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Styrene-Divinylbenzene Copolymers*

VII. Stability of the Porous Structures Formed in Toluene — Cyclohexanol Mixtures

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SUMMARY:

The pore stability of styrene-divinylbenzene (S-DVB) copolymers prepared in toluene-cyclohexanol mixtures as inert diluents was investigated as a function of the DVB concentration, diluent composition, and dilution. The stability of the porous structures increases with increasing DVB concentration and, to some extent, with increasing dilution. At a fixed degree of equilibrium volume swelling in toluene, the pore stability also increases with increasing solvating power of the diluent. The density of S-DVB copolymers increases during the sulfonation reaction with chlorosulfonic acid, but the stability of porosity remains unchanged.

ZUSAMMENFASSUNG:

Die Porenstabilität von Styrol-Divinylbenzol-Copolymeren (S-DVB), hergestellt in Toluol-Cyclohexanol-Mischungen, wurde in Abhängigkeit von der DVB-Konzentration, der Lösemittelzusammensetzung und der Verdünnung untersucht. Die Stabilität der Porenstrukturen nimmt mit steigender DVB-Konzentration zu und — in gewissem Ausmaß — auch mit steigender Verdünnung. Bei einem festgelegten Grad der Gleichgewichtsquellung in Toluol nimmt die Porenstabilität auch mit steigender Lösefähigkeit des Verdünnungsmittels zu. Die Dichte der S-DVB-Copolymeren steigt während der Sulfonierung mit Chlorsulfonsäure an, aber die Stabilität der Poren bleibt unverändert.

Introduction

A characteristic feature of porous styrene-divinylbenzene (S-DVB) copolymers is the change in their porosities during drying or during the intro-

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* Part VI: cf.[12].

duction of functional groups[1]. It is known that the drying process of S-DVB copolymers swollen in good solvents may lead to a partial or total collapse of the pores[2-4]. Moreover, the actual pore structure formed during the network formation process, namely the maximum porosity, can be preserved if the swollen copolymers were treated with solvents with decreasing solvating power (solvent exchange) before the drying process[5-6]. Previous studies have shown that, during the drying process of the copolymers, the pores collapse in the rubbery rather than in the glassy state[7]. Thus, the "average" glass transition temperature of polymer-solvent system and its fluctuation along the network regions due to the compositional inhomogeneity are the most important factors determining the pore stability of S-DVB copolymers[8-11].

In the present study, the pore stability of S-DVB copolymers prepared in toluene-cyclohexanol mixtures as inert diluents was investigated as a function of the DVB concentration, diluent composition, and dilution. For this purpose, the copolymers after synthesis were dried from toluene to find the stable part of their porosities, and the results were then compared with their maximum porosity values reported in a recent study[12]. The change in the porosity during the sulfonation reaction was also investigated.

Experimental

The S-DVB copolymer beads prepared in[12] were used for this study. The copolymer samples were swollen to equilibrium in toluene and then dried in vacuo at room temperature.

The sulfonated products were prepared by adding chlorosulfonic acid (6 g; 51.5 mmol) to 5 g of the copolymer beads swollen to equilibrium in 35 ml 1,2-dichloroethane at $0\,^{\circ}C$. The reaction was conducted for 5 h at $0\,^{\circ}C$ and then for 20 h at room temperature. The products were washed successively with 1,2-dichloroethane, dioxane, and finally with water, and then dried in vacuo at room temperature.

The apparent density of the copolymers, d_0, was determined by the mercury pycnometric method. The stable porosity, P' (%), was calculated 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 fraction of the stable porosity was calculated as P'/P where P is the maximum porosity of the copolymers[12].

Results and Discussion

Two series of copolymers were investigated for their pore stability (Tab. 1). The copolymers in series I were prepared at a fixed diluent-monomer volume ratio, r, but with various amounts of DVB. The volume fraction of cyclohexanol in the diluent mixture, v_{CH-OH}, was taken as 0.50 and 0.75. In series II, the copolymers were prepared at a fixed DVB concentration and diluent composition, but the diluent-monomer volume ratio, r, was varied between 0.73 and 4.00.

The change in the apparent density of the copolymers as a function of the DVB concentration and dilution are given in Fig. 1 and Fig. 2, respectively. The dotted curves in Fig. 1 and 2 represent the apparent densities of copoly-

Tab. 1. Composition and properties of copolymers[a].

Series	DVB (mol-%)	v_{CH-OH}	r	d_0 (g/cm³)	P′ (%)	P′/P	$(d_0)_{sulf}$ (g/cm³)
I	5	0.50		1.04	4	—	—
		0.75		1.05	3	—	1.47
	10	0.50		1.06	2	—	1.41
		0.75		1.06	2	0.03	1.46
	15	0.50		1.05	3	0.27	1.38
		0.75	1.00	1.02	6	0.15	1.44
	20	0.50		1.00	7	0.34	1.31
		0.75		0.89	18	0.42	1.06
	25	0.50		0.99	8	0.35	1.31
		0.75		0.715	34	0.79	1.02
	30	0.50		0.92	15	0.56	1.26
		0.75		0.66	39	0.89	0.98
II	20	0.75	0.73	1.04	4	0.42	
	20	0.75	1.00	0.89	18	0.42	
	20	0.75	1.50	0.99	8	0.18	
	20	0.75	2.00	0.43	60	0.96	
	20	0.75	3.00	0.41	62	0.90	
	20	0.75	4.00	0.59	45	0.64	

[a] v_{CH-OH} = Volume fraction of cyclohexanol in the diluent mixture, r = diluent-monomer volume ratio, d_0 = apparent density, P′ = stable porosity of the copolymers, P′/P = fraction of the stable porosity, and $(d_0)_{sulf}$ = apparent density of the sulfonated copolymers.
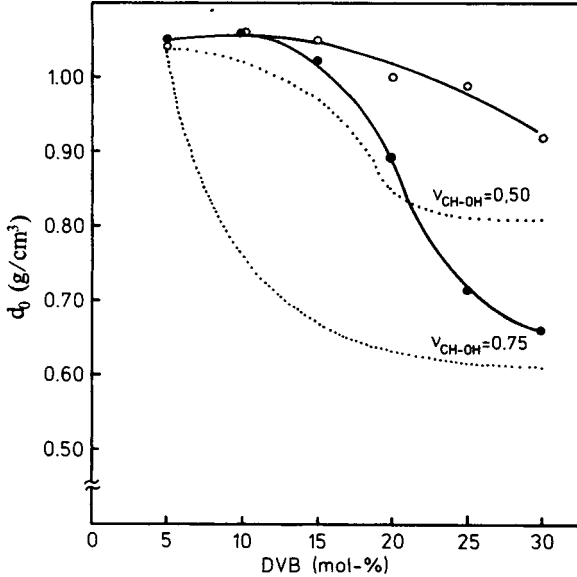
Fig. 1. Dependence of the apparent density, d_0, on the DVB concentration for co-polymers in series I. $v_{CH-OH} = 0.50$ (○) and 0.75 (●). The dotted curves represent the d_0 values of copolymers dried after the solvent exchange[12].

mers dried after the solvent exchange. At a fixed dilution (Fig. 1), the apparent density decreases, i.e., the stable porosity increases with increasing DVB concentration. For $v_{CH-OH} = 0.75$, the stable porosity increases abruptly between 15 and 30 mol-% DVB, and at 30 mol-% DVB 90% of the pores are preserved on drying in the swollen state (Tab. 1).

The stable porosity also increases with increasing dilution, and the apparent density approaches to its value after the solvent exchange at $r = 2.00$ (Fig. 2). At this point 96% of the pores are stable on drying. With a further increase in dilution, a slight decrease in the stable porosity was observed up to $r = 4.00$.

The results given in Fig. 1 and Fig. 2 can be collected in a single diagram if the equilibrium swelling ratio of the copolymers in toluene was taken as a measure of the pore stability. In Fig. 3, the fraction of stable porosity, P'/P, is plotted against the swelling ratio in terms of v_2, which is the volume fraction of copolymer in the swollen gel. The copolymers from both series show an increase in P'/P with increasing v_2. Thus, the pore stability increa-

Fig. 2. Dependence of the apparent density, d_0, on the diluent-monomer volume ratio in the starting monomer mixture, r, for copolymers in series II. The dotted curve represents the d_0 values of copolymers dried after the solvent exchange[12].
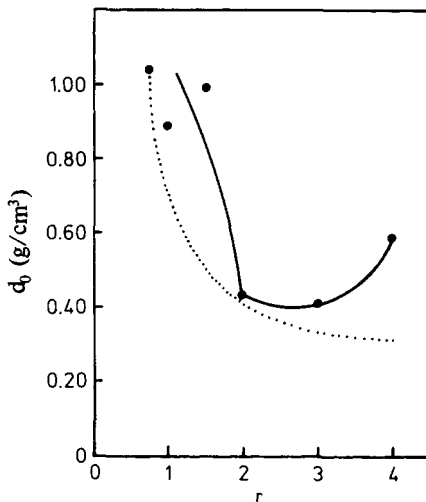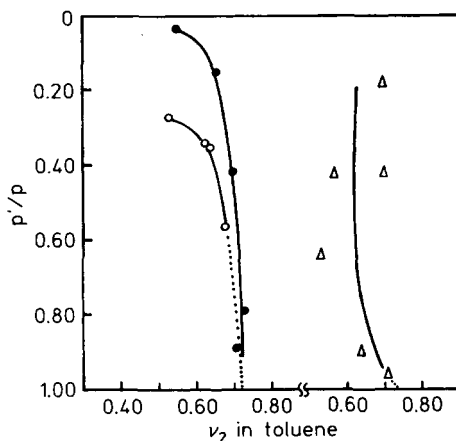
Fig. 3. Dependence of the fraction of stable porosity, P'/P, on the volume fraction of copolymer in the swollen gel, v_2. Shown are copolymers from series I with $v_{CH-OH} = 0.50$ (○) and 0.75 (●), and from series II (△).

ses with decreasing swelling ratio of the copolymers. Furthermore, the increase in the pore stability is abrupt at about $v_2 = 0.7$, and the extrapolation of the curves to P'/P = 1.00 leads to a v_2 value between 0.7 and 0.8. This value of v_2 corresponds to the critical v_2 value for glassy transition of S-DVB copolymers swollen in toluene at room temperature[9]. Another point illustrated by Fig. 3 is that, at a given value of v_2, the pores in a copolymer prepared in the presence of thermodynamically poorer diluents are less stable than those prepared in better diluents. For instance, at $v_2 = 0.65$, the

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fraction of stable porosity decreases from 0.35 to 0.15, as the cyclohexanol volume fraction in the diluent mixture increases from 0.50 to 0.75. This situation can be explained by the increasing inhomogeneity in porous S-DVB copolymers with decreasing solvating power of the diluent. An increase in the compositional inhomogeneity leads to the formation of less crosslinked regions in the network which can collapse on drying in the swollen state.

The apparent densities of the copolymers from series I before and after the sulfonation reaction are given in Tab. 1. The apparent density increases with the sulfonation reaction. Such an increase in the density was not observed during the sulfonation reaction with sulfuric acid, as reported previously[7]. To calculate the porosity of sulfonated copolymers according to Eq. (1), the density values of 1.4 to 1.5 g/cm^3 at 5 and 10 mol-% DVB were taken as the density of homogeneous copolymers (d_2). In this way, the calculated porosities of sulfonated products can be compared with the stable porosities of starting copolymers. As seen in Fig. 4, the porosity of the copolymers does not change with the sulfonation reaction.
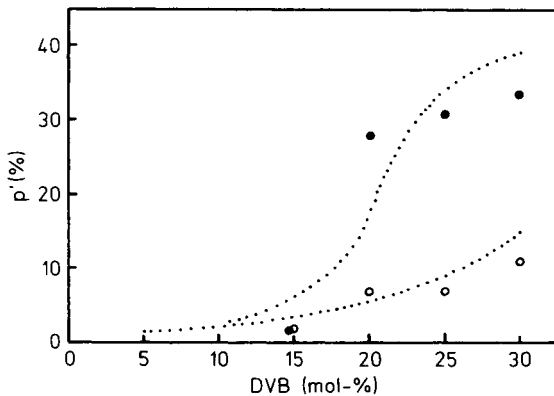

Fig. 4. Dependence of the stable porosity, P', on the DVB concentration for sulfonated copolymers. v_{CH-OH} = 0.50 (○), 0.75 (●). The dotted curves represent the stable porosities of the starting copolymers in series I.

The experimental results regarding the pore stability of S-DVB copolymers prepared in toluene-cyclohexanol mixtures as inert diluents can be summarized as follows:

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1. The equilibrium swelling ratio of the copolymers in toluene determines the stability of the porous structures; the pores are stable at $v_2 \geq 0.7 - 0.8$. This is in accord with our previous results[9, 10].

2. For a given value of v_2, the pore stability increases with increasing solvating power of the diluent.

3. The density of the copolymers increases during the sulfonation reaction with chlorosulfonic acid, but the stability of porosity remains unchanged.

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