Microfibrillar Foams

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Fiber Formation by Highly CO_2-Soluble Bisureas Containing Peracetylated Carbohydrate Groups**

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Supercritical carbon dioxide ($scCO_2$) has attracted interest as an environmentally benign solvent,[1] but its practical usage is limited by the low CO_2-solubility of polar and high-molecular-weight compounds. To enhance the CO_2-solubility of such compounds, CO_2-philic surfactants,[2,3] dispersants,[4,5] thickeners,[6] and polymers[5,7] have been designed. Early success was achieved by the use of polyfluoroalkyl groups: various derivatives incorporating these groups showed enhanced CO_2-solubility. In an attempt to develop "greener" CO_2-philes,[8–11] several investigators have explored other highly CO_2-philic compounds composed solely of carbon, hydrogen, and oxygen. For example, the CO_2-solubilities of poly(ether carbonate)s are comparable to that of poly(hexafluoropropylene oxide), probably owing, in part, to the concentration of negative charge density on the carbonyl oxygen atom of the carbonate units.[8] The acetate group was also recognized as having the potential to be very CO_2-philic and has the advantage of easy introduction into polymers and surfactants.[11–17] Peracetylated sugars, such as sorbitol,[18] sugar amides, peracetylated cyclodextrins,[19] maltose octaacetate,[20] glucose pentaacetate, and galactose pentaacetate[21,22] also exhibit extraordinary solubility in $scCO_2$. A Lewis acid–base interaction between the acetyl oxygen atom and the carbon atom of CO_2, and weak C–H···O hydrogen bonding between the acetyl methyl group and the oxygen atoms of CO_2 are believed to be responsible for the CO_2-affinity of the acetyl group.[21,23]

We have previously shown that self-aggregating organic compounds containing both hydrogen-bonding urea groups and fluorinated CO_2-philic tails could modestly increase the viscosity of $scCO_2$.[9] Upon depressurization, these solutions produced free-standing foams, which represent organic analogues of silicate aerogels, with submicron-sized fibers and a bulk density reduction of greater than 90% of the parent material.[9] A critical feature of these systems is the presence of strong and directional hydrogen bonding between the carbonyl oxygen atoms and the NH units in the urea groups of adjacent molecules, which leads to the formation of two-dimensional sheet-like structures (Figure 1).[24,25] The sheets

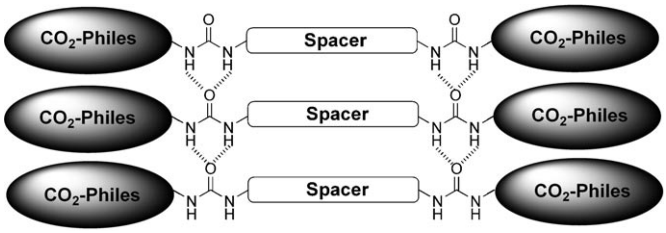

Figure 1. Two-dimensional network formed by the intermolecular hydrogen bonding of bisureas containing CO_2-philic arms.

likely further associate through noncovalent contacts to form viscosity-enhancing networks in solution and, subsequently, free-standing foams upon removal of the CO_2.

The objective of the present work was to design nonfluorous hydrogen-bonding molecules capable of dissolving in CO_2 and self-associating to form novel materials. An inexpensive and readily available source of multiple hydroxy groups is the family of mono-, di-, and oligosaccharides. These molecules can be readily converted into their peracetylated derivatives, which should have a density of electronegative groups similar to that of perfluoroalkanes. In particular, gluconic acid is readily available from glucose by oxidation and should be easily converted into its peracetylated derivative. Thus, gluconic acid and commercially available D-glucamine were chosen as nonfluorous CO_2-philic appendages for connection to less soluble hydrogen-bonding groups.

The synthesis of bisureas **1** began with the peracetylation of commercially available D-glucamine (**3**). In contrast to the longer four-step synthesis of pentaacetylated D-glucamine (**4**) reported by Hoeg-Jensen et al.,[26] we could selectively acetylate the hydroxy groups in D-glucamine with acetyl chloride under acidic conditions[27] directly. Pentaacetylated D-glucamine (**4**) reacted with the commercially available diisocyanates at room temperature to give the desired bisureas **1** in high yield (Scheme 1).

An alternative design places the peracetylgluconate groups further from the urea groups, through the insertion of ethanolamine or ethylenediamine spacers, as in bisureas **2**. Esters and amides of gluconic acid (**8**) were synthesized by

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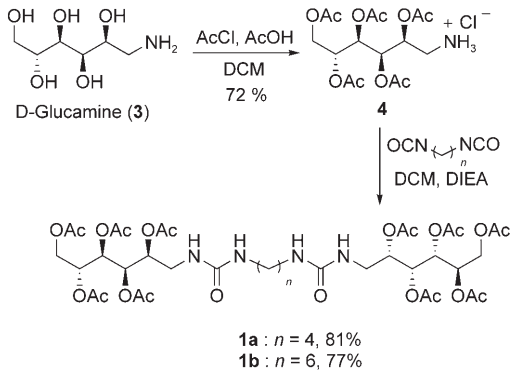
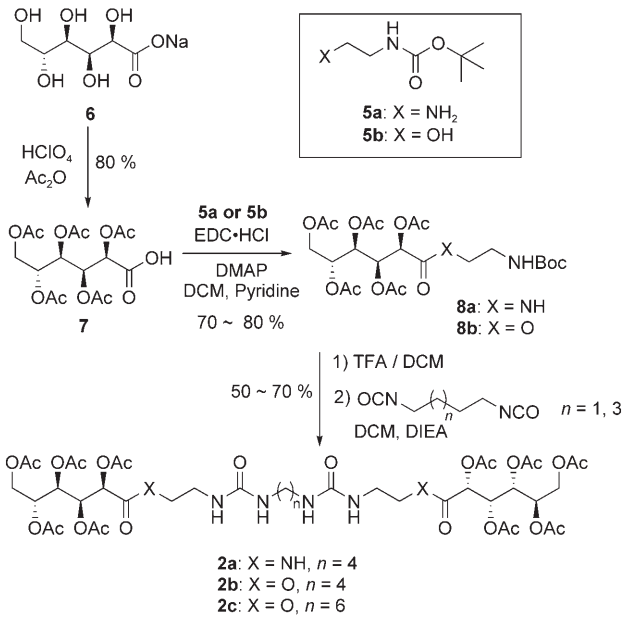


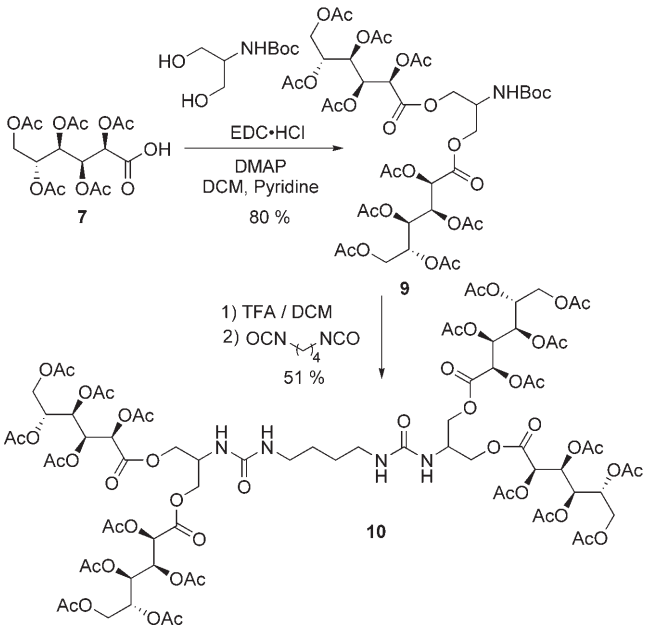
Scheme 1. Synthesis of bisureas **1a** and **b**. DCM = dichloromethane, DIEA = *N*,*N*-diisopropylethylamine.

using the coupling agent 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) hydrochloride. After removal of the *tert*-butyloxycarbonyl (Boc) protecting groups from the esters or amides, the resulting free amines were treated with diisocyanates to form the desired bisureas **2** in moderate to high yields (Scheme 2).



Scheme 2. Synthesis of bisureas **2a–c**. DMAP = *N*,*N*-dimethylaminopyridine, TFA = trifluoroacetic acid.

The simplicity of this method made it readily applicable to branched species containing multiple peracetylgluconate groups. Cooper et al. have previously shown that a hydrophilic dendrimer, DAB-*dendr*-$(NH_2)_{32}$ (a dendrimer with a diaminobutane (DAB) core and 32 terminal amino groups) functionalized with perfluoropolyether chains is highly CO_2-soluble.[10] A similar, albeit more limited, approach could be taken to increase the CO_2-solubility of self-assembling dendrimer-like bisureas, through the attachment of multiple CO_2-philic groups, as in **10**. The Boc-protected diester amine **9** was converted, using the same reaction conditions as in the syntheses of **1** and **2**, to the bisurea derivative **10**, which has four CO_2-philic groups (Scheme 3).



Scheme 3. Synthesis of bisurea **10**.

At ambient temperature, bisureas **1a** and **b** were not soluble in $scCO_2$, even at pressures up to the limit of the instrument (68.95 MPa) and temperatures up to 100 °C. Chain length (butyl vs. hexyl spacers) did not have any effect on the solubility of these compounds in $scCO_2$. It is possible that the close proximity of the peracetylated moieties to the urea groups may inhibit both solvation by CO_2 and aggregation through hydrogen bonding. Bisureas **2a–c**, which contain an ethylene spacer, were synthesized to test the effect of an increased distance between the CO_2-philic peracetylated moieties and the bisurea groups. Bisurea **2a** did not dissolve in $scCO_2$ at any temperature and pressure, possibly owing to the CO_2-phobic nature of the amide linkages. However, replacement of the amides by ester groups gave the more CO_2-philic bisureas **2b** and **c** (Scheme 2). At 298 K, these highly acetylated bisureas dissolve to 1 wt% in CO_2 at pressures of 62 (**2b**) or 65 MPa (**2c**).

The transparent, single-phase solutions obtained under these conditions were metastable. After 2–5 min, a suspension of fine fibers began to form in the solutions. Apparently, under isothermal and isobaric conditions, the dissolved compounds slowly aggregate, resulting in the formation of fibers. Within 20 min, the sample volumes were filled with fibers, and upon removal of the CO_2, very brittle, freestanding microfibrillar foams formed. In phase-behavior studies for bisurea **2b** at lower (13.5 °C) and higher (37.5 °C) temperatures and at a pressure of 62 MPa, a transparent, single-phase solution was never attained. Nonetheless, the powdery compound initially charged into the cell (Figure 2a) dissolved and then precipitated in the form of fibers. At low temper-

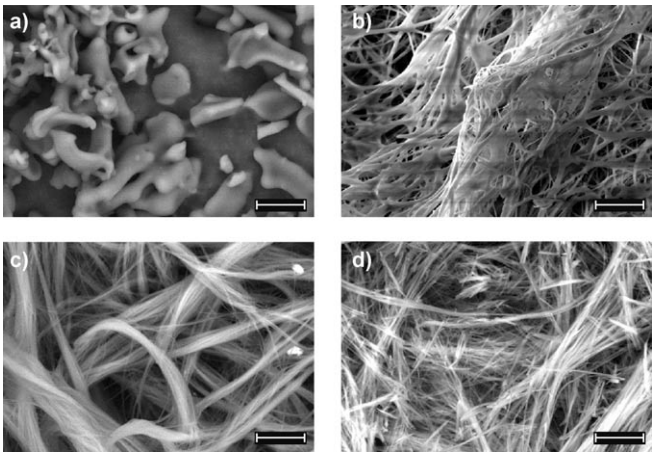


Figure 2. SEM images of a) **2b** before the introduction of CO_2, and of the fibers of **2b** formed in $scCO_2$ at a pressure of 62 MPa and a temperature of b) 13 °C, c) 25 °C, or d) 37.5 °C. Scale bars = 10 μm.

ature, **2b** produced a foam with a highly interconnected microfibrillar structure and fiber diameters of less than 1 μm (Figure 2b). The foam produced from **2b** at ambient temperature consists of major fibers with diameters of 1–3 μm, which are composed of submicron fibers (Figure 2c); this foam has a higher porosity than that formed at low temperature. The foam produced at 37.5 °C was very brittle and had a fiber diameter of approximately 1 μm (Figure 2d).

The improvements in the CO_2-solubility of **2b** and **c** encouraged us to prepare the dendrimer-like bisurea **10**, which contains four CO_2-philic peracetylated moieties around a bisurea core (Scheme 3). In contrast to **2b** or **c** (1 wt% dissolution at 62 or 65 MPa), bisurea **10** dissolved more readily to 1 wt% in CO_2 at a notably lower pressure of 27 MPa. Compound **10** dissolved to 1–5 wt% in liquid CO_2 at 25 °C and in $scCO_2$ at 44 °C. This compound is the first CO_2-soluble dendrimer-like molecule composed solely of carbon, hydrogen, nitrogen, and oxygen. Unlike the linear bisureas **2b** and **c**, **10** formed a powder, rather than a rigid foam upon removal of the CO_2.

In conclusion, nonfluorous CO_2-philic compounds with two highly oxygenated arms and a core of two urea groups separated by a short alkyl chain (**2b** and **c**) were dissolved to 1 wt% in $scCO_2$ at 298 K. Upon dissolution, microfibrillar foams with fiber diameters of approximately 1–3 μm formed, and these brittle networked materials retained their integrity upon depressurization of the CO_2. A nonfluorous bisurea with four peracetylated arms (**10**) was soluble to 5 wt% in liquid CO_2 and $scCO_2$. The phase behavior of **10** in CO_2 is presented in Figure 3a in the form of pressure–concentration isotherms at 25 and 44 °C. The room-temperature curve constitutes a small portion (indicated by the red box) of the overall phase diagram of this binary mixture at 25 °C (Figure 3b). The results presented herein indicate that acetylation provides an environmentally benign pathway to the generation of nonfluorous CO_2-soluble hydrogen-bonding molecules and dendrimers.

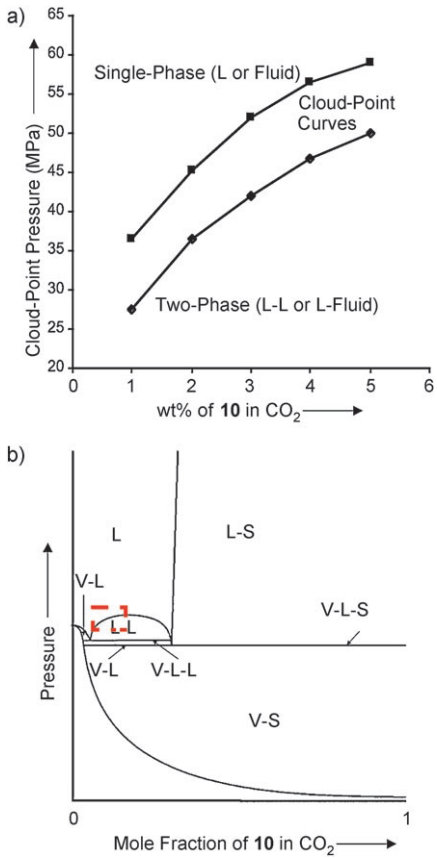


Figure 3. a) Cloud-point curves for bisurea **10** in CO_2 at temperatures of 25 °C (◆) and 44 °C (■). b) The isothermal phase diagram for the binary mixture at 25 °C; the portion corresponding to the curve in (a) is indicated by the red box. V = vapor, L = liquid, S = solid.

Experimental Section

Cloud-point pressures were determined using a standard visual nonsampling technique involving slow isothermal compressions and expansions of binary mixtures of the bisurea and CO_2 of known overall composition. The cloud-point pressure is defined as the highest pressure at which a minute amount of the denser, bisurea-rich phase remains in equilibrium with the CO_2-rich fluid phase. Typically, when this pressure is realized, the transparent single-phase solution becomes essentially opaque as the "cloud" of the second phase appears. Phase-behavior studies were performed using a high-pressure variable-volume windowed cell (DB Robinson and Associates) in a constant-temperature air bath. Details of phase-behavior investigations using this cell have been presented elsewhere.[14] Experimental details for the syntheses of bisureas **1**, **2**, and **10** are presented in the Supporting Information.

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