PETER KRAJNC
University of Maribor
Faculty of Chemistry and Chemical Engineering
Smetanova 17, Maribor, Slovenia
e-mail: peter.krajnc@uni-mb.si

The influence of some polymerization conditions on the morphology of poly(styrene-*co*-divinylbenzene) monoliths

Summary — High internal phase emulsion (HIPE) precursors were used to prepare emulsions which were submitted to radical polymerization to yield poly(styrene-*co*-divinylbenzene) monolithic polymers. The morphology and mechanical properties of the resulting materials were studied in relation to selected polymerization conditions. As the amount of diizovinylbenzene (crosslinking agent) was increased, 10 *vs.* 50%, the cell size in the porous structure of the material fell. The hydrophile—lipophile balance (HLB) value of the surfactant used (sorbitan mono and/or trioleate) was found to be the crucial factor influencing the morphology: the lower HLB (from 4.3 to 3.5) surfactant resulted in smaller cells. Curing procedure (open *vs.* tightly closed containers) also affected the structure, *viz.*, the latter case yielded more fragile and chalky polymers.

Key words: monolithic polymers, high internal phase emulsions, morphology of porous poly(styrene-*co*-divinylbenzene) materials.

The acronym polyHIPE signifies porous polymer materials prepared by polymerizing the continuous phase of a high internal phase emulsion (HIPE) [1]. The emulsion is produced by vigorous mixing; the internal phase is comprised of water droplets and the continuous organic phase is comprised of monomers. Divinylbenzene is used as a crosslinking agent. The high internal phase emulsion has a very large volume fraction of water droplets, up to 99%. Polymerization and subsequent removal of water yields a highly porous polymer material of a low density. Such materials are usually endowed with an open cellular structure in which every cavity is connected to its neighboring cavities. Large surface areas is another distinction of polyHIPE polymers. Cameron and co-workers [2] have prepared polystyrene polyHIPE with surface areas up to 550 m^2/g by the use of inert solvents (porogens). This is especially important for applications such as solid-phase extraction and reverse phase HPLC. Since polymerization of a high internal phase emulsion is usually triggered thermally, the stability of the emulsion is of paramount importance. To prevent phase separation, the emulsion must be stable up to the temperature of polymerization. To enhance the stability, surfactants are added. The hydrophile—lipophile balance (HLB) system of surfactant characterization is widely used [3].

The pioneering work on polyHIPE materials has been done by the researchers at Unilever Laboratories [1, 4] and, in recent times, many research groups are involved in the investigations on polyHIPEs, most notably the group led by N. R. Cameron at the University of Durham [2, 5—8]. The various applications of novel materials already reported include monolithic polymers for separation of heavy metals [9, 10], monolithic solid-phase acid catalysis [11], monoliths as precursors for supported species [12] *etc.*

A lot of work has recently been done on the comparison of the use of polymers as supports between sphered polymer particles (polymer beads) and monolithic porous polymers [13, 14]. With polymer beads, swelling in solvents is of vital importance since the vast majority of reactive sites are positioned inside the sphere. With polyHIPE monolithic polymers, sites are accessible *via* pores and swelling can be controlled or eliminated making the use of continuous flow techniques easier. High back pressures and non-uniform flow patterns (channeling) are drawbacks to the use of polymer beads. PolyHIPE monoliths offer low back pressures.

So far, the morphology of polystyrene polyHIPE materials has been studied in relation to crosslinking degree, but the influences of surfactant and curing procedures on the morphology have not been reported as yet. This paper sets out to describe the results of the study on the effect of polymerization conditions, namely, crosslinking degree, surfactant HLB values and curing procedure, on the morphology of the resulting materials.

EXPERIMENTAL

Materials and measurements

Divinylbenzene (DVB) [Merck's (55:45) and (80:20 w/w) isomeric divinylbenzene—ethylstyrene mixtures] and styrene (Merck) were washed with aqueous 5% NaOH to remove the inhibitors. Sorbitan monooleate (Aldrich's Span 80), sorbitan trioleate (Aldrich's Span 85), potassium persulfate (Fluka), calcium chloride hexahydrate (Fluka) and ethanol (Fluka) were used as received.

FT-IR spectra were taken on a Perkin—Elmer FT-IR 1650 spectrometer.

Scanning electron micrographs were taken on a Jeol JSM—840A electronic microscope.

Preparation of polyHIPE monolithic polymer

Procedure 1: 4.500 g styrene, 1.000 g 55% DVB, and 1.000 g Span 80 were put in a three-necked round bottom flask equipped with an overhead stirrer and stirring was set at 300 rpm. A mixture of 50 mg potassium persulfate and 493 mg calcium chloride hexahydrate in 45 mL deionized water was degassed under reduced pressure for 15 min and added dropwise to the solution in the flask in 30 min. The mixture was stirred for another hour and 50 mL of the resulting emulsion was transferred to PET containers and cured for 48 h (1a — at 60°C in an open container; 1b — at 60°C in a tightly closed container; 1c — at room temperature for 24 h and at 60°C for 24 h in an open container).

Procedure 2: 2.688 g styrene, 2.812 g 80% DVB, and 1.000 g Span 80 were put in a three-necked round bottom flask equipped with an overhead stirrer and stirring was set at 300 rpm. A mixture of 50 mg potassium persulfate and 493 mg calcium chloride hexahydrate in 45 mL deionized water was degassed under reduced pressure for 15 min and added dropwise to the solution in the flask in 30 min. The mixture was stirred for another hour and 50 mL of the resulting emulsion was transferred to PET containers and cured for 48 h (2a — at 60°C in an open container; 2b — at 60°C in a tightly closed container; 2c — at room temperature for 24 h and at 60°C for 24 h in an open container).

Procedure 3: 4.500 styrene, 1.000 g 55% DVB, and 0.6800 g Span 80 and 0.320 g of Span 85 were put in a three-necked round bottom flask equipped with an overhead stirrer and stirring was set at 300 rpm. A mixture of 50 mg potassium persulfate and 493 mg calcium chloride hexahydrate in 45 mL deionized water was degassed under reduced pressure for 15 min and added dropwise to the solution in the flask in 30 min. Mixture was stirred for another hour and 50 mL of the resulting emulsion transferred to PET containers and cured for 48 h (3a — at 60°C in an open container; 3b — at 60°C in a tightly closed container; 3c — at room temperature for 24 h and at 60°C for 24 h in an open container).

In order to obtain dry samples without any inclusions, the polymer products were removed from the containers, washed in a Soxhlet apparatus with deionized water for 24 h and with ethanol for 24 h and dried in vacuo at 50°C for 3 h.

Characterization of the products

Samples for scanning electron microscopy (SEM) were prepared by immersing the polymer in liquid nitrogen and cutting thin (*ca.* 0.5 mm) slices which were coated with a thin film of vaporized gold. SEM micrographs of various parts of samples were taken at various magnifications.

For FT-IR spectroscopy, samples were crushed, mixed with KBr and pressed to form tablets to be FT-IR scanned.

Mechanical properties (in qualitative sense) were tested by cutting, crushing and rubbing of samples.

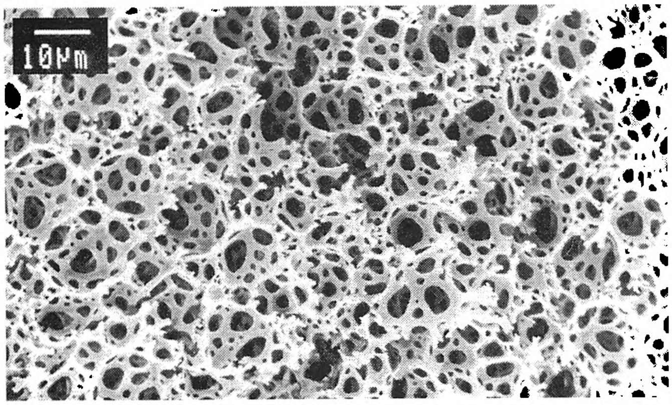
RESULTS AND DISCUSSION

The crosslinking degree (mass percentage of divinylbenzene in the mixture of monomers) was found to influence the flexibility of the polymer backbone in polymer beads and, thus also to affect functionalizations of the resins [15—17]. The effect of crosslinking degree on the morphology of polystyrene polyHIPE materials was studied by using 10% and 50% crosslinked polystyrene. Different polymers were prepared by using the same surfactant, sorbitan monooleate (Span 80), the same procedure, and different amounts of divinylbenzene. SEM revealed a noticeable effect of crosslinking degree on the cell size (Fig. 1, Table 1): the open cellular morphology type is seen to be identical, but cells in sample 2a (50% DVB) are smaller than cells in sample 1a (10% DVB).

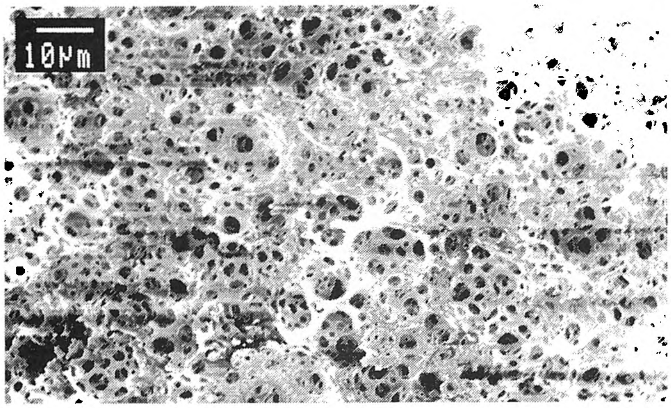
Table 1. Morphological and mechanical characteristics of polystyrene polyHIPE monolithic polymers

Polymer product	HLB value	DVB content %	Approx. average cell size µm	Homogeneity	Mechanical properties
1a	4.3	10	10	good	solid, non chalky
1b	4.3	10	10	good	solid, non chalky
1c	4.3	10	8—10	poor	crumbles easily, leaves chalky residue
2a	4.3	50	8	good	solid, non chalky
2b	4.3	50	8	good	solid, non chalky
2c	4.3	50	8	poor	crumbles easily, leaves chalky residue
3a	3.5	10	1	good	solid, non chalky
3b	3.5	10	2	good	solid, non chalky
3c	3.5	10	1—3	poor	crumbles easily, leaves chalky residue

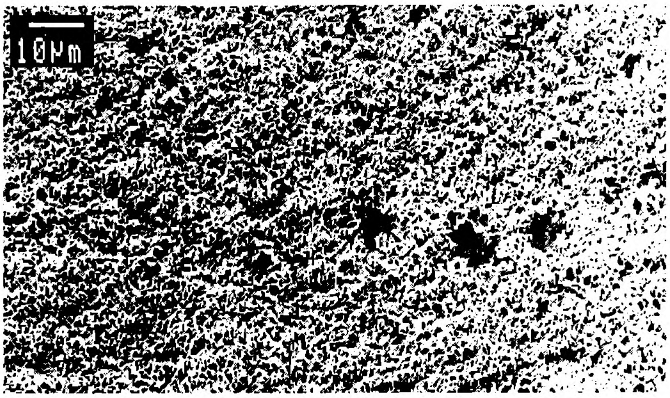
Fig. 1. Scanning electron micrographs of polymers 1a, 2a, 3a, 2b and 2c



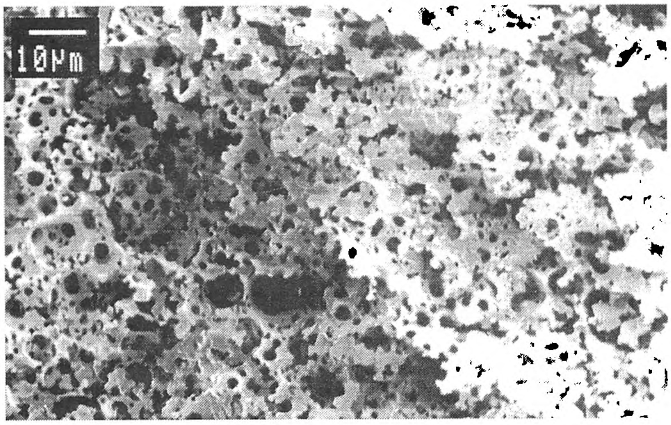
1a (10% DVB, HLB 4.3)



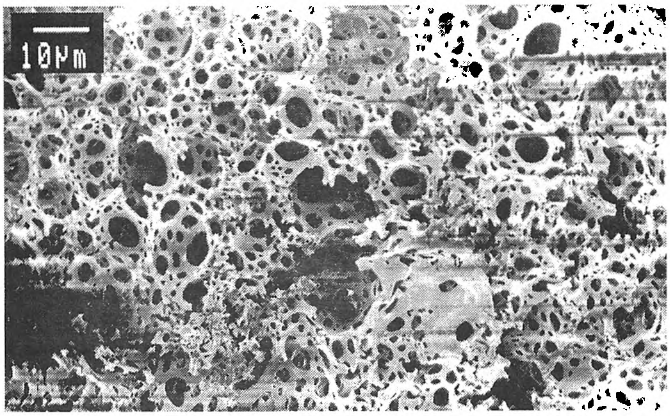
2a (50% DVB, HLB 4.3)



3a (10% DVB, HLB 3.5)



2b (50% DVB, HLB 4.3)



2c (50% DVB, HLB 4.3)

This effect can probably be attributed to the lower interfacial tension between the organic and the water phase in the case of the higher crosslinking degree. Both samples had a very homogeneous cell size distribution and no larger cavities in the materials were formed during the emulsion polymerization. Both products were mechanically strong and crushed only if a substantial force was applied. No chalky residue was left after rubbing of the materials. It was also of interest to see if lowering of the HLB value of the surfactant influenced the structure of the products. The question was how low HLB value can be used to get a still mechanically useful material. As seen in Fig. 1, replacement of sorbitan monooleate (HLB value of 4.3) with a mixture of sorbitan monooleate and sorbitan trioleate (HLB value of 3.5) produced a material with strikingly smaller cells. FT-IR spectroscopy showed no difference in the absorption of crushed and pressed samples 1a and 3a (Fig. 2) as expected. Further lowering of the HLB value of the surfactants produced unstable emulsions upon polymerization. No dramatic change was found to occur in the mechanical properties of sample 3a (HLB value of 3.5) as compared with those of 1a (HLB value of 4.3): both remained solid after cutting.

Water evaporates during the curing procedure; therefore, obstructing the evaporation during polymerization could influence the resulting structure of the polymer material. For this reason, the effect of different curing procedures was tested on the morphology of polystyrene polyHIPE monolithic polymers. All the three emulsions were polymerized in open PET containers (1a, 2a and 3a), in tightly closed PET containers (1b, 2b and 3b), both at

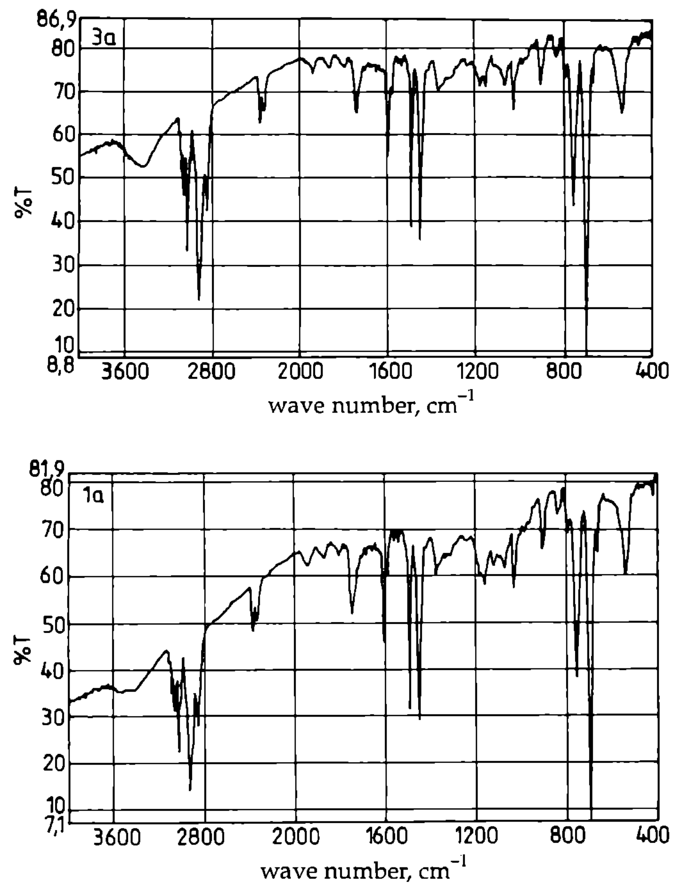


Fig. 2. FT-IR spectra of polymers 1a and 3a

60°C for 48 hours and in open PET containers at room temperature for 24 h and 60°C for 24 h (1c, 2c, 3c). Scanning electron micrographs of the products, polymerized in open containers at room temperature and at 60°C showed no notable difference in the morphology. On the other hand, the scanning electron micrographs of the products polymerized in tightly closed PET containers at 60°C (1b, 2b and 3b) showed (Fig. 1), when compared with the patterns of 1a, 2a and 3a, lower homogeneity and larger cavities formed in the products, presumably on account of coalescing water droplets. These samples were also much weaker mechanically, easy to crush between fingers and they left chalky residues when rubbed. FT-IR spectroscopy again showed no notable differences caused by different curing procedures.

CONCLUSION

As evident from SEM of polystyrene polyHIPE polymers, morphology and also mechanical properties of the resulting materials can be controlled by optimizing the emulsion preparation and polymerization conditions. Tailoring cell size and mechanical properties is of great importance for further functionalization and applications. The HLB value of the surfactant proved to be the most important factor affecting the cell size of polyHIPE materials; the crosslinking degree plays a role, too. The curing procedure, whether performed in open or in tightly closed containers influenced the homogeneity of the material and also the mechanical properties. Samples polymerized in tightly closed containers proved to be more fragile and chalky.

Further studies will be necessary to investigate the influence of morphology on functionalizations of the polymers.

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