Polymer Bulletin 33, 487–491 (1994)

Polymer Bulletin

Structure and properties of styrene-divinylbenzene copolymers

II. Mixtures of different diluents with heptane as pore forming agents

D. Rabelo and F. M. B. Coutinho*

Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro,
P.O. Box 68.525, 21945-970 Rio de Janeiro, RJ, Brazil

ABSTRACT

The influence of binary mixtures of heptane with different diluents on the porous structure of styrene-divinylbenzene (Sty-DVB) copolymers was investigated. It was found that the porosity produced by the diluent mixtures depends not only on the affinity of each diluent for the copolymer but also on the interaction of the diluent molecules with themselves. In this work it was observed that some polar aromatic solvents when mixed with heptane presented cosolvency effects. In general, the accessible pore volumes were higher than the fixed pore ones, indicating the formation of elastic internuclear chains.

INTRODUCTION

In a previous paper, we have investigated the influence of the solvating power of pure diluents on the porous structure formation and swelling properties of Sty-DVB copolymers (1). It was found that three-dimensional solubility parameters were better predictors than Hildebrand solubility parameters. When the diluent solvating power is reduced, the microspheres and macropores become bigger, the microspheres become more rigid and compact, and the nuclear and internuclear chains entangle and coil.

The porous structure formation can be controlled by using diluent mixtures as pore forming agents. In general, diluent mixtures composed of a good and a bad solvent produce intermediate pore sizes (2-5). Therefore, the solubility parameter (δ) of a diluent mixture can be considered as an average value of the pure diluent δ_s. In the case of three-dimensional solubility parameters, the coordinates (δ_d, δ_p, δ_h) of a diluent mixture can be calculated by equation I (6):

$$\delta_{m_i} = \phi_1 \, \delta_{1,i} + \phi_2 \, \delta_{2,i} \qquad \text{(I)}$$

where ϕ_1 and ϕ_2 are the volume fractions of diluents 1 and 2, and $\delta_{1,i}$ and $\delta_{2,i}$ (i = d, p, h) are the coordinates of diluents 1 and 2,

---

*Corresponding author

respectively. The polymer-diluent distance in a three-dimensional diagram (D_o) for a diluent mixture is given by equation II:

$$D_o = \left[(\delta_{md} - \delta_{3d})^2 + (\delta_{mp} - \delta_{3p})^2 + (\delta_{mh} + \delta_{3h})^2 \right]^{1/2} \qquad \text{(II)}$$

where δ_{mi} and δ_{3i} (i = d,p,h) are the coordinates of the diluent mixture and polymer, respectively.

The aim of this work was to investigate the effects of different diluents mixed with heptane on the formation of porous structure. The prediction of polymer-diluent affinity by D_o values were compared with the experimental results.

EXPERIMENTAL

Sty-DVB copolymers were synthesized by suspension polymerization in the presence of binary mixtures of heptane (Hep) with different diluents and purified as previously described **(5)**. The diluent, combined with Hep were: acetophenone (ACP), benzyl alcohol (BA), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), di-2-ethylhexyl phthalate (DOP), toluene (Tol), decalin (Dec), ethyl acetate (EtAc), butyl acetate (BuAc), isoamyl acetate (i-AmAc), methylisobutylketone (MIBK). The volume fraction of Hep for all mixtures was 0.55. The dilution degrees employed were 120 and 200% in relation to the total volume of monomers. The DVB content was kept at approximately 15% in relation to the monomer weight.

The copolymer samples were characterized by apparent densities (d_{ap}), fixed pore volumes (V_{fp}), surface areas (S), average pore diameters ($\bar{D}$), toluene uptakes (U_{Tol}) and heptane uptakes (U_{Hep}) according to methods previously described **(7,8)**.

RESULTS AND DISCUSSION

Tables 1 and 2 show the characteristics of Sty-DVB copolymers synthesized in the presence of binary mixtures of Hep with different diluents. As expected, the higher the D_o values, the higher were the porosities of the copolymers. However, some deviations were observed: DIBP/Hep and DOP/Hep produced higher V_{fp} than Tol/Hep, and Dec/Hep produced higher V_{fp} than acetate/Hep mixtures.

In general, mixtures of solvents and non-solvents produce porous structures with intermediate characteristics of those produced by the pure diluents. However, several diluent mixtures produced lower V_{fp} than the pure diluents: BA/Hep (V_{fp} = 0,09), BA (V_{fp} = 0.65), Hep (V_{fp} = 0.99); DEP/Hep (V_{fp} = 0.16), DEP (V_{fp} = 0.47); DIBP/Hep (V_{fp} = 0,43); DIBP (V_{fp} = 0.57); DOP/Hep (V_{fp} = 0.60), DOP (V_{fp} = 0.88) (The results for the pure diluents are presented in ref **1**). These diluent mixtures were better solvents, than the pure diluents. In the case of the BA/Hep system the cosolvency, i.e., the solvating power increase of the mixture in relation to the pure diluents, can be explained by the decrease of D_o value: BA/Hep (D_o = 9.9); BA (D_o = 11.4), Hep (D_o = 14.0). But for the phthalate/Hep mixtures the cosolvency cannot be explained by the D_o values which predict intermediate solvating power: DEP/Hep (D_o = 10.4), DEP (D_o = 8.3), DIBP/Hep (D_o = 10.3), DIBP (D_o = 7.5), DOP/Hep (D_o = 11.1), DOP (D_o = 9.5).

ACP/Hep, DEP/Hep and BA/Hep were better solvents than Tol/Hep although Tol was a better solvent than ACP, DEP and BA **(1)**.

Dec/Hep was a poorer solvent than the acetate/Hep and MIBK/Hep mixtures, although Dec was a better solvent than the acetate series and MIBK **(1)**.

TABLE 1 - Characteristics of Sty-DVB copolymers synthesized in presence of mixtures of different diluents with heptane

Diluent mixtures	Dilution (%)	D_o ($MPa^{1/2}$)	d_a g/cm^3	V_{fp} cm^3/g	S m^2/g	$\bar{D}$ (Å)	U_{Tol} cm^3/g	U_{Hep} cm^3/g	U_{Tol} - U_{Hep} cm^3/g	V_{ap}^*/ /V_{fp}
ACP/Hep	120	9.4	0.63	0.04	0	-	1.33	0.41	0.92	10.3
BA/Hep	120	9.9	0.57	0.09	0	-	1.19	0.67	0.52	7.4
DIBP/Hep	120	10.3	0.44	0.43	94	183	1.45	1.14	0.31	2.7
DEP/Hep	120	10.4	0.54	0.16	116	55	1.40	0.96	0.44	6.0
DOP/Hep	120	11.1	0.38	0.60	114	211	1.70	1.39	0.31	2.3
Tol/Hep	120	11.1	0.53	0.27	114	95	1.78	1.02	0.76	3.8
Dec/Hep	120	11.4	0.42	0.55	114	193	1.55	1.30	0.25	2.4
EtAc/Hep	120	11.7	0.51	0.32	53	242	1.35	1.02	0.33	3.2
BuAc/Hep	120	12.1	0.46	0.42	-	-	1.75	1.21	0.54	2.9
i-AmAc/Hep	120	12.4	0.45	0.43	91	189	1.59	1.17	0.42	2.7
MIBK/Hep	120	12.8	0.45	0.43	-	-	1.48	1.13	0.35	2.6
ACP/Hep	200	9.4	0.51	0.27	82	132	2.23	1.18	1.05	4.4
BA/Hep	200	9.9	0.52	0.23	-	-	1.68	1.05	0.63	4.6
DIBP/Hep	200	10.3	0.36	0.66	-	-	2.36	1.94	0.42	2.9
DEP/Hep	200	10.4	0.40	0.55	178	124	2.18	1.46	0.72	2.7
DOP/Hep	200	11.1	0.30	1.02	177	231	2.40	2.13	0.27	2.1
Tol/Hep	200	11.4	0.53	0.56	162	138	2.36	1.70	0.66	3.0
Dec/Hep	200	11.7	0.32	1.02	104	392	2.64	2.03	0.61	2.0
EtAc/Hep	200	12.1	0.40	0.61	124	197	1.65	1.39	0.26	2.3
BuAc/Hep	200	12.4	0.34	0.87	-	-	2.63	2.24	0.39	2.6
i-AmAc/Hep	200	12.8	0.37	0.79	96	329	2.65	2.12	0.53	2.7
MIBK/Hep	200	13.2	0.36	0.78	-	-	2.49	2.03	0.46	2.6

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

We can conclude that apolar solvents were more affected by the presence of Hep than polar ones. Therefore, the porosity produced by a diluent mixture depends not only on the affinity of each diluent for the copolymer but also on the interaction of the diluent molecules with themselves.

The presence of Hep improved or did not change the solvating power of polar aromatic solvents like phthalates, BA and ACP, while for polar aliphatic solvents, like the acetate series and MIBK, the solvating power was reduced. The cosolvency presented by polar aromatic solvents mixed with Hep can be related to orientation and autoassociation of polar molecules (9). We think that the aromatic structures containing polar groups are stiff enough to present molecular orientations similar to those presented by liquid crystals. Hep mixed with these polar aromatic liquids can interact with them and provoke disorientation. As a result a more random distribution of the diluent is attained and therefore better solvents are produced. In the case of acetates and MIBK, the molecules are not stiff enough to produce ordered structures so that the presence of Hep preferencially reduces the solvating power.

In general, the average pore diameters ($\bar{D}$) decreased when the solvating power increased. V_{fp} and $\bar{D}$ increased with the dilution enhancement.

The nuclei swelling given by the $U_{Tol}-U_{Hep}$ differences and the elasticity of internuclear chains given by the V_{ap}/V_{fp} ratios showed a tendency to increase when the porosity diminished. The nuclei swelling was rather small (<1.0 cm^3/g) and the V_{ap}/V_{fp} ratios were rather high (>2.0). These results indicate that in the presence of diluents mixed with Hep, the precipitated chains in the early stages of polymerization form entangled nuclei, but the growing internuclear chains are solvated to produce elastic macroporous structures. Therefore, we can except that the copolymer beads present more accessible polymer surfaces in the solvated state than in the dry one.

ACKNOWLEDGEMENTS

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Conselho de Ensino para Graduados e Pesquisa (CEPG/UFRJ), Comissão Nacional de Energia Nuclear (CNEN) and Nitriflex S.A. Indústria e Comércio.

REFERENCES

1. Rabelo, D.; Coutinho, F.M.B.; Polym. Bull., see previous article (Part I).
2. Sederel, W.L.; Jong, G.J.; J. Appl. Polym. Sci., 17, 2835(1973).
3. Poinescu, I. C.; Beldie, C.; Angew. Makromol. Chem., 164, 45(1988).
4. Coutinho, F.M.B.; Cid, R.C.A.; Eur. Polym. J., 26, 1185(1990).

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

6. Froehling, P.E.; Koenhen, D.M.; Bantjes, A.; Smolders, C.A.; Polymer, 17, 835 (1976).

7. Rabelo, D.; Coutinho, F.M.B.; Eur. Polym. J., in press.

8. Rabelo, D.; Coutinho, F.M.B.; Polymer Bull., 30, 725 (1993).

9. Fernández-Piérola, I.; Horta, A.; Makromol. Chem., 182, 1705 (1981).

Received: 16 February 1994/Revised version: 14 June 1994/ Accepted: 17 June 1994