presence of a bad solvent, the precipitated polymer tends to agglomerate rapidly to form large microspheres, consequently, the diluent distributes preferencially among the microsphere agglomerates to form big pores. On the other hand, the microspheres are rather small when they are formed in the presence of a solvating diluent which distributes inside and outside of the microspheres. During the polymerization, the entanglement degree of the nuclear and

internuclear chains is particularly affected by the diluent solvating power. In presence of a nonsolvating diluent, the precipitated polymer extracts unreacted monomer from the monomer/diluent solution. The nuclear chains become more entangled as the extracted monomer polymerizes. Due to the tendency of the precipitated polymer to agglomerate, there is a lack of diluent between the nuclei so that the internuclear chains are rather short and entangled. The opposite situation is found in presence of a solvating diluent. In this case, the diluent competes with the monomer to swell the nuclei, i.e., the nuclear chains become less entangled because they are solvated during does polymerization. The low tendency of nuclei to agglomerate favours the formation of longer and less entangled internuclear chains in presence of a solvating diluent.

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