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Morphological changes induced by the chloromethylation reaction as a function of the chloromethylation conditions with TMCS/$(CH_2O)_n$

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Chloromethylation degree and morphological changes of some macroporous styrene-divinylbenzene (St-DVB) copolymers, with paraformaldehyde $(CH_2O)_n$/ trimethylchlorosilane (TMCS) as chloromethylation reagent and $FeCl_3$ as catalyst, as a function of copolymer porosity, concentration of chloromethylation reagent and catalyst content were followed in the paper. An increase of the chloromethylation degree with the increase of both the St/$(CH_2O)_n$/TMCS molar ratio and the increase of the reagent concentration was found. Morphological changes, manifested in the increase of the specific surface area and the decrease of the average pore radius, accompanied the chloromethylation reaction comparative with the starting S-DVB copolymers, the level of changes being correlated with the chloromethylation conditions.

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1. Introduction

The chemical modification of polystyrene (PSt) and styrene-divinylbenzene (St-DVB) copolymers, especially the chloromethylation reaction [1,2], is a subject of considerable interest from both theoretical and practical reasons, including the obtaining of precursors for functional membranes, coatings, ion exchange resins, ion exchange fibers, selective permeable film, and so on. There are two procedures available for the preparation of polymers with reactive functionalities. One approach is polymerization or copolymerization of the functional monomers. Many functional monomer precursors of reactive vinyl polymers are now commercially available, including species such as (chloromethyl)styrene, 4-vinylpyridine, 4-chlostyrene, 4-bromostyrene and 4-acethyloxystyrene. Another procedure is chemical modification of non-functional or functional (co)polymers, which has been extensively used in the preparation of reactive polymers. The chemical modification of PSt and St-DVB copolymers is no doubt the process which has drawn the most attention to date due to the very desirable properties of these copolymers, which combine good chemical reactivity with ease of preparation and mechanical stability. Currently, the most functional polymers are derived from chloromethylated PS [3].

Conventional chloromethylation method of St-DVB copolymers is based on the Friedel-Crafts type alkylation using chloromethyl methyl ether in the presence of Lewis acids as catalysts [4]. Since strong carcinogenic property was evidenced for this chloromethylating agent [5], commercial chloromethyl methyl ether is less used, the interest in finding other chloromethylating reagents being more and more intensive, a new safe method or reagent being strongly desired. One of a few modified methods reported consists in the use of chloromethyl alkyl ethers having long alkyl chains such as chloromethyl octyl ether, whose boiling point is much higher than that of the methyl ether. Another alternative method used methoxyacethyl chloride which generated chloromethyl methyl ether and carbon monoxide in the presence of a Lewis acid [6]. The combination of dimethoxyethane, thionyl chloride and a Lewis acid was also reported to provide chloromethylated PSt resin [7]. Ford et al. [8] reported an interesting approach of chlorination of the methyl groups of poly(4-methylstyrene) with aqueous sodium hypochlorite under phase transfer conditions. A more recent approach has been developed by Itsuno et al. [9, 10] who studied the chloromethylation of PSt resins with a different reagent made from trimethylchlorosilane (TMCS) and trioxane, in the presence of $SnCl_4$ as catalyst, in chloroform ($CHCl_3$). The mixture of commercial paraformaldehyde $(CH_2O)_n$ with an equimolar amount of TMCS, and $SnCl_4$ as catalyst, has been used as a new chloromethylation agent for the chloromethylation of linear polymers [11]. This reagent has been also successfully used in the functionalization of the macroporous St-DVB copolymers as precursors in the synthesis of some macroporous strong base anion exchangers [12].

The goal of this study is to report on the chloromethylation degree and the modifications of morphological characteristics after the chloromethylation reaction of macroporous St-DVB copolymers prepared in the presence of n-butyl alcohol (nBA) as porogen, using CH_2O/TMCS as chloromethylation reagent, in the presence of $FeCl_3$ as catalyst, in $CHCl_3$ as reaction medium, as a function of the reaction conditions.

2. Experimental

2.1. Materials

Styrene (St), technical grade (99% purity) was distilled at 3 mm Hg before use. DVB, technical grade (54.5% o-DVB, m-DVB, p-DVB, 36.2% ethyl styrene and 9.3% inert compounds, by gas chromatography) was used throughout the experiments. nBA reagent grade was used as received. Benzoyl peroxide (BPO) was employed as a radical polymerization initiator. Paraformaldehyde, technical grade, was used as received. $FeCl_3$ and TMCS purchased from Fluka Chemical Co. (Buchs, Switzerland) were used without further purification. Chloroform purified and dried by the conventional methods was used as reaction medium.

2.2 Synthesis of St-DVB copolymers

Macroporous St-DVB copolymers, as beads with diameters within the range 90-200 μm, were prepared by suspension copolymerization according to the method presented in detail elsewhere [13]. Typically, BPO (1 wt% relative to monomers) was added to monomers and then the corresponding amount of nBA to form the organic phase. The organic phase was then added in a volume ratio of 1/2.5 to the aqueous phase containing 0.22% ammonium salt of styrene-maleic acid copolymer, 0.22% food grade gelatine and 2% NaCl. The polymerization was allowed to proceed at 60 ^oC, 80 ^oC and 85 ^oC for 1 h, 10 h and 3 h, respectively. Afterwards, the copolymer beads were filtered and sieved under water, and finally washed with warm water to remove the dispersing agents. The removal of nBA was performed by static methanol extraction [12]. Dilution of the monomer mixture, D, was calculated as the ratio between the volume of nBA and the volume of the whole organic phase [$D = \frac{V_{nBA}}{V_m + V_{nBA}}$].

2.3. Chloromethylation of macroporous St-DVB copolymers

A mixture of commercial $(CH_2O)_n$ and TMCS in an equimolar ratio, as chloromethylation agent, and $FeCl_3$, as catalyst, were used for the chloromethylation reaction in this work, in $CHCl_3$ as a reaction medium, at 50 ^oC. Chloromethylated copolymers (CMC) were separated from the reaction mixture, washed three times with methanol, two times with water/methanol (1/1, v/v) and finally with methanol. CMC samples were dried at 40 ^oC for 48 h and then characterized by the total chlorine content, Schöniger's method, and morphological characteristics, as it will be described bellow.

2.4. Morphological characterizations of macroporous structures in dry state

The apparent density (ρ_{ap}) was determined using a mercury pycnometer at 10^{-4} Torr [14]. The real density (ρ_r) was measured in n-heptane. For the starting St-DVB copolymers and CMC, the average values of the real density, experimentally determined, were as follows: 1.045 and 1.1329 g/cm^3, respectively. The specific surface area (S_{sp}) was determined by the nitrogen adsorption at the boiling temperature of liquid nitrogen, by the Haul-Dümbgen method on a Ströhlein Area Meter apparatus [15]. The average pore radius, $\bar{r}_p$ was calculated using the following equation, cylindrical shape of pores being assumed:

$$\bar{r}_P = (\frac{2V_P}{S_{sp}}) \times 10^3 \quad \text{(nm)} \qquad (1)$$

where: $V_P = \frac{1}{\rho_{ap}} - \frac{1}{\rho_r}$, pore total volume, cm^3/g.

Secondary Electron Images (SEI) have been performed with a scanning electron microscope (SEM) Tesla BS 301. The samples were obtained with an acceleration tension of 20 kV.

3. Results and discussion

The main goal of this study was to follow first the influence of the chloromethylation conditions on the functionalization degree and the morphological changes comparative with the starting St-DVB copolymer and to select the chloromethylation conditions, which allow to perform the chloromethylation reaction with a maximum chloromethylation degree and a minimum degree of secondary reactions. It is well known that the self-alkylation reaction between the pendent CH_2Cl groups and the nonfunctionalized aromatic rings as a secondary reaction could induce further crosslinks reflected in morphological changes of the St-DVB substrate. This aspect is very important when the chloromethylated copolymers are used as precursors in the synthesis of different anion exchangers, the access of the low molar mass reagents to the reactive groups being more difficult.

In this study, the chloromethylation conditions established in the previous paper for the chloromethylation of some macroporous St-DVB copolymers, prepared in the presence of 2-ethyl-1-hexanol (2EH) as porogen [12], were used as starting conditions. Thus, the starting parameters in the chloromethylation reaction of the macroporous copolymers with different porosities, prepared in the presence of nBA, were as follows: a molar ratio of St/$(CH_2O)_n$/TMCS/$FeCl_3$ of 1:8:8:0.5, 8 h at

50 °C, in $CHCl_3$ as reaction medium. The influence of the copolymer concentration in $CHCl_3$ (weight of St-DVB copolymer in 100 mL $CHCl_3$) and of the St/$FeCl_3$ molar ratio were also followed in this paper.

3.1. Morphological changes after chloromethylation reaction as a function of St-DVB copolymer porosity

Macroporous copolymers with a constant DVB content of 8%, prepared in the presence of nBA at different dilutions, were chloromethylated with a molar ratio St/$(CH_2O)_n$/TMCS/$FeCl_3$ of 1:8:8:0.5, the pore volume, V_p, and the average pore radius, $\overline{r}_p$, being plotted in Fig. 1. As Figure 1 shows, the pore volume of the chloromethylated copolymers increased from 0.3429 mL/g up to 1.0667 mL/g and the average pore radius increased from 8.8 nm up to 71.11 nm with the increase of the dilution from 0.40 up to 0.48 mL/mL.

A significant decrease of both the pore volume and pore radius were observed after the chloromethylation comparative with the values corresponding to the starting St-DVB copolymers (results presented elsewhere [13]).

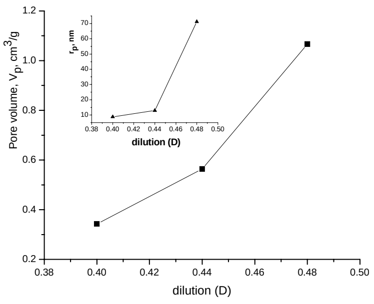

Fig. 1. The pore volume (!) and average pore radius (7, the inset) of chloromethylated copolymers as a function of dilution (D).

3.2. Morphological changes after chloromethylation reaction as a function of the reagents concentration

The results obtained when two different concentration of the chloromethylation reagent were used in the chloromethylation reaction of a macroporous St-DVB copolymer were collected in Table 1.

As Table 1 shows, the increase of the St/$(CH_2O)_n$ / TMCS molar ratio from 1:8:8 up to 1:15:15, the $FeCl_3$ concentration being kept constant, caused an increase of the Chloromethylation degree, reflected in the increase of chlorine content from 13.25 % up to 15.23 %.

Table 1. *Morphological characteristics of a macroporous St-DVB copolymer and of the corresponding chloromethylated copolymer as a function of the reagent concentration*

St-DVB Copolymer[a] CMC[b]	St/$(CH_2O)_n$/ TMCS/$FeCl_3$	Cl, (%)	ρ_{ap}, (g/cm^3)	V_p, (cm^3/g)	S_{sp}, (m^2/g)	$\overline{r}_p$, (nm)
St-DVB - 2	–	–	0.5248	0.8605	25.46	67.76
CMC - 2.1	1 : 8 : 8 : 0.4	13.25	0.7463	0.4572	62.10	14.72
CMC - 2.2	1: 15 : 15 : 0.4	15.23	0.7050	0.5357	70.50	15.20

[a] Starting copolymer with 8% DVB and a dilution of 0.44 mL/mL;

[b] Chloromethylation in chloroform, 10 g copolymer/100 mL chloroform, at 50 °C, 8h.

Comparative with the starting copolymer, a significant decrease of the pore volume and of the average pore radius, on the one side, and an abrupt increase of the specific surface area, on the other side, werw observed after chloromethylation reaction irrespective of the reagent concentration. The influence of the system dilution (content of copolymer in $CHCl_3$, g copolymer/100mL $CHCl_3$) on the chloromethylation degree and on the morphological characteristics, comparative with the starting copolymer, the other parameters being kept constant, is presented in Table 2.

Table 2. *Morphological characteristics of a macroporous St-DVB copolymer and of the corresponding chloromethylated copolymer as a function of copolymer concentration in $CHCl_3$*

St-DVB Copolymer[a]/ CMC[b]	Copolymer, g/100 mL $CHCl_3$	Cl, (%)	ρ_{ap}, (g/cm^3)	V_p, (cm^3/g)	S_{sp}, (m^2/g)	$\overline{r}_p$, (nm)
St-DVB - 2	–	–	0.5248	0.8605	25.87	67.76
CMC - 2.3	15	19.43	0.7134	0.5190	69.86	14.86
CMC - 2.4	10	16.61	0.7463	0.4572	62.10	14.72
CMC - 2.5	5	14.32	0.8200	0.3368	82.40	8.17

[a] Starting copolymer with 8 wt.% DVB and a dilution of 0.44 mL/mL;

[b] Chloromethylation with the molar ratio St/$(CH_2O)_n$/TMCS/$FeCl_3$ of 1:8:8:0.5, at 50 °C, 8h.

As one can see from Table 2, it seems that the increase of the copolymer content in the reaction medium has a positive influence on the chloromethylation degree, an increase of the chlorine content from 14.32% up to 19.43% being reached when the copolymer content in $CHCl_3$ increased from 5 up to 15 g/100 mL $CHCl_3$. Some morphological changes can be easily observed. A slight decrease of the pore volume and a slight increase of the specific surface area were found with the increase of the copolymer content in $CHCl_3$ from 10 to 15 g/100 mL. On the other side, the decrease of the copolymer content from 10 to 5 g/100 mL $CHCl_3$ caused a significant decrease of the pore volume and an increase of the specific surface area. Finally, the average pore radius decreased from 14.72 to 8.17 nm. These results show that further crosslinks are generated in all chloromethylating conditions, but the level of cronsslinking by self-alkylation is clearly influenced by the dilution of the reaction medium.

3.3 Morphological changes after chloromethylation reaction as a function of the catalyst content

Morphological changes in the chloromethylation step of the St-DVB copolymer with 10% DVB and D = 0.44 mL/mL (St-DVB 10:0.44) as a function of the ratio between St and catalyst ($FeCl_3$) can be seen in Table 3.

Table 3. *Morphological characteristics of a macroporous St-DVB copolymer and of the corresponding chloromethylated copolymer as a function of the St/$FeCl_3$ molar ratio.*

St-DVB Copolymer[a]/ CMC[b]	St/$(CH_2O)_n$/ TMCS/$FeCl_3$	Cl, (%)	ρ_{ap}, (g/cm^3)	V_p (cm^3/g)	S_{sp}, (m^2/g)	$\bar{r}_P$ (nm)
St-DVB - 4	–	–	0.470	1.1707	41.1	56.9
CMC - 4.1	1 : 8 : 8 : 0.5	14.49	0.7567	0.4389	67.0	13.10
CMC - 4.2	1 : 8 : 8 : 0.1	9.72	0.7004	0.5451	52.0	20.96

[a] Starting copolymer with 10% DVB and a dilution of 0.44 mL/mL;

[b] Chloromethylation at a copolymer content of 10 g/100 mL $CHCl_3$, at 50 °C, 8h.

The decrease of the St/$FeCl_3$ molar ratio from 1:0.5 to 1:0.1, the molar ratio between styrene and chloromethylation reagent being constant (St/$(CH_2O)_n$/TMCS = 1:8:8), determined an increase of the volume from 0.4389 cm^3/g up to 0.5451 cm^3/g and of catalyst content in the reaction medium the probability of the self-alkylation and thus of further crosslinkings is also decreased.the average pore radius from 13.10 nm up to 20.96 nm. These results demonstrate that by the decrease of the pore

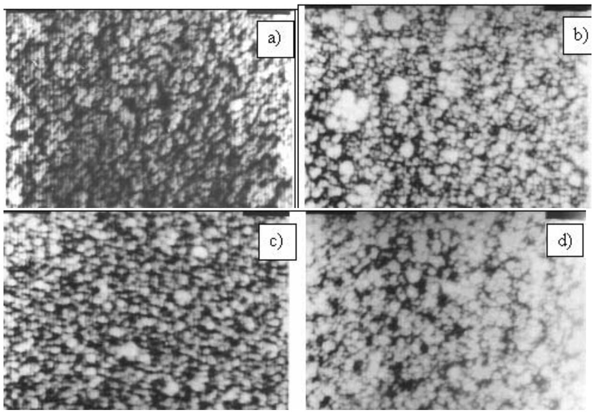

Fig. 2. SEM images of the outer part of the St-DVB beads before (a) and after chloromethylation reaction (b, c, d) in different conditions (x16 000): a) starting copolymer with 8 % DVB and D = 0.44 mL/mL; b) St-DVB copolymer after chloromethylation at a concentration of 5 wt.% in $CHCl_3$; c) St-DVB copolymer after chloromethylation at a concentration of 10 wt.% in $CHCl_3$; d) St-DVB copolymer after chloromethylation at a concentration of 15 wt.% in $CHCl_3$.

By SEM, it was demonstrated that a drastic decrease of the pore volume occurred after the chloromethylation reaction (Figure 2b, 2c and 2d)

Agglomerations of microspheres with sizes much higher than those observed in the starting copolymer (Figure 2a) were evident after the chloromethylation reaction (Figures 2b - 2d). As a consequence, the total pore volume and the mean pore radius diminished. However, the influence of the copolymer concentration in the reaction medium on the morphology of the chloromethylated copolymer can be also observed. Thus, at a concentration of 5 wt.% copolymer in $CHCl_3$, the highest sizes of the microspheres aggregates can be observed (Figure 2b). This shows the highest swollen state of the copolymer is stabilized by the further crosslinks, which accompanied the chloromethylation reaction in these conditions. At a concentration of 10 wt.% in $CHCl_3$, the sizes of microspheres aggregates are lower than in the previous conditions of chloromethylation, and furthermore the distribution of pores between the agglomeration of microsheres seems to be more uniform than in the case of starting St-DVB copolymer. Total pore volume and the mean pore radius are higher, and confirm the results presented in Table 2. As Figure 2d shows, a higher concentration of copolymer in the reaction medium led to a lower swelling of the globules, and as a consequence at a lower decrease of the interstices between the aggregates of microspheres.

4. Conclusions

Functionalization by chloromethylation with CH_2O/TMCS in the presence of $FeCl_3$ as catalyst, in

$CHCl_3$ as reaction medium, of the porous St-DVB copolymers, prepared in the presence of nBA as porogen, has been examined in this work. Chloromethylation degree and morphological changes after the chloromethylation reaction were correlated with the chloromethylation conditions and were supported by SEM images. The probability of the self-alkylation reaction decreased with the decrease of the catalyst content in the reaction medium.

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