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$$\left| \frac{P'}{F_0} \right|^2 = \frac{1 + \omega^2 \tau^2}{(1 - \alpha\mu)^2 + \omega^2 \tau^2}$$

$$\tan(\phi) = \frac{\alpha\mu\omega\tau}{1 - \alpha\mu + \omega^2\tau^2}$$

For conditions on the approximations in Eq. 5, see (27). The coupling coefficients α and μ are positive and $\alpha\mu < 1$ so that the positive feedbacks do not become unstable. In Fig. 3, $\alpha\mu = 0.5$.
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The Gelation of CO₂: A Sustainable Route to the Creation of Microcellular Materials

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Compounds with strong thermodynamic affinity for carbon dioxide (CO_2) have been designed and synthesized that dissolve in CO_2, then associate to form gels. Upon removal of the CO_2, these gels produced free-standing foams with cells with an average diameter smaller than 1 micrometer and a bulk density reduction of 97 percent relative to the parent material.

Carbon dioxide is nonflammable, relatively nontoxic, and naturally abundant, and is consequently promoted as a sustainable solvent in chemical processing. Carbon dioxide's "green" properties have provided the driving force for development of a number of new applications, such as replacement of organic solvents in polymerization (1), as a medium for conducting hydrogenations and oxidations in the absence of transport limitations (2), as a solvent in biocatalysis (3), and as a raw material in synthesis (4). Many of these applications have been made possible by the relatively recent discovery that certain functional groups, subsequently denoted "CO_2-philic" (see below), enable miscibility of target compounds with CO_2 at moderate pressures (5). Development of CO_2-soluble surfac-

tants, for example, permits CO_2-based emulsion polymerization and dry cleaning. The design and synthesis of CO_2-philic phosphine ligands has spawned a number of CO_2-soluble metal catalysts. By combining concepts in CO_2-philic design with an understanding of molecular assembly in solution, we have generated compounds that gel CO_2 at concentrations below 5 weight %. Creation of gels in CO_2 has allowed us to generate cellular polymers with a bulk density <5% of that of the parent polymer and cells <1 μm. Generation of gels, and more recently foams, using CO_2 thus provides a technically and environmentally satisfying solution to a material fabrication problem.

A one-step, CO_2-based route for generation of low bulk density, microcellular materials is of particular technical interest because these materials—organic analogs to silicate aerogels—have some intriguing applications (catalyst and separation supports, low-dielectric materials, insulation, tissue engineering scaffolds), and be-

cause current routes to organic and inorganic aerogels involve multiple process steps and large volumes of solvent. Commercial foaming processes using CO_2 are by contrast "greener," but they do not generate the combination of low bulk density and submicrometer pore size. These processes either add CO_2 to a polymer melt in an extruder or mix CO_2 with (polyurethane) precursor materials before polymerization. In either case, the pressure used is relatively low (30 to 100 atm), and thus the amount of CO_2 mixed with the polymer is usually <5 weight %. Foam with a very low bulk density (>95% density reduction relative to the parent polymer) is produced, but its cells can be as large as 1 mm (6). Research conducted during the 1980s and 1990s showed that high-pressure CO_2 (pressures up to 500 atm) can be used to swell thermoplastic polymers by as much as 30%, and that subsequent rapid depressurization produces a microcellular foam. Such methods readily produce foams with cells <2 μm, but density reductions rarely exceed 65% (7). There would be considerable utility in a single-step process by which one could generate organic, low-density, microcellular materials with a benign foaming medium such as CO_2.

As a means to generate low-density microcellular foam, we synthesized molecules that would dissolve in CO_2 under relatively moderate pressures, then associate in solution to form gels. Previous work has shown that gels can be created in traditional organic solvents through hydrogen bonding (8), association between ionic groups (9), or association between electron-donating and electron-accepting moieties (10). To form foams from such gels, it is necessary to preserve the supramolecular aggregates created in solution, both during and after solvent removal. Although it is possible to design molecules that aggregate in solution, for example through multipoint hydrogen-bond formation (11), only

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Fig. 1. (A) Foam produced using 1 at 4.86% initial composition in CO_2. (B) Foam produced using 2 at 4.0% initial composition in CO_2. (C) Foam produced using 1 at 2.2% initial composition in CO_2. (D) Foam produced using 10 at 5% initial composition in CO_2. (E) Foam produced using 12 at 4.7% initial composition in CO_2. (F) Foam produced using 11 at 4.8% initial composition in CO_2. All panels are SEM images; scale bars, 5 μm (A, C, and F), 10 μm (B and E), and 500 μm (D).
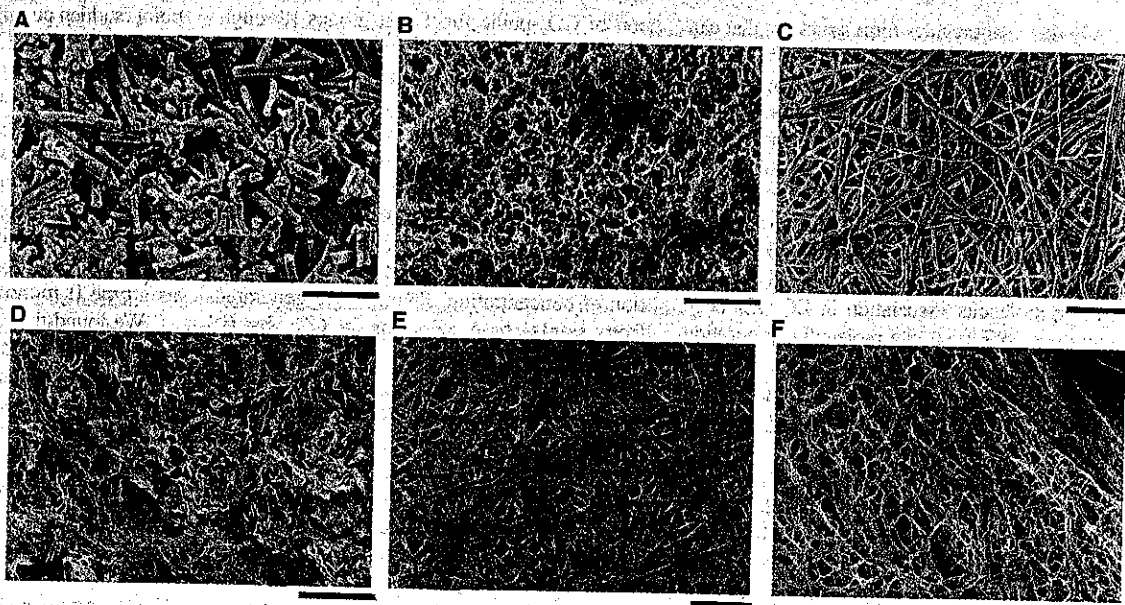
terial (Fig. 1C) with submicrometer pores, a fibrillar morphology, and a bulk density comparable to that of the material in Fig. 1A (the monolith comprises less material but does not fill the entire volume available in the view cell). Some but not all of the materials in Table 1 exhibit a morphology-concentration correlation, but it is not yet clear how the chemical structure of the agents governs this correlation.

Changing the R group from alkyl to aromatic in class B compounds changes the behavior from type II (monoliths) to type III (precipitated as powders). Here, although the elevated temperature allows dissolution of these type III materials, the formation of large aggregates with type II morphology is apparently inhibited by the aromatic structures, even for 5, where the R group contains aromatic groups with a highly CO_2-philic fluoroether spacer. When fluoroether groups are used in the aspartate residue (the Z group), as in 6, type I foams with a more traditional cellular appearance are formed.

As we expected, reducing the number of

Fig. 2. SEM image of foam produced from terpolymer of 1H,1H,2H,2H-perfluorodecyl acrylate (84 mol %), styrene (11 mol %), and sulfonated styrene (5 mol %) at 1.1 initial weight % in CO_2. Scale bar, 5 μm. For more details of the terpolymer synthesis, see Science Online (www.sciencemag.org/feature/data/1044209.shl).

urea groups from two to one (class A structures) produces type I materials more readily, yet still allows for types II and III to form, depending on the structure of the R group. Somewhat surprisingly, R groups that might be suspected to be relatively CO_2-philic (p-fluorophenyl and p-trifluoromethyl phenyl in 7 and 8), and hence to lead to solubility at room temperature, instead produced type II and III behaviors, requiring elevated temperature for dissolution. Addition of the second trifluoromethyl group (8) is needed for the molecule to dissolve at room temperature. The agents that produced type I behavior generally produced foams with a traditional porous morphology, with cells larger than 1 μm (see Fig. 1D). However, the methacrylate-functional compound (12) exhibits type I behavior and also produces a foam with a fibrillar structure (Fig. 1E). The phenyl-functional material (11) exhibited type II behavior and produced very low density, microcellular foam monoliths that filled the view cell, like those produced from 1, with a fibrillar microstructure (Fig. 1F).

Although the foams generated with these compounds are stable upon removal of the CO_2 (they easily support their own weight with no dimensional changes after days or weeks), they can be readily redissolved in CO_2. Foams with a greater degree of permanence can be generated using compounds such as 12 (methacrylate-functional material) or an analog of 1 or 2 where a diyne functionality is included in the R group. Irradiation after foam formation would polymerize these materials.

CO_2-soluble associating polymers were also generated (15) by copolymerization of the highly CO_2-philic 1H,1H,2H,2H-perfluorodecyl acrylate with 12, or with styrene followed by partial sulfonation of the phenyl groups. Copolymers of the fluorinated acrylate and 12 dissolved readily in CO_2 at room temperature and produced stable, transparent gels at concen-

trations of 5 weight % and below. Unlike the type I structures shown in Table 1, the viscosity enhancement created by these polymers was two to three orders of magnitude. Removal of the CO_2 produced free-standing foam monoliths with a very low bulk density (>97% density reduction) but larger cells (>10 μm) than those described above. Gels and foams were produced even at levels of 12 in the copolymer as low as 6 mol %. Terpolymers of the fluorinated acrylate, styrene, and sulfonated styrene also produced transparent gels in CO_2 and foam monoliths with this type of microstructure (Fig. 2). Copolymers of the fluorinated acrylate with monomers that do not promote association in solution did not produce a large viscosity increase in CO_2, nor did they produce foam monoliths upon depressurization. Rather, the cellular materials produced from these copolymers collapsed upon removal of the CO_2.

A number of issues remain to be explored, including understanding the mechanism for morphology development in the foams, and hence why we have observed such striking changes in morphology upon changing either molecular structure or concentration. The CO_2 gels produced with the agents described above are not only precursors to microcellular materials, but could also have applications themselves. Gelation of CO_2 could be used to enhance the tertiary recovery of petroleum from aging fields and could also support CO_2-based coating processes. Each of these applications requires less expensive, and hence nonfluorinated, analogs of the compounds described above, and some of these are now under development (16).

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