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Short Communication

Styrene — Divinylbenzene Copolymers, IV

Porosity Changes During Chloromethylation

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SUMMARY:

The change in the porosity of styrene-divinylbenzene (S-DVB) copolymers during the chloromethylation reaction was investigated using apparent densities and equilibrium swelling in toluene. Maximum porosity of S-DVB copolymers does not change appreciably with the chloromethylation reaction. Only a slight decrease in the maximum porosity was observed in rigid networks, probably due to the partial destruction of the pore structure. However, with the substitution by chloromethyl groups, the degree of swelling decreases, which results in an increase in the stability of the porous structure in chloromethylated copolymers.

ZUSAMMENFASSUNG:

Die Änderung der Porosität von Styrol-Divinylbenzol-Copolymeren (S-DVB) während der Chlormethylierung wurde mit Hilfe von Dichtemessungen und Quellungsversuchen in Toluol untersucht. Die maximale Porosität von S-DVB-Copolymeren ändert sich während der Chlormethylierung nicht wesentlich. Es wurde nur ein leichter Abfall der maximalen Porosität in starren Netzwerken beobachtet, was vermutlich auf die teilweise Zerstörung der Porenstruktur zurückzuführen ist. Andererseits aber sinkt der Quellungsgrad mit der Substitution durch Chlormethylgruppen, was zu einer vergrößerten Stabilität der porösen Struktur in den chlormethylierten Copolymeren führt.

Introduction

Chloromethyl-substituted styrene-divinylbenzene (S-DVB) copolymers are key intermediates in many resin preparations for ion-exchange reactions[1]. Chloromethyl groups are introduced most often by Friedel-Crafts alkylation with chloromethyl methyl ether and in the presence of aluminium chloride or

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stannic chloride as catalyst. The introduction of chloromethyl groups into the heterogeneous S-DVB matrices results in a change in the solvent regain as well as in the porosity of the starting materials[2,3]. Moreover, the porosity of S-DVB copolymers also varies with the type of solvent in which the copolymer is swollen before drying[3-11]. For instance, the copolymers dried from bad solvents such as methanol or water show a "maximum porosity"[5], which is close to the porosity in the swollen state[8]. The drying process of the copolymers swollen in good solvents such as toluene may lead to a partial or total collapse of the pores. Thus, the porosity of S-DVB copolymers consists of two parts, namely stable and unstable porosities.

This communication is concerned with an investigation of changes in the porous properties of S-DVB copolymers during the chloromethylation reaction. For this purpose, a set of porous S-DVB copolymer beads was chloromethylated under identical conditions. The change in the maximum and stable porosities was observed by measuring the apparent densities of the samples before and after the chloromethylation reaction. Swelling of the copolymers in toluene was also measured by the centrifugation method.

Experimental

Materials

All monomers and reagents were purified and distilled prior to use. The S-DVB copolymer beads of 0.35 to 1.00 mm in diameter were obtained by the suspension polymerization method, as described previously[11,12]. Cyclohexanol was used as the diluent at a fixed volume fraction of the organic phase (0.50). After drying at room temperature, 3 g of the copolymer beads were swollen in 30 ml 1,2-dichloroethane and then they were chloromethylated by 3.4 ml chloromethyl methyl ether (CMME) at 40 °C for 3 h in the presence of 1.5 g $AlCl_3$ as catalyst. (Copolymer : CMME : $AlCl_3$ molar ratio 1 : 1.6 : 0.4). At the end of the reaction time, the products were filtered off and washed with 3 : 1 dioxane-water and 3 : 1 dioxane-3N aqueous HCl. The copolymers were then successively washed with the following solvents, respectively: water, dioxane, toluene, acetone, methanol, and water.

After treatment with water as a final solvent, the samples were dried in vacuo at room temperature. For comparison, a part of the samples swollen in toluene was dried without the solvent exchange in vacuo at 70 °C.

Methods

The apparent density of the copolymers, d_0, was determined by the mercury pycnometric method[13]. The porosity, P %, was calculated from d_0 as,

$$P\,\% = (1 - d_0/d_2) \times 100\% \qquad (1)$$

where d_2 is the density of homogeneous S-DVB copolymers taken as 1.08 g/cm^3. The weight swelling ratio in toluene was determined by the centrifugation method[14]. The volume fraction of the copolymer in the swollen gel, v_2, was calculated as in ref.[11].

The chloromethyl content of the copolymers was determined as follows[15]: A weighed portion (about 200 mg) of the resin was quarternized in 5 ml boiling n-butyl amine for 6 h. The mixture was then poured into 50 ml water. After acidification of the mixture with nitric acid, the chlorine content was determined titrimetrically using a 0.1 M silver nitrate solution. Good agreement was found between the values obtained with the titrimetric method and those calculated from the elemental analysis.

Results and Discussion

The chloromethylated S-DVB copolymer beads were found to have in all cases a chloromethyl content between 2.8 and 3.2 mmol/g (45% substitution).

Tab. 1. Composition and properties of copolymers before and after the chloromethylation reaction[a] ((1) and (2), respectively).

Sample No.	DVB (wt.-%)	v_2 in toluene		P_T%		P_w%		Cl-content (mmol/g)
		(1)	(2)	(1)	(2)	(1)	(2)	
1	6.2	0.47	0.59	5	2	22	20	3.1
2	12.3	0.57	0.66	5	34	33	38	3.2
3	14.8	0.73	0.75	8	38	46	41	2.9
4	21.0	0.81	0.84	39	—	47	42	2.9
5	24.7	0.83	0.94	47	46	50	45	2.8

[a] v_2 = volume fraction of copolymer in the swollen gel, P_T% = total porosity of copolymers dried from toluene (stable porosity) and P_w% those dried from water (maximum porosity).

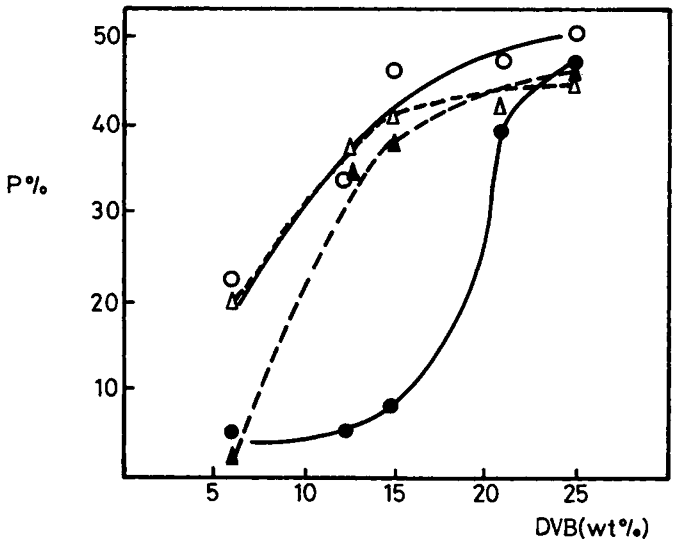

Fig. 1. Dependence of the total porosity, P%, on the DVB concentration for copolymers before (———) and after the chloromethylation reaction (- - -): maximum (○ and Δ) and stable porosities (● and ▲) of starting and chloromethylated copolymers, respectively.

As expected, the swelling degree in toluene decreases or the v_2 value increases with the introduction of chloromethyl groups into the copolymer matrices (Tab. 1). The decrease in the degree of swelling is due to the increase of the polarity of copolymer matrices. In addition, the Friedel-Crafts conditions may also lead to a further crosslinking in the network by interpolymer alkylation.

The porosities of the starting materials and their chloromethylated derivatives are plotted against the DVB concentration in Fig. 1. The porosity of samples dried from water, i.e., the maximum porosity does not change up to 12.3% DVB with the chloromethylation reaction. With a further increase in the DVB concentration, the chloromethylated copolymers show slightly lower maximum porosity values than the starting copolymers. The slight decrease in the maximum porosity may be attributed to the partial destruction of the rigid pore structure during the reaction. Such a destruction in rigid S-DVB copolymers was found previously during the sulfonation and chloromethylation reactions[3].

The stable porosity, i.e. the porosity of copolymers dried from toluene, increases abruptly over a narrow range of the DVB concentration, i.e. between 15 – 25% DVB for starting copolymers and between 6 – 15% DVB for their chloromethylated derivatives (Fig. 1). It seems that the critical DVB concentration required for the stability of the porous structure shifts to the lower values with the chloromethylation reaction.

The stable porosity of starting copolymers is close to the maximum porosity at a DVB content between 20 – 25%, corresponding to a v_2 value appr. 0.80 (Tab. 1). As we showed earlier, this value of v_2 represents a borderline between rubbery and glassy state[11]; i.e., the S-DVB copolymers swollen in toluene with v_2 values above 0.80 are in the glassy state. Therefore, the porous structure of such copolymers does not collapse on drying in the swollen state. With the substitution by chloromethyl groups on the matrices, v_2 reaches the value of 0.80 earlier, namely between 15 – 21% DVB, corresponding to the onset of the pore stability. This suggests that the decreasing swelling of S-DVB copolymers with the chloromethylation reaction is the reason of the increasing pore stability of chloromethylated samples.

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