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# Microporous and Mesoporous Materials

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## Dry- and swollen-state morphology of novel high surface area polymers

Stefano Sterchele<sup>a</sup>, Paolo Centomo<sup>a</sup>, Marco Zecca<sup>a</sup>, Libuše Hanková<sup>b</sup>, Karel Jeřábek<sup>b,\*</sup><sup>a</sup> Department of Chemical Science, University of Padova, Via Marzolo 1, I35131 Padova, Italy<sup>b</sup> Institute of Chemical Process Fundamentals of the ASCR, v.v.i., 165 02 Prague, Czech Republic

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### ABSTRACT

This study looked into the morphology of novel mesoporous divinylbenzene polymers with extremely high surface areas, both in the dry state using a conventional nitrogen adsorption/desorption method and in the swollen state by inverse steric exclusion chromatography. By comparing the dry- and swollen-state morphologies it was possible to obtain a more comprehensive understanding of the porous structure of the material. The novel poly(divinylbenzene) was found to have a foam-like morphology in which the polymeric matrix formed a continuous phase with thin walls surrounding bubble-like cavities generated by a microsineresis mechanism. Such a morphology is completely different from that of other styrenic polymers with high-surface areas.

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### 1. Introduction

Crosslinked polymers are very versatile materials that can be used for applications like heterogeneous catalysis, solid phase synthesis and separation processes performed under solid–liquid conditions. When the compatibility between the polymer matrix and the reactants is good, the solvation of the polymer chains (swelling) is potentially the most effective way of ensuring the access of the reactants from the fluid phase to functional groups attached to the polymer. However, solvation is not always possible and hence, porous polymeric supports that are stable even in the dry state have been developed to enable their application under conditions of poor or no swelling.

For this purpose, monomers are generally diluted with a suitable porogenic solvent and during such heterogeneous polymerization, syneresis and phase separation effects create a porous morphology of the produced polymer. Mechanisms related to the formation of a porous structure during polymerization are discussed in a review by Okay [1] and special attention is devoted to the preparation of polymer particles – the most frequently used porous polymers – in the recent comprehensive review by Gokmen and Du Perez [2].

The morphology of porous polymers is controlled by the porogen amount as well as the composition and crosslinking of the polymer matrix. Synthesis of porous polymers has been extensively studied especially for the preparation of beaded polymers by suspension polymerization [2,3]. The last twenty

years has also seen the development of porous polymer monoliths, especially for monolithic chromatographic columns [4]. However, Svec and Frechet found that influences of synthesis conditions, such as the composition of the polymerization mixture or reaction temperature on the pore morphology, would differ when preparing particulate polymers by suspension polymerization as opposed to during “bulk” polymerization of monolithic materials [5,6].

It is considered that phase separation and syneresis form the pore morphology mainly through the precipitation of gel-like nuclei that continue to grow with the continuing polymerization and gradually aggregate into larger clusters with less individualized textures [3,4]. Pores are then formed as spaces between these nuclei or clusters. In order to prevent their collapsing during drying, the polymer matrix must have a certain rigidity and this is achieved with an appropriate level of crosslinking. Essentially, the higher the crosslinking, the higher is the level of dispersity of the solid phase that can be attained.

The specific surface area as measured from nitrogen adsorption data using the BET equation is a widely accepted parameter to assess the degree of dispersity. In styrene-co-divinylbenzene polymers, increasing the content of divinylbenzene (cross-linker) renders it possible to achieve apparent specific surface areas as high as 700–800 m<sup>2</sup>/g. Even higher apparent surface areas, up to 2000 m<sup>2</sup>/g, can be obtained upon post-polymerization crosslinking. This can be accomplished, as proposed by Tsyurupa and Davankov [7,8], by chloromethylation of the phenyl rings in styrene-co-divinylbenzene polymers and the subsequent transformation of the chloromethyl groups into methylene crosslinking bridges. An alternative way is to exploit the residual vinyl groups existing in polymers with high divinylbenzene contents. This is done through

\* Corresponding author. Tel.: +420 220390332.

E-mail address: [kjer@icpf.cas.cz](mailto:kjer@icpf.cas.cz) (K. Jeřábek).

Friedel-Craft alkylation of the phenyl rings [9,10], and can lead to the formation of further cross-links.

However, in practically all these polymers, it is the presence of very narrow pores with characteristic dimensions smaller than 2 nm (“micropores” according to the IUPAC classification [11]) that is responsible for the high apparent surface area. Microporous polymer materials are popular as adsorbents [e.g. [12]], but due to steric hindrances they have a relatively limited utility as anchor points for functionalities.

Recently, some Chinese colleagues described a novel approach to synthesize porous polymers based on a “solvothermal” synthetic method using a mixture of tetrahydrofuran and water as the porogenic solvent in the homo-polymerization of divinylbenzene [13]. Their polymers (poly-divinylbenzene, poly(DVB)) were prepared as monoliths at a relatively high polymerization temperature (100 °C) in an autoclave. These rather unusual polymerization conditions led to materials with very high specific surface areas and relatively large pore sizes.

The morphological properties of these novel polymers have so far only been evaluated from nitrogen adsorption/desorption data obtained on dried samples. Although this approach is quite common, it cannot provide fully relevant information when it comes to the influence of the preparation conditions on the formation process of a porous polymer morphology since the original polymer morphology created when in contact with the liquid porogen becomes inevitably deformed by the drying. This is probably why the reported effects of varying the synthesis conditions on the morphology are limited to simply listing achieved values of the standard parameters, such as the BET surface area or pore volume, without attempting to propose a hypothesis about the mechanism of the morphology formation.

There is a much better chance of understanding the mechanisms of the pore morphology development during the polymerization process by gathering information of the uncollapsed, swollen morphology of the polymer matrix which has not been deformed by drying. Such data can be obtained by inverse steric exclusion chromatography (ISEC) [14]. The present study was thus devoted to the evaluation of the morphology of novel “hydrothermally” prepared poly(DVB) materials, both in the dry and swollen states, using respectively conventional nitrogen adsorption/desorption porosimetry and ISEC. On the basis of this more complex information, conclusions were drawn regarding specific features of the morphology of the novel polymers and the characteristics of the pore formation process.

## 2. Experimental

Porous polymer monoliths were prepared under conditions that were essentially identical to those described by Feng-Shou and co-workers [13]. In a typical experiment, a clear, homogeneous mixture of 6.0 g (6.6 cm<sup>3</sup>) of divinylbenzene (tech. grade 80%), 60 cm<sup>3</sup> of tetrahydrofurane (THF), 6 cm<sup>3</sup> of water and 165 mg of 2,2′ azobis(2-methylpropionitrile) (AIBN) as the initiator was maintained in a closed autoclave under autogenic pressure

(2.1 bar) at 100 °C for 48 hours. h. After cooling to room temperature, a white, opaque cylinder of relatively soft polymer was removed and left to dry at room temperature for 10 days. The polymer

(referred to as A) was then pestled in a mortar and dried at 100 °C overnight. A second sample (referred to as B) was prepared with a double amount of DVB and AIBN as the initiator, i.e., 12.0 g (13.2 cm<sup>3</sup>) and 170 mg, respectively, and otherwise under identical conditions as those applied for A.

The morphology of the dried polymers was assessed with nitrogen adsorption/desorption measurements at the temperature of liquid nitrogen using a computerized ASAP 2010 apparatus and the associated software (Micromeritics, USA). The characterization of the swollen-state morphology of both A and B was performed by ISEC with THF as the mobile phase using a standard HPLC equipment connected to a computer data acquisition system programmed for precise evaluation of the elution volumes. The polymers were ground and sieved in order to separate the particles smaller than 0.2 mm. They were further purified from fines by decantation and packed in a chromatographic column of known volume.

Solutes with known effective molecular sizes (from 320 nm for polystyrene, MW = 10,000 KDa, down to 0.55 nm for n-pentane) were then eluted through the filled column where the polymer acted as the stationary phase. Their elution volumes were utilized as the basis for a mathematical treatment that provided a description of the swollen polymer morphology. The latter was modeled as a set of discrete pore fractions, each characterized by a single size of pores of simple geometrical shape. Pores with an effective size >10 nm, undoubtedly too big to be part of the swollen polymer gel (the so-called “true” pores) [14], were characterized using the cylindrical pore model.

The morphology of smaller pores, possibly spaces within the swollen polymer gel, could be conveniently modeled using Ogston’s model [15], which describes the pores as spaces amongst randomly oriented cylindrical rods representing the polymer chains. In this case, the concentration of polymer chains (in units of length per unit of volume of the gel) replaced the pore diameter as the parameter characterizing the pore size. By using ISEC on a swollen polymer, it was expected that polymer chain concentrations in the range of about 0.1–1.5 nm/nm<sup>3</sup> could be detected. Details on the experimental procedure and data treatment can be found elsewhere [16].

## 3. Results and discussion

The morphological properties in the dry state of polymers A and B, as determined from nitrogen adsorption/desorption data, are shown in Table 1. Both samples of poly(DVB) prepared under “solvothermal” conditions exhibited exceptionally high surface areas as assessed both by BET measurements and *t*-plot analysis according to Harkins and Jura [17]. However, the results from the latter, in which the adsorbed amount of nitrogen is represented as a function of the adsorbed layer thickness, also showed a negligible amount of microporosity (Fig. 1).

**Table 1**

Dry-state porosity of the polymers prepared under “solvothermal” conditions as evaluated from nitrogen adsorption/desorption measurements.

Polymer	Solvent-monomer volume ratio	BET surface area, m <sup>2</sup> /g	External surface area from <i>t</i> -plot slope <sup>a</sup> , m <sup>2</sup> /g	Micropore volume <sup>b</sup> , cm <sup>3</sup> /g	Cumulative surface area in pores >4 nm <sup>c</sup> , m <sup>2</sup> /g	Total pore volume, cm <sup>3</sup> /g
A	10:1	1096	1091	0.008	436	2.07
B	5:1	899	922	0.000	392	1.89

<sup>a</sup> See Fig. 1.

<sup>b</sup> From *t*-plot., see text.

<sup>c</sup> from pore-size distribution data.

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