

NOVEL CO<sub>2</sub>-THICKENERS FOR IMPROVED MOBILITY CONTROL

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By  
Dr. Robert M. Enick and Dr. Eric J. Beckman, University of Pittsburgh  
Dr. Andrew Hamilton, Yale University

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Prepared for  
U.S. Department of Energy  
Assistant Secretary for Fossil Energy

Jerry F. Casteel, Project Manager  
National Petroleum Technology Office  
P.O. Box 3628  
Tulsa, OK 74101

Prepared by  
University of Pittsburgh  
Department of Chemical & Petroleum Engineering  
1249 Benedum Engineering Hall  
Pittsburgh, PA 15261

Yale University  
Chemistry Department  
2250 Prospect Avenue  
New Haven, CT 06520-8107



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## Abstract

The carbon dioxide-solubility and carbon dioxide-thickening potential of the following compounds were evaluated: hydrocarbon-fluorocarbon copolymers, sulfonated hydrocarbon-fluorocarbon copolymers, semifluorinated trialkyltin fluorides, and small hydrogen-bonding compounds.

Random copolymers of heptadecafluorodecyl acrylate and styrene were synthesized, with the amount of styrene ranging between 22-40 mol%. The pressure required to dissolve the copolymer at a specified concentration increased with the mole fraction of styrene. Falling cylinder viscometry results indicated that the 29%styrene-71%fluoroacrylate copolymer induced the most significant increase in carbon dioxide viscosity yet recorded. For example, at 295K and 34.5 MPa, the viscosity of carbon dioxide increased by a factor of 10, 60 and 250 at concentrations of 1, 3 and 5wt%, respectively. This very significant increase was attributed to the "stacking" of the aromatic rings of the copolymer, causing the copolymer in solution to form linear macromolecular structures.

The sulfonation of a portion of the styrene monomers in the copolymers affected both the carbon dioxide-solubility and viscosity behavior of the solution. Due to the polar nature of the sulfonate groups, carbon dioxide solubility decreased. The association of these polar groups in solution resulted in an increase in viscosity.

A semifluorinated trialkyltin fluoride was found to exhibit carbon dioxide-solubility and viscosity-enhancing potential. An increase of carbon dioxide viscosity by a factor of 3 at a concentration of 4wt%. This increase is attributed to the formation of transient, linear, weakly associating polymer in solution.

Small H-bonding compounds were synthesized and characterized. Several of these compounds (usually white powders or waxes) have been evaluated in carbon dioxide. Some required heating of the carbon dioxide and the compound to achieve dissolution. Although many of these compounds precipitated out of solution upon cooling, several precipitated in the form of an interlocking network of fibers. These compounds are being redesigned to increase carbon dioxide-solubility, eliminate the need to heat for dissolution, and retain the ability to form viscosity-enhancing macromolecules.





## Executive Summary

The objective of this contract is to design, synthesize, and characterize thickening agents for dense carbon dioxide and to evaluate their solubility and viscosity-enhancing potential in CO<sub>2</sub>. Previously, fluoroacrylate homopolymers and fluorinated telechelic ionomers were shown to increase the viscosity of carbon dioxide by a factor of 3-4 at concentrations of 2-3 at concentrations of 4-5 wt%. This report details the findings for several new types of carbon dioxide thickening candidates. Hydrocarbon-fluorocarbon random copolymers, sulfonated hydrocarbon-fluorocarbon random copolymers, semifluorinated trialkyltin fluorides and small hydrogen-bonding compounds were evaluated.

Random copolymers of styrene and heptadecafluorodecyl acrylate were synthesized. The amount of styrene varied between 22-40 mole% in the copolymer. The fluoroacrylate monomer is very carbon dioxide-philic, while the styrene monomer is can be considered relatively carbon dioxide-phobic. Homopolymers of fluoroacrylate are extremely carbon dioxide-philic, while polystyrene is insoluble in carbon dioxide. Therefore, it was expected that as the fraction of styrene in the copolymer increased, carbon dioxide solubility would decrease. This was the case, in that the pressure required to dissolve a specified concentration of copolymer in carbon dioxide increased with the mole fraction of styrene in the polymer. Very large increase in viscosity were observed using these polymers. For example, falling cylinder viscometry results indicated that the 29%styrene-71%fluoroacrylate copolymer induced the most significant increase in carbon dioxide viscosity yet recorded. At 295K and 34.5 MPa, the viscosity of carbon dioxide increased by a factor of 10, 60 and 250 at copolymer concentrations of 1, 3 and 5wt%, respectively. This very significant increase may be the result of inter- and intramolecular "stacking" of the aromatic rings of the copolymer, causing the copolymer in solution to fold and form linear macromolecular structures. This copolymer also exhibited an "optimal" composition. The increase in carbon dioxide viscosity reached a maximum value for 29mol% styrene.

It was expected that the sulfonation of a portion of the styrene in the copolymer would lead to even more substantial viscosity increases. Previously, we demonstrated that the prescence of sulfonate groups on telechelic ionomers led to the formation of macromolecular networks as the polar, carbon dioxide-phobic sulfonate groups associated in solution. Therefore the sulfonation of a portion of the styrene of the fluoroacrylate-styrene copolymer was also expected to increase the ability to form macromolecular structures. Therefore, a copolymer of 78mol% fluoroacrylate and 22mol% styrene was synthesized. 27% of the styrene in the copolymer was then sulfonated. The carbon dioxide thickening capability of the copolymer did increase, as the carbon dioxide miscibility diminished. For example, at 41.3 MPa and 295K, a 5 wt% solution of the fluoroacrylate-styrene copolymer was 65 times as viscous as neat carbon dioxide. When the sulfonated analog of the compound was tested, it increased the solution viscosity by a factor of 85. As pressure was lowered to 20.7 MPa, the

copolymer remained soluble to at least 5wt%, but the sulfonated copolymer solubility decreased to about 3wt%.

A semifluorinated trialkyltin fluoride was also evaluated. (The hydrocarbon analog of this compound is a well-known alkane thickener.) This type of compound can establish linear, transient, weakly associating polymers in non-polar solvents. Therefore, tri(nonafluorohexyl) tin fluoride,  $(F(CF_2)_4(CH_2)_2)_3SnF$ , was synthesized under the direction of Dr. Dennis Curran of the University of Pittsburgh. This compound increased the viscosity of carbon dioxide by a factor of 3 at a concentration of 4wt%. A lower molecular weight compound, tri(trifluorobutyl) tin fluoride,  $(F(CF_2)(CH_2)_3)_3SnF$  was also synthesized. Carbon dioxide solubility and viscosity enhancing potential of this compound have not yet been determined.

A number of small hydrogen-bonding compounds designed to dissolve in carbon dioxide and increase the viscosity of carbon dioxide were also synthesized. The most promising candidates have urea functionalities for hydrogen-bonding that leads to the formation of viscosity-enhancing macromolecules. Fluoroalkane or fluoroether functionalities in the structure impart carbon dioxide-solubility and steric stability of the macromolecule. Many variations of these molecules are being considered to permit the rapid dissolution of the compound in carbon dioxide followed by the formation of macromolecular structures in solution. Polymerizable versions of these compounds are being designed that would enable the structure to be covalently bonded after the hydrogen-bonded orientation has been established.

## 1. Introduction

Carbon dioxide is used extensively as a solvent for enhanced oil recovery and as a well-fracturing fluid. In both applications, the low viscosity of the dense carbon dioxide diminishes the effectiveness of the process. For example, at reservoir conditions, CO<sub>2</sub> has a viscosity of only 0.03-0.10 mPa·s, while the oil being displaced has a viscosity between 0.1 and 50 mPa·s. Therefore carbon dioxide tends to “finger” from the injection well to the production well rather than sweeping through the formation in a more uniform manner. A substantial increase in the viscosity of the carbon dioxide is required to achieve this improved sweep efficiency. Well-fracturing with liquid carbon dioxide would also be more effective if the viscosity of carbon dioxide could be increased. “Thickened” CO<sub>2</sub> would be able to propagate wider fractures, diminish fluid leak-off and carry larger sand proppant particles further into the fracture.

Many investigators have attempted to address this problem by dissolving a small amount (0.1-2.0 wt%) of a “thickener” in CO<sub>2</sub>. The small amount of thickening additives is desirable to minimize process cost and formation damage caused by the deposition of the thickener in the reservoir. Our strategy for identifying a thickener is to impart carbon dioxide solubility via the incorporation of highly carbon dioxide-philic groups into the compound. Further, carbon dioxide-thickening capability is introduced by adding carbon dioxide-phobic functional groups that lead to inter- and intra-molecular interactions that form macromolecular structures in solution.

The new compounds investigated this quarter will be discussed in the following order: sulfonated and non-sulfonated fluoroacrylate-styrene random copolymers, semifluorinated trialkyltin fluorides, and small hydrogen-bonding compounds.

## 2. Random copolymers of fluoroacrylate and styrene

### 2.1 Experimental procedure

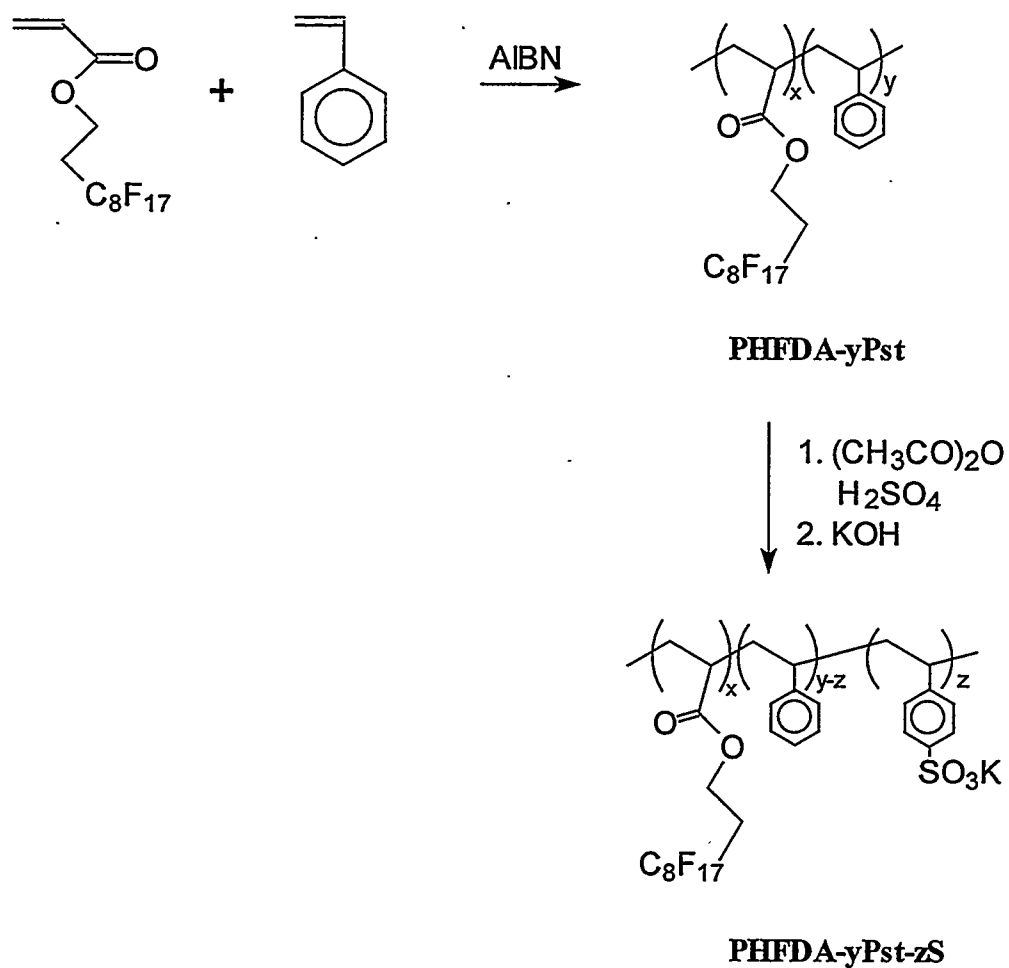
#### *Materials*

Styrene was purchased from Aldrich and was distilled under vacuum before use. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10,10-heptafluorodecyl acrylate (HFDA) was obtained from Aldrich and was purified in order to remove inhibitor before use. Other reagents and solvents were also from Aldrich and were used without further purification.

#### *Synthesis of copolymers and sulfonated copolymers*

Copolymers from HFDA and styrene monomers were obtained by bulk free radical polymerization using AIBN as initiator. The composition of the copolymers is listed in Table 1.

Copolymers were lightly sulfonated at 50 °C in 1,1,2-trichlorotrifluoroethane using acetyl sulfate as the sulfonating agent according to the procedure of Makowski et al<sup>1</sup>.



Scheme 1. Synthesis of copolymers and sulfonated copolymers

Table 1. Composition of copolymers

Polymer	Content of Polystyrene (mol.%)	
	Theoretical	By $^1\text{H}$ NMR
PHFDA-0.22Pst	0.22	0.258
PHFDA-0.25Pst	0.25	0.273
PHFDA-0.29Pst	0.29	0.292
PHFDA-0.33Pst	0.33	0.347
PHFDA-0.40Pst	0.40	0.403

Then the sulfonated copolymers were neutralized by using 0.1N KOH solution. . The average sulfonation level was determined by  $^1\text{H}$ -NMR. Scheme 1 shows the synthesis procedure.

#### *Characterization*

All samples were characterized by Mattson FT-IR and Bruker 300MHz NMR spectroscopies.

#### *Phase behavior and viscosity measurements*

See previous description in first quarterly report.

## *2.2 Results and discussion*

#### *Phase behavior*

It has been reported previously in the literature<sup>2</sup> and subsequently confirmed in our last quarterly report that the homopolymer of HFDA was very soluble in liquid carbon dioxide as indicated by low cloud pressure (below 1450 psi) up to 5 wt.%. Figure 1 illustrates the two-phase boundaries of mixtures of carbon dioxide and the copolymers. Apparently, the copolymer becomes difficult to dissolve in carbon dioxide with increasing the content of styrene in the copolymeric chain because styrene part is highly  $\text{CO}_2$ -phobic. When the content of styrene reaches 40 mol.%, at more that 3 wt.%, the copolymer will not dissolve in carbon dioxide at room temperature and pressure below 7000 psi.

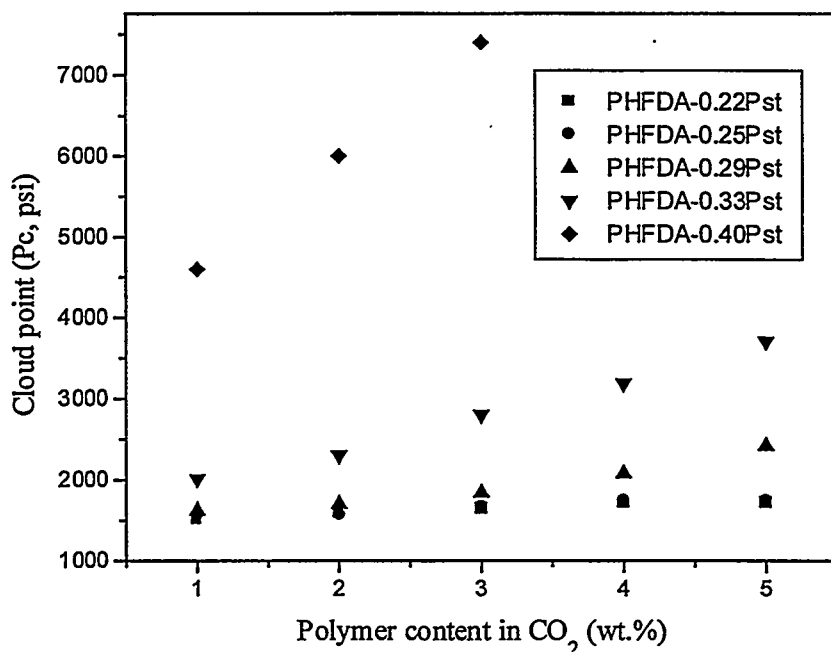


Figure 1. Phase behavior of copolymers in liquid carbon dioxide ( $T=25\text{ }^\circ\text{C}$ ).

The neutralized sulfonated copolymer (NSC) is more difficult to dissolve in carbon dioxide than the copolymer because the high-polarity salt is more CO<sub>2</sub>-phobic. Figure 2 illustrates the cloud point of NSC (PHFDA-0.22Pst-0.027S) solution in carbon dioxide at different concentration. Compare to the unsulfonated copolymer (PHFDA-0.22Pst), it is more difficult to dissolve in carbon dioxide, especially at high concentration. (.27 refers to 27% of the styrene in the copolymer being sulfonated.)

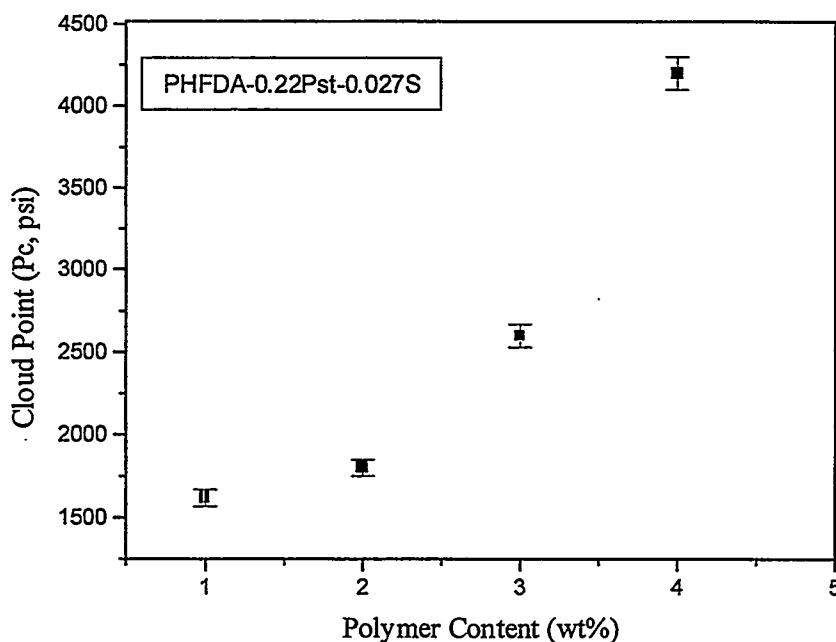


Figure 2. Phase behavior of neutralized sulfonated copolymers (PHFDA-0.22Pst-0.027S) in liquid carbon dioxide (T=25 °C).

#### *Viscosity behavior*

As sulfonated polystyrene exhibits thickening viscosity behavior in many non-polar organic solvent, the neutralized sulfonated copolymer (NSC) was found that it can significantly enhance the solution viscosity in liquid carbon dioxide. Figure 3 shows the relative viscosity of PHFDA-0.22Pst-0.027S – CO<sub>2</sub> solution to neat carbon dioxide. Obviously, this NSC copolymer can increase the solution viscosity by 90 fold at only 5 wt% concentration. In the meantime, we found that unsulfonated copolymer PHFDA-0.22Pst can also exhibit this kind viscosity-thickening behavior, although the degree of viscosity-thickening is lower than the former. Figure 4 shows the relative viscosity of PHFDA-0.22Pst – CO<sub>2</sub> solution to neat carbon dioxide. For NSC – CO<sub>2</sub> system, we believe that association of the acid or salt groups in the polymeric chain plays an important role in enhancing the solution viscosity. However, in unsulfonated copolymer

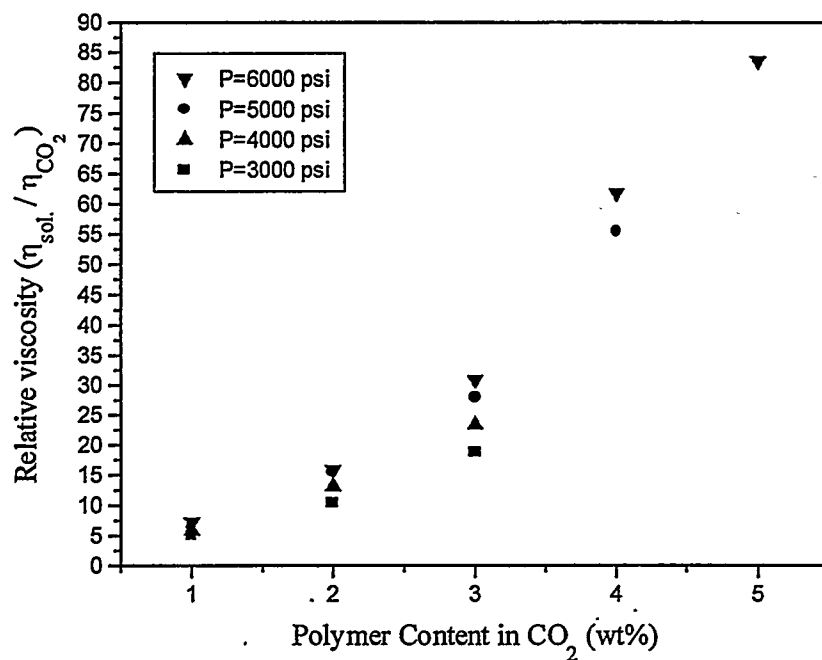


Figure 3. Relative viscosity of PHFDA-0.22Pst-0.27S of various polymer content in liquid carbon dioxide at room temperature.

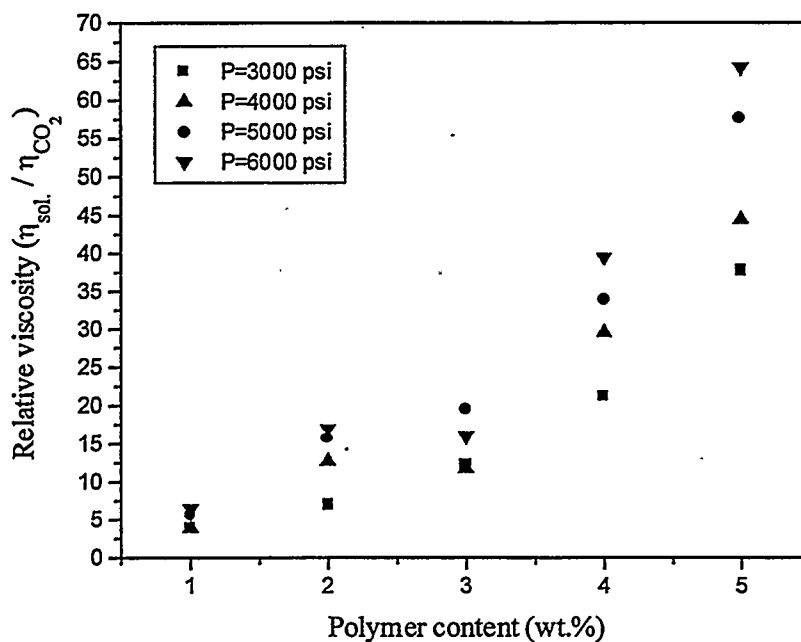


Figure 4. Relative viscosity of PHFDA-0.22Pst of various polymer content in liquid carbon dioxide at room temperature.



— CO<sub>2</sub> system, the packing of styrene groups may be the main reason to increase the solution viscosity, because we found that copolymers of fluorinated acrylate and hydrocarbon acrylate (N,N-dimethylamino ethyl acrylate) which *do not* have the aromatic packing structure *did not* exhibit thickening viscosity behavior.

The above results lead us to study the viscosity behavior of other unsulfonated copolymers. Figure 5 illustrates the relative viscosity of unsulfonated copolymer – CO<sub>2</sub> solution to neat carbon dioxide. It was found that the sample of PHFDA-0.29Pst has highest efficiency in increasing the viscosity. Figure 6 shows this result. At low concentration, these polymers do not exhibit significant viscosity-thickening behavior, except that PHFDA-0.29Pst sample can increase the solution viscosity to 11 folds at concentration of 1 wt.% (Figure 7).

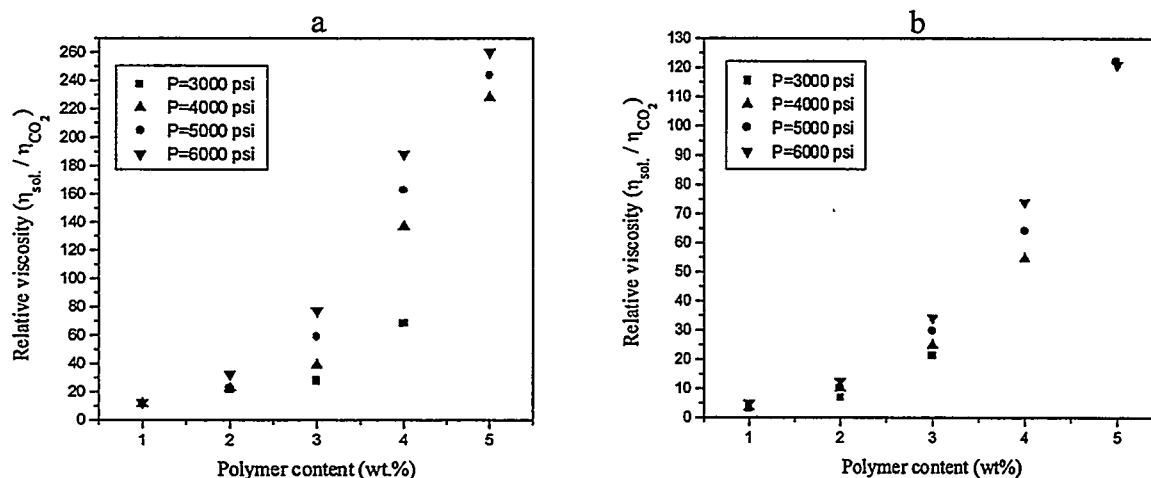


Figure 5. Relative viscosity of copolymers of various polymer content in liquid carbon dioxide at room temperature. (a) PHFDA-0.29Pst (b) PHFDA-0.33Pst

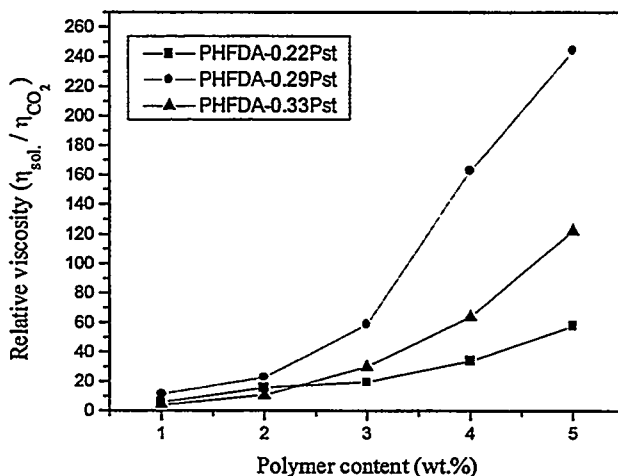


Figure 6. Relative viscosity of copolymers in liquid carbon dioxide at room temperature and pressure of 5000psi.

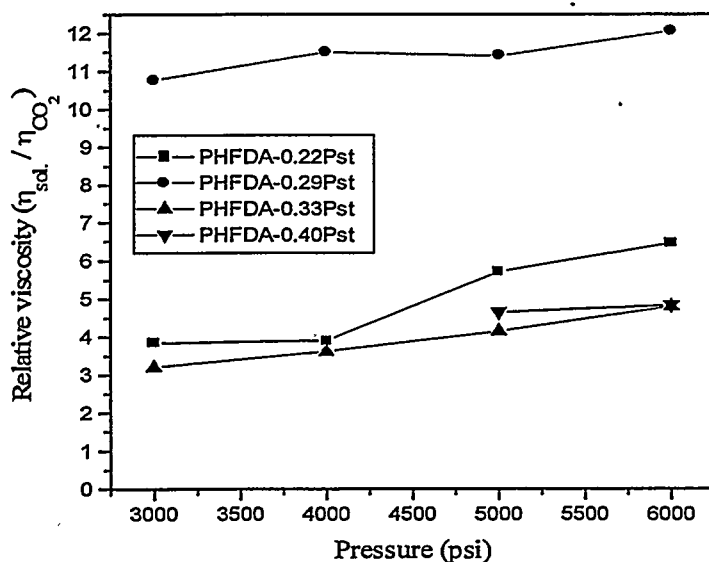


Figure 7. Relative viscosity of copolymer with concentration of 1 wt.% in liquid carbon dioxide at room temperature.

#### *Repeat measurement*

Due to influence of shear rate of the falling cylinder, the obtained relative viscosity may be different by using cylinders with different falling velocity in carbon dioxide. We repeated to measure the relative viscosity of PHFDA-0.29Pst sample by using a fast falling cylinder. Figure 8 illustrates the relative velocity of two falling cylinders (F and S). The velocity of cylinder F is about as 3 times as that of cylinder S that was used in former measurements. Figure 9 shows the relative viscosity of PHFDA-0.29Pst – CO<sub>2</sub> solution to neat carbon dioxide with cylinder F and S, respectively. Obviously, the copolymer exhibits significant thickening viscosity behavior, although the cylinder with high falling velocity was used.

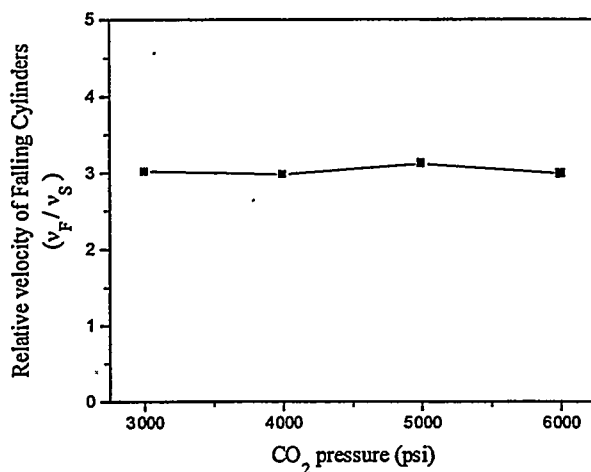


Figure 8. Relative falling velocity of cylinder F to cylinder S.

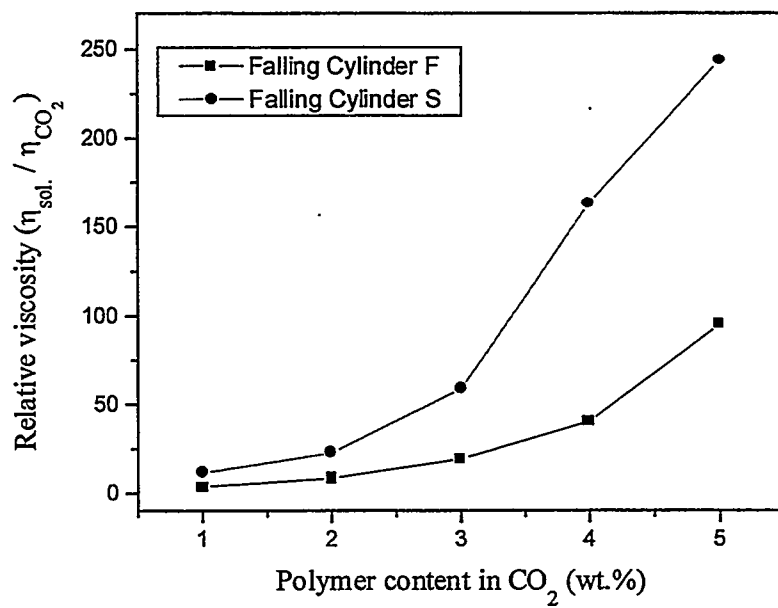


Figure 9. Relative viscosity of PHFDA-0.29Pst in liquid carbon dioxide by using cylinders F and S, respectively. (P=5000psi, room temperature)

### 3. Low Molecular Weight Associating Compounds, Semifluorinated Trialkyltin Fluorides and Hydrogen-bonding compounds

#### 3.2 Introduction

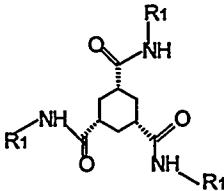
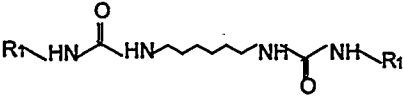
Two types of low molecular weight associating compounds were synthesized: (1) compounds that are able to associate through hydrogen bonding interactions of amide and urea groups; (2) tin-fluoride compounds that are believed to associate through the interactions between the electronegative fluorine atoms and electropositive tin atoms.

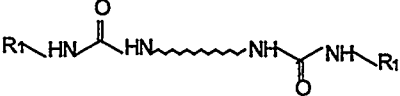
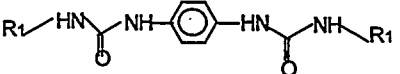
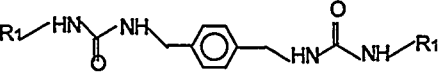
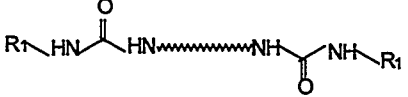
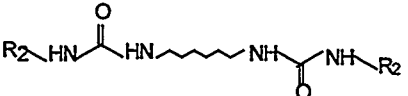
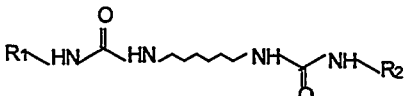
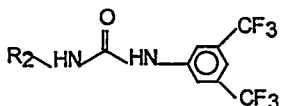
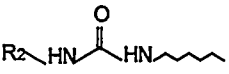
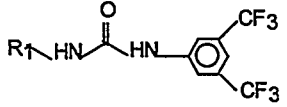
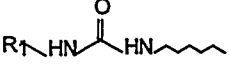
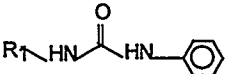
#### 3.2 H-Bonding Compounds

Researchers have found that some simple low molecular weight compounds can form linear rod-shaped structures through hydrogen bonding interactions when dissolved in organic solvents and lead to formation of gels at concentrations of approximately 1 wt%. Usually, due to the polar hydrogen bonding groups present in the molecular structures, heating is required to disrupt the hydrogen bonding in solid samples and dissolve the compounds in organic solvents. Upon cooling, the hydrogen bonding between diluted compound molecules directs the formation of aggregates in the solvent environment, which is the macroscopic "gel formation". The hydrogen bondings are so strong that even at concentrations lower than 1 wt%, thermoreversible gels can form in some organic liquids to achieve significant viscosity increase.

In the compound that we synthesized, Amide or urea functionalities were chosen to provide intermolecular interaction sites. Fluoroalkyl and fluoroether functionalities—previously proven to be CO<sub>2</sub>-philic—were incorporated into the molecular structure to increase the compound solubility in CO<sub>2</sub>. These fluorinated side chains are presumed to be able to further associate through Van der Waals interactions to form infinite networks.

The H-bonding compounds that we synthesized are listed below:

Compounds	structures	H-bonding functionalities	presumed structure network
cyclohexane-1,3,5-triamide		3	one-dimensional
hexyl-1,6-bisurea		2	two-dimensional

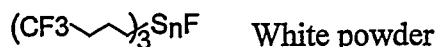
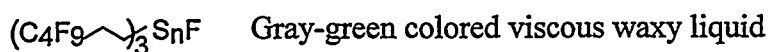
1,12-dodecyl bisurea		2	two-dimensional
1,4-phenylene bisurea		2	one-dimensional
1,4-xylene bisurea		2	two-dimensional
fluoroether backbone bisurea		2	two-dimensional
fluoroether paddle 1,6-hexyl bisurea		2	two-dimensional
fluoroether fluoroalkyl hybrid paddle 1,6-hexyl bisurea		2	two-dimensional
fluoroether bis(trifluoromethyl)phenyl urea		1	one-dimensional
fluoroether hexyl urea		1	one-dimensional
fluoroalkyl bis(trifluoromethyl)phenyl urea		1	one-dimensional
fluoroalkyl hexyl urea		1	one-dimensional
fluoroalkyl phenyl urea		1	one-dimensional

\* R<sub>1</sub>: fluoroalkyl aspartate; R<sub>2</sub>: fluoroether aspartate.

### 3.3. Tin-Fluoride Compounds

Trialkyltin fluorides were found to be effective thickening agents for light alkanes. This type of compounds dissolve in light alkanes at room temperature and form stable, highly viscous and transparent solutions even at a concentration as low as 0.2 wt%. The possible mechanism is that the electronegative fluorine atoms interact with the electropositive tin atoms in another molecule, thus form a linear macromolecular structure and the solvents were accordingly thickened. Common trialkyltin fluorides are not soluble in CO<sub>2</sub>, however, which leads to our development of CO<sub>2</sub>-soluble fluorinated analogues: semifluorinated trialkyltin fluorides.

Two fluorinated trialkyltin fluorides were synthesized with the following structures.



### 3.4 Synthesis and Characterization

For the synthesis of the above urea or amide samples, deprotected fluoroalkyl or fluoroether aspartate amines were first synthesized, and later reacted with commercially available isocyanates or acid chloride to give the final products.

#### 3.4.1. Synthesis of Deprotected Fluoroalkyl Aspartate Amine

Typically, in a 100ml 3-neck flask equipped with a stirring bar, charge 100ml dichloromethane, 7.88g 1H,1H,2H,2H perfluorodecanol (0.017mol) was added and the flask was cooled in an ice bath. 2g N-Boc-Asp (0.0086mol) and 3.28g (0.017mol) EDCI were subsequently charged to the reaction mixture. Start stirring until most of the reactants were dissolved. 1.05g DMAP (0.0086mol) was then introduced. The reaction mixture was kept in the ice bath for 30 min, then the ice bath was removed and reaction was kept at room temperature overnight.

The reaction mixture was then diluted with 100ml chloroform and transferred to a separatory funnel. The organic layer was washed with 50ml 1%HCl twice, and 50ml brine once and dried over sodium sulfate. Solvents were later removed to yield a pale yellow solid. The solid was dissolved in a minimal amount of dichloromethane (freon was added if necessary). The solution was transferred to a silica column and washed with chloroform. A pale translucent product layer was recovered and solvent removed under vacuum. White solid aspartate was obtained with 80% yield.

The obtained aspartate diester was subject to deprotection with trifluoroacetic acid. Typically, 5g aspartate was deprotected with 10ml trifluoroacetic acid in 20ml

dichloromethane for 4 hours. The solvent was removed under reduced pressure. Chloroform was added and removed under vacuum until a white solid formed. The solid was recrystallized from 200ml ethanol and cooled in a fridge for 3 hours. The solid was collected and dried under reduced pressure. The deprotected aspartate amine was a needle-shaped white solid with 78% yield.

#### *3.4.2.Synthesis of Deprotected Fluoroether Aspartate Amine*

Similar to the synthesis of fluoralkyl aspartate, fluoroether aspartate was synthesized in 100ml cooled ethyl acetate-freon mixture (1:1 v/v) with Krytox fluoroether alcohol and N-CBZ-Asp as the reactants. After reaction, most solvents were removed and the concentrated oil was washed with 50ml ethyl acetate twice, 50ml ethanol once, and 100ml 1% HCl twice. The residue was then diluted with 50ml freon and dried over sodium sulfate. Vacuum evaporate most freon until the residue reached a volume of 20-30ml. The yellow-colored solution was then purified over a silica column and washed down with 1:1 ethyl acetate-freon mixture. Solvents were later evaporated and yield a colorless oil.

The fluoroether aspartate diester were then deprotected by hydrogenation with  $\text{Pd}(\text{OH})_2$  as the catalyst. Typically, 5.0g fluoroether aspartate diester was dissolved in 20ml perfluoro1,3-dimethyl cyclohexane, 0.25g palladium hydroxide on carbon catalyst was added.  $\text{N}_2$  was passed through the reaction flask to displace air before hydrogen was introduced. The diester was deprotected with hydrogen for 12 hours, then catalyst was removed by filtration (Whatman #1 filter), residual fine catalyst powder was removed by Millipore membrane filter (0.45 $\mu\text{m}$ ). The solvent was removed under vacuum and residue washed with ether. Yellowish oil sample was then dried under vacuum.

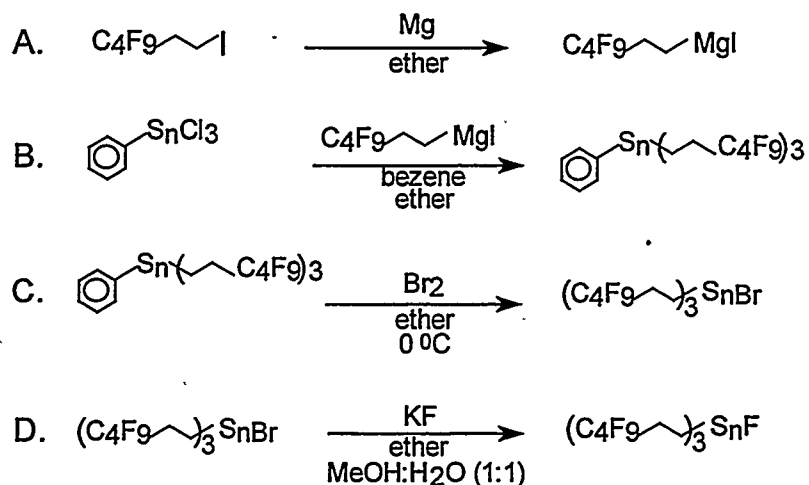
#### *3.4.3.Synthesis of Amide and Ureas*

The deprotected fluoroalkyl or fluoroether aspartate amines were then reacted with stoichiometric amounts of different commercially available isocyanates to give ureas of different structures. Fluoroalkyl aspartate amine was reacted with 1,3,5-cyclohexane triacid chloride to give the triamide product.

Typically, the reaction between fluoroalkyl amine and isocyanates were carried out in 50ml dichloromethane with triethylamine as the catalyst. The product fluoroalkyl ureas are white solids and collected by filtration and washed with 1% HCl and hexanes and then dried under vacuum. The fluoroether ureas were obtained by reacting the deprotected fluoroether amine with different isocyanates in 50ml freon, with triethylamine as the catalyst. After reactions, solvent was removed by reduced pressure and oily product washed with 1% HCl and hexanes and dried. The fluoroalkyl-fluoroether hybrid paddle bisurea was obtained in two steps. The first step generated a urea with isocyanate end functionality by using excessive amount of isocyanate. In the second step, the remaining isocyanate was reacted with a different amine to yield the hybrid structure.

### 3.4.4. Synthesis of Fluorinated Trialkyltin Fluorides

The synthesis of the two fluorinated tin fluoride analogues were carried out with the help of Dr. Curran's group in Chemistry Department at University of Pittsburgh. The synthesis routes are described below, with semifluorinated trihexyl tin fluoride synthesis as an example.



### 3.5. Characterization

The synthesized ureas were characterized by taking IR spectra on a Mattson Polaris FT-IR. Solid samples were mixed with KBr and compressed into pellets before taking the spectra. Liquid samples were prepared in the form of thin films between NaCl windows.

The IR spectra for fluoroalkyl ureas are similar, showing N-H stretching absorbance at  $3350\text{--}3360\text{ cm}^{-1}$ , C-H stretching at  $2940\text{--}2990\text{ cm}^{-1}$ , carbonyl absorbance around  $1735\text{--}1745\text{ cm}^{-1}$ , N-H scissoring absorbances at  $1630$  and  $1570\text{ cm}^{-1}$  respectively.

The IR spectra for fluoroether ureas usually show N-H stretching absorbances at  $3340\text{--}3350\text{ cm}^{-1}$ , C-H stretching at  $2940\text{--}2980\text{ cm}^{-1}$ , carbonyl absorbance around  $1760\text{--}1770\text{ cm}^{-1}$ , and two N-H scissoring absorbances at  $1650$  and  $1570\text{ cm}^{-1}$ .

### 3.6 $\text{CO}_2$ Solubility and Viscosity Results

#### 3.6.1. Solubility of H-Bonding Compounds and Network Formation in $\text{CO}_2$

The solubility and network formation/viscosity increase results of the H-bonding compounds in  $\text{CO}_2$  were listed in the table below. Solubility and gelling results in fluorinated liquids were also shown.



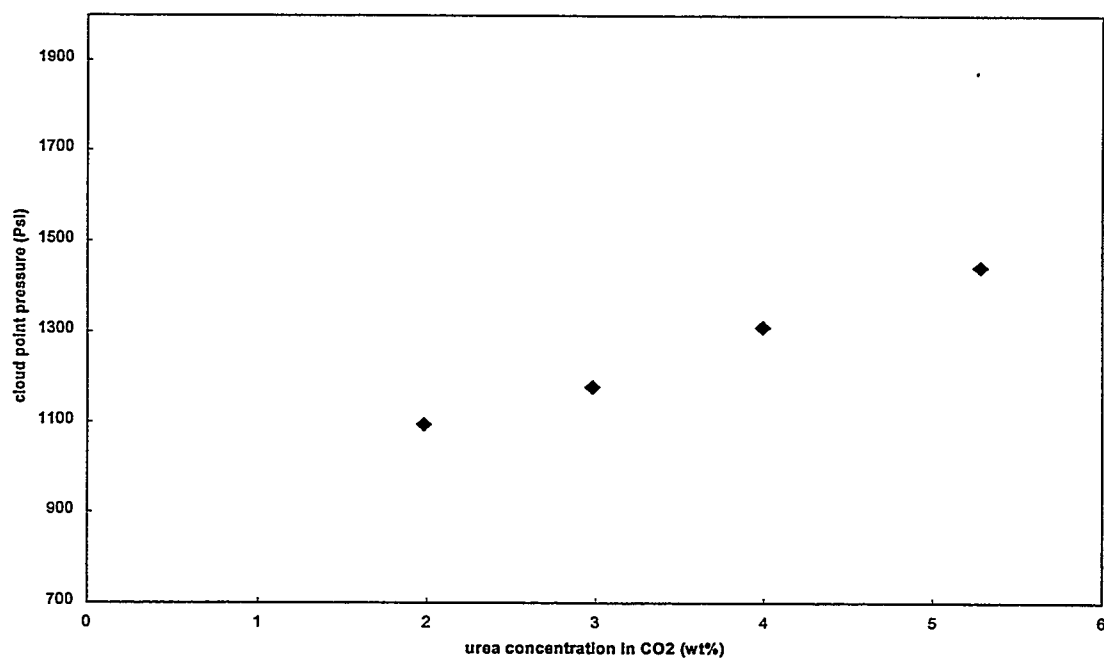
Compounds	Fluorinated Liquids		CO <sub>2</sub>
	Freon 113	PFDMCH	
cyclohexane-1,3,5-triamide	insoluble	insoluble at room T soluble when heated gel at 1wt%	soluble at 90 °C, 6000 Psi, 2.5wt% precipitated as fine powder upon cooling
hexyl-1,6-bisurea	insoluble	insoluble at room T soluble when heated gel at 1wt%	soluble at 90 °C, 6000 Psi, <4.86wt% When cooled, integrated rigid network at 2.95-4.86wt%; collapsed network at 2.18%; gel formed at 4.26% urea, 22.53%PFDMCH, 73.21% CO <sub>2</sub> , see SEM.
1,12-dodecyl bisurea	insoluble	insoluble at room T soluble when heated gel at 1wt%	soluble at 90 °C, 6000 Psi, 3.96 wt%. When cooled, form collapsed network, see SEM.
1,4-phenylene bisurea	insoluble	insoluble at room T soluble when heated gel at 1wt%	soluble at 100 °C, 6000 Psi 1.94 wt%. When cooled, precipitated as powder
1,4-xylene bisurea	insoluble	insoluble at room T soluble when heated gel at 1wt%	soluble at 100 °C, 6000 Psi 3.35 wt%. When cooled, precipitated as powder
fluoroether backbone bisurea	insoluble	insoluble at room T form loose network at 1wt%	soluble at 90 °C, 6000 Psi 4.82, 2.46 wt%. When cooled form loose floating fibers

fluoroether paddle 1,6-hexyl bisurea	soluble	soluble at room T no gel	soluble at room T, 2200 Psi, 1.5-5 wt%, no gel, no viscosity increase
fluoroether fluoroalkyl hybrid paddle 1,6- hexyl bisurea	insoluble	insoluble	soluble at 80 °C, 6000 Psi precipitated when cooled
fluoroether bis(trifluoro- methyl)phenyl urea	soluble	soluble no gel	not tested
fluoroether hexyl soluble urea	no gel	soluble	not tested
fluoroalkyl bis (trifluoro- methyl)phenyl urea	soluble gel at 5wt%	soluble gel at 1-5wt%	<b>soluble at room T, 2200 Psi no gel, viscosity to be tested 5.28wt%. network formed on venting CO<sub>2</sub>, see SEM</b>
fluoroalkyl hexyl urea	soluble gel at 1wt%	insoluble gel at 1wt%	<b>soluble at room T, see fig.1. for phase behavior, viscosity to be measured. Network formed on venting CO<sub>2</sub>, see SEM</b>
fluoroalkyl phenyl urea	insoluble gel at 1wt%	insoluble gel at 1wt%	to be tested

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The important thing about these H-bonding compounds is that by finely adjust the structures, the compounds can be made to be soluble in CO<sub>2</sub> and form networks as proven by SEM characterization. Currently we found two compounds with only one urea functionality in the molecular structures to be soluble in CO<sub>2</sub>. The fluoroalkyl bis(trifluoromethyl)phenyl urea and the fluoroalkyl hexyl urea. The former formed a microcellular foam, and the latter formed an open-cell foam structure when CO<sub>2</sub> was vented. The fluoroalkyl hexyl urea was soluble at concentration up to 4.33 wt% at room T, 6000Psi over a long time span. When the pressure was decreased to 5000 Psi, loose fibillar networks fell out of solution. The fluoroalkyl bis(trifluoromethyl)phenyl urea, however, was quite soluble in CO<sub>2</sub> as can be seen from the phase behavior data in Fig.1.

**Fig.1. Phase Behavior of Fluoroalkyl Bis(trifluoromethyl)phenyl Urea-  
CO<sub>2</sub> Solution, T=26 °C**



**Fig.2. Phase Behavior of Semifluorinated Trihexyl Tin Fluoride-  
CO<sub>2</sub> Solution, T=24 °C**

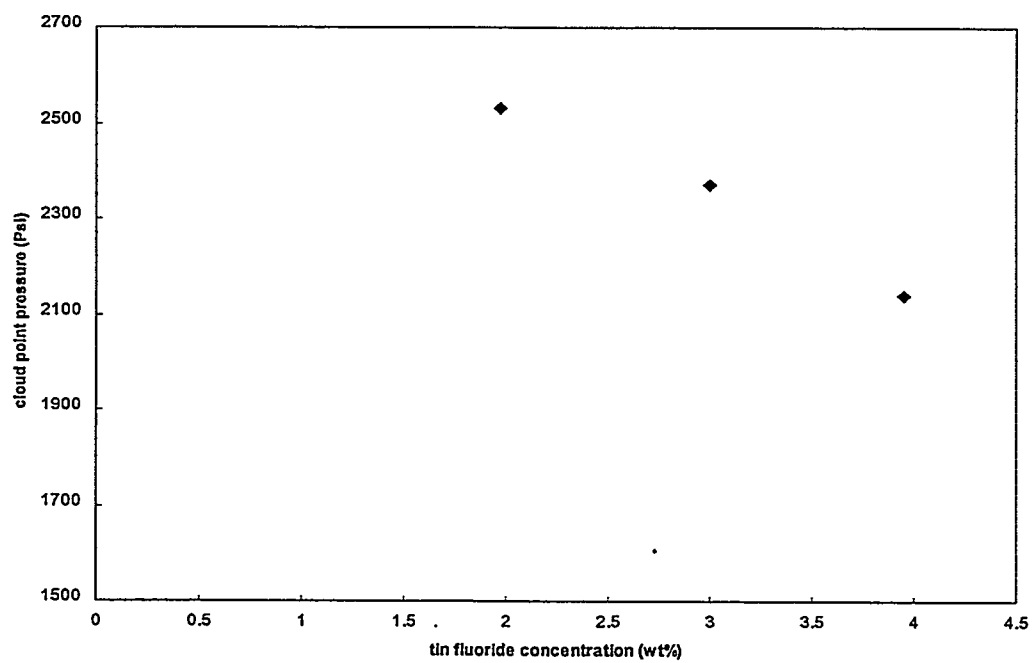
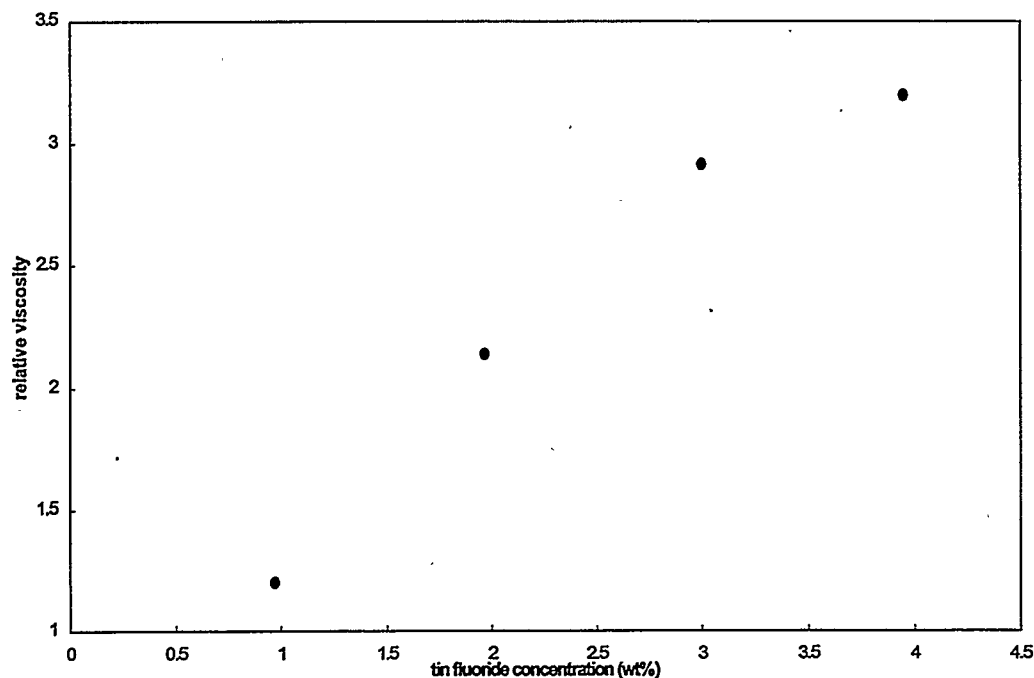


Fig.3. Relative Solution Viscosity of semifluorinated trihexyl tin fluoride-CO<sub>2</sub> solution, T=24 °C



### 3.2. Phase Behavior and Viscosity Increase of Fluorinated Tin Fluoride in CO<sub>2</sub>

The semifluorinated trihexyl tin fluoride were tested in CO<sub>2</sub> and the phase behavior and solution viscosity were shown in Fig 2. and 3. It can be seen that the fluorinated analogue was quite soluble in CO<sub>2</sub> at room T and is able to increase solution viscosity by about 3 times at a concentration of 3.95 wt%.

## 4.0 Advanced hydrogen-bonding compounds

During the past project period we (Dr. Hamilton's group at Yale University) have made important progress in our search for novel and effective gelators of supercritical CO<sub>2</sub>. In particular we have been focusing on analysis and optimization of the gelation properties of a series of bis-urea derivatives. In order to facilitate rapid analysis and identification of good gelling agents we have investigated the gel properties of these derivatives in perfluorinated organic solvents, before sending the optimized compounds to our collaborators in Pittsburgh for study in CO<sub>2</sub>.

### *4.1 Structure - Gelation activity relationship*

We have now prepared a small family of mono- and bis-urea derivatives and analyzed their ability to gel perfluorinated organic solvents. The structures and gelling properties of these compounds are shown below.

### *4.2 Synthesis and polymerization of diacetylene-bis-urea derivatives*

We are investigating different routes to polymerize our family of bis-urea organogelators for two reasons :

- a) Stabilization of the gels by covalently linking the strands.
- b) The polymerization would give us some insight of the primary structure of the strands because of spatial disposition of the acetylenes for polymerization to occur.

In order to test our hypothesis of diacetylene bis urea polymerization we have synthesized three alkyl substituted bis-ureas. (Fig 1) The butyl, octyl and benzyl substituents were synthesized in 69, 77 and 51 % respectively.

The octyl and benzyl substituents turned light blue as they were being filtered, indicating a small amount of polymerization. This has been also observed by others when polymerizing molecules of similar type.

However the octyl substituted derivative remained a cream color. This compound was dissolved in DMSO with slight heating. When it was allowed to cool to room temperature small clear crystals formed.

Following are some observation made about these crystals:

- a) Within 24 hours the crystals turn light blue in color and cannot be redissolved in DMSO.
- b) When the light blue crystals are irradiated with short UV wave radiation for 30 minutes they turn red-violet.
- c) When the light blue crystals are heated they turn red.
- d) The light blue crystals will remain that color for up to 2 weeks. However after 3 weeks they turn a shiny black color, which indicates polymerization and metal like conjugation.

Attempts to grow x-ray quality crystals of the octyl derivative are currently in progress.

Polymerization of bis-urea diacetylene compounds occurs at room temperature at a relatively slow rate (ideal for easy manipulation of such compounds). Therefore the synthesis of a polymerizable

organogelator was undertaken (Fig 2) This compound shows gelation of acetonitrile and hexanes. The acetonitrile gel is cloudy, but when irradiated with short wave UV radiation the gel turns a salmon color.

When the solvent evaporates the color changes to red and the compound does not redissolve in the solvent.

We are currently investigating the full implications of these color changes as they relate to the polymerized state of the gelator and the thermal stability of the gel.

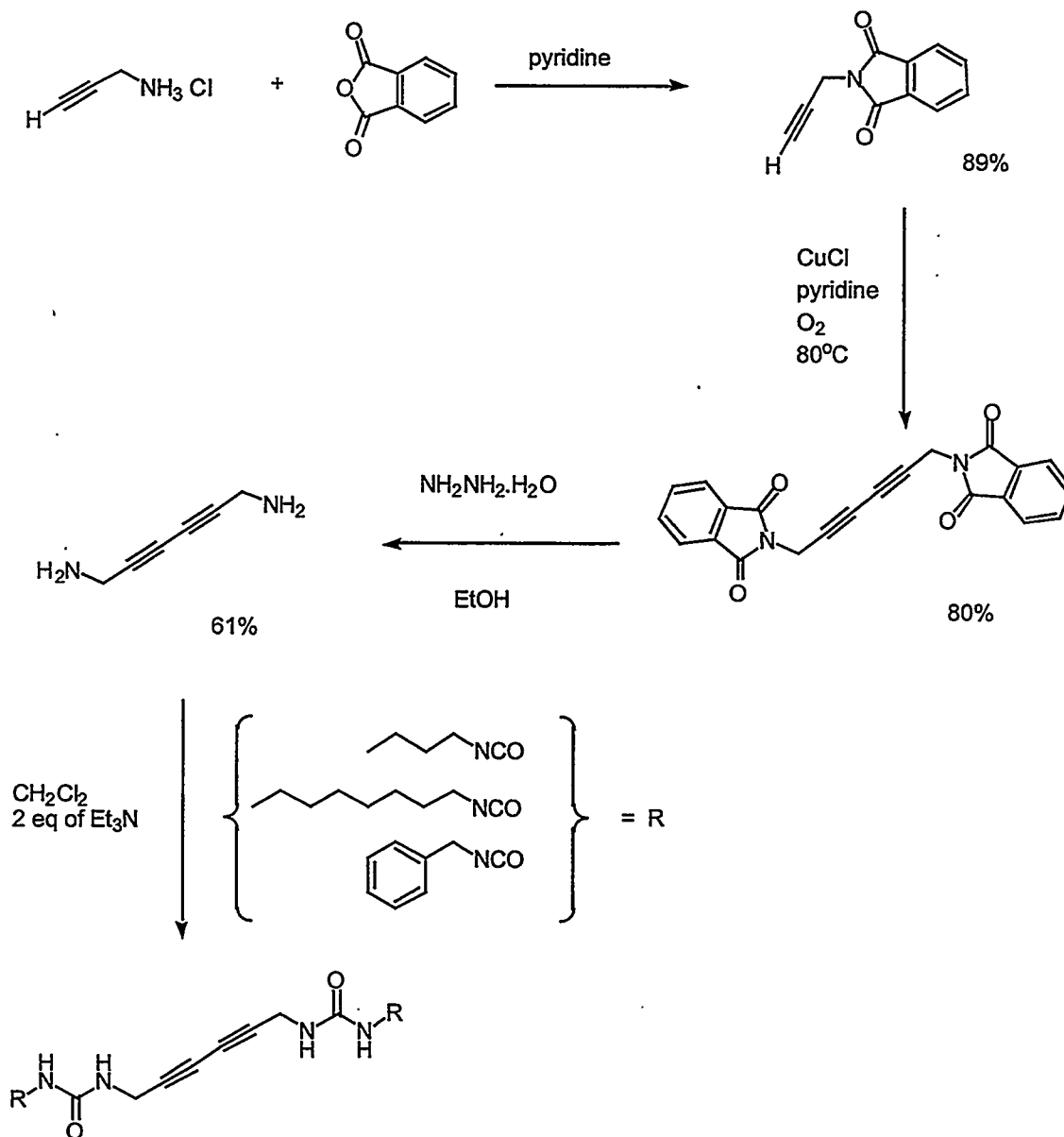


Fig 1. Synthesis of alkyl substituted bis-ureas.

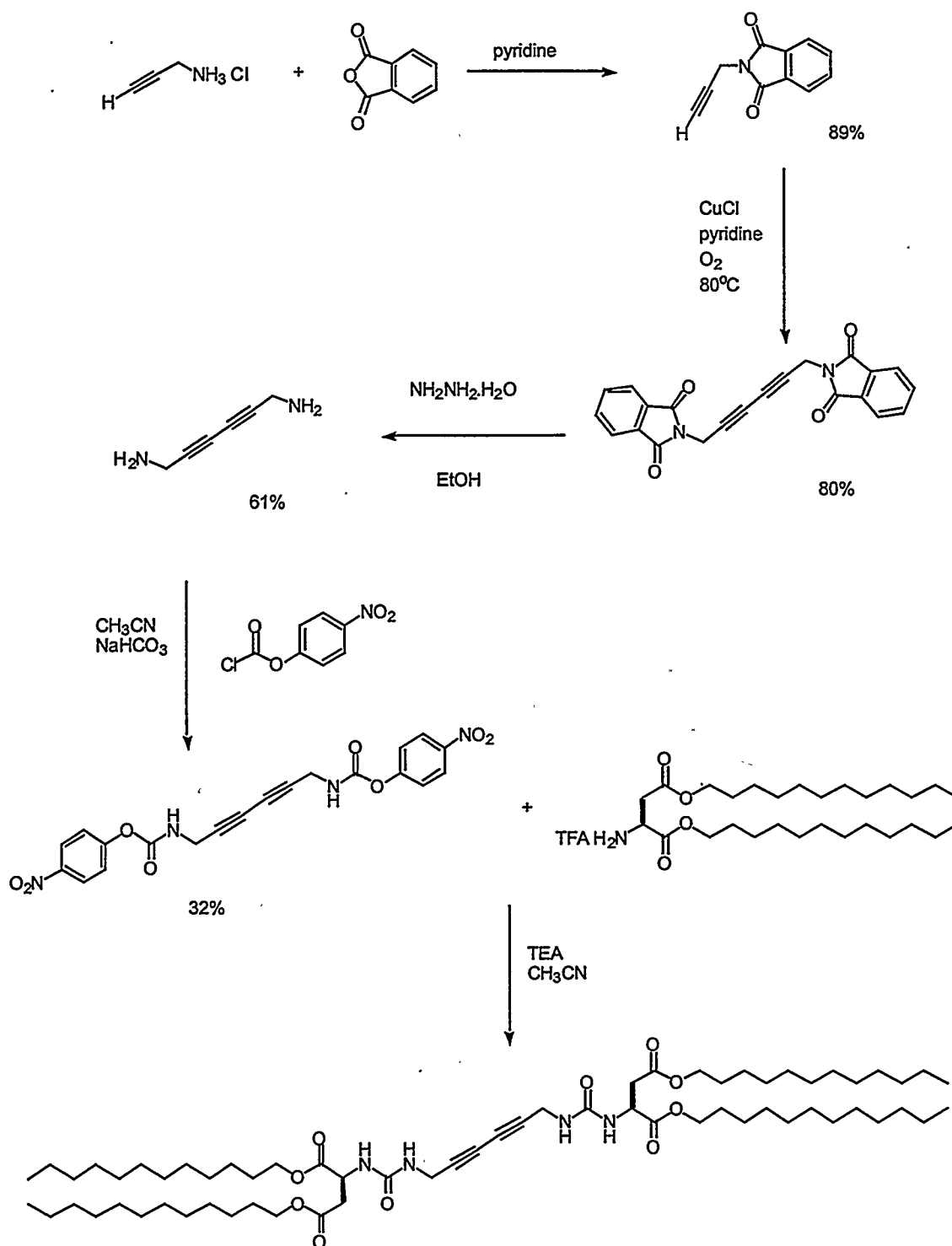


Fig 2. Synthesis of bis-urea diacetylene organogelators.





## 5. References

1. Makowski, H.S., Lundberg, R.D., Singhal, G.H., U.S. Patent 3,870,841, 1975
2. Enick, R.; Beckman, E.; Shi, C.; Karmana, E.; *J. Supercritical Fluid*, **13**, 127-34, 1998.