Enhancement of the Viscosity of Carbon Dioxide Using Styrene/Fluoroacrylate Copolymers

Zhihua Huang, Chunmei Shi, Jianhang Xu, Sevgi Kilic, Robert M. Enick, and Eric J. Beckman*

Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

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ABSTRACT: Copolymers of a fluorinated acrylate and styrene were synthesized to enhance the viscosity of liquid carbon dioxide. The phase behavior of mixtures of these polymers with carbon dioxide was measured at 295 K and pressures from 6.70 to 48.28 MPa. Miscibility pressures decreased with a decrease in the styrene content and increased as molecular weight increased. These polymers were also found to significantly enhance the viscosity of carbon dioxide, by a factor of ca. 5 to 400 at concentrations from 1 to 5 wt %. The optimal composition for viscosity enhancement was 29 mol % styrene−71 mol % fluoroacrylate.

Introduction

Carbon dioxide has been promoted as a green solvent for a variety of industrial applications because it is nonflammable, nonhazardous, low cost, and environmentally benign. Carbon dioxide thus offers new opportunities in chemical manufacturing including polymer processing,[1,2] formation of microcellular materials,[3] heterogeneous reactions and polymerization,[4−6] protein extraction,[7,8] complexation of organic acids[9] and heavy metals,[10] and separations processes such as cleaning and purification. For many years, carbon dioxide has also been used as a solvent for enhanced oil recovery and as a well-fracturing fluid by the oil and gas industry.[11,12] The foremost disadvantage of carbon dioxide for enhanced oil recovery is that its viscosity is only 0.03−0.10 cP at reservoir conditions, while the reservoir oil viscosity varies between 0.1 and 50 cP. The areal sweep efficiency of a CO_2 flood can thus be very low, because the carbon dioxide "fingers" toward the production wells rather than displacing the oil ahead of it. Vertical sweep efficiency in stratified reservoirs can also be diminished as the CO_2 preferentially flows into high permeability layers. If the viscosity of the carbon dioxide could be increased to a value comparable to the oil being displaced, a 2−20-fold increase in most cases, a significant increase in the rate of oil recovery and the cumulative amount of oil recovered would result. Well fracturing with liquid carbon dioxide would also be more effective if the viscosity of the carbon dioxide could be increased. "Thickened" carbon dioxide would be able to propagate wider fractures, carry larger sand proppant particles further into a fracture, and reduce "leak-off" of CO_2 into the faces of the fractures.

Many researchers have attempted to "thicken" carbon dioxide by using organic compounds that associate in solution. Initial attempts focused on compounds known to thicken oils,[13,14] although these efforts were unsuccessful due to the very low CO_2 solubility of conventional hydrocarbon-based polymers, telechelic ionomers, organometallic compounds, surfactants, and ammonium carbamates. Although viscosity enhancement was observed in some cases when an organic cosolvent such as toluene or ethanol was introduced,[15−17] identification of a viscosity-raising agent for neat carbon dioxide remained elusive. Recent attempts to identify CO_2-soluble thickeners have been more productive, because novel thickeners have been designed to achieve high solubility in liquid carbon dioxide. DeSimone and coworkers[18−20] have recently conducted homogeneous polymerizations in liquid and supercritical carbon dioxide, and fluoropolymers and silicones have been shown to be greatly soluble in CO_2. Poly(1,1-dihydroperfluorooctyl acrylate),[21] with molecular weight (MW) of ca. 1.4×10^6, was miscible with CO_2 and was able to induce a significant increase in solution viscosity as measured in a falling sinker viscometer. At 50 °C, 6.7 wt % polymer increased carbon dioxide's viscosity from 0.08 to 0.2−0.6 cP, the first successful "thickening" of neat carbon dioxide. Although the target level of viscosity enhancement at the very low concentrations desired for enhanced oil recovery (less than 1 wt %) was not attained, DeSimone's results indicated that it was possible to generate high molecular weight, CO_2-soluble polymers capable of increasing the viscosity of dense carbon dioxide.

Recently, Shi et al.[22,23] synthesized CO_2-soluble fluorinated polyurethane disulfates with molecular weights (MW) up to 32 500 g/mol. Falling cylinder viscometry results showed that at a concentration of 4 wt % a fluorinated disulfate with MW of 32 500 increased the solution viscosity 2.7-fold relative to neat carbon dioxide at room temperature and 34.5 MPa.

To significantly enhance the viscosity of carbon dioxide when present in dilute concentration, thickening agents should create the macromolecular structures of very high molecular weight via noncovalent association. It has been reported[24,25] that random, lightly sulfonated polystyrene can greatly increase solution viscosity in nonpolar organic solvents through the association of the acid or salt groups in the polymeric chain. Unfortunately, polystyrene does not dissolve in dense carbon dioxide at reasonable pressures and temperatures.

In this paper, we report that highly CO_2-soluble styrene/fluorinated acrylate copolymers can enhance the viscosity of CO_2 by factors greater than 100 at concentrations of about 5 wt %; 3−10-fold increases in viscosity are realized for 1 wt % solutions at shear rates much greater than those associated with EOR. Therefore, this

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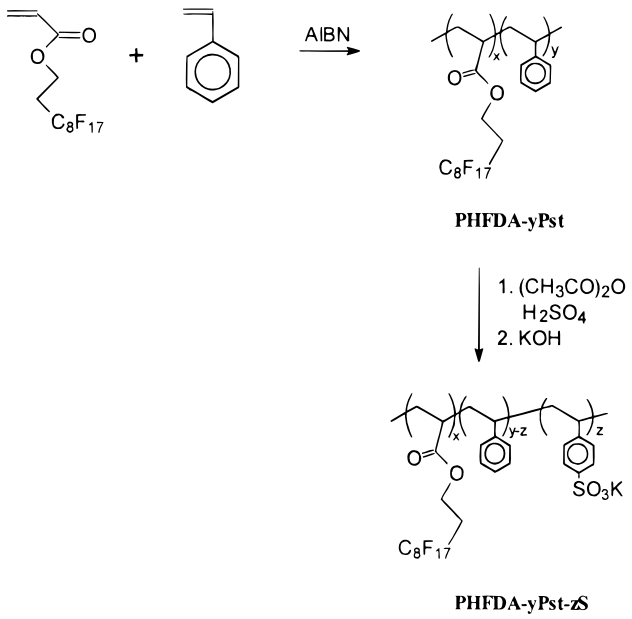
Scheme 1



type of copolymer has the potential to attain the desired level of viscosity enhancement at low shear rates when present in dilute concentration

Experimental Section

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-Heptadecafluorodecyl acrylate (HFDA) was obtained from Aldrich and was purified in order to remove inhibitor before use. All other reagents and solvents were received from Aldrich and were used without further purification unless otherwise indicated.

General Procedures. Copolymers from HFDA and styrene monomers were obtained by bulk free radical polymerization using AIBN as initiator (Scheme 1). Under an inert N_2 atmosphere, a 50 mL glass ampule was charged with 5.18 g of monomer HFDA (0.01 mol), 0.42 g of styrene (4.0 mmol), and 4.6 mg of AIBN. The ampule was sealed and placed in a water bath at 65 °C for 12 h. The reaction mixture was cooled and then dissolved in 1,1,2-trichlorotrifluoroethane. The polymer was precipitated in methanol, washed, and dried under reduced pressure. Copolymers were lightly sulfonated at 50 °C in 1,1,2-trichlorotrifluoroethane using acetyl sulfate according to the procedure of Makowski et al.[27]

Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Mattson FTIR using KBr disks at a resolution of 4 cm^{-1}. ^1H NMR was recorded on a Bruker 300M NMR instrument. Intrinsic viscosities of the polymers were determined in 1,1,2-trifluorotrichloroethane at 25 °C using an Ubbelohde viscometer.

Phase Behavior and Viscosity Measurements. The phase behavior and viscosity measurements were performed at room temperature using a high-pressure, variable-volume, windowed cell as shown in Scheme 2. Isothermal compressions and expansions of mixtures of specified overall composition were used to initiate phase separation. Visual observations of the initial appearance of a second phase (cloud points or bubble points) indicated location of the phase boundary.

The viscosity of single-phase polymer−CO_2 solutions was determined by falling cylinder viscometry (see Scheme 3). This technique was selected because of its simplicity in monitoring large viscosity increases in fluids as indicated by reductions in the terminal velocity (μ_t) of a falling object:

$$\eta_f = \frac{K(\rho_s - \rho_l)}{\mu_t} \quad (1)$$

where K is the calibration constant, ρ_s is the solid cylinder density, ρ_l is the liquid carbon dioxide density, and η_f is the fluid viscosity. Although eq 1 is only valid for Newtonian fluids, it can also be used for estimating the viscosity of non-Newtonian fluids provided that the shear rate is low and shear dependence of the viscosity is not considered.[28,29] Although K is typically determined using calibration fluid of known viscosity, it is also possible to calculate K on the basis of the geometry of the viscometer.[30,31] The apparent shear rate range for the viscosity measurement can be calculated from a Newtonian fluid model for annular fluid flow around a falling cylinder which is displacing the fluid according to eq 2.[30,31]

$$\text{shear rate} = \frac{dU_z}{dr} = U_t\left[\frac{-2r_c - (r_t^2 - r_c^2)\dfrac{1}{r_c \ln(r_c/r_t)}}{r_t^2 - r_c^2 + \ln(r_c/r_t)(r_t^2 + r_c^2)} + \frac{1}{r_c \ln(r_c/r_t)}\right] \quad (2)$$

where U_z is the fluid velocity in the z direction, U_t is the falling cylinder terminal velocity in the z direction, r_t is the inside radius of the glass tube, r_c is the radius of the falling cylinder, and r is the distance from the central line of the cylinder. In this study, the apparent shear rate range is 20−7000 s^{-1}.

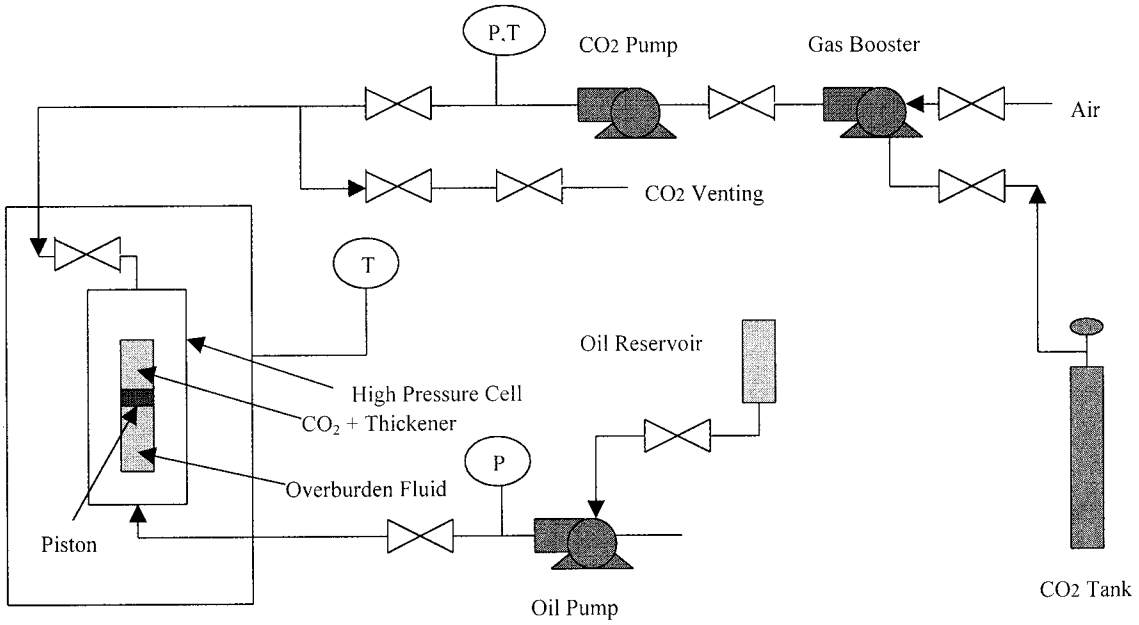
The viscosity tests were performed using the phase behavior apparatus. As shown in Scheme 3, a finely machined aluminum cylinder was placed in the cylindrical sample volume before the polymer sample, and the mixing balls were added. After equilibration of the system, the cell was rapidly inverted, and the fall time of the cylinder across a certain distance was measured, from which the terminal velocity was obtained for viscosity calculations. Experimental measurements indicated that the cylinder reached its terminal velocity well before the observation levels at the bottom half of the viscometer, especially for very viscous fluids, as expected by theoretical predictions of the acceleration length of the falling piston.[30,31] Therefore, the fall time measurements were carried out in the bottom part of the viscometer. The falling aluminum cylinder was calibrated using neat carbon dioxide. 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, and thus the relative viscosity was equivalent to the terminal velocity ratio (terminal velocity in neat carbon dioxide/terminal velocity in solution). The fall time measurement was repeated five times at each concentration, and the average apparent relative viscosity (the ratio of the average terminal velocity of the cylinder falling through the solution to the terminal velocity of the cylinder falling through neat CO_2) of the solution results was reported.

Results and Discussion

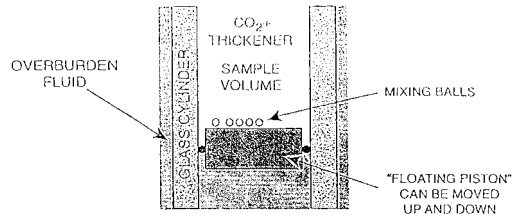
Copolymers of styrene and the fluoroacrylate were characterized using ^1H NMR and intrinsic viscosity in 1,1,2-trichlorotrifluoroethane (TCTFE). Results are reported in Table 1.

Phase Behavior of Polymers in Liquid Carbon Dioxide. Although carbon dioxide, in both its liquid and supercritical states, is miscible with many small molecules, it is a relatively poor solvent at easily accessible conditions (temperature <100 °C and pressure <50 MPa). Materials that exhibit low or negligible solubility in pure carbon dioxide include most polymers (except amorphous or low-melting fluoropolymers and silicones), waxes, heavy oils, proteins, salts, and metal oxides. It has been reported[23] in our laboratory that the homopolymer of HFDA is soluble in liquid carbon dioxide at concentration of 5 wt % at room temperature and low pressure (below 10 MPa). DeSimone and co-workers[21] have reported on the high solubility of poly(1,2-dihydroperfluorooctyl acrylate) (polyFOA) in supercritical carbon dioxide at low pressure as well.

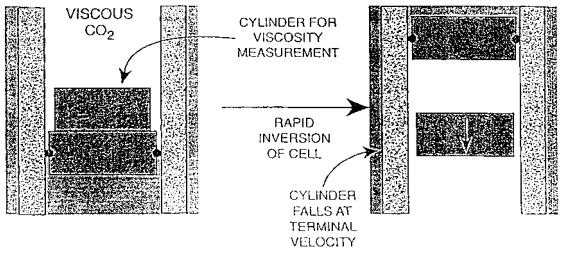
Scheme 2. High-Pressure, Variable Volume, Windowed Cell (D. B. Robinson Cell)



Scheme 3



SOLUBILITY ARRANGEMENT



VISCOSITY MEASUREMENT

Figure 1 shows that the experimental cloud point curves of PHFDA−*x*PSt copolymers in carbon dioxide at 25 °C with concentration varying from 1.0 to 5.0 wt %. The copolymer becomes more difficult to dissolve in carbon dioxide as styrene content increases, because styrene repeat units are known to be CO_2-phobic. When the styrene content reaches 40 mol %, concentrations of more than 3 wt % copolymer do not completely dissolve in carbon dioxide at 25 °C below 50 MPa. It should be noted that the polymers shown in Table 1 exhibit differences in molecular weight (as shown by intrinsic viscosity for samples with same styrene content) as well as styrene content. Ordinarily, the cloud point pressure increases sharply as polymer molecular weight increases, and thus the data in Figure 1 reflect both molecular weight and styrene content variations. However, if we compare the cloud point curves that represent the two copolymers with the same styrene content (29 mol %) and different molecular weight

Table 1. Composition of Copolymers

polymer[a]	content of polystyrene (mol %) theoretical	by ^{1}H NMR	intrinsic viscosity[c] (g/mL)
PHFDA−0.258PSt	22.0	25.8	117.8
PHFDA−0.273PSt	25.0	27.3	
PHFDA−0.292PSt	29.0	29.2	175.4
PHFDA−0.299PSt[b]	25.0	29.9	196.4
PHFDA−0.347PSt	33.0	34.7	145.8
PHFDA−0.403PSt	40.0	40.3	

[a] Polymerization conditions: [AIBN]/[monomers] = 0.2 mol %, 60 °C, 24 h. [b] This polymer was synthesized by bulk polymerization using 2,3-dicyano-2,3-diphenylsuccinic acid diethyl ester as initiator.[26] Reaction conditions: [initiator]/[monomers] = 0.05 mol %, 70 °C, 4 days. [c] Intrinsic viscosity was determined in 1,1,2-trichlorotrifluoroethane at 25 °C.

(intrinsic viscosity of 175 and 196, respectively), it appears that styrene content plays a more significant role than molecular weight in determining the location of the phase boundary for these copolymers.

The neutralized sulfonated copolymer (NSC) is more difficult to dissolve in carbon dioxide than its unsulfonated analogue because the high-polarity salt is more CO_2-phobic. Figure 2 shows the cloud points of NSC (PHFDA−0.258PSt−0.027S) in carbon dioxide vs concentration. Compare to its unsulfonated analogue (PHFDA−0.258PSt), it exhibits much higher cloud point pressures, especially at high concentration.

Viscosity Behavior of the Polymers. In an earlier attempt to raise the viscosity of liquid carbon dioxide, we previously synthesized and evaluated telechelic (sulfonate-teminated) fluorinated polyurethanes,[23] polymers that may undergo association in solution. The relative viscosity approached 3 at concentrations of 5 wt % polymer, a significant enhancement but far short of what would be necessary to effectively practice CO_2-based enhanced oil recovery (EOR). Therefore, we evaluated materials with other means for association in solution in the current study. It is known that phenyl groups can "stack" in organic solvent.[32] This stacking of phenyl groups in the copolymers would provide a fundamental force for intermolecular association needed to raise the viscosity of the solution. Figure 3 illustrates

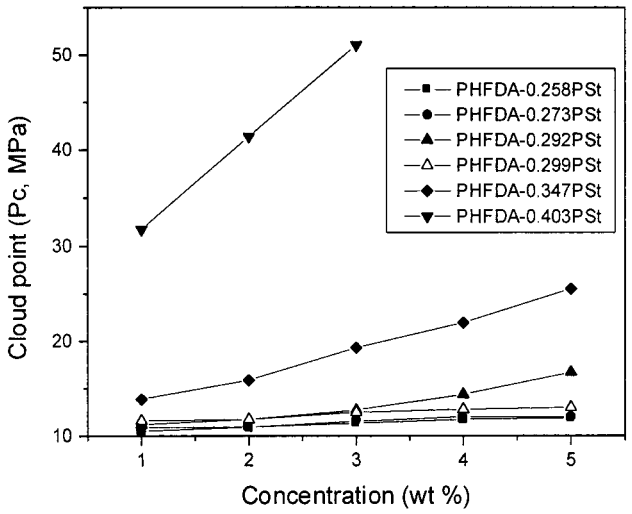


Figure 1. Experimental results of poly(HFDA)−polystyrene copolymers cloud point behavior in CO_2 at 25 °C.

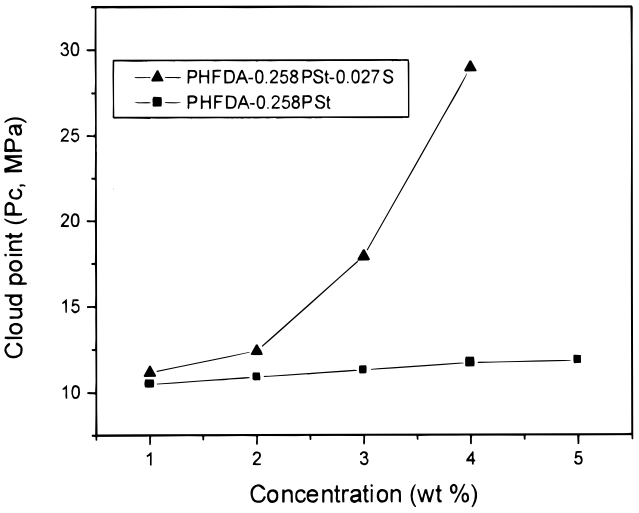


Figure 2. Cloud point result of the neutralized lightly sulfonated copolymer (PHFDA−0.258PSt−0.027S) in CO_2 at 25 °C.

the viscosity behavior of the copolymers in liquid carbon dioxide with concentrations varying from 1 to 5 wt % at 25 °C and 34.48 MPa. All of the copolymers enhance the viscosity of neat liquid carbon dioxide, yet not to the same degree. As shown in the figure, there exists an optimum level of styrene (approximately 29 mol %) insofar as viscosity enhancement is concerned. For copolymers (PHFDA−0.292PSt and PHFDA−0.299PSt) with the same composition and different molecular weight, not surprisingly, the one with higher molecular weight shows a higher extent of viscosity enhancement. It might be expected that if $\pi-\pi$ stacking is governing the viscosity enhancement of these copolymers solutions, then increasing the number of phenyl groups (increasing the styrene content) would produce a monotonic increase in the viscosity, rather than the behavior shown in Figure 3. However, the phase behavior results show that increasing the styrene content in the copolymers renders the polymer−solvent thermodynamics less favorable. (CO_2 is a poorer solvent for copolymers with higher styrene contents.) Hence, the polymer coils will not be as expanded in solution at higher styrene contents, potentially leading to fewer interchain associations and a larger number of intrachain associations.

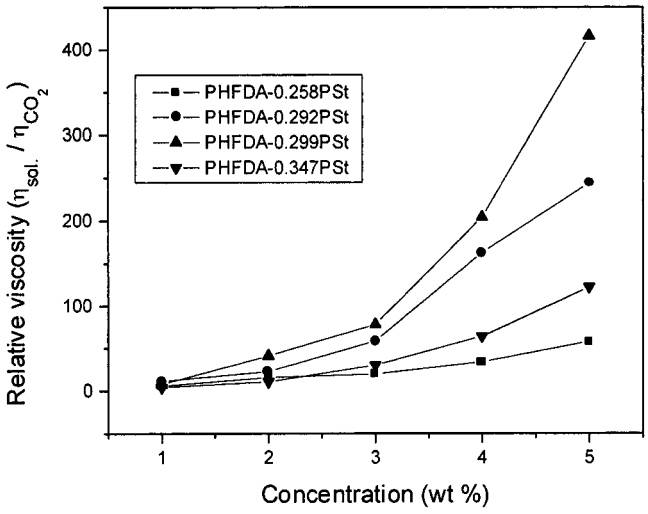


Figure 3. Apparent relative viscosity of copolymer solutions in CO_2 as a function of concentration at pressure of 34.48 MPa and 25 °C.

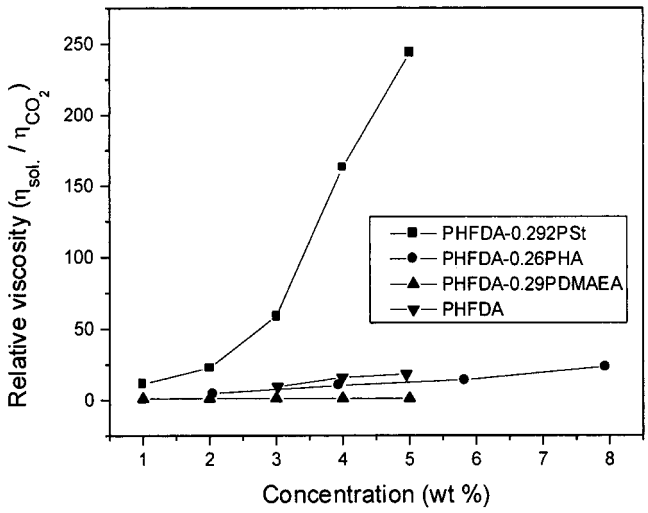


Figure 4. Apparent relative viscosity of CO_2−polymer solutions as a function of polymer type and concentration at pressure of 34.48 MPa and 25 °C. PHA = poly(hexyl acrylate); PDMAEA = poly(2-(dimethylamino)ethyl acrylate).

We surmise that $\pi-\pi$ stacking between phenyl groups is contributing to the strong viscosity enhancement effect of the copolymers, because copolymers lacking the aromatic group produce a much lower degree of viscosity enhancement in carbon dioxide. We synthesized copolymers, for example, from the fluorinated acrylate and hydrocarbon acrylates ((*N*,*N*-dimethylamino)ethyl acrylate (DMAEA) and hexyl acrylate (HA), respectively). Experimental results show that these polymers do not exhibit significant viscosity enhancement in neat liquid carbon dioxide, as shown in Figure 4.

The solution viscosity increases as pressure increases. Figure 5 shows the viscosity behavior of the copolymer (PHFDA−0.292PSt) in carbon dioxide at concentrations varying from 1 to 5 wt % and pressures from 20.69 to 41.38 MPa. It is known that increasing pressure will increase the viscosity of pure CO_2 (viscosity is a function of fluid density), but this dependence is already accounted for because the data in Figure 5 are reported as relative viscosities. However, solution viscosity could be a strong function of polymer volume fraction, given by

$$\phi_p = \frac{1}{1 + \frac{\rho_p}{\rho_c}\left(\frac{1-\omega}{\omega}\right)}$$

where the ρ's are the density of the polymer and CO_2, and w is the weight fraction polymer. Hence, as pressure increases, the volume fraction of polymer increases even though the weight fraction remains constant, given that CO_2 is much more compressible than the polymer. However, even this adjustment would not account for the large relative viscosity increase with increasing pressure. The pressure-induced increase in viscosity enhancement shown in Figure 5 may derive from the fact that CO_2 is a better solvent at higher pressures, and thus the polymer coils will be more expanded in solution at higher pressures. Greater coil expansion could lead to higher viscosity through larger numbers of interchain association points.

Just as lightly sulfonated polystyrene exhibits viscosity-thickening behavior in conventional organic solvents, the neutralized lightly sulfonated copolymers from styrene and fluorinated acrylate were found to significantly enhance the solution viscosity in neat liquid carbon dioxide. Figure 6 shows the viscosity behavior of a neutralized lightly sulfonated copolymer (PHFDA−0.258PSt−0.027S) and its unsulfonated analogue (PHFDA−0.258PSt) in carbon dioxide at concentrations from 1 to 4 wt % at 34.48 MPa and 25 °C. The neutralized lightly sulfonated copolymer can increase the viscosity to a higher extent than its unsulfonated analogue due to ionic association in solution. Unfortunately, the neutralized lightly sulfonated copolymer is more difficult to dissolve in carbon dioxide at reasonable conditions.

Consequently, we performed a series of experiments on the polyfluoroacrylate-*co*-polystyrene (29 mol % styrene) where either the polymer concentration or the falling cylinder radius was varied (note that each of these will affect the terminal velocity). Consequently, we could evaluate the effect of shear rate (defined by eq 2) on the viscosity, as shown in Figure 7. From these data we conclude that these copolymer/CO_2 solutions are shear thinning. The shear rate range associated with EOR is approximately 10 s^{-1}; therefore, Figure 7 indicates that it may be possible to achieve a 2−20-fold increase in solution viscosity at concentrations much less than 1.0 wt %.

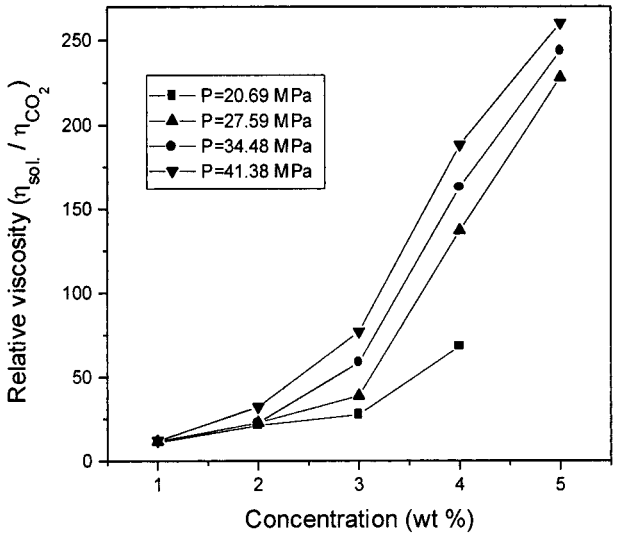


Figure 5. Apparent relative viscosity of copolymer PHFDA−0.292PSt solution in CO_2 as a function of concentration at pressure varying from 20.69 to 41.38 MPa and 25 °C.

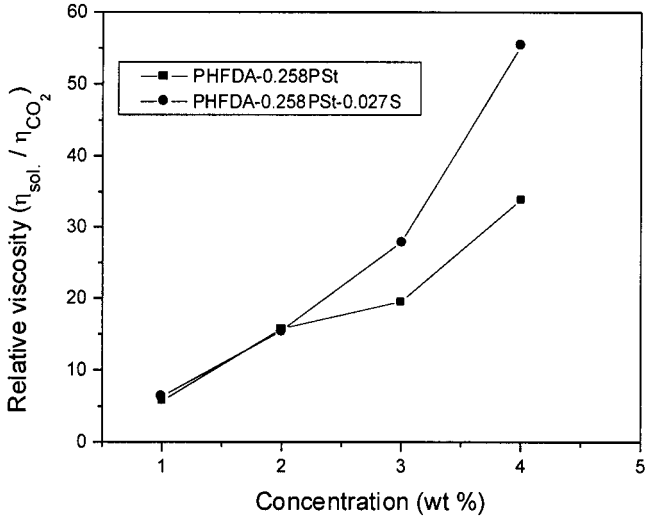


Figure 6. Apparent relative viscosity of solutions of copolymer PHFDA−0.258PSt and its neutralized lightly sulfonated polymer PHFDA−0.258PSt−0.027S in CO_2 as a function of concentration at pressure of 34.48 MPa and 25 °C.

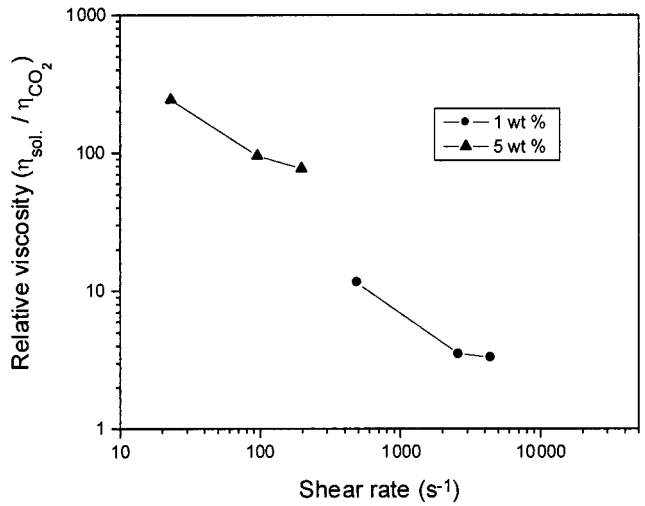


Figure 7. Apparent relative viscosity of copolymer PHFDA−0.292PSt solution in CO_2 as a function of shear rate at pressure of 34.48 MPa and 25 °C.

Currently, more data are being collected over a wide range of compositions and shear rates, and a power-law viscosity model of the solutions will be employed (rather than the Newtonian fluid assumption) to more accurately describe the CO_2−copolymer solutions. Nonfluorinated analogues of these thickeners are also under development.

Conclusions

Highly CO_2-soluble copolymers from perfluoroacrylate and styrene monomers were synthesized by free radical polymerization. Cloud point experiments indicate that the solubility of the polymers decreases with increasing styrene content in the polymer chain. A neutralized, lightly sulfonated polymer was also obtained, and it was more difficult to dissolve in liquid carbon dioxide than its unsulfonated analogue because of ionic association in the solution. All of these copolymers can enhance the viscosity of carbon dioxide by several orders of magni-

tude at relatively low concentration at room temperature, possibly because of "stacking" of phenyl groups in the solution. In addition, an optimum level of styrene (approximately 29 mol %) with regards to viscosity-thickening behavior in carbon dioxide was observed. The study of shear rate effect on viscosity behavior of polymer−CO_2 solution shows that the relative viscosity decreases as shear rate increases. We are actively investigating changes to molecule structure of the polymer that will provide high viscosity-thickening behavior in carbon dioxide at low concentration (<1 wt %) and reduction in the weight percent fluorine in the associating molecules or replacement of fluorine with new, less expensive CO_2-philic groups.

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