

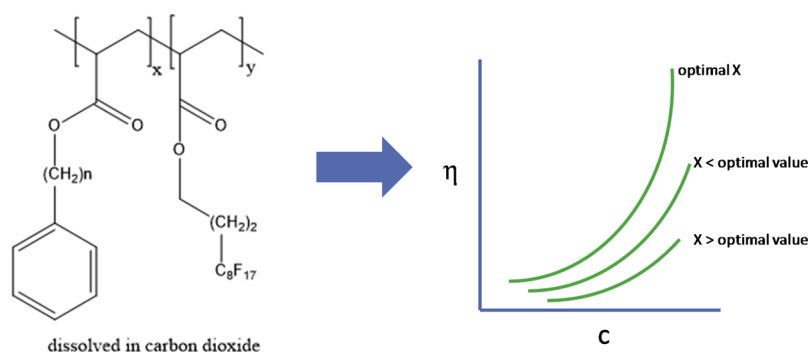
Fluoroacrylate-aromatic acrylate copolymers for viscosity enhancement of carbon dioxide

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GRAPHICAL ABSTRACT



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ABSTRACT

The effect of the structure of aromatic acrylate-fluoroacrylate copolymers on CO₂ viscosity at elevated pressures was investigated. These copolymers were all found to be miscible with CO₂ at pressures between 10–15 MPa (295 K) and induce an increase in the viscosity to some degree. It appears that stacking of aromatic rings is the key factor in viscosity enhancement. The results showed that viscosity of the solution increases with the increasing content of the aromatic acrylate unit in the copolymer, but a point is reached beyond which additional comonomer causes the relative viscosity to drop, suggesting that the aromatic rings associate through intramolecular rather than intermolecular interactions beyond the optimum value. The most effective CO₂ thickener identified in this study was the 29% phenyl acrylate-71% fluoroacrylate copolymer. However, the presence of a spacer (methyl or ethyl) between the backbone and the aromatic group substantially diminished the viscosity enhancement.

1. Introduction

A number of fluid-based techniques, including the use of high pressure CO₂, fall under the broad heading of Enhanced Oil Recovery (EOR) [1]. In CO₂ flooding, high-pressure CO₂ is injected into the oil-bearing porous media at reservoir temperatures that range between 298 K and 393 K. The minimum miscibility pressure (MMP) for a CO₂

displacement process is the pressure required to ensure that CO₂ is a strong enough solvent to recover essentially all of the crude oil that it contacts. The minimum miscibility pressure (MMP) is not the critical point. Rather, the MMP for a CO₂ displacement process is the pressure required to ensure that CO₂ is a strong enough solvent to recover essentially all of the crude oil that it comes into contact with as it flows through porous media. During this process, the injected CO₂

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extracts light hydrocarbon components from the crude oil, developing a CO₂/hydrocarbon composition that is miscible with the crude oil that it subsequently contacts. MMP values are determined by injecting CO₂ into long pieces of narrow tubing packed with unconsolidated sand and saturated with crude oil; these tubes are so narrow that viscous fingers cannot form and the CO₂ is able to sweep through and contact all of the oil in the porous media. The unconsolidated porous media is so permeable that the displacement occurs at nearly isobaric conditions. Therefore, CO₂ can attain a very high displacement efficiency of nearly 100% (i.e. the percentage of oil that can be recovered by solvent flowing through the porous media where the oil resides) at pressure values at or above the MMP. At pressures below the MMP the recovery of oil is incomplete, with poorer recovery occurring with decreasing pressure. MMP is a function of crude oil composition and temperature, and typically ranges from roughly 10 MPa at 298 K to about 30 MPa at 393 K. However, when CO₂ is injected into a well in an oilfield where the production well is located hundreds of feet away, the CO₂ has the ability to finger through the formation and not contact significant portions of oil-bearing rock because its viscosity of 0.03–0.10 cP at reservoir conditions [2] is roughly 10–100 times less than that of the light crude oil being displaced from the sandstone or limestone formation. Therefore, the CO₂ bypasses much of the oil in the formation [3]. As a result, operators must recycle the produced CO₂ and combine it with purchased CO₂ for extended periods of time in order to effectively sweep the formation. If CO₂ could be made more viscous, or thickened, such that its viscosity was comparable to that of the oil being displaced, viscous fingering would be suppressed and more oil could be recovered more quickly using less CO₂ [4].

There is a long history of attempts to increase the viscosity of CO₂ via the dissolution of polymers or small associating molecules in CO₂ [4,5]. Although one can also employ water-soluble or CO₂-soluble surfactants in CO₂ [6,7] in an attempt to generate high apparent viscosity CO₂-in-brine foams containing as much as 95 vol% CO₂ [8], these foams are inherently unstable and difficult to control within a sandstone or limestone formation.

There has been very limited success in significantly thickening CO₂ with thermodynamically stable, single-phase solutions of small associating molecules in CO₂. A handful of CO₂-soluble fluorinated self-assembling compounds have been synthesized that induce very modest changes in CO₂ viscosity [4,5]. Although our group recently used slightly more than 1 wt% of a non-fluorous benzene trisurfactant with three CO₂-philic dimethylsiloxane oligomeric arms to thicken CO₂ by more than an order of magnitude, the dissolution of the compound in CO₂ required the addition of at least 18 wt% organic co-solvent to the (72% or less) CO₂ [9].

Attempts to directly thicken CO₂ via the dissolution of high molecular weight oil-soluble polymers have also yielded little success. Although it is possible to thicken liquid propane, butane or pentane with dilute concentrations of an oil-soluble poly- α -olefin with an extraordinarily high molecular weight of at least 20 million [10], this polymer is insoluble in CO₂. Heller and coworkers [11] investigated numerous hydrocarbon polymers and identified 18 polymers that exhibited limited solubility (0.24–1.1 wt%) in CO₂ at EOR conditions. However, only several of the polymers induced very slight viscosity increases when they were dissolved in CO₂. Subsequent attempts by Heller and co-workers to maximize the entropy of mixing, and thereby the polymer solubility in CO₂, focused on the synthesis [12] and evaluation of poly α -olefins, such as poly α -hexene, however none were effective thickeners. Our group found that 2 wt% of polyvinyl acetate (PVAc) of molecular weight 11,000 was not able to induce an appreciable CO₂ viscosity increase [13]. An attempt to circumvent the low solubility of polymers in CO₂ by polymerizing CO₂-soluble monomers in dense CO₂ only resulted in the precipitation of the polymer [14].

Chevron researchers [15–17] selected candidates that exhibited solubility parameters less than ~ 7 (cal/cc)^{0.5} in an attempt to match the temperature- and pressure-dependent solubility parameter of CO₂ [18]

at reservoir conditions, which is roughly 5–6 (cal/cc)^{0.5}. It was determined that very high molecular weight silicone oil (polydimethylsiloxane (PDMS), with molecular weight of 197,000, kinematic viscosity of 600,000 cSt and solubility parameter of 7.3 (cal/cc)^{0.5}), could effectively thicken CO₂, but only if a significant amount of a co-solvent such as toluene (solubility parameter = 8.9 (cal/cc)^{0.5}) was added. For example, a 4 wt% PDMS, 20 wt% toluene, 76% CO₂ mixture had a viscosity of 1.2 cP, while pure CO₂ at the same condition exhibits a viscosity of only 0.04 cP [16].

The first high molecular weight polymer capable of dissolving in CO₂ at moderate pressures comparable to CO₂ EOR MMP values without the need for a co-solvent was reported by DeSimone and coworkers [19]. These researchers found that poly(1,1-, dihydroperfluorooctyl acrylate), (PFA, with molecular weight of 1,400,000, which is insoluble in both water and oil) could dissolve in CO₂ and induce a significant increase in viscosity as measured with a falling object viscometer. For example, at 323 K and 3.4 wt/vol% PFA in CO₂, the solution viscosity was ~ 0.25 cP at ~ 30.0 MPa, about 2.5 times greater than the viscosity of pure CO₂ at the same condition. Polyfluoroacrylate remains the most CO₂-soluble polymer that has been identified. Nonetheless, the concentration of the PFA (and hence the cost) was too high to be practical for CO₂ flooding. Enick, Beckman, and co-workers [20–22] developed an associative co-polymeric thickener based on a perfluoropolyacrylate in the hope of reducing the amount of thickener needed to attain a specified viscosity. Associating polymers provide the thermodynamic illusion of a dramatically increased molecular weight of the dissolved polymer. Because higher molecular weight polymers induce larger viscosity changes at the same mass concentration than lower molecular weight polymers or non-associating analogs, associating polymers are more effective thickeners at a specified mass fraction. The most effective thickener was a random co-polymer composed of ~ 79 mol% of a CO₂-philic fluoroacrylate monomer (1,1-,2-,2-tetrahydro heptadecafluorodecylacrylate) and 21 mol% styrene, a mildly CO₂-phobic monomer. The resultant fluoroacrylate-styrene copolymer (polyFAST) induced viscosity increases [20–22] greater than those reported for PFA [19] due to the aromatic rings, which are known to associate with one another via “ π - π stacking” that results from a different electron density along the periphery of the aromatic ring than in the core of the ring. Further, this polyFAST is reasonably soluble in CO₂ at temperature and pressure conditions similar to CO₂ EOR conditions [20]. An attempt to replace the fluoroacrylate of polyFAST with an inexpensive non-fluorous CO₂-philic monomer, vinyl acetate, yielded a low molecular weight polymer that required pressures much greater than MMP to attain dissolution, while inducing viscosity increases of only 25% at a concentration of 2 wt% [13]. Reviews of non-fluorous polymer solubility found in several review papers [23,24] further illustrate that no known hydrocarbon-based or oxygenated hydrocarbon-based high molecular polymer dissolves in CO₂ in sufficient concentration at EOR conditions to induce a significant increase in CO₂ viscosity.

In this study, we have explored the impact of fluoroacrylate copolymer structure on the ability of such materials to efficiently enhance the viscosity of CO₂. We employed several types of aromatic groups as associating moieties in fluoroacrylate based copolymers. Our initial hypothesis was that if we were to increase the distance between the aromatic group and the copolymer backbone, we might improve the ability for the aromatic groups to freely associate, and hence more effectively enhance the viscosity of their associated CO₂ solutions.

This study was conducted using a heptadecafluorodecylacrylate monomer that contains the C₈F₁₇ functionality, which can degrade via hydrolysis to perfluorooctanoic acid (PFOA). Because this monomer is no longer used in commercial products due to the bio-persistence of PFOA, we recommend that future studies employ analogous polymers made with the C₆F₁₃ fluorinated side chain. The C₆F₁₃-based chemistry enjoys global regulatory approval in a wide variety of commercial applications and C₆F₁₃-based compounds are safe and effective

replacements for the older C_8F_{17} -based analogs, especially because data in non-human primates indicate that they have substantially shorter half-lives in these animals than PFOA and are less toxic than long-chain perfluoroalkyl carboxylic acid (PFCA) chemicals. Therefore, in 2013, the EPA affirmed that compounds containing C_6F_{13} groups would not be targeted by EPA's 2009 Long-Chain Perfluorocarbon Action Plan Proposal (Poston and Connell 2013) [25]. Further, it has been previously shown that fluoroacrylate polymers containing C_6F_{13} functionalities retain a high degree of CO_2 -solubility [5].

2. Experimental procedure

2.1. Materials

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl acrylate (FA, 97%, $M_w = 518.17$ g/mol, density = 1.637 g/cm³) was obtained from Aldrich. 2-phenylethyl acrylate (PEA, $M_w = 176.22$ g/mol, density = 1.034 g/cm³) was purchased from Polysciences, Inc., naphthyl acrylate (NA, $M_w = 198.22$ g/mol, density = 1.1 g/cm³) from Monomer-Polymer & Dajac Lab. Inc., benzyl acrylate (BEA, 100%, $M_w = 162.19$ g/mol, density = 1.06 g/cm³) and cyclohexyl acrylate (CHA, 98%, $M_w = 154.21$ g/mol, density = 0.98 g/cm³) from Scientific Polymer Products, Inc. and phenyl acrylate (PA) from Lancaster, Inc. All monomers were purified using an inhibitor remover column (Aldrich) prior to use. Initiator, 2,2'-azobis(isobutyronitrile) (AIBN, 98%, Aldrich) was recrystallized twice from ethanol. 1,1,2-trichlorotrifluoroethane (TCTFE, 99.8%, Aldrich) and methanol (99.9%, Aldrich) were used as received.

2.2. Synthesis of copolymers of aromatic acrylates with fluoroacrylate

The copolymerization of aromatic acrylates with fluoroacrylate was performed free radically in bulk. In a typical experiment, an ampule equipped with stir-bar was flushed with argon. A known amount of aromatic acrylate, fluoroacrylate and AIBN (0.11 wt% of monomers) was added. The ampule was degassed, flame-sealed and placed in an oil bath at $T = 335 \pm 1$ K. At the point where the magnetic stir-bar ceased to spin, which was typically 30–45 min later, the reaction was stopped by quenching the ampule in liquid N_2 . Allowing the polymerization to proceed to higher conversions often yielded insoluble gels due to intramolecular and intermolecular H-abstraction (chain transfer) reactions during the course of polymerization [26–29]. Copolymers were purified via dissolution in TCTFE followed by precipitation into methanol (three times). Residual solvent was then removed under vacuum.

2.3. Synthesis of copolymers of cyclohexyl acrylate with fluoroacrylate

Cyclohexyl acrylate-fluoroacrylate copolymers were synthesized following the procedure given for the synthesis of aromatic acrylate-fluoroacrylate copolymers.

2.4. Structural characterization

Chemical characterization of the resulting products was accomplished via ¹H NMR spectroscopy; copolymer samples were dissolved in TCTFE in an 8 mm O.D. inner tube, which was then placed in a 10 mm O.D. outer tube containing deuterated chloroform and tetramethylsilane. Aromatic and acrylate proton peaks were used for calculation of comonomer compositions because they were well resolved in the spectra. *St-FA Copolymer*: δ 4.3 (broad, 2H, -CO-O-CH₂-CH₂-CF₂), δ 7.2 (broad, 5H, Ar). *PHA-FA Copolymer*: δ 4.3 (broad, 2H, -CO-O-CH₂-CH₂-CF₂), δ 7.2 (broad, 5H, Ar). *BEA-FA Copolymer*: δ 4.4 (broad, 2H, -CO-O-CH₂-CH₂-CF₂), δ 5.05 (broad, 2H, -CO-O-CH₂-Ar), δ 7.3 (broad, 5H, Ar). *PEA-FA Copolymer*: δ 4.3 (broad, 2H, -CO-O-CH₂-CH₂-CF₂), δ 4.1 (broad, 2H, -CO-O-CH₂-CH₂-Ar), δ 7.2 (broad, 5H, Ar). *NA-FA Copolymer*: δ 4.4 (broad, 2H, -CO-O-CH₂-CH₂-CF₂), δ 7.3 (broad, 7H, Ar)

CHA-FA Copolymer: δ 4.36 (broad, 2H, -CO-O-CH₂-CH₂-CF₂), δ 4.8 (broad, H, -CO-O-CH). The synthesis was found to be reproducible enough to attain the same molar concentration of each monomer in the copolymer to one percentage point or less. Determination of the molecular weight of fluoroacrylate copolymers was not performed. Analysis of copolymers containing more than 40 mol% fluoroacrylate is only possible using GPC with a solvent such as hexafluoro isopropanol (HFIP) because these highly fluorinated polymers are not soluble in non-fluorinated, non-corrosive solvents to the degree that allows for accurate molecular weight detection. Unfortunately HFIP is a corrosive solvent that will damage a GPC over a fairly short time frame of several months.

2.5. Phase behavior measurements

The phase behavior measurements were performed at 295 K using a high pressure, windowed, agitated, invertible, variable-volume wind-owed cell with a cylindrical sample volume (Schlumberger), as detailed in our prior studies [6,9,20–22,24]. Isothermal expansions and compressions of mixtures of specified overall composition were used to determine the two-phase boundary. A known amount of polymer was introduced to the sample volume. High pressure liquid carbon dioxide was then metered via a positive displacement pump (Schlumberger) into the sample volume. Addition of carbon dioxide was performed isothermally and isobarically by simultaneously withdrawing the transparent silicone oil overburden fluid at the same time with a second positive displacement pump (Schlumberger). This overburden fluid served to apply pressure to the floating cylinder at the base of the variable-volume cylindrical sample volume. The CO_2 -polymer mixture was pressurized and mixed with a small impeller at the top of the sample volume until a transparent single phase resulted. The system was then slowly depressurized by withdrawing the overburden fluid and thus expanding the sample volume. As the system pressure slowly diminished, a slight haze would appear as the least CO_2 -soluble components of the polydisperse polymer would come out of solution. As the pressure was reduced to slightly lower values (about 0.2 MPa lower than the first appearance of any haze), a pressure was attained at which all of the fluid in the sample volume was cloudy due to a second polymer-rich phase formation; this pressure was taken as the cloud point pressure of that mixture at that concentration. Measurements were repeated by compressing the mixture (re-pressurizing) until a single, clear phase was observed and then expanding (de-pressurizing) the system again. The average of 3–4 measurements was recorded as the cloud point pressure. Experiments were conducted over a range of compositions, thus the P-x diagram was established; typical variability in our cloud point measurements is less than ± 0.7 MPa.

2.6. Relative viscosity measurements

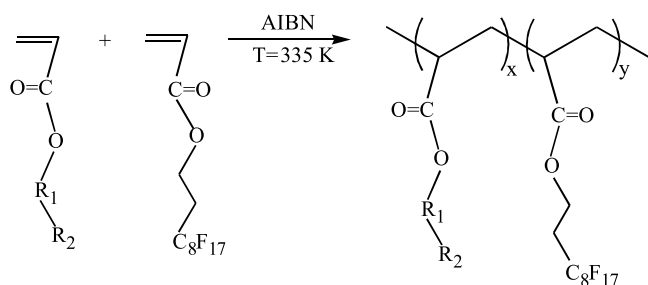
The relative viscosity of CO_2 -polymer solutions was determined using the same high-pressure variable-volume view cell equipment used for phase behavior experiments. The viscosity of transparent, single-phase CO_2 -polymer (i.e. thickened CO_2) solution was determined by a falling cylinder viscometer as described previously [9,10,20]. In a typical measurement of fluid viscosity, a finely machined aluminum cylinder (3.1597 cm in diameter) was placed into the cylindrical sample volume (3.1750 cm inside diameter) before the polymer sample and the mixing balls were added. Upon equilibration of the system at the specified CO_2 and polymer concentrations, temperature and pressure of interest (typically this process required 15 min of gentle stirring followed by 15 min of the system remaining quiescent) resulting in a single, transparent phase, the cell was rapidly inverted. Measurements taken at different positions of the glass cylinder indicated that the falling cylinder reaches its terminal velocity within the first 1/10 of the length of its fall. The fall time of the aluminum cylinder was recorded over a fixed distance at constant temperature and pressure. The

measurement was repeated at least 5 times for each CO₂-polymer mixture composition, temperature and pressure and the average value was determined and reported. Experiments were repeated in neat CO₂ as well. It was assumed that the difference between the density of the CO₂-polymer solution and the density of neat CO₂ at the same temperature and pressure was small compared to the 1.681 g/cm³ density difference between aluminum (2.700 g/cm³) and CO₂ (e.g. 1.019 g/cm³ at 295 K and 41.4 MPa). Therefore the relative viscosity is calculated from the ratio of fall times ($\eta_{\text{solution}}/\eta_{\text{CO}_2} = t_{\text{solution}}/t_{\text{CO}_2}$), where t_{solution} and t_{CO_2} are the amounts of time required for the cylinder to fall a specified distance through the high pressure polymer solution and neat CO₂, respectively. Because the fluoroacrylate-based polymers synthesized in this study contain a high mole fraction of the heptadecafluorodecyl acrylate monomer (M_w 518.17, 1.637 g/cm³) combined with a hydrocarbon monomer (0.98–1.1 g/cm³), the density of the fluorinated polymers was estimated to be about 1.5 g/cm³. The density of the single phase CO₂-polymer solutions that were present in the sample volume during viscosity measurements, which contained 1–5 wt % of the fluorinated polymer (1.5 g/cm³) and 99–95 wt% CO₂ (e.g. 1.019 g/cm³ at 295 K and 41.4 MPa), would have been roughly 1.011–1.055 times greater than that of neat CO₂. Therefore the actual density difference between the aluminum cylinder and the CO₂-polymer solution (e.g. 2.700 – 1.075 g/cm³ = 1.625 g/cm³ for a 5 wt% polymer solution) was slightly smaller than the density difference between aluminum and pure CO₂ (2.700 – 1.019 g/cm³ = 1.681 g/cm³). Consequently the CO₂-polymer viscosity values obtained from the ratio $\eta_{\text{solution}}/\eta_{\text{CO}_2} = t_{\text{solution}}/t_{\text{CO}_2}$ are overestimated by about 3% or less.

3. Results and discussion

3.1. Phase behavior results of the copolymers in dense CO₂

The copolymers of interest were composed of a fluoroacrylate monomer and another monomer intended to promote intermolecular associations while not rendering the copolymer CO₂-insoluble. We chose to include aromatic rings that can associate by forming non-covalent bonds via stacking [30–35]. Carbonyl groups were also included in the aromatic co-monomer, because it is well known that they exhibit favorable Lewis acid-Lewis base interactions with CO₂ [36–38]. It was also postulated that the acrylate group would extend the aromatic ring further from the backbone than the styrene used in poly-FAST, perhaps facilitating the π - π stacking. The general structure of the aromatic acrylate-fluoroacrylate copolymers is shown in Scheme 1.



	Phenyl Acrylate (PHA)	Benzyl Acrylate (BEA)	Phenyl Ethyl Acrylate (PEA)	Naphthyl Acrylate (NA)	Cyclohexyl Acrylate (CHA)
R ₁	-	-CH ₂ -	-CH ₂ -CH ₂ -	-	-
R ₂					

Scheme 1. Synthetic route for preparation of copolymers.

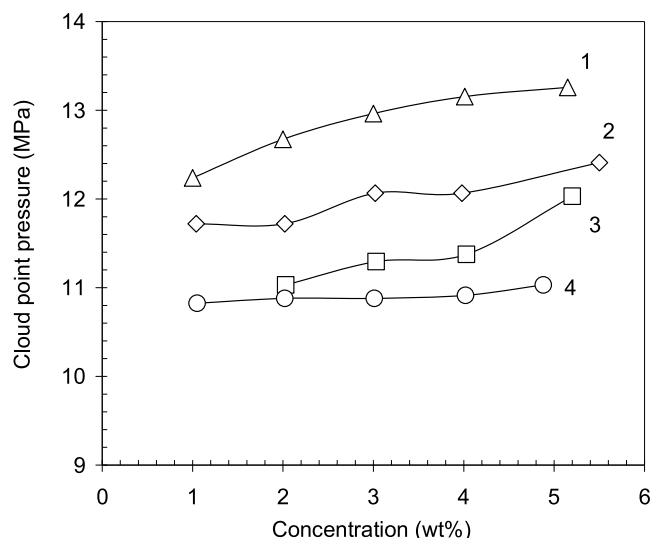


Fig. 1. Phase Behavior of PHA-FA Copolymer in CO₂ at T = 295 K (PHA: Phenyl Acrylate, FA: Fluoroacrylate) 1) 31%PHA-69%FA, 2) 29%PHA-71%FA, 3) 26%PHA-74%FA, 4) 23%PHA-77%FA.

The phase behavior of PHA-FA copolymers is illustrated in Fig. 1 as a function of concentration at various copolymer compositions. (Note that in all figures, the size of the data markers is slightly greater than or equal to the size of the ± 0.5 MPa error bars, therefore the data markers provide a direct indication of the error bar for the data measurement at that condition.) As can be seen in Fig. 1, as the aromatic acrylate content increases in the copolymer, the miscibility pressure of the copolymers rises slightly; given that the typical error in cloud point measurements is ± 0.7 MPa, the data in Fig. 1 show that the impact of the aromatic content in these copolymers is not large. The 23–31% PHA range may seem narrow; although polymers with less than 23% PHA would have exhibited even lower cloud point pressures, and (as will be shown later) have imparted little viscosity enhancement. Likewise, polymers with greater than 31% PHA would have increased the cloud point pressure substantially relative to the 31% PHA polymer, and (as will be shown later) have imparted little viscosity enhancement. Similar behavior was also observed with the BEA-FA and PEA-FA copolymers [39]. Further, despite the bulkiness of the naphthyl group, the location of the phase boundary does not change significantly with increasing content of naphthyl acrylate in the copolymer either (Fig. 2). Not surprisingly, increasing the length of the spacer between the aromatic groups and the carbonyl had no significant effect on miscibility pressures of the copolymers (Fig. 3). We surmise that the favorable interactions between the fluoroacrylate repeats and CO₂ (as well as weak fluoroacrylate self-interactions) dominate the thermodynamics of mixing and hence the location of the phase boundary for all of the copolymers evaluated.

The effect of the number of aromatic rings in the acrylate unit on miscibility is illustrated in Fig. 4. As seen in the figure, despite its bulkiness, the presence of naphthyl unit in the copolymer does not significantly increase the miscibility pressures (increased miscibility pressures reflect decreased miscibility and diminished polymer solubility in CO₂). The miscibility pressure curve of a NA-FA copolymer is located very close to that of a PHA-FA copolymer of the same aromatic acrylate content. As before, it is suggested that the highly CO₂-philic fluoroacrylate unit dominates the miscibility behavior of the copolymers in CO₂.

The miscibility pressures of various acrylate copolymers at similar compositions are compared in Fig. 5. Again, given the typical ± 0.7 MPa error in such measurements, the miscibility pressures for the copolymers are not substantially different.

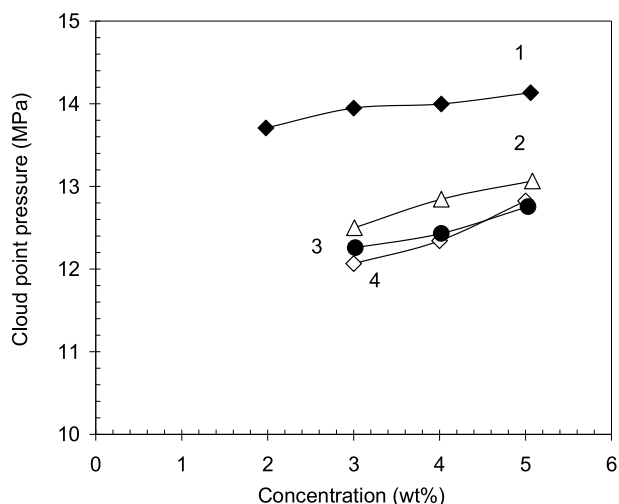


Fig. 2. Phase Behavior of NA-FA Copolymer in CO₂ at T = 295 K (NA: Naphthyl acrylate, FA: Fluoroacrylate), 1) 32%NA-68%FA, 2) 17%NA-83%FA, 3) 22%NA-78%FA, 4) 19%NA-81%FA.

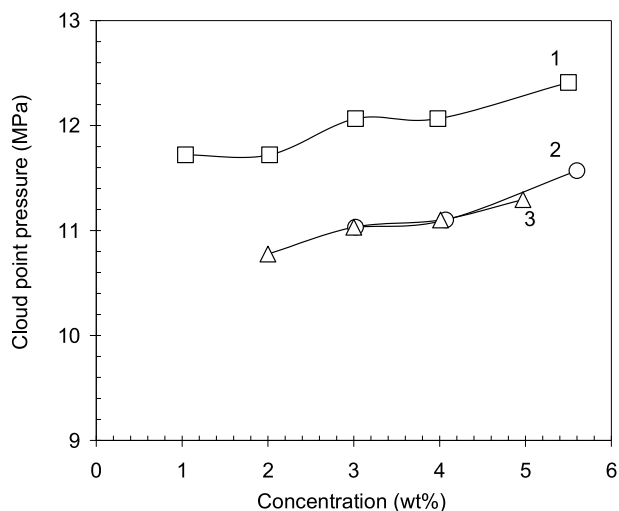


Fig. 3. Effect of spacer length on the phase behavior of copolymers in CO₂ at T = 295 K (PHA: Phenyl acrylate, BEA: Benzyl acrylate, PEA: Phenyl ethyl acrylate, FA: Fluoroacrylate), 1) 29%PHA-71%FA, 2) 29%BEA-71%FA, 3) 29%PEA-71%FA.

3.2. Viscosity behavior results of copolymers in dense CO₂

All of the aromatic acrylate copolymers studied in the current work were found to increase the viscosity of neat CO₂ to varying degrees. Unless otherwise noted, a pressure of 41.4 MPa (6000 psi) was selected to ensure that single-phase conditions were achieved for the viscometry testing; this pressure was not intended to represent the typical MMP values for EOR, which are significantly lower (on the order of 10 MPa at 295 K [4,5]). The viscosity of pure CO₂ at 295 K and 41.4 MPa is 0.129 cP [2]. Based on the average of five measurements ranging between 0.999 and 0.103 cm/s, the terminal velocity of the aluminum cylinder (3.1597 cm in diameter) falling coaxially within the cylinder (inside diameter of 3.1750 cm) charged with CO₂ at 295 K and 41.4 MPa was 0.101 cm/s (1.01 mm/s). (The terminal velocity of the same cylinder falling through the CO₂-polymer solution at the same temperature and pressure can be determined by dividing this velocity of 0.101 cm/s by the relative viscosity values reported in the following results at the same temperature and pressure.) The five viscosity values for each polymer solution at a specified temperature, pressure and polymer concentration are provided in the Supplementary Material,

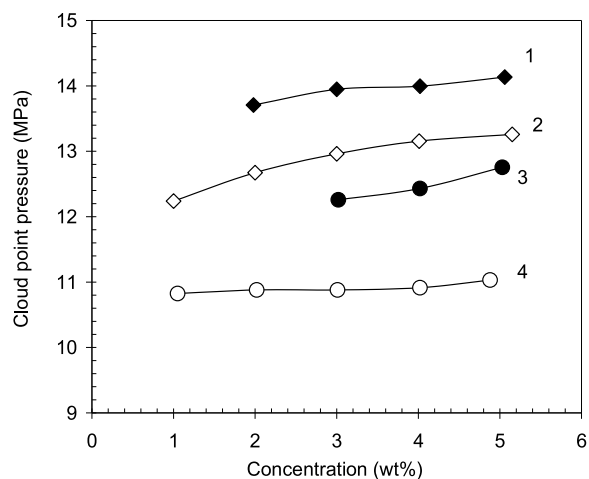


Fig. 4. Phase Behavior of NA-FA and PHA-FA Copolymers in CO₂ at T = 295 K (NA: Naphthyl acrylate; PHA: Phenyl acrylate, FA: Fluoroacrylate), 1) 32%NA-68%FA, 2) 31%PHA-69%FA, 3) 22%NA-78%FA, 4) 23%PHA-77%FA.

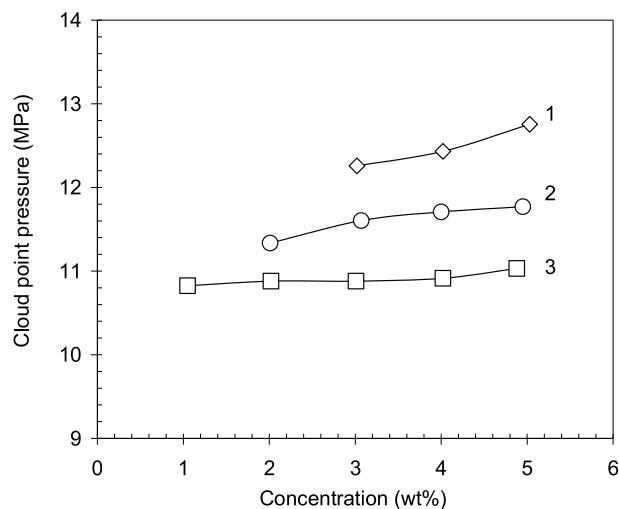


Fig. 5. Phase Behavior of NA-FA, CHA-FA and PHA-FA Copolymers in CO₂ at T = 295 K (CHA: Cyclohexyl acrylate, NA: Naphthyl acrylate; PHA: Phenyl acrylate, FA: Fluoroacrylate), 1) 22%NA-88%FA, 2) 22%CHA-78%FA, 3) 23%PHA-77%FA.

along with the standard deviation of each datum. The extent of the increase in viscosity depended strongly upon the structure of the aromatic acrylate and its content in the copolymer (from Figs. 6–8), and there was not a direct correlation between miscibility and viscosity. In other words, the most CO₂-soluble polymers (those with the least aromatic content) were not the most effective CO₂ thickeners at a given mass concentration. As seen in Fig. 6, viscosity increases with the addition of phenyl acrylate to the copolymer; but after a certain composition, additional increases in the content of the aromatic acrylate in the copolymer cause viscosity to drop. The same effect was previously observed with styrene-fluoroacrylate copolymers [20]. The optimum composition for PHA-FA copolymers for maximum viscosity enhancement is 29% PHA. 29 mol% is the same optimal composition of styrene in polyFAST [20–22]. Although one might expect that increasing the aromatic acrylate content would increase the number of association points, leading to a monotonic increase in viscosity, we believe that after an optimum composition, the hydrodynamic volume of the coils decreases due to the relatively CO₂-phobic nature of the aromatic acrylates. A number of studies have investigated the change in polymer coil dimension as a function of solvent density in supercritical fluids [40,41]. Those works indicated that the polymer chains expand as the

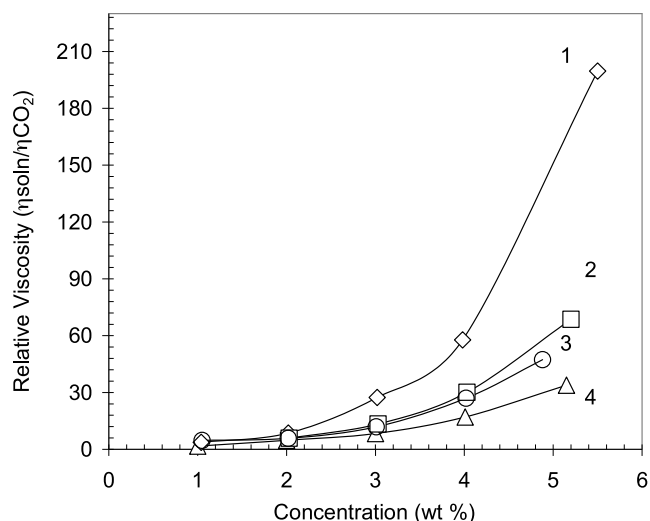


Fig. 6. Relative viscosity of x%PHA-y%FA copolymer solutions in CO₂ as a function of concentration at T = 295 K at varying copolymer composition, P = 41.4 MPa, (PHA: Phenyl Acrylate, FA: Fluoroacrylate), 1) 29%PHA-71%FA, 2) 26%PHA-74%FA, 3) 23%PHA-77%FA, 4) 31%PHA-69%FA.

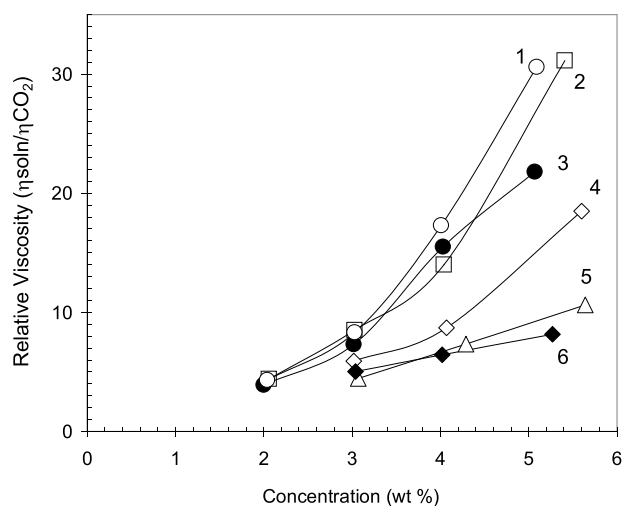


Fig. 7. Relative viscosity of x%BEA-y%FA copolymer solutions in CO₂ as a function of concentration at T = 295 K at varying copolymer composition, P = 41.4 MPa, (BEA: Benzyl Acrylate, FA: Fluoroacrylate), 1) 18%BEA-82%FA, 2) 21%BEA-79%FA, 3) 27%BEA-73%FA, 4) 29%BEA-71%FA, 5) 38%BEA-62%FA, 6) 54%BEA-46%FA.

density of supercritical fluid increases, screening attractive intra-chain forces. In our case, we believe that as the coils shrink owing to added aromatic acrylate, the aromatic rings associate more through intramolecular than intermolecular interactions, resulting in lower viscosity enhancement.

By contrast with the PHA-FA results in Fig. 6, viscosity enhancement by BEA-FA copolymers indicated decreasing trend with increase of BEA mol % in the BEA-FA copolymer (Fig. 7). These results suggest that optimum concentration for maximum viscosity increase is 18 wt% or below for BEA. Similar to PHA-FA copolymers, PEA-FA copolymers showed increase in relative viscosity with the increase of PEA content from 25% to 36% in the copolymer (Fig. 8).

The effect of increasing pressure is illustrated in Fig. 9. As the pressure increases, CO₂ becomes a better solvent for any given copolymer, hence inducing greater swelling (expansion) of the polymer coils and allowing for a higher chance for inter-chain associations. Therefore, the relative viscosity, the ratio of the CO₂-polymer solution viscosity to

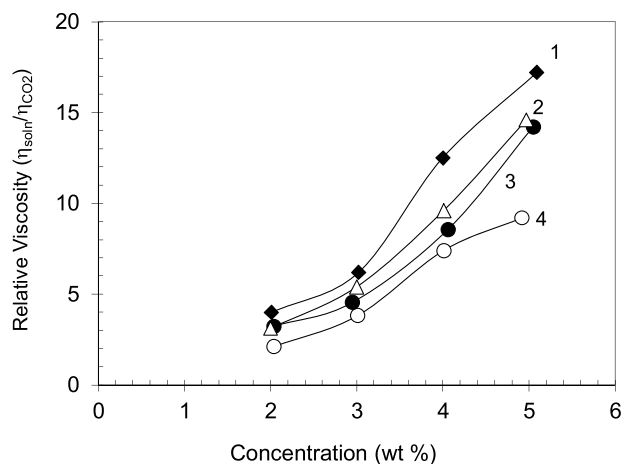


Fig. 8. Relative viscosity of x%PEA-y%FA copolymer solutions in CO₂ as a function of concentration at T = 295 K at varying copolymer composition, P = 41.4 MPa, (PEA: Phenyl ethyl acrylate, FA: Fluoroacrylate), 1) 36%PEA-64%FA, 2) 29%PEA-75%FA, 3) 26%PEA-74%FA, 4) 25%PEA-71%FA.

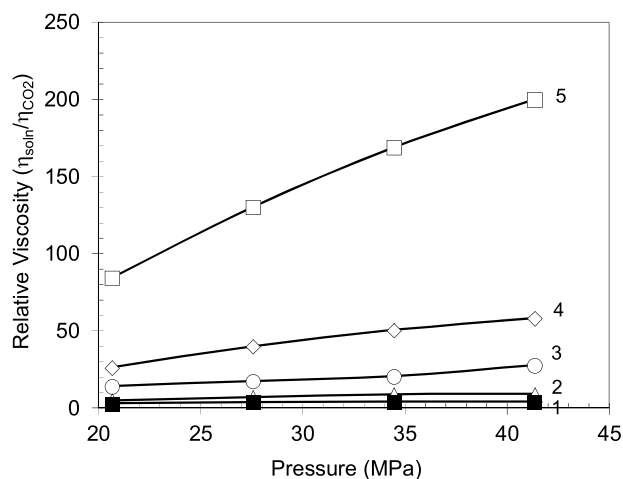


Fig. 9. Relative viscosity of 29%PHA-71%FA copolymer solutions in CO₂ as a function of pressure at T = 295 K at varying copolymer concentration in CO₂ (PHA: Phenyl Acrylate, FA: Fluoroacrylate), 1) 1 wt% copolymer concentration, 2) 2 wt%, 3) 3 wt%, 4) 4 wt%, 5) 5.5 wt%.

the viscosity of neat CO₂ at the same temperature and pressure, increases substantially with increasing pressure. Therefore, even as the viscosity of CO₂ increases with pressure (for example at 295 K, CO₂ viscosity at 20.7 and 41.4 MPa is 0.100 and 0.129 cP, respectively), the relative viscosity of the CO₂-polymer solution increases at a more rapid rate. This effect of increasing relative viscosity with increasing pressure was observed with all the copolymers examined in this study.

We established in Fig. 3 that spacer length has little impact on polymer solubility in CO₂ for the pendent phenyl group. Nonetheless, we had initially hypothesized that use of a spacer of one or two carbons between the aromatic moiety and the acrylate might allow for a more dramatic change in viscosity due to the enhanced ability of the aromatic groups to associate with one another, leading to enhanced viscosity in CO₂. The ability to modify the length of the alkyl spacer provides a useful tool for altering the viscosity-enhancing potential of the polymer in an attempt to maximize the concentration required to attain a desired level of thickening. Contrary to this hypothesis, we experimentally observed that increasing spacer length had a negative effect on viscosity enhancement, at least with regards to those copolymers possessing a single aromatic ring in the aromatic acrylate repeat unit (Fig. 10); PHA-FA, which has no alkyl spacer, thickened CO₂ more effectively than

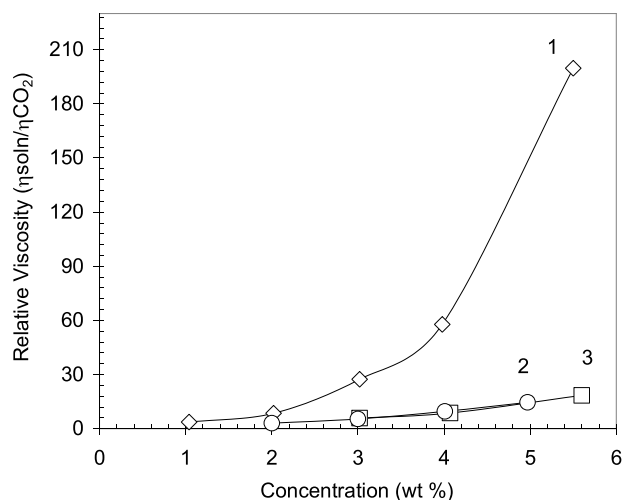


Fig. 10. Effect of spacer length on CO₂-viscosity enhancement of copolymer solutions as a function of concentration at T = 295 K and P = 41.4 MPa, (BEA: Benzyl Acrylate, PHA: Phenyl acrylate, PEA: Phenyl ethyl acrylate, FA: Fluoroacrylate), 1) 29%PHA-71%FA, 2) 29%PEA-71%FA, 3) 29%BEA-71%FA.

either BEA-FA (-CH₂- spacer) or PEA-FA (-C₂H₄- spacer). We surmise that the difference between anticipated and the actual behavior results from a change in electronic nature of the aromatic ring, which is electron-rich in its core and electron-poor in the peripheral torus of hydrogens, owing to a change in substituent that joins it to the polymer backbone from (aromatic ring-O-C(O)-backbone) to (aromatic ring-(CH₂)_x-O-C(O)-backbone). It was previously suggested that one could alter the magnitude of the interactions between closely aligned aromatic rings [30], which would both affect the electron density of the ring and the steric barriers to interactions. By introducing a less bulky, less-electron-withdrawing, alkyl spacers, we expected increased aromatic self-interaction and thickening, however it appears that this change also enhanced the strength of interaction between CO₂ and the aromatic and/or the accessibility of the aromatic groups with CO₂, which reduced the copolymer's ability to increase the viscosity of CO₂.

One might question whether the association of the aromatic rings is the key factor governing viscosity enhancement of CO₂ by these copolymers. In order to examine this, copolymers of fluoroacrylate with cyclohexyl acrylate at varying compositions were synthesized. Fig. 11

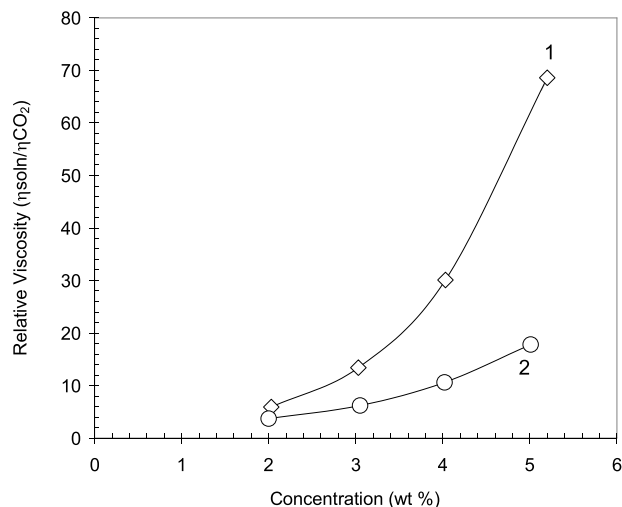


Fig. 11. Comparison of aromatic and non-aromatic rings on CO₂-viscosity enhancement at similar compositions at T = 295 K and P = 41.4 MPa as a function of concentration (PHA: Phenyl Acrylate; CHA: Cyclohexyl Acrylate; FA: Fluoroacrylate), 1) 26%PHA-74%FA, 2) 27%CHA-73%FA.

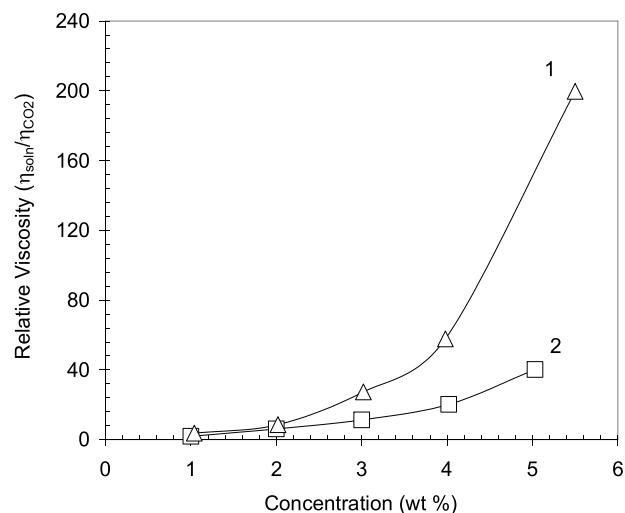


Fig. 12. Comparison of aromatic and non-aromatic rings on CO₂-viscosity enhancement at their most favorable composition at T = 295 K and P = 41.4 MPa as a function of concentration (PHA: Phenyl Acrylate; CHA: Cyclohexyl Acrylate; FA: Fluoroacrylate), 1) 29%PHA-71%FA, 2) 16%CHA-84%FA.

provides a direct contrast between the viscosity enhancement associated with aromatic rings and cyclohexyl rings, comparing the viscosity enhancement due to CHA-FA and PHA-FA copolymers at similar compositions, and Fig. 12 does so at the most favorable composition of 29%PHA-71%FA for the PHA-FA copolymer and the more favorable composition of 16%CHA-84% of the two CHA-FA compositions studied in this work (23%CHA-77%FA and 16%CHA-84%FA). As seen in these figures, the increase in viscosity is far more pronounced when a phenyl ring is included in the copolymer, which was as expected due to the π - π stacking that occurs with interacting aromatic rings. Although the results of the phenyl acrylate-fluoroacrylate (PHA-FA) copolymer and the previously studied styrene-fluoroacrylate copolymer polyFAST are not directly compared in Fig. 12 because they were obtained at slightly different temperatures and with cylinders of different diameter, it is clear that the results for the more favorable phenyl acrylate-fluoroacrylate composition (29% PHA - 71% FA) are similar to the results for the optimal fluoroacrylate-styrene copolymer (polyFAST) composition (29% styrene - 71% FA) from our previous work [20]. For example at 5 wt% the relative viscosity of polyFAST was 245 [20], while 5% of 29% PHA - 71% FA increased the relative viscosity to 205. It is also evident that the presence of the phenyl ring in PHA-FA or polyFAST copolymers results in significantly greater viscosity enhancement than it can be achieved with cyclohexyl groups.

We surmised that one might obtain higher viscosity enhancement in CO₂ by increasing the surface area of the aromatic groups [40,42]. Fig. 13 compares the effect of size of the aromatic functional group on viscosity of CO₂ via contrast of the phenyl and naphthyl groups, where it is clear that the use of the single aromatic ring provides superior results. As noted above, this could be due to enhanced CO₂ aromatic interaction [43–45] or decreased aromatic-aromatic interaction due to bulkiness and close proximity of the rings to the backbone in the naphthyl case.

One may think that the differences we observed in relative viscosities between various copolymers might be a result of differences in molecular weights. As previously noted, we could not measure the molecular weight of the polymers studied due to their insolubility in traditional GPC solvents such as THF and NMP. To estimate the effect of molecular weight variations on observed relative viscosities, we examined the Huggins equation:

$$\eta_{rel} = 1 + c[\eta] + K_H[\eta]^2c^2 \quad (1)$$

where $[\eta]$ and c are the intrinsic viscosity (dl/g) and the concentration

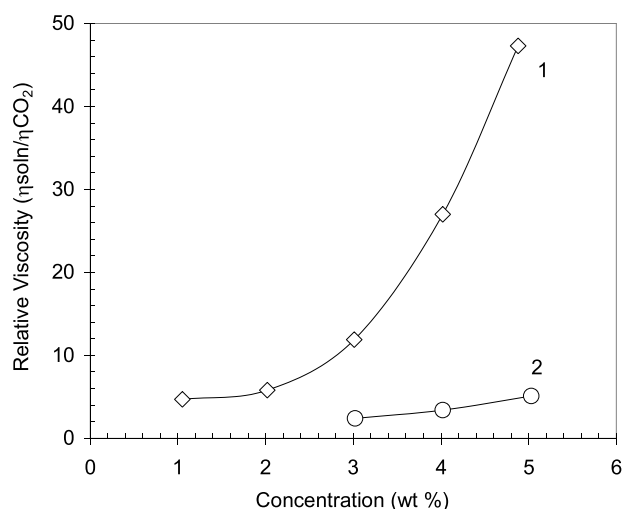


Fig. 13. Comparison of effect of size of aromatic rings on viscosity enhancement ability of CO₂ at two different compositions as a function of concentration. T = 295 K and P = 41.4 MPa (PHA: Phenyl acrylate; NA: Naphthyl acrylate; FA: Fluoroacrylate). (1) 23%PHA-77%FA, 2) 22%NA-78%FA.

(g/dl), respectively. K_H is the Huggins coefficient, which is approximately 0.3 for polymers in thermodynamically “good” solvents. In that high pressure CO₂ can dissolve 5 or more weight percent of many fluoroacrylate-rich copolymers and at least 15 wt percent of fluoroacrylate homopolymers [46], it can be considered to be a good solvent. Using the Mark-Houwink relationship ($[\eta] = K \cdot M^a$, where K and a are constants specific to each polymer-solvent pair), we can then estimate the effect of molecular weight variation on relative viscosity for polymers in “good” solvents. Given typical Mark-Houwink parameters for polyacrylates, methacrylates, and polystyrene in good solvents (benzene, chloroform) at a concentration of 5 g/dl (~ 5 wt % at high pressure), we find that changes in relative viscosity at constant concentration would be essentially proportional to changes in molecular weight. Although the insolubility of these polymers in solvents typically used for characterization prevented the determination of molecular weights, there is no reason to suspect that dramatic changes in molecular weight would occur as a result of our previously described synthetic techniques. Further, our previous study of fluoroacrylate-styrene copolymer intrinsic viscosity in trichlorotrifluoroethane, along with measurements of phase behavior and viscosity, demonstrated that dramatic differences in CO₂-thickening capability of copolymers was primarily attributable to the ratio of styrene to monomer, rather than differences in copolymer molecular weight [20]. Therefore we believe that the nearly order of magnitude changes in viscosity that we observed in this study upon altering co-monomer structure (e.g. from Figs. 9–13) are primarily due to changes in molecular structure and composition.

4. Conclusions

The effect of the structure of aromatic acrylate-fluoroacrylate copolymers on the viscosity of CO₂ was investigated. In general, these copolymers were all found to be miscible with CO₂ at 295 K at pressures below 15 MPa and induce an increase in the viscosity to some degree, depending upon the type and content of aromatic acrylate unit in the copolymer. It appears that stacking (association) of aromatic rings and the swelling of polymer coils are the key factors in viscosity enhancement. The location of the miscibility pressure curves of the copolymers was not strongly affected by the type and/or content of the aromatic acrylate unit. This was attributed to the dominance of the highly CO₂-philic fluoroacrylate unit in the copolymer on miscibility.

The results showed that viscosity of the phenyl acrylate-

fluoroacrylate copolymer solutions increases with the increasing content of the aromatic acrylate unit in the copolymer, but a point is reached beyond which additional increase causes the relative viscosity to drop. Existence of such an optimum composition suggests that, beyond an optimum, the aromatic rings associate through intramolecular rather than intermolecular interactions, resulting in a decrease in viscosity enhancement. It is surmised that decreasing affinity of CO₂ for the copolymer with increasing content of aromatic acrylate unit in the copolymer (i.e. decreasing hydrodynamic volume) is the reason for this effect. Consistent with this explanation, viscosity enhancement was found to be dependent on the pressure of the solution; higher viscosities were produced at higher pressures. This is again simply due to CO₂ becoming a weaker solvent for the polymer at lower pressures, resulting in a switch in the type of association from intermolecular to intramolecular. The most effective CO₂ thickener identified in this study was a 29 mol% phenyl acrylate-fluoroacrylate copolymer, which thickened CO₂ to a degree that was comparable to that of a 29 mol% styrene-fluoroacrylate copolymer, polyFAST [20–22].

Fluoroacrylate copolymers have been shown to increase the viscosity of CO₂ with falling cylinder viscometry and the mobility measurements of CO₂ flowing through porous media [21]. Being aware of the high cost of the fluoroacrylates and their environmental and biological persistence, we have been in parallel investigating inexpensive, non-fluorous, CO₂-philic polymers to replace the fluoroacrylate component out and thus to improve the viability of the EOR process. We have also recently demonstrated that more environmentally benign (but still expensive) fluorinated homopolymers of tridecafluorooctyl acrylate (i.e. the -C₆F₁₃ acrylate monomer) [47] are just as CO₂-soluble as homopolymers of the heptadecafluorodecyl acrylate (i.e. the -C₈F₁₇ acrylate monomer) [48,49]; exhibiting nearly identical cloud point pressure values at 1 wt% polymer concentration in CO₂ at 297–298 K.

Acknowledgements

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.supflu.2019.01.001>.

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