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Design of polymeric microparticles with improved structural properties: Influence of ethylstyrene monomer and of high proportions of crosslinker

Cristina Garcia-Diego *, Jorge Cuellar

Department of Chemical Engineering, University of Salamanca, Plaza de los Caidos 1-5, 37008 Salamanca, Spain

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Abstract

Macroreticular poly(styrene-co-divinylbenzene) microparticles with high proportions of divinylbenzene have been synthesized and the effects of the operating conditions and of the proportion of ethylstyrene, which is the monomer accompanying divinylbenzene in commercial divinylbenzene, on the structural characteristics of the microparticles have been investigated. The use of commercial divinylbenzene with a purity of 80% enabled the synthesis of microparticles with a high grade of crosslinking, which showed enhanced structural properties, such as BET specific surface areas (some types of particles reached more than 500 $m^2 g^{-1}$) or pore volumes (mesopore volumes higher than 0.7 $cm^3 g^{-1}$, and macropore volumes higher than 0.5 $cm^3 g^{-1}$). At the same time, microparticles with the same percentage of divinylbenzene but a different percentage of ethylstyrene were synthesized by using, as raw material, two types of commercial divinylbenzene with purities of 80% and 55%, respectively. Comparison of the properties of both these types of particle indicated that ethylstyrene has a significant effect on macropore volume in the case of the lowest proportion of porogen in the synthesis mixture, within the range of values investigated.

Keywords: Macroreticular polymeric microparticles; Poly(styrene-co-divinylbenzene); Ethylstyrene; Modelling

1. Introduction

Macroreticular poly(styrene-co-divinylbenzene) microparticles, plain or with diverse functionalizations, are widely used as ion exchangers, chromatographic packings, in solid-phase synthesis, as catalysts, in solid-phase extraction, etc. [1–3]. These microparticles are synthesized through the copolymerization of styrene and divinylbenzene, the latter acting as a crosslinker, in the presence of an inert diluent (or porogen). After the polymerization has been completed, the inert diluent is removed from the microparticles, leaving a porous polymeric network.

The research carried out to date has indicated that the type and concentration of the crosslinker and of the diluent are the synthesis parameters with the greatest influence in the porous structure of the microparticles, while the polymerization temperature and the type of initiator are of less importance,

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* Corresponding author. Tel.: +34 923294479; fax: +34 923294574.
E-mail address: cristinagd@usal.es (C. Garcia-Diego).

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this influence being due to the role that each parameter plays in the evolution of the polymerization process [4]. The qualitative influence of these variables in the structural properties of the microparticles has already been studied and described on several occasions [4–9] and recently, in the case of macroreticular poly(styrene-co-divinylbenzene) microparticles using *n*-heptane as porogen, the quantitative influence of the porogen and of the crosslinker concentration in certain structural characteristics of the microparticles has also been determined [10,11].

The factor that relates the concentrations of monomers in the polymerization mixture, and whose effect has been investigated extensively, is the weight percentage of pure divinylbenzene in the monomeric mixture. The effect of ethylstyrene, which is the monomer accompanying divinylbenzene in commercial divinylbenzene, does not seem to have been studied. However, this monomer is present at a considerable proportion in the polymerization mixture. For instance, in the case of 55% commercial divinylbenzene, the proportion of ethylstyrene is 45%. This proportion is very high and, since ethylstyrene is not a crosslinker, its effect on the structural characteristics of the microparticles, if it exists, should be different from the effect of divinylbenzene. In this case, investigation of its effect is important because it could enable beads with better properties to be obtained.

However, since the ratio between divinylbenzene and ethylstyrene for a given commercial divinylbenzene is fixed, in principle it is not possible to separate the effect of both monomers. This may be why the effect of ethylstyrene on the porous structure of polymeric microparticles has not yet been studied. Nevertheless, if experiments were carried out with two different commercial divinylbenzenes – that is, with two different ratios between the divinylbenzene and ethylstyrene –, it might be possible to design experiments aimed at studying the influence of ethylstyrene. In this sense, two types of available commercial divinylbenzene can be used: 55% commercial divinylbenzene (this concentration is the usual purity in the investigations carried out), and 80% commercial divinylbenzene (this type is used only occasionally).

Furthermore, the results of investigation on the synthesis of macroreticular poly(styrene-co-divinylbenzene) microparticles indicate that such particles can be obtained with enhanced adsorption and structural properties and high mechanical strength if high concentrations of divinylbenzene are used in the polymerization mixture [11]. These results seem to justify research aimed at finding out whether it might be possible to further increase these properties by using higher proportions of divinylbenzene.

In consequence, the dual aim of the present work was to obtain information about: (a) the influence of very high percentages of divinylbenzene in the BET specific surface area, and in the micropore, mesopore and macropore volumes, of the microparticles; and (b) the effect of ethylstyrene monomer on the structural characteristics of the microparticles. To attain these two objectives, the synthesis of polymeric microparticles with high proportions of divinylbenzene, using 80% commercial divinylbenzene, was carried out. The structural characteristics of the microparticles were determined and correlated with their synthesis conditions. They were also compared with those obtained in experiments performed with 55% commercial divinylbenzene, in order to elucidate the influence of ethylstyrene in the porous structure of the microparticles.

2. Experimental

2.1. Materials

Commercial styrene (St, 99%) and divinylbenzene (80% of DVB, the remainder ethylstyrene) supplied by Aldrich (Madrid, Spain) were used as monomers. Both monomers were washed with a 10% aqueous NaOH solution to remove the 4-*tert*-butylcatechol inhibitor and then with deionized water until neutralization. The other reagents were used as received. As the polymerization initiator, benzoyl peroxide was used (BPO, 70%, remainder water, obtained from Aldrich, Madrid, Spain). The porogen was *n*-heptane (HEP, synthesis grade), supplied by Panreac (Barcelona, Spain). Poly(vinyl alcohol) (PVA, with a weight-average molar mass of 88,000 and a degree of hydrolysis of 88%) was used as the suspension agent and was obtained from Acros Organics (Geel, Belgium). To wash the microparticles obtained, acetone (reagent grade) and methanol (HPLC grade) were used. Both were supplied by Scharlau (Barcelona, Spain). Aqueous solutions were prepared using deionized water.

2.2. Synthesis of microparticles

Macroreticular polymeric microbeads with different structural characteristics were obtained by the suspension polymerization technique, as described elsewhere [10,11]. Some synthesis conditions of the microparticles are summarized in Table 1. The beads were obtained in a 500 mL three-necked round-bottomed jacketed glass reactor fitted with a mechanical stirrer, a condenser, and a thermometer. The aqueous phase was a solution of 250 mL of 0.5 wt% PVA. The organic phase was composed of monomers (styrene, divinylbenzene and ethylstyrene), *n*-heptane as porogen, and benzoyl peroxide as initiator (0.5 wt% of the monomers used). The organic phase was added slowly to the aqueous phase previously prepared under stirring at 65 °C, employing a ratio of aqueous phase/organic phase of 5/1 in the polymerization. The reaction was carried out at 85 °C for 8 h at a stirring speed of 400 rpm. Then, the microparticles thus obtained were first washed with hot water, extracted with acetone in a Soxhlet apparatus, and washed with methanol. Finally, the microparticles were dried under vacuum in an oven at 45 °C for at least 24 h, after which they were sieved. Synthesis yields were in the 65–88 wt% range. The fractions of microparticles with a size of 90–200 μm were used in this work.

2.3. Structural characterization of the microparticles

The microparticles were characterized structurally using nitrogen adsorption–desorption porosimetry (Micromeritics Gemini V 2380 v1.00) and mercury porosimetry (Micromeritics Pore Sizer 9320). The BET specific surface areas of the microparticles (S_{BET}, $m^2\,g^{-1}$) were determined from the nitrogen adsorption data [12]. The micropore volume (V_{micro}, $cm^3\,g^{-1}$) was determined using the *t* method [13]. The mesopore and macropore volumes (V_{meso} and V_{macro}, respectively, expressed in $cm^3\,g^{-1}$), and the pore size distributions of the microparticles, were determined by combining the data obtained from nitrogen adsorption, following the Barret–Joyner–Halenda (BJH) method [14], and from the mercury porosimetry data. Polymeric beads were also characterized by scanning electron microscopy (SEM), using a Philips ESEM XL-30 microscope.

2.4. Planning the experiments

As explained in Section 1, the aims of this work were: (a) to prepare polymeric microparticles with enhanced properties (high BET specific surface areas, and high volumes of micropores, mesopores and macropores) and to study the effect of very high concentrations of divinylbenzene and that of *n*-heptane on their structural characteristics, and (b) to study the effect of ethylstyrene monomer on such characteristics.

To achieve the first objective, polymeric microparticles were synthesized with commercial divinylbenzene containing 80%DVB isomers. The design of experiments methodology [15] was used to plan the experiments to be carried out, in order to establish quantitative relationships between certain structural characteristics of the polymeric microparticles (response) and their synthesis conditions (factors). The factors studied were the DVB concentration

Table 1
Synthesis conditions and structural characteristics of macroreticular poly(styrene-co-divinylbenzene) microparticles synthesized according to the 2^2 factorial central composite design

Adsorbent number	Synthesis conditions				Structural characteristics			
	%DVB[a]		F_m[b]		S_{BET} ($m^2\,g^{-1}$)	V_{micro} ($cm^3\,g^{-1}$)	V_{meso} ($cm^3\,g^{-1}$)	V_{macro} ($cm^3\,g^{-1}$)
	Real value	Coded value	Real value	Coded value				
1	60.0	−1	0.55	−1	465.3	0.0759	0.677	0.460
2	80.0	+1	0.55	−1	520.6	0.0746	0.763	0.549
3	60.0	−1	0.65	+1	454.7	0.0776	0.632	0.154
4	80.0	+1	0.65	+1	498.4	0.0821	0.657	0.077
5	70.0	0	0.60	0	502.8	0.0842	0.718	0.291
6	70.0	0	0.60	0	487.1	0.0726	0.720	0.336
7	60.0	−1	0.60	0	463.3	0.0782	0.668	0.320
8	80.0	+1	0.60	0	524.1	0.0787	0.773	0.302
9	70.0	0	0.55	−1	513.5	0.0825	0.734	0.444
10	70.0	0	0.65	+1	463.9	0.0728	0.643	0.160

[a] %DVB, %wt/wt; that is, the weight percentage of DVB isomers in the monomeric mixture.

[b] F_m, v/v; that is, the volume fraction of the monomers in the organic phase.

in the monomeric mixture (%DVB, %wt/wt; that is, the weight percentage of DVB isomers in the monomeric mixture) and the monomeric fraction in the organic phase (F_m, v/v; that is, the volume fraction of the monomers in the organic phase). The responses studied were the BET specific surface area of the microparticles, and their volumes of macropores, mesopores and micropores. Attempts were made to correlate these four responses with the synthesis conditions through multiple linear regression analysis.

Based on quantitative relationships reported in a previous work [10], the research was planned in a range of DVB and *n*-heptane concentrations within which it would be expected to obtain microparticles with enhanced structural properties. Thus, the range of values chosen for the synthesis conditions was 60–80% for the DVB concentration, and 0.55–0.65 for the monomeric fraction. A 2^2 factorial central composite design was selected to study this region in detail (experiments are represented as squares in Fig. 1). Also, the centre point was replicated to estimate the error due to experimental or random variability. Hence, 10 experiments were carried out to perform the first objective of this investigation. The design matrix, with the corresponding coded scheme of the values of the factors, is given in Table 1.

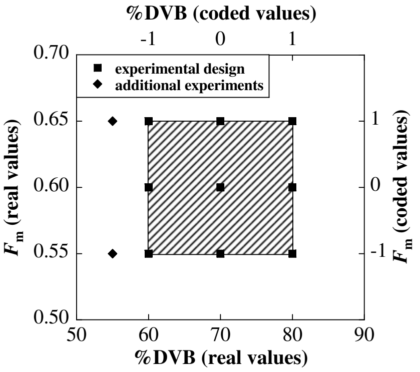


Fig. 1. Levels of the factors used in the 2^2 factorial central composite design (■) and in the additional experiments (◆). The shaded region indicates the application range for the correlations obtained.

To attain the second objective, that is, to check the effect of the concentration of ethylstyrene monomer (%ES, %wt/wt – the weight percentage of ethylstyrene monomer in the monomeric mixture –) on the structural characteristics of the microparticles, in a first step, two additional experiments (depicted as rhombi in Fig. 1) and their corresponding replicates were performed (experiments 11–14, in Table 2) with a DVB concentration of 55%, using commercial divinylbenzene with a purity of 80%. The synthesis conditions used in the experiments and the values obtained for the structural characteristics are given in Table 2. The next step was to contrast these results with those obtained in experiments performed with 55% commercial DVB (with 45% of ethylstyrene), because this is the easiest way to separate the effect of DVB from the effect of ethylstyrene. Thus, Table 2 also shows the synthesis conditions of microparticles obtained with a DVB concentration of 55% using commercial divinylbenzene with a purity of 55% (experiments 15–18), whose synthesis and characterization have been already published [11].

Table 2
Synthesis conditions and structural characteristics of macroreticular poly(styrene-co-divinylbenzene) microparticles of the additional experiments

Adsorption number	Synthesis conditions			Structural characteristics			
	%DVB	F_m	%ES[a]	S_{BET} ($m^2\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)	V_{meso} ($cm^3\ g^{-1}$)	V_{macro} ($cm^3\ g^{-1}$)
11[b]	55	0.55	14	450.7	0.0762	0.702	0.404
12[b]	55	0.55	14	452.4	0.0765	0.668	0.478
13[b]	55	0.65	14	426.0	0.0751	0.580	0.113
14[b]	55	0.65	14	420.2	0.0667	0.621	0.138
15[c]	55	0.55	45	447.1	0.0600	0.692	0.322
16[c]	55	0.55	45	461.8	0.0696	0.691	0.396
17[c]	55	0.65	45	413.4	0.0703	0.545	0.049
18[c]	55	0.65	45	408.7	0.0620	0.517	0.059

[a] %ES, %wt/wt; that is, the weight percentage of ethylstyrene monomer in the monomeric mixture.

[b] Microparticles synthesized with 80% commercial DVB.

[c] Microparticles synthesized with 55% commercial DVB.

3. Results and discussion

3.1. Nitrogen porosimetry: BET analysis and evaluation of microporosity

The nitrogen adsorption–desorption isotherms obtained for the adsorbents synthesized are depicted in Fig. 2.

With respect to microparticles synthesized with 60–80%DVB (Fig. 2a–c), it may be seen that only the isotherm of microparticles obtained in experiment 4 is, as expected, of Type IV according to IUPAC classification [16], because the most compact structure of the microparticles, in terms of macropores, is achieved with the highest concentration of DVB and the lowest percentage of porogen.

Regarding the microparticles synthesized with 55%DVB (Fig. 2d and e), a high degree of similarity can be seen among the isotherms of the microparticles obtained with the same monomeric fraction, regardless of the ethylstyrene concentration.

The specific surface areas of each adsorbent were calculated from the nitrogen adsorption isotherms using the BET method (Tables 1 and 2). As a consequence of the high values of the DVB concentration used, the values of S_{BET} obtained are very high, and even higher than the values obtained for microparticles synthesized in previous experimental designs [10,11,17–19].

There are hardly any differences between the S_{BET} values obtained for microparticles synthesized in experiments 11, 12, 15 and 16 (55%DVB, $F_m = 0.55$); that is, no appreciable effect of the ethylstyrene concentration on the BET specific surface area of the microparticles synthesized with a monomeric fraction of 0.55 can be seen. Nevertheless,

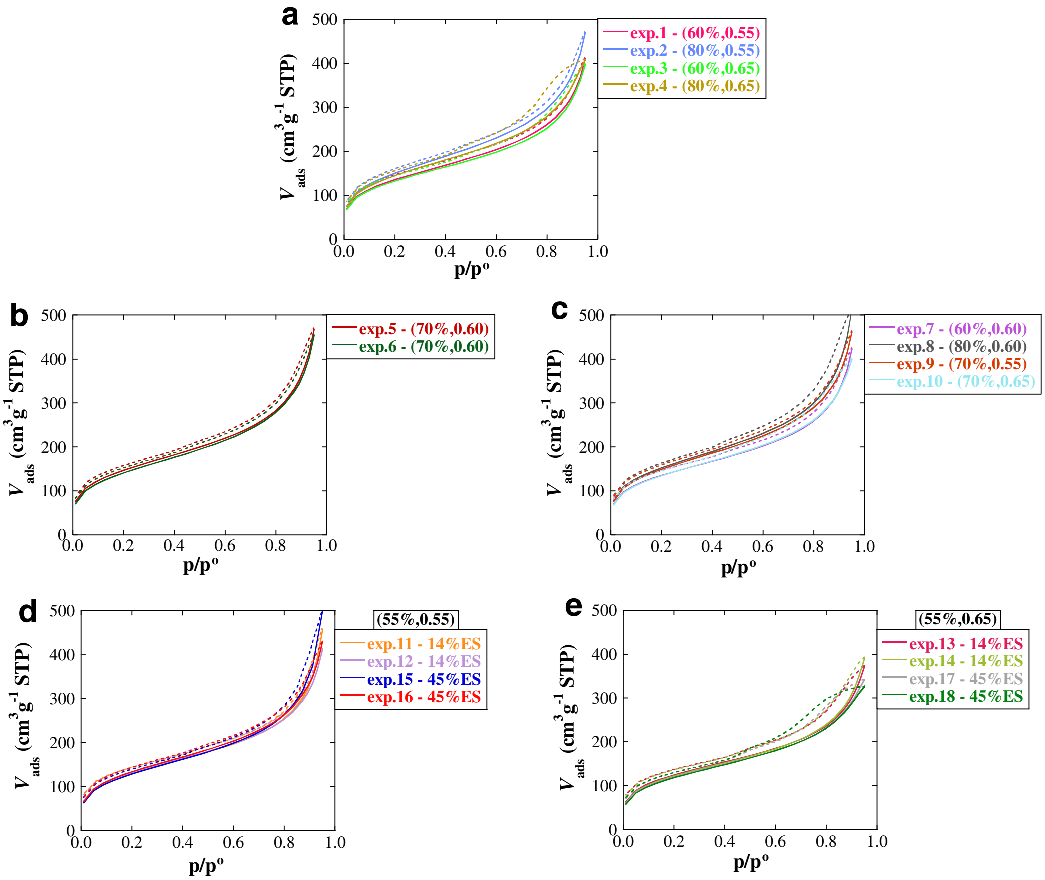


Fig. 2. Nitrogen adsorption–desorption isotherms of macroreticular poly(styrene-co-divinylbenzene) microparticles obtained in the experimental design (a, b and c), and in the additional experiments to check the influence of ethylstyrene monomer (d and e). Solid curves correspond to the adsorption branch and dashed curves to the desorption branch. Values in brackets represent the divinylbenzene concentration and monomeric fraction.

slight differences among the S_{BET} values of the microparticles obtained in experiments 13, 14, 17 and 18 (55%DVB, $F_m = 0.65$) are observed.

Additionally, the micropore volume of each type of microparticles was determined using the *t* method. The values obtained are shown in Tables 1 and 2. The high values obtained for V_{micro}, due to the high concentrations of DVB employed in the synthesis of the microparticles, can be seen.

3.2. Mercury porosimetry

The mercury intrusion curves for the microparticles synthesized in the experimental design and in the additional experiments were obtained; they are plotted in Fig. 3.

In Fig. 3a–c, it can be clearly observed that the microparticles synthesized with the highest proportion of porogen (or the smallest monomeric fraction), at a given pressure, admitted the highest amount of mercury: experiments 1 and 2 ($F_m = 0.55$) vs. experiments 3 and 4 ($F_m = 0.65$) in Fig. 3a, and experiment 9 ($F_m = 0.55$) vs. experiment 10 ($F_m = 0.65$) in Fig. 3c. With intermediate values of the monomeric fraction, intermediate volumes of mercury penetrated into the microparticles: experiments 5, 6, 7 and 8 ($F_m = 0.60$), in Fig. 3b and c. With regard to the DVB concentration, no trend in the effect of this factor on the structural characteristics of the microparticles is observed.

Concerning the use of commercial DVB of different purities as raw material, it can be observed that

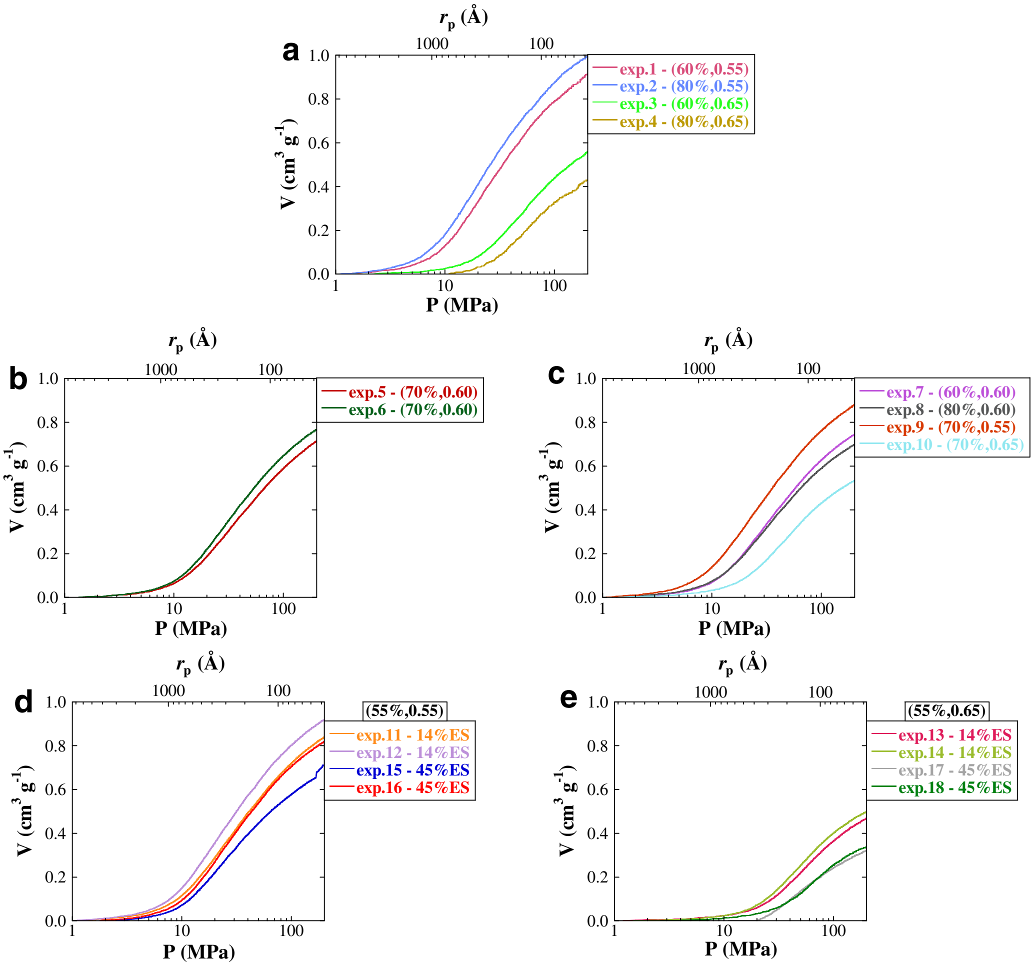


Fig. 3. Mercury intrusion curves of macroreticular poly(styrene-co-divinylbenzene) microparticles obtained in the experimental design (a, b and c), and in the additional experiments to check the influence of ethylstyrene monomer (d and e). Values in brackets represent the divinylbenzene concentration and monomeric fraction.

there is no clear effect of the ethylstyrene concentration on the structural characteristics of the microparticles synthesized with a monomeric fraction of 0.55 (experiments 11 and 12 vs. experiments 15 and 16, in Fig. 3d). In contrast, it may be seen that the concentration of ethylstyrene affects the presence of pores for microparticles synthesized with a monomeric fraction of 0.65 (experiments 13 and 14 vs. experiments 17 and 18, in Fig. 3e); that is, the lower the ethylstyrene content, the higher the amount of mercury penetrating the microparticles at a given pressure.

3.3. Study of the mesoporosity and macroporosity

In this part of the work, the mesoporosity and macroporosity of the microparticles synthesized in the experimental design and in the additional experiments was studied. To achieve this objective, the cumulative pore volume curves and the pore size distributions of the microparticles were obtained. These curves were calculated from the nitrogen adsorption isotherms together with the data on mercury intrusion.

The cumulative pore volume curves are shown in Fig. 4. These curves allowed the mesopore and macropore volumes, shown in Tables 1 and 2, to be determined.

Additionally, the pore size distributions of the microparticles, according to the pore volume, were obtained, as shown in Fig. 5.

In Figs. 4 and 5 it may be observed that increases in the DVB concentration (experiment 1 vs. experiment 2 –$F_m = 0.55$–, experiment 7 vs. experiment 8 –$F_m = 0.60$–, experiment 3 vs. experiment 4 –$F_m = 0.65$–), and decreases in the monomeric fraction (experiments 3, 7 and 1 –%DVB = 60%–, and experiments 4, 8 and 2 –%DVB = 80%–) induce the

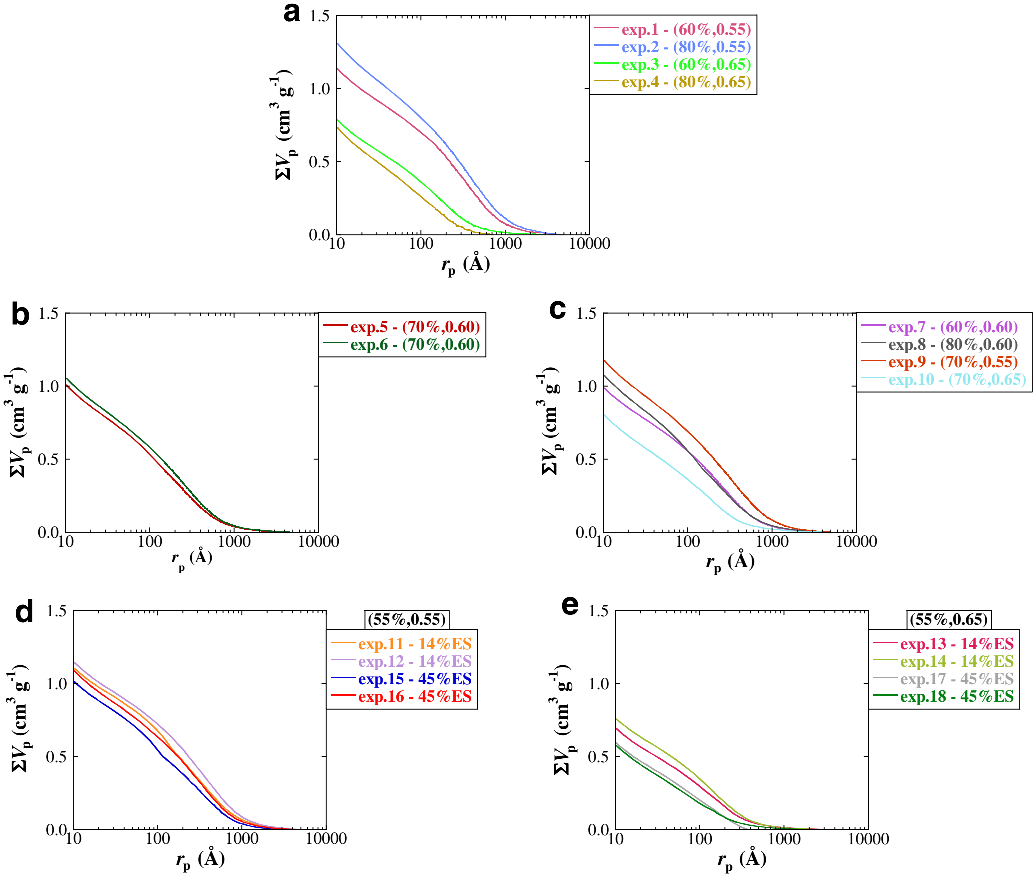


Fig. 4. Cumulative pore volume curves of macroreticular poly(styrene-co-divinylbenzene) microparticles obtained in the experimental design (a, b and c), and in the additional experiments to check the influence of ethylstyrene monomer (d and e). Values in brackets represent the divinylbenzene concentration and monomeric fraction.

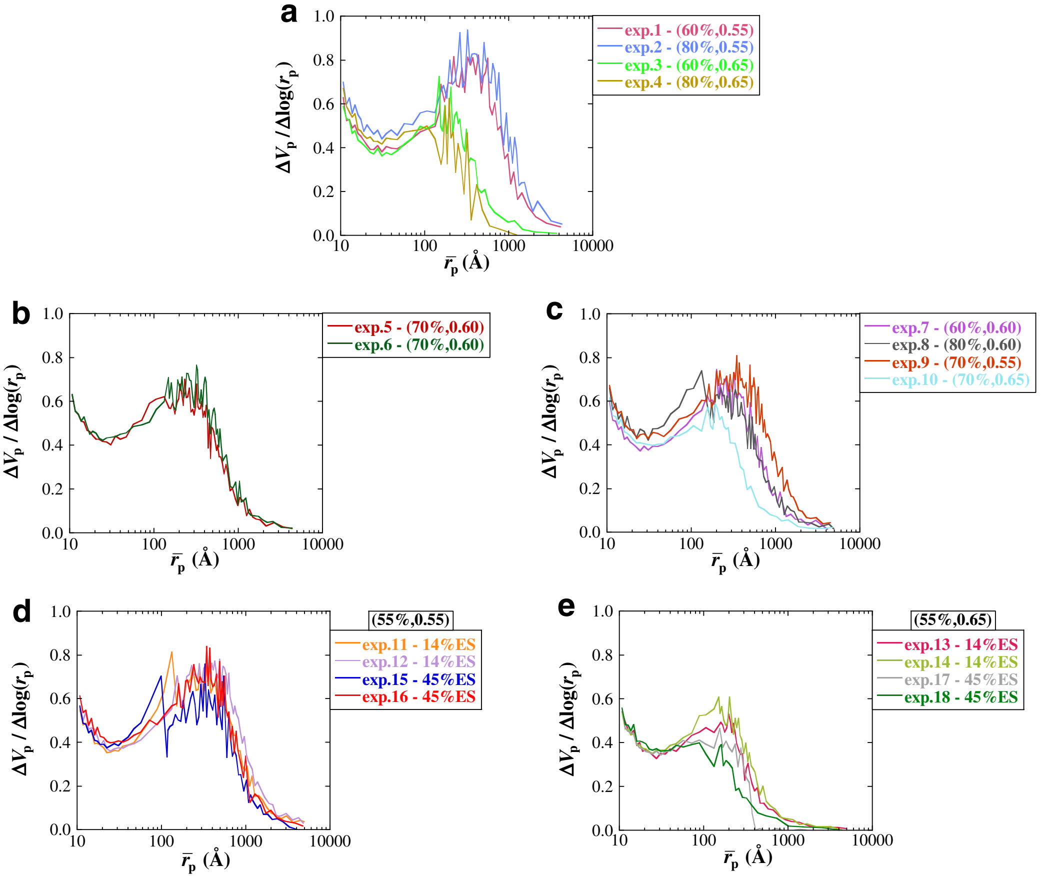


Fig. 5. Pore size distribution curves, according to the pore volume, of macroreticular poly(styrene-co-divinylbenzene) microparticles obtained in the experimental design (a, b and c), and in the additional experiments to check the influence of ethylstyrene monomer (d and e). Values in brackets represent the divinylbenzene concentration and monomeric fraction.

formation of more mesopores. Indeed, the values of the mesopore volume for the microparticles synthesized in this experimental design are higher than those obtained for microparticles synthesized in previous experimental designs [10,11].

Regarding the presence of macropores, it may be seen that high concentrations of porogen in the synthesis of the microparticles promote the formation of this kind of pores, while no effect of the concentration of DVB on the amount of macropores in the microparticles was observed.

With respect to the influence of the ethylstyrene concentration, no appreciable effect of the purity of this reactant on the amount of mesopores and macropores formed was observed in microparticles synthesized with a monomeric fraction of 0.55, as can be seen in Figs. 4d and 5d. Nevertheless, for microparticles synthesized with a monomeric fraction of 0.65 (Figs. 4e and 5e), it can be observed that the highest mesopore and macropore volumes are obtained when the percentage of commercial DVB used is 80%; that is, when the lowest concentration of ethylstyrene is used during the synthesis of the microparticles.

Taking into account the above results, it may be deduced that the concentration of ethylstyrene only affects microparticles synthesized with a monomeric fraction of 0.65: the higher the concentration of ethylstyrene in the organic phase during the synthesis of the microparticles, the lower the specific BET surface area, and the mesopore and macropore volumes.

3.4. Scanning electron microscopy

The morphology of the copolymer microparticles can be seen in Fig. 6, which depicts two SEM photographs of the microparticles synthesized in

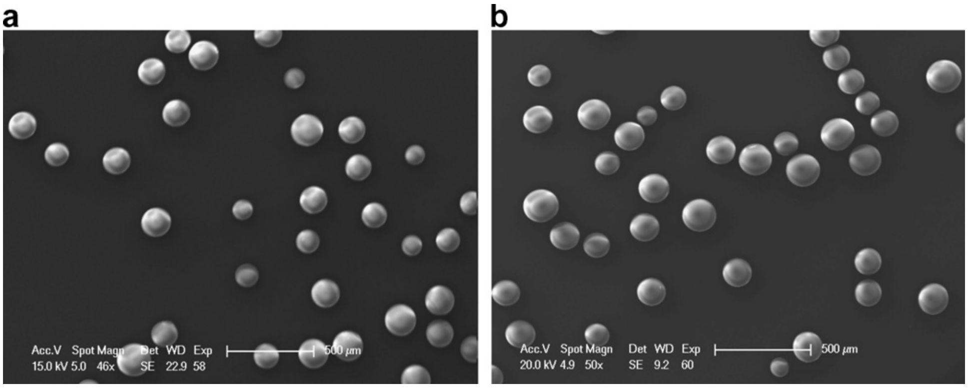
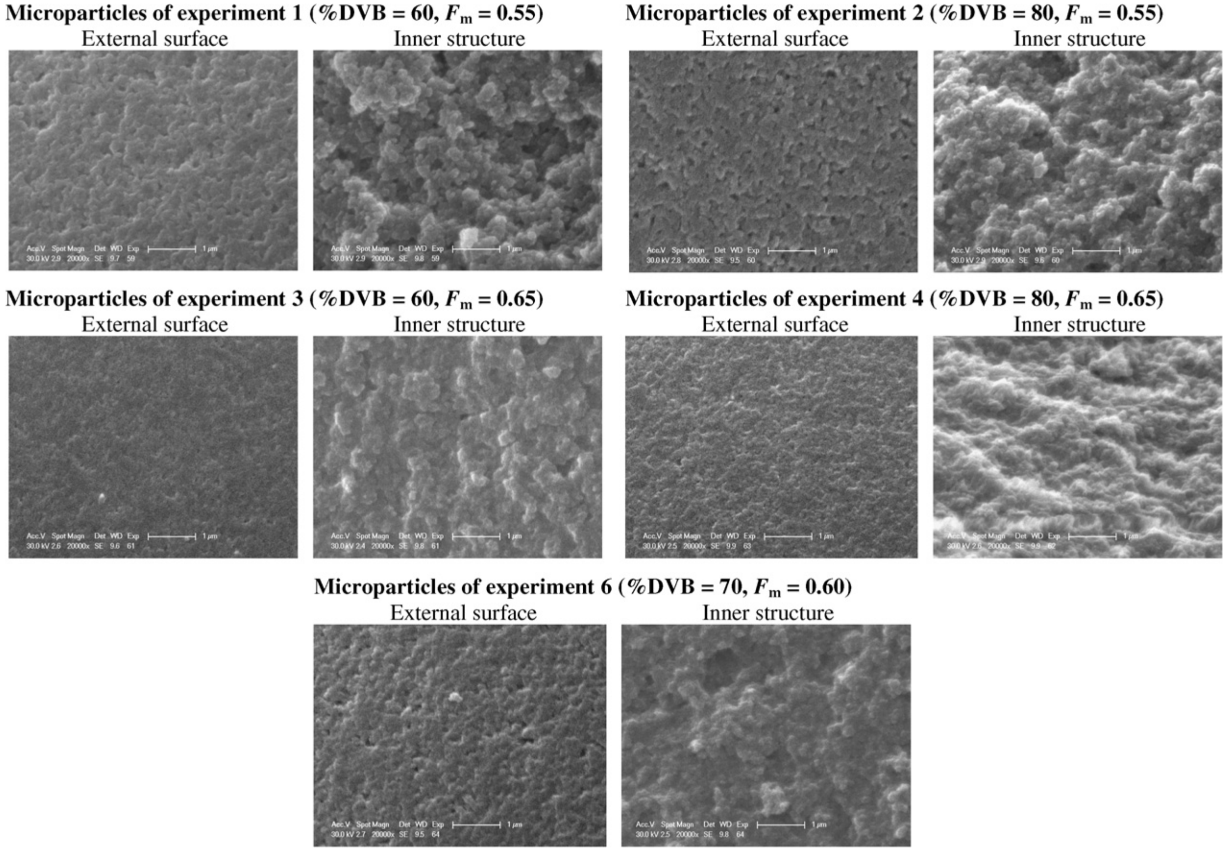


Fig. 6. SEM photographs of the morphology of the microparticles synthesized in: (a) experiment 1, and (b) experiment 2. In both cases scale bar is 500 μm.

experiments 1 and 2 as examples to show their perfect spherical form. Furthermore, SEM photographs of the external surface and inner structure of some of the microparticles synthesized in the experimental design are given in Fig. 7.

Two extreme cases are shown in Fig. 7. The most open structure is seen in the photographs of the first row of Fig. 7, which depict the microparticles synthesized with the highest amounts of porogen, while the photographs of the second row of Fig. 7 represent the most compact structure, owing to the low amounts of porogen used during the synthesis of the microparticles. An intermediate case is observed in the photographs of the last row of Fig. 7, corresponding to


Microparticles of experiment 1 (%DVB = 60, F_m = 0.55)
External surface Inner structure

Microparticles of experiment 2 (%DVB = 80, F_m = 0.55)
External surface Inner structure

Microparticles of experiment 3 (%DVB = 60, F_m = 0.65)
External surface Inner structure

Microparticles of experiment 4 (%DVB = 80, F_m = 0.65)
External surface Inner structure

Microparticles of experiment 6 (%DVB = 70, F_m = 0.60)
External surface Inner structure

Fig. 7. SEM photographs of macroreticular poly(styrene-co-divinylbenzene) microparticles. Magnification is 20,000×. Scale bar is 1 μm.

SEM photographs of microparticles synthesized under intermediate operating conditions.

3.5. Analysis of results

Our first objective was to determine the correlations that relate the structural characteristics of the microparticles with their synthesis conditions. To obtain such correlations, multiple linear regression analysis was applied to fit a response surface model, for each response, to the data of the runs of the experimental design (experiments 1–10). The regression coefficients of a second-order response surface model for each response were estimated by the least squares method (Table 3), affording the following equations:

$$\hat{S}_{\mathrm{BET}} = 495.7 + 26.6x_{\%\mathrm{DVB}} - 13.7x_{F_\mathrm{m}} - 2.9x_{\%\mathrm{DVB}}x_{F_\mathrm{m}} - 2.8x^2_{\%\mathrm{DVB}} - 7.8x^2_{F_\mathrm{m}} \quad (1)$$

$$\hat{V}_{\mathrm{micro}} = 0.07844 + 0.00062x_{\%\mathrm{DVB}} - 0.00008x_{F_\mathrm{m}} + 0.00145x_{\%\mathrm{DVB}}x_{F_\mathrm{m}} - 0.00004x^2_{\%\mathrm{DVB}} - 0.00084x^2_{F_\mathrm{m}} \quad (2)$$

$$\hat{V}_{\mathrm{meso}} = 0.721 + 0.036x_{\%\mathrm{DVB}} - 0.040x_{F_\mathrm{m}} - 0.015x_{\%\mathrm{DVB}}x_{F_\mathrm{m}} - 0.003x^2_{\%\mathrm{DVB}} - 0.035x^2_{F_\mathrm{m}} \quad (3)$$

$$\hat{V}_{\mathrm{macro}} = 0.310 - 0.001x_{\%\mathrm{DVB}} - 0.177x_{F_\mathrm{m}} - 0.042x_{\%\mathrm{DVB}}x_{F_\mathrm{m}} + 0.004x^2_{\%\mathrm{DVB}} - 0.006x^2_{F_\mathrm{m}} \quad (4)$$

where $\hat{S}_{\mathrm{BET}}$, $\hat{V}_{\mathrm{micro}}$, $\hat{V}_{\mathrm{meso}}$ and $\hat{V}_{\mathrm{macro}}$ represent the predicted values of the S_{BET}, V_{micro}, V_{meso} and V_{macro} responses; and the regression variables $x_{\%\mathrm{DVB}}$, x_{F_m}, $x_{\%\mathrm{DVB}}x_{F_\mathrm{m}}$, $x^2_{\%\mathrm{DVB}}$ and $x^2_{F_\mathrm{m}}$ denote the coded values of % DVB, F_m, their interaction and their quadratic terms (Table 1).

To check the adequacy of the models, ANOVA tests were performed for the significance of the regressions (Table 4) and, from the P-values, it was deduced that at least one of the five regressor variables, corresponding to %DVB, F_m, $\%\mathrm{DVB} \cdot F_\mathrm{m}$, $\%\mathrm{DVB} \cdot \%\mathrm{DVB}$ and $F_\mathrm{m} \cdot F_\mathrm{m}$ terms, had a non-zero regression coefficient in all the prediction equations, except in the model of V_{micro} (Eq. (2)), which was unable to explain the variability of the experimental data. The next step, to determine which regressor variables contributed significantly to the rest of models, was to test the significance of the individual regression coefficients. Thus, their P-values were calculated, which are shown in Table 3. The regression coefficients are statistically significant, with a level of significance of 0.05, if the P-values are lower than 0.05. Therefore, the regressor variables whose regression coefficients have P-values higher 0.05 can be eliminated from the corresponding models. Thus, new response surface models for the S_{BET}, V_{meso} and V_{macro} responses, with only the significant regressor variables in each case, were obtained by again applying a multiple linear regression analysis to the experimental data (runs 1–10):

$$\hat{S}_{\mathrm{BET}} = 489.4 + 26.6x_{\%\mathrm{DVB}} - 13.7x_{F_\mathrm{m}}$$
$$R^2 = 0.877; R^2_{\mathrm{adj}} = 0.842 \quad (5)$$
$$P\text{-value for lack of fit} = 0.680$$

$$\hat{V}_{\mathrm{meso}} = 0.720 + 0.036x_{\%\mathrm{DVB}} - 0.040x_{F_\mathrm{m}} - 0.035x^2_{F_\mathrm{m}}$$
$$R^2 = 0.916; R^2_{\mathrm{adj}} = 0.874$$
$$P\text{-value for lack of fit} = 0.055 \quad (6)$$

$$\hat{V}_{\mathrm{macro}} = 0.309 - 0.177x_{F_\mathrm{m}}$$
$$R^2 = 0.940; R^2_{\mathrm{adj}} = 0.933 \quad (7)$$
$$P\text{-value for lack of fit} = 0.858$$

Eqs. (5)–(7) are given in terms of coded factors. However, since it is desirable to enable a prediction of the structural characteristics at any combination of the synthesis conditions without having to code

Table 3
Values of the regression coefficients and of their statistical significance in the models given by Eqs. (1)–(4)

Term	S_{BET} (m^2 g^{-1})		V_{micro} (cm^3 g^{-1})		V_{meso} (cm^3 g^{-1})		V_{macro} (cm^3 g^{-1})	
	Coefficient	P-value	Coefficient	P-value	Coefficient	P-value	Coefficient	P-value
Constant	495.7	<0.001	0.07844	<0.001	0.721	<0.001	0.310	<0.001
%DVB	26.6	0.005	0.00062	0.808	0.036	0.004	−0.001	0.948
F_m	−13.7	0.044	−0.00008	0.974	−0.040	0.003	−0.177	<0.001
%DVBF_m	−2.9	0.643	0.00145	0.645	−0.015	0.117	−0.042	0.078
%DVB%DVB	−2.8	0.731	−0.00004	0.993	−0.003	0.784	0.004	0.886
$F_\mathrm{m}F_\mathrm{m}$	−7.8	0.362	−0.00084	0.837	−0.035	0.025	−0.006	0.823

Table 4
ANOVA for the significance of the models given by Eqs. (1)–(4)

Model	Source of variation	Sum of squares	Degrees of freedom	Mean square	F	P-value	
Eq. (1) S_{BET}	Regression	5603	5	1121	8.34	0.031	Significant
	Residual error	537	4	134			
	Lack of fit	414	3	138	1.12	0.586	Non-significant
	Pure error	123	1	123			
	Total	6140	9				
	$R^2 = 0.912$; $R^2_{\mathrm{adj}} = 0.803$						
Eq. (2) V_{micro}	Regression	0.000012	5	0.000002	0.07	0.993	Non-significant
	Residual error	0.000136	4	0.000034			
	Lack of fit	0.000069	3	0.000023	0.34	0.815	Non-significant
	Pure error	0.000067	1	0.000067			
	Total	0.000148	9				
	$R^2 = 0.084$; $R^2_{\mathrm{adj}} =< 0.001$						
Eq. (3) V_{meso}	Regression	0.021497	5	0.004299	18.43	0.007	Significant
	Residual error	0.000933	4	0.000233			
	Lack of fit	0.000931	3	0.000310	155.19	0.059	Non-significant
	Pure error	0.000002	1	0.000002			
	Total	0.022430	9				
	$R^2 = 0.958$; $R^2_{\mathrm{adj}} = 0.906$						
Eq. (4) V_{macro}	Regression	0.194956	5	0.038991	31.56	0.003	Significant
	Residual error	0.004942	4	0.001236			
	Lack of fit	0.003930	3	0.001310	1.29	0.556	Non-significant
	Pure error	0.001013	1	0.001013			
	Total	0.199898	9				
	$R^2 = 0.975$; $R^2_{\mathrm{adj}} = 0.944$						

them, these models are also given in terms of the real values of the factors ($y_{\%\mathrm{DVB}}$ and $y_{F_{\mathrm{m}}}$ in Eqs. (8)–(10)), where obviously the same values of R^2, R^2_{adj} and P-value for lack of fit are obtained:

$$\hat{S}_{\mathrm{BET}} = 467.7 + 2.7y_{\%\mathrm{DVB}} - 274.7y_{F_{\mathrm{m}}} \tag{8}$$

$$\hat{V}_{\mathrm{meso}} = -4.148 + 0.004y_{\%\mathrm{DVB}} + 16.193y_{F_{\mathrm{m}}} - 14.167y^2_{F_{\mathrm{m}}} \tag{9}$$

$$\hat{V}_{\mathrm{macro}} = 2.433 - 3.540y_{F_{\mathrm{m}}} \tag{10}$$

The surface and contour plots of these models (Eqs. (8)–(10)) are shown in Fig. 8. From these figures, it may be concluded that: (a) with respect to the BET specific surface area (Fig. 8a), high values of S_{BET} are promoted with high values of DVB concentration and low values of monomeric fraction, although the effect of the monomeric fraction is less significant; (b) regarding the mesopore volume (Fig. 8b), the higher the concentration of porogen and of DVB, the higher the volume of mesopores; and finally (c) the monomeric fraction has a significant negative effect on the macropore volume (Fig. 8c), that is, the lower the monomeric fraction, the higher the macropore volume. With regard to micropore volume, no factor has a significant effect on the response, as deduced from the values given in Tables 3 and 4.

The use of commercial divinylbenzene with a purity of 80% in the synthesis of polymeric microparticles thus enables the synthesis of beads with higher values of the BET specific surface area and mesopore volume than those obtained for microparticles synthesized in the previous experimental designs [10,11], thereby accomplishing the first aim of this part of the investigation: to obtain microparticles with improved structural properties.

Moreover, since it was observed that the proportion of ethylstyrene influences the structural characteristics of poly(styrene-co-divinylbenzene) microparticles, a more detailed study was carried out.

First, taking into account experiments 11, 12 and 15, 16 – that is, experiments in which the microparticles were synthesized with a monomeric fraction of 0.55, a divinylbenzene concentration of 55%, and different ethylstyrene concentrations – a one-way analysis of variance was performed for each response (Table 5). According to this, there is no effect of the concentration of ethylstyrene on the

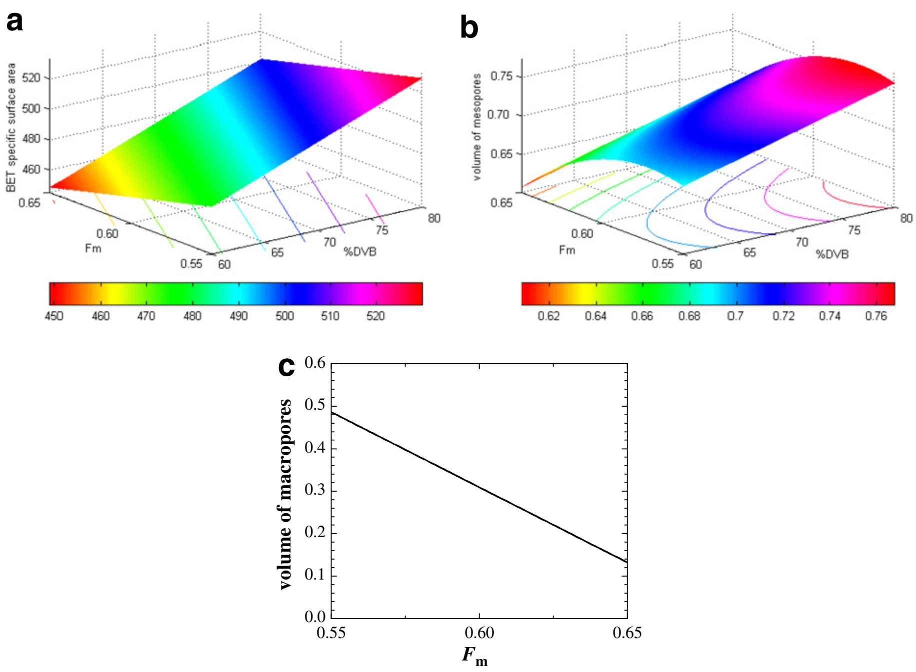


Fig. 8. Plots of the models for: (a) BET specific surface area (Eq. (8)), (b) volume of mesopores (Eq. (9)), and (c) volume of macropores (Eq. (10)).

Table 5
One-way analysis of variance for the structural characteristics (experiments 11, 12 and 15, 16: experiments with a monomeric fraction of 0.55)

One-way ANOVA	Level	Mean	Standard deviation	*P*-value
S_{BET} (m^2 g^{-1})	Percentage 14 %ES	451.6	1.2	0.733
	Percentage 45 %ES	454.4	10.4	
V_{micro} (cm^3 g^{-1})	Percentage 14 %ES	0.0764	0.0002	0.138
	Percentage 45 %ES	0.0648	0.0068	
V_{meso} (cm^3 g^{-1})	Percentage 14 %ES	0.685	0.024	0.739
	Percentage 45 %ES	0.692	0.001	
V_{macro} (cm^3 g^{-1})	Percentage 14 %ES	0.441	0.052	0.258
	Percentage 45 %ES	0.359	0.052	

structural characteristics of the microparticles synthesized with a monomeric fraction of 0.55.

Following this, experiments 13, 14 and 17, 18 ($F_m = 0.65$, %DVB = 55%, and different ethylstyrene concentrations) were considered in order to perform the one-way analysis of variance for each response (Table 6). In this case, as previously expected, a significant effect of the ethylstyrene concentration was observed only on the macropore volume; in other words, the higher the concentration of ethylstyrene in the organic phase during the synthesis of the microparticles, the lower the macropore volume. As seen in Fig. 5e, the pore size distributions of the microparticles synthesized with an ethylstyrene concentration of 14% (experiments 13 and 14) are not shifted towards higher pore radii with respect to the curves obtained for experiments 17 and 18, indicating that the increase in macropore volume is not due to the formation of wider pores, but only to the increase of the number of pores with a diameter similar to those of microparticles of experiments 17 and 18. Taking into account that high percentages of porogen afford high macropore volumes as a consequence of the formation of larger pores, and hence microparticles with low mechanical strength [10,11], this result indicates that the use of

Table 6
One-way analysis of variance for the structural characteristics (experiments 13, 14 and 17, 18: experiments with a monomeric fraction of 0.65)

One-way ANOVA	Level	Mean	Standard deviation	*P*-value
S_{BET} (m^2 g^{-1})	Percentage 14 %ES	423.1	4.1	0.084
	Percentage 45 %ES	411.0	3.3	
V_{micro} (cm^3 g^{-1})	Percentage 14 %ES	0.0709	0.0059	0.506
	Percentage 45 %ES	0.0662	0.0059	
V_{meso} (cm^3 g^{-1})	Percentage 14 %ES	0.600	0.029	0.107
	Percentage 45 %ES	0.531	0.020	
V_{macro} (cm^3 g^{-1})	Percentage 14 %ES	0.126	0.018	0.034
	Percentage 45 %ES	0.054	0.007	

commercial DVB of high purity may be useful in the synthesis of microparticles oriented to applications where an acceptable macropore volume and high mechanical strength are required.

4. Conclusions

The use of high percentages of DVB (80% commercial DVB) in the polymerization mixture enabled us to obtain macroreticular poly(styrene-co-divinylbenzene) microparticles with enhanced structural characteristics. Besides, by comparing these results with those obtained for particles synthesized with 55% commercial DVB, the effect of ethylstyrene on these characteristics has been also elucidated.

Microparticles synthesized with 80%DVB show higher BET specific surface area values, and mesopore volumes, than those synthesized with lower percentages of DVB. These improvements may be of great use in the future if the microparticles are to be used in the adsorption of macromolecules, because they should exhibit enhanced equilibrium and kinetic adsorption properties. The results were modelled as a function of the coded and real values of the %DVB and F_m factors. Thus, the BET specific surface area, and the mesopore and macropore volumes of the microparticles can be predicted with these models within the range of the values of the factors investigated in this work.

Regarding the influence of the proportion of ethylstyrene in the structural characteristics of the microparticles, the use of two types of commercial DVB (with a purity of 80% and 55%) enabled us to obtain microparticles with the same percentage of DVB but different percentages of ethylstyrene. It was observed that the highest macropore volume was obtained when the microparticles were synthesized with the lowest percentage of ethylstyrene in the case of the lowest proportion of porogen in the synthesis mixture. Therefore, the use of divinylbenzene with a purity of 80% permits the collection of microparticles with an acceptable macropore volume and high mechanical strength.

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