

Recent Developments in Materials Synthesis and Processing Using Supercritical CO₂**

By *Andrew I. Cooper**

The chemical and physical properties of carbon dioxide in the liquid or supercritical state differ quite strongly from those of conventional liquid organic solvents. These differences may be exploited in a wide variety of materials applications.

Here we describe recent research involving the use of dense carbon dioxide in the areas of porous organic materials, coatings and lithography, metal nanoparticle synthesis, and biomaterials processing.



1. Introduction

Supercritical carbon dioxide (scCO₂) has attracted much interest recently as an alternative solvent for materials synthesis and processing.^[1] Researchers have promoted CO₂ as a sustainable and “green” solvent because it is non-toxic, non-flammable, and naturally abundant. In fact, the economics of using dense CO₂ on an industrial scale are usually complex and must be assessed on a case-by-case basis.^[2] Issues such as capital costs associated with high-pressure equipment and the energy requirements for compressing CO₂ into the dense state may prove prohibitive in many instances. Nevertheless, it is widely accepted that the advantages associated with this solvent are likely to lead to a number of new CO₂-based processes. The level of interest in supercritical fluid (SCF) technology can be gauged from the growing number of participating academic and industrial research groups world-wide. We highlight here four research areas of special interest in the field of advanced materials. We describe how the unusual physical properties of CO₂ (i.e., low toxicity, easy separations, variable density, low viscosity, low surface tension, and polymer plasticization) are exploited in each case.

2. Results and Discussion

2.1. Porous Organic Materials

Carbon dioxide has been studied extensively as an alternative solvent for polymer synthesis.^[3] Several groups have investigated the production of porous polymeric materials

using scCO₂ as a solvent and/or foaming agent. Beckman and Hamilton have developed a one-step process that uses scCO₂ to produce low-density microcellular fluorinated materials.^[4] Fluorinated compounds (Fig. 1a) were designed and synthesized, which dissolve in scCO₂ and then associate to form gels. Upon removal of the CO₂ phase, the gels pro-

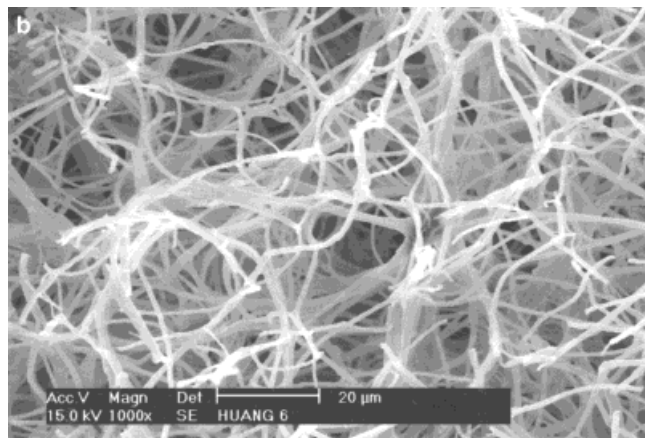
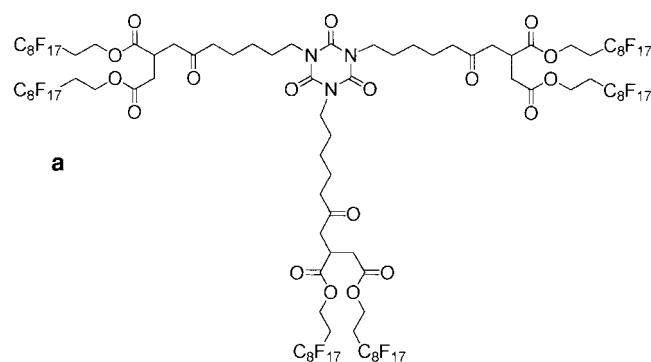


Fig. 1. a) A CO₂-soluble trifunctional urea. b) Scanning electron microscopy (SEM) image of a free-standing foam produced from this urea by gelation of a 5 wt.-% solution in scCO₂ (scale bar = 20 μm). Bulk density of the foam is approximately 0.09 g/cm³.

[*] Dr. A. I. Cooper
Donnan and Robert Robinson Laboratories
Department of Chemistry
University of Liverpool
Crown Street, Liverpool, L69 3BX (UK)
E-mail: aicooper@liv.ac.uk

[**] Dr. Cooper is grateful to the Royal Society for provision of a Royal Society University Research Fellowship.

duced free-standing foams with cell diameters smaller than 1 μm and density reductions of 97% relative to the parent compound (Fig. 1b). We developed a technique involving the gelation of CO₂ to form well-defined macroporous materials based on acrylate monomers.^[5] The figure in the abstract shows a sample of a monolithic, cross-linked polyacrylate adjacent to the high-pressure reactor in which it was synthesized. Materials of this type can be considered as organic analogues of silicate aerogels^[6] and have intriguing potential applications (e.g., catalyst scaffolds and separation supports, low-dielectric materials, and insulation). Unlike current routes to organic aerogels, neither of these methods^[5,6] involves multiple process steps or large volumes of organic solvents. Furthermore, a scCO₂-based route may allow the in-situ preparation of porous materials in containment vessels where solvent separation is problematic (e.g., direct formation of porous packings within narrow-bore silica capillaries).

Supercritical fluids are highly compressible and the density can be “tuned” over a considerable range by varying the pressure. We have exploited this in order to achieve structural control in porous polymers. This concept was first explored in the preparation of macroporous monolithic materials, as mentioned above.^[5] More recently, we have extended the same idea to the synthesis of porous polymer beads by suspension polymerization. Well-defined macroporous polymer beads were formed without using any organic solvents—just water and CO₂ (Fig. 2). Furthermore, the surface area of the beads could be tuned over a wide range (5–500 m²/g) by varying the CO₂ density, thus using the supercritical fluid as a “pressure-adjustable porogen”.^[7] We believe that this is the most dramatic example yet of a system where polymer properties can be tuned by varying the SCF density.

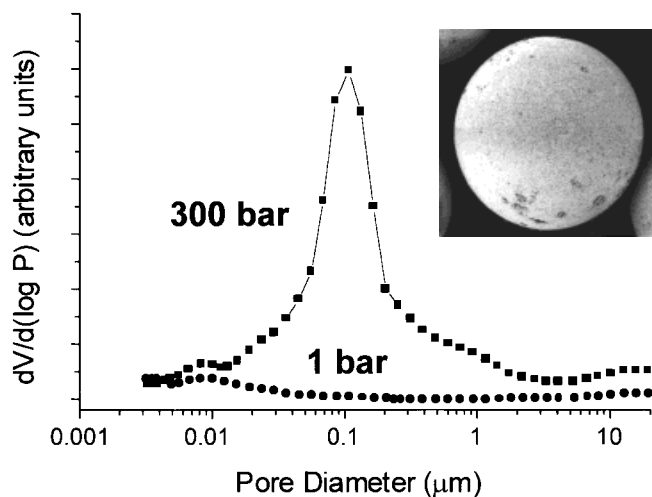


Fig. 2. Mercury intrusion porosimetry data for porous beads synthesized in the presence of CO₂ at 1 bar and at 300 bar [7]. Average pore size for the sample produced at 300 bar is 100 nm (specific surface area = 253 m²/g). The inset shows an SEM image of a single porous bead (average bead diameter = 130 μm).

2.2. Coatings and Lithography

Supercritical fluids tend to have much lower viscosities than liquid solvents. The viscosity of CO₂ is also low in the liquid state. Moreover, liquid CO₂ has extremely low surface tension and surface energy—lower even than many perfluorocarbons—which give this solvent remarkable wetting properties. Coupled with the possibility of easy separations and reductions in organic solvent usage, these factors have led to a growing interest in the areas of coating and lithography using dense CO₂. Ober has developed diblock copolymer resists for 193 nm wavelength lithography using scCO₂ as the developing solvent.^[8] Lithographic resolutions as low as 0.2 μm can be achieved using these methods (Fig. 3). This may be due in part to interfacial segregation behavior exhibited by the

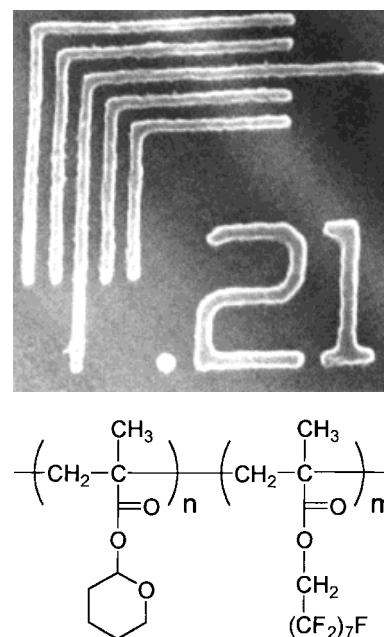


Fig. 3. SEM image of a 193 nm wavelength photolithographic image developed using scCO₂ [8]. The structure of the CO₂-soluble diblock copolymer resist is shown below the image.

diblock copolymers resists. Ober suggests that scCO₂ development could play a key role in the fabrication of high aspect-ratio features because of the absence of surface-tension forces.^[8] Presently, millions of gallons of wastewater from semiconductor processing facilities are treated annually. Supercritical solvents offer a simpler and more energy-efficient method for solvent recycling. In this context, Carbonell and DeSimone have developed techniques for spin-coating polymer resists onto silicon wafers directly from liquid CO₂.^[9] This suggests the intriguing possibility of a new photolithographic technology that uses no organic or aqueous solvents whatsoever, either in the coating or developing steps.

A further distinction between liquid solvents and supercritical fluid solvents is the degree of miscibility with gaseous reagents. For example, hydrogen has low solubility in most organic solvents but is highly miscible with scCO₂. This has

been exploited by Watkins in the formation of high-purity, conformal metal films from CO₂-soluble organometallic precursors via the technique of “chemical fluid deposition” (CFD) (Fig. 4).^[10] This is a process that genuinely exploits the gas–liquid “hybrid” properties of scCO₂: it is solution based (therefore eliminating precursor volatility constraints) while retaining most of the rapid transport properties and conformal coverages associated with chemical vapor deposition. The primary restriction for CFD is that the reduction chemistry must proceed readily at low temperatures.^[10]

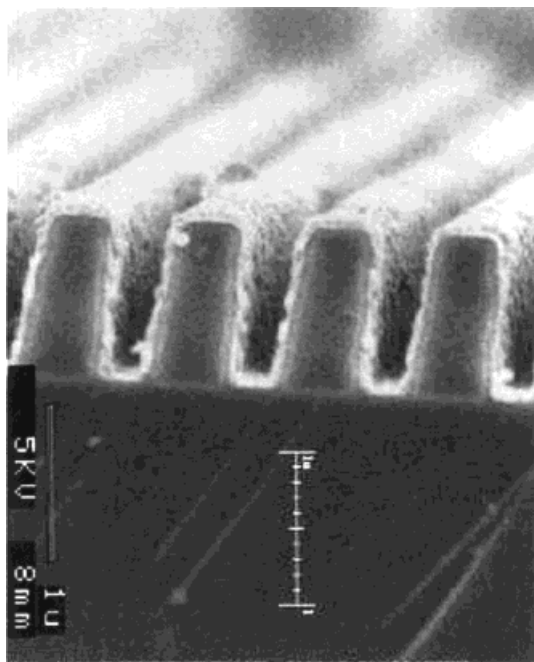


Fig. 4. Conformal palladium film grown on a patterned silicon wafer by chemical fluid deposition from scCO₂ (scale bar = 1 μm). A 0.26 wt.-% solution of CpPd(π -C₄H₇) in CO₂ was reduced using H₂ to produce the film.

2.3. Metal Nanoparticles

Given the enormous level of interest in the field of nanomaterials, it is perhaps not surprising that supercritical fluid solvents have been explored in this context. Recent reports suggest that the synthesis and processing of nanoparticles is an area where fine control over solvent properties may offer distinct advantages. For example, recent studies by Schiffrin and coworkers show that the variable density associated with SCFs may be exploited in the size-fractionation of functionalized metal nanoparticles.^[11] Fulton and Wai have described a process for synthesizing and dispersing silver nanoparticles in a water-in-scCO₂ microemulsion.^[12] A microemulsion of aqueous sodium nitrate solution was stabilized in scCO₂ by the addition of a mixed surfactant system involving sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and a perfluoropolyether-phosphate ether. Addition of a reducing agent [NaBH(OAc)₃] led to the formation of Ag⁰ nanoparticles with

an average diameter of about 4 nm, as estimated from ultraviolet-visible (UV-vis) bandwidth analysis and from transmission electron microscopy (TEM) imaging. Both the precursor solution and the reduced Ag-particle solution formed stable, optically clear microemulsions throughout the entire reaction sequence. More recently, Wai outlined a process for synthesizing silver halide nanoparticles (diameters = 3–15 nm) by mixing two different water-in-scCO₂ microemulsions—one containing silver nitrate and the other containing a sodium halide (X = Cl, Br, I).^[13] In this case, nanoparticle formation involves several processes, such as droplet collision, intermicellar exchange, and reaction between silver ion and halide ion. The formation of nanoparticles in supercritical fluid solvents offers potential advantages, which include rapid solvent separation, accelerated reaction rates (due to high diffusivities), and the possibility of depositing particles in situ in porous materials, thereby taking advantage of the unique properties of the SCF phase.^[12,13] However, conventional approaches to nanoparticle synthesis and processing are not always directly transferable. For example, alkanethiol-capped nanoparticles have not been found to disperse readily in scCO₂ due to the very low van der Waals forces and polarizability exhibited by this solvent. Johnston and Korgel have addressed this problem by synthesizing robust fluorocarbon-capped silver nanocrystals, which may be dispersed in pure liquid or supercritical CO₂.^[14] The synthesis and processing of metal nanoparticles capped with fluorinated ligands (e.g., 1H,1H,2H,2H-perfluorodecanethiol)^[14] could prove important, for example, in memory storage applications where a low dielectric constant coating material may help to insulate the active charge-storing devices. Johnston and coworkers have also used alkanethiol-coated gold nanocrystals (2.5 nm diameter) as uniform seeds for the growth of defect-free silicon nanowires from SCF solution.^[15] It was found that the orientation of the nanowires could be controlled by varying the reaction pressure, once again taking advantage of the variable density associated with SCFs.

2.4. Biomaterials Processing

Tissue engineering scaffolds and controlled drug-delivery devices are polymeric composites designed to release precise quantities of guest species (e.g., growth factors, pharmaceuticals) at rates matching the physiological needs of the biological tissue. A major challenge is to incorporate the biologically active guest species into the polymer host without loss of activity. For example, there are well-documented problems in maintaining protein activity under conventional processing methods due to either the presence of an organic/aqueous interface (e.g., double emulsion techniques), elevated temperatures (e.g., polymer melt processing), or vigorous mechanical agitation. A further challenge is to control the morphology of the composites (e.g., to generate porosity that optimizes release characteristics or allows cell infiltration into a scaffold).

fold). Howdle and coworkers have reported a supercritical fluid mixing technology that overcomes many of these limitations in a single processing step.^[16] Carbon dioxide is known to plasticize a wide variety of amorphous polymers and to cause a significant reduction in the glass transition temperature (T_g). This plasticization effect was used to lower the viscosity of biodegradable polymers such as poly(D,L-lactide), poly(lactide-co-glycolide), and polycaprolactone to such an extent that bioactive guests could be mixed into the polymer at temperatures close to ambient (e.g., 35 °C, 200 bar). Efficient agitation of the CO₂-swollen polymer led to a homogeneous distribution of the guest particles throughout the matrix (Fig. 5). Furthermore, foaming occurs upon venting the CO₂ and this introduces a high degree of porosity into the composite material. Composites were formed encapsulating enzymes (e.g., ribonuclease A, catalase, β -D-galactosidase) and it was found that the enzyme activity was retained. Carbon dioxide is a very attractive solvent for processes of this type because of the complete lack of toxic solvent residues introduced into the materials.

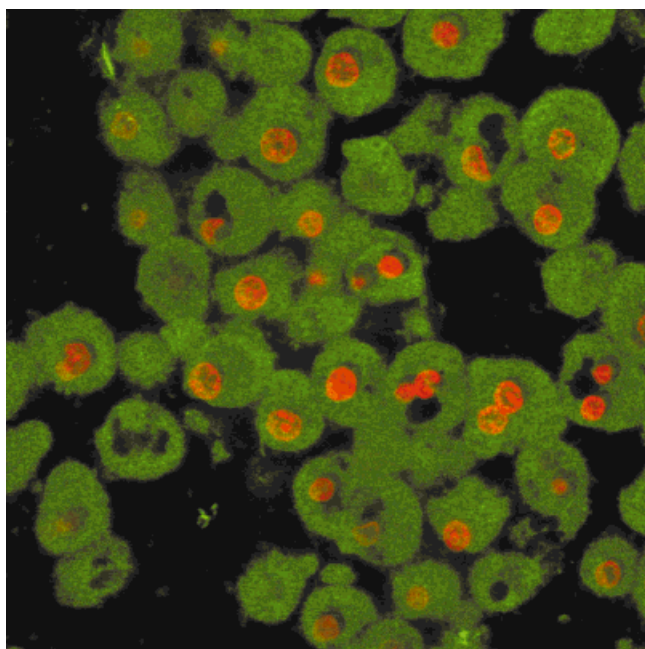


Fig. 5. Hepatocyte liver cells growing on a poly(lactic acid) scaffold produced using supercritical fluid mixing. Reflectance microscopy of the polymer surface reveals the cell outline (green) and specific staining shows the cell nuclei (red). These two images have been superimposed.

3. Conclusions and Outlook

The use of carbon dioxide as a solvent offers unique opportunities for the synthesis and processing of a range of advanced materials. Given the additional cost and complexity associated with high-pressure technology, it is clear that SCFs are not necessarily a sensible answer for all materials problems. However, in certain large-scale, solvent-intensive processes (e.g., photolithography), reductions in organic solvent usage and aqueous waste streams may be compelling reasons for considering this approach. In more specialized, smaller-scale applications, the use of scCO₂ (and other fluids) could provide routes to well-defined materials that would otherwise be difficult to obtain. Some of the most interesting opportunities will be found in systems where a specific limitation is imposed by the use of conventional liquid solvents.

- [1] P. G. Jessop, W. Leitner, *Chemical Synthesis Using Supercritical Fluids*, WILEY-VCH, Weinheim **1999**. A. I. Cooper, *J. Mater. Chem.* **2000**, *10*, 207. J. A. Darr, M. Poliakoff, *Chem. Rev.* **1999**, *99*, 495. E. Reverchon, *J. Supercrit. Fluids* **1999**, *15*, 1.
- [2] M. Perrut, *Ind. Eng. Chem. Res.* **2000**, *39*, 4531.
- [3] J. M. DeSimone, Z. Guan, C. S. Elsbernd, *Science* **1992**, *257*, 945. J. M. DeSimone, E. E. Maury, Y. Z. Menciloglu, J. B. McClain, T. J. Romack, J. R. Combes, *Science* **1994**, *265*, 356. P. A. Charpentier, K. A. Kennedy, J. M. DeSimone, G. W. Roberts, *Macromolecules* **1999**, *32*, 5973. J. L. Kendall, D. A. Canelas, J. L. Young, J. M. DeSimone, *Chem. Rev.* **1999**, *99*, 543.
- [4] C. Shi, Z. Huang, S. Kilic, J. Xu, R. M. Enick, E. J. Beckman, A. J. Carr, R. E. Melendez, A. D. Hamilton, *Science* **1999**, *286*, 1540.
- [5] A. I. Cooper, A. B. Holmes, *Adv. Mater.* **1999**, *11*, 1270.
- [6] D. A. Loy, E. M. Russick, S. A. Yamanaka, B. M. Baugher, K. J. Shea, *Chem. Mater.* **1997**, *9*, 2264. H. Wakayama, Y. Fukushima, *Chem. Mater.* **2000**, *12*, 756.
- [7] C. D. Wood, A. I. Cooper, *Macromolecules* **2001**, *34*, 5.
- [8] C. K. Ober, A. H. Gabor, P. Gallagher-Wetmore, R. D. Allen, *Adv. Mater.* **1997**, *9*, 1039. S. Yang, J. G. Wang, K. Ogino, S. Valiyateetil, C. K. Ober, *Chem. Mater.* **2000**, *12*, 33. N. Sundararajan, S. Yang, K. Ogino, S. Valiyateetil, J. G. Wang, X. Y. Zhou, C. K. Ober, S. K. Obendorf, R. D. Allen, *Chem. Mater.* **2000**, *12*, 41.
- [9] E. N. Hoggan, J. L. Kendall, D. Flowers, R. G. Carbonell, J. M. DeSimone, *Abstr. Pap.—Am. Chem. Soc.* **1999**, *218*, 52.
- [10] J. J. Watkins, J. M. Blackburn, T. M. McCarthy, *Chem. Mater.* **1999**, *11*, 213. J. M. Blackburn, D. P. Long, J. J. Watkins, *Chem. Mater.* **2000**, *12*, 2625. D. P. Long, J. M. Blackburn, J. J. Watkins, *Adv. Mater.* **2000**, *12*, 913.
- [11] N. Z. Clarke, K. A. Johnson, J. Satherley, D. J. Schiffrin, unpublished.
- [12] M. Ji, X. Y. Chen, C. M. Wai, J. L. Fulton, *J. Am. Chem. Soc.* **1999**, *121*, 2631.
- [13] H. Ohde, J. M. Rodriguez, Y. Xiang-Rong, C. M. Wai, *Chem. Commun.* **2000**, 2353.
- [14] P. G. Shah, J. D. Holmes, R. C. Doty, K. P. Johnston, B. A. Korgel, *J. Am. Chem. Soc.* **2000**, *122*, 4245.
- [15] J. D. Holmes, K. P. Johnston, R. C. Doty, B. A. Korgel, *Science* **2000**, *287*, 1471.
- [16] S. M. Howdle, M. S. Watson, M. J. Whitaker, V. K. Popov, M. C. Davies, F. S. Mandel, J. D. Wang, K. M. Shakesheff, *Chem. Commun.* **2001**, 109.