

Morphological Study on the Reactivity of Styrene-Divinylbenzene Copolymers in a Chloromethylation Reaction

Viviane G. Teixeira,¹ Fernanda M. B. Coutinho²

¹Departamento de Química Analítica, Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro 21941-909, Brazil

²Departamento de Processos Químicos, Instituto de Química, Universidade do Estado do Rio de Janeiro, Rua São Francisco Xavier, 524, Maracanã, Rio de Janeiro 20550-900, Brazil

Received 12 May 2009; accepted 2 February 2010

DOI 10.1002/app.32203

Published online 22 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Styrene-divinylbenzene (S-DVB) copolymers with different kinds of porous structures were synthesized by aqueous suspension polymerization using *n*-heptane as the pore forming agent. The amount of this solvent (monomer dilution degree) and the DVB content in the organic phase were varied. The combination of three different dilution degree values and three DVB contents yielded three series of copolymers with a variety of porous structures. The three series were composed by copolymers with pore diameters (*D*) in the following ranges: $D < 500 \text{ \AA}$, $500 < D < 1000 \text{ \AA}$, and $D > 1000 \text{ \AA}$, respectively. The effect of synthesis conditions on the pore size distribution and on the copolymer matrix rigidity was evaluated. These copolymers were submitted to a chloromethylation reaction with a paraformaldehyde/gaseous HCl mixture

in the presence of zinc chloride as a Lewis acid catalyst and 1,2-dichloroethane as solvent. The effect of the copolymer porosity on the chloromethylation reaction extension was evaluated. It was possible to observe that a gel copolymer with a high swelling capacity in the reaction medium achieved the same chloromethylation yield observed for a high porous copolymer. This result thus indicates that, in the case of the chloromethylation reaction studied here, the high swelling capacity of the gel copolymer can counterbalance its limited surface area, turning this type of polymer structure as reactive as a macroporous one. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2389–2396, 2010

Key words: functionalization of polymers; crosslinking; ion exchangers; chloromethylation; porosity

INTRODUCTION

Styrene-divinylbenzene (S-DVB) copolymers obtained by suspension polymerization are the main precursors of ion-exchange and chelating resins. They are also used as supports for size exclusion chromatography, adsorbents for solid phase extraction, heterogeneous catalysts, and so forth.^{1–4} The knowledge about controlling the porous structure of these materials and their easy chemical modifications make them very attractive for such purposes.^{5–7} For all applications mentioned above, styrene-divinylbenzene copolymers must contain an immobilized reactive group, which is chosen in accordance with the final objective.⁸

Many of the reaction pathways adopted to modify S-DVB copolymers are based on a preliminary chloro-

methylation step catalyzed by a Lewis acid. The presence of the labile chlorine atom eases the immobilization of a large variety of groups by its nucleophilic substitution making the chloromethylated copolymer an interesting intermediate for many synthetic routes. These chloromethylated copolymers are sometimes called Merrifield resins when they are synthesized with a low crosslinking degree.⁹ The classical route applied to chloromethylate S-DVB copolymers is based on the use of chloromethyl ether or bischloromethyl ether. Both reagents produce high yields of chloromethylation but they are extremely carcinogenic. Because of this characteristic, many efforts have been done to use safer reagents. However, the cost of substituting the classical process by an alternative one should also be evaluated and it will determine the possibility of an industrial application.¹⁰ There are many works in the literature presenting alternative chloromethylation routes of styrene copolymers and other materials. These works are based on the modification of the alkyl chain size of the halomethylating ether to lower the reagent volatility, as proposed by Warshawsky and Deshe,¹¹ or on the modification of the reaction type, as the

Correspondence to: V. G. Teixeira (vgomes@iq.ufrj.br).

Contract grant sponsors: Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

use of chloroacetylation, proposed by Wu et al.¹⁰ for membrane modifications. Moulay and Mehdi¹² used two different systems in the chloromethylation of polystyrene catalyzed by stannic chloride: formaldehyde/thionyl chloride and paraformaldehyde/trimethylchlorosilane, being the first one the most effective. A mixture of paraformaldehyde and phosphorus trichloride in the presence of zinc chloride was applied in the chloromethylation of poly(ether imide) membranes.¹³ A substitution degree of 0.22 chloromethyl group per unit of poly(ether imide) was attained. Trimethylchlorosilane, paraformaldehyde, and some different Lewis acid catalysts composed the chloromethylating system used by Dragan et al.¹⁴ in the synthesis of strong basic anion exchangers. SnCl₄ and FeCl₃ were effective catalysts for the reaction.

HCl/paraformaldehyde mixture is an alternative chloromethylating agent, but the degree of chloromethylation attained by this system is not as high as those achieved by the classical reagents. Studies on the catalyst, as the one described by Dragan et al.,¹⁴ have been made with the aim of improving the reaction yields. This was also the choice presented by Kishida et al. when they chloromethylated aromatic hydrocarbons in the presence of rare-earth metal triflates. These compounds were effective as catalysts and showed the advantage of being reusable.¹⁵

In the case of the chemical modification of styrene-divinylbenzene copolymers, we should not consider only the chemical characteristics of the reagents. The heterogeneous characteristic of the overall reaction medium, i.e. substrate and reagents solution, is another limiting factor. If so, the yield can be greatly enhanced by the choice of the kind of material porous structure and by the affinity between the two heterogeneous phases. Copolymers synthesized with a gel-type structure present a good ability of swelling in thermodynamically good solvents, though no permanent porosity is present. These materials are efficient as heterogeneous catalysts when the reaction medium is able to swell their polymer matrix, producing a high surface area in the swelling state. The other class of styrene copolymers, the macroporous one, is composed by materials with a high proportion of fixed pores. Consequently, this kind of material presents a higher surface area that eases the contact with the reagent solution, though its swelling capacity is reduced. Because of these characteristics, they are generally used as chromatographic packing materials.^{8,16} The knowledge about controlling the porosity of styrene-divinylbenzene copolymers is well established. Many research groups have demonstrated the influence of the amount of DVB and kind/amount of solvent used in the synthesis as the determining parameters for the material porous structure. In other words, the governing factors for polymer chains precipitation in the reaction system

are those responsible for the porosity formation in the copolymer matrix.^{4,17}

Although the number of works inferring about chemical modifications on styrene-divinylbenzene copolymer is high and also high is the number of works treating about the synthesis conditions of porous copolymers, there are few works describing the dependency between the extension of the modification reactions and the porous structure. These relations are of great importance in determining good reaction conditions for copolymers with different kinds of porous structure. With this aim, we chose the chloromethylation reaction using HCl/p-formaldehyde mixture as a model reaction to evaluate its extension on styrenic materials with varied porous structures. The necessary conditions that should be applied to improve the reaction in each kind of porous copolymer were also of interest. The choice for that chloromethylating system was based on its low reaction yields, since a more effective reaction could not be limited by the copolymer porous structure.

EXPERIMENTAL PART

Reagents

Styrene (S) and divinylbenzene (DVB) were of technical grade. These monomers were donated by Petroflex Ind. Com. S.A. and Nitriflex S.A. Ind. Com., respectively, and purified by washing with 5% w/v NaOH (Vetec Química Fina Ltda.) aqueous solution and water. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol solution. Zinc chloride (Vetec Química Fina Ltda.) was dried at 110°C. All the other reagents (Vetec Química Fina Ltda. - PA grade) were used as received.

Instruments

The surface area and the pore size distribution curves of copolymers were determined by nitrogen adsorption on a Micromeritics ASAP 2010. Pore size distribution was also evaluated by mercury intrusion using a Quantachrome Co. Autoscan 33 mercury porosimeter. The morphology of S-DVB copolymers was observed in a Jeol JSM5610LV scanning electron microscope (SEM). Potentiometric titration of chloride ions was carried out with the aid of an Analyser 300 potentiometer with an Analyser 6A09 silver ring oxidation-reduction electrode. FTIR spectra were obtained by using a diffuse reflectance accessory in a Perkin Elmer 1720X spectrometer.

Synthesis of S-DVB copolymers

S-DVB copolymers were synthesized by suspension polymerization initiated by AIBN. Poly(vinyl alcohol)

TABLE I
Synthesis Conditions and Porous Properties of S-DVB Copolymers

Copolymer	Dilution (%) (<i>n</i> -heptane)	DVB/S	d_a^a (g cm ⁻³)	V_p^b (cm ³ g ⁻¹)	V_{pf}^c (cm ³ g ⁻¹)	A^d (m ² g ⁻¹)	I_{tol}^e (%)	I_{hep}^f (%)
06	50	15/85	0.64	nm ^g	0.01	nm ^g	79	6
08		25/75	0.59	0.15	0.03	6	61	32
09		40/60	0.50	0.27	0.26	90	30	25
10	100	15/85	0.35	0.87	0.73	74	59	24
11		25/75	0.33	0.94	0.80	92	41	26
12		40/60	0.30	1.14	1.06	127	24	16
15	200	15/85	0.30	1.22	1.03	51	114	55
16		25/75	0.21	2.11	1.85	69	47	25
18		40/60	0.19	2.26	2.18	142.8	28	22

^a d_a = apparent density.

^b V_p = fixed pore volume determined by mercury porosimetry.

^c V_{pf} = fixed pore volume determined by water uptake.

^d A = surface area.

^e I_{tol} = swelling degree in toluene.

^f I_{hep} = swelling degree in *n*-heptane.

^g nm = not measurable.

was used as suspension agent and sodium chloride as salting-out agent. *n*-Heptane was used as diluent for the monomers in different proportions. All reactions were carried out at 80°C for 24 h.

Chloromethylation of S-DVB copolymers

All copolymers were chloromethylated by the method described in a previous paper.¹⁸ HCl(g) was produced by adding H₂SO₄ (98%) to concentrated HCl aqueous solution. HCl(g) was bubbled in a suspension of copolymer, paraformaldehyde, and ZnCl₂ in 1,2-dichloroethane (DCE). The system under stirring was heated at 80°C during 3 h. After that period, the copolymer was initially washed with ethanol and then with water until neutrality was reached.

Characterization of copolymers porous structure

The porous structure of the copolymers was characterized by determining: apparent density; pore volume by water uptake; volumetric swelling degree in toluene and *n*-heptane;¹⁹ pore size distribution by mercury intrusion and nitrogen desorption (BJH method); and surface area by nitrogen adsorption (BET method). The polymer appearance was observed by optical microscopy and the morphology by SEM. For this last analysis, samples were previously coated with a thin layer of gold. Secondary electrons and an accelerating voltage of 20 keV were used.

Determination of chloromethyl group content in the copolymers

This method is a modification of the one described by Feinberg and Marrifield²⁰ which was adapted considering the different porosities of the copolymers analyzed in this work.²

Characterization of copolymers chemical structure

The modifications carried out in the chemical structure of the copolymers were evaluated by FTIR spectrometry using a diffuse reflectance accessory. Twenty scans and a 2 cm⁻¹ resolution were used.

RESULTS AND DISCUSSION

Synthesis and porous characteristics of styrene-divinylbenzene copolymers

With the aim of evaluating the extent of chloromethylation reaction in copolymers with different kinds of porous structure, three series of S-DVB copolymers were synthesized. The synthesis conditions are summarized in Table I. The first series was constituted by copolymers with pore diameters below 500 Å. The copolymers synthesized in the second series presented a pore diameter distribution varying from 500 to 1000 Å, while the third series was composed by copolymers with pore diameters above 1000 Å. To prepare these three series of materials, *n*-heptane was used as diluent to the monomers in different proportions during their synthesis. This solvent has low affinity to the growing chains of S-DVB copolymer. It can be explained by comparing the solubility parameter of *n*-heptane, 15.1 MPa^{1/2}, with that one of the S-DVB copolymer, 18.6 MPa^{1/2}. There is a difference of 3.5 unities between these two values and, according to the Hildebrand theory, this difference must be almost zero for a good interaction between the polymer chains and the solvent.^{6,21}

The process of the formation of the porous structure of S-DVB copolymers in the presence of a diluent is governed by precipitation parameters. If the diluent used in the synthesis has a poor affinity to the copolymer, phase separation will readily occur

and the polymer chains will precipitate in a more entangled way. In this stage, the precipitation of nuclei occurs allied to their agglomeration and linkage of linear chains. This process results in the formation of microspheres. If the diluent is a poor solvent for the copolymer, as *n*-heptane is, the compactness of the microspheres is enhanced and the final material presents higher pore volume. In the presence of high amounts of a poor solvent, the precipitation process is faster. The nuclei formed in this condition are more entangled and pores with higher diameters are formed. Considering the mechanism of pore formation, the copolymer porous structure can thus be controlled by the kind and amount of diluent used in the synthesis.^{22,23} In this study, the use of *n*-heptane in different dilution degrees offered the possibility of obtaining copolymers with gel or macroporous structures. If a good solvent had been chosen as pore forming agent in place of *n*-heptane, it would be difficult to obtain copolymers with pores larger than 1000 Å, which was necessary in order to evaluate the extent of chloromethylation.

The copolymer pore size is not the only parameter responsible for the extent of the modification reactions on the polymer matrix. We also wanted to evaluate the influence of polymer matrix rigidity on the reaction yield. The rigidity is mainly governed by the DVB content. However, the amount of DVB is also a parameter responsible for phase separation during the copolymer synthesis. The synergism of the effects of a high dilution degree and a high DVB content allows the formation of materials with a high porosity and low mechanical resistance.

According to these considerations, three monomer dilution degrees with *n*-heptane were used in the synthesis of the three series of copolymers: 50, 100, and 200%. The DVB content in the mixture of the monomers was also varied. Contents of 15, 25, and 40% of DVB in the monomer mixture were used (Table I). The pore size distribution curves of the copolymers determined by mercury intrusion are showed in Figure 1. Figure 2 shows the curves for the same parameters now determined by nitrogen desorption (BJH method). We must consider that nitrogen adsorption or desorption data are only valid in determining pore sizes until 250 Å. Data for size distributions above this value must not be considered.²⁴ On the other side, mercury intrusion is not adequate to measure micropores. Thus, the combination of these two techniques can provide a good overview of a wide pore diameter range.

Figures 1 and 2 show that the changes in the dilution degree promoted more intense variations on the pore size distributions than the DVB content did. The combination of three dilution degrees and three DVB contents resulted in the production of three

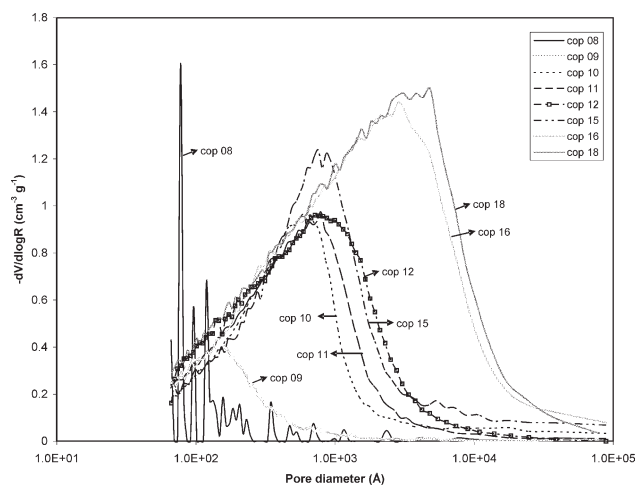


Figure 1 Pore size distribution curves of S-DVB copolymers obtained by mercury porosimetry.

S-DVB copolymers series with different pore size distribution. In each series, copolymers with comparable pore size distributions but different matrix rigidity were obtained.

Copolymers synthesized with the dilution degree of 50% present a high concentration of pores with diameter around 100 Å. There was no mercury intrusion in the copolymer synthesized with 15% DVB and its pore volume was insignificant. The volume of water uptake (V_{pf}) after copolymer treatment with methanol is considered as a measure of fixed pore volume, which increases with the amount of *n*-heptane and DVB used in the synthesis. The V_{pf} value for this copolymer was almost zero (Table I), what is in accordance with the results offered by the other techniques. These results reveal the gel structure of this copolymer. As the amount of DVB increased to 25 and 40%, more porous structures were formed. The copolymer synthesized with 25% DVB has a higher pore volume in the range from 80

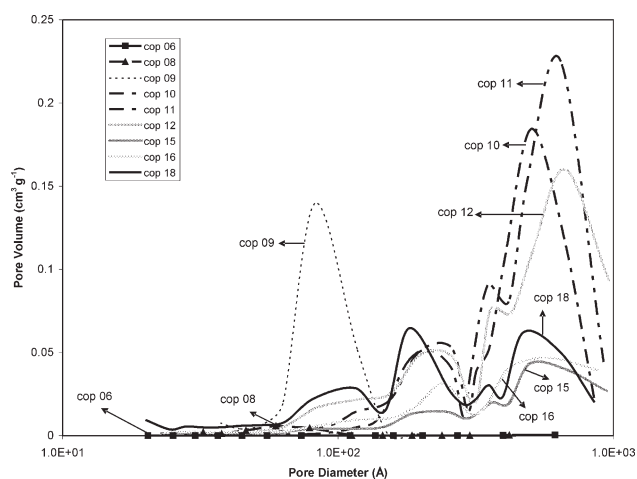


Figure 2 Pore size distribution curves of S-DVB copolymers obtained by nitrogen adsorption.

to 100 Å. When 40% DVB was used in the monomer mixture, the pore size distribution shifted to the range between 100 to 300 Å. The volume of fixed pores also increased and the apparent density of the copolymers decreased as the DVB amount in the monomer mixture was increased. These results confirm the development of a true porosity in the copolymers when the highest amounts of crosslinking agent were used in the synthesis, even maintaining a low dilution degree value. The increase in the DVB content produces more rigid networks and this can be confirmed by the copolymer swelling ability in solvents like toluene and *n*-heptane, a solvent and a nonsolvent to S-DVB copolymer, respectively. A decrease of the copolymer swelling in toluene for the highest DVB contents was observed, but the swelling in *n*-heptane increased. This behavior indicates a smaller proportion of gel regions and a higher volume of fixed pores. When 40% DVB was used, the copolymer swelling abilities in both solvents were close what suggests, for this DVB content, a very rigid structure characteristic of a hypercrosslinked material.⁴ The surface area of the copolymers synthesized at the dilution degree of 50% was significant only when 40% of the mixture of monomers was composed by DVB (Table I).

The copolymers synthesized with the dilution degree in *n*-heptane of 100%, keeping the same amounts of DVB employed in the synthesis of the first copolymers series, showed an improvement in fixed porosity, what can be evaluated by the decrease of their apparent density and in the swelling degree in toluene and also by the increase of the water uptake volume (Table I). The pore diameter distribution curves in Figures 1 and 2 show a high concentration of pores with sizes around 1000 Å. An enlargement of the distribution curves profile obtained by mercury intrusion with the increase of DVB content can also be observed. The higher heterogeneity of the more crosslinked polymer networks can explain this behavior. The distribution curves obtained by the BJH method do not show pores smaller than 250 Å and confirm that the pore size distributions were shifted to higher values. In opposition to the 50% dilution degree series, the copolymers synthesized with the degree of dilution of 100% showed a significant value of surface area, even when only 15% of the mixture of monomers was composed by DVB. The swelling degree in toluene for copolymers synthesized in the second series was not as high as those of the first series, indicating that the crosslinking degree is not the only factor responsible for polymer rigidity. The swelling degree in *n*-heptane decreased as the DVB content increased, what is expected due to the higher rigidity of the polymer matrix. This behavior is different from that observed in the copolymer series synthesized with

dilution of 50%. In the first series, the parameter responsible for the swelling behavior in *n*-heptane was the development of a fixed porosity with the increase of the DVB content. The presence of true pores allowed the permeation of *n*-heptane through the copolymer matrix. By comparing the copolymers synthesized with 40% DVB in the two series, it is possible to notice a comparable swelling behavior of these copolymers in the two solvents, suggesting a similarity in their network rigidity. Thus, when high amounts of DVB are present in the monomer mixture, the crosslinking degree seems to be the parameter that determines the polymer network elasticity, despite the dilution degree value.

The third and last series of S-DVB copolymers was synthesized with a dilution degree of 200% with *n*-heptane. The aim of using this high amount of diluent was the synthesis of a copolymer series with pore diameters above 1000 Å. The pore diameter distribution curves (Figs. 1 and 2) show that this goal was attained. The copolymer synthesized with 15% DVB presents a high abundance of pores with diameters around 1000 Å, while copolymers synthesized with 25 and 40% DVB show distribution curves shifted to the range from 2000 to 3000 Å. The enlargement of the distribution curves profile with the increase in the DVB content was also observed in this copolymer series. However, the same behavior can be observed by comparing the distribution curves of the materials synthesized with the same DVB content but different dilution degrees. Therefore, the DVB content is not the only factor responsible for the polymer network heterogeneity. The increase in *n*-heptane content promotes a faster and more disordered precipitation of the polymer chains, leading to the formation of pores with different sizes. Distribution curves obtained by BJH method reveal the presence of only a little amount of pore diameters lower than 250 Å, confirming the shift in the pore sizes. The porous characteristics of copolymers synthesized using 200% dilution degree confirm the high porosity of these materials, i.e. low apparent density and high fixed pore volume. Because of their large pore size, the surface area of these materials was not enhanced when compared to those of the second series of copolymers. The swelling properties of the materials synthesized with 100 and 200% dilution degree were comparable, but the behavior of the copolymer synthesized with 15% DVB and degree of dilution of 200% was anomalous. The swelling degrees observed for this material were higher than expected. The synthesis was repeated and a material with the same properties was obtained. This behavior can be attributed to the high mobility that polymer chains can attain when they are synthesized in the presence of high solvent amounts. On the other hand, the swelling behavior

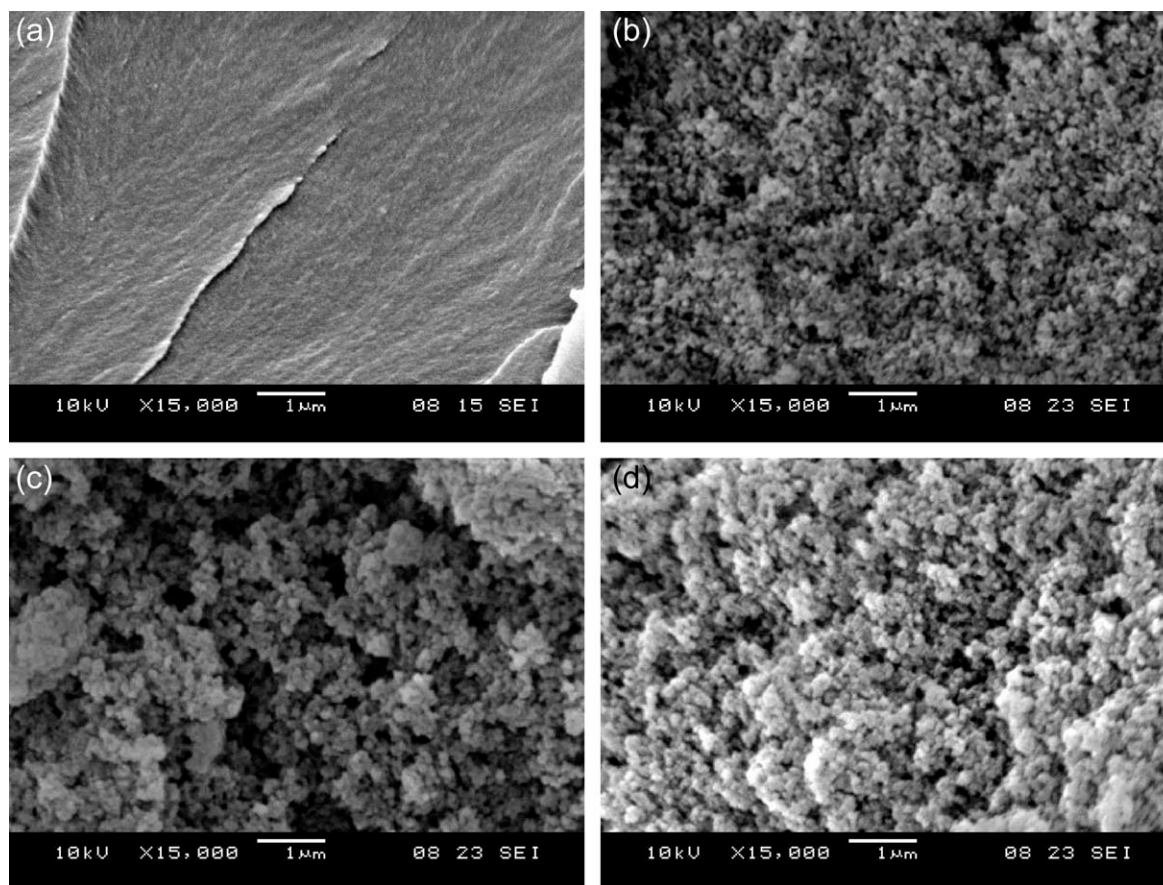


Figure 3 SEM micrographs of the inner regions of S-DVB copolymers 06 (a); 10 (b); 15 (c); and 12 (d).

of the copolymers synthesized with the highest DVB contents (25 and 40%) confirmed the important influence of dilution degree on the rigidity of the polymer matrix, even when high amounts of DVB were used in monomer mixture.

Figure 3 shows scanning electron micrographs of copolymers 06, 10, and 15, synthesized with the same DVB content (15%) in the presence of *n*-heptane at three different dilution degrees (50, 100, and 200%). The increase of the pore diameters as the dilution degree increases can be observed. The enhancement of porosity can also be observed when the amount of DVB was increased from 15% to 40% and the dilution degree was kept constant at 100% (copolymers 10 and 12).

The synthesis conditions applied in this work allowed the formation of materials with a large variety of porous structures. Changes only in the DVB content (keeping constant the dilution degree with *n*-heptane) yielded copolymers with differences in the matrix rigidity but with comparable pore size distributions. When the dilution degree was varied and the DVB amount in the mixture of monomers was kept constant, a series of copolymers with different pore size distributions was obtained, but their matrix rigidities were comparable.

All those copolymers were submitted to the chloromethylation reaction using a mixture of HCl(g) and paraformaldehyde in the presence of ZnCl₂ and DCE. Therefore, the extent of this electrophilic aromatic substitution reaction could be evaluated in a large variety of S-DVB copolymers porous structures.

Chloromethylation of S-DVB copolymers with different porous structures

A study on chloromethylation conditions was presented in a previous paper.¹⁸ That paper describes in detail the determination of the best conditions for S-DVB copolymers chloromethylation using the alternative route based on the reaction by HCl(g)/paraformaldehyde mixture and zinc chloride as catalyst. The mechanism proposed for this reaction is shown in Figure 4. In the first step, the oxygen atom of the aldehyde carbonyl is protonated. The electrophile formed is attacked by the copolymer's aromatic ring leading to the formation of an alcohol which is transformed into the halide by the nucleophilic substitution with the chloride ion. The methylene bridges formation by a Friedel-Crafts alkylation is a side reaction controlled by limiting the amount of catalyst used. In order to evaluate the

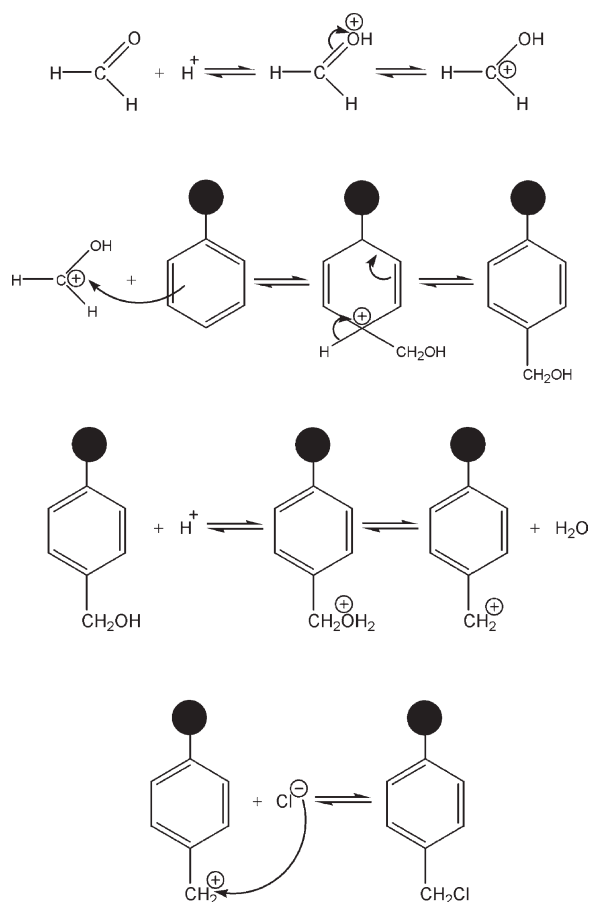


Figure 4 Proposed mechanism for S-DVB copolymers chloromethylation by formaldehyde/HCl (g) mixture.

extent of chloromethylation on S-DVB copolymers with different kinds of porous structure, the best chloromethylation condition determined in the previous study was applied in this work (see Experimental Part). The chloromethylation degree attained for the previously studied copolymer was $0.498 \text{ mmol g}^{-1}$, which is 10-fold lower than the degree generally attained by the classical method. However, no methylene bridges seemed to be formed, what was verified by the maintenance of the copolymer swelling properties after the chloromethylation process. Even being a low extent reaction, this amount of chloromethyl groups yielded was enough to evaluate the reaction extension in the three synthesized copolymers series.

As mentioned before, the morphology of the synthesized copolymers varied from gel to macroporous. Copolymer 06, a gel-like one, was not functionalized during the chloromethylation reaction. The absence of fixed pores was responsible for this result. Thus, we decided to introduce a step of swelling of the materials in the chloromethylation solvent (DCE). This procedure turned the reaction conditions into homogeneous for all the copolymers. Figures 5 and 6 do not show any trend in the behavior

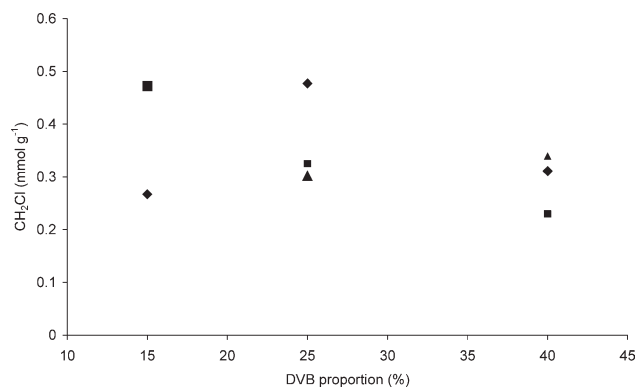


Figure 5 Influence of DVB amount on the chloromethylation degree of S-DVB copolymers obtained with 50 (◆), 100 (■), and 200% (▲) dilution degree in *n*-heptane.

of copolymers chloromethylation degree, neither when the degree of dilution was kept constant and the DVB amount was varied nor when the opposite was done. All the values were comparable and copolymer 15 was not functionalized. The 1264 cm^{-1} absorption band is observed in the FTIR spectrum of copolymer 10 (Fig. 7), confirming the occurrence of the chloromethylation and discharging the possibility of a contamination with chloride ions in copolymer beads. These results show that the step of swelling in DCE, a good solvent for S-DVB copolymer, leveled the reaction extension through the different kinds of porous structures. It is known that gel polymers need to swell in the reaction medium to permit the reaction occurrence throughout the matrix but, in this work, we could observe that, after swelling, this kind of copolymer can be functionalized inside the gel structure at the same extent that a porous copolymer can be on its surface. In other words, a gel copolymer can be considered as reactive as a porous one for the studied reaction, since its swelling equilibrium is obeyed.

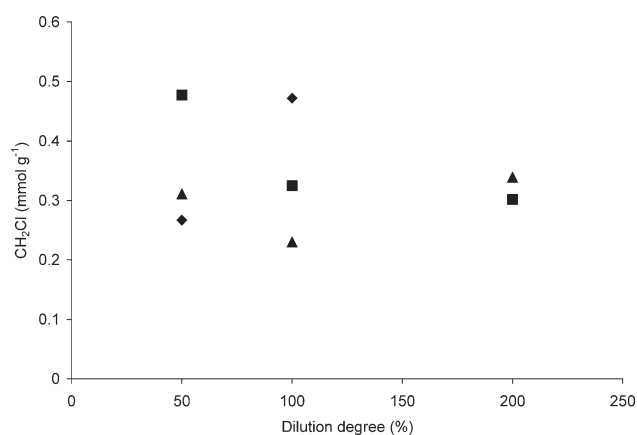


Figure 6 Influence of dilution degree in *n*-heptane on the chloromethylation degree of S-DVB copolymers obtained with 15 (◆), 25 (■), and 40% (▲) of DVB in the monomer mixture.

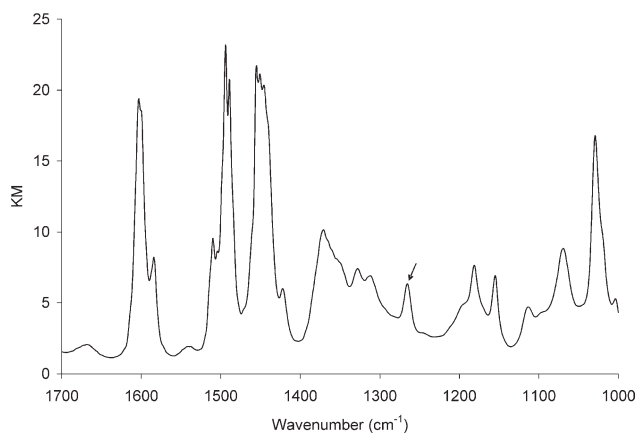


Figure 7 DRIFT spectra of chloromethylated S-DVB copolymer 10.

A swelling period of 24 h was enough to make the gel structures reach the equilibrium state in DCE. Even macroporous structures have a gel domain that is also swelled during this period. Though these rigid porous structures do not swell as the gel one does, its higher accessible surface area promotes an easier contact with the reaction medium.

Concluding, the polymer swelling capacity in the reaction medium must be considered in a chemical modification process. In the case of porous copolymers, their swelling capacity in the solvent used is not so important because fixed pores allow the diffusion of the reagents through the polymer matrix. Considering the characteristics of the copolymers synthesized in this work, we can say that the higher swelling ability of gel materials in the reaction medium and the higher surface area of the macroporous ones promoted the same global effect in the yield of the chloromethylation reaction here studied. Therefore, the choice of the kind of polymer porosity must be done in accordance to the final application of the material and not considering the *pseudo*-limited reactivity of the gel type copolymers. If the final material will be applied in a good solvent medium, the gel structure can be satisfactory chosen, but if the copolymer do not swell in the medium where it will be applied, a porous copolymer will be a better choice.

CONCLUSIONS

The combination of different DVB contents in the mixture of monomers and dilution degrees with *n*-heptane produced a variety of porous S-DVB copolymers. When only the DVB proportion was enhanced, the copolymers showed higher pore volumes, but the average pore diameter did not vary significantly. On the other side, it varied strongly when the dilu-

tion degree was increased. This behavior characterizes the different influences of those synthesis parameters on the mechanism of formation of porous structure in S-DVB copolymers.

Chloromethylation of S-DVB copolymers by HCl/paraformaldehyde mixture can be attained in different kinds of porous structures, but the reaction extent in the polymer matrix is defined by the swelling property of the material in the reaction media and by its surface area. Gel structures can be functionalized in the same extent that porous structures can but a swelling pretreatment must be applied before conducting the chloromethylation reaction. These results suggest that the thermodynamic affinity between the solvent and the copolymer can be used as a controlling parameter for the yield of the modification reaction.

The authors thank Nitriflex and Lanxess for monomers donation and Instituto Nacional de Tecnologia (INT) for mercury porosimetry analysis.

References

- Coutinho, F. M. B.; Teixeira, V. G.; Barbosa, C. C. R. *J Appl Polym Sci* 1998, 67, 781.
- Teixeira, V. G.; Coutinho, F. M. B.; Petrocínio, F. M.; Gomes, A. S. *J Braz Chem Soc* 2005, 16, 951.
- Coutinho, F. M. B.; Rezende, S. M.; Soares, B. G. *J Appl Polym Sci* 2006, 102, 3616.
- Tsyurupa, M. P.; Davankov, V. A. *React Funct Polym* 2006, 66, 768.
- Kun, K. A.; Kunin, R. *J Polym Sci Part A-1: Polym Chem* 1968, 6, 2689.
- Rabelo, D.; Coutinho, F. M. B. *Polym Bull* 1994, 33, 479.
- Okay, O. *Polymer* 1999, 40, 4117.
- Guyot, A.; Hodge, P.; Sherrington, D. C.; Widdecke, H. *React Polym* 1992, 16, 233.
- Merrifield, R. B. *J Am Chem Soc* 1963, 85, 2149.
- Wu, L.; Xu, T.; Yang, W. *J Membr Sci* 2006, 286, 185.
- Warshawsky, A.; Deshe, A. 1985, 23, 1839.
- Moulay, S.; Mehdi, N. *Chin J Polym Sci* 2006, 24, 627.
- Cheng, Z.; Zhu, X.; Kang, E. T.; Neoh, K. G. *Macromolecules* 2006, 39, 1660.
- Dragan, E. S.; Avram, E.; Axente, D.; Marcu, C. *J Polym Sci Part A: Polym Chem* 2004, 42, 2451.
- Kishida, T.; Yamauchi, T.; Komura, K.; Kubota, Y.; Sugi, Y. *J Mol Catal A* 2006, 246, 268.
- Kunin, R.; Meitzner, E.; Bortnick, N. *J Chem Soc* 1962, 84, 305.
- Okay, O. *Prog Polym Sci* 2000, 25, 711.
- Teixeira, V. G.; Coutinho, F. M. B.; Gomes, A. S. *Polímeros: Ciência e Tecnologia* 2004, 14, 267.
- Rabelo, D.; Coutinho, F. M. B. *Eur Polym J* 1994, 30, 675.
- Feinberg, R. S.; Merrifield, R. B. *Tetrahedron* 1974, 30, 3209.
- Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press, Inc: Boca Raton, 1985.
- Millar, J. R.; Smith, D. G.; Kressman, T. R. E. *J Chem Soc* 1965, 304.
- Howard, G. J.; Midgley, C. A. *J Appl Polym Sci* 1981, 26, 3845.
- Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic Press: London, 1982.