

# The Influence of the Diluent System on the Porous Structure Formation of Copolymers Based on 2-Vinylpyridine and Divinylbenzene. Diluent System. III. Heptane/Methylethylketone

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**ABSTRACT:** The effects of the diluent mixture's composition and crosslinking degree [divinylbenzene (DVB)] on the porous characteristics of the anion-exchange resins based on 2-vinylpyridine (2VP) and DVB, synthesized by suspension polymerization, in the presence of a diluent mixture constituted of heptane (HEP) and methyl ethyl ketone (MEK) at different proportions, were evaluated. The resins were characterized by mercury porosimetry, nitrogen adsorption (Brunauer–Emmett–Teller (BET) method surface area determination), apparent density, and swelling in

methanol. The optical appearance of the copolymer beads was examined by optical microscopy. It was found that the development of porosity was attained whenever the content of methyl ethyl ketone in the diluent mixture was increased for all DVB contents employed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 666–669, 2004

**Key words:** 2-vinylpyridine; crosslinking; copolymerization; macroporous polymers; morphology

## INTRODUCTION

Macroporous copolymers, because of their better performance than those conventional gel-type materials, have been widely employed as support for ion exchange resins, polymeric catalysts, and as column packing materials for gel permeation chromatography.<sup>1</sup> The porous structure formation of these copolymers is governed by the occurrence of phase separation during the copolymerization reaction.<sup>2</sup> That process is achieved by the addition of pure diluents (so-called porogens) or mixtures of them to the reaction mixture (monomers and initiator). This way, polymer networks with porous properties dependent on the concentration of the crosslinking agent and on the concentration and nature of the diluent system are produced.

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.<sup>3–17</sup> However, there has been a growing interest in vinylpyridine copolymers, which can be directly used as ion exchange resins in the

recovery of metals, as polymeric reagents, catalysts, and catalyst supports, and they are also being employed in the removal of organic contaminants from wastewater.<sup>18</sup>

In previous articles, we described the influence of the content of pure heptane<sup>19</sup> and their mixtures with diethylphthalate<sup>20</sup> and toluene<sup>21</sup> on the porous structure formation of copolymers based on 2-vinylpyridine (2VP) and divinylbenzene (DVB) at different divinylbenzene proportions. In this article, we extended the investigation about the effect on the porosity formation of 2VP–DVB copolymers to the mixtures constituted of heptane (HEP) and methyl ethyl ketone (MEK).

## EXPERIMENTAL

### Materials

2VP and DVB (both monomers donated by Nitriflex Indústria e Comércio, Rio de Janeiro, Brazil) were vacuum distilled after washing with a 5% NaOH aqueous solution. The initiator 2,2'-azobisisobutyronitrile (AIBN) (E. Merck AG, Germany) was purified by recrystallization from methanol (Prosint SA, Rio de Janeiro, Brazil). The other chemicals, MEK (Vetec Química Fina LTDA, Rio de Janeiro, Brazil), HEP (Vetec Química Fina LTDA), sodium hydroxide (Reagen-Quimibrás Indústria Química SA, Rio de Janeiro, Bra-

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TABLE I  
Characteristics of the Resins

DVB (%)	HEP/MEK (V/V) (%)	$V_p^a$ (cm <sup>3</sup> /g)	$S$ (m <sup>2</sup> /g)	$d_{ap}$ (g/cm <sup>3</sup> )	Swelling in methanol (%)	Optical appearance
20	0-100	nd	<1	0.65	134	T
	10/90	nd	<1	0.66	111	T
	30/70	0.05	<1	0.67	109	T
	50/50	0.15	1.6	0.49	92	Tr
40	0-100	nd	<1	0.66	65	T
	10/90	nd	<1	0.65	52	T
	30/70	0.06	<1	0.67	69	T
	50/50	0.19	20.2	0.51	57	Tr
60	0-100	nd	<1	0.65	61	T
	10/90	nd	<1	0.64	50	T
	30/70	0.12	<1	0.59	65	Tr
	50/50	0.24	36.7	0.55	51	O

<sup>a</sup> T, transparent; Tr, translucent; O, opaque; nd, not determined;  $V_p$ , pore volume;  $S$ , surface area;  $d_{ap}$ , apparent density.

zil), gelatin (Union Carbide do Brasil SA, Brazil), and 2-hydroxyethylcellulose (Union Carbide do Brasil SA, São Paulo, Brazil), were used as received. The aqueous solutions were prepared with distilled deionized water.

### Polymerization

The copolymer beads were synthesized by the 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.<sup>21</sup> A typical procedure is described as follows. At room temperature, the reactor was charged with the aqueous phase that was composed by gelatin (0.2 wt % in relation to water), 2-hydroxyethylcellulose (0.2 wt % in relation to water), and NaCl (2 wt % in relation to water). The organic phase, a mixture of 2VP (0.3 mol), DVB (mol % in relation to vinylpyridine), AIBN (1 mol % in relation to monomer mixture), and the diluent system (vol % in relation to monomer mixture), was added to the aqueous phase and suspended by stirring (400 rpm). The proportion 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 I. The ratio between aqueous and organic phases was set at 3 : 1. After establishing a nitrogen atmosphere in the reactor, the temperature was raised to 70°C and kept at this temperature by a thermostated oil bath during the reaction period (8 h). The produced beads were separated and washed with water, methanol, again with water, and then wet sieved. The obtained fractions were washed with methanol and finally dried in an oven at 70°C for 24 h.

### Copolymer characterization

Copolymer characterizations were carried out by using a fraction (50–80 mesh range) of sieved beads. The

porosity of the beads was determined by Hg porosimetry in a Quantachrome porosimeter Model Autoscan 33; the surface area was determined by N<sub>2</sub> adsorption in a Micrometrics Model ASAP 2010 area meter according to the Brunauer–Emmett–Teller (BET) method,<sup>22</sup> and the apparent density was determined by the graduated cylinder method, a modification of the ASTM D 1895-69 method.<sup>23,24</sup> The swelling experiments in methanol (contacting time = 48 h) were also carried out in a graduated cylinder, as described previously.<sup>21</sup> The visual appearance of the copolymer beads was examined by optical microscopy.

## RESULTS AND DISCUSSION

The results illustrated in Table I are in agreement with those obtained in our earlier studies on the synthesis and characterization of copolymers based on 2DV and DVB.<sup>19–21</sup> At a fixed DVB content, as the diluent mixture was enriched with the bad solvating diluent (heptane), the pore volume increased and, in consequence, both the apparent density and the swelling in metha-

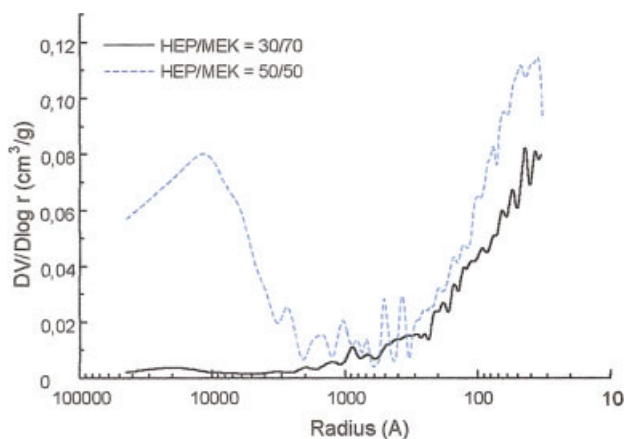
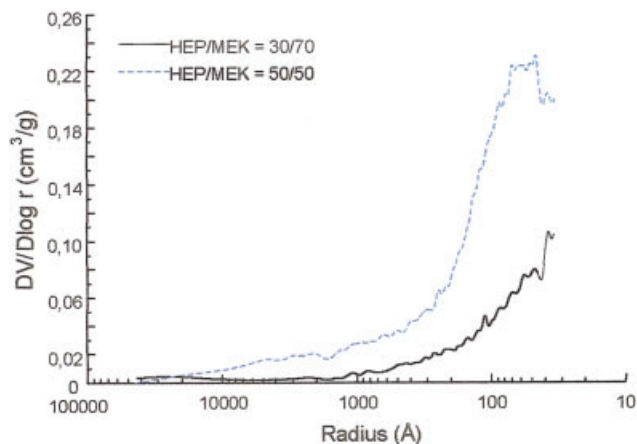


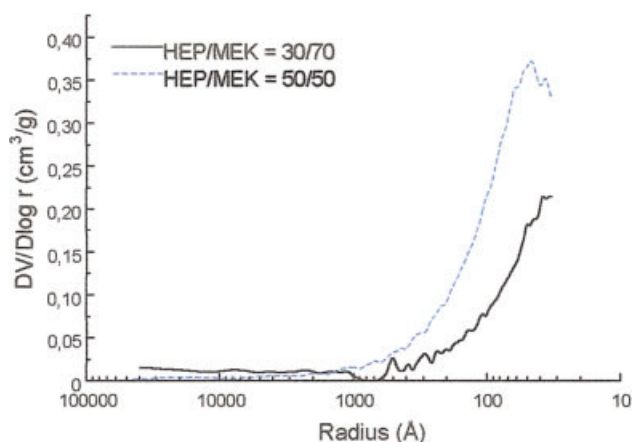
Figure 1 Differential pore-size distribution of the copolymers synthesized with 20% DVB at two diluent compositions.



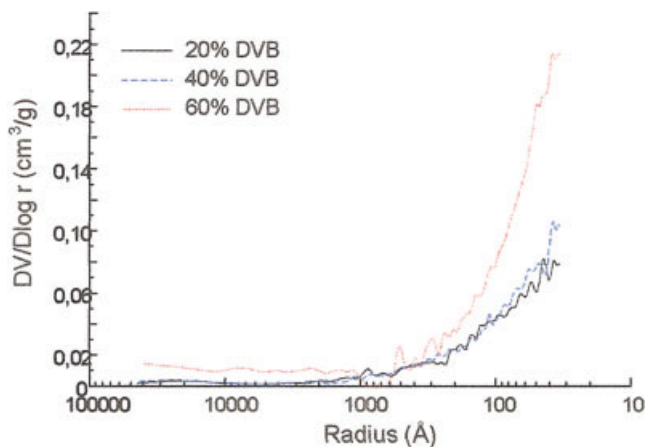
**Figure 2** Differential pore-size distribution of the copolymers synthesized with 40% DVB at two diluent compositions.

nol decreased. That behavior is explained by the formation of a macroporous copolymer.<sup>3,4</sup> Because of the occurrence of phase separation and the decrease in the solvating power of the diluent provoked by the increase of heptane proportion, larger pores were formed, resulting in a more rigid polymer structure.

Figures 1-3 show the effect of the diluent mixture composition on the pore-size distribution curves at a fixed DVB content. At 20% DVB, the increase in heptane proportion resulted in a broad distribution of pore sizes ranging greater than 1000 Å. As the DVB content was increased to 40 and 60% (Figs. 2 and 3), the pore-size distribution curves became quite similar, showing, as expected, an increase in a pore volume as the heptane proportion increased, with pores smaller than 1000 Å. It is interesting to notice that, even at low DVB content, an accentuated pore formation was observed for the copolymers based on 2VP/DVB synthesized with different diluent mixtures, heptane being the bad solvating diluent.<sup>19-21</sup> This behavior can be



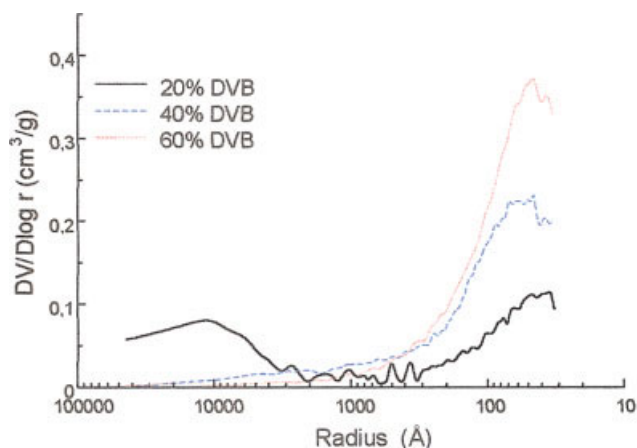
**Figure 3** Differential pore-size distribution of the copolymers synthesized with 60% DVB at two diluent compositions.



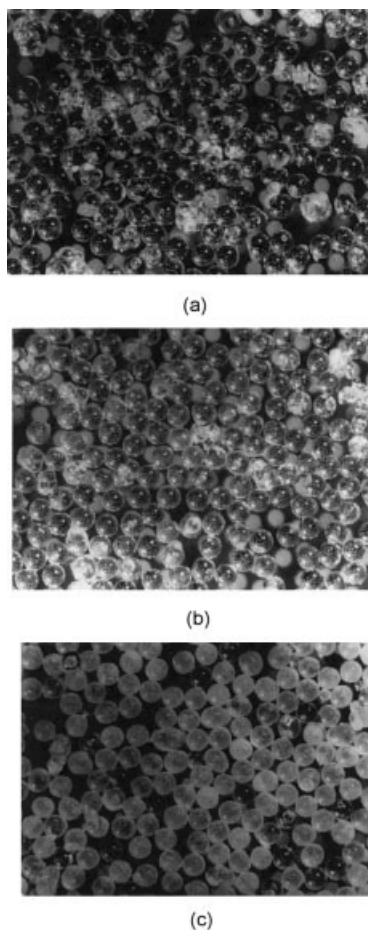
**Figure 4** Differential pore-size distribution of the copolymers synthesized with diluent composition HEP/MEK = 30/70 at various DVB contents.

attributed to the difference in the reactivities between the monomers, 2VP and DVB.<sup>25</sup> This way, it is possible that because of the higher reactivity of the DVB, in the initial stages of the polymerization, the nuclei are preferentially formed by DVB units, leading to the formation of copolymers rich in linear poly(vinyl pyridine) segments that contribute to the more accentuated phase separation occurrence as the heptane content increases. As the DVB content increases, the growing chains present a less pronounced linearity with a more homogeneous distribution of the two vinyl monomers, and thus, the phase separation will occur later.

The effect of DVB content on the copolymers porosity, at a fixed diluent mixture composition, is illustrated in Figures 4 and 5. Again, the distribution curves are quite similar and, as verified, as the DVB content increases, the pore volume increases for both (30/70 and 50/50 HEP/MEK) diluent compositions. It



**Figure 5** Differential pore-size distribution of the copolymers synthesized with diluent composition HEP/MEK = 50/50 at various DVB contents.



**Figure 6** Optical appearance of 2VP/DVB copolymers synthesized in the presence of HEP/MEK (30/70 V/V) at varied proportions of DVB: (a) 20% DVB; (b) 40% DVB; (c) 60% DVB.

is interesting to observe that, at diluent composition of HEP/MEK = 30/70, the distribution curves (Fig. 4) for 20 and 40% DVB content are practically coincident. Moreover, Table I shows that the pore volumes are low, having the same magnitude, and the copolymers are transparent [optical appearance; Fig. 6(a, b)], typical of gel-like materials. These results can be attributed to the high solvating power of the diluent mixture enriched with MEK, a better solvent than HEP and, as consequence, the phase separation will occur later or will be incipient. As the DVB content increases to 60%, the phase separation is more pronounced, as a consequence of increasing in the copolymers crosslinking density. This way, the distribution curve increases abruptly and the copolymer presents a translucent appearance [Fig. 6(c)], indicating a mesoporous morphology. Increasing the HEP/MEK ratio to 50/50 (Fig. 5), the pore size distribution curves present the same pattern, but are more separated, because of the more intense phase separation occurrence determined by increasing both HEP and DVB contents. The pore-size distribution curves also indicate that the porosity

increasing is practically due to the increase in the number of pores of small diameter. Because these pores contribute for most of the surface area, this observation is in accordance with the results of surface area (Table I).

## CONCLUSION

Copolymers based on 2VP and DVB were synthesized in the presence of a diluent consisting of mixtures of HEP and MEK at varied compositions. Macroporous networks were formed, as a result of a phase separation, whenever the diluent mixture was enriched with the bad solvent (heptane) at a fixed DVB content, or with the increase of DVB content at a fixed diluent mixture composition. It was also observed that the copolymers presented low surface areas, as published in our previous studies on copolymers based on 2VP and DVB.

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