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NOVEL CO₂-THICKENERS FOR IMPROVED MOBILITY CONTROL

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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.

A series of falling cylinder viscometry experiments were conducted that demonstrated the shear-thinning behavior of the fluoroacrylate-styrene carbon dioxide-thickening agents. Further, it was demonstrated that approximately 0.2 wt% of these compounds must be employed to yield a significant (factor of at least 2) increase in carbon dioxide viscosity. At concentrations up to 5wt%, several hundred-fold increases in viscosity were detected.

An extensive amount of research was conducted on the small H-bonding compounds. Some of these agents were able to increase the viscosity of carbon dioxide by a factor of 2-3 at concentrations up to 5 wt%. Many of these compounds yielded highly porous, rigid, microcellular or microfibrillar foams upon colloing and/or depressurization. Although not desirable for CO₂ viscosity-enhancement in porous media, these high porosity (>95%) microcellular (cells less than 10 microns) foams may be useful materials for other applications.

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 CO₂. Previously, 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 yielded substantial increases in viscosity. The amount of styrene varied between 22-40 mole% in the copolymer. Falling cylinder viscometry results indicated that the 29%styrene-71%fluoroacrylate copolymer induced (at 295K and 34.5Mpa) increases of 10, 60 and 250 at copolymer concentrations of 1, 3 and 5wt%, respectively.

This report details the shear rate dependence of the viscosity of these solutions. Close-clearance falling cylinder viscometry was used to measure the solution viscosity. Aluminum cylinders of varying diameter (and therefore terminal velocity) were used to determine the effect of shear rate on viscosity. Further, concentrations as low as 0.2wt% were tested in an attempt to identify the least amount of thickener required to enhance the viscosity of dense carbon dioxide.

A second semifluorinated trialkyltin fluoride, tri(trifluorobutyl) tin fluoride, $(F(CF_2)(CH_2)_3)_3SnF$ was synthesized. This compound was not soluble in carbon dioxide. Therefore this type of thickener was considered to be not viable.

A number of small hydrogen-bonding compounds designed to dissolve in carbon dioxide and increase the viscosity of carbon dioxide were also synthesized. Although increases in carbon dioxide viscosity have been detected, the magnitude of these increases has been by a factor of 3 or less. Several of these compounds have yielded high porosity, microcellular foams upon cooling and or depressurization of the carbon dioxide-thickener solution.

1. Introduction

Carbon dioxide is non-flammable, relatively non-toxic, 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 [1-3], as a medium for conducting hydrogenations and oxidations in the absence of transport limitations [4, 5], as a solvent in biocatalysis [6], and as a raw material in synthesis [7,8]. Many of these applications have been made possible by the relatively recent discovery that certain functional groups, subsequently christened "CO₂-philic", enable miscibility of target compounds with CO₂ at moderate pressures [9]. Development of CO₂-soluble surfactants, for example, has rendered CO₂-based emulsion polymerization and dry cleaning feasible. Design and synthesis of CO₂-philic phosphine ligands has spawned a number of CO₂-soluble metal catalysts. In this paper we show how combination of concepts in CO₂-philic design with an understanding of molecular assembly in solution has allowed us to gel CO₂. Creation of gels in carbon dioxide allows us to attack two problems that have frustrated engineers for decades: (a) how to raise the viscosity of CO₂ to permit more efficient enhanced oil recovery, and (b) how to generate cellular polymers with a bulk density less than 10% of the parent polymer and cells smaller than 10 microns. Generation of gels in CO₂ provides solutions to these problems that are both technically and environmentally satisfying.

The pressure gradient between oil-bearing porous media and a production well is initially the force that moves oil to the wellhead. As the formation pressure drops during production, a flooding agent (usually water) is pumped into the oil-bearing formation to maintain the reservoir pressure and to displace additional petroleum to production wells [10]. Although the water sweeps efficiently through the formation, it displaces only a small fraction of the oil it encounters because water and oil are effectively immiscible. Dense carbon dioxide is miscible with petroleum, and thus will displace (tertiary recovery) the oil left behind by water-flooding. However, the viscosity of CO₂ can be 100 times lower than the viscosity of the oil, and thus carbon dioxide "fingers" its way through the petroleum rather than sweep the oil before it. The displacement efficiency is very high where the CO₂ actually contacts the oil, but by fingering the CO₂ bypasses most of the petroleum in the formation. Petroleum engineers have tried for decades to

design an additive [11] that can raise the viscosity of carbon dioxide (at low concentration) to a level comparable to the oil being displaced, thereby inhibiting the formation of "fingers". Success, unfortunately, has been elusive. Additives have been synthesized that enhanced the viscosity of simple *hydrocarbons*, yet which were not soluble in CO₂ without the use of impractically high fractions of co-solvent [12,13]. On the other hand, surfactants have been designed that are CO₂-soluble, but their effect on the viscosity has been minimal.

Creation of compounds that will enhance the viscosity of CO₂ would allow more efficient recovery of oil from older fields, possibly reducing the need for creation of new fields. In addition, enhanced oil recovery (EOR) ultimately sequesters CO₂ in rock formations, and thus CO₂-based EOR would be an important part of an overall sequestration strategy [14]. What is at first glance simply a technical problem in petroleum engineering has significant environmental ramifications as well.

Foaming of polymers using CO₂ is considered to be a sustainable process because it promotes efficient use of raw materials, the final products are excellent thermal insulators, and because CO₂ is a more benign "blowing agent" than CFC's or HFC's. A one-step, CO₂-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 because current routes to aerogels (organic and inorganic) involve multiple process steps and significant volumes of solvent.

Commercial CO₂-based foaming processes either add CO₂ to a polymer melt in an extruder, or mix CO₂ with polyurethane precursor materials just prior to polymerization. In either case, the pressure is relatively low (30 to 100 bar), and thus the amount of CO₂ mixed with the polymer is usually less than five percent by weight. These processes produce foam with a very low bulk density (greater than 95% density reduction vs. the parent polymer) but with cells that are often 1 mm in diameter [15]. Research conducted during the 1980's and 90's showed that high pressure CO₂ (pressures up to 500 bar) can be used to swell thermoplastic polymers significantly, often by 20-30%, and that subsequent rapid depressurization produces a microcellular foam. Such methods readily produce foams with cells smaller than 2 microns, but density reductions rarely exceed 65% [16].

There would be considerable utility in a single-step process by which one could generate organic, low density, microcellular materials using a benign foaming medium such as CO₂.

2. Gelation of Carbon Dioxide

We hypothesized that each of these seemingly unrelated technical problems could be addressed by the creation of molecules that would dissolve in carbon dioxide under relatively moderate pressures, then associate in solution. To enhance the viscosity of CO₂, the agents would create the thermodynamic illusion of very high molecular weight via non-covalent association. Previous work has shown that polymers with terminal ionic groups associate in organic solvent and thus produce viscosity increases of several orders of magnitude [17]. Recent work by Maita and coworkers has shown that gels can also be created in solution through association of electron donating and electron accepting functional groups [18]. To form foams from these solutions, the aggregates formed in solution would need to be preserved during and after solvent (CO₂) removal. Considerable research has shown that one can design molecules that aggregate in solution owing to multi-point hydrogen bond formation [19], however only rarely do the aggregates form structures that can be preserved following removal of the solvent [20-21]. We surmised that by changing the temperature-pressure conditions of the initial solution of our model agents in CO₂, we could induce a phase separation, producing an organic analog to the aerogel upon depressurization. Unlike traditional aerogel generation, we proposed to form these microcellular materials in a single step in CO₂ without the use of any additional solvent. Although molecular association in CO₂ has been previously observed, the molecules in question (surfactants) were designed to form spherical micelles, whereas we desire formation of supramolecular networks that will enhance viscosity or exist as stable entities in the absence of CO₂.

In this report, we show how one can design molecules that are both highly CO₂-soluble and which aggregate in solution. When associating polymers are employed, we have observed the 2 order of magnitude increase in viscosity necessary to conduct CO₂-based EOR without "fingering". When a low molecule weight compound which can exhibit multi-point hydrogen bonding is employed, monolithic aggregates composed of cells or interlocking microfibers are formed in CO₂. These supramolecular structures

become freestanding microcellular foams when the CO₂ is removed, and exhibit over 90% density reduction and cells smaller than 10 microns.

3. Experimental

Monomeric gelling agents were synthesized as in reference 22. Polymers were synthesized as shown in reference 23. The viscosity of polymer and monomer-CO₂ solutions was measured using a high-pressure falling cylinder apparatus as described in reference 24, where the shear rate was varied by using cylinders of different diameters in the apparatus. Relative viscosity, the ratio of the viscosity of the solution to that of pure CO₂, is reported. The viscosity of all monomer and polymer solutions was measured in the single-phase region, as determined from cloud point measurements using a variable volume view cell as described in reference 25. Foam samples were fractured, sputter-coated with gold, then examined using scanning electron microscopy (SEM) as in reference 26.

4. Results and Discussion

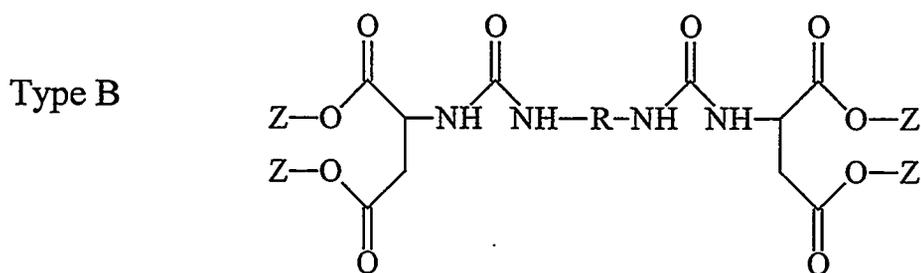
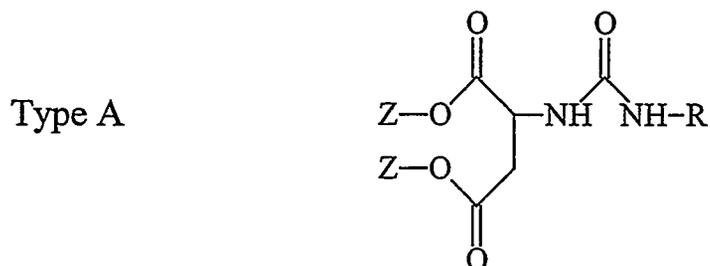
To form gels in CO₂, molecules must dissolve under experimentally accessible temperature and pressure conditions. Consequently, all of the compounds synthesized and evaluated for this work incorporate "CO₂-philic" functional groups. A small number of compounds have been found, experimentally, to exhibit miscibility with CO₂ at relatively moderate pressures; these have since been labeled CO₂-philic to distinguish them from traditional lipophilic and hydrophilic moieties. It has been hypothesized that "CO₂-philicity" derives from inclusion of functional groups that interact specifically with the carbon atom in CO₂, and/or from weak self-interaction of the solute. Further, it is thought that the latter manifests itself as a low solubility parameter, low interfacial tension, and/or a low softening temperature. Experiment has shown that effective CO₂-philes include fluoroalkyl, fluoroether, and siloxane functional materials.

5. Formation of Microcellular Materials using Monomeric Gelling Agents

The use of multi-point hydrogen bonding to form macromolecular, yet non-covalent architectures in solution has been explored extensively in recent years [19-21, 27, 28]. Molecules have been synthesized, which, when

dissolved under appropriate conditions, form transparent gels via self-assembly into macromolecular rigid rods, disks, and 3-dimensional networks. Although the architectures that one can form vary widely as the shape and functionality of the precursors vary, many of these materials share common hydrogen bonding functional groups. These include amides, ureas, ureidopyrimidone, etc. --- functional groups that contain both hydrogen bond donors and acceptors and are thus self-complimentary. Consequently, we have prepared a number of "monomers" that contain one or two urea groups (to induce aggregate formation) plus fluorinated functional groups to promote solubility in carbon dioxide at moderate pressures. The general structure of these compounds is shown in Figures 1a and 1b.

Figure 1. Two types of H-Bonding Structures:



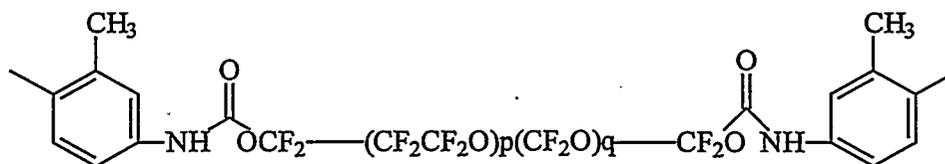
The use of aspartate residues in the construction of the compounds allows easy incorporation of "CO₂-philic" functional groups (via di-ester formation) as well as generation of the urea groups needed for hydrogen bonding (via reaction with isocyanates).

We evaluated the ability of several variations of the structures in Figure 1 to form cellular materials in CO₂ (Table 1).

Table 1: Behavior of various monomeric gelling agents in CO₂ (See Figure 1 for definitions of Z, R, Types A and B); behavior types (I,II, III) defined in the text

Comp. #	Str. (A or B)	-CO ₂ -phile (Z)	R Group	Concentration (weight %)	Behavior (I - III)
1.	B	(CH ₂) ₂ (CF ₂) ₇ CF ₃	(CH ₂) ₆	2.2 - 4.9	II
2.	B	(CH ₂) ₂ (CF ₂) ₇ CF ₃	(CH ₂) ₁₂	4.0	II
3.	B	(CH ₂) ₂ (CF ₂) ₇ CF ₃	1,4 phenyl	1.9	III
4.	B	(CH ₂) ₂ (CF ₂) ₇ CF ₃	1,4 xylyl	3.35	III
5.	B	(CH ₂) ₂ (CF ₂) ₇ CF ₃	fluoroether ^a	2.5 - 4.8	III
6.	B	fluoroether ^b	(CH ₂) ₆	1.5 - 5.0	I
7.	A	(CH ₂) ₂ (CF ₂) ₇ CF ₃	p-fluoro phenyl	4.5	II
8.	A	(CH ₂) ₂ (CF ₂) ₇ CF ₃	p-CF ₃ phenyl	2.5	III
9.	A	(CH ₂) ₂ (CF ₂) ₇ CF ₃	3,5 bis-CF ₃ phenyl	6.0	I
10.	A	(CH ₂) ₂ (CF ₂) ₇ CF ₃	(CH ₂) ₅ CH ₃	1-5	I
11.	A	(CH ₂) ₂ (CF ₂) ₇ CF ₃	phenyl	5.05	II
12.	A	(CH ₂) ₂ (CF ₂) ₇ CF ₃	ethyl methacrylate	4.7	I

a -- Fluorolink B, Ausimont, molecular weight = 3000



b -- oligomer of hexafluoropropylene oxide, molecular weight = 1200 (DuPont)

First, the phase behavior was measured to determine those conditions where a single-phase solution could be produced as a function of concentration. Foams were generated from single-phase solutions in CO₂ by either (a) lowering the temperature, (b) lowering the pressure, or (a) followed by (b). When formed, aggregates were recovered following venting of the CO₂ for SEM analysis. Behavior in CO₂ could be separated into three general categories:

- I. These compounds (typically powders) could dissolve in CO₂ at concentrations exceeding five weight percent at room temperature (above a given threshold pressure that varied with molecular structure of the agent but was below 300 bar for all cases). Measurement of the resulting viscosity of the solution showed enhancement that was significant, but by less than a factor of 3. Removal of the CO₂ via pressure reduction left behind a foamed material (solid at room temperature and pressure) that was stable and could easily be handled and examined via SEM.
- II. These compounds were less than 0.1 weight percent soluble in CO₂ at room temperature at pressures up to the limit of the instrument (500 atmospheres), but would dissolve at concentrations exceeding five weight percent at elevated temperature (typically 70 - 90C). Upon cooling at constant pressure (300 atmospheres), the solution would exhibit a sharp phase separation point (sudden complete opacity of the mixture). Removal of the CO₂ by gradual depressurization left behind a monolithic cellular or fibrillar material that was stable and could be handled and examined via SEM.
- III. These compounds, like those of type II, were soluble in CO₂ at elevated temperature, although slow cooling of the solution led to precipitation of the material as a powder or free floating fibers, rather than as a type II monolithic foam.

We found that small variations to the structure of the associating molecules led to large changes in their behavior in carbon dioxide. With the exception of compound 6, type B structures exhibited type II or III behavior, and hence required elevated temperature to dissolve in CO₂. Apparently, the two urea groups in type B molecules require elevated temperature to break the strong self-interaction in the compound and allow dissolution. Alterations to the R group of type B structures produce substantial changes

in behavior. For example, compound 1, when dissolved in CO₂ at slightly less than 5 weight percent, produces a cellular material (via type II behavior) which exhibits a morphology of "stacks" of small parallelograms. Despite the dense appearance of this material, its bulk density is 97% less than that of the parent material (the five weight percent solution produces a monolith that fills the entire view cell). The pores (the space between the parallelograms) are sub-micron. Lengthening the R group from hexyl to dodecyl produces a foam with a more conventional porous structure, larger cells, and a higher bulk density.

Surprisingly, changing the concentration of the agents in solution could produce dramatic changes in the morphology of the foams. For example, lowering the concentration of compound 1 in CO₂ to below 2.5 weight percent (all other conditions the same) produces a material with a fibrillar morphology and a comparable bulk density (the monolith comprises less material but does not fill the entire volume available in the view cell) of the previously described foam. Again, the pores (spaces between the fibers) are sub-micron. We have found that some, but not all of the materials in Table 1 exhibit a morphology-concentration correlation, but it is not clear at this time how the chemical structure of the agents governs this correlation.

Changing the R group from alkyl to aromatic in Type B structures changes the behavior from II (monolith formation) to III (precipitation as powder). Here, although the elevated temperature allows dissolution of these type III behavior materials, the formation of large aggregates (and thus the morphology of the type II's) is apparently inhibited by the aromatic structures. This is even the case for compound 5, where the R group contains aromatic groups with a highly CO₂-philic fluoroether spacer. When fluoroether groups are used in the aspartate residue (the Z group), as in compound 6, type I behavior results, with production of foams with a more traditional cellular appearance.

As we expected, reducing the number of urea groups from two to one (type A structures) produces type I behavior more readily, yet still allows for other behaviors, depending upon the structure of the R group. Somewhat surprisingly, the R groups that one might *a priori* suspect would be relatively CO₂-philic (p-fluoro phenyl and p-trifluoromethyl phenyl), and hence lead to solubility at room temperature, instead produce type II and III behaviors, requiring elevated temperature for dissolution. Only upon addition of the second trifluoromethyl group (compound 8) does the

molecule dissolve at room temperature. The agents that exhibited type I behavior generally produced foams with a traditional porous morphology, with cells larger than 1 micron. However, the methacrylate-functional compound (#12) exhibits type I behavior and also produces a foam with a fibrillar structure. The phenyl-functional material (Table 1, compound 11), exhibited type II behavior and produced very low density, microcellular foam monoliths that filled the view cell, much like those of compound 1.

It should be noted that while the foams generated using these compounds are stable upon removal of the CO₂ (they easily support their own weight with no dimensional changes after days or weeks), they can be readily re-dissolved in CO₂. To generate foams with a greater degree of permanence, one could employ compounds such as number 12 (methacrylate functional material) or an analog of numbers 1 and 2 where a diyne functionality is included in the R group. Irradiation following foam formation would polymerize these materials.

In summary, these compounds have demonstrated significant aggregation into macromolecules. Several of these H-bonding chemicals have increased the viscosity of carbon dioxide by a factor as high as 3 at concentrations up to 5wt%. We continue to modify the structure to attain more significant increase in solution viscosity. Surprisingly, we have found that these compounds are also able to form foams upon cooling or depressurization. Although these foams are not suitable for viscosity enhancement in porous media, they represent a useful, new means of generating high porosity, microcellular rigid foams.

6. Raising the Viscosity of CO₂ using Associating Polymers

In an earlier attempt to raise the viscosity of CO₂, we synthesized and evaluated telechelic (sulfonate-terminated) fluorinated polyurethanes [29]. Relative viscosity approached 3 at concentrations of 5 weight percent polymer, a significant enhancement but far short of what would be necessary to effectively practice CO₂-based EOR. Hence, we evaluated materials with multiple points of interaction along the chain, rather than just at the two end groups.

As in the case of the monomeric agents, the target polymers incorporate both CO₂-philic groups and moieties that we believed would promote associate in solution. For the former, we chose a 1H, 1H, 2H, 2H perfluorodecyl acrylate monomer, as previous work has shown that homo- and copolymers of this material exhibit miscibility with CO₂ at moderate pressures. For the latter, we at first assumed that groups with hydrogen bond donors and acceptors would be required. In a surprising result, a simple random copolymer of styrene and the fluoroacrylate exhibited a two order of magnitude enhancement in CO₂ -- well above what is observed for the fluoroacrylate homopolymer (see Figure 3). In addition, as shown in Figure 4, there exists an optimum level of styrene (approximately 30 mole %) insofar as viscosity enhancement is concerned. We surmise that pi-pi stacking between phenyl groups is contributing to the strong enhancement effect of this simple copolymer. Copolymers lacking the aromatic side group, and thus where the comonomer is not likely to associate (Figure 3) produce a much lower degree of viscosity enhancement in CO₂. We have also found that the associating styrene-fluoroacrylate copolymers exhibit shear-thinning behavior in CO₂ (Figure 5), an important advantage in that it allows the solution to be pumped (at higher shear rates) into the injection well and near-wellbore vicinity. The viscosity would increase to the levels shown in Figure 4 as the CO₂ flowed more slowly through the formation displacing the oil.

Given that a simply phenyl side chain (styrene) helped produce as substantial viscosity enhancement in CO₂, we were curious to see the result when groups with hydrogen bond donors and acceptors were included. Toward that end, we copolymerized the methacrylate-functional aspartate gelling agent (Table 1, compound 12) with the fluoroacrylate (78 mole % fluoroacrylate, 22% aspartate monomer). At five weight percent in CO₂, this copolymer produced a transparent gel of such high viscosity that the cylinder

(in our falling cylinder viscometer) could not move during the experiment - even raising the temperature to 90C did not drop the viscosity sufficiently to allow cylinder movement. We are currently examining the effect of aspartate methacrylate content on the behavior of this polymer in CO₂.

Figure 3: Relative viscosity of CO₂-polymer solutions as a function of polymer type and concentration at 340 bar and room temperature; PHFDA: Poly(heptadecafluorodecyl acrylate); PSt: Polystyrene; PHA: Poly(hexyl acrylate); PDMAEA: Poly(2-dimethylamino ethyl acrylate)

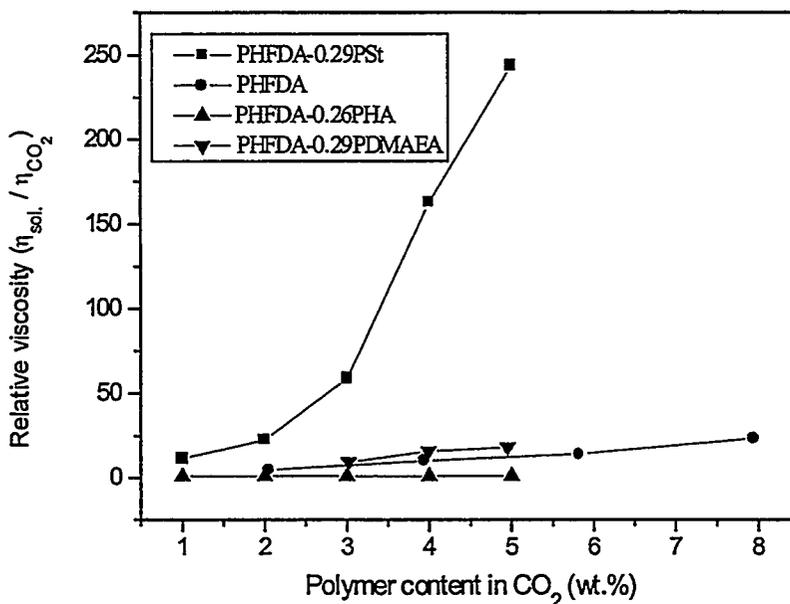
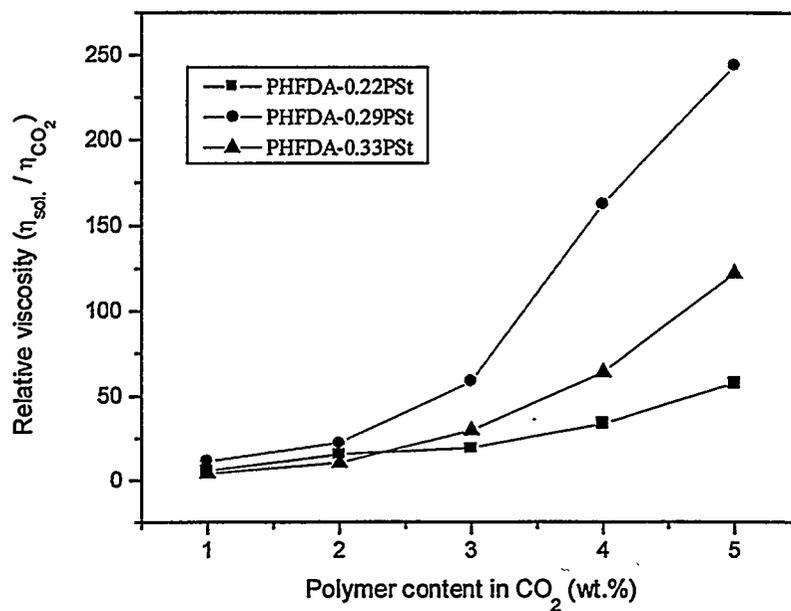


Figure 4: Relative viscosity of CO₂ solutions of poly(fluoroacrylate-co-polystyrene) copolymers as a function of styrene content and concentration



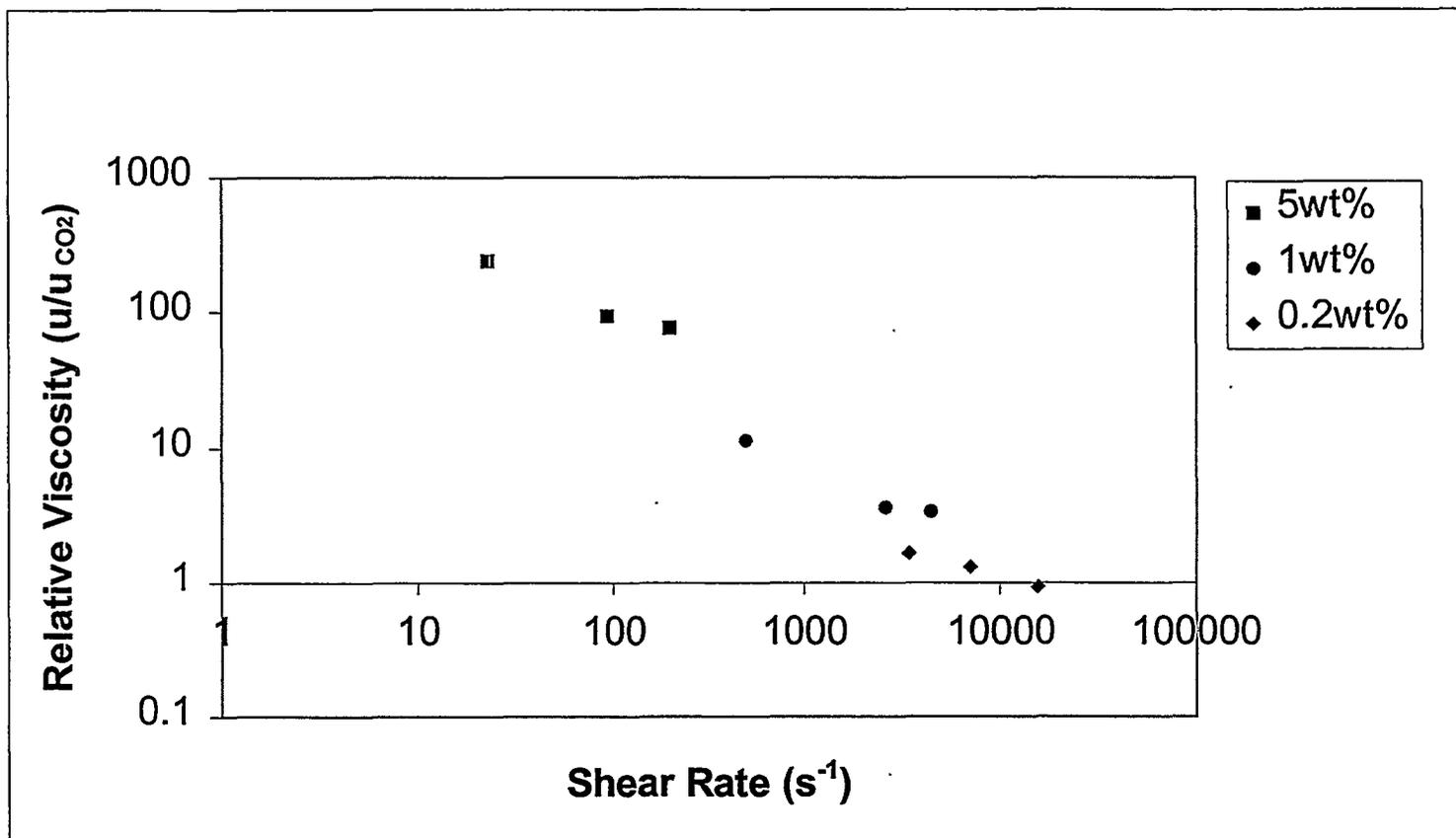


Figure 5: Relative viscosity of CO₂ solutions of poly(fluoroacrylate-co-polystyrene) copolymers as a function of shear rate and concentration

7. Summary

We have shown that by combining concepts surrounding the design of "CO₂-philic" materials with results from the literature on the design of associating monomers and polymers, we can generate materials that enhance the viscosity of CO₂ by several orders of magnitude at relatively low concentration, or that promote formation of low bulk density, microcellular materials. Thus the technical hurdles to use of high viscosity CO₂ in EOR or in organic aerogel formation can be overcome through appropriate molecular design. Despite this technical success, additional work needs to be performed in order to render this approach completely practical. While technically successful, the use of a fluorinated CO₂-philic group is very expensive. Consequently, to render the use of associating molecules in these applications feasible, we are actively investigating (a) changes to molecular structure that will shift the viscosity curves (such as those in Figure 6) to the left (such as by use of the aspartate methacrylate monomer), and (b) reduction in the weight percent fluorine in the associating molecules or replacement of fluorine with new, less expensive CO₂-philic groups [30]. Finally, there are a number of scientific questions that remain unanswered, including understanding the mechanism for morphology development in the foams, and hence why we have observed such dramatic changes in morphology upon changing either molecular structure or concentration.

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22. The bis urea gelling agents were prepared by esterification of N-Boc-aspartic acid in dichloromethane with EDCl, DMAP and 1H,1H,2H,2H-perfluorodecanol followed by deprotection with 50% TFA/CH₂Cl₂ and reaction with the appropriate mono or bis-isocyanates in CH₂Cl₂ with excess triethylamine. The resultant bisureas were filtered off and washed with CH₂Cl₂, 1% aqueous HCl, water and more CH₂Cl₂. All compounds gave spectroscopic characteristics consistent with their structure and were shown to be >95% pure.

23. Monomers (styrene, N,N dimethyl amino ethyl methacrylate, n-hexyl acrylate, 1H, 1H, 2H, 2H perfluorodecyl acrylate) were received from Aldrich and purified using conventional procedures (washing to remove inhibitors, drying, vacuum distillation as appropriate). Copolymers were prepared via bulk polymerization at 65C using AIBN (0.2 mole %, recrystallized from methanol). Copolymers were purified via dissolution in 1,1,2 trichloroethane or perfluoromethyl cyclohexane, then precipitation into methanol. Copolymer content was quantified using ¹H NMR. The aspartate methacrylate monomer was prepared using the scheme shown in reference 22 and 2-isocyanato ethyl methacrylate (Aldrich).

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