# Porogenic Solvents Influence on Morphology of 4-Vinylbenzyl Chloride Based PolyHIPEs

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ABSTRACT: Poly(high internal phase emulsion) materials were prepared from concentrated emulsions containing 4-vinylbenzyl chloride as the reactive monomer and divinylbenzene as the cross-linker. Emulsions consisted of 80 vol. % aqueous phase (water, $CaCl_2$, initiator) and 20 vol. % of organic phase (monomers, surfactant Span 80 and a porogenic solvent). Polymerized samples were purified and investigated for morphology and porosity by scanning electron microscopy, nitrogen adsorption/ desorption and inverse steric exclusion chromatography (ISEC). It was found that no substantial additional *dry* porosity was achieved by the addition of solvents (as determined by nitrogen adsorption) while *wet* microporosity was substantially improved as determined by the ISEC method. The process of drying the polyHIPE materials also influenced the *wet* porosity.

## Introduction

Polymer supports bearing benzyl chloride moieties and cross-linked with divinylbenzene are well-established media for solid phase organic synthesis and have been used in numerous applications since Merrifield's peptide synthesis.[1] Widespread use of chloromethylated polystyrene has led to the commercialization of the resin in form of beads with various degrees of porosity.[2] The chloromethyl group in the polymer offers numerous possibilities for chemical modification, and many derivatives of polymer supported reagents and catalysts, made from chloromethylated polystyrene are known.[3] Recently, monolithic polymer supports are gaining a lot of attention in the view of supports, especially flow through techniques.[4–6] When using a support in a flow-through mode rather than in a batch mode, monolithic supports have certain advantages over particulate type of supports. Usually, monolithic supports pose permanent porosity and do not significantly compress under flow. Furthermore, channeling of the solution is not possible, when monoliths are used in appropriate housings. However, monoliths must exhibit good permeability so that an efficient process can be run without applying high pressures. This normally means larger pore sizes, but this, in return, results in a material with a lower capacity of reactive sites. To overcome this problem, techniques such as grafting can be used.[7,8] Another, already established method to produce porous permeable monoliths, is to apply a high internal phase emulsion (HIPE; in a HIPE the internal, or droplet, phase content is 74% or greater; this value represents the maximum volume part of uniform nondeformable spheres when packed in the most efficient manner), including the monomers in the continuous phase while using the droplet phase for void generation. During the polymerization the forming film of polymer shrinks and the result is a highly porous material with interconnected voids. Styrene/DVB polyHIPEs[9] are well established and studied and have been used in various applications.[10–17] The influence of the surfactant used in the process of stabilizing the HIPEs during the formation has also been studied.[18,19] Both water in oil (W/O) and oil in water (O/W) HIPEs can be used for monolithic polymers preparation. Besides already mentioned styrene/DVB based polyHIPEs, examples of W/O derived polyHIPEs include materials based on 4-vinylbenzyl chloride,[20–28] aryl acrylates,[29–31] and glycidyl methacrylate.[32,33] Much less literature can be found on the use of O/W HIPEs for the production of porous polymers; known products include acrylic acid,[34] polysaccharide,[35,36] and hydroxyethyl methacrylate.[37] Supercritical $CO_2$ has also been used as the internal phase for the production of acrylamide based polyHIPEs.[38–40]

VBC-based polymer supports are already well established as media for solid phase organic synthesis (SPOS) and polyHIPE materials based on VBC are known.[20,23–25] Cameron et al. studied the influence of VBC to DVB ratio on the morphology and surface area of the resulting material.[21] VBC-based polyHIPEs have since been used as precursor media for polymer-assisted solution phase chemistry[22] and for SPOS.[27]

PolyHIPE materials normally do not have a very high surface area (typically around 20 $m^2/g$), while with the addition of more cross-linking agent or the addition of porogenic solvents the surface area can rise significantly; examples of polyHIPE materials with BET surface areas higher than 700 $m^2/g$ are known.[41]

However, more cross-linking means less capacity as VBC is replaced by DVB. Furthermore, higher cross-linking hampers swelling of polymer matrix in contact with liquids which may open access to more active centers than it could be accommodated on the dry polymer surface. Another way to increase porosity of the polymer matrix is the addition of porogenic solvents to the monomer mixture forming the continuous (oil) phase. An increase in surface area resulting from the addition of porogenic solvents has been noticed in the case of DVB[19] and aryl acrylate based polyHIPEs.[30]

For the determination of surface area and pore size distribution so far mostly mercury porosimetry and nitrogen adsorption/ desorption methods have been used, evaluating the texture properties in the dry state only. In the present study of preparation of solvent-modified polyHIPE materials besides conventional tools like scanning electron microscopy or surface measurements by nitrogen adsorption, also inverse steric exclu-

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Table 1

| polymer | $m_{\text{styrene}}$ (g) | $m_{\text{DVB}}$ (g) | $m_{\text{VBC}}$ (g) | $V_{\text{solvent}}$ (mL) | Span80 (g) | aqueous phase (mL) |
|---|---|---|---|---|---|---|
| AD7 | 0.75 | 0.41 | 2.46 | 5.41 (PhCl) | 1.85 | 36 |
| AD8 | 0.76 | 0.40 | 2.45 | 5.43 (T) | 1.86 | 36 |
| AD10 | 0.75 | 0.40 | 2.45 | 5.42 (DCM) | 1.86 | 36 |
| AD11 | 2.05 | 1.10 | 6.75 |  | 2.01 | 39 |

sion chromatography was used, providing information on the morphology in fully expanded swollen state. This could be more relevant for the working state of functional polymers than the dry state related data.

## Experimental Section

**Materials.** Divinylbenzene (DVB; 80 vol % *m*- and *p*-divinylbenzene, the remainder *m*- and *p*-ethylstyrene), styrene and 4-vinylbenzyl chloride (VBC) were purified by passing through a column of basic alumina. Commercially available dichloromethane (DCM, Merck), toluene (T, Aldrich), chlorobenzene (Aldrich), tetrahydrofuraneee (THF, Aldrich), ethanol (Aldrich) were used as received.

**Preparation of Poly(4-vinylbenzyl chloride-*co*-divinylbenzene) PolyHIPE Samples.** PolyVBC polyHIPE materials were prepared as follows: VBC (2.46 g, 14.14 mmol), DVB (0.41 g, 2.46 mmol), styrene (0.75 g, 7.21 mmol), solvent (4.09 mL of dichloromethane or 5.43 mL of toluene or 5.41 mL of chlorobenzene) and Span 80 (1.85 g, 4.76 mmol) were placed in a three-necked 250 mL round-bottomed flask, fitted with an overhead stirrer (glass rod fitted with a D-shaped PTFE paddle), and the mixture was purged with nitrogen gas for 15 min. The aqueous phase was prepared separately by dissolving potassium persulfate (0.072 g, 0.27 mmol) and calcium chloride hexahydrate (0.638 g, 4.95 mmol) in deionized water (36 mL), and the resulting solution was purged with nitrogen for 15 min (preparation data for polymer supports are in Table 1). The organic solution was stirred at ca. 300 rpm, and the aqueous phase was added dropwise under constant stirring in a period of 30 min. After complete addition of the aqueous phase, stirring was continued for 1 h to produce a homogeneous emulsion. The emulsion was poured into a PE bottle and polymerized in an oven at 70 °C for 48 h. The polyHIPE was retrieved by disassembling the bottle and extracted in a Soxhlet apparatus with deionized water for 24 h and ethanol for a further 24 h. The monolith was dried in vacuo at 50 °C for 48 h.

**Morphology Investigations.** Dry-state morphology of the investigated materials was characterized on the base of nitrogen adsorption/desorption data. Measurements were performed using the computerized apparatus DigiSorb 2600 (Micromeritcs), including the evaluation of porosimetric information by the built-in software. SEM microphotographs were obtained using the device JSM 6400 (JEOL, Japan). Swollen-state morphology was characterized by the inverse steric exclusion chromatography (ISEC) in tetrahydrofuranee using n-alkanes and polystyrenes as standard solutes. ISEC apparatus consists of Model 7725i syringe loading sample injector (Rheodyne), stainless steel column 4.1 mm × 250 mm, refractometric detector RIDK 101 (LP Praha, Czech Republic) and computer data acquisition system synchronized with the chromatography setup trough a drop counter probe. The porosity evaluation is based on the modeling of real morphology as a set of discrete pore fractions, each characterized by its pore size. The evaluation of macropores ($d_p > 10$ nm) was based on the cylindrical pore model with pore diameter as the pore size characteristic parameter. For the description of morphology of swollen polymer mass was used the Ogston model,[42] depicting the pores as spaces between randomly oriented cylindrical bodies. In this model, the characteristic parameter is the density of the cylindrical bodies representing the polymer chains expressed in units of length per unit of volume, i.e. $\text{nm}^{-2}$. The treatment of chromatographic data then provides information on volumes of individual model fractions. Details of the experimental procedure and data treatment were reported elsewhere.[43,44]

Table 2. Results of BET Surface Area Measurements of Differently Dried Samples

|  | BET surface area, $\text{m}^2$/g |  |
|---|---|---|
| polymer | dried from THF | dried from ethanol |
| AD7 | 0.9 | 6.5 |
| AD8 | 2.1 | 7.8 |
| AD10 | 6.2 | 7.1 |
| AD11 | 8.1 | 10.2 |

## Results and Discussion

The most common standard method for the characterization of morphology of porous materials is the evaluation of their BET surface area. Before measurements of BET surface area the VBC polyHIPE samples were dried either from a good swelling solvent (THF) or were deswollen by washing with a nonswelling solvent (ethanol) prior to drying. Varying the solvent treatment before polymer drying makes it possible to assess the rigidity of the polymer skeleton. During the drying from a good swelling solvent (e.g., THF) the pores in less rigid polymers may collapse due to the capillary forces generated in the menisci of liquid filling the pores. Porous structure could be better preserved if before drying the polymer is deswollen by washing with a nonswelling solvent (e.g., ethanol), which precipitates the polymer and increases its resistance to the collapse during drying. Difference of dry-state morphologies achieved by these two solvent treatments may be used as an indicator of the structural stability of the examined polymers. Comparison of apparent BET surface areas of the examined polymers determined before and after the postpolymerization treatment and dried from different solvents is shown in Table 2.

The influence of the method of drying on BET surface area indicates that the polymers AD7 and AD8 exhibit significantly lower rigidity than AD10 and AD11. Morphology of the polyHIPE materials on a micrometer-scale level is well shown in SEM microphotographs (Figure 1). It is possible to clearly see the granular morphology of the polymer matrix of the samples AD7, AD8 and AD10 created during the polymerization by phase separation between cross-linked polymer and the solvents added to the mixture of monomers. The pictures also confirm the differences in the rigidity of the polymer skeletons of the samples AD7 and AD8 vs the samples AD10 and AD11 as revealed by the influence of the drying method on their morphology.

Investigation of the swollen state porosity by ISEC brought information on submicrometer features of the polymer morphologies. Pores with diameter more than about 500 nm, prominent in the SEM microphotographs, were too big to be detected by the molecular probes employed by ISEC and for this method they appeared as a part of the interparticle space. Overview of the ISEC results is shown in Table 3.

In all the polyHIPE materials, substantial porosity was detected by ISEC outside the size range which may exist in the swollen polymer gel (“true” pores >10 nm). Surface area of these pores is significantly greater than the BET surface found in dried polymer samples and this indicates that in the polyHIPE materials swelling opens some additional porosity, which is collapsed in the dry state. This evidently apply both for the materials polymerized in the presence of porogenic solvents (AD7, AD8, AD10) and for the AD11 prepared using the oil phase composed of monomers only.

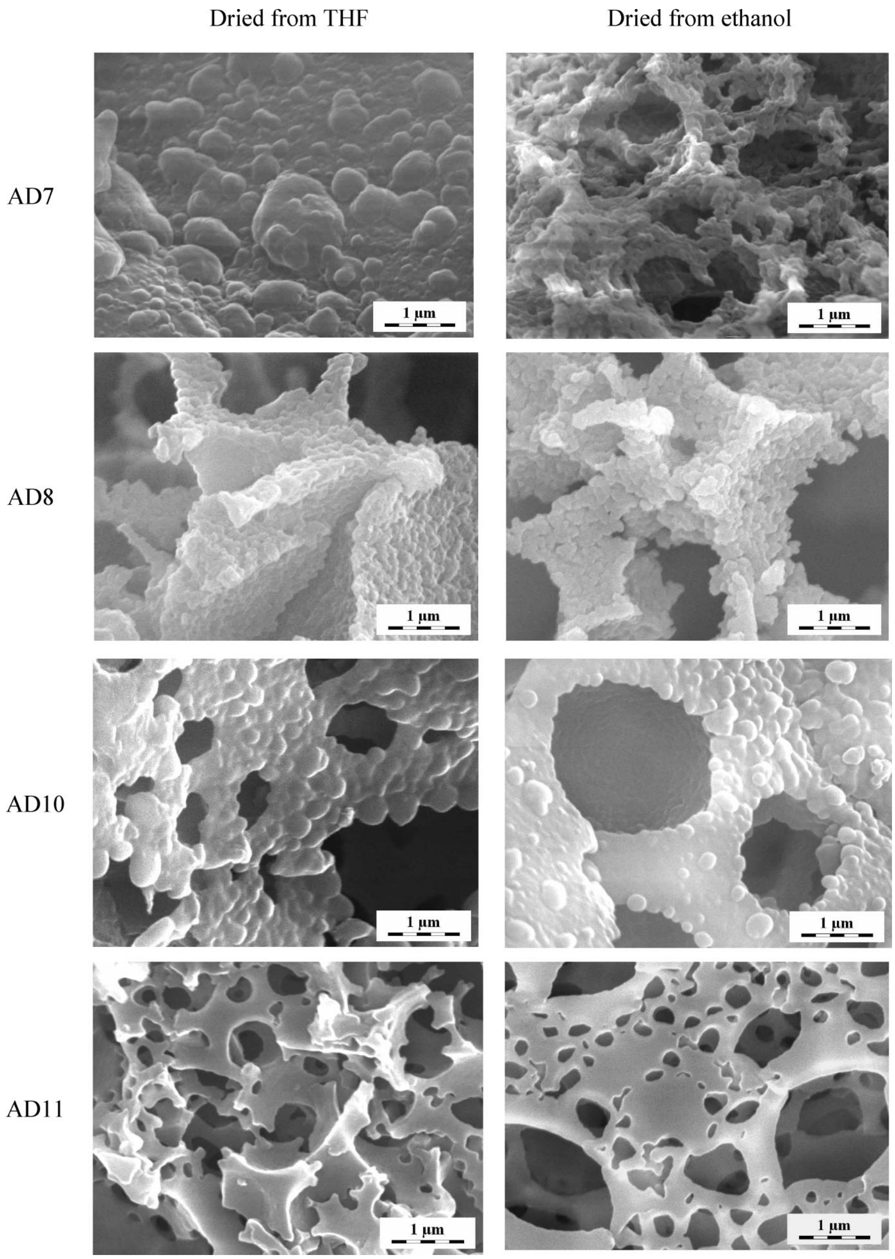

**Figure 1.** SEM micrographs of differently dried samples (magnification 20 000×).

**Table 3. Results of the Characterization of Swollen Morphology of Examined Polymers by ISEC**

| polymer | AD7 | AD8 | AD10 | AD11 |
|---|---|---|---|---|
| “true” pores | | | | |
| median pore diameter, nm | 40 | 20 | 210 | 120 |
| pore volume, cm$^3$/g | 2.04 | 0.27 | 1.33 | 2.68 |
| surface area,[a] m$^2$/g | 223 | 51 | 25 | 87 |

Porosity of Swollen Polymer Gel

| polymer chain density, nm/nm$^3$ | polymer fraction volume, cm$^3$/g | | | |
|---|---|---|---|---|
| | AD7 | AD8 | AD10 | AD11 |
| 0.1 | 0 | 0 | 0 | 0 |
| 0.2 | 0 | 0 | 0 | 0 |
| 0.4 | 0.48 | 0 | 0 | 0 |
| 0.8 | 1.53 | 0 | 0 | 0.04 |
| 1.5 | 0 | 0.43 | 0.71 | 1.69 |

[a] Surface area of cylindrical pore walls computed from the pore volume and median pore diameter.

For the description of the porosity of the swollen gel matrix the Ogston model was used depicting pores as spaces between randomly oriented cylindrical rods representing polymer chains. Instead of the pore diameter this model uses density of the polymer chains expressed as their concentration in units of length per unit of volume. As it is evident from the ISEC results represented in the Table 3, only the polymer matrix of the sample AD7 was able to expand considerably, exhibiting presence of polymer fraction with density 0.4 and 0.8 nm/nm$^3$. Porogenic solvent used in the preparation of this polymer was chlorobenzene, solvent of chemical nature similar to the main component of the monomeric mixture, 4-vinylbenzyl chloride. The similarity facilitated solvation of the growing polymer chains minimizing their entanglement and physical cross-linking. The other solvents, toluene and dichloromethane apparently acted as precipitants and due to higher polymer chain entanglement, their polymer matrix has lower swellability. Functionalized monomers have a tendency to form intermolecular interactions increasing the probability of polymer chain entanglement resulting in physical cross-linking.[45] The effect that only the porogen most similar to the functional monomer is able to reduce the physical cross-linking was already observed during the preparation of copolymers of 4-vinylpyridine and divinylbenzene.[46] Similarly "compact" polymer matrix was formed in the absence of modifying solvents during the preparation of polymer AD11. The strongest tendency to the formation of the least swelling polymer matrix (highest physical cross-linking) seems to be apparent in the case of toluene. A slightly more expandable polymer nework was created in the presence of chlorinated solvent, dichloromethane. The higher expandability of the polymer AD11 prepared in the absence of modifying solvent is probably due to the solvation of growing polymer chains during the polymerization by unreacted monomers reducing their entanglement, but because eventually all the monomers are consumed, this cannot be as efficient as the effect of a "good" porogenic solvent in the case of the polymer AD7.

## Conclusions

This study showed that employing porogenic solvents in the synthesis of polyHIPE materials usefully widens the possibilities for tuning their morphology. BET surface measurements by nitrogen adsorption/desorption alone do not show the complete picture on the porosity characteristics of VBC polyHIPEs with added solvents. The ISEC method applied to this type of material has shown substantial changes of their morphology induced by the contact with solvents. As in the majority of applications polyHIPE materials are used in liquid environment and information on their swollen state morphology provided by ISEC could be very useful for understanding the relations between application properties and morphology or optimization of polyHIPE materials for specific use.

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