Pergamon

Eur. Polym. J. Vol. 34, No. 5/6, pp. 805–808, 1998

Printed in Great Britain
0014-3057/98 $19.00 + 0.00

PII: S0014-3057(97)00195-X

COSOLVENCY EFFECT ON THE POROUS STRUCTURE FORMATION OF STYRENE DIVINYLBENZENE COPOLYMERS

FERNANDA M. B. COUTINHO*, MARíA LUZ LA TORRE and DENILSON RABELO
Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, P.O. Box 68.525, Rio de Janeiro, 21945-970 RJ, Brazil

(Received 21 October 1996; accepted in final form 14 April 1997)

Abstract—A series of styrene-divinylbenzene copolymers were synthesized by suspension polymerization using two types of diluent systems: diethylphthalate (DEP)/*n*-heptane (Hep) and diethylphthalate (DEP)/isoamylacetate (*i*-AmAc). The influence of DEP/Hep and DEP/*i*-AmAc ratios on the formation of the porous structure and swelling of the copolymers were investigated. The mixtures of these diluents produced copolymers with lower pore volumes than those produced with the pure diluents. These results were attributed to the cosolvency effect provoked by the interaction and association between the components of the diluent systems. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Porous Sty-DVB copolymers have been synthesized by suspension polymerization in the presence of inert diluents. The main differences on the porous structure formation are governed by the solvating power of the diluent system and can be summarized as: critical concentrations for the polymer precipitation during the early stages of the polymerization, the tendency of precipitated polymer to agglomerate in microspheres, and the entanglement degree of nuclear and internuclear chains [1].

Solvating diluents, generally, produce expanded networks, microspheres which collapse upon diluent removal, or small fixed pores, depending on the dilution degree and DVB content [2, 3].

As the diluent solvating power decreases polymer precipitation occurs earlier in the polymerization process, the microspheres and macropores become rather larger fixed pores and the nuclear and internuclear chains become more entangled. In general, mixtures of solvating and non-solvating diluents produce pores of intermediate size [4, 5]. The solubility parameters (δ) are useful to predict the formation of porous structures of Sty-DVB copolymers synthesized in the presence of different pure diluents or their mixtures [6]. The greater the affinity of the diluent for the copolymer the smaller their difference in δ. 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. 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, may result in a diluent system with increased solvating power because their average δ will be closer to the δ of the copolymer than the pure diluents.

In previous works [6, 7], it had been found that some polar aromatic solvents when mixed with heptane presented cosolvency effects. It had also been suggested that in the case of diluent mixtures, 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.

In the present work, we have investigated the effect of cosolvency that occurs with the mixtures diethylphthalate/*n*-heptane and diethylphthalate/isoamylacetate on the formation of porous structures and swelling properties of Sty-DVB copolymers.

EXPERIMENTAL

Materials

Commercial styrene (donated by Nitriflex S/A) and divinylbenzene (donated by Nitriflex S/A) were washed with 10% aqueous hydroxide solution, deionized water, dried over anhydrous calcium chloride and finally distilled under reduced pressure. The purity of the supplied DVB was 55%. The diluents, diethylphthalate (DEP, Química Taubaté S/A), *n*-heptane (Hep, Rio-Lab., Ltd.) and *i*-amylacetate (*i*-AmAc, Rio-Lab.) with P. A. purities were used as received. The initiator 2,2′-azobisisobutyronitrile (AIBN) (donated by Metacril S/A) was purified by recrystallization from methanol solution. The components of the aqueous phase: gelatin (Otker Produtos Alimenticios), hydroxyethylcellulose (donated by Union Carbide do Brasil) and NaCl (Vetec Química Fina) were obtained commercially and used as received.

Polymerization

Sty-DVB copolymers were synthesized by suspension polymerization in the presence of two diluent systems: diethylphthalate/*n*-heptane (DEP/Hep) and diethylphthalate/isoamylacetate (DEP/*i*-AmAc) according to a pro-

---

*To whom all correspondence should be addressed.

Table 1. Characteristics of Sty-DVB copolymers synthesized with diethylphtalate (DEP), *n*-heptane (Hep) and mixtures of DEP/Hep

DEP/Hep V/V (%)	δ_{mix} (MPa)$^{1/2}$	d_a (g cm^{-3})	S (m^2 g^{-1})	D (Å)	V_{fp} (cm^3 g^{-1})	U_{Tol} (cm^3 g^{-1})	U_{Hep} (cm^3 g^{-1})	$U_{Tol}-U_{Hep}$ (cm^3 g^{-1})	U_{Hep}/V_{fp} (cm^3 g^{-1})
100/0	20.5	0.44	137	126	0.43	1.21	1.05	0.16	2.4
90/10	19.9	0.47	84	157	0.33	1.20	0.97	0.23	2.9
75/25	19.2	0.58	–	–	0.06	1.04	0.87	0.17	14.5
65/35	18.6	0.58	0	–	0.05	0.96	0.68	0.28	13.6
50/50	17.8	0.60	0	–	0.03	0.96	0.67	0.29	22.3
45/55	17.6	0.61	0	–	0.02	0.90	0.60	0.30	30.0
25/75	16.6	0.56	8	450	0.09	0.97	0.71	0.26	7.9
10/90	15.6	0.47	85	146	0.31	1.05	0.91	0.14	2.9
0/100	15.1	0.41	99	291	0.72	1.20	1.02	0.18	1.4

cedure described in an earlier paper [2]. The dilution degree employed was 80% in relation to the total volume of monomers. The DVB content was 45% in relation to the molar concentration of styrene.

Characterization of the copolymers

The copolymer samples were characterized by apparent density (d$_a$), fixed pore volume (V_{fp}), surface area (S), average pore diameter (D), toluene uptake (U_{Tol}) and heptane uptake (U_{Hep}) according to methods described in earlier papers [3, 8].

RESULTS AND DISCUSSION

The solubility parameters of DEP, Hep, *i*-AmAc and Sty-DVB copolymers are 20.5, 15.1, 16.0, and 18.6 (MPa)$^{1/2}$, respectively [9, 10]. The values of solubility parameters for the diluent mixtures (δ_{mix}) were calculated as shown in Ref. [6]. According to their solubility parameters DEP and *i*-AmAc are classified as intermediary solvents while Hep as poor solvent for styrene-divinylbenzene copolymers [1].

For the diluent systems DEP/Hep and DEP/*i*-AmAc the δ_{mix} value of a given diluent mixture will be closer to the δ of the copolymer than that of the pure diluents. Consequently, the solvating power of these mixtures is expected to be higher than the solvating power of the pure diluents.

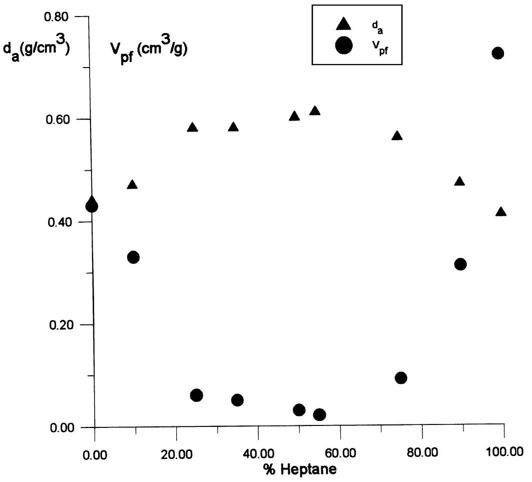

Fig. 1. Effect of the composition of Dep/Hep mixture on the apparent density and the fixed pore volumes of Sty-DVB copolymers

Table 1 shows the characteristics of Sty-DVB copolymers synthesized with DEP, Hep and DEP/Hep mixtures. These mixtures produced copolymers with smaller porosities than those produced by the pure diluents. When the proportion of Hep in the diluent mixture increased, the porosity diminished until a minimum value and then it began to increase up to the complete DEP substitution (Fig. 1). The

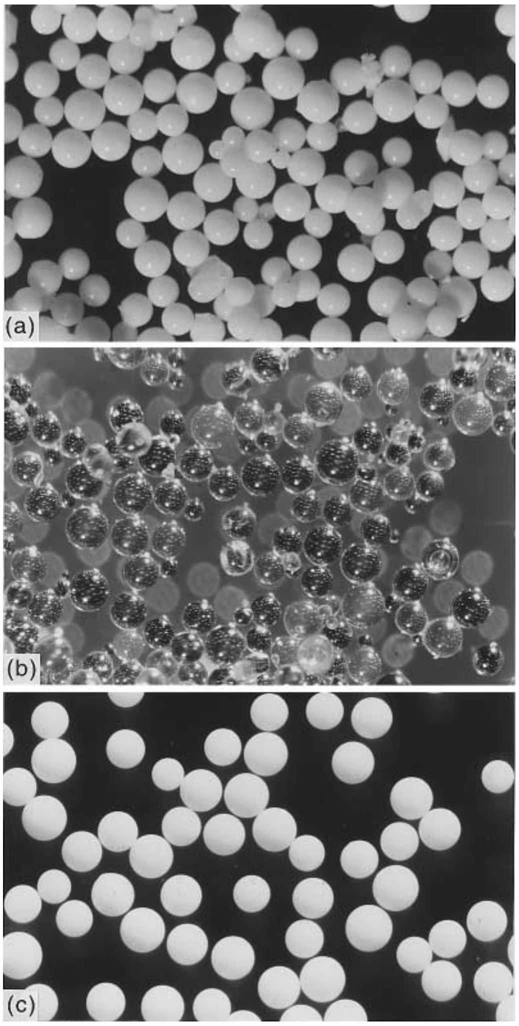

Fig. 2. Photomicrographs of optical microscopy of the Sty-DVB copolymers produced at DEP/Hep ratios: (a) 100/0, (b) 45/55, and (c) 0/100 (magnification: 40×)

Table 2. Characteristics of Sty-DVB copolymers synthesized with diethylphtalate (DEP), isoamylacetate (*i*-AmAc) and mixtures DEP/*i*-AmAc

DEP/*i*-AmAc V/V (%)	δ_{mix} (MPa)$^{1/2}$	d_a (g cm^{-3})	S (m^2 g^{-1})	D (Å)	V_{fp} (cm^3 g^{-1})	U_{Tol} (cm^3 g^{-1})	U_{hep} (cm^3 g^{-1})	U_{Tol}–U_{Hep} (cm^3 g^{-1})	U_{Hep}/V_{fp} (cm^3 g^{-1})
100/0	20.5	0.44	137	126	0.43	1.21	1.05	0.16	2.4
90/10	20.1	0.48	82	166	0.34	1.22	1.02	0.20	3.0
75/25	19.4	0.55	44	246	0.27	1.15	0.95	0.20	3.5
45/55	18.0	0.60	0	–	0.09	1.00	0.71	0.29	7.9
25/75	17.2	0.60	0	–	0.10	1.08	0.82	0.26	8.2
10/90	16.4	0.50	97	157	0.38	1.12	0.90	0.22	2.4
0/100	16.0	0.48	90	173	0.39	1.15	0.97	0.18	2.5

apparent density (d_a) attained a maximum value and the fixed pore volume (V_{fp}) was minimum at DEP/Hep = 45/55. The best cosolvent mixtures were DEP/Hep = 65/35, 50/50 and 45/55, whose δ_{mix} are the closer to the δ of the copolymer. The cosolvency effect of DEP/Hep mixtures resulted in a lower tendency of the precipitated nuclei to agglomerate producing microspheres and small agglomerates. The diluent distributed inside and outside of the microspheres and produced very small pores which collapsed upon diluent removal ($S \approx 0$, $V_{fp} < 0.10$ cm^3 g^{-1} and $U_{Hep} > 0.10$ cm^3 g^{-1}).

Figure 2(a)–(c) shows the optical appearance of those copolymers prepared in presence of DEP/Hep = 100/0; 45/55 and 0/100 respectively. The copolymers synthesized with DEP/Hep = 45/55 were transparent and presented collapsed type structure unlike the copolymers synthesized with DEP/Hep = 100/0 and 0/100 which were opaque as result of the light scattering caused by their heterogeneous structure (macroporous structure).

The polymeric nuclei swelling given by the difference between U_{Tol} and U_{Hep} (U_{Tol}–U_{Hep}) and the internuclear elasticity given by the ratio between U_{Hep} and V_{fp} (U_{Hep}/V_{fp}) showed a tendency to increase when the porosity diminished [1].

Table 2 shows the characteristics of Sty-DVB copolymers synthesized with DEP, *i*-AmAc and DEP/*i*-AmAc mixtures. These copolymers presented higher porosities than those produced in presence of DEP/Hep mixtures. The best cosolvent systems were DEP/*i*-AmAc = 45/55 and 25/75 (Fig. 3). Figure 4 shows the optical appearance of these copolymers.

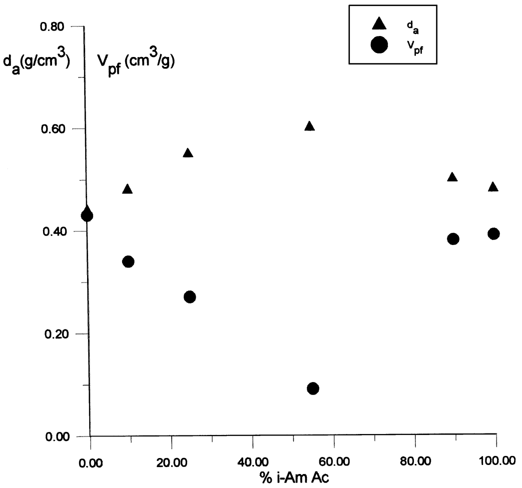

Fig. 3. Effect of the composition of DEP/*i*-AmAc mixture on the apparent density and the fixed pore volumes of Sty-DVB copolymers

Both diluent systems showed small U_{Tol}–U_{Hep} differences but the U_{Hep}/V_{fp} ratios were higher in DEP/Hep mixtures than in DEP/*i*-AmAc mixtures.

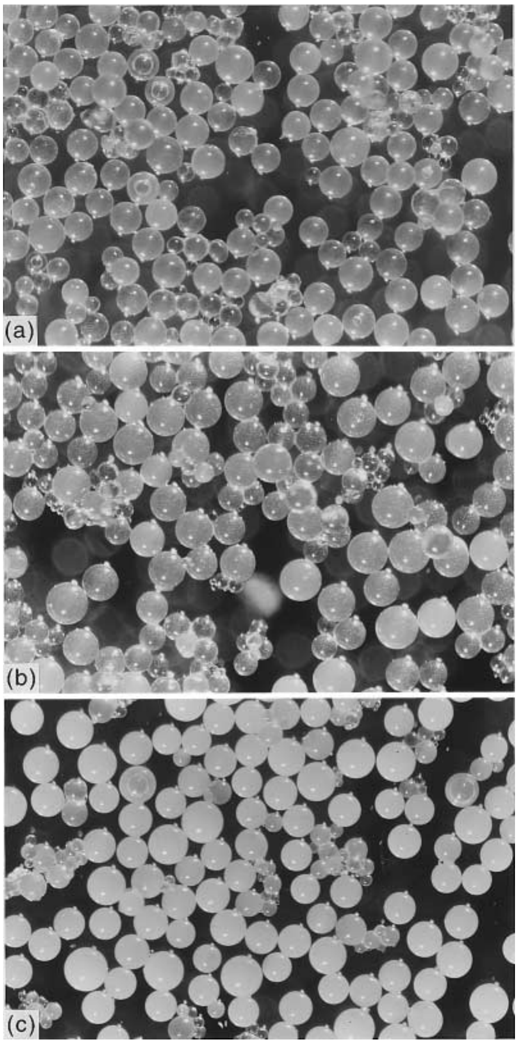

Fig. 4. Photomicrographs of optical microscopy of the Sty-DVB copolymers produced at DEP/*i*-AmAc ratios: (a) 45/55, (b) 25/75, and (c) 0/100 (magnification: 40×)

These results indicate that the precipitated chains in the early stages of the polymerization formed entangled nuclei, but the growing internuclear chains in the case of DEP/Hep diluent system were more elastic than the ones produced with DEP/*i*-AmAc.

The occurrence of cosolvency with these 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 DEP/Hep system, DEP presents an ordered stiff structure, thus the dilution effect of heptane provokes a disorientation of the molecules of the aromatic compound (DEP) resulting in mixtures with a higher capacity to interact with the copolymer [7]. In the case of DEP/*i*-AmAc, as the two diluents are polar, the interaction and association of both components cause a decrease of the interaction with the copolymer and therefore these mixtures are less solvating than DEP/Hep mixtures.

CONCLUSION

The occurrence of cosolvency between diethylphthalate (DEP) and *n*-heptane (Hep), and between diethylphthalate and isoamylacetate (*i*-AmAc) was verified in this work during the synthesis of styrene-divinylbenzene copolymers by suspension polymerization using those solvent pairs as diluent systems for the monomers.

Collapsed-type structures were produced by using cosolvent mixtures and macroporous ones were obtained when the pure solvents were employed as diluent systems.

Acknowledgements—The authors thank PADCT/CNPq, CNPq, CAPES, Metacril and Nitriflex S.A., Indústria e Comércio for their support of this work.

REFERENCES

1. Rabelo, D. and Coutinho, F. M. B., *Polym. Bull.*, 1994, **33,** 479.
2. Rabelo, D. and Coutinho, F. M. B., *Eur. Polym. J.*, 1992, **28,** 1553.
3. Rabelo, D. and Coutinho, F. M. B., *Polym. Bull.*, 1993, **30,** 725.
4. Poinescu, I. C. and Beldie, C., *Angew. Makromol. Chem.*, 1988, **164,** 45.
5. Coutinho, F. M. B. and Cid, R. C. A., *Eur. Polym. J.*, 1990, **26,** 1185.
6. Rabelo, D. and Coutinho, F. M. B., *Polym. Bull.*, 1993, **31,** 585.
7. Rabelo, D. and Coutinho, F. M. B., *Polym. Bull.*, 1994, **33,** 487.
8. Rabelo, D. and Coutinho, F. M. B., *Eur. Polym. J.*, 1994, **30,** 675.
9. Brandrup, J. and Immergut, E. H. (ed.), *Polymer Handbook*, 2nd edn. Wiley, New York, 1975.
10. Barton, A. F., *Handbook of Solubility Parameters and Cohesion Parameters*. CRC Press, Boca Raton, 1983.