

# New Porous Materials from Natural Polymers Processed by Supercritical CO<sub>2</sub>

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## Abstract

Supercritical carbon dioxide (CO<sub>2</sub>) has been widely used for processing polymeric materials in a variety of applications. Polymer foaming is the production of porous materials through the interaction (e.g. sorption, plasticization, desorption) of CO<sub>2</sub> with a polymer matrix. Natural polymers such as cellulose, chitin, gelatin, and chitosan are crystalline and do not absorb CO<sub>2</sub> in the solid state. Also, they do not exhibit any temperature transitions (glass transition or melting point) before their decomposition temperature and, thus, the polymer foaming technique cannot be applied to them. We report here the CO<sub>2</sub> foaming of such polymers through an intermediate hydrogel state (hydrogel foaming). In an alternative route, the water in these gels can be replaced by an alcohol. The alcohol-gels can also be processed by CO<sub>2</sub> (critical point drying) resulting in interesting nanoporous materials (aerogels). The above mentioned two techniques were applied to various polymers. The influence of different processing parameters, such as pore size or density, on the properties of the obtained materials is investigated. Also, a mechanism for the hydrogel foaming is proposed and compared with the plain polymer foaming mechanism.

## Introduction

Porous polymeric materials are used in a broad spectrum of applications including separation processes, packaging, thermal insulation, as absorptive materials, as tissue engineering scaffolds, etc. [1,2]. Particular interest is observed in the production of novel porous materials by processing polymers with supercritical carbon dioxide (CO<sub>2</sub>) through a variety of approaches, like foaming, phase inversion, formation of emulsions, critical point drying, etc. [1- 7].

Phenomena associated with polymer-CO<sub>2</sub> interactions have been studied, both, experimentally and theoretically [8-11]. A key step and a crucial associated phenomenon during the production of the porous structure via CO<sub>2</sub> sorption by a polymer matrix, is the plasticization of the polymer, which is induced by this sorption. If supersaturation is caused in a polymer-CO<sub>2</sub> system (either by pressure decrease or temperature increase), nucleation and pore growth occurs when the polymer remains in the rubbery state. The produced porous structure stabilizes when the polymer enters the glassy state. This polymer foaming method can be applied to amorphous or semi-crystalline polymers with low to moderate degrees of crystallinity (that exhibit glass to rubber transition). The presence of a highly crystalline structure prohibits the CO<sub>2</sub> sorption by the polymer. However, if the CO<sub>2</sub> processing occurs above the melting point of the polymer, sorption of CO<sub>2</sub> and production of porous structure is possible [12]: Stabilization of the produced structure, in this case, is achieved by cooling and crystallisation of the polymer.

In this study, a novel route is described for processing polymers that do not absorb CO<sub>2</sub> in the solid state and do not exhibit any thermal transition. The process involves the foaming of polymeric hydrogels and has been applied to chitin, cellulose, cellulose- hydroxyapatite composite, gelatine and gelatine-chitosan blend. A mechanism for this process is proposed. Also, the well known technique of

critical point drying has been successfully applied to cellulose and chitin for the production of aerogels.

## Experimental

The solvent for chitin was dimethylacetamide (DMA) + LiCl mixture, while the solvent for cellulose was the ionic liquid ally-methyl-imidazolium chloride (AmimCl). After the gelation process, extensive washings with water were applied (regeneration process). This process results in highly swollen dispersions of chitin and cellulose in water with typical characteristics of hydrogels.

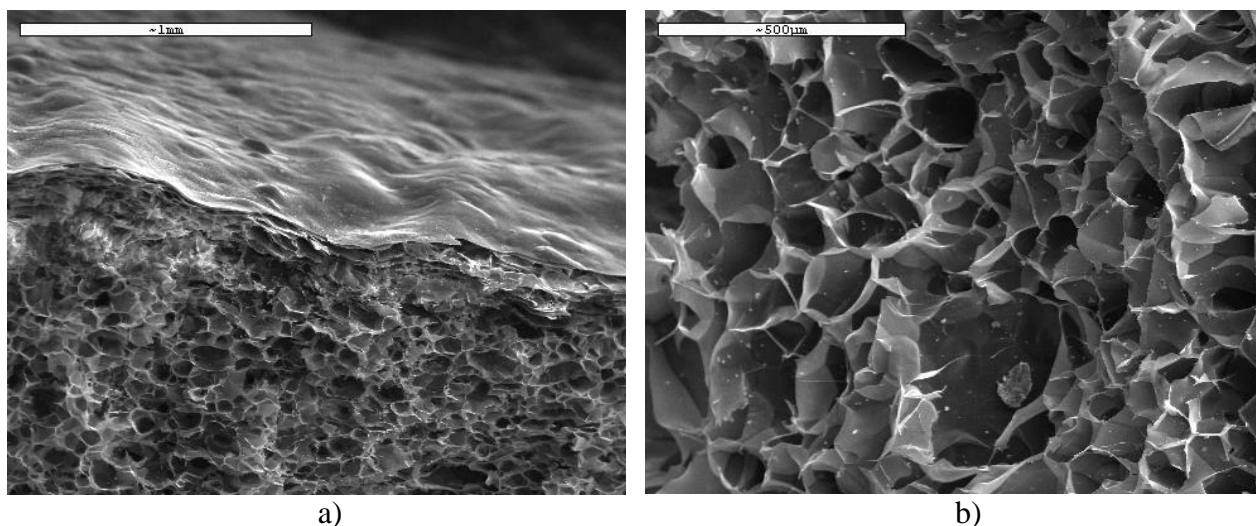
Gelatine was dissolved in water and gelatine-chitosan blend was dissolved in 2% (v/v) acetic acid aqueous solution by heating at 50 °C. The solutions, when cooled to room temperature, solidify and were crosslinked with glutaraldehyde vapour for 1 day. After washing with glycine aqueous solution and distilled water, crosslinked hydrogels were obtained.

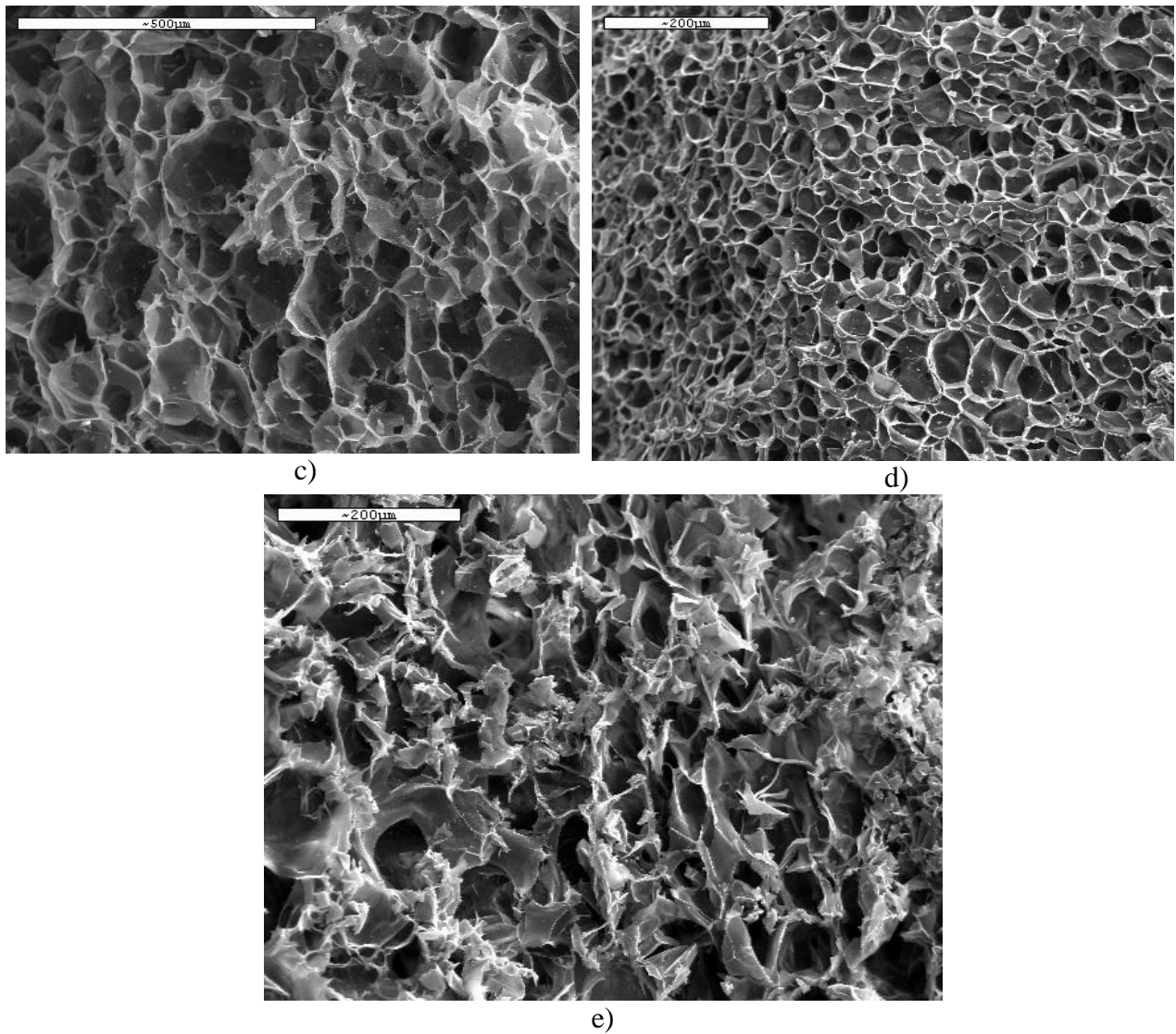
The apparatus used for the high pressure experiments is described elsewhere in detail [3,4]. Briefly, it consists of a high pressure cell of internal volume of 40 cm<sup>3</sup>, an ISCO syringe pump for pumping CO<sub>2</sub>, and pressure and temperature controllers for keeping pressure (accuracy ±0.1bar) and temperature (accuracy ±0.1 °C) constants at the desired values. A freeze drying setup was used and it consisted of a Haake constant temperature bath (model G) with a D1 circulator, a Savant refrigerated condensation trap (model RT-100A), and a rotary vane vacuum pump (Vacuubrand, type RZ5). The morphology of porous samples was examined using scanning electron microscopy (Jeol, model JSM-840A). Also a Seifert, model XRD3003TT X-ray diffractometer (Fe,  $\lambda=1.9373 \text{ \AA}$ ) and a Rigaku Miniflex X-ray diffractometer (Cu,  $\lambda=1.5405 \text{ \AA}$ ) were used.

For the critical point drying, methanogels were used. These gels were prepared by immersing repeatedly the hydrogels in methanol. Detailed description of experimental condition can be found in recent publications [7, 13-15].

## Results and discussion

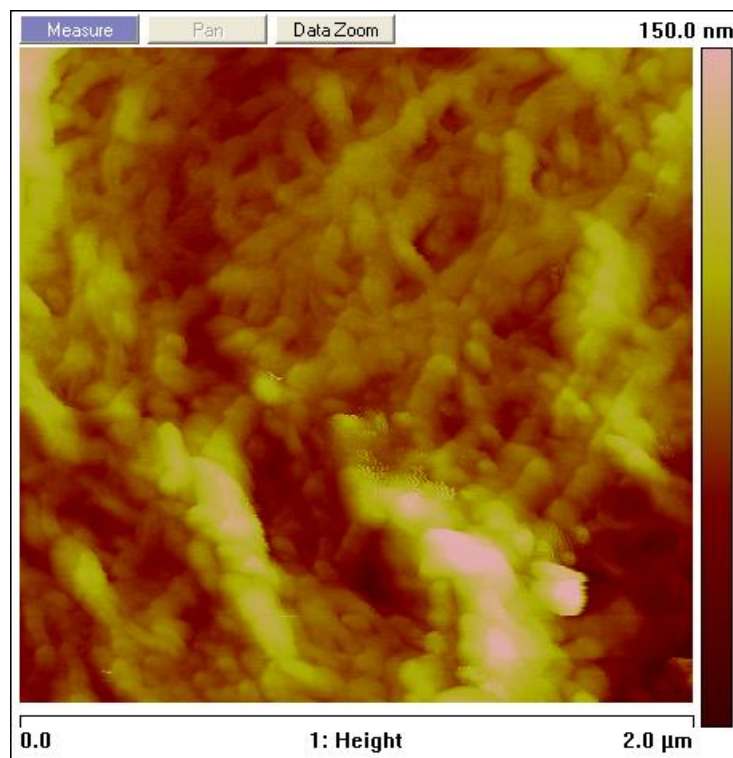
The morphology of different porous polymer samples prepared by the hydrogel foaming method is presented in figure 1. As can be seen, different pore size distributions and morphologies can be obtained for the different samples.





**Figure 1.** SEM pictures of different samples prepared by hydrogel foaming: a) chitin, b) cellulose, c) cellulose-hydroxyapatite composite, d) gelatine, e) gelatine-chitosan blend.

In the case of methanogels, the foaming process is not equally effective. However, the critical-point-drying method resulted in high surface area aerogels ( $300 \text{ m}^2/\text{g}$ ) of chitin and cellulose. An AFM image of the cellulose aerogel is presented in figure 2, while the nitrogen adsorption isotherm at 77K by a chitin aerogel is presented in figure 3 along with the corresponding pore size distribution.

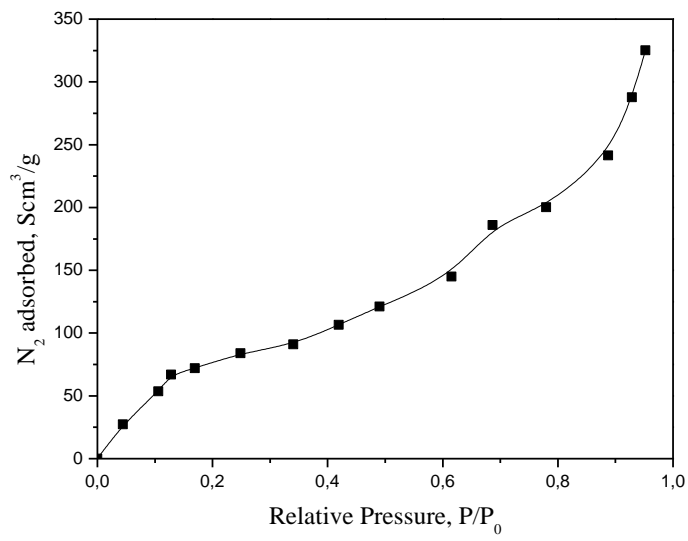


**Figure 2.** AFM image of cellulose aerogel.

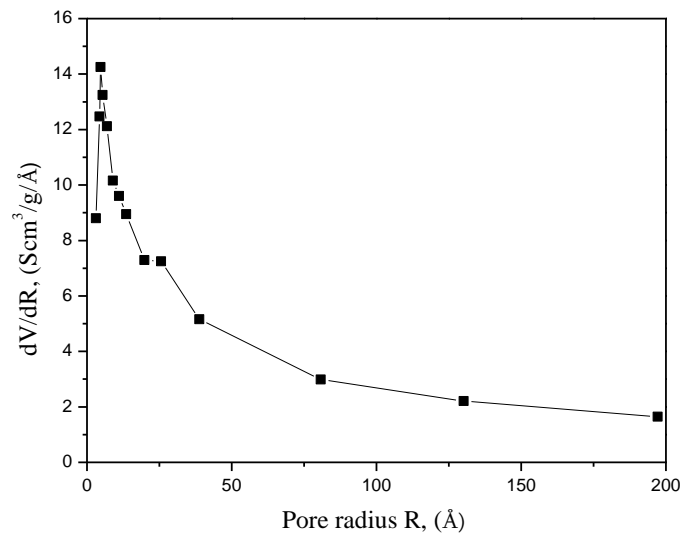
The foaming of hydrogel is a rather unexpectedly successful process. The CO<sub>2</sub> sorption is even more unexpected, since these polymers do not absorb in the solid state while the mutual solubilities of carbon dioxide and water are very low. However, the amorphous nature of hydrogels might be the explanation for this. As can be seen from the XRD patterns of different polymeric hydrogels (figure 4), they are in an amorphous state and thus, besides dissolution in water, CO<sub>2</sub> sorption by the amorphous polymer is possible.

In addition, the amorphous soft matter (hydrogel) can be resembled to an amorphous polymer in the rubbery state (e.g. short relaxation time in contrast to a polymer in the glassy state). Thus, upon pressure decrease, the stresses applied by the CO<sub>2</sub> formed nuclei (micro-phases) are capable of rearranging the flexible polymer molecules in the rubbery or in the hydrogel state but not in the glassy state.

Since the hydrogel possess a high interfacial area, the nucleation of CO<sub>2</sub> is more likely to occur heterogeneously at the water-polymer interface, in contrast to the polymer foaming where the nucleation is homogeneous. Finally, in polymer foaming, the produced structure is stabilised upon vitrification. In hydrogel foaming, the cooling during expansion (due to the Joule-Thomson effect) can cause the freezing of the hydrogel and thus can stabilize the produced structure. However, this is a temporary stabilization which becomes permanent by freeze drying (removal of water). The above discussion about the mechanism of hydrogel and polymer foaming is graphically presented in figure 5.

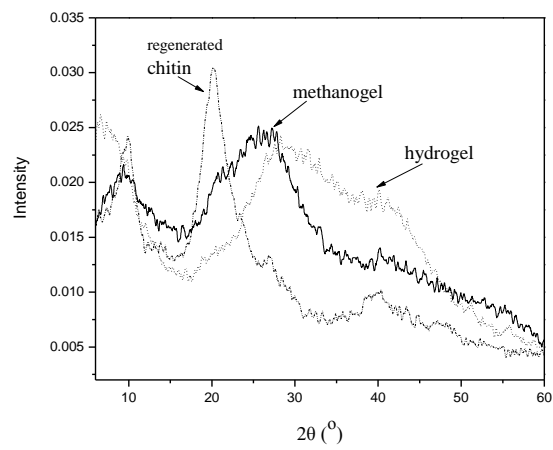


a)

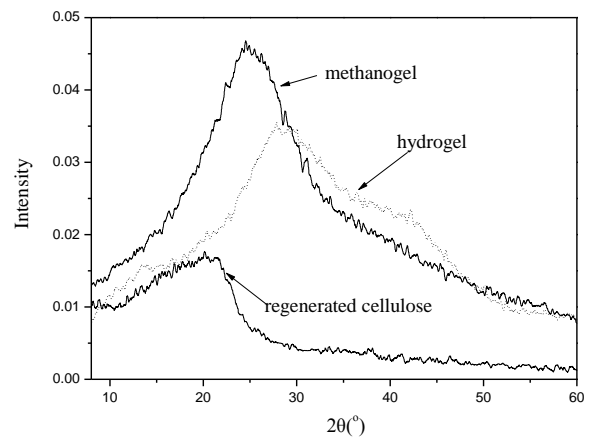


b)

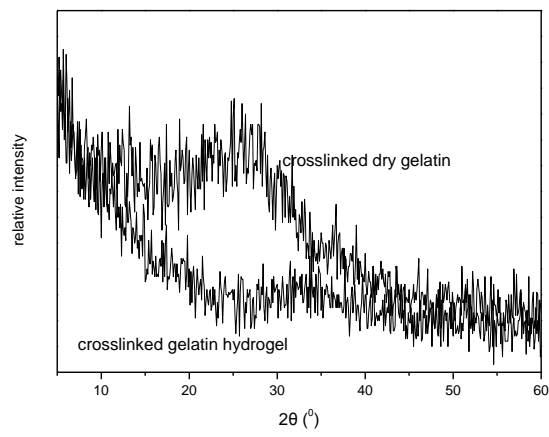
**Figure 3.** a) Nitrogen adsorption isotherm at 77K and b) pore size distribution for a chitin aerogel.



a)

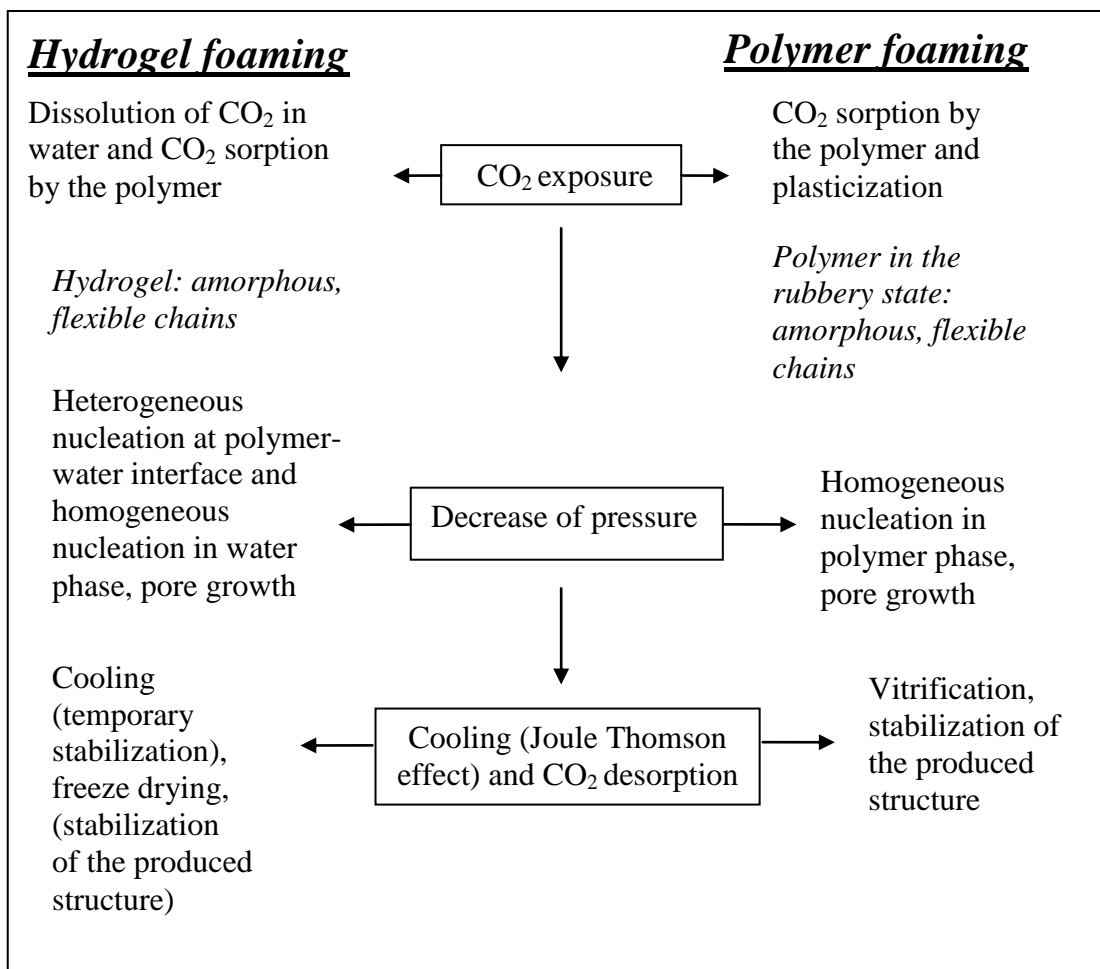


b)



c)

**Figure 4.** XRD patterns of a) chitin, b) cellulose and c) gelatine in the solid state and in the gel state.



**Figure 5.** Proposed mechanism for the hydrogel foaming and comparison with polymer foaming.

## Conclusions

Hydrophilic crystalline polymers, that do not exhibit any phase transitions below thermal decomposition temperature and/or do not absorb CO<sub>2</sub> in their solid state, can be foamed with CO<sub>2</sub> by bringing them to an intermediate hydrogel state and following a process analogous to classical polymer foaming. After foaming of the hydrogel, freeze drying must be applied to remove water. A key factor related to the physicochemical mechanism of the hydrogel foaming is the amorphous character of the polymer in hydrogels. CO<sub>2</sub> is retained in the hydrogel through dissolution in water and through sorption by the amorphous polymer. Depending on the constitution of the hydrogel, it may exhibit mechanical strength sufficient for the foaming process. The structure is stabilized temporarily by the freezing caused by the rapid depressurization, while the final structure is stabilized by the removal of water in the mild freeze drying step.

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