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Pellicular ion exchange resins based on divinylbenzene and 2-vinylpyridine

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Abstract

A semi-suspension polymerization process was used in this work in order to prepare ion exchange pellicular resins. This technique allowed us to produce cores of polydivinylbenzene or poly(divinylbenzene-*co*-2-vinylpyridine) with narrow particle size distribution. The shell structure was formed by a porous thin layer of a functional polymer based on poly(divinylbenzene-*co*-2-vinylpyridine) grafted to the core. The characterization of cores and pellicular resins was carried out through the determination of apparent density, surface area, particle average diameter and ion exchange capacity. The morphological characterization of the core-shell particles was carried out by electron microscopy. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Semi-suspension polymerization; Pellicular resins; Synthesis

1. Introduction

Macroreticular (macroporous) resins have been widely employed as chromatographic packings, polymer-supported catalysts, adsorbents, ion-exchange resins, etc. due to the facility of obtaining these materials with high control of morphology (porous structure) and to their high chemical resistance [1–4].

The variation of synthesis conditions results in morphological structures ranging from gel-type to macroporous. The gel-type resins do not have porosity in the dry state. The ions to be exchanged have to diffuse through the swollen gel structure. However, when macroporous resins are used, their porosity permits that large ions be completely and quickly removed from external solutions during the resins regeneration processes [4]. Macroporous resins have longer operational lifetime and, generally, are more selective than microporous ones. However, the macroporous resins capacity is lower than the gel-type ones. Studies about the influence of the resins morphology on the functional groups access and on the ion exchange capacity and kinetics have been carried out in our laboratory [5–8]. The major problem identified by us included the production of resins with high capacities where the active sites were readily accessible. These two combined characteristics are the main purpose of our present research on ion exchange resins.

Recent studies have resulted in the development of a new type of resin with better morphological characteristics than the conventional macroporous ones. This new type, denominated pellicular or core-shell resin, consists of a porous layer of a functional polymer grafted onto an inert microporous core. These resins show an ion exchange kinetics faster than the conventional macroporous ones due to the shorter distance (shell) for the ions diffusion to the active sites (easier access to the active sites) [9–11].

In this work, the semi-suspension polymerization was used to prepare ion exchange pellicular resins, consisting of a thin shell based on poly(divinylbenzene-*co*-2-vinylpyridine) grafted onto cores of polydivinylbenzene or poly (divinylbenzene-*co*-2-vinylpyridine).The grafting reaction occurred onto the core residual double bonds of the divinylbenzene units. The pellicular resins were characterized by their apparent density, surface area (BET), particle average diameter, ion exchange capacity and electron scanning microscopy.

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Table 1
The cores synthesis conditions

First step (bulk prepolymerization in a shaker bath)[a]	
Reaction mixture	Concentration
2-VP	0 or 5% (mol)
DVB	100 or 95% (mol)
AIBN	1% (mol)[b]
Reaction variables	Conditions
Temperature	50°C
Reaction time	0.5 h
Stirring speed	50 cycles/min
Second step (suspension polymerization)	
Additives of the aqueous phase	Concentration
Gelatin	0.5% (wt/wt)[c]
NaCl	0.6% (wt/wt)[c]
Organic phase	Concentration
Prepolymerized reaction mixture[d]	First step total mixture
Toluene (dilution degree)[e]	50 or 100% (v/v)
Reaction variables	Conditions
Aqueous phase/organic phase[f]	4/1 (v/v)
Temperature	70°C
Reaction time	7 h
Stirring speed	500 rpm

[a] Maximum conversion attained = 5%.
[b] In relation to the monomers.
[c] In relation to the weight of water (wt/wt%).
[c] Prepolymerized mixture = polymer + non-reacted monomer + non-reacted initiator.
[d] In relation to the volume of the prepolymerized mixture (v/v%).
[e] Organic phase = prepolymerized mixture + toluene.

Table 2
Pellicular resins synthesis conditions (suspension polymerization)

Organic phase	Concentration
Cores[a]	Relative to the shell monomers
2-VP	80 or 60% (mol)
DVB	20 or 40% (mol)
Dilution degree (50/50% tol/hep)	100 or 200%[b]
AIBN	1% (mol)[b]
Additives of the aqueous phase	
Gelatin	0.5% (wt/wt)[c]
NaCl	2.0% (wt/wt)[c]
Reaction variables	
Aqueous phase/organic phase[d]	4/1
Temperature	70°C
Reaction time	24 h
Stirring speed	400 rpm

[a] Core/shell monomers = 60/40 (wt/wt%).
[b] In relation to the shell monomers.
[c] In relation to water.
[d] Organic phase for the calculus of water volume = shell monomers volume + diluent volume.

2. Experimental procedures

2.1. Materials

Commercial 2-vinylpyridine (2-VP) (from Nitriflex) was vacuum distilled. The initiator, 2-2′-azobisisobutyronitrile (AIBN) (from Metacril), was purified by recrystallization from methanol. The diluents *n*-heptane (hep) and toluene (tol) (from SHELL QUIMICA) and commercial divinylbenzene (DVB) (from NITRIFLEX) were used as received.

2.2. Pellicullar resins synthesis

The synthesis of pellicular (core-shell) resins was carried out in two stages. In the first stage, the cores were prepared and in the second stage the cores were grafted with the shell monomers (DVB and 2-VP) to produce the core-shell structure.

2.2.1. Cores synthesis

The synthesis conditions to prepare the cores are summarized in Table 1. The core beads were obtained, in two steps, by semi-suspension polymerization [12]. In the first step, a mixture of monomers and initiator was prepolymerized (conversion <5 wt%) in a shaker bath, and afterwards the reaction mixture (polymer, non-reacted monomer and residual initiator) was dissolved in toluene. In the second step, the resultant toluene solution was added to a 1-L three-necked round-bottomed flask, fitted with a condenser and a mechanical stirrer, containing the aqueous phase (water, gelatin and sodium chloride) at room temperature. The resultant mixture was stirred at 500 rpm for 10 min, and afterwards the temperature was raised to 70°C and kept constant by a thermostated oil bath during the reaction period. The suspension polymerization was conducted to almost complete conversion. After the reaction period (7 h), the polymer beads were washed with water and methanol, filtered, and screened through a series of sieves of standard mesh size to determine particle size distribution. The fraction in the range from 0.354 to 0.177 mm (45–80 mesh) was collected, and used to prepare the pellicular resins.

2.2.2. Pellicular resins preparation

The pellicular resins (Table 2) were formed by suspension polymerization using the cores produced in the first stage. The cores were swollen with the reaction mixture (AIBN, DVB, 2-VP and diluent mixture (50/50 tol/hep v/v% at a dilution degree of 100 or 200%) and afterwards dispersed in the aqueous phase (water, gelatin and sodium chloride) for the synthesis (suspension polymerization) of the shell. At the end of the polymerization period, the resultant beads were thoroughly washed with water and then with ethanol to ensure the complete removal of impurities.

Table 3
Characteristics of the cores (d_a = apparent density; S = surface area; $d\bar{p}$ = particle average diameter)

DVB/2-VP (mol/mol%)	Dilution degree (v/v%)	d_a (g/cm^3)	S (m^2/g)	$d\bar{p}$ (μm)	Yield 45–80 mesh (%)
100/0	50	0.55	87	206.2	68.2
	100	0.43	511	199.6	72.1
95/5	50	0.52	45	223.7	65.4
	100	0.45	431	202.9	70.7

2.3. Characterization

The cores and pellicular resins were characterized by several methods. The surface area (S) was determined by nitrogen adsorption measurements following the BET method [13]. The apparent density was measured by the graduated cylinder method [14]. The particle average diameter was determined by laser light scattering in a Mastersizer Malvern Instrument [15]. The ion exchange capacity of the pellicular resins was determined by titration.

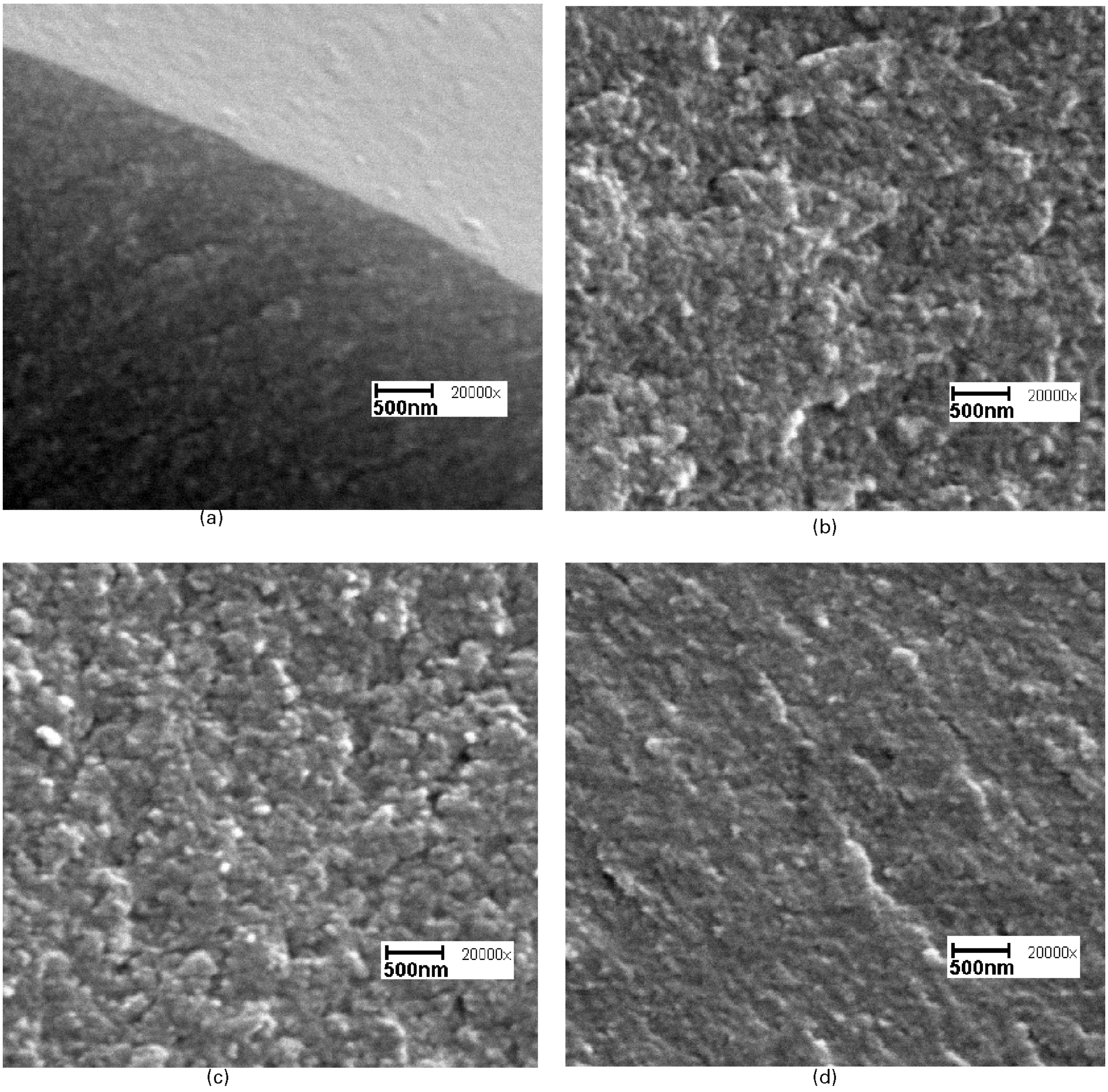

Fig. 1. SEM micrographs of the bulk of the cores synthesized with: 100% DVB (a) 50% dilution and (b) 100% dilution; 95% DVB/5% 2-VP (c) 50% dilution; and (d) 100% dilution.

Table 4
Characteristics of pellicular resins (d_a = apparent density; S = surface area; $d\bar{p}$ = particle average diameter)

Original core		Pellicular resins					
DVB/2-VP (mol/mol%)	Dilution degree[a] (v/v%)	Dilution degree[b] (v/v%)	DVB/2-VP (mol/mol%)	d_a (g/cm^3)	S (m^2/g)	$d\bar{p}$ (μm)	Capacity (meq/g)
100/0	50	200	20/80	0.47	20	210.6	0.29
			40/60	0.51	117	206.0	0.12
	100		20/80	0.38	281	196.9	0.35
			40/60	0.47	237	217.0	0.11
95/5	50	100	20/80	0.51	1	225.8	0.10
			40/60	0.53	2	259.7	0.16
	100		20/80	0.40	96	200.1	0.21
			40/60	0.54	137	218.2	0.14

[a] Diluent = toluene.
[b] Diluent = 50/50 (v/v%) tol/hep.

Following the IUPAC recommendations [16], the resins were converted to the chloride-form (Cl-form) and the ion exchange capacity was determined by titration with a standard aqueous $AgNO_3$ solution [17]. The internal and external morphologies of the beads' surfaces were observed by scanning electron microscopy.

3. Results and discussion

3.1. Polymeric cores

The polymer cores presented particle size in the range from 199 to 224 μm (the highest yield) with a relatively narrow particle size distribution.

Table 3 summarizes the structural characteristics of the cores. The increase of dilution degree in the core synthesis (from 50 to 100% of toluene) provoked an increase in the surface area and a decrease in the apparent density.

These results are evidences of the increase in the cores' porosity with predominance of micropores. The increase of the proportion of micropores provoked an increase in the surface area, and, as a consequence, a decrease in the apparent density.

Macroporous resins when examined by electron microscopy show aggregates (clusters) of microgel particles (microspheres) glued together at their interfaces. The porosity arises from the voids within the clusters, and the spaces between the microspheres from which the aggregates are built [4].

Scanning electron microscopy of the different cores produced in this work (Fig. 1(a)–(d)) showed that the increase of dilution degree (from 50 to 100% of toluene) provoked a slight increase in the size of the aggregates of microspheres that compose the bulk morphology of the cores.

That change in morphology, with the increase of the dilution degree, is in accordance with the decrease of the apparent density and increase in the surface area. All results indicate an increase in the porosity.

3.2. Pellicular resins

The structural characteristics of the pellicular resins are shown in Table 4. The dilution degrees selected in this work were the result of swelling experiments of the core particles [18]. If an excess of diluent were used, the cores would not be able to absorb the total amount of the reaction mixture (monomers/initiator/diluents), provoking a copolymerization out of the cores, making new beads instead of forming a grafted shell. However, if the amount of diluent were insufficient to swell all cores, the shell would not be formed in all cores. The presence of a macroporous shell on the cores' surface was responsible for the decrease of its surface area and resulted in a decrease of mass per volume. Consequently, in a general way, the apparent density decreased (Table 4).

The shell grafting on the polymer core, in a general way, provoked an increase in particle average diameter. This increase indicates the presence of an additional layer on the cores surface. However, in some cases the results did not show this behavior. This fact may be explained by the presence of small beads formed out of the cores during the second stage of the pellicular resin synthesis.

The presence of a porous shell on the polymer core surface can be seen in the SEM micrographs shown in Fig. 2.

3.2.1. The influence of DVB content on apparent density

The results in Table 4 show that the increase of DVB content in the shell monomers composition provoked an increase in the apparent density. That result is in accordance with the mechanism of phase separation [6,7]. The higher the amount of DVB, the lower the difference between the solubility parameters of diluent (mixture 50/50 v/v% tol/hep) and polymer. The solubility parameter of 2-VP and its polymer is higher than the solubility parameter of the diluent, while the solubility parameter of DVB and its polymer is closer to the diluent. Thus the phase separation during the shell formation is not so drastic, resulting in a less

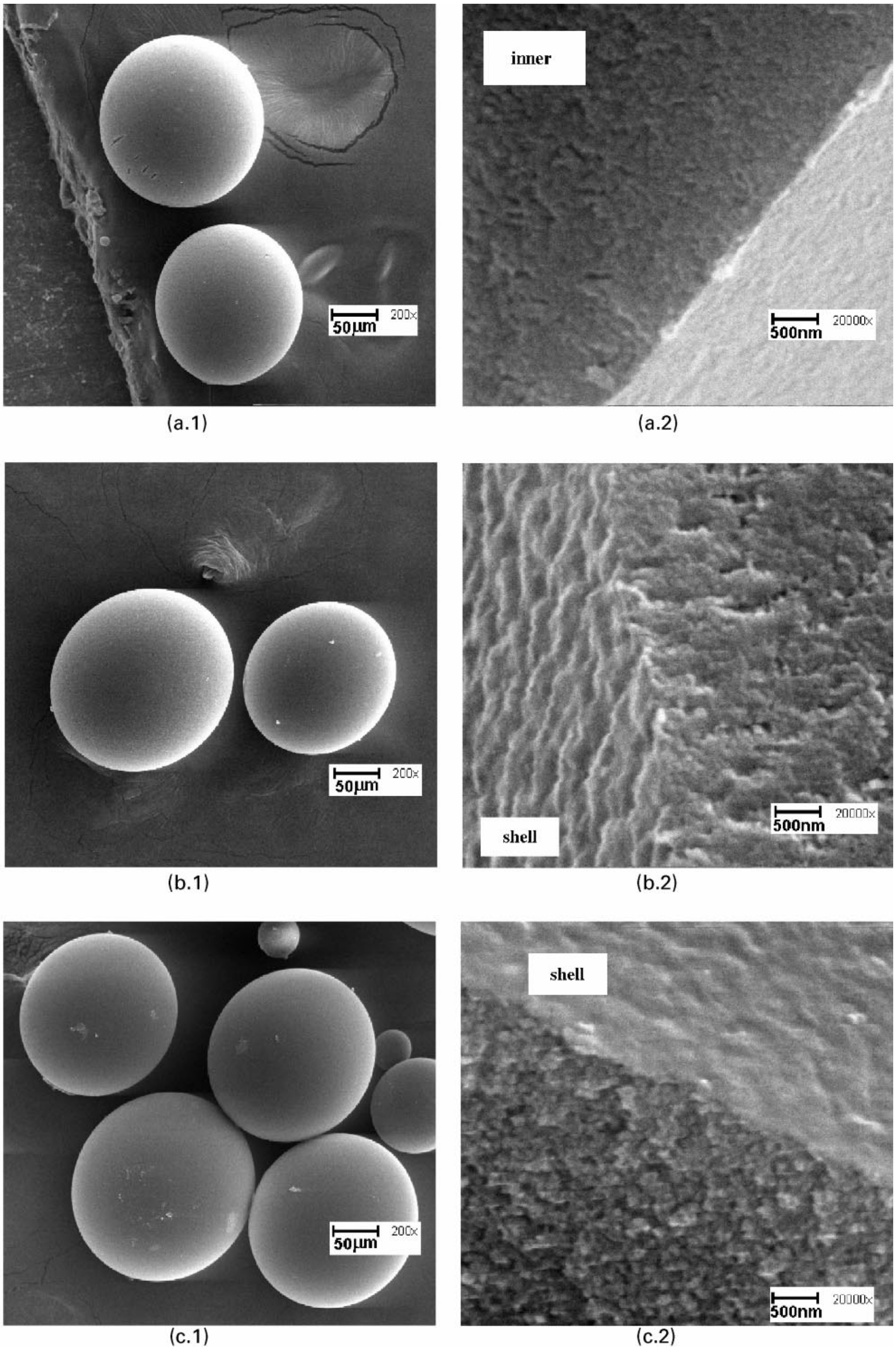

Fig. 2. SEM micrographs: (a) core 95% DVB/5%2-VP—100% dilution; (b) pellicular resin 20% DVB/80% 2-VP —100% dilution; (c) pellicular resin 40% DVB/60% 2-VP—100% dilution.

porous structure and consequently with higher apparent density.

3.2.2. *The influence of DVB content on surface area*

In general, the increase in DVB content in the shell monomer composition promoted an increase in the resin surface area (Table 4). That behavior is a consequence of the formation of pores with smaller diameters resultant of a less drastic phase separation. That explanation is supported by the results obtained when it was used at dilution degree of 100%. In that case, the phase separation was more drastic, due to the lower content of diluent, resulting in larger pores and as a consequence in lower surface areas [19].

3.2.3. The influence of DVB content on ion exchange capacity

Generally, as expected, the increase of DVB content provoked a decrease in ion exchange capacity of the resins (Table 4). As the active sites are derived from 2-VP, the lower the amount of 2-VP, the lower the ion exchange capacity. Additionally, more reticulated structures have a higher micropore proportion, where the access to active sites (pyridine nitrogen) is steric obstructed, that may also provoke a decrease in ion exchange capacity. However, one resin did not show this behavior. That fact may be related to the presence of beads formed out of the cores surface that would contribute for the increase in ion exchange capacity.

4. Conclusions

It was verified in this work that the semi-suspension polymerization is a possible technique to synthesize cores with narrow particle size distribution.

The increase in dilution degree resulted in increase in surface area and decrease in apparent density of the cores. The presence of 2-vinylpyridine in the core composition provoked a decrease in the surface area and did not influence the apparent density.

In general, the pellicular resins had smaller surface area and larger particle average diameter than their cores. The increase of DVB content in the shell monomers composition resulted in increase in apparent density and, in a general way, the surface area also increased. Generally, as expected, the increase of DVB content provoked a decrease in resins ion exchange capacity.

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