Communication

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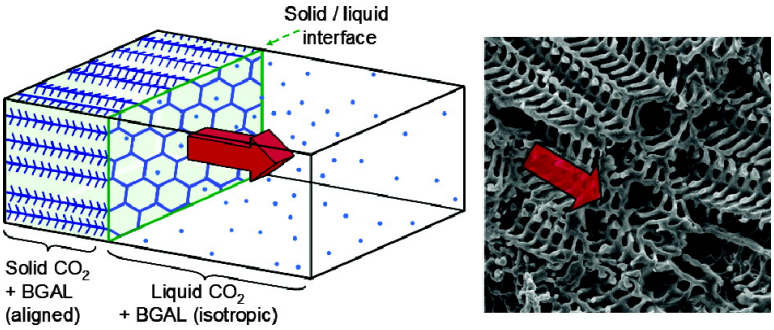
J. Am. Chem. Soc., **2005**, 127 (39), 13482-13483• DOI: 10.1021/ja054353f • Publication Date (Web): 13 September 2005



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Published on Web 09/13/2005

Aligned Porous Materials by Directional Freezing of Solutions in Liquid CO_2

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Received July 1, 2005; E-mail: aicooper@liv.ac.uk

Carbon dioxide has received much attention recently as an inexpensive, nontoxic, and nonflammable solvent replacement for materials synthesis and processing.[1] CO_2 is a particularly versatile medium for the preparation of porous materials, and a number of new approaches have been developed in the past few years.[2] Current routes include foaming,[3] CO_2-induced phase separation,[4] reactive-[5] and nonreactive[6] gelation of CO_2 solutions, nanoscale casting using supercritical CO_2,[7] and CO_2-in-water (C/W) emulsion templating.[8] Each of these methods uses a different mechanism to generate the porosity in the material. Foaming[3] involves expansion of a molten or highly plasticized polymer when the compressed CO_2 is depressurized. Gelation approaches[5,6] employ CO_2 as a "porogenic solvent" in the same way that organic porogens are used in suspension polymerization,[9] although this may also be combined in some cases with an expansive foaming step upon depressurization.[6] Nanoscale casting using supercritical CO_2 [7] employs preformed organic porous materials as scaffolds for modification with inorganic precursors. Only one method—C/W emulsion templating[8]—exploits the CO_2 phase (in the form of emulsion droplets) as a shape-specific "template" to define the porosity in the resulting material.

We present here an entirely new approach to preparing porous materials by templating the structure of *solid* CO_2. This method differs fundamentally from the other CO_2-based techniques[3−8] and offers the unique advantage of generating materials with aligned pore structures. Materials with aligned microstructures and nanostructures are of interest in a wide range of applications such as organic electronics,[10] microfluidics,[11] molecular filtration,[12] nanowires,[13] and tissue engineering.[14]

A general approach to producing materials with aligned CO_2-templated pores is illustrated schematically in Figure 1.

A sugar acetate, 1,2,3,4,6-pentaacetyl β-D-galactose (BGAL), was used in our experiments because it is highly soluble in CO_2 and is a solid at ambient temperatures.[15] To form a porous structure, BGAL (12 wt %) was dissolved in liquid CO_2 at 75 bar/21 °C within a stainless steel column (5.3 mm diameter). A sonicating bath was used to ensure complete dissolution of the BGAL. The column was lowered vertically into liquid nitrogen at a rate of 3.2 mm/min until the column was completely submerged, at which point the sample was no longer under excess pressure since all of the CO_2 had been frozen into the solid state. The column was then transferred into a beaker containing dry ice and a venting valve opened to allow the gaseous CO_2 to escape from the column as it sublimed from the sample during slow warming. The BGAL sample (which was supplied as a powder) could then be recovered directly from the tube as a continuous monolith. Figure 2 shows an electron micrograph of the porous structure observed in the processed BGAL material.

Our new CO_2-based process can be compared with aqueous directional freezing routes for the production of aligned silica fibers[16] and microhoneycombs[17] where the porous structure is directed by the advancing ice crystallites.[16,17] By analogy, the aligned pore structure shown in Figure 2 can be explained by the phase separation that occurs during the directional freezing process. We propose that freeze concentration of BGAL causes constitutional supercooling at the interface, leading to Mullins−Sekerka instability and solid CO_2 cell growth with a well-defined periodic separation whereby the BGAL becomes concentrated between the cells (Figure 1), as described previously for the unidirectional freezing of aqueous polymer solutions.[18] The aligned tubular pores shown in Figure 2 are templated from the structure of the solidified CO_2 which is then removed from the material by direct sublimation. We propose that the detailed "fish bone" morphology (Figure 2) in the material results from the side branches that form when the BGAL freeze−concentrates around the primary solid CO_2 cells, causing secondary instability formation perpendicular to the freezing direction. As such, the aligned tubular pores in Figure 2 (diameter ≈ 20 μm) result from the primary periodicity of the aligned CO_2 crystallites while the smaller pores (diameter ≈ 5−10 μm) arise from secondary

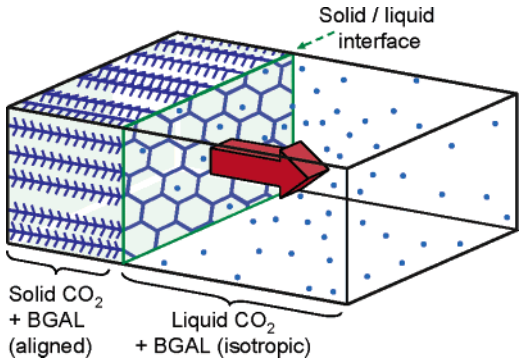

Figure 1. Preparation of an aligned porous sugar acetate material by unidirectional freezing of a solution of 1,2,3,4,6-pentaacetyl β-D-galactose (BGAL) in liquid CO_2. The red arrow represents the freezing direction. The solid CO_2 is removed subsequently by direct sublimation to yield a porous, solvent-free structure with no additional purification steps.

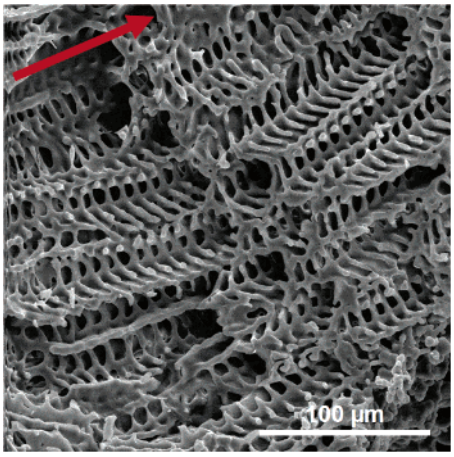

Figure 2. Aligned porous BGAL produced by directional freezing of a liquid CO_2 solution. The red arrow represents the approximate direction of freezing.

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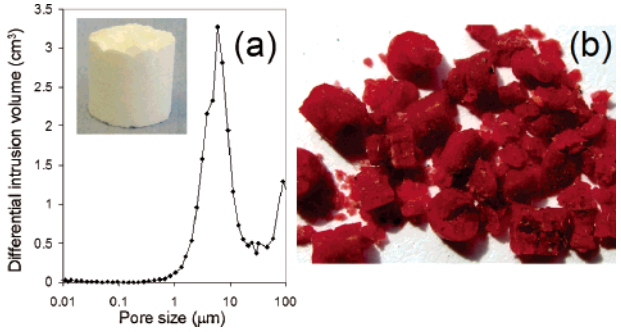

Figure 3. (a) Pore size distribution (mercury intrusion porosimetry) for aligned porous BGAL material produced by directional freezing of a solution in liquid CO_2. (Inset) Photograph of a monolithic material produced by this route (height = 4.4 mm, diameter = 4.5 mm). (b) Porous BGLU composite material produced by directional freezing of a solution of BGLU and Oil Red in liquid CO_2. The Oil Red loading was 3.3 wt % based on the total mass of composite.

instability wavelengths and the formation of side branches.[18] The macropores of the material were characterized using mercury porosimetry (Figure 3a).

A clear peak in the pore size distribution was observed at 8 μm corresponding to the interconnected "side-branch" pores. The total macropore volume for the material was determined to be 2.0 cm^3/g. The surface area of the material was found to be relatively low (<5 m^2/g) due to the exclusively macroporous nature of the sample. Macropores in this size range would be suitable for applications such as tissue engineering.

Microscopy at a lower magnification[19] revealed that the pores in the BGAL material were aligned over a more extended distance—at least on the order of a few millimeters—by using the simple preparative procedure outlined above. At the molecular level, the structure of the BGAL was not found to be altered by processing—that is X-ray diffraction and thermal analysis suggested that the percentage crystallinity was unchanged.[19] This is in accordance with studies involving the crystallization of BGAL from supercritical CO_2,[20] even though the process by which the aligned material was formed (freezing followed by sublimation) is fundamentally different from the slow expansion "SESS" process used in these previous crystallization studies.[20]

Other sugar acetates, α-1,2,3,4,6-pentaacetyl-D-glucose (AGLU) and β-1,2,3,4,6-pentaacetyl-D-glucose (BGLU), could also processed by the same method to give similar porous structures. It was also found that it was possible to form composite materials by this route—for example, porous BGLU materials were produced loaded with a CO_2-soluble dye, Oil Red,[21] distributed homogeneously throughout the composite (Figure 3b).

In addition to producing materials with aligned porosity, there are a number of additional advantages associated with this new technique. The method avoids the use of any organic solvents, thus eliminating toxic residues in the resulting material. The CO_2 can be removed by simple sublimation, unlike aqueous-based processes where the water must be removed by freeze-drying.[16,17] Moreover, the method can be applied to relatively nonpolar, water-insoluble materials (such as BGAL). These aligned porous structures may find numerous applications, for example, as biomaterials. Aligned porous materials with micrometer-sized pores are of importance in tissue engineering where modification with biological cells is required. We are particularly interested in the use of such porous materials as scaffolds for aligned nerve cell growth. This latter application will be greatly facilitated by the recent development of biodegradable CO_2-soluble hydrocarbon polymers as potential scaffold materials.[22]

Acknowledgment. We thank EPSRC for financial support (EP/C511794/1) and the Royal Society for a Royal Society University Research Fellowship (to A.I.C). We thank Dr. D. Bradshaw and Dr. N. Winterton for assistance with X-ray diffraction and thermal analysis, respectively.

Supporting Information Available: SEM images, X-ray data, and thermal analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA054353F