Macromol. Symp. ***151**, 399–405 (2000)*

Modified Suspension Polymerization of Styrene-Divinylbenzene for Application in Size Exclusion Chromatography

Fernanda M.B. Coutinho*[1,2], Gizelda M. Alves[3], Márcia A.F.S. Neves[1]
Marcos L. Dias[1], Beatriz S. Chagas[1]

[1]Instituto de Macromoléculas Professora Eloisa Mano/UFRJ, P.O. Box 68.525, Rio de Janeiro,RJ, 21945-970, Brasil,
[2]Departamento de Processos Industriais/IQ/UERJ, Rio de Janeiro, RJ, Brasil,
[3]Faculdade de Engenharia Química de Lorena, Lorena, SP, Brasil
*e-mail: fern@ima.ufrj.br

SUMMARY : Styrene-divinylbenzene copolymers were synthesized by modified suspension polymerization using a diluent system constituted of a solvating and a non-solvating diluent. These copolymers were used as packing materials for size exclusion chromatography columns. The examined columns presented exclusion limit in range from 2800 to 447000.

Introduction

Size exclusion chromatography (SEC) is one of the most powerful techniques to characterize the molecular weight of polymers. This particular application needs columns packed with porous spherical particles of narrow size distribution .

Styrene-divinylbenzene copolymers in the form of porous spherical particles with diameters around 10 μm for application in size exclusion chromatography have been studied since the 80s$^{1)}$. Small spherical particles can be obtained by a modified suspension polymerization. In this polymerization technique predetermined amounts of monomers, initiator and solvents are mixed and added to a determined amount of water having a suspension stabilizer dissolved therein. The resultant mixture is then subjected to high speed stirring for a specified time interval to obtain the desired particle size. Afterwards, the polymerization is continued as a conventional suspension polymerization$^{1,2)}$. This method is an excellent one and also very simple to produce small particles, but for application in SEC, not only the particle size is important, but also the porous structure and the swelling properties. The pore size distribution is the parameter that determines the molecular weight in which occurs the polymer molecules separation during

CCC 1022-1360/00/$ 17.50+.50/0

the SEC analysis. The porous structure of the beads can be controlled by using porogens during the copolymerization process (the beads synthesis)$^{3)}$. The presence of a nonsolvating diluent, acting as porogen, in the reaction mixture during the copolymerization causes phase separation on the copolymer structure, resulting in a macroporous material (polymer beads). This material is formed by agglomerates of microspheres linked together by the reaction of residual monomers at the end of the polymerization process$^{4)}$. Another important parameter for the porous properties and mechanical stability of the copolymers is the concentration of the crosslinking agent, in this case, divinylbenzene. The Figure 1 shows the internal and external surface morphology of particles of styrene-divinylbenzene copolymers synthesized by the modified suspension polymerization$^{5)}$. As can be seen the external surface is less porous than the inner surface. The inner surface is formed by agglomerates of microspheres as proposed in the mechanism formation of the beads porous structures$^{4)}$.

This paper describes the effect of the diluent (porogen agent) composition and divinylbenzene concentration on the copolymer porous properties and chromatographic behavior.

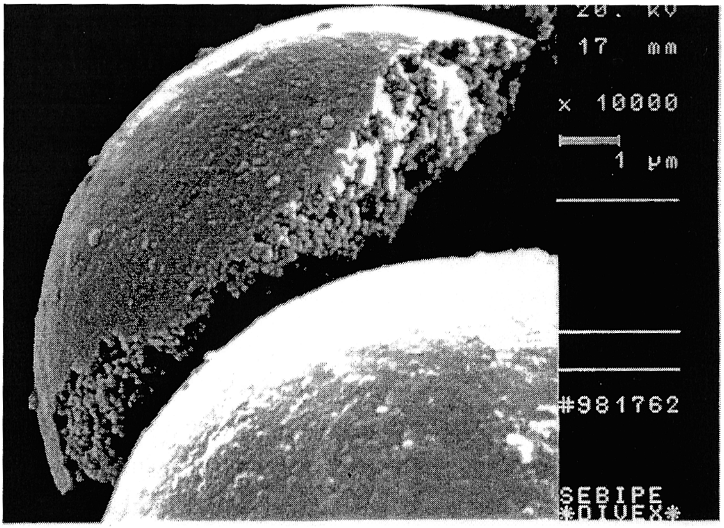

Figure 1: Electron micrograph of the internal and external surfaces of a styrene-divinylbenzene copolymer bead

Experimental

Materials

Styrene (Sty) and commercial divinylbenzene (56% DVB) were distilled under reduced pressure. The initiator 2,2'-azobisisobutironitrile (AIBN) was purified by recrystallization from methanol and 1% (mol/mol) based on monomers was used. Poly(vinyl alcohol) (hydrolysis degree = 88% and polymerization degree = 2400), 0.5% (w/w) in relation to water, was used as steric stabilizer. The diluents, toluene and heptane, were used as received and their contents were expressed as volume percent at the total volume of the monomers. The toluene/heptane (tol/hep) ratios were expressed as (v/v). The relation between the two phases (aqueous/organic) was 4/1 for all reactions.

Polymerization

Styrene-divinylbenzene copolymers were synthesized by suspension polymerization as described previously$^{2)}$. The organic phase formed by styrene, divinylbenzene, diluents and initiator was poured into a flask containing the aqueous phase (water and steric stabilizer) and submitted to a high speed stirring (20,500 rpm) at 10°C for 10 minutes to obtain the desired particle size. The flask was then fitted with a mechanical stirrer, condenser and mercury seal. The reaction temperature was then raised to 70°C and the stirring speed kept at 400 rpm during the reaction period (24 h). In the first part of this work, toluene was used as diluent in differents dilution degrees of dilution (volume percent in relation to the total volume of monomers). The divinylbenzene concentration was varied from 60% to 100% in molar relation to styrene. In the second part of this work, a mixture of toluene/heptane (Tol/hep) (expressed as v/v) was used as diluent at 200% of dilution degree and varied proportions of DVB were employed.

After 24 h reaction, the resulting beads were separated from the aqueous phase and washed with distilled water (23-25°C), warm distilled water (60-65°C) and acetone to ensure the complete removal of impurities. The beads were finally washed with methanol and vacuum dried at 50°C for 48h.

Characterization

The surface area (S) and pore volume (Vp) were obtained from nitrogen adsorption data, using BET and BJH methods, respectively$^{6)}$. The average pore diameter (D) was calculated by the relation between Vp and S. Particle size and particle size distribution were determined by laser light scattering[7,8]. Swelling was carried out in toluene and heptane and the correspondent uptakes were determined by the centrifugation method as described previously[2]. The solvent uptake is the volume of solvent retained by determined amount of the dry copolymer.

Chromatographic Evaluation

The styrene-divinylbenzene copolymer beads dispersed in chloroform (10%w/v) were packed into a stainless-steel column (30cm x 7.6mm) as described previously[9]. The columns were packed using chloroform as eluent by slurry method. The final pressure packing attained was approximately 90 kg/cm^2. The SEC calibration curves were plotted using solution of polystyrene standards (MWD = 1.0) in chloroform (1.0 ml/min). The exclusion limit of each column was obtained with the aid of the calibration curves. After the column packing, the operating backpressure was determined at a flow rate 1.0 ml/min in chloroform.

Results and Discussion

Table 1 shows the characteristics and chromatographic properties of the copolymers beads prepared using only a solvating diluent (toluene) and varying the dilution degree and the divinylbenzene proportion. These copolymers did not present measurable fixed pores in the dry state when analysed by nitrogen adsorption measurements.

The toluene and heptane uptake values demonstrated that these copolymers present pores in the presence of solvent, i.e., in swelling state. Rabelo[10] related that in a general way toluene uptake of the styrene-divinylbenzene copolymers may be considered as resultant of three contributions: filling of fixed pores, expansion of fixed or collapsed pores and swelling of polymeric nuclei. On the other hand the heptane uptake may be resultant of two contributions: filling of fixed pores and expansion of fixed or collapsed pores. As the first series copolymers prepared in this work did not present pores in dry state, the toluene uptakes is resultant of the contribution of two factors: expansion of collapsed pores and swelling of polymeric nuclei and heptane uptake is only due to expansion of collapsed pores. Thus, when the styrene-divinylbenzene copolymers are applied in SEC, the changes on the porous structure by swelling must be considered, since the separation of molecules by size exclusion occurs in the presence of solvent.

At 80% of dilution degree, the increase of DVB proportion pratically did not affect the toluene uptakes. The exclusion limit of the columns packed with these copolymers did not vary, probably the pore size distribution in the swelling state did not change significantly with the change of DVB content. The columns packed with these copolymers presented a low exclusion limit (2800) due to the small pores developed in the swollen state. But, the increase of DVB content, provoked an increase in the mechanical stability of the packing material, indicated by the decrease of the operating backpressure, at a flow rate of 1.0 ml/min using chloroform as eluent. Less crosslinked particles can be deformed more easily and as a consequence the pressure in the columns will increase during the packing procedures and SEC operation.

When the DVB content was fixed at 60% and at 100%, the increase of the dilution degree increased the toluene uptakes and heptane uptakes, and as a consequence, the exclusion limit of these columns also increased. The heptane uptake in this case is only responsible for the expansion of the collapsed pores. Probably, when the pores were formed in presence of larger amounts of toluene, larger collapsed pores were produced. The highest exclusion limit was obtained with the column packed with the beads synthesized with 100% of DVB.

In the second part of this work, a mixture of toluene and heptane was used as diluent at 200% of dilution degree and the divinylbenzene content was varied from 80% to 120% (Table 2). These copolymers presented measurable fixed pores in the dry state verified by nitrogen adsorption measurements. For 80% DVB content, the fixed pore volume pratically did not significantly change as the heptane proportion in the diluent mixture increased, but the average pore diameter increased. As a consequence the exclusion limit also increased. The toluene uptake values did not vary with the increase of heptane in the diluent mixture, but the heptane uptake increased. In this case the toluene uptake is considered as resultant of three contributions: filling of fixed pores, expansion of fixed or collapsed pores and swelling of polymeric nuclei. The heptane uptakes is resultant of two contributions: filling of fixed pores and expansion of fixed or collapsed pores. As the heptane uptake increased and toluene uptake was constant, that means the swelling of polymeric nuclei diminished as the heptane proportion in the diluent mixture increased. At 100 and 120% of DVB, the copolymers synthesized with 70% of heptane in the diluent mixture presented the highest values of fixed pore volume and high average pore diameter. The columns packed with these copolymers presented the highest values of exclusion limit. This result is in accordance with the pore characteristics of these copolymers. The fact that heptane uptakes were lower than the toluene uptakes, demonstrates that swelling of the polymeric nuclei has occurred. The increase of DVB content also influences the mechanical stability of the packing material. The operating backpressure of the columns packed with these copolymers (200% of dilution) also decreased with the increase of DVB content due to the high rigidity (low elasticity) of the polymeric structure.

Table 1: Characteristics and chromatographic properties of the styrene-divinylbenzene copolymers synthesized using toluene as diluent in different dilution degrees and varied divinylbenzene contents

Dilution	DVB (% molar)	Uptake$_{tol}$ (cm^3/g)	Uptake$_{hep}$ (cm^3/g)	$\bar{d}p^{(a)}$ (μm)	EL$^{(b)}$	P$^{(c)}$ (kg/cm^2)
	60	0.96 ± 0.03	0.82 ± 0.03	9.3	2800	29
80	80	0.98 ± 0.03	0.88 ± 0.03	10.8	2800	20
	100	0.99 ± 0.03	0.95 ± 0.03	11.6	2800	13
80		0.96 ± 0.03	0.82 ± 0.03	9.3	2800	29
100	60	1.14 ± 0.03	0.96 ± 0.03	10.5	3900	38
120		1.34 ± 0.03	1.18± 0.03	9.9	7600	41
80		0.99 ± 0.03	0.95 ± 0.03	11.6	2800	13
100	100	1.22 ± 0.03	1.15 ± 0.03	12.4	9700	13
120		1.37 ± 0.03	1.24 ± 0.03	12.3	12500	15

(a) $\bar{d}p$: average particle diameter, (b) EL: exclusion limit, (c) operating backpressure

Table 2: Characteristics and chromatographic properties of the styrene-divinylbenzene copolymers synthesized using toluene/heptane mixtures at 200% of dilutions degree and varied the divinylbenzene contents

DVB (% molar)	Tol/hep (v/v)	V$_p^{(a)}$ (cm^3/g)	$\bar{D}^{(b)}$ (Å)	Uptake$_{tol}$ (cm^3/g)	Uptake$_{hep}$ (cm^3/g)	$\bar{d}p^{(c)}$ (μm)	EL$^{(d)}$	P$^{(e)}$ (kg/cm^2)
	70/30	0.4	81	2.47 ± 0.03	1.77 ± 0.03	11.5	112000	30
80	50/50	0.6	111	2.46 ± 0.03	1.88 ± 0.03	13.1	158500	31
	30/70	0.4	136	2.48 ± 0.03	2.44 ± 0.03	14.7	282000	26
	70/30	0.6	77	2.14 ± 0.03	2.06 ± 0.03	15.2	126000	24
100	50/50	0.5	111	2.15 ± 0.03	2.05± 0.03	14.5	158000	21
	30/70	1.1	187	2.29 ± 0.03	2.20 ± 0.03	14.5	447000	15
	70/30	0.6	75	2.18 ± 0.03	2.11 ± 0.03	15.9	158500	13
120	50/50	0.8	104	2.29 ± 0.03	2.16 ± 0.03	16.6	224000	10
	30/70	1.2	175	2.35 ± 0.03	2.26 ± 0.03	14.9	447000	14

(a) V$_p$: fixed pore volume, (b) $\bar{D}$: average pore diameter, (c) dp: average particle diameter, (d) EL: exclusion limit, (e) P: operating backpressure

ACKNOWLEDGMENT

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

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