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Macroporous styrene-divinylbenzene copolymers: Formation of stable porous structures during the copolymerization

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Summary

The variation of the pore structure of styrene-divinylbenzene (S-DVB) copolymer beads depending on the polymerization time was investigated. Macroporous S-DVB copolymer beads with 10 mol % DVB content were prepared in the presence of cyclohexanol as a diluent. It was found that the stable pores in S-DVB copolymers mainly form at an early stage of the copolymerization, i.e., at the gel point. Thus, the early phase separated portions of the network, where the crosslink density is locally high, do not collapse on drying and illustrate the stable part of the porosity of S-DVB copolymers. The number of stable pores does not change much during the whole course of the copolymerization. The maximum porosity first decreases on rising the post-gelation time due to the decreasing degree of dilution of the gel phase. Then, it increases continuously due to the increasing crosslink density of the gel. The pores formed at a later stage of the copolymerization are unstable and they collapse during the drying process. This is due to the lower crosslink density of the network regions forming later.

Introduction

Macroporous (heterogeneous) styrene - divinylbenzene (S-DVB) copolymer networks are widely used as starting materials for ion exchangers and as specific sorbents. These materials are prepared by free-radical crosslinking copolymerization of S and DVB monomers in the presence of an inert diluent (1-4). The diluent, which is a solvent, a nonsolvent, or a linear polymer, is included in the reaction system as a pore forming agent, and plays an important role in the design of the pore structure of these crosslinked materials. Heterogeneities in the network structure appear if the diluent separates out of the gel phase during the polymerization reactions. The incipient phase separation during the crosslinking copolymerization may occur before the onset of macrogelation; this results in the formation of a polymer dispersion in the liquid phase. Otherwise, if the system phase separates beyond the gel point, the gel shrinks and results in a dispersion of the expelled liquid droplets in the network phase (5,6). In both cases, after complete conversion of the monomers, a heterogeneous S - DVB network consisting of network and diluent phases is obtained. Removing of the diluent from the network creates voids (pores) of sizes 10 A^0 up to 1 μm in the glassy state. Relationships between the synthesis conditions and the structure of macroporous S-DVB networks have been the subject of intensive studies during the last four decades (1-4). Experiments showed that a phase separation during the gel formation process is promoted, i.e., the volume of the diluent

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phase (pore volume) in the network increases as the concentration of the crosslinker (DVB) or that of the diluent increases, or as the solvating power of the diluent decreases.

Although the final pore structure of a S - DVB network is fixed during the gel formation process, that is, when the network is in a rubbery state, its structural characterization is performed with the polymer sample in the glassy state. Krska et al. were first pointed out the difference in the pore structure of S-DVB copolymers between the swollen and the dried states (7). It was shown that the copolymers dried from nonsolvents such as methanol show a “maximum porosity”, which is close to the porosity in the swollen state. The drying process of the copolymers swollen in good solvents such as toluene may lead to a partial or total collapse of the pores (8-15). These experimental findings indicate that the pore structure of S-DVB copolymers consists of two parts: the stable part which does not collapse during the post-treatment process, and the unstable part which collapses during the drying process in a rubbery state. It seems that the stability of the pores is closely related to the degree of inhomogeneity in crosslink distribution of the network; the pores in the loosely crosslinked (rubbery) regions of the material collapse during the drying process, whereas those in the highly crosslinked (glassy) regions remain unchanged.

This study aims to determine the polymerization times required for the formation of stable and unstable pores in S - DVB copolymers. These polymerization times are important because they also correspond to the formation times of network regions differing in crosslink density. For this purpose, S - DVB copolymerization reactions were carried by the suspension polymerization technique at 10 mol % DVB content. Cyclohexanol, a poor solvent for S - DVB copolymer was used as a diluent. The changes in the pore structure of S-DVB copolymer beads depending on the polymerization time were investigated by mercury porosimetry using copolymer samples dried from methanol and toluene.

Experimental

Materials

Styrene (S, Sabic), divinylbenzene (DVB, Riedel-de Haen), dibenzoyl peroxide (DBP, Elf Atochem), tert-butyl perbenzoate (TBP, Interchem), cyclohexanol (Merck), tricalcium phosphate (TCP, Budenheim), calcium chloride (Kemira Kemi), dodecylbenzene sodiumsulfonate (DBS, Henkel) were used as received. DVB consisted of 62 % DVB isomers with the rest being mostly ethylvinyl benzenes (35 %). Fresh distilled water was used in the synthesis of the copolymers.

The S-DVB copolymer beads were obtained by the suspension polymerization technique (16). Cyclohexanol was used as the diluent of the organic phase. The DVB concentration in the monomer mixture and the volume fraction of the monomers in the organic phase (monomer - diluent mixture) were taken to be constant at 10 mol % and 0.5, respectively. DBP and TBP were used as the initiator of the low and high temperature period of the free-radical copolymerization, respectively. Suspension polymerization was conducted in a 1 L Buchi jacketed glass reactor fitted with a mechanical stirrer, nitrogen inlet, condenser, temperature and pressure indicators. 550 mL of 3 % aqueous NaCl solution, the diluent cyclohexanol (100 mL) and the S - DVB monomer mixture (100 mL) were first introduced into the reactor, heated to 70°C, and 100 mL of an aqueous suspension agent containing $CaCl_2$ (0.095 g), TCP (7.430 g), and DBS (0.017 g) were then added to the reactor under nitrogen atmosphere at 300 rpm. The reaction mixture was heated to 90°C and the initiators DBP (0.500 g) and TBP (0.035 g) were feeded to the mixture to initiate the polymerization reactions. The reaction was allowed to proceed at 90°C for 5.5 h and at 120°C for 1.5 h under nitrogen atmosphere and at 300 rpm. In order to follow the formation of porous structures and the monomer conversions during the copolymerization, at predetermined reaction times, samples of approximately 20 mL in volume were withdrawn from the reactor. One part of the sample was mixed with a dilute HCl solution to dissolve TCP surrounding the beads. After filtration of the copolymer beads, they were sieved using ASTM sieves under vibration. All the beads were within the size range of 0.5 to 1.4 mm in diameter. They were first washed with water and then extracted with acetone for 6 h in a Soxhlet apparatus. To determine the monomer conversion, another part of the sample taken from the reactor was also treated with HCl solution; then, the organic phase was separated and poured slowly into methanol under agitation. The precipitated copolymer was dried at 160 °C and then weighed. The fractional monomer conversion x was calculated as the amount of polymer formed per gram of the monomer present initially.

Solvent Treatment

The copolymer beads thus obtained were swollen to equilibrium in toluene for at least one week. Then, they were washed first with acetone and finally with pure methanol. Using this solvent exchange procedure, the good solvent toluene in the swollen gel was replaced with the nonsolvent methanol and, thus, the gel was transferred from the rubbery to the glassy state before the drying process. The copolymer beads after treatment with methanol as a final solvent were dried *in vacuo* at room temperature for 15 h. For comparison, part of the copolymer beads swollen in toluene was dried, without the solvent exchange, for 30 h at 80°C.

Methods

The pore volume and the pore size distribution of copolymer beads were determined by mercury intrusion porosimetry on a Micromeritics 9305 model porosimeter. The distribution function ΔV / Δ **log(*r*)** was used to express the pore size distribution, where AV is the pore volume change when the radius of a cylindrical pore was changed from r to $r - \Delta r$. The total porosity, defined as the cumulative volume of the pores in one gram of the copolymer, was estimated from the intruded mercury volumes of the pores larger than 3 nm radius (intruded pressures smaller than 30000 psi).

Results and discussion

Macroporous S-DVB copolymer beads with 10 mol % DVB were prepared in the presence of cyclohexanol as an inert non-solvating diluent. The initial volume fraction of the monomers in the organic phase was taken to be constant at 0.5 throughout the present study, and only the polymerization time was varied. Figures 1A and 1B illustrate the differential pore size distribution curves of S - DVB copolymers isolated at different polymerization times. Open symbols in the figures represent the porosities of the copolymer samples dried from methanol; thus, they correspond to the swollen state (“maximum”) porosities because the swelling agent toluene was replaced with the nonsolvent methanol before the drying process (10). The filled symbols belong to the copolymer samples dried from toluene, i.e., they represent the stable porosities.

At the very early stage of the copolymerization, the polymer was completely soluble in toluene. The insoluble material started to appear between a polymerization time of 20 and 25 min. The first sample for the porosity measurements was taken from the reactor after 30 min of polymerization. As seen from Figure 1A, this sample exhibits large number of pores of sizes 10^2 - 10^4 A° in radius, if it dried from methanol. However, these pores are unstable and, they totally disappear during the drying process from toluene.

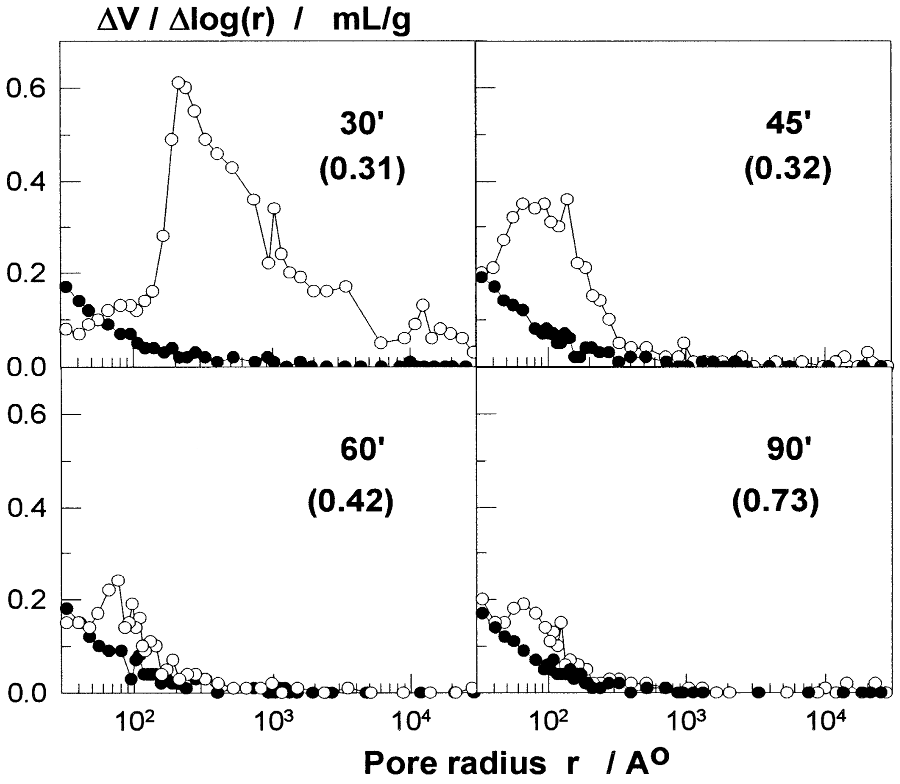

Fig. 1A. Differential pore size distribution of S-DVB copolymers dried from toluene (filled symbols) and from methanol (open symbols) at different reaction times. DVB = 10 mol %. Monomer concentration in the organic phase = 50 (v/v) %, Diluent = cyclohexanol. The reaction times and the monomer conversions (in parenthesis) are indicated in the figures.

As the polymerization time increases from 30 to 90 min, i.e., as the monomer conversion x increases from 0.3 to 0.7, the number of pores of 10^2 - 10^4 A° in radius found in the first sample decreases and finally disappears. Therefore, we may conclude that the pores of larger than 10^2 A° in radius appearing just beyond the gel point form due to the unreacted monomers and the sol polymers acting as an intrinsic diluent of the reaction system. Continuing polymerization converts monomer and sol polymer to the gel, so that the voids inside the network gradually fill up with the gel material, resulting in a decrease in porosity on increasing the polymerization time from 30 to 90 min.

Further polymerization up to 420 min creates new pores of 40 to 100 A° in radius (Figure 1B). The number of these pores increases and the pore size distribution shifts toward the larger pores on increasing the polymerization time. This increase in the porosity is first slight up to a polymerization time of 300 min but then ($x > 0.98$) rapid, due to the increasing crosslink density of the gel by the reaction of pendant vinyl groups with macroradicals to form crosslinks and multiple crosslinks. However, these pores formed at a later stage of the copolymerization are unstable and they collapse during the drying process.

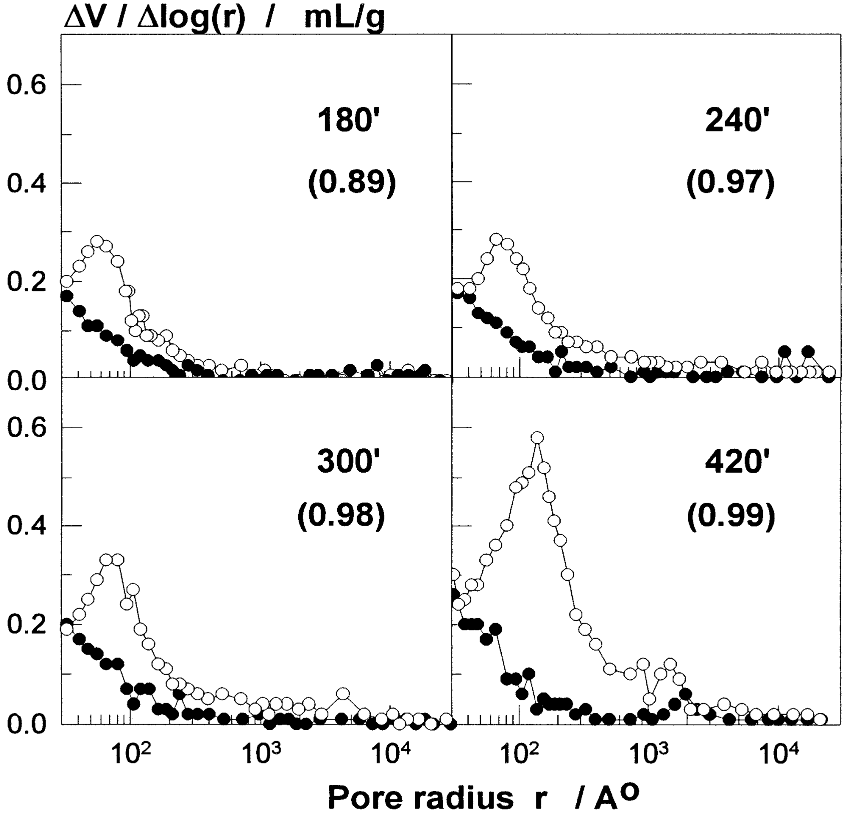

Fig. 1B. Differential pore size distribution of S-DVB copolymers dried from toluene (filled symbols) and from methanol (open symbols) at different reaction times. See Figure 1A caption for explanations.

Interesting is the observation that the stable pores of sizes less than 100 A° in radius appearing at the gel point exist during the whole course of the polymerization reaction (filled symbols in Figures 1A and 1B). These experimental results demonstrate that the stable pores in S-DVB copolymers form just beyond the macrogelation. This is probably due to the higher reactivity of the DVB monomers compared to styrene (17-21); at the beginning of the copolymerization, much more DVB is incorporated into the copolymer than is expected based on the initial composition of the monomer mixture. Accordingly, the first formed nuclei and their agglomerates (microspheres) are highly crosslinked than those formed in a later stage of the copolymerization when the major part of the DVB monomers have been used up. Thus, the pores inside the first formed regions of the network remain stable during the drying process because these regions will have higher crosslink density. However, the pores formed at higher monomer conversions are unstable due to the lower crosslink density of the network regions forming later.

In Figure 2, the total porosities of copolymers dried from methanol (expanded state) and toluene (collapsed state) are shown as a function of the polymerization time. It is seen that the stable porosity, i.e., the porosity of the copolymer dried from toluene does not change much during the whole course of the polymerization reactions. Its value is fixed with the onset of macrogelation. However, the maximum porosity first decreases on rising the post-gelation time due to decreasing degree of dilution of the gel phase. Thereafter, it increases continuously on rising the reaction time due to the increasing crosslink density of the gel.

The structure of macroporous S-DVB copolymers is known to consist of globules (22); the smallest, rather spherical particles of about 100 - 200 A° in diameter are the nuclei, and the aggregation of these nuclei results in the microspheres. The pores are defined as the spaces between the nuclei, microspheres and the aggregated microspheres. According to this picture, the first formed nuclei and their agglomerates are stable whereas those formed later are unstable. The unstable pores in the copolymer collapse when it is dried from a good solvent like toluene. As we observed recently, the collapsed pores in S-DVB copolymer reexpand if the copolymer is swollen again in toluene and then dried from methanol (23). This collapse - reexpansion process of the unstable pores was found to be reversible, indicating that the actual pore structure formed during the crosslinking copolymerization is memorized by the copolymer network (23). According to Figure 2, a macroporous S - DVB copolymer with a maximum memory of pores, that is, with a maximum number of variable pores can be obtained if the network is isolated beyond the gel point.

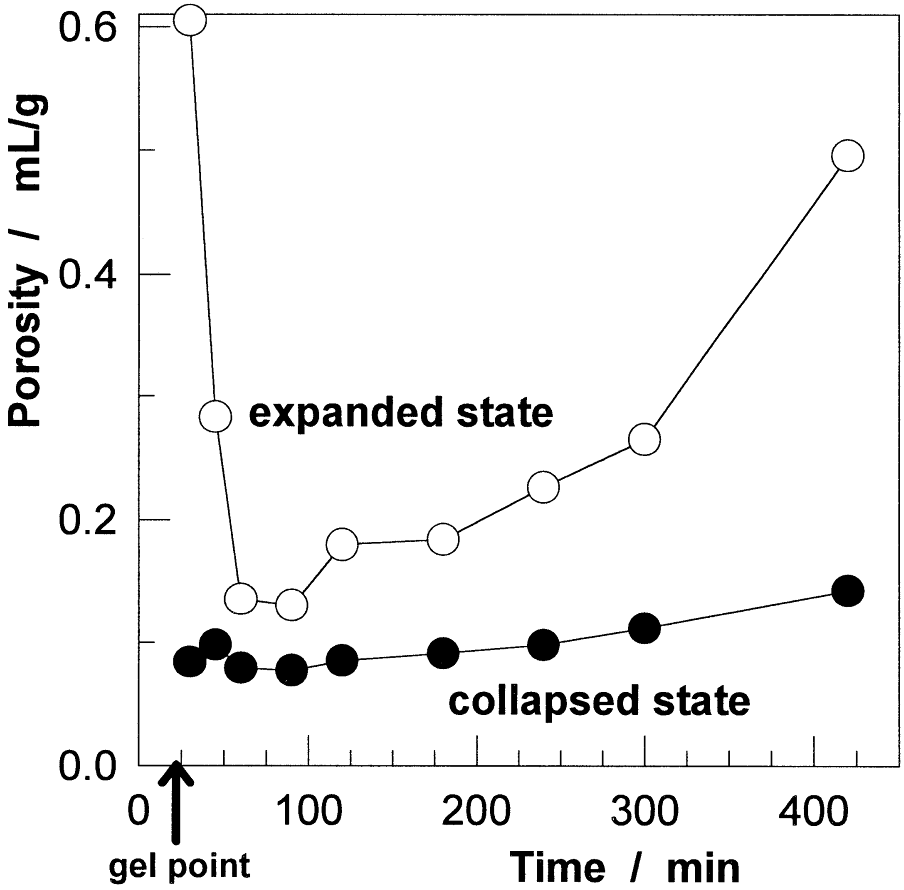

Fig. 2. Total porosity of copolymer samples dried from toluene (filled symbols) and from methanol (open symbols) shown as a function of the reaction time of S - DVB copolymerization.

Conclusions

1) Experimental data demonstrate that the stable pores in S-DVB copolymers mainly form at an early stage of the copolymerization, i.e., at the gel point. Thus, the early phase separated portions of the network, where the crosslink density is locally high, do not collapse on drying and illustrate the stable part of the porosity of S-DVB copolymers. The number of stable pores does not change much during the whole course of the copolymerization.
2) The maximum porosity first decreases on rising the post-gelation time due to the decreasing degree of dilution of the gel phase. Then, it increases continuously due to the increasing crosslink density of the gel. The pores formed at a later stage of the copolymerization are unstable and they collapse during the drying process. This is due to the lower crosslink density of the network regions forming later.

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