

Porous Structure and Swelling Properties of Styrene–Divinylbenzene Copolymers for Size Exclusion Chromatography

FERNANDA M. B. COUTINHO, MÁRCIA ANGÉLICA F. S. NEVES, MARCOS L. DIAS

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 4 September 1996; accepted 6 November 1996

ABSTRACT: Small spherical particles of styrene–divinylbenzene copolymers have been synthesized by modified suspension polymerization. The effects of divinylbenzene (DVB) contents, dilution degree of the monomers and diluent composition on the porous structure and swelling properties of the copolymers were investigated. Toluene uptakes of macroporous copolymers were considered as a result of three contributions: filling of the fixed pores, expansion of the fixed or collapsed pores, and nuclei swelling and heptane uptakes as a result of the two first contributions. The increase of DVB content in the copolymers synthesized in presence of a solvating diluent (toluene) provoked a decrease on the nuclei swelling. The increase of dilution degree with solvating diluents changed the toluene and heptane uptakes, and when the diluent–copolymer affinity was reduced, the fixed pore volume increased. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1257–1262, 1997

Key words: styrene–divinylbenzene copolymers; size exclusion chromatography (SEC); porous structure

INTRODUCTION

The increasing interest for porous styrene–divinylbenzene copolymer beads in recent years is due to their diversified applications as polymer-supported catalysts, polymer-immobilized extractants, starting materials for the synthesis of ion exchange resins, and chromatographic packing for size exclusion chromatography (SEC).^{1–4}

The objective of our present research is the development of gels of styrene–divinylbenzene copolymers to be employed as packing materials for SEC columns. To that end, the technique of suspension polymerization in the presence of diluents such as toluene and heptane was selected, primarily be-

cause it allows the production, in a single reaction, of materials with the proper porous structure, swelling properties, and particle size in the desired range (5–10 μm). The porous structure and swelling properties can be controlled by addition of inert diluents at specified dilution degree of the monomers and by the amount of crosslinking agent employed in the copolymer synthesis.^{5,6} The diluents employed in suspension polymerization for the production of porous copolymers can be classified into three types: solvating, nonsolvating, and linear polymers or mixtures of them, which will generate different profiles of pore size distributions.⁷ During the copolymerization process the diluent may remain in the network phase (gel) or may separate out of the gel. These two situations will produce respectively, expanded networks or macroporous structures.⁸

When one resin is being designed for SEC application, the changes on the porous structure by swelling must be taken into consideration. Sty-

Correspondence to: F. M. B. Coutinho.
Contract grant sponsors: CNPq; CEPG/UFRJ; PADCT/
CNPq; Nitriflex S.A.
© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/071257-06

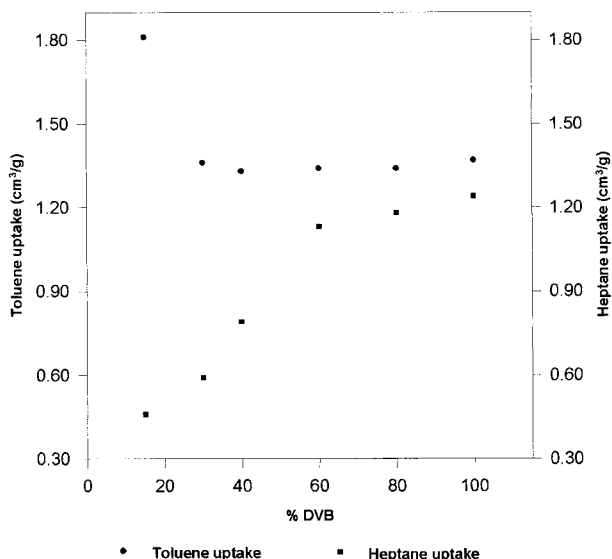


Figure 1 Influence of DVB content on toluene and heptane uptakes of Sty-DVB copolymers synthesized with pure toluene as the diluent at 120% dilution.

rene-divinylbenzene copolymers synthesized in the presence of solvating diluents may lead to a partial or total collapse of the porous structure after solvent is removed.⁹ In a solvating diluent, macroporous copolymers are only obtained when the DVB content and the monomer dilution are high. On the other hand, when nonsolvating diluents are used, the macroporosity appears at considerably lower DVB contents and lower dilutions so that the total pore volume and the pore size of the copolymers are greater than the similar copolymer prepared in the presence of solvating diluents.⁶

The objective of this work is the preparation and characterization of gel beads of styrene-divinylbenzene copolymers having different porosities and swelling abilities to be applied as packing material for size exclusion chromatography.

EXPERIMENTAL

Materials

Styrene (Sty) and divinylbenzene (DVB) free of inhibitors were distilled under reduced pressure. The initiator 2,2'-azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. The diluents, toluene (solvating) and heptane (nonsolvating) were used as received and their contents were expressed as volume percent of the

total volume of the monomers. The toluene/heptane ratio was expressed as (v/v). Poly(vinyl alcohol) (hydrolysis degree = 88% and polymerization degree = 2400), 0.5% (w/w) in relation to water was used as steric stabilizer. The ratio between the two phases (aqueous/organic) was 4/1 (v/v) for all reactions.

Polymerization

The solution formed by the monomers, diluents, and initiator was poured into a flask containing the aqueous phase at 10°C and submitted to a high-speed stirring (20,500 rpm) for 10 min to obtain the desired particle size.¹⁰ Examination under a microscope showed drops with an average diameter of 10 μm . The flask was then fitted with a mechanical stirrer, condenser, and Hg seal. The temperature was maintained at 70°C and the stirring speed kept constant at 400 rpm during the polymerization period (24 h).

After the reaction period, the resulting beads were separated by filtration and successively washed with water (23–25°C), hot water (60–65°C), and acetone to ensure the complete removal of impurities. The beads were then washed with methanol and finally dried at 50°C for 48 h.

Characterization

The texture of the beads in the dry state, surface area (S), and pore volume (V_p), were analyzed by

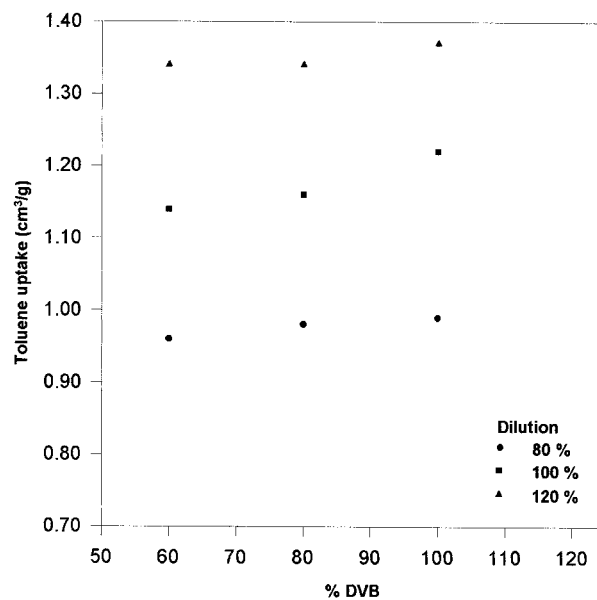


Figure 2 Influence of DVB content and dilution using pure toluene as the diluent on toluene uptake of Sty-DVB copolymers.

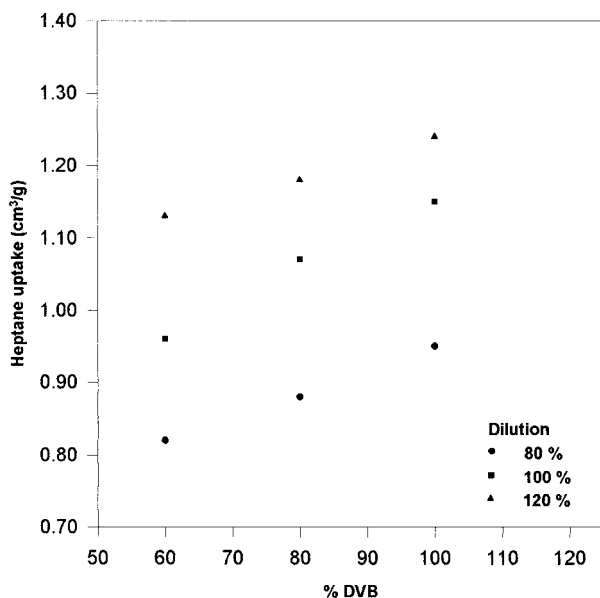


Figure 3 Influence of DVB content and dilution using pure toluene as the diluent on heptane uptake of Sty-DVB copolymers.

nitrogen adsorption measurements using respectively BET and BJH methods.¹¹

The average pore diameter (\bar{D}) was calculated according to the equation

$$\bar{D} = \frac{4 \times 10^4 \times V_p}{S}$$

where \bar{D} is the average pore diameter (\AA), V_p is the total pore volume (cm^3/g), and S is the surface area (m^2/g).

The cylindrical model for the pores was assumed.

For the evaluation of porous structure, swelling experiments were carried out in toluene and heptane, and correspondent uptakes were determined by the centrifugation method¹² using the equation

$$\text{Uptake} = \frac{W_{\text{sol}}}{W_{\text{cop}} \times \rho_{\text{solv}}}$$

where Uptake is the volume of solvent retained by determined amount of dry copolymer (cm^3/g), W_{cop} is the weight of dry copolymer (g), W_{sol} is the weight of solvent (g), and ρ_{solv} is the solvent specific gravity (g/cm^3).

RESULTS AND DISCUSSION

The first study of this article is centered on the effect of DVB content on the porous structure and swelling properties for small particles, i.e., beads with sizes around $10 \mu\text{m}$, prepared by suspension polymerization employing pure toluene as diluent.

Figure 1 shows the toluene and heptane uptakes for the Sty-DVB copolymers prepared at a dilution degree of 120% using pure toluene as diluent and varying the DVB content in the range from 15 to 100%. The toluene uptake was the highest for low amounts of DVB (15%) and decreased as the DVB content increased reaching a constant level at about 30% of DVB. On the other hand, in the same figure it can be seen that heptane uptake increased as the DVB content increased. These copolymers presented nonmeasurable fixed pores and surface areas in the dry state, as we have already observed in an earlier work⁵ where the DVB content was increased up to 40%. The increase of crosslinking promotes phase separation, which in the case of solvating diluent is characterized by the formation of micropores. These micropores collapse or totally or partially with the solvent removal. Thus, the increase of heptane uptake may be a consequence of the opening of the collapsed micropores. Jun et al.¹³ working with high DVB contents and high dilution

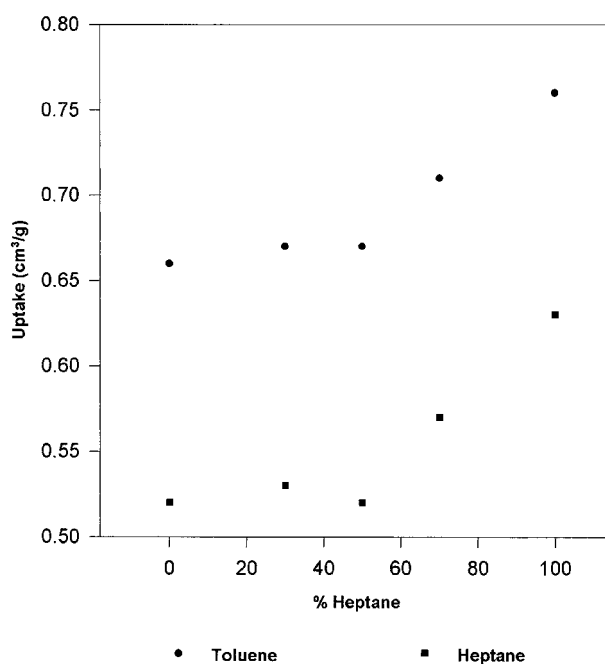


Figure 4 Influence of toluene/heptane ratio on toluene and heptane uptake of Sty-DVB copolymers using 60% DVB and 50% dilution.

degree ($\geq 200\%$) observed that as the DVB content was increased, the toluene uptake decreased and the heptane uptake increased. The values of heptane uptake were always higher than the fixed pore volume. When high dilution degree was employed, even in a solvating diluent, macroporous structures were obtained. The authors explained their results in the same line of thinking as Davankov and Tsyurupa,¹⁴ who consider that Sty-DVB copolymers highly crosslinked have a similar behavior as macronet isoporous styrene copolymers. That is, the existence of strain in the internuclear chains, so the swelling of the copolymers is accompanied by an increase of their volume, which is favorable to the release of strain. Thus, a weak polymer-solvent interaction is enough to provoke the swelling of the copolymers. We consider the explanation based on expansion of fixed or collapsed pores a better one because even at low DVB content, where the strain would be absent, the value of heptane uptake was higher than the fixed pore volume.

The increase of DVB content can produce two different effects on toluene uptake. It may decrease because of the low nuclei swelling or may increase by favoring the phase separation.

At 15% of DVB, the toluene uptake is only responsible for nuclei swelling because the heptane uptake is low, but with the increase of DVB the toluene uptake becomes constant and heptane uptake increases. As heptane does not have the ability to cause nuclei swelling, this contribution is probably only due to the expansion of the internuclear

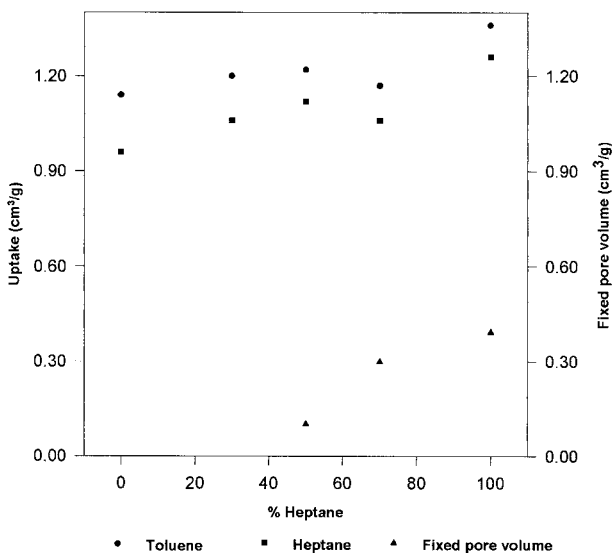


Figure 5 Influence of toluene/heptane ratio on toluene and heptane uptake and fixed pore volume of Sty-DVB copolymers using 60% DVB and 100% dilution.

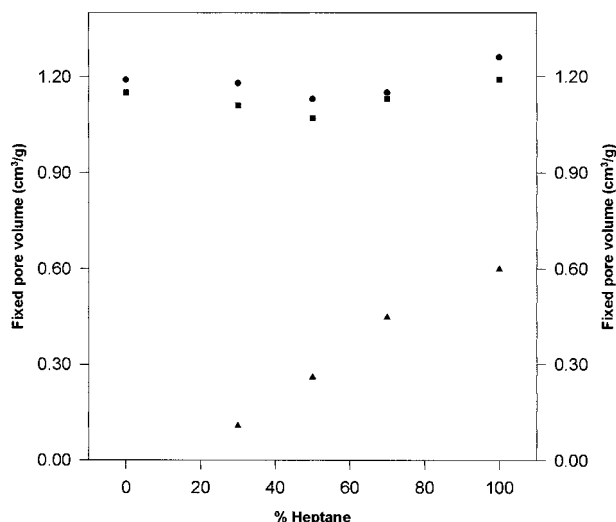


Figure 6 Influence of toluene/heptane ratio on toluene and heptane uptakes and fixed pore volume of Sty-DVB copolymers using 100% DVB and 100% dilution.

chains. Thus, as heptane uptake increased and toluene uptake remained constant, we may conclude that the nuclei swelling decreased as a consequence of the increase of DVB content.

Figure 2 shows the change of toluene uptake with the variation of DVB content and dilution degree. For the copolymers produced at different dilution degrees, the variation of DVB content only slightly affected the toluene uptakes. The variation of the dilution at the same DVB content strongly affected the toluene uptake. The same general behavior may be observed in Figure 3, which shows the variation of heptane uptake with the variation of DVB content and dilution degree. The dilution degree had a greater influence on the heptane uptake than the DVB content. The effect of DVB content on the heptane uptake was stronger, however, than on the toluene uptake. For these copolymers the fixed pore volume and surface area were not measurable. These results suggest that high DVB content produced copolymers with more entangled polymeric nuclei. Although heptane cannot swell the nuclei, it can solvate and expand the internuclear chains.

Figures 2 and 3 show that the increase of dilution for all DVB contents caused increase of toluene and heptane uptakes. At high DVB contents the increase of dilution with solvating diluents provokes enhancement of phase separation, after the diluent elimination the total collapse of the micropores occurs, but in contact with solvent these pores will be reexpanded. Thus, the increase of dilution degree with solvating diluents enhances the phase separation and produces more flexible internuclear chains.

The toluene uptake of macroporous copolymers can be considered as the result of three contributions: filling of the fixed pores, expansion of fixed and collapsed pores, and nuclei swelling. The heptane uptake only has the two first contributions because heptane cannot swell the nuclei. Figure 4 shows the influence of the diluent mixture composition on the uptakes of toluene and heptane at 60% DVB and 50% dilution degree. One can see that the increase of heptane content up to 50% particularly did not change the uptakes of toluene and heptane, but additional increase of heptane content resulted in a considerable increase of the solvent uptakes. Because the fixed pore volume for these copolymers were zero, even pure heptane, at this dilution (50%) was not enough to obtain porous Sty-DVB copolymers in the dry state due to the overshadowing solvating effects of the monomers over the small amount of the diluent. The toluene and heptane uptakes presented close values. The uptake of toluene was only slightly higher than the uptake of heptane, likely due to the high degree of crosslinking. Thus, the increase of toluene and heptane uptakes as the heptane proportion in the diluent increased was basically due to one factor: expansion of collapsed pores. High heptane contents employed in the copolymer synthesis were responsible for the production of high proportion of collapsed pores.

When the dilution was increased to 100%, the increase of heptane proportion in the diluent produced fixed pores. At 60% DVB, 50% of heptane was enough to produce fixed pores. However, when the DVB was increased to 100% at the same dilution, the phase separation occurred earlier during the polymerization and a smaller content of heptane

was sufficient to generate fixed pores. The increase of heptane content, for example, the decrease of diluent solvating power produced Sty-DVB copolymers with higher porosities. That is shown on Figures 5 and 6 by the increase of the fixed pore volume of the copolymers.

The effects of the increase of DVB content on the porosity formation depend on the diluent composition. For the copolymers prepared with low heptane content (0 and 30%) the fixed pore volume was zero for 60 and 100% DVB. The copolymers with 50% heptane only produced fixed pores with 100% DVB. The copolymers synthesized with high heptane content (70 and 100%) presented an increase of the fixed pore volume with the increase of heptane and DVB contents.

Table I shows the variation of copolymer texture parameters, as the DVB content and diluent composition employed in the synthesis were varied.

The copolymer surface area depends on the relative contribution of pore volume and average diameters of the pores. At 60% DVB, the surface area increased, passed through a maximum at 70% heptane, and then decreased. The fixed pore volume showed a different behavior, increased as the heptane content increased. At 100% DVB the surface area showed the same behavior as the fixed pore volume, increased as the heptane content increased.

Figures 5 and 6 show, as expected, that toluene and heptane uptakes were always higher than the fixed pore volumes, but both uptakes present the same behavior. The heptane uptakes are the result of two contributions: filling of the fixed pores and expansion of fixed or collapsed pores and the toluene uptakes are the result of three contributions: filling of the fixed pores, and expansion of fixed or collapsed pores and nuclei swelling.

Table I Surface Area (S), Fixed Pore Volume (V_p), and Average Pore Diameter (\bar{D}) of Sty-DVB Copolymers Synthesized with 100% Dilution

DVB (% molar)	Tol/Hep (v/v %)	S (m ² /g)	V_p (cm ³ /g)	\bar{D} (Å)
60	100/0	^a	^a	—
	70/30	^a	0.00	—
	50/50	56	80.10	85
	30/70	102	0.30	121
	0/100	92	0.39	170
100	100/0	^a	^a	—
	70/30	79	0.11	54
	50/50	165	0.26	63
	30/70	169	0.45	106
	0/100	189	0.60	127

^a Not measurable.

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), the Conselho de Ensino para Graduados e Pesquisa (CEPG/UFRJ), the Programa de Apoio ao Desenvolvimento Científico e Tecnológico (PADCT/CNPq), and Nitriflex S.A., Indústria e Comércio.

REFERENCES

1. D. C. Sherrington, *Nouv. J. Chim.*, 661 (1982).
2. R. Kunin, *Ion Exchange Resin*, 2nd ed., R. E. Krieger Publishing, Melbourne, 1972.
3. J. C. Moore, *J. Polym. Sci.*, **A2**, 835 (1964).

4. S. Belfer, Y. Egozy, and E. Korngold, *J. Appl. Polym. Sci.*, **29**, 3825 (1984).
5. D. Rabelo and F. M. B. Coutinho, *Eur. Polym. J.*, **30**, 675 (1994).
6. D. Rabelo and F. M. B. Coutinho, *Macromol. Symp.*, **84**, 341 (1994).
7. W. L. Sederel and G. J. Jong, *J. Appl. Polym. Sci.*, **17**, 2835 (1973).
8. O. Okay, *Angew. Makromol. Chem.*, **157**, 1 (1988).
9. O. Okay, *Angew. Makromol. Chem.*, **157**, 15 (1988).
10. x. Tanaka., U.S. Pat. 4,338,404 (1982).
11. T. Allen, *Particle Size Measurement*, 4nd ed., Chapman and Hall, London, 1990.
12. K. W. Pepper, *J. Appl. Chem.*, **I**, 124 (1951).
13. Y. Jun, X. Rouganan, and Y. Juntan, *J. Appl. Polym. Sci.*, **38**, 45 (1989).
14. V. A. Davankov and M. P. Tsyurupa, *Angew. Makromol. Chem.*, **91**, 127 (1980).