

The influence of the diluent system on the porous structure formation of copolymers based on 2-vinylpyridine and divinylbenzene.

Diluent system: II-*n*-heptane/toluene

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Abstract

Anion-exchange resins based on 2-vinylpyridine (2VP) and divinylbenzene (DVB) were synthesized by suspension polymerization in the presence of a diluent mixture of *n*-heptane (HEP) and toluene (TOL) at different compositions. The effects of the composition of the diluent mixture and crosslinking degree (DVB content) on the porous properties of the resins were evaluated. It was found that the development of porosity was attained whenever the content of *n*-heptane in the diluent mixture was increased for all DVB contents employed. The resins were characterized by mercury porosimetry, BET surface area determination, and apparent density, swelling in methanol. The optical appearance and surface morphology of the copolymer beads were examined by optical and scanning electron microscopies (SEM), respectively. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: 2-vinylpyridine; Divinylbenzene; Porous copolymers

1. Introduction

Macroporous copolymers, because of their better performance than those conventional gel-type materials, have been widely employed as column packing materials for gel permeation chromatography, as the supports for ion exchange resins and polymeric catalysts [1–3]. The synthesis of these materials has been extensively studied and reviewed in the literature, mainly the synthesis of those based on styrene and divinylbenzene monomers [4,5]. The porous structure formation of these copolymers is governed by the occurrence of phase separation during the copolymerization reaction [6–8]. The addition of pure diluents (so-called porogens) or mixtures of them to the reaction mixture (monomers and initiator) achieve that process. This way polymeric networks with porous properties dependent on the concentration of the crosslinking agent, and on the concentration and nature of the diluent system are produced [9–25]. Although the production of macroreticular structures for the above-mentioned applications has been reported for many polymer systems, there are few studies in the literature about macroporous copolymers

based on vinylpyridines [26–34], which can be directly used as ion exchange resins. These resins find applications as catalysts or catalysts supports and as polymer reagents, in metal recovery and in the pollution control of waters by metal contaminants [35].

In a previous paper [35] we described the influence of the contents of the diluents, *n*-heptane (HEP) and diethylphthalate (DEP), pure or as mixtures, and the crosslinking agent divinylbenzene (DVB) on the porous structure formation of copolymers based on 2-vinylpyridine and divinylbenzene (2VP–DVB). The purpose of this present paper is to extend the investigation about the effect of diluent mixtures, namely those constituted of *n*-heptane and toluene, on the porosity formation of 2VP–DVB copolymers.

2. Experimental

2.1. Materials

Commercial 2-vinylpyridine (2VP) and divinylbenzene (DVB) (both monomers donated by Nitriflex Indústria e Comércio, Brazil) were vacuum distilled after washing with a 5% NaOH aqueous solution. The initiator 2, 2'-azobisisobutyronitrile (AIBN) (E. Merck AG, Germany) was

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Table 1
Characteristics of the resins

DVB (%)	HEP/TOL (vol%/vol%)	V_p (cm ³ /g)	S_2 (m ² /g)	d_{ap} (g/cm ³)	Swelling (%) ^a	Optical appearance ^b
20	0–100	nd ^c	nd	0.62	141.4	T
	25–75	nd	nd	0.62	131.2	T
	50–50	0.18	3.1	0.60	174.2	O
	75–25	0.85	0.4	0.31	57.7	O
40	0–100	nd	nd	0.66	100.0	T
	25–75	nd	nd	0.66	101.1	T
	50–50	0.26	11.1	0.53	89.3	O
	75–25	0.91	21.1	0.33	29.5	O
60	0–100	nd	nd	0.69	92.1	T
	25–75	nd	nd	0.68	92.2	T
	50–50	0.26	24.3	0.58	92.0	O
	75–25	0.93	63.8	0.33	20.0	O

^a Swelling in methanol.

^b T = transparent. Tr = translucent. O = opaque.

^c Not determined.

purified by recrystallization from methanol (Prosint SA, Brazil). The other chemicals: *n*-heptane (Vetec Química Fina LTDA, Brazil), toluene (Vetec Química Fina LTDA, Brazil), sodium hydroxide (Reagen-Quimibrás Indústria Química SA, Brazil), gelatin (Union Carbide do Brasil SA, Brazil) and 2-hydroxyethylcellulose (Union Carbide do Brasil SA, Brazil), were used as received. The aqueous solutions were prepared with distilled deionized water.

2.2. Polymerization

The copolymer beads were obtained by usual aqueous suspension polymerization method in a 1 l, three-necked, round-bottomed flask reactor fitted with mechanical stirrer, reflux condenser with a Hg seal at its top and a nitrogen gas inlet tube as described previously [36]. At room temperature, the flask was charged with the aqueous phase that was composed of gelatin (0.2 wt% in relation to water), 2-hydro-

xyethylcellulose (0.2 wt% in relation to water) and NaCl (2 wt% in relation to water). The organic phase, a mixture of 2-vinylpyridine (0.3 mol), divinylbenzene (mol% in relation to vinylpyridine), diluent system and AIBN (1 mol% in relation to monomer mixture), was added to the aqueous phase and suspended by stirring (400 rpm). The content of the diluent mixture was fixed at 100% in relation to the volume of the monomer mixture and its composition was varied according to the data given in Table 1. The ratio between aqueous and organic phase was set at 3:1. After establishing a nitrogen atmosphere in the flask, the temperature was raised to 70°C and kept constant by a thermostatic oil bath during the reaction period (8 h). The produced beads were decanted, washed with methanol, wet sieved, washed again with methanol, and finally dried in an oven at 70°C for 24 h.

2.3. Copolymers characterization

Copolymers characterization was carried out with a fraction of sieved beads in the range of 50–80 mesh. The copolymers beads were characterized by Hg porosimetry (pore volume = V_p) in a Quantachrome porosimeter Mod. Autoscan 33, the surface area (S) was determined by N₂ adsorption in a Micromeritics Mod. ASAP 2010 area meter accordingly to the BET method [37], and the apparent density (d_{ap}) and swelling in methanol (contacting time = 48 h in swelling experiments) were determined in a graduated cylinder as described previously [31]. The visual appearance and surface morphology of the copolymer beads were examined by optical and scanning electron microscopies, respectively.

3. Results and discussion

Table 1 presents the characteristics of the copolymers synthesized in the presence of diluent mixtures at various proportions of the crosslinking agent (DVB). It was

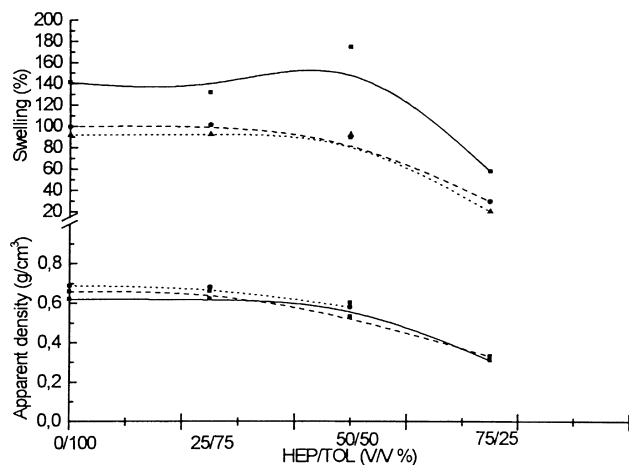


Fig. 1. The influence of the diluent mixture composition used in the polymerization on the swelling in methanol and on the apparent density of the resins synthesized with (—) 20% DVB, (---) 40% DVB and (···) 60% DVB.

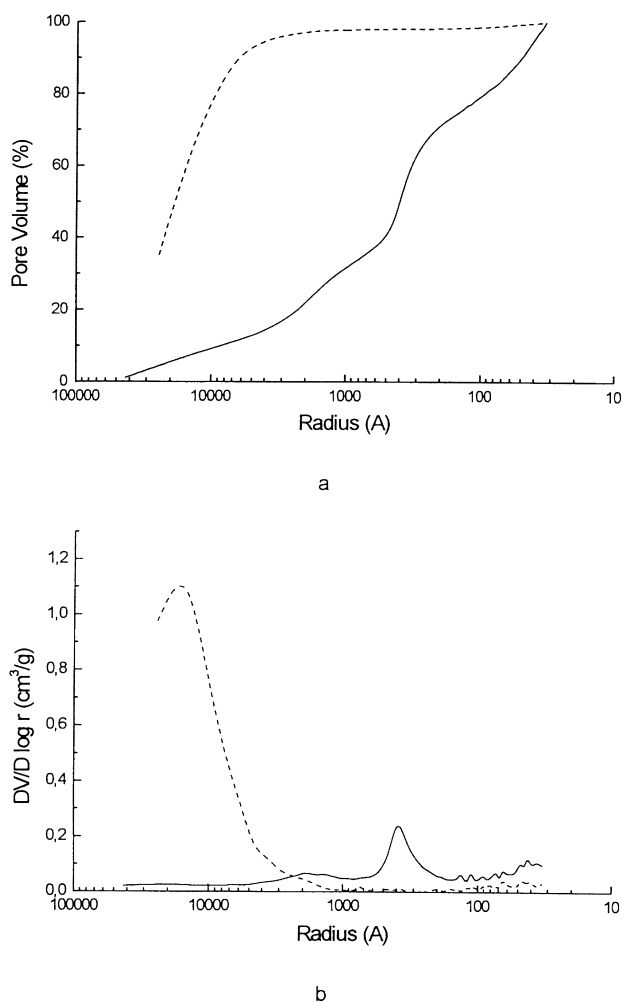


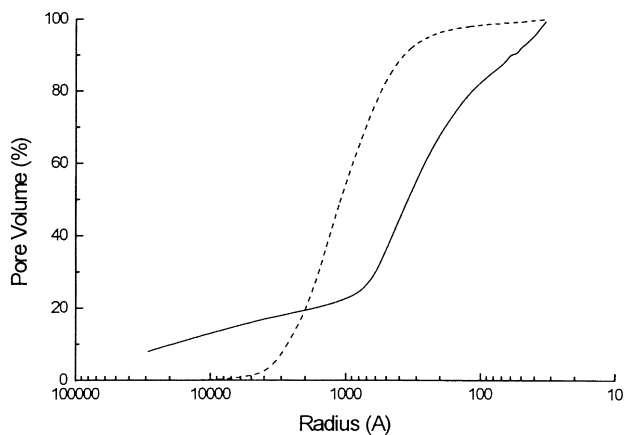
Fig. 2. Cumulative (a) and (b) differential pore size distribution of the resins synthesized with 20% DVB at diluent compositions of: HEP/TOL (%) = (—) 50/50 and (---) 75/25.

observed that the resins synthesized in the presence of pure toluene or at low heptane proportion in the diluent mixture (HEP/TOL = 25/75) were transparent, gel-type like materials, although toluene is cited as a non-solvating diluent to the poly(2-vinylpyridine) [38]. As the heptane content in the diluent mixture was increased, at a fixed DVB content (Table 1), the pore volume increased and, in consequence, the apparent density decreased (Fig. 1), since those characteristics are complementary. In the same way, except for the resins synthesized with 20% DVB using HEP/TOL = 50/50 as the diluent, as the porosity increased the swelling in methanol decreased (Fig. 1). That result may be attributed to the formation of more rigid structures due to the presence of larger pores, resultant from the occurrence of phase separation during the early stages of the polymerization. This same anomalous behavior at 20% DVB in relation to the swelling, showing a maximum in the curve, was observed in a previous study for the resins based on 2VP/DVB synthesized using pure heptane [31] or heptane-diethylphthalate as diluent [39]. This behavior was also

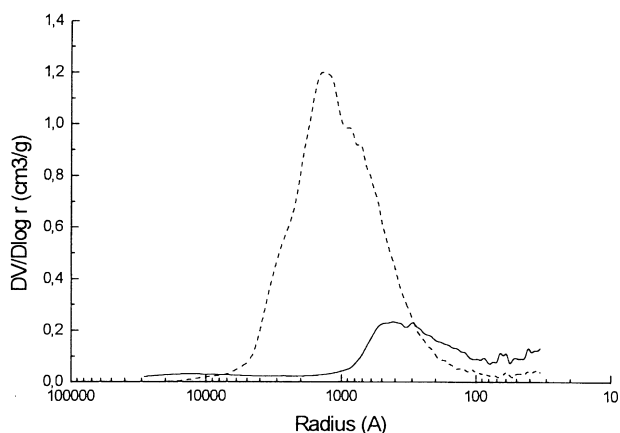
related in the literature for resins based on styrene/DVB [40]. A possible explanation for this behavior, is that at a low DVB content, at the early stages of polymerization, the addition of a small amount of heptane to the diluent mixture, contributes more to the solvation of the growing chains of poly(2-vinylpyridine) than to the phase separation process. In those conditions, the phase separation will occur later, as the polymer chains grow due to the incorporation of 2VP units. This way, the polymer chains formed at low DVB and heptane contents are formed in a more expanded way than those formed at higher heptane content. Thus these chains are able to swell when put into contact with a good solvent like methanol. As the heptane contents increases, the phase separation becomes more predominant leading to the formation of more rigid structures and as a consequence the swelling decreases as observed in Fig. 1. At higher DVB contents, this behavior is minimized since the polymer chains are more entangled due the higher degree of cross-linking between the chain segments and thus, the swelling decreases. When both, the heptane and DVB content attain a critical value in the reaction mixture, again the phase separation occurrence leads to the decrease in the swelling.

Figs. 2–4 show the influence of the diluent mixture, at same DVB proportion, on the porous structure of the resins illustrated by their pore size distribution curves obtained by mercury porosimetry. It was observed that, for all DVB contents, the increase in heptane proportion in the diluent mixture, the pore size distributions tended to shift toward larger pore size region. That behavior was the result of the occurrence of a more pronounced phase separation due to the decrease of the solvating power of the diluent mixture provoked by the increase of the heptane proportion. This behavior was more pronounced to the resins synthesized with 20% DVB where pores of about 20,000 Å were detected (Fig. 2) for the resin synthesized in the presence of a diluent mixture HEP/TOL = 75/25. The presence of large pores provoked a decrease in the surface area (Table 1). The SEM micrographs of the beads and their inner cross-section surface are illustrated in Figs. 5 and 6. These figures show a marked change in the morphology of the resins resultant of the increase in the heptane content. At 40 and 60% DVB (Figs. 3 and 4), the tendency to form very large pores diminished, however the population of pores of intermediary diameters increased and, as consequence the surface area also increased (Table 1). The increase in the pore volume and in the pore diameter with the increase in the proportion of non-solvating diluent (heptane), is in agreement with those results obtained previously for the resins based on 2VP/DVB synthesized with pure heptane [31], and their mixtures with diethylphthalate [35] or methyl ethyl ketone [30]. This behavior is also similar to that observed for the resins based on styrene/DVB [1,13–15].

The results of the Table 1 show that an initial increase in the concentration of DVB, provoked an increase in the pore volume values of the resins, which practically did not vary when the DVB content was further increased to 60%. Since



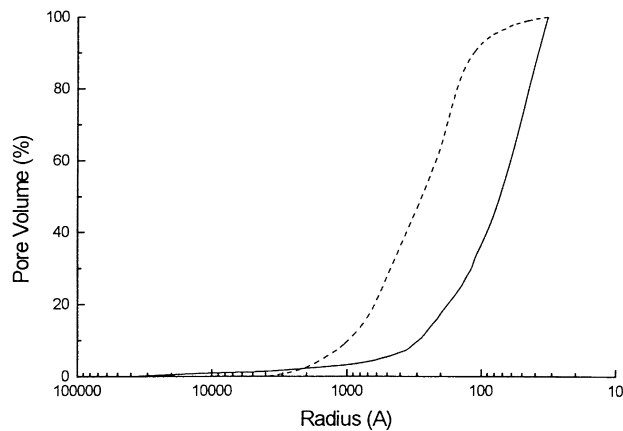
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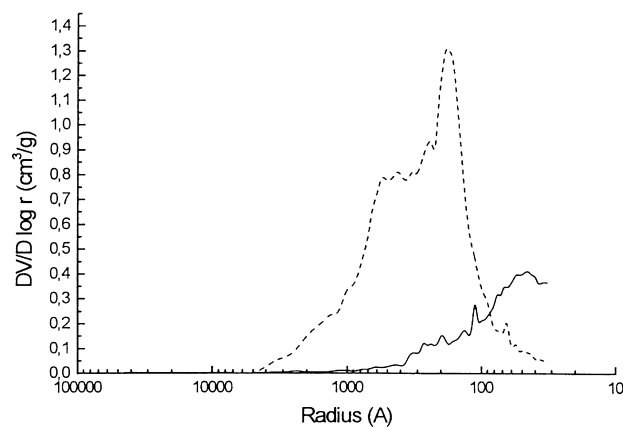
b

Fig. 3. Cumulative (a) and (b) differential pore size distribution of the resins synthesized with 40% DVB at diluent compositions of: HEP/TOL (%) = (—) 50/50 (---) 75/25.

the increase of DVB proportion has provoked a slight enhancement in the porosity, the increase in the apparent density with the increase in DVB content, can be explained as being due to the formation of a more dense structure because of the entanglement provoked by the increase in the crosslinking degree. As expected, the swelling in methanol decreased as a consequence of the formation of more rigid structures due to the higher degree of crosslinking and to the presence of larger pores (Table 1). The effect of the DVB content on the porous structure of the resins, are better illustrated in Figs. 7 and 8 through their distribution curves. In a general way, as the DVB increased, the pore size distribution curves shifted toward smaller pore region. The resin synthesized using a diluent mixture HEP/TOL = 50/50 and 20% DVB (Fig. 7), showed a pore size distribution with three distinct pore size ranges, localized between 1000 and 5000 Å, between 200 and 1000 Å, and those below 100 Å. These pore families are visualized in the SEM micrographs illustrated in Fig. 9a. The larger pores, those



a



b

Fig. 4. Cumulative (a) and (b) differential pore size distribution of the resins synthesized with 60% DVB at diluent compositions of: HEP/TOL (%) = (—) 50/50 (---) 75/25.

in the range of 1000–5000 Å and 200–1000 Å are localized between the aggregates of microspheres. The other pores, smaller than 100 Å, are those localized in the interstices between the microspheres. At 40% DVB, except for the largest pore size range family that disappeared, the distribution curve (Fig. 7) show a pattern similar to that of the resins synthesized with 20% DVB with a broadening of the distribution of the intermediary pores with a maximum at about 400 Å. The SEM micrograph of this resin (Fig. 9b), shows this effect. In the same figure can be seen that the size of the microspheres and their aggregates diminished and are closely together and, as a consequence, the surface area increased (Table 1). At 60% DVB the pore size distribution curve (Fig. 7) tended to be unimodal and characterized by the presence of a crescent and complex distribution of pores smaller than 1000 Å. Again, the SEM micrograph of this resin (Fig. 9c) confirms this effect. The aggregates of microspheres are even more closely together than those of the resin synthesized with 40% DVB. The voids among those aggregates diminished and, in the same way as observed at

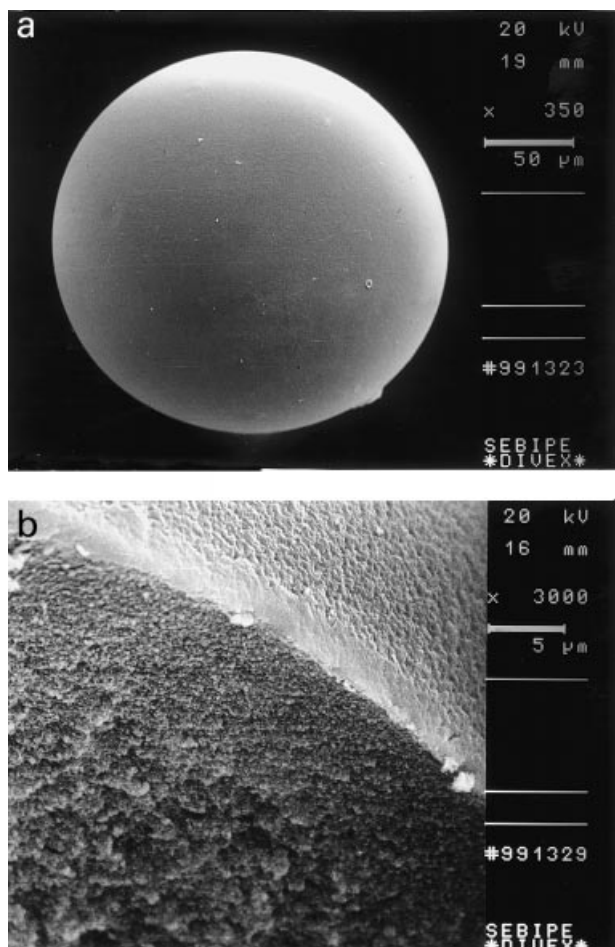


Fig. 5. SEM micrographs of the resins synthesized with HEP/TOL ratio = 50/50 and 20% DVB.

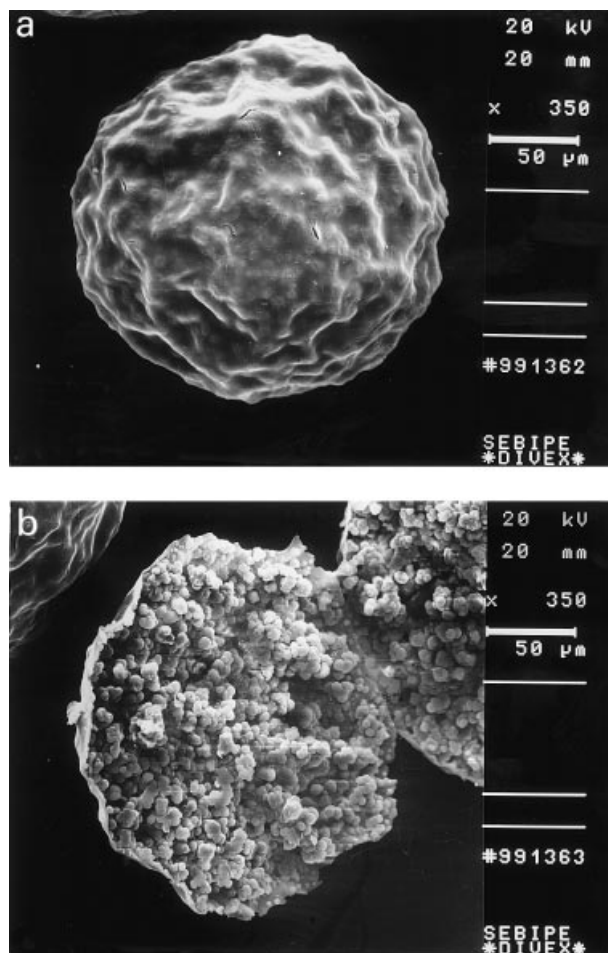


Fig. 6. SEM micrographs of the resins synthesized with HEP/TOL ratio = 75/25 and 20% DVB.

40% DVB, the decrease in the size of pores and microspheres provoked an increase in the resin surface area (Table 1).

The resins synthesized with HEP/TOL = 75/25, suffered a more pronounced effect in their structures, when the DVB proportion was increased, than those previously discussed. That effect can be seen in the pore size distribution curve illustrated in Fig. 8 and in the SEM micrograph (Fig. 10). The resins with 20% DVB showed very large pores, as mentioned above, compared with the resins synthesized at higher DVB contents. At 40 and 60% DVB, the pore sizes diminished markedly. The SEM micrographs of these resins, at a higher magnification (Fig. 11), show that the increase in the DVB content provoked a more accentuated decrease in the size of microspheres and their aggregates leading to the increase in the resin surface area (Table 1).

These results indicate that the porous structure formation of the 2VP/DVB copolymers is more strongly influenced by the nature and composition of the diluent or diluent mixture than the copolymers based on styrene/DVB. This fact can be attributed to the difference in the polarity existing between the monomers 2VP and DVB, in contrast with the styrene/DVB system where both monomers having low polarities,

present chemical similarity. Thus, the presence of diluents of different solvating capacities in the diluent mixture has a minor effect in the polymer chains formation of these copolymers (sty/DVB) compared with 2VP/DVB ones. As was already discussed in this paper, the most accentuated influence of the heptane was found at low DVB and toluene proportions. As the DVB and toluene proportions were increased, the pore size and the size of microspheres and their aggregates decreased as a consequence of the combined effects of toluene and DVB. Since the resins synthesized with pure toluene were gel-type, this suggests that the nuclei are formed in a more swollen state, caused by the preferential solvation of these nuclei, rich in DVB units due to the difference in the monomers reactivity (DVB is more reactive than 2VP) [26]. In the same way, outside the nuclei, the growing chains are formed mainly by 2VP units, crosslinked with DVB and having pendant DVB units. These DVB units show a higher affinity in relation to toluene. That seems to be a reasonable explanation for the mechanism pore structure formation of 2VP/DVB resins as gel-type in presence of toluene. As the heptane content in the diluent mixture reaches a critical value, the phase

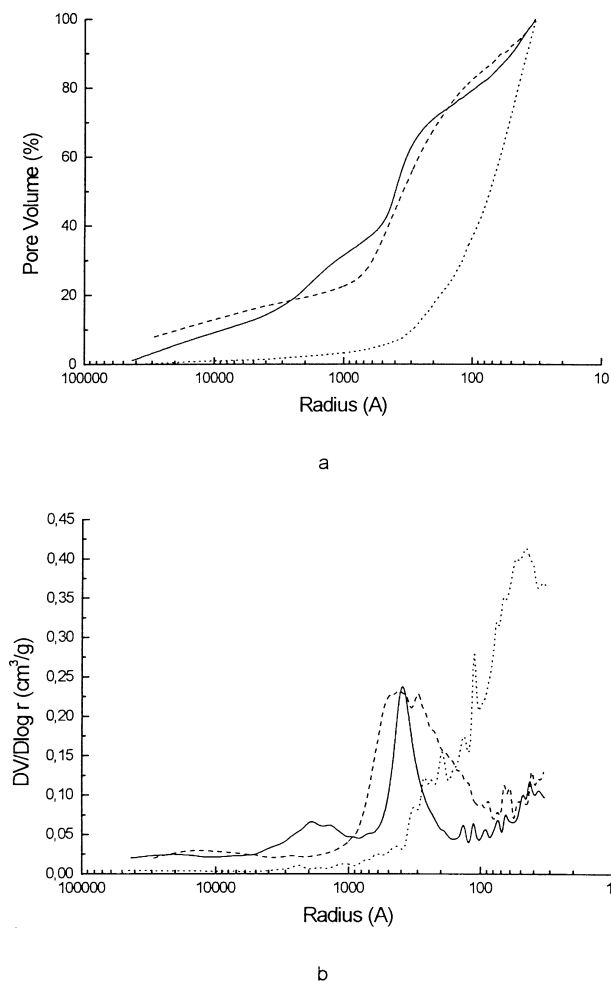


Fig. 7. Cumulative (a) and (b) differential pore size distribution of the resins synthesized with diluent composition HEP/TOL = 50/50 at various DVB content (%) = (—) 20%, (---) 40% and (···) 60%.

separation occurs at a stage that depends on the length of the segment chains constituted by 2VP units that are governed by the content of DVB and the proportion of toluene in the diluent mixture.

Comparing the results related in this paper with those obtained previously [31,36], one finds that the resins based on 2VP/DVB presented the highest porosities when synthesized with the diluents utilized in these studies in this order: pure heptane, heptane/diethylphthalate (HEP/DEP), heptane/toluene (HEP/TOL). When the pure aromatic diluents were employed, the resins were characterized as gel-type materials. When heptane was present in the diluent mixture higher porosity was achieved by the addition of DEP than by the addition of TOL. That result may be attributed to the higher polarity of DEP as compared with TOL. Thus, the diluent mixtures HEP/DEP are more precipitant (poorer solvent) than the diluent mixtures of HEP/TOL in relation to the polymer chains constituted of 2VP units. As a consequence the diluent mixtures HEP/DEP are able to form larger pores (earlier occurrence of phase separation) than the

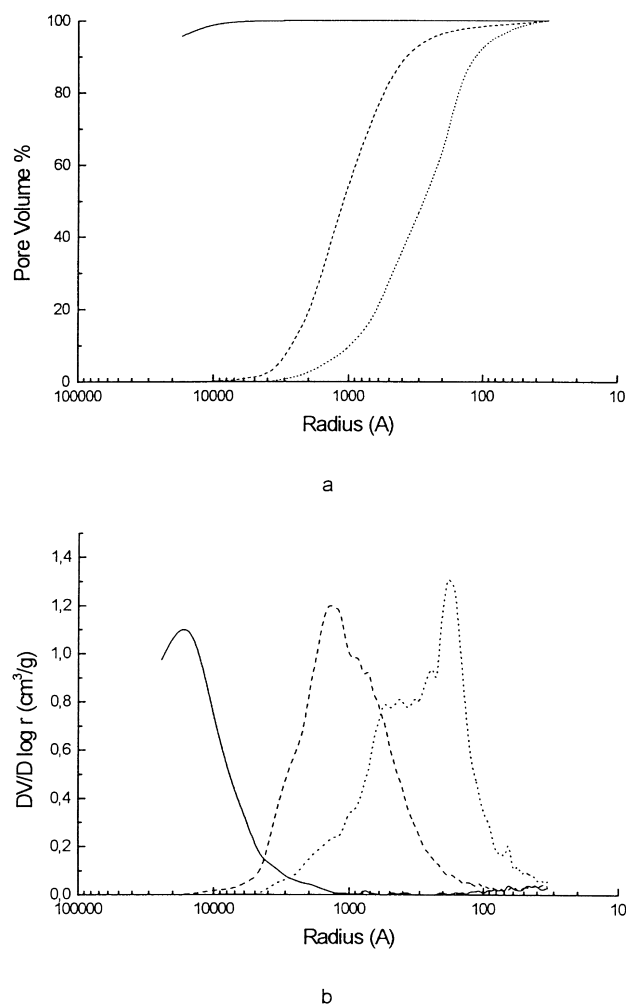


Fig. 8. Cumulative (a) and (b) differential pore size distribution of the resins synthesized with diluent composition HEP/TOL = 75/25 at various DVB content (%) = (—) 20%, (---) 40% and (···) 60%.

diluent mixture HEP/TOL, as was already verified in a previous paper [36].

4. Conclusions

Macroporous resins based on 2VP/DVB were synthesized in presence of diluent mixtures consisting of heptane and toluene at different compositions and varied DVB content. The results indicated that, as in the case of styrene/DVB copolymers, the increase of both, the proportion of the non-solvating diluent (heptane) and DVB content, increased the pore volume. However, the resins showed a more accentuated influence of the nature of the diluent and DVB content than the copolymers based on styrene/DVB. That difference was attributed to the difference in the polarity existing between the comonomers 2VP and DVB. The difference seems to provoke a preferential solvation of

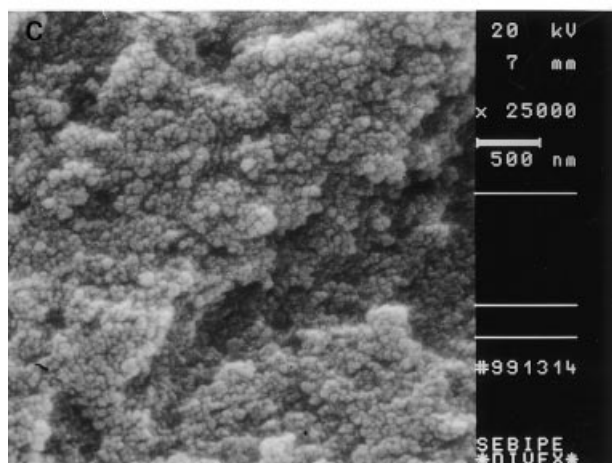
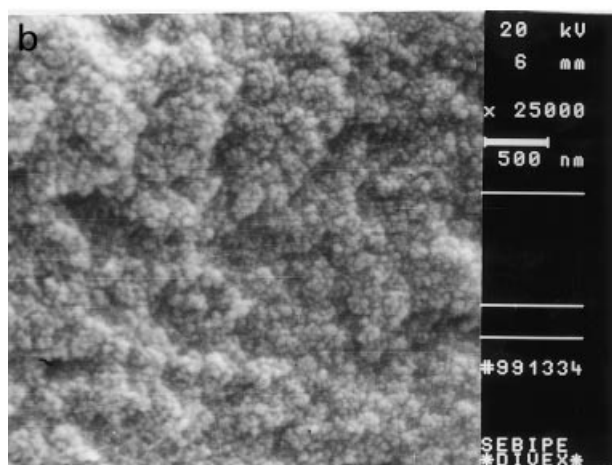
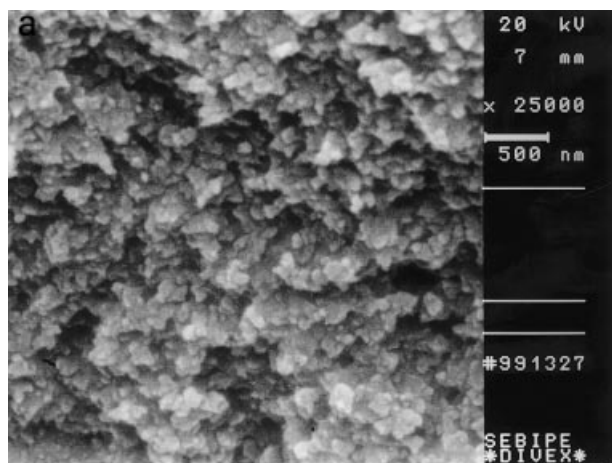


Fig. 9. SEM micrographs of the resins synthesized with HEP/TOL ratio = 50/50 and (a) 20% DVB (b) 40% DVB and (c) 60% DVB.

one of the monomers depending on the nature of the diluent mixture and on the DVB content.

In order to know more about the porous structure formation of the resins based on 2VP/DVB, other studies are being carried out and will be the object of future papers.

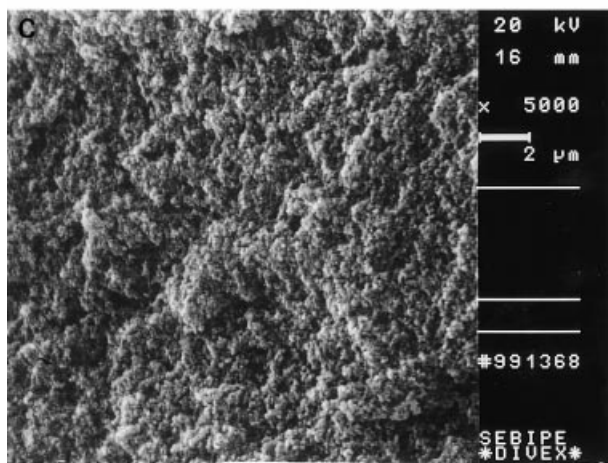
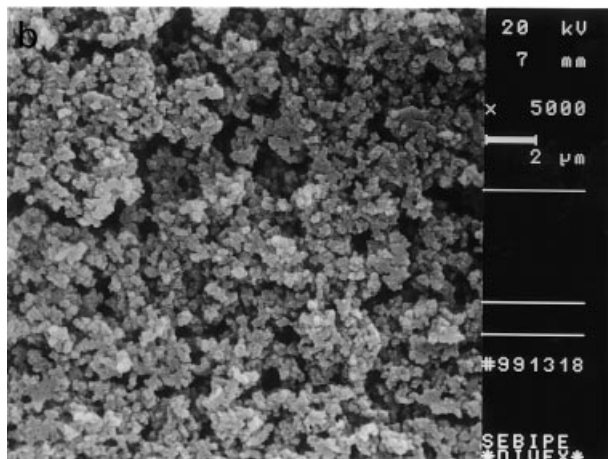
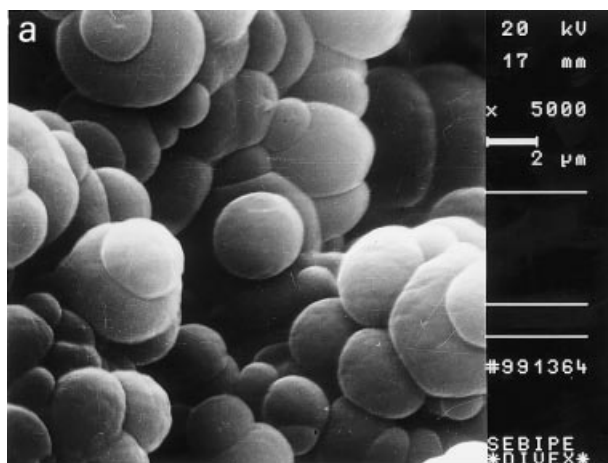


Fig. 10. SEM micrographs of the resins synthesized with HEP/TOL ratio = 75/25 and (a) 20% DVB (b) 40% DVB and (c) 60% DVB.

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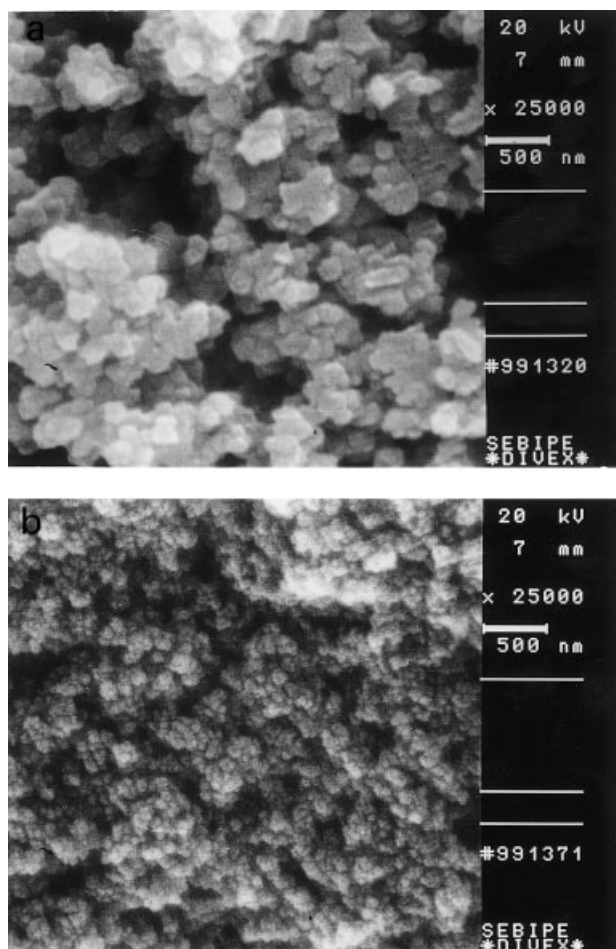


Fig. 11. SEM micrographs of the resins synthesized with HEP/TOL ratio = 75/25 and (a) 40% DVB (b) 60% DVB.

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