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Novel CO₂-Thickeners for Improved Mobility Control

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Abstract

The ability of a polymer and an end-functionalized polymer to increase the viscosity of liquid carbon dioxide was evaluated. The polymer was a high molecular weight, highly CO₂-soluble polyfluoroacrylate that dissolved rapidly in liquid carbon dioxide over a wide range of concentrations at ambient temperature. This polyfluoroacrylate increased the viscosity of carbon dioxide by a factor of 1.60 and 1.75 at a concentration of 4.0 and 4.8wt%, respectively. A lower molecular weight telechelic ionomer, a fluorinated polyurethane disulfate (a fluorinated polyurethane polymer with a sulfate group at each end of the polymer) was then synthesized. This compound required greater pressures to dissolve in carbon dioxide, but it was able to induce more significant viscosity changes. This was attributed to the ability of these compounds to associate in solution (the polar sulfate groups aggregate), forming a macromolecular structure. The viscosity of liquid carbon dioxide increased by a factor of 1.5 and 2.7 at concentrations of 2.7 and 4.0 wt%, respectively. *This is the first reported increase in carbon dioxide viscosity using an associating compound that does not need a cosolvent.*

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. During the first quarter of this contract, two carbon dioxide thickeners have been identified, a polymer and a telechelic ionomer. These results are very promising, and subsequent research will be directed at making them more effective thickeners at lower concentrations. Synthesis of H-bonding compounds began this quarter. No work was performed on tin fluorides this quarter.

Fluorinated polyurethane disulfates with molecular weights (MW) up to 32500 g/mol were synthesized by reacting a fluorinated diisocyanate or 1,6-bis(diisocyanato-hexane) with a fluorinated diol. The CO₂-solubility of the lower MW telechelic ionomers, MW<19500, increased with MW due to the enhanced carbon dioxide-philicity of the fluoropolymer backbone, despite the increased MW of the compound. The fluorinated disulfate with MW of 19500 exhibited the greatest carbon dioxide solubility. The effect of increasing MW was more significant than increased carbon dioxide-philicity for MW>19500, however, causing CO₂-solubility to decrease with increasing MW. Dilute concentrations of telechelic ionomers increased solution viscosity via the association of the polar end groups, leading to the development of a macromolecular network. Falling cylinder viscometry results indicated that at a concentration of 4 wt%, a fluorinated disulfate, MW = 32500, increased the solution viscosity by a factor of 2.7 (relative to neat carbon dioxide) at 293 K and 34.5 MPa. The CO₂-viscosity enhancing capacity of these telechelic ionomers was then compared to a high MW polyfluoroacrylate. Poly(heptadecafluorodecyl acrylate) was highly soluble in liquid carbon dioxide,

exhibiting a flat two-phase boundary at about 8 MPa with concentrations between 1-5 wt% at 293 K. The viscosity increase was slightly less than that observed for the telechelic ionomer. For example, the solution viscosity increased by a factor of 1.6 at 4 wt% polyfluoroacrylate.

1. Introduction

Carbon dioxide is used extensively as a solvent for enhanced oil recovery [1-11] and as a well-fracturing fluid [12]. In both applications, the low viscosity of the dense carbon dioxide diminishes the effectiveness of the process. For example, at reservoir conditions, CO₂ 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” CO₂ 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 CO₂. 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. Initial attempts focused on compounds known to thicken oils. These efforts were unsuccessful because of the very low CO₂-solubility of conventional hydrocarbon-based polymers, telechelic ionomers, organometallic compounds, surfactants, hydroxystearic acid and ammonium carbamates [6,7]. Although substantial viscosity increases were observed in some cases when large amounts of an

organic co-solvent (e.g. 10~20 vol% toluene or ethanol) were introduced, the identification of a viscosity-enhancing agent for neat carbon dioxide remained elusive. [3-5,10,11].

Rather than testing conventional chemicals in neat CO₂ or CO₂-cosolvent mixtures, several investigators have recently developed highly carbon dioxide-soluble compounds by molecular design. DeSimone and coworkers have carried out numerous polymerizations in liquid and supercritical CO₂ [8,9,12-14]. During a study of homopolymerization of a CO₂-soluble monomer and polymer in carbon dioxide, they reported a significant solution viscosity increase with poly(1,1-dihydro perfluoro octyl acrylate), MW=1.4×10⁶ g/mol. At 323 K, 6.7 wt/vol% polymer increased CO₂ viscosity from 0.08 mPa s (cp) to 0.2-0.6 mPa s in the 23-35 MPa pressure range [9]. This increase was attributed to the intermolecular entanglement of the solvent expanded polymer chains, and was the first successful “thickening” of neat carbon dioxide. Although the targeted level of viscosity change (a 10-100 fold increase using 0.1 – 2.0wt% thickener) was not attained, DeSimone’s results indicated that it was possible to generate high MW, CO₂-soluble polymers capable of increasing the viscosity of carbon dioxide

Beckman and Enick also identified or synthesized numerous polymers, surfactants, dispersants, and chelating agents that exhibited high solubility in carbon dioxide [15-19]. These compounds were based on a carbon dioxide-philic fluoroether functionality. Highly carbon dioxide-soluble amphiphiles, such as dispersants, chelating agents and surfactants were successfully synthesized. Attempts to increase the viscosity of carbon

dioxide with fluoroether polymers at concentrations up to 10wt% (MW<30000) were unsuccessful because this MW was too low, and higher MW fluoroethers exhibited extremely low carbon dioxide solubility. CO₂-soluble fluoroether-based hydroxy aluminum disoaps were also unsuccessful thickeners because the flexible fluoroether tail did not promote the formation of viscosity-enhancing cylindrical micelles [7,16]. Although semifluorinated alkanes gelled liquid carbon dioxide, these “gels” were actually dispersions of semifluorinated alkanes microfibers in liquid carbon dioxide [7].

The objective of this study was to incorporate carbon dioxide-philic functionalities into the structure of a telechelic ionomers in an attempt to design a carbon dioxide-thickener. Alkyl analogs of these end-functionalized polymers have been successfully employed in dilute concentration to increase the viscosity of organic liquids or to induce gelation [20-25]. The ionic end-groups associate in solution, establishing a viscosity-enhancing macromolecular structure. More dramatic viscosity changes have been attained at very dilute concentrations with low MW associating compounds than with ultra-high MW polymers. The apparent molecular weight of the associative network greatly exceeds the MW of the covalently-bonded polymer in solution, yet the relatively low molecular weight of the compound favors its solubilization.

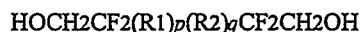
A fluoroether polyurethane oligomer backbone was selected to impart CO₂ solubility. The ionomer was end-capped with hydrophilic sulfate groups to facilitate the formation of the macromolecular structure. A high molecular weight fluorinated

polyacrylate was also synthesized [8,9]. The carbon dioxide solubility and viscosity enhancing capability of this fluoropolymer was compared to the telechelic ionomers.

2. Materials and methods

2.1. Fluorinated liquids

The precursors to make fluorinated polyurethane backbones are fluorinated diol and diisocyanate macromers. They are commercially available under the trade name of Ausimont Fluorolink D and B. Fluorolink D is a difunctional, hydroxyl-terminated fluorinated polyether with an average molecular weight of 2000 g/mol:

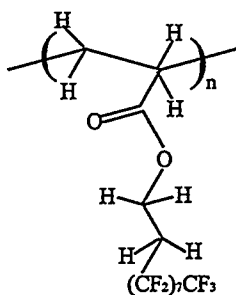


Fluorolink B is a difunctional, isocyanate terminated fluorinated polyether with an average molecular weight of 3000 g/mol:



where $\text{R}_1 = \text{CF}_2\text{CF}_2\text{O}$, $\text{R}_2 = \text{CF}_2\text{O}$, and Ar = an aromatic group. In both fluorinated macromonomers, the difunctional contents are greater than 95% as characterized by NMR analysis. Ausimont describes both compounds as polydisperse, although quantitative measures of polydispersity were not available.

The monomer for fluorinated polyacrylate synthesis is heptadecafluorodecyl acrylate (97%, inhibited, Aldrich). The monomer was inhibited with 100ppm monomethyl ether hydroquinone. Homopolymerization of this monomer yields the following polyfluoroacrylate,



2.2. Other reagents

1,6-Bis(diisocyanato hexane), or HDI (Aldrich), was used as received. It is an alternate reagent used to form linear fluorinated polyurethane backbone with Fluorolink D. Dibutyltin dilaurate (95%, Aldrich), chlorosulfonic acid (99%, Aldrich) and sodium methoxide (25 wt% solution in methanol, Aldrich) were used as received. Solvent 1,1,2-trichlorotrifluoroethane (Freon 113, 99.8%, Aldrich) was dried over molecular sieves. Tetrahydrofuran (THF, 99.5+%, Aldrich) was distilled over sodium before use. Acetone (99.9+%, HPLC grade, Aldrich) and chloroform (99.8%, Aldrich) was used as received. Nitrogen (Ultra high purity, Praxair), carbon dioxide (bone dry grade, 99.9%, Liquid Carbonic), methanol (anhydrous, Mallinckrodt) and sodium hydroxide (pellets, J.T. Baker) and α,α,α -trifluorotoluene (99%, Aldrich) were used as received. AIBN (2, 2'-azobisisobutyronitrile, 98%, Aldrich) was recrystallized from methanol twice before use. Heptadecafluorodecyl acrylate monomer (97%, Aldrich) was washed with 5% sodium hydroxide solution three times to remove the inhibitor.

2.3. Synthesis procedures

2.3.1. Fluorinated disulfate based on fluorolink D

Typically, 10g(0.005 mol) of Fluorolink D was dissolved in 50ml Freon, and 0.67ml(0.01mol) HClSO_3 was added dropwise to the alcohol solution. The reaction was carried out at 293 K under a nitrogen blanket. After 2 hours, the reaction was stopped and Freon removed by vacuum evaporation. The obtained acid was dissolved in 50ml Freon-THF (3:1 mixture), and 2.3ml (0.01mol) NaOCH_3 (25wt% solution in methanol) was added dropwise for neutralization. The reaction mixture was kept at 293 K for 24 hours. Most of the reaction solvent was then removed by vacuum evaporation. The resulted pasty liquid was washed three times with 100ml of acetone. The product was then dried in a vacuum oven at 30 mmHg, 323 K for 48 hours before characterization and CO_2 -solubility evaluation. For the synthesis of diols with MW=7000 and 12000 g/mol, Fluorolink B was used as the chain-extending agent. Typically, 11g of Fluorolink D (a 5% excess) was dissolved in 50ml of Freon and 2 drops of dibutyltin dilaurate catalyst were added. 7.5g (for MW=7000) or 10g (for MW=12000) of Fluorolink B was dissolved in 50ml Freon and added dropwise through an addition funnel. The reactions were kept at room temperature for 24 hours before the solvent was removed by rotary evaporation. The viscous, pasty liquid products were then washed three times with 100ml of chloroform to remove residual catalysts. Diols with MW of 15000, 17200, 19300, 32300, used 1,6-bis(diisocyanato hexane), HDI, as the chain-extending agent. The reaction procedures were similar to that for chain-extension reaction between Fluorolink B and D. By varying the ratio of Fluorolink D to HDI, diols with different chain length

could be made. All of the extended diol products were dried in a vacuum oven at 30 mmHg, 323 K for 12 hours. Subsequent acidification and neutralization procedures were similar to those for disulfate formation directly from Fluorolink D. Detailed reaction procedures are shown in Fig.1. with disulfate of triblock polyurethane backbone as an example.

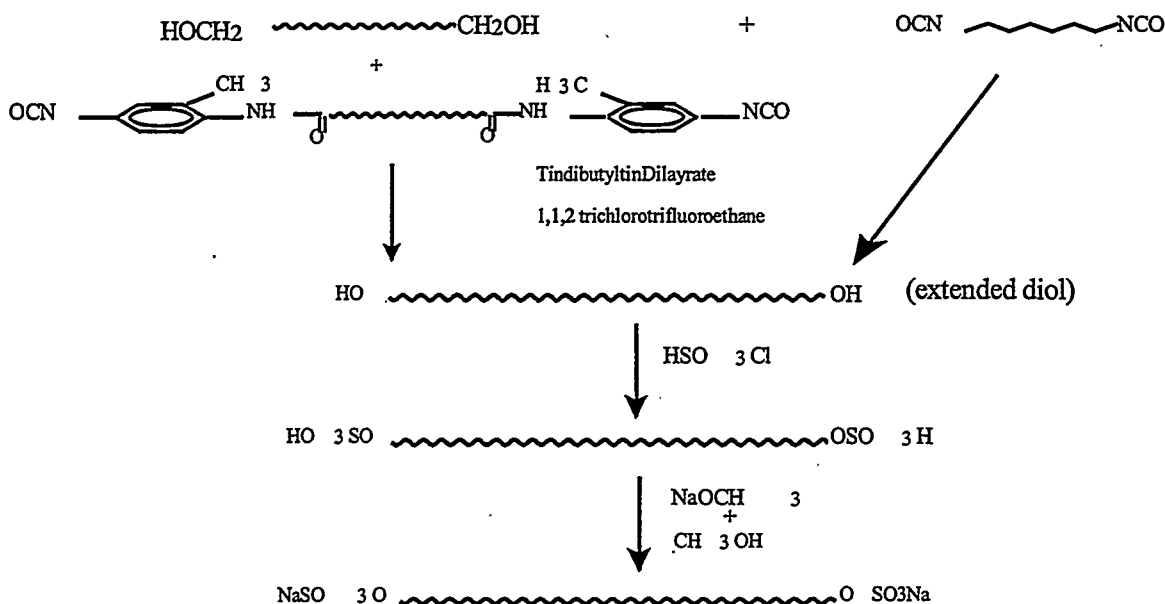


Fig. 1. Reaction procedures to make telechelic disulfates with fluorinated urethane backbones. By varying the proportions of diol and diisocyanates, end products of disulfates of different backbone lengths can be synthesized.

2.3.2. Poly(*heptadecafluorodecyl acrylate*)

The synthesis used for the generation of polyfluoroacrylate was similar to that proposed by DeSimone [8,9]. Typically, 10g monomer (inhibitor removed) and 5mg initiator AIBN were measured and transferred into a 50ml ampule. 10ml of trifluorotoluene was then added. The reaction mixture was then purged with nitrogen for

3min and sealed with flame. The reaction was carried out in an oil bath at 333 K for 48 hr. After reaction, the polymer solution was precipitated into 500ml methanol three times. The polymer was then dried in a vacuum oven overnight. The product polymer is white powder, yield 84%. Although the MW of the polymer was not determined, previously reported MW for polyfluoroacrylates synthesized in this manner were as high as 1.4×10^6 [9].

2.4 Chemical characterization

Chemical structures were characterized via IR spectroscopy with a Mattson FT-IR and ^1H -NMR spectroscopy with Bruker 300 MHz NMR respectively. The IR characterizations were done by thin-layer technique. The NMR spectroscopy was carried out by placing a Freon (in some cases deuterated-DMSO was added to dissolve the sample) solution of samples in an 8 mm O.D. inner tube and deuterated chloroform and tetramethylsilane in a 10 mm O.D. outer tube for analysis. The complete reaction of diisocyanates was shown by the disappearance of the isocyanate absorbance around 2280 cm^{-1} in IR. The complete neutralization of acid intermediates was confirmed by the disappearance of the peak for acid proton around 10.5 –12.0 ppm in the ^1H NMR spectroscopy.

2.5 Phase behavior and viscosity measurements

The phase behavior and viscosity measurements were performed at 293 K using a high pressure, variable-volume, windowed cell, with a cylindrical sample volume, Fig. 2.

Isothermal compressions and expansions of mixtures of specified overall composition were used to determine the two-phase boundary. Visual observations of the initial appearance of a second phase (cloud points or bubble points) indicated the presence of the second phase.

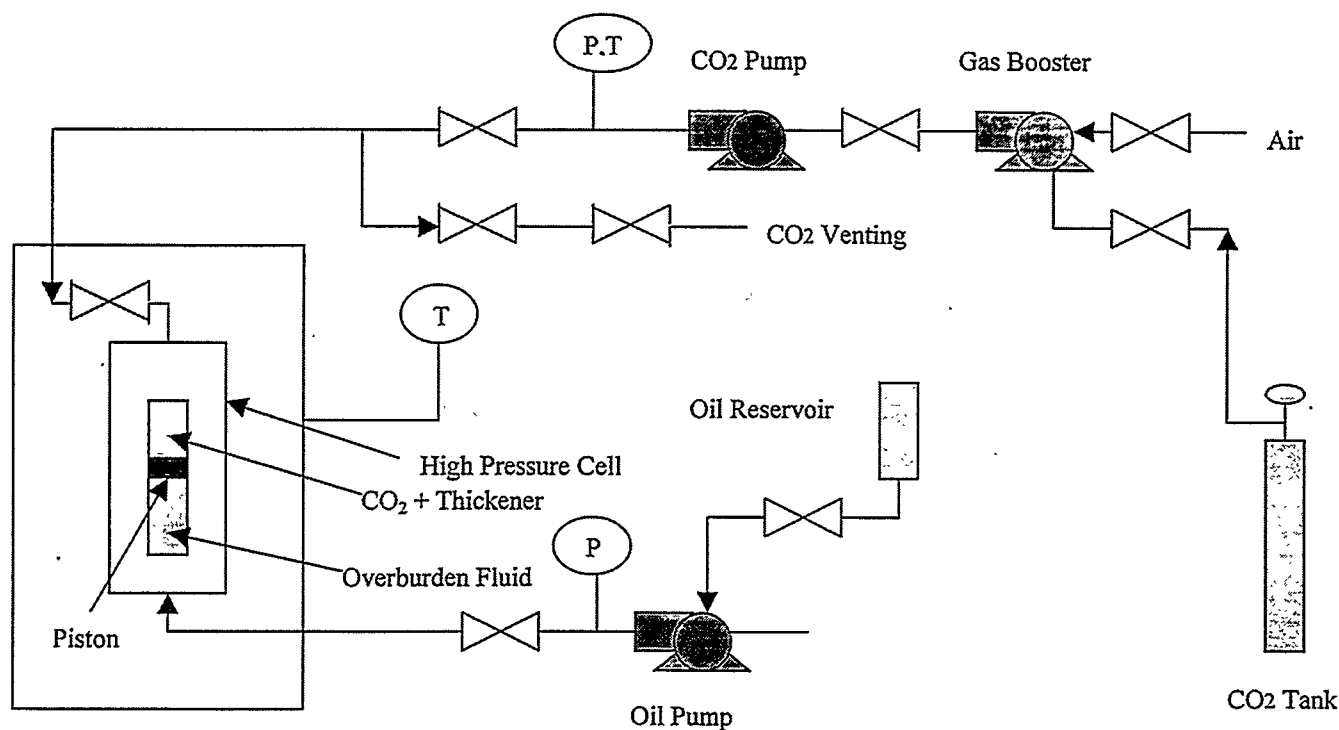


Fig. 2. High Pressure, Variable Volume, Windowed Cell (D. B. Robinson Cell)

The viscosity of single-phase disulfate-CO₂ solutions was determined by falling cylinder viscometry. This technique was selected because of its simplicity in monitoring large viscosity increases in fluids as indicated by reductions in the terminal velocity of a falling object. Visual observations enable one to verify that the reduced terminal velocity, u_t , is attributed to solution viscosity increase, and not to the small amounts of a

solid phase between the object and the cell wall inhibiting the fall of the object (when low viscosity solutions are evaluated, close clearances between the cylindrical cell wall and the falling cylinder exist). In equation 1, K is the calibration constant, ρ_s is the solid

$$\mu = \frac{K(\rho_s - \rho_l)}{u_t} \quad (1)$$

cylinder density, ρ_l is the liquid carbon dioxide density, and μ_f is the fluid viscosity. Although other viscosity measurements, (e.g. capillary viscometry and pressure drop through porous media) provide more comprehensive and precise assessments of viscosity as a function of shear rate, falling object (ball, sphere, cylinder, needle) viscometry remains a simple technique that rapidly provides an indication of significant viscosity changes. The viscosity tests were also performed using the phase behavior apparatus.

An aluminum cylinder was put into the cylindrical sample volume before the polymer sample and the mixing balls were added. After equilibration of the system in the single phase was achieved, the cell was rapidly inverted and the terminal velocity of the cylinder was measured. The falling aluminum cylinder viscometer was calibrated using neat carbon dioxide at 293 K and 34.5 MPa. The velocity of the falling cylinder in CO₂-telechelic ionomer solutions at the same temperature and pressure was used to determine the solution viscosity. Changes in the solution density relative to that of neat carbon dioxide were assumed to be small relative to the density difference between aluminum and carbon dioxide. Therefore the relative viscosity (solution viscosity/viscosity of neat carbon dioxide) was equivalent to the terminal velocity ratio (terminal velocity in neat carbon dioxide/terminal velocity in solution). Terminal velocities were determined by dividing the length of the cylinder's fall by the duration of the fall. The experiment was

repeated five times at each concentration, with the average relative viscosity results reported in Figure 4.

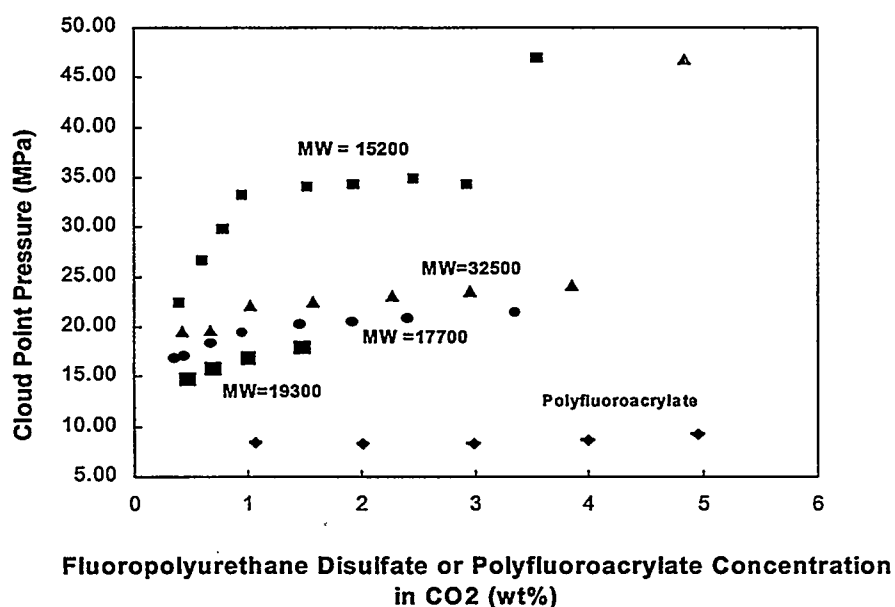
3. Results and discussion

3.1 Phase behavior

Telechelic ionomers synthesized from Fluorolink D directly (MW=2200), and from Fluorolink B and D (MW=7200, 12200 g/mol) were insoluble at 0.5wt% in liquid CO₂ below 48.2 MPa at 293 K. The disulfates synthesized from HDI and Fluorolink D, however, exhibited solubility in liquid CO₂ at 293K. The two-phase boundaries (dew point loci) of mixtures of CO₂ and these fluoroether polyurethane disulfates are illustrated in Fig. 3. A single phase liquid occurred at conditions above the dew point locus, while liquid-liquid phase behavior existed at conditions below the dew point pressure. The disulfate ionomer with MW of 15200 g/mol was the lowest MW sample that was soluble in liquid carbon dioxide below 34.5 MPa. As the molecular weight increased from 15200 to 17400 and then to 19500 g/mol, the cloud pressure decreased significantly. The increased miscibility with increasing MW can be attributed to the enhanced carbon dioxide-philicity of the ionomer. Because the hydrophilic sulfate segments remained unchanged as the CO₂-philic fluorinated polyurethane backbone increased with MW, the ionomer became more CO₂-philic. At higher MW, however, as MW increased, a decrease in solubility was observed due to stronger effect of unfavorable entropy of mixing than marginal increases in CO₂-philicity. Polyfluoroacrylate was very soluble in liquid CO₂ as indicated by the low cloud point pressure (below 10 MPa) up to 5

wt%. This high solubility is in agreement with the fluoropolymer solubility results of DeSimone [9] and Mawson, et al [26].

Fig. 3. Phase behavior of telechelic disulfate with fluorinated urethane backbones in liquid CO₂, T=298 K



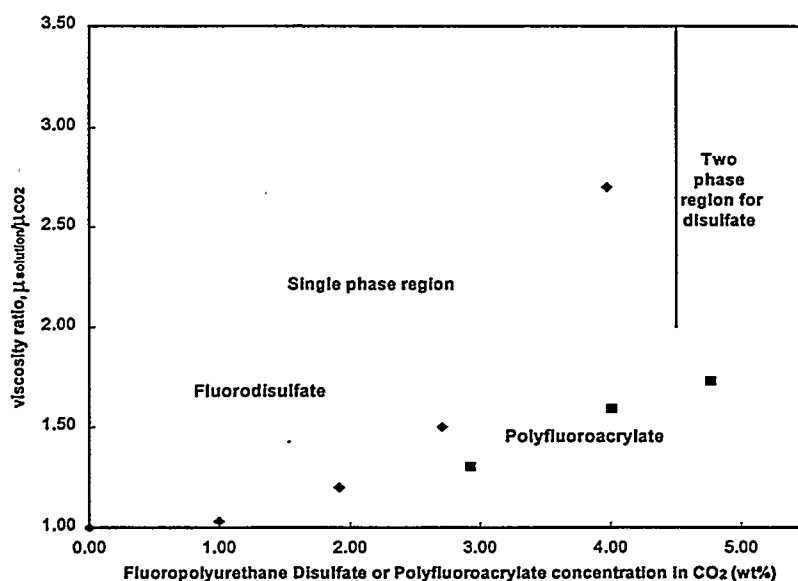
3.2 Viscosity measurements

Previous studies of telechelic ionomers in organic liquids have indicated that significant viscosity increases are most readily attained with dilute concentrations of high MW ionomers. Therefore, the highest MW telechelic ionomer that was soluble in CO₂ at pressures below 34.5 MPa was evaluated as a carbon dioxide-thickener. The viscosity

of single-phase mixtures of CO₂ and fluorinated polyurethane disulfate (MW=32500 g/mol, 0-4wt%) was measured at 298 K and 34.5 MPa.

Higher concentrations were not considered because the disulfate was not soluble in CO₂ at concentrations above 4wt%, as shown in Fig. 3.

Fig. 4. Disulfate-CO₂ solution viscosity change with disulfate concentration measured by falling cylinder viscometry, disulfate MW=32,500 g/mol, T=298 K, P=34.5 MPa



3.2 Viscosity Results

The viscosity results are presented in Figure 4. The change in viscosity relative to the viscosity of neat carbon dioxide at identical temperature and pressure conditions is

plotted against concentration of the fluorinated polyurethane telechelic ionomer. The viscosity measurements were performed at 293 K and 34.5 MPa. At 1wt%, there was no detectable increase in viscosity. However, as the disulfate concentration increased to 4wt%, the relative viscosity increased to a factor of 2.7. This indicated that the CO₂-soluble fluorinated polyurethane telechelic disulfate was capable of significantly increasing the viscosity of CO₂ at relatively low concentrations. Although the relative viscosity curve was increasing rapidly at this concentration, further viscosity increases were not attained because the solubility limit of the telechelic ionomer in carbon dioxide was slightly greater about 4.5 wt% (Fig. 4). An increase in the solution viscosity was also realized with the polyfluoroacrylate. The degree of the increase was less than that achieved with the disulfate at an equivalent concentration (wt%). For example, at 4wt% polyfluoroacrylate, the solution viscosity was 1.6 times greater than that of neat carbon dioxide, while the relative viscosity of the telechelic ionomer at the same concentration was 2.7.

Current research is directed at synthesizing higher MW, carbon dioxide-soluble telechelic ionomers that induce induce higher relative viscosities (10-100) at lower concentrations (0.1-1.0wt%).

4. Conclusions

Telechelic disulfates with extensively fluorinated polyurethane backbones were synthesized from the reaction between fluorinated diol and 1,6 bis(diisocyanato hexane).

Ionomers with molecular weights in the range of 15200-32500 g/mol exhibited significant solubility in liquid CO₂ at 293 K pressures below 34.5 MPa. Due to the competing effects of CO₂-philic fluorinated backbone content and the total molecular weight of the polymer, an optimal molecular weight, about 19500 g/mol, occurred for the miscibility of the disulfates with CO₂. The viscosity of carbon dioxide-fluorinated disulfate (MW 32500 g/mol) solutions was measured at 293 K and 34.5 MPa. The results indicated that the viscosity of the 4 wt%disulfate-CO₂ solution was 2.7 times greater than that of neat carbon dioxide. This telechelic ionomer was slightly more effective carbon dioxide thickening agent (at equivalent wt%) than poly(heptadecafluorodecyl acrylate).

Although these results are promising, they need to be improved. It is still desirable to obtain a greater viscosity increase at a lower concentration of the thickener. Therefore, we will evaluate higher MW telechelic ionomers based of polyfluoroacrylates. No further work will be done on non-functionalized polymers because they do not appear to have the potential to be effective at concentrations of 1wt% or less. We will also initiate the evaluation of H-bonding compounds and tin fluorides during the next quarter.

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