

# Generation of Microcellular Materials via Self-Assembly in Carbon Dioxide

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Received March 29, 2002. Revised Manuscript Received August 13, 2002

Fluoroalkyl urea compounds were designed to generate foams via dissolution in CO<sub>2</sub>, self-assembly in solution, and critical point drying via pressure reduction. The fluoroalkyl groups imparted CO<sub>2</sub>-philicity while hydrogen bonding between urea groups led to the formation of macromolecular structures. Monourea and bisurea compounds yielded collapsed foams of overlapping fibers because the association site density was not sufficient to form a rigid macrostructure. Triureas with a symmetric spacer in the hydrogen bonding core formed stable foams most readily. These foams were able to support their own weight and exhibited density values of 0.03–0.09 g/cm<sup>3</sup> and a thermal conductivity of 0.04 W/m·K. Although a fluorinated polyacrylate urea copolymer was designed to exhibit the greatest density of urea sites for associations, the high proportion of these CO<sub>2</sub>-phobic groups diminished CO<sub>2</sub> solubility. Further, strong intramolecular associations prevented the intermolecular self-assembly required for the generation of foams.

## Introduction

Carbon dioxide is nonflammable and relatively non-toxic, and it 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,<sup>1,2</sup> as a medium for conducting hydrogenations and oxidations in the absence of transport limitations,<sup>3</sup> as a solvent in biocatalysis,<sup>4</sup> and as a raw material in synthesis of carbonate copolymers.<sup>5</sup> Gelation of CO<sub>2</sub>, a sustainable route to the creation of microcellular and microfibrillar materials, was first reported<sup>6</sup> in our laboratory in 1999.

The gelation of organic solvents by low-molecular-weight organic compounds has progressed from discovery by chance to use of reasonably well-defined guidelines.<sup>7</sup> Gelation is attributed to the self-assembly of molecules into supramolecular structures (cylinders, etc.), forming interlocking networks of fibers that entrap solvent.<sup>8</sup> Considerable previous research has shown that

molecular aggregates can form in both the solid state and in solution through intermolecular hydrogen bonding. The aggregates in solution can form a three-dimensional network encapsulating the solvent, even at concentrations as low as 1 wt %, producing a solvent-rich gel. If one performs the self-assembly in carbon dioxide, solvent removal can be accomplished easily. Here, structure formation and critical point drying are performed sequentially in the same solvent (CO<sub>2</sub>), greatly reducing the time required to create the materials versus that of the traditional structure formation → solvent displacement → critical point drying procedure.

Compounds that exhibit both hydrogen bond donors and acceptors are not, however, expected to be soluble in carbon dioxide at moderate temperature and pressure conditions. Carbon dioxide has been shown to be rather a feeble solvent, and hence the strong solute–solute interactions that permit the formation of supramolecular aggregates also inhibit the dissolution of the associating compounds in CO<sub>2</sub>. While CO<sub>2</sub> is indeed a weak solvent, previous research has identified functional groups that are relatively "CO<sub>2</sub>-philic", that is, their presence in a molecule promotes dissolution in carbon dioxide at moderate pressures. Known CO<sub>2</sub>-philes include fluorinated polyacrylates, fluorinated polyethers, fluoroalkyl groups, and to a lesser extent silicones (dimethyl siloxane polymers). By combining concepts in CO<sub>2</sub>-philic design with an understanding of molecular assembly in solution, we have generated organic compounds that gel CO<sub>2</sub> at low concentration.<sup>6,9</sup> Furthermore, creation of gels in CO<sub>2</sub> has allowed us to

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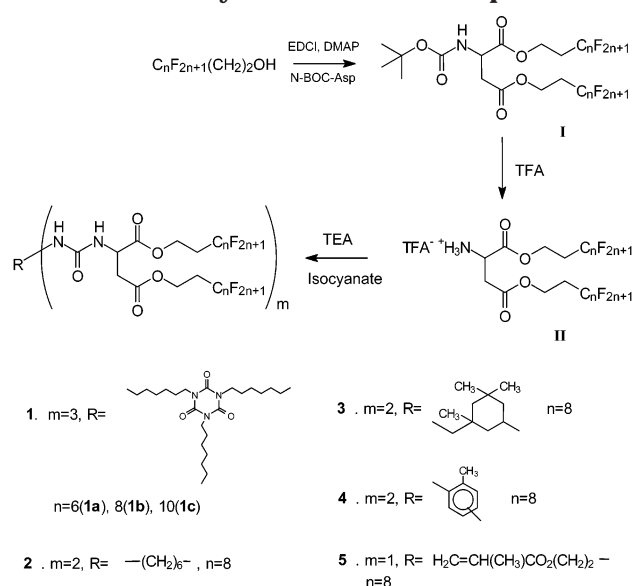
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## Scheme 1. Synthesis of Urea Compounds



generate microcellular or microfibrillar products with very low bulk density. Previous work on use of  $CO_2$  as a “blowing agent” has shown that one can readily obtain materials with low bulk density or with small cells, but not both. Generation of gels, and more recently foams, using  $CO_2$  thus provides a technically and environmentally satisfying solution to a material fabrication problem.

In this paper, we present the results on hydrogen bonding small compounds and copolymers that can increase the viscosity of gel dense  $CO_2$  in solution and/or form low density, low thermal conductivity, microfibrillar foams upon removal of the  $CO_2$  via depressurization.

## Experimental Section

**Materials.** *N*-*t*-BOC protected aspartic acid (*N*-*t*-BOC-*L*-Asp) was obtained from Sigma Chemical Co. and stored below  $0^\circ C$  before use. 1*H*,1*H*,2*H*,2*H*-Perfluorooctanol (97%), 1*H*,1*H*,2*H*,2*H*-perfluorodecanol (97%), and 1*H*,1*H*,2*H*,2*H*-perfluorododecanol (97%) were purchased from Synquest Labs., Inc. 1-[3-(Dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI, 98+%) and 4-(dimethylamino)pyridine (DMAP, 99+%) were obtained from Aldrich Chemical Co. and used as received. 1,6-Diisocyanatohexane (98%), isophorone diisocyanate (98%), and toluene 2,4-diisocyanate (tech. 80%) were obtained from Aldrich and used as received. Aliphatic polyisocyanate (Desmodur N 3600) was obtained from Bayer Corporation.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl acrylate (97%) was purchased from Aldrich. The inhibitor was removed by washing with 5% aqueous NaOH solution and then passing through an alumina column. The monomer was subsequently dried over  $MgSO_4$  and stored at  $0^\circ C$  prior to use. 2-Isocyanatoethyl methacrylate (Aldrich) was used as received for the synthesis of fluorinated aspartate methacrylate urea monomer. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol twice before use. All other chemicals and solvents were obtained from Aldrich and used as received.

NMR spectra were obtained using a Bruker 300 MHz instrument (TMS as reference), while FT-IR spectra were recorded using a Matson Research Series instrument.

Carbon dioxide (instrument grade) was obtained from Praxair.

**Bisureas and Triureas (Scheme 1).** Di(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-*N*-*t*-BOC-*L*-aspartate (**I**). Typically, 100 mL of dichloromethane was charged to a 250 mL three-neck flask equipped with a stirring bar. Subsequently, 7.88 g of 1*H*,1*H*,2*H*,2*H*-perfluorodecanol (0.017 mol) was added and the flask was cooled to  $0^\circ C$  in an ice bath. 2 g of *N*-Boc-Asp (0.0086 mol) and 3.28 g (0.017 mol) of EDCI were subsequently charged to the reaction mixture, which was stirred until the reactants dissolved. 1.05 g of DMAP (0.0086 mol) was then introduced. The reaction mixture was kept in the ice bath for 30 min and then slowly warmed to room temperature and allowed to stand for 12 h. The reaction mixture was then diluted with 100 mL of chloroform and transferred to a separatory funnel. The organic layer was washed with 50 mL of 1% HCl in water and 50 mL of brine; then it was dried over sodium sulfate. Solvents were removed under vacuum to yield a pale yellow solid. The solid was then dissolved in dichloromethane, and the solution was passed through a silica column. The solvent was subsequently removed under vacuum, and a white solid aspartate product was obtained in 80% yield.

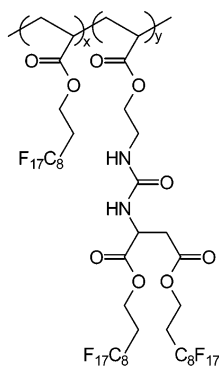
Di(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-*L*-aspartate Trifluoroacetic Acid Salt (**II**). Typically, 5 g of compound **I** was deprotected with 10 mL of trifluoroacetic acid (TFA) in 20 mL of dichloromethane for 3 h. The solvent was removed under reduced pressure, another 20 mL portion of TFA/dichloromethane was added, and the reaction was stirred for another 1 h. An off-white solid was obtained upon removal of the solvent under reduced pressure. The solid was recrystallized from 200 mL of ethanol, collected, and dried under vacuum, resulting in the formation of thin, white needles with 78% yield.  $^1H$  NMR ( $CDCl_3/50\%$   $CD_3COCD_3$ , ppm): 4.89 (m,  $O=C(CH_2)NH$ ), 4.22–3.80 (m,  $O=C(CH_2)CH$ ), 3.18 (m,  $C_8F_{17}CH_2(CH_2)O$ ), 2.62 (m,  $C_8F_{17}(CH_2)CH_2$ ).

**Synthesis of Bisureas and Triureas.** Compounds **II** ( $n = 6, 8, 10$ ) were reacted with stoichiometric amounts of commercially available diisocyanates to form bisureas (**2**, **3**, **4**) and with triisocyanate to form triurea (**1a**, **1b**, **1c**). Typically, the reactions were carried out in 50 mL of dichloromethane with triethylamine as a catalyst and stirred overnight under dry nitrogen. The white products were collected by filtration, washed with cold dichloromethane, 1% HCl, and ether, and then dried under vacuum. The FTIR spectra for the various bisureas/triureas are similar, showing N–H at 3350–3360  $cm^{-1}$ , C=O at 1735–1745  $cm^{-1}$ , and the absence of residual isocyanate (2150–2270  $cm^{-1}$ ).

2-(Di-1*H*,1*H*,2*H*,2*H*-perfluorodecyl-*L*-aspartyl) Carbonylaminoethyl Methacrylate (**5**). 5 g (4.3 mmol) of compound **II** were charged to a 125 mL Erlenmeyer flask and 50 mL of dichloromethane was added. 1.5 mL of triethylamine was then added while stirring to dissolve the aspartate salt. After the salt completely dissolved, 0.63 mL (4.4 mmol) of 2-isocyanatoethyl methacrylate was subsequently added dropwise. As the reaction proceeded, the solution gelled, presumably owing to intermolecular hydrogen bonding between the urea groups. The reaction flask was heated to a temperature not exceeding  $40^\circ C$  for 4 h to complete the reaction. The solvent was then removed under vacuum, and the product was washed with 1% HCl and hexanes and then dried under vacuum. The product was a white solid with 66% yield. FTIR (KBr): 3368, 1747, 1638  $cm^{-1}$ . There was no evidence of residual isocyanate (2150–2270  $cm^{-1}$ ).

**Random Copolymers of 2-(Di-1*H*,1*H*,2*H*,2*H*-perfluorodecyl-*L*-aspartyl) Carbonylaminoethyl Methacrylate and Heptadecafluorodecyl Acrylate (Scheme 2).** Copolymer **6** of 2-(Di-1*H*,1*H*,2*H*,2*H*-perfluorodecyl-*L*-aspartyl) Carbonylaminoethyl Methacrylate (**5**) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl Acrylate (HFDA). Copolymers with varying molar ratios of the two monomers were synthesized via free radical polymerization. The synthesis of a copolymer with a fluorinated acrylate (HFDA) to urea (**5**) molar ratio of 15:1 was conducted as follows: 1.0 g (0.93 mmol) of **5** and 7.2 g (14 mmol) of HFDA were charged to a 50 mL flask; 4.9 mg (0.03 mmol) of initiator (azobis(isobutyronitrile), or AIBN) was subsequently added. The flask was purged with argon for 15 min and then sealed and put into an oil bath and heated to

### Scheme 2. Structure of Copolymer from Urea Monomer 5



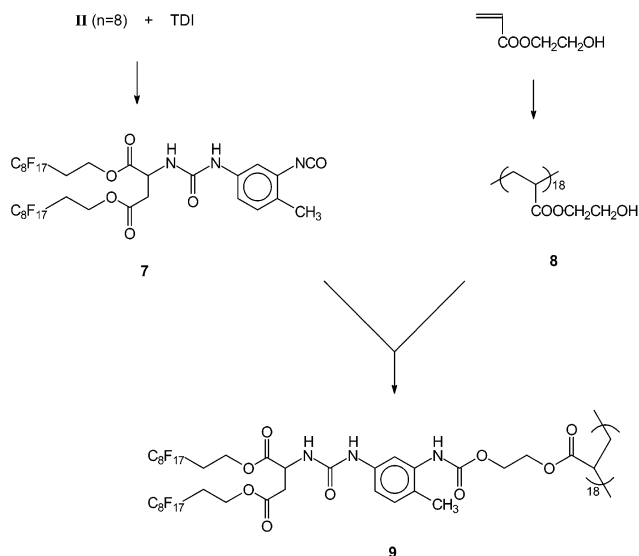
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6a: x:y = 2.7

6b: x:y = 14.3

6c: x:y = 19.5

### Scheme 3. Synthesis of Poly-urea Compound



60 °C. The reaction mixture was maintained at 60–65 °C for 2 days. The obtained polymer block was cut into several pieces, dissolved in 1,1,2-trichlorotrifluoroethane, and then precipitated into 200 mL of methanol (total of three reprecipitations). The white polymer was dried under vacuum overnight.

The compositions of the copolymers were characterized via  $^1\text{H}$  NMR using peaks for methylene protons in the pendant fluoroacrylate urea chains ( $\text{COOCH}_2\text{CH}_2\text{NH}$ ) that appeared between 5 and 6 ppm and peaks for methylene protons in the pendant fluoroacrylate chains ( $\text{COOCH}_2\text{CH}_2\text{C}_8\text{F}_{17}$ ) at 4.55 ppm (samples were dissolved in mixtures of 1,1,2 trichlorotrifluoroethane/deuterated acetone). We were unable to determine the molecular weight of the samples by GPC because these fluorinated copolymers were not soluble in THF or other conventional GPC eluents. Further, GPC measures molecular weight through hydrodynamic volume—these copolymers are known to associate in solution, which would complicate the analysis of molecular weight via either GPC or light scattering.

**Polymers Derived from a Fluorinated Aspartate Urea-Urethane Acrylate Monomer (Poly(FAUUA), Compound 9 in Scheme 3).** Fluorinated Isocyanate (7). 3.0 g of compound II was charged in a 100 mL round flask with 50 mL of dichloromethane, and 0.5 mL of triethylamine was added. Once the salt was dissolved, 0.46 g of Mondur TDS (toluene diisocyanate) was added. The reaction was stirred overnight under dry nitrogen. The white solid was collected by filtration, washed with cold dichloromethane, and then dried under vacuum. FTIR (KBr): 3356, 2278, 1746, 1645, 1601, 1553  $\text{cm}^{-1}$ .

**Poly(2-hydroxyethyl acrylate) (8).** Poly(2-hydroxyethyl acrylate) was synthesized using atomic transfer radical polymerization (ATRP).<sup>10</sup> Typical ratios of the reactants were monomer/initiator/CuBr/ligand = 43:1:1:2. In a reaction tube, 1.35 g (8 mmol) of 2,2'-bipyridine, 0.62 g (4 mmol) of CuBr, 0.48 mL (4 mmol) of 2-bromopropionate, and 20 mL (0.172 mol) of 2-hydroxyethyl acrylate were combined and degassed via three freeze-pump-thaw cycles. The tube was then sealed under vacuum and placed in an oil bath at 90 °C for 2 h. The tube was then frozen in liquid nitrogen and opened. The product was dissolved in 20 mL of DMF, and the solution was passed over alumina. The polymer was obtained after removal of the solvent under vacuum at 60 °C. The molecular weight of the polymer was determined by  $^1\text{H}$  NMR via comparison of peak areas representing end groups and repeat units, following the method described by Coca and co-workers.<sup>10</sup> The resonance representing the end group ( $-\text{CH}_3$  from the methyl 2-bromopropionate) appears as a broad multiplet at 1.1 ppm while the resonances from the backbone H's appear at 2.25 ppm ( $-\text{CH}$ ) and from 1.3 to 2.0 ppm ( $-\text{CH}_2$ ). Integration of these peaks and comparison provided a number average molecular weight of 2200. Coca and colleagues found this route provided comparable results to those found using MALDI-tof spectrometry.

**Fluorinated Polyacrylate Urea (Poly(FAUUA), 9 in Scheme 3).** 2.4 g of compound 7 was charged to a 100 mL round-bottom flask with 50 mL of DMF; several drops of dibutyltin dilaurate were then added. Once the solid was dissolved, 0.25 g of poly(2-hydroxyethyl acrylate) (8) were added. The reaction was stirred overnight under dry nitrogen; the reaction was stopped when an FT-IR spectrum showed the disappearance of the isocyanate peak at 2278  $\text{cm}^{-1}$ . The white solid was collected by filtration, washed with DMF, and then dried under vacuum.

**Phase Behavior.** The experimental apparatus (high-pressure, variable-volume view cell) for phase behavior measurements has been described elsewhere.<sup>11</sup>

**Scanning Electron Microscopy (SEM).** The foam samples were prepared for SEM by fracturing the surfaces to be examined after cooling in liquid nitrogen. Micrographs were recorded using a JEOL 35 scanning electron microscopy instrument.

**Foam Formation.** We evaluated the ability for compounds 1–9 (described above) to form microcellular foams via self-assembly in  $\text{CO}_2$ . For these studies, given amounts of the compounds were added to  $\text{CO}_2$  in our variable-volume, high-pressure view cell. The cell was charged with carbon dioxide to a pressure of 27.6 MPa. If the compound did not dissolve, the pressure of the system was then elevated to 48.3 MPa. The temperature was raised while maintaining the pressure at a constant 48.3 MPa via movement of the piston that expanded the volume of the variable-volume view cell. Compounds used in this study tended to dissolve either at room temperature or at temperatures above 343 K. If the compound required elevated temperature to achieve dissolution, the temperature of this single fluid phase was then lowered (at constant pressure) until phase separation (complete opacity within the view cell) occurred. The temperature was subsequently lowered to 295 K, and the  $\text{CO}_2$  slowly bled from the view cell. The cell was then opened and the foamed material removed intact. In cases where the compound dissolved at room temperature and elevated pressure, the foam was created via lowering the pressure through movement of the piston, and ultimately bleeding of the  $\text{CO}_2$  from the view cell.

Foam bulk densities were determined from their masses and the volume of water they would displace.

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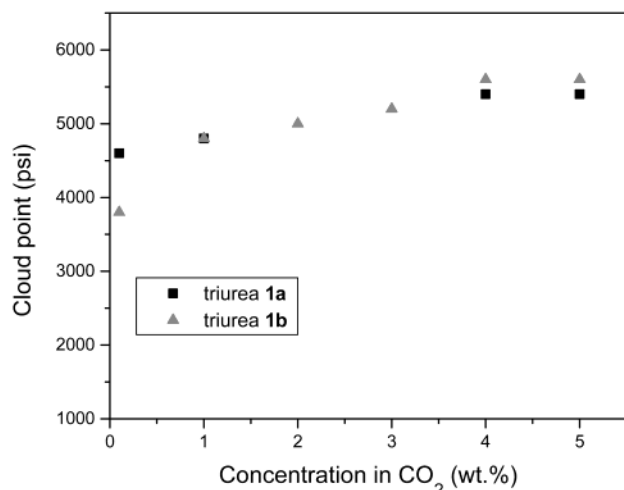
**Table 1. Phase Behavior of the Urea Compounds in CO<sub>2</sub> at 373 K**

sample	conc in CO <sub>2</sub> (wt %)	phase behavior in CO <sub>2</sub>
<b>1a</b>	0.1, 1.0–5.0	insoluble at 298 K and 48.3 MPa; soluble at 373 K
<b>1b</b>	0.1, 1.0–5.0	insoluble at 298 K and 48.3 MPa; soluble at 373 K
<b>1c</b>	5.0	insoluble at 298 K and 48.3 MPa; soluble at 373 K and 37.2 MPa
<b>2</b>	5.0	insoluble at 298 K and 48.3 MPa; soluble at 363 K and 33.1 MPa
<b>3</b>	4.0	soluble at 298 K and 10.3 MPa
<b>4</b>	4.0	insoluble at 298 K and 48.3 MPa; soluble at 373 K and 37.2 MPa
<b>9</b>	1.0	insoluble at 298 K and 48.3 MPa; soluble at 373 K and 43.4 MPa

**Table 2. Solubility and Gel Formation Results for Fluorinated Aspartate Methacrylate Urea–Fluoroacrylate Copolymers in Carbon Dioxide**

sample	entry	conc (wt %)	behavior at 298 K	behavior at 353 K
<b>5</b> (monomer)	E1	4.7	soluble at 10.3 MPa	
<b>6a</b>	E2	3.19–5.0	single-phase swollen polymer gel	single-phase swollen polymer gel
	E3	1.2	swollen polymer gel (1/2) <sup>a</sup> + CO <sub>2</sub> -rich phase	swollen polymer gel (1/2) + CO <sub>2</sub> -rich phase
<b>6b</b>	E4	4.0–4.82	single-phase swollen polymer gel	single-phase swollen polymer gel
	E5	3.0	swollen polymer gel (1/3) + CO <sub>2</sub> -rich phase	swollen polymer gel (1/3) + CO <sub>2</sub> -rich phase
	E6	2.0	swollen polymer gel (1/4) + CO <sub>2</sub> -rich phase	single-phase swollen polymer gel; remains single phase when cooled to 25 °C
<b>6c</b>	E7	5.0	single-phase swollen polymer gel	single-phase swollen polymer gel

<sup>a</sup> Estimated volume fraction of the CO<sub>2</sub>-swollen polymer phase in the two-phase systems observed with a cathetometer.

**Figure 1.** Cloud point curves of triureas **1a** and **1b** at 373 °C; the error in the phase behavior measurements is  $\pm 150$  psi.

## Results and Discussion

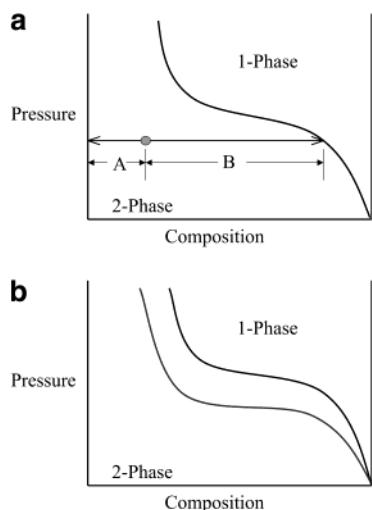
**Phase Behavior.** The urea compounds we obtained can be separated into three types: nonpolymeric bisurea and trisurea compounds **1–5**, acrylate copolymers **6**, and poly(FAUUA) **9**.

**Bisureas and Trisureas.** The phase behavior of the nonpolymeric ureas in carbon dioxide is summarized in Table 1. Figure 1 shows the experimental cloud point curves (phase boundaries) of triureas **1a** and **1b** at 373 K at concentrations varying from 0.1 to 5.0 wt %; the phase behavior of the two compounds in carbon dioxide is essentially the same. As the results from Table 1 indicate, all of the urea compounds synthesized and evaluated can dissolve in carbon dioxide below 48.3 MPa, albeit most at elevated temperature. The CO<sub>2</sub>-philic fluorinated alkyl tails promote solubility in carbon dioxide and stability of the macromolecular structures, while the elevated temperature diminishes the probability of hydrogen bonding interactions that would inhibit dissolution. Most of the compounds developed for this study show poor CO<sub>2</sub> solubility at ambient temperature, except the bisurea **3**. The central, isophorone isocyanate-derived portion of the bisurea **3** is

asymmetric, hindering molecular assembly and hence reducing the probability for strong solute–solute interactions. This promotes higher solubility in carbon dioxide at lower temperatures while likely decreasing the potential that the molecules will aggregate in solution.

**Random Copolymers of 2-(Di-1H,1H,2H,2H-perfluorodecyl-L-aspartyl) Carbonylaminoethyl Methacrylate and Heptafluorodecyl Acrylate.** The phase behavior of acrylate copolymers in carbon dioxide is summarized in Table 2. The monomer (**5**) is a monourea compound and exhibits high solubility in liquid carbon dioxide at room temperature and modest pressures. From Scheme 2, it can be seen that the primary structural difference between polymers **6a**, **6b**, and **6c** is the relative ratios of fluoroacrylate and urea-containing monomers. If we treat the urea-containing monomers as potential physical cross-link points (through hydrogen bonding), then the cross-link density of the copolymer decreases as we move from **6a** to **6b** to **6c**. The trends shown in Table 2 can be rationalized if we examine the likely phase behavior of an analogous covalently cross-linked material in the presence of a compressible solvent such as CO<sub>2</sub>, as shown in the isothermal pressure–composition diagram, Figure 2a. In this analogy, the covalent cross-link corresponds to hydrogen bonded physical cross-links in our materials. Consider the “point” in this figure, which corresponds to a mixture with a specified overall polymer mole fraction at a given pressure. The system splits into two phases, a swollen gel whose volume is  $A/(A+B)$  and an essentially pure CO<sub>2</sub> phase with volume  $B/(A+B)$ . As the number of cross-link points along the chain is increased (via increases in the number of urea-containing monomers, **6c**  $\rightarrow$  **6b**  $\rightarrow$  **6a**), there is a decrease in the molecular weight between “cross-links”, and the phase boundary will tend to move to the right, as shown in Figure 2b. This corresponds to a reduced extent of swelling as the cross-link density increases. Conversely, if the cross-link density decreases, the curve shifts to the left.

Using the generic phase diagrams in Figure 2, we can rationalize the behavior of the gels formed from our model copolymers shown in Table 2. Entries (E6  $\rightarrow$  E5  $\rightarrow$  E4) correspond to an increasing concentration of



**Figure 2.** Phase behavior of a cross-linked material in the presence of a compressible solvent (such as CO<sub>2</sub>).

copolymer **6b** in CO<sub>2</sub>, which is equivalent to moving horizontally to the right in Figure 2a. Hence, it is not surprising that the volume of the swollen polymer phase increases (as segment A increases in Figure 2a), and then ultimately a single-phase system is produced as we cross the phase boundary. The same trend holds for entries (E3 → E2), corresponding to an increasing concentration of **6a** in carbon dioxide.

Raising temperature is equivalent to lowering the cross-link density because the extent to which the urea groups will associate through hydrogen bonding decreases steadily as the temperature is raised. Consequently, in entry E6 we see that raising the temperature serves to transform a two-phase mixture (25% swollen gel plus pure CO<sub>2</sub> phase) to a single-phase mixture of CO<sub>2</sub> and gel. However, surprisingly, this did not occur in E4 or E5, where a higher concentration was used—it is not clear why the system did not form a single phase.

Also somewhat surprising is the fact that the single-phase solution formed by heating the system in entry E6 to 353 K remains single phase upon cooling the system back down to 298 K. This could be due to a change upon heating from a system that is dominated by intrachain interactions to one where interchain interactions dominate. For example, Nguyen and Iverson<sup>12</sup> synthesized a polymer that contained both electron donors and acceptors in the main chain. Initially, this polymer adopted a helical configuration in solution owing to intrachain interactions between the electron donating and accepting groups. Upon heating, these interactions were eliminated; upon cooling a number of interchain interactions formed, creating a single-phase gel.

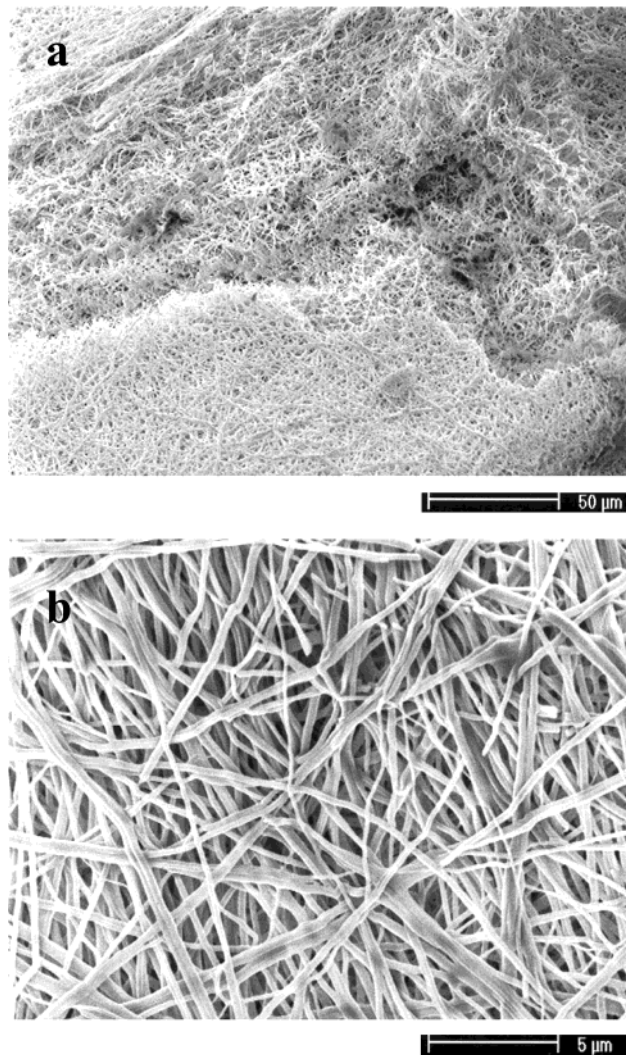
**Fluorinated Polyacrylate Urea (Poly(FAAUA)).** The results in Table 3 indicate that the fluorinated polyacrylate urea **9** was only soluble to 1 wt % in CO<sub>2</sub>. As this material has the highest “cross-link” density of any of the polymers, it is not surprising that it is the most difficult to dissolve in carbon dioxide.

**Gelation Behavior and Generation of Foams via CO<sub>2</sub> Removal.** In general, the behavior of the various

**Table 3.** Gelation Behavior of the Uea Compounds in Carbon Dioxide at 48.3 MPa (7000 psi)

sample	conc in CO <sub>2</sub> (wt %)	gelation behavior
<b>1a</b>	0.1, 1.0–5.0	stable foam
<b>1b</b>	0.1, 1.0–5.0	stable foam
<b>1c</b>	5.0	stable foam
<b>2</b>	5.0	foam <sup>a</sup>
<b>3</b>	5.0	powder
<b>4</b>	4.0	powder
<b>5</b>	4.7	foam <sup>a</sup>
<b>6a</b>	1.2–5.0	foam forms, collapses
<b>6b</b>	2.0	foam forms, collapses
<b>6c</b>	5.0	foam forms, collapses
<b>9</b>	1.0	powder

<sup>a</sup> Foam visibly exhibits shrinkage following complete CO<sub>2</sub> removal.

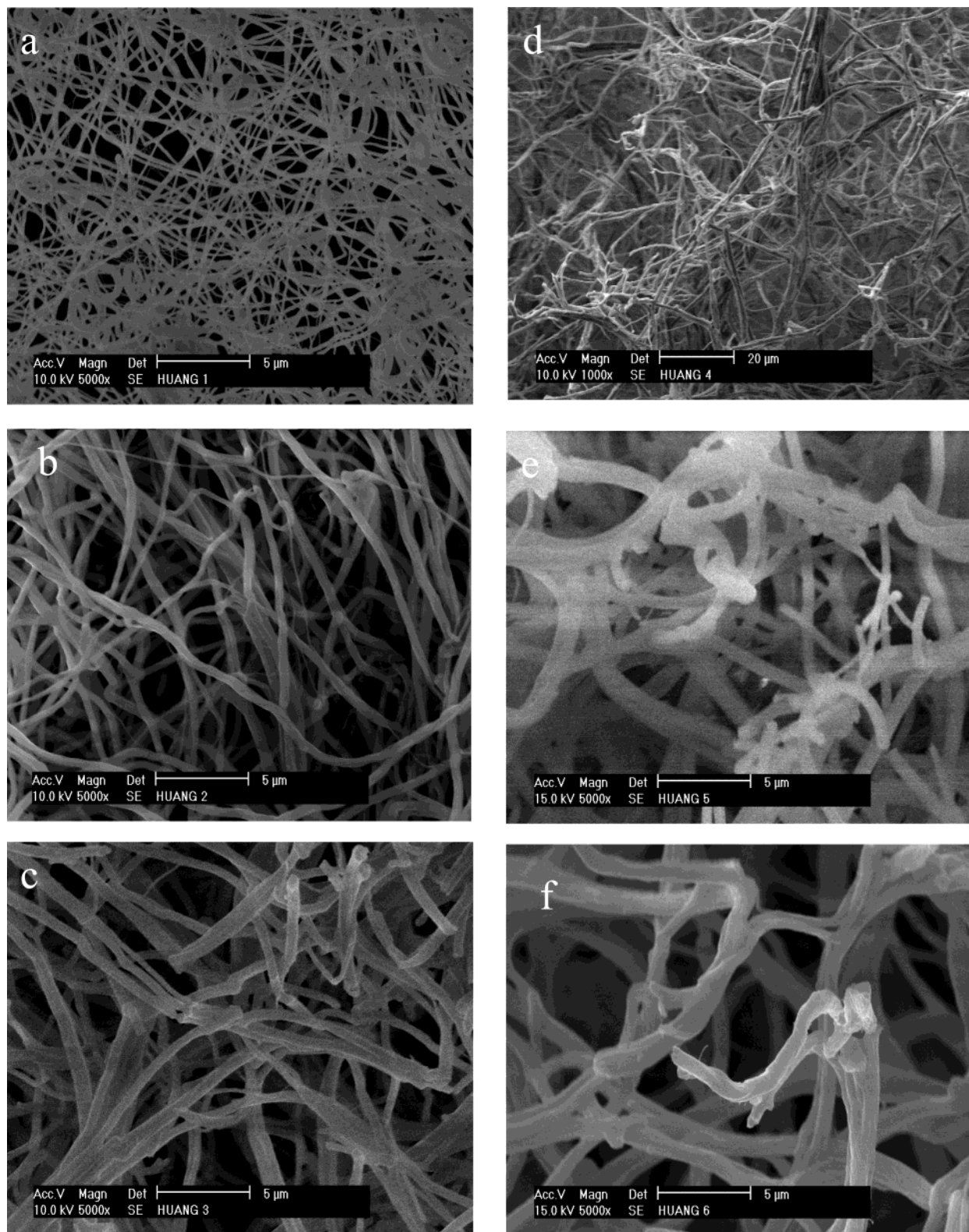


**Figure 3.** SEM images of the foams from carbon dioxide: (a) compound **5**, from a concentration of 4.7 wt % in carbon dioxide; (b) compound **2**, from a concentration of 2.2 wt % in carbon dioxide.

compounds in CO<sub>2</sub> reflects the degree to which they self-associate (number of physical cross-link points, strength of the interactions) versus the degree to which solute–CO<sub>2</sub> interactions dominate. If self-association via hydrogen bonding is too strong, the material will either not dissolve in CO<sub>2</sub> or will precipitate as a powder. If self-association is too weak versus interaction with CO<sub>2</sub>, the compound will dissolve easily but will require significant depressurization prior to precipitation, and

(12) Nguyen, J. Q.; Iverson, B. L. An Amphiphilic Folding Molecule That Undergoes an Irreversible Conformational Change. *J. Am. Chem. Soc.* **1999**, *121*, 2639.



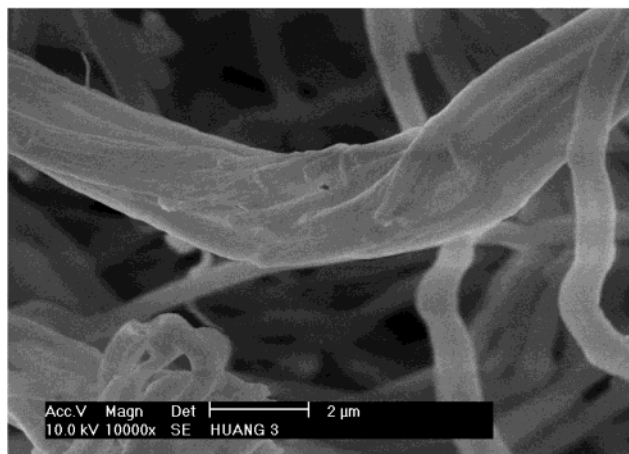


**Figure 4.** SEM images of the foams from triurea compound **1b** in carbon dioxide from concentrations of (a) 0.1 wt %, (b) 1.0 wt %, (c) 2.0 wt %, (d) 3.0 wt %, (e) 4.0 wt %, and (f) 5.0 wt %.

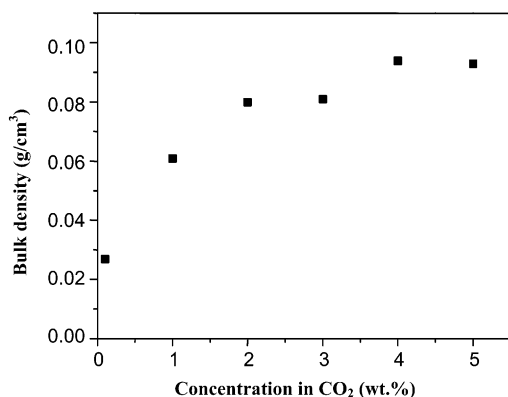
then the resulting foam will exhibit relatively large cells owing to less-than-adequate self-assembly.

The behavior of the various urea compounds with respect to foam formation in CO<sub>2</sub> is shown in Table 3. The compounds listed in Table 3 (see Schemes 1–3 for structures) exhibit differences in the number of urea groups per molecule, as well as differing extents of steric hindrance to self-assembly. For example, we note that

compounds **1a–1c** (3 ureas per molecule) and **2** (2 ureas per molecule) formed monolithic foams upon phase separation from CO<sub>2</sub>. Compounds **6a–6c** are polymeric, each containing over three urea groups per molecule. The polymer with the lower “urea density”, compound **6c**, dissolves easily at relatively high weight fraction (5%) but does not produce a foam that sustains its own weight following depressurization. Although the urea



**Figure 5.** Enlarged SEM image of the foam from triurea **1b** in CO<sub>2</sub> at a concentration of 2 wt %.



**Figure 6.** Bulk density of the foams from triurea compound **1b** in carbon dioxide at concentrations varying from 0.1 wt % to 5.0 wt %.

groups allow for the formation of physical cross-links, the fluoroacrylate comonomer promotes a low glass transition temperature ( $T_g$ ) for the copolymer, and hence the foam produced through depressurization is not physically stable at room temperature. Increasing the “urea density”, moving from **6c** → **6b** → **6a** makes it more difficult to achieve a single phase between polymer and CO<sub>2</sub>, yet formation of a stable foam is still not possible, owing to the low glass transition of the copolymer. Hence, in these materials, even though we can alter the balance of solute–solute interactions and solute–CO<sub>2</sub> interactions through alterations to the number of urea groups, the low glass transition of the fluoroacrylate comonomer prevents formation of a stable foam.

Copolymer **9** has the highest “urea density” of the various copolymers evaluated; it is therefore not surprising that elevated temperature is required to dissolve this material (even at only 1 wt %) in CO<sub>2</sub>. Copolymer **9** has a high enough  $T_g$  such that it is a solid at room temperature, but the self-interaction of this copolymer is sufficiently strong that powder, rather than a microcellular material, is produced upon lowering the temperature. Here the balance has swung too far toward solute–solute interaction, inhibiting dissolution in CO<sub>2</sub> and hence formation of a cellular material.

Compounds **3** and **4**, despite having only two urea groups per molecule, also precipitated as powders, possibly because the asymmetry in the precursor iso-

cyanate prevented extensive assembly in solution and hence the formation of a supramolecular network. Compound **5** (1 urea per molecule) was able to form a foam, but the material collapsed following removal of the CO<sub>2</sub>, suggesting that a single urea group per molecule does not provide enough sites for physical cross-link formation.

The SEM images of the foams formed from compounds **5** and **2** show a network of fibers (see Figure 3). Each of these foams exhibited shrinkage following removal of the CO<sub>2</sub> (after temperature-induced phase separation). Compound **5** produced a foam with visibly greater shrinkage than that for **2**, perhaps because **5** contains only one association point (urea) per molecule and hence cannot form a network to the same extent as compound **2**.

Triurea compounds **1a**, **1b**, and **1c** have more hydrogen bond donors and acceptors than the monourea and bisurea compounds, which should promote more effective aggregation and subsequent fiber formation. These compounds also have symmetric spacers between the hydrogen bonded moieties that contain some flexible and rigid functional groups; this combination should promote self-assembly of the molecules in solution. Compounds **1a–1b** produce similar foams through phase separation from CO<sub>2</sub>; the length of the fluoroalkyl “ponytails” did not significantly influence the phase behavior or foam morphology. Figure 4 shows the SEM images of the foams from triurea compound **1b** in carbon dioxide at concentrations varying from 0.1 to 5.0 wt %. Unlike the case of the foams from monourea and bisurea compounds (see Figure 3), there is significant void space between the fibers in the foam microstructure. The SEM images further revealed that the fibers formed at high substrate concentration in CO<sub>2</sub> appeared to be generated through assembly of thinner fibrils (Figure 5). The foams from triurea compound **1b** exhibit bulk densities lower than 0.09 g/cm<sup>3</sup> (see Figure 6). Compared to the case of the parent material, the bulk density of the foam is reduced by 92% to 98%.

**Thermal Conductivity.** The thermal conductivity of a triurea foam composed of **1a** was measured by Mathis Instruments using a hot disk thermal analyzer. The thermal conductivity of **1a** was 0.044 W/m·K. A conventional rigid polyurethane foam, for example, would exhibit a bulk density of approximately 0.03 g/cc (versus 0.03–0.09 g/cm<sup>3</sup> for compounds **1a–1c**) and a thermal conductivity of 0.022 W/m·K. It should be noted, however, that a rigid polyurethane foam generally exhibits a closed-cell morphology, while the foams generated here are “open-cell” types.

## Summary

Fluorinated urea compounds were designed and synthesized to form physical gels in supercritical carbon dioxide, forming microcellular foams upon removal of the carbon dioxide. As expected, hydrogen bond density and the structure of urea compounds play important roles in forming strong foams. The triurea compounds with a symmetric spacer in the hydrogen bond core and three association points per molecule provide an optimum structure to generate the strong microcellular foams. The SEM images show that these relatively strong foams have an open microstructure of interlock-

ing fibers with bulk density values of 0.03–0.09 g/cm<sup>3</sup> and thermal conductivity of 0.044 W/m·K. Collapsed foams with overlapping fibers were generated from monourea and bisurea compounds due to the diminished amount of hydrogen bonding sites per molecule. Although the fluorinated polyacrylate urea contained the greatest density of urea sites for associations, the high density of these CO<sub>2</sub>-phobic groups diminished CO<sub>2</sub> solubility. Further, strong intramolecular associations prevented the intermolecular self-assembly required for the generation of foams.

While the use of carbon dioxide as the solvent in a foam-making process has a number of “green” attributes, it is not clear that use of fluorinated building blocks for the foams is also sustainable (or economical).

As such, a major current<sup>13</sup> and future research thrust in our group is to design a truly CO<sub>2</sub>-philic material that does not include fluorine.

**Acknowledgment.** The authors would like to thank the U.S. DOE National Petroleum Technology Office for the financial support under Contract DOE-RA26-98BC15108. We would also like to thank Air Products, Cabot Oil and Gas, Bayer, and Universal Well Services for their support of this project.

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