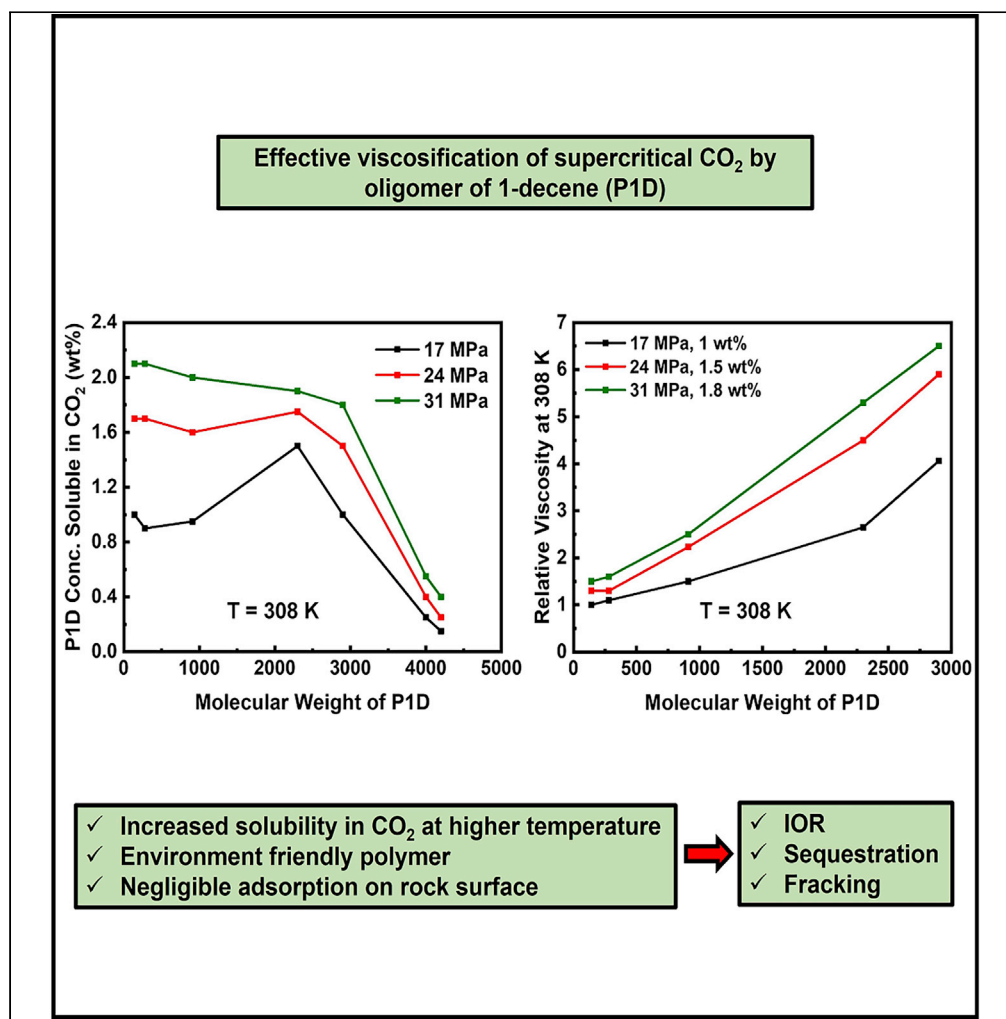


## Article

## Effective viscosification of supercritical carbon dioxide by oligomers of 1-decene



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**Highlights**

Increasing P1D size has non-monotonic solubility trend in CO<sub>2</sub> at moderate pressures

P1D solubility in CO<sub>2</sub> has monotonic trend at higher pressures

Methyl groups enhance solubilization in CO<sub>2</sub>

An exponential trend observed for relative viscosity with polymer molecular size

## Article

## Effective viscosification of supercritical carbon dioxide by oligomers of 1-decene

Taniya Kar<sup>1</sup> and Abbas Firoozabadi<sup>1,2,3,\*</sup>

## SUMMARY

**Viscosification of carbon dioxide by polymers can make large scale CO<sub>2</sub> sequestration safe and efficient. We present solubility of branched hydrocarbon oligomers in CO<sub>2</sub> and viscosification measurements at relevant subsurface conditions. Polymers of 1-decene (P1D) with about 20 repeating units are found to be effective in CO<sub>2</sub> viscosification, increasing it by 6.5-fold at 1.8 wt% concentration at 308 K and 31 MPa. We reason that methyl groups and branching promote solubility and viscosification. Low molecular weight oligomers can have lower solubility in CO<sub>2</sub> than higher molecular weight ones and the trend in solubility is non-monotonic at constant pressure and temperature. Analysis of solubility trend of P1D oligomers in CO<sub>2</sub> advances our understanding of molecular structure and functionality and opens the path to engineering of oligomers effective in viscosification and widespread use of CO<sub>2</sub>.**

## INTRODUCTION

The United States Geological Survey (USGS) in 2013 estimated the potential carbon dioxide storage capacity of the United States to be around 3000 metric gigatons. The US Energy Information Administration (EIA) estimates that the total CO<sub>2</sub> emission from various sources in 2020 was about 5.1 billion metric tons in the USA and about 33.1 billion metric tons worldwide. Hydrocarbon energy production has made major advances to minimize release of pollutants and toxic substances into the atmosphere and oceans. Hydrocarbon fuels have also become clean-burning resources. The major issue is climate change from emission of substantial amounts of CO<sub>2</sub> into the atmosphere. Numerous studies based on concentration of CO<sub>2</sub> in the atmosphere and temperature have found a correlation between the two (Petit et al., 1999). In the past 400,000 years, there have been several cycles of global warming. The cycles correspond to the period of higher CO<sub>2</sub> concentration (Firoozabadi, 2016). From around 1960, there has been a continuous increase in CO<sub>2</sub> concentration in the atmosphere from a yearly average of around 318 to 412 ppm in 2018. Until about 1900, the concentration of CO<sub>2</sub> had been close to or below 300 ppm. There may be delays in global warming from CO<sub>2</sub> concentration, but the general belief in the scientific community is that global warming and other consequences may arrive somewhat later. There is no shortage of space in the subsurface to permanently sequester CO<sub>2</sub> (Firoozabadi and Myint, 2010). Advanced technologies for carbon capture are being investigated with the focus on using metal-organic frameworks (MOF) compared to the conventional amine absorption methods (Britt et al., 2009; Liang et al., 2019). The captured CO<sub>2</sub> can be used in the production of useful chemicals (Fiorani et al., 2015), including synthesis of cyclic organic carbonates (Ara-yachukiat et al., 2017; Al Maksoud et al., 2020; Natongchai et al., 2021). Use of CO<sub>2</sub> may also help to drastically improve efficiency of oil recovery (CO<sub>2</sub>-IOR) and hydraulic fracturing (Feng et al., 2021). CO<sub>2</sub> sequestration in saline aquifers, CO<sub>2</sub>-IOR, and CO<sub>2</sub> fracturing depend on CO<sub>2</sub> viscosification. CO<sub>2</sub> has a liquid-like density but gas-like viscosity at subsurface conditions. Its low viscosity makes it inefficient for improved oil recovery (IOR) because of low sweep efficiency. CO<sub>2</sub> may give rise to early breakthroughs from displacement of liquids in cores and from injection in large scale fields.

Viscosification of CO<sub>2</sub> by low concentration of polymers has been investigated since the early 1980s (Heller et al., 1985; Enick et al., 2012). Numerous studies using polymers have been conducted to determine the increase in viscosity of CO<sub>2</sub> (Hunter et al., 1993; Huang et al., 2000; Davani et al., 2012). There has not been much progress to find cost-effective and environmentally friendly materials for the intended applications. The polymers which seem effective without porous media become ineffective in contact with porous media (Zaberi et al., 2020). Owing to complexities in mixing and measurements, some of the results in the literature vary by a wide range between different authors. Fluorine-based polymers are commonly studied; they are found to be readily soluble

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**Table 1. Methods used in solubility and viscosity measurements by various authors**

Study	Main component for solubility test	Temperature (K)	Pressure (MPa)	Mixing mechanism for solubility apparatus	Viscometer type
Heller et al. (1985)	Sapphire tube (entire sample volume visible)	298–331	10–24	Magnetic stirring bar	Falling cylinder
Bae and Irani (1993)	Ruska double windowed cell	328	17	Oscillating shaft, manual rocking	Capillary
Huang et al. (2000)	Variable volume, windowed cell	295	6–48	Rocking of cell	Falling cylinder
Xu and Enick (2001)		298–373	45		
Kilic et al. (2019)		295	10–15	Impeller fixed at top of sample volume	
Zhang et al. (2011)	See-through, windowed cell	329	21	Not mentioned	Capillary
Shi et al. (2015)	Fixed volume view chamber with two sapphire windows on opposite walls	318–343	21	Installed stirrer, maximum speed of 1,200 rpm	N/A
Sun et al. (2018)	Variable volume cell, windows made of quartz glass	308	15–30	Magnetic stirrer	Falling ball
Al-Hinai et al. (2018)	Windowed cell	377	55	No stirrer	Capillary
Chen et al. (2020)	Autoclave with adjustable volume (visibility)	308	5–40	Not mentioned	Falling ball

in CO<sub>2</sub> (Xu and Enick, 2001), viscosifying CO<sub>2</sub> by two to three orders of magnitude at 4 to 5 wt%. Recently, close to a 4-fold viscosity increase by 1 wt% polyfluoroacrylate has been reported at temperature and pressure conditions of 297 K and 21 MPa (Zaberi et al., 2020). Fluoropolymers are expensive, potentially harmful for the environment, and adsorb strongly onto the rock formation (Trickett et al., 2010). Hydrocarbon polymers have also been examined by various authors. Poly-1-decene (P1D) with six repeating units and poly vinyl ethyl ether (PVVE) (Gu et al., 2013) show limited effectiveness. P1D with six repeating units has been found to be more effective in CO<sub>2</sub> viscosification compared to other hydrocarbon polymers (Heller et al., 1985; Zhang et al., 2011; Al Hinai et al., 2018). Zhang et al. (2011) report large increase in CO<sub>2</sub> viscosity by P1D with six repeating units. Their work has been disputed in the literature. Al-Hinai et al. (2018) use the same commercial P1D (molecular weight of around 910) at pressure and temperature conditions of 50 to 55 MPa and 358 to 377 K, respectively. They report CO<sub>2</sub> viscosity to increase by a factor of 1.2 to 2.77 for P1D concentrations of 0.8 to 5 wt% at the aforementioned pressure and temperature ranges. Lemaire et al. (2021), in a recent review paper, investigate P1D with six repeating units along with other oligomers and heavy molecular weight polymers and report 0–10% increase in viscosity for 2 and 4 wt% of P1D in CO<sub>2</sub> at 34 and 48 MPa, respectively, at temperature of 297 K. A main suggestion in the recent literature review of CO<sub>2</sub> viscosification by Lemaire et al. (2021) is that CO<sub>2</sub>-soluble low molecular weight polymers and oligomers should be considered as modest thickeners, increasing relative viscosity by say less than a factor of two. The use of nanoparticles in combination with hydrocarbon polymers is being investigated to viscosify CO<sub>2</sub> (Gandomkar and Sharif, 2020; Gallo et al., 2021). Gandomkar and Sharif (2020) added up to 500 ppm of graphene oxide to a very high molecular weight P1D (MW 640000) and measured a considerable increase in relative viscosity from 4.5 to 22.9 using 300 ppm of graphene oxide at 353 K, with a reduction in cloud point from 24 to 16 MPa. Gallo et al. (2021) found silicone resins to be efficient in thickening supercritical CO<sub>2</sub> (relative viscosification of 4.2 at 328 K and 18 MPa, for 6.90 wt% nanoparticle concentration). Nanoparticles have also been mixed with CO<sub>2</sub> to achieve better mobility control in EOR applications (Jafari et al., 2015; Dezfuli et al., 2020). In another recent review article, Pal et al. (2022) have reiterated the advances made in CO<sub>2</sub> viscosification for applications in EOR and fracking and classified the CO<sub>2</sub> thickeners into five main categories, including cosolvents, polymeric materials, and small molecule-associating compounds.

Visual cells with mechanical mixing are generally used to measure solubility of various chemicals and polymers in CO<sub>2</sub>. The viscosity of CO<sub>2</sub>-polymer fluid is commonly measured by capillary tubes or by falling cylinder viscometers. A brief summary of different setups from the literature is presented in Table 1.

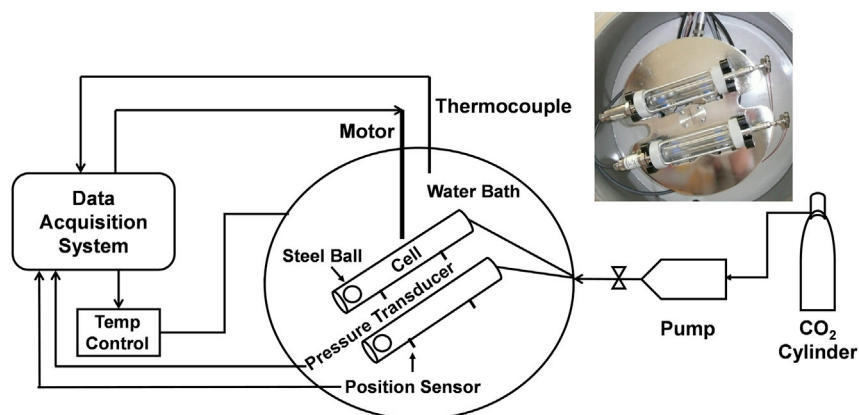
Goicochea and Firoozabadi (2019a) have investigated molecular structures of CO<sub>2</sub> with heptadecafluorodecyl acrylate (HFDA), P1D, and PVEE polymers via dissipative particle dynamics (DPD) simulations and then determine the increase in viscosity of CO<sub>2</sub> by these polymers (Goicochea and Firoozabadi, 2019b). The branched structure of P1D with six repeating units is found to be more effective in solubilizing in CO<sub>2</sub> compared to linear chains. For non-fluorinated polymers, the viscosity increase with concentrations is linear as opposed to power law viscosity increase with concentration for fluorinated polymer HFDA. The intermolecular  $\pi$ -stacking from the styrene functionality strongly increases the aggregation, leading to significant increase in viscosity. The effect of water on the solubility and viscosification of CO<sub>2</sub> by the polymers is also examined. Water is observed to promote folding of PVEE molecules, thereby increasing the CO<sub>2</sub> viscosity because of higher resistance to flow provided by the aggregation of folded molecules. Conversely, P1D and HFDA molecules are not affected by water from molecular simulations.

After the publication of the work of Goicochea and Firoozabadi in 2019 (2019a; 2019b), Zakeri et al. (2020) have studied the solubility and CO<sub>2</sub> thickening effect of polyfluoroacrylate (PFA). At  $T = 297$  K, the cloud point pressure is measured to range from 9.5 to 10 MPa for 1 to 8 wt% PFA concentration in CO<sub>2</sub>. The solubility of PFA is significantly reduced in the presence of light hydrocarbons in CO<sub>2</sub>, with cloud point pressure increasing to 21 MPa for a concentration of 0.5 wt% PFA in a mixture of 85 wt% CO<sub>2</sub> and 15 wt% hydrocarbons consisting of n-hexane (C<sub>6</sub>) to eicosane (C<sub>20</sub>), at  $T = 297$  K. Close to four-time increase in CO<sub>2</sub> viscosity is obtained by 1 wt% PFA at  $T = 297$  K and  $P = 21$  MPa. Even with increased viscosity, PFA is rendered not applicable for CO<sub>2</sub> mobility control because of high adsorption of the polymer onto rock surface. Increase in pressure drop by a factor of 30 is recorded during coreflooding in Berea sandstone rock using the CO<sub>2</sub>-PFA mixture.

Zhang et al. (2021) have synthesized polyether-based polymers by adding heptamethyltrisiloxane to improve solubility of the polymer in CO<sub>2</sub> through reduced polymer-polymer interaction and improved chain flexibility. They add phenyl groups to the polymer to increase intermolecular  $\pi$ - $\pi$  association and increase the CO<sub>2</sub> viscosification of the polymer. At  $P = 20$  MPa and  $T = 308$  K, a 4.8-fold increase in CO<sub>2</sub> viscosification is obtained using the polymer with 18.7 mole percent of phenyl group at a concentration of 1 wt% polymer in CO<sub>2</sub>. This ratio gives the optimal amount of phenyl group to achieve maximum thickening and further increase in phenyl group content is found to reduce the viscosity. The increase in intramolecular  $\pi$  stacking rather than intermolecular association leads to a decrease in effectiveness. Despite the fact that the molecules synthesized by Zhang et al. (2021) are very effective in viscosification, strong adsorption to the rock surface may make their performance similar to the results of Zakeri et al. (2020). Chen et al. (2020) report on CO<sub>2</sub> thickening by poly ether carbonates and find CO<sub>2</sub> viscosity to increase by a factor of 11 and 3.9 by addition of 0.95 wt% of phenyl-centered four-chain poly (ether-carbonate) and 0.72 wt% phenyl-centered tri-chain poly (ether-carbonate), respectively, at  $P = 30$  MPa and  $T = 308$  K. Ether group has one oxygen atom directly connected to an alkyl group. The presence of the heteroatoms is likely to have adverse adsorption effects on rock surface. In our work, we observe strong sandstone rock adsorption by polymers with phenol functionality.

There are six important characteristics of functional molecules for CO<sub>2</sub> viscosification in relation to CO<sub>2</sub> sequestration and some other important applications. These essential features relate to: 1- solubility, 2- viscosification, 3-adsorption onto the rock surface, 4- solubility in the aqueous phase, 5- shear thinning and reversibility in performance, and 6- environmental considerations. Solubility and viscosification are the key elements of the process. In addition, low adsorption, low solubility in water and brine, reversibility in shear from change in pressure, and environmental friendliness are also required in the application of viscosified CO<sub>2</sub>. Based on the above six considerations, the published molecules may not be effective in CO<sub>2</sub> sequestration. High adsorption is a serious issue in both fluorinated and oxygen-containing polymers. These considerations rule out the use of published molecules for the intended applications. The objective of this work is introduction of a molecule that meets the six requirements and can be used in increasing the efficiency and safety of CO<sub>2</sub> sequestration.

As discussed earlier, there have been a number of publications on the performance of P1D with six repeating units on solubility in CO<sub>2</sub> and viscosification. There are major differences among various authors in CO<sub>2</sub> solubility and even wider differences in reported viscosity. Recent publications report a viscosity increase of only a few percent. One objective of this work is to present accurate measurements for the solubility and viscosification of P1D with six repeating units and then evaluate the potential for polymers with various number of 1-decene repeating units and provide a clear understanding of solubility in CO<sub>2</sub> and



**Figure 1. Schematic of the Sapphire Rocking Cell Setup (insert image shows the cells with steel balls)**

viscosification. P1D with six repeating units has a molecular weight of about 910, but it has much higher solubility in CO<sub>2</sub> compared with normal alkanes of half of its molecular weight. Our work covers a wide range of repeating units in P1D. The molecular weight of 1-decene and P1D molecules in our investigation vary from 140 to approximately 4200. Solubility of polymers and viscosification effects in CO<sub>2</sub> are determined at pressures of 17, 24, and 31 MPa, and temperatures of 308 and 323 K. Throughout this work, the terms oligomer and polymer are used interchangeably, denoting polymers of low molecular weight with a maximum approximate molecular weight of 4200.

## RESULTS AND DISCUSSION

The schematic of solubility and viscosity measurements are shown in Figures 1 and 2, respectively. Detailed description of the procedure is included in the STAR Methods section.

### Solubility measurements

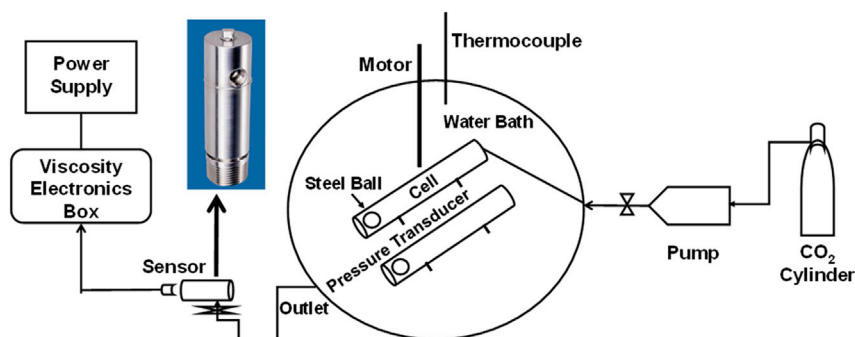
Figure 3 presents the essence of our measurements on solubility of 1-decene and P1D of various monomer units in CO<sub>2</sub> at 308 K and three pressures of 17, 24, and 31 MPa. At 17 and 24 MPa, the highest solubility in CO<sub>2</sub> is for P1D of 2300 MW: 1.5 wt% and 1.75 wt%, respectively. The non-monotonic trend in solubility is unusual and different from the monotonic trend in solubility of normal alkanes in CO<sub>2</sub> as we will discuss shortly. At 31 MPa, the trend becomes monotonic but still one region (low MW P1D) shows slow decrease in CO<sub>2</sub> solubility followed by a sharp decrease for heavy P1D molecules with 1-decene and P1D with 2 repeating units having highest solubility (2.1 wt%). There may be a probable shift in maximum with more data on P1D of repeating units between 3 and 6. The impurity in 1-decene and P1D molecules are not known. There may be some effect from impurity; however, the overall trend will not change. The non-monotonic solubility trend has not been reported previously for CO<sub>2</sub> viscosification to the best of our knowledge.

The effect of increase in temperature on P1D solubility is examined at two temperatures: 308 and 323 K at constant pressure of 24 MPa (see Figure 4). There is a consistent trend of increase in solubility with increase in temperature. This is opposite to the solubility trend for n-alkanes (Shi et al., 2015) but in agreement with that of aromatics like toluene as reported in the literature (Ng and Robinson, 1978; Kim et al., 1986). Figures 3 and 4 reveal that the effect of pressure is greater than the effect of temperature in increasing the polymer solubility. The increase in solubility of P1D in CO<sub>2</sub> with temperature is in agreement with literature data (Al Hinai et al., 2018).

The solubility measurements for a commercially available P1D with six repeating units (MW 910) from the literature are compared with our results in Figure 5. Our measurements agree with data of Heller et al. (1985) as well as data of Lemaire et al. (2021) at 296 K. Difference in measurements may be because of different techniques used in mixing; a summary of techniques is presented in Table 1.

### Solubility of alkanes and alkenes in CO<sub>2</sub> with increasing molecular weight

For n-butane and 1-butene, the solubility is comparable in CO<sub>2</sub> at  $T = 273$  K and  $P = 0.3$ – $3.4$  MPa (Nagahama et al., 1974). CO<sub>2</sub> is in liquid state under these conditions. Solubility of 1-hexene is lower than that

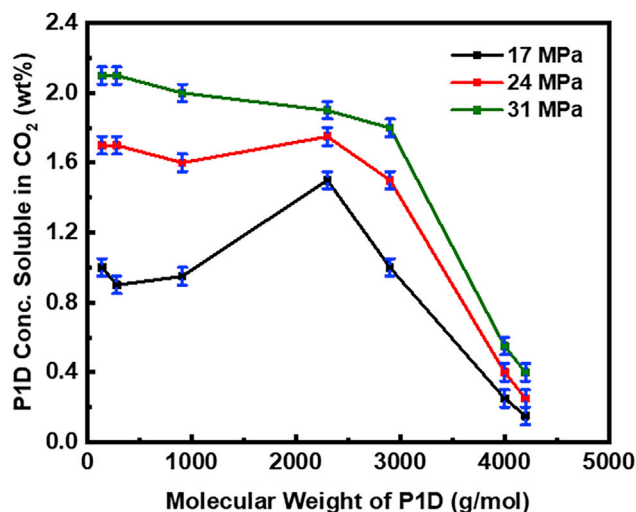


**Figure 2.** Schematic of viscosity measurement by the moving piston viscometer

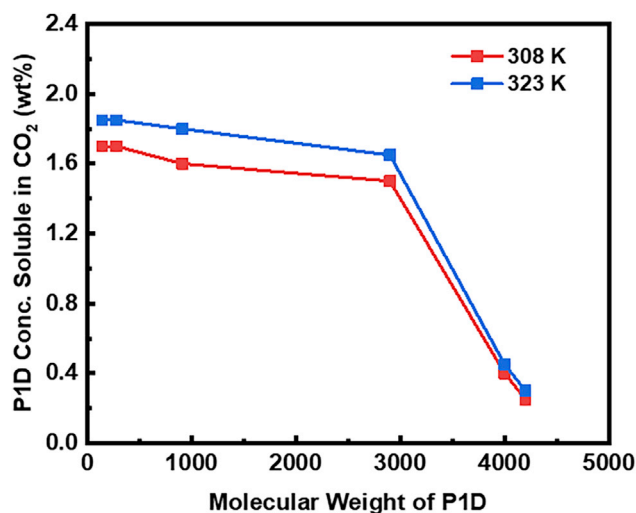
of n-hexane in supercritical CO<sub>2</sub> based on the work by Wagner and Wichterle (1987). They performed measurements at different temperatures and found 1-hexene solubility to increase with increase in temperature. The observation is supported by another study (Jennings and Teja, 1989). The increase in solubility with increase in temperature is in line with our measurements of 1-decene and P1D polymers. From our results, we see a significant lowering of solubility of 1-decene than that of n-decene at the same pressure and temperature conditions. The solubility data for n-decene, along with other heavier hydrocarbons, as extracted from literature studies, is presented in the next section. There is limited data in literature on solubility of heavier alkenes in supercritical CO<sub>2</sub>.

### Effect of branching on hydrocarbon solubility in supercritical CO<sub>2</sub>

Molecular structure and shape and functionality may affect solubility in CO<sub>2</sub>. In this work, we find that the methyl group has a very strong effect on CO<sub>2</sub> solubility. Figure 6 presents the solubility data for nC<sub>10</sub>, nC<sub>16</sub>, nC<sub>18</sub> (Shi et al., 2015), nC<sub>20</sub> (Schmitt and Reid, 1988), nC<sub>28</sub>, nC<sub>29</sub>, and nC<sub>32</sub> (Chandler et al., 1996; Reverchon et al., 1993) alkanes as well as C<sub>30</sub> branched alkane (squalane) (Sovova et al., 1997) and alkene (squalene) (Saure, 1996) at various pressures at temperature of 318 K. There is agreement for nC<sub>28</sub> solubility from two separate studies. A decline in solubility is observed with increase in molecular weight of normal alkanes. The molecular weights of nC<sub>10</sub> and nC<sub>32</sub> are 142 and 450, respectively. When there is branching in alkane structure (addition of methyl group), there is a significant jump in solubility (see Figure 6). Squalane (C<sub>30</sub>H<sub>62</sub>) with eight methyl groups is around eight times more soluble in supercritical CO<sub>2</sub> than nC<sub>32</sub> with two methyl groups. Squalene has six double bonds and eight methyl groups. The two molecules (squalane and squalene) have comparable solubility in CO<sub>2</sub>. The implication is that the vast difference in CO<sub>2</sub> solubility of squalene and nC<sub>32</sub> of comparable molecular weight alkane is because of methyl functionality.

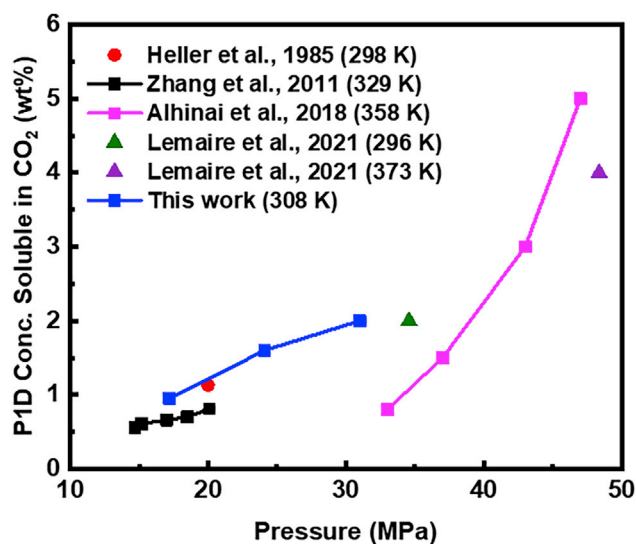


**Figure 3.** Solubility of 1-decene and poly-1-decene (P1D) molecules (different molecular weights) in supercritical CO<sub>2</sub> at T = 308 K and P = 17, 24, and 31 MPa [Blue bars show the standard deviation of measured data]



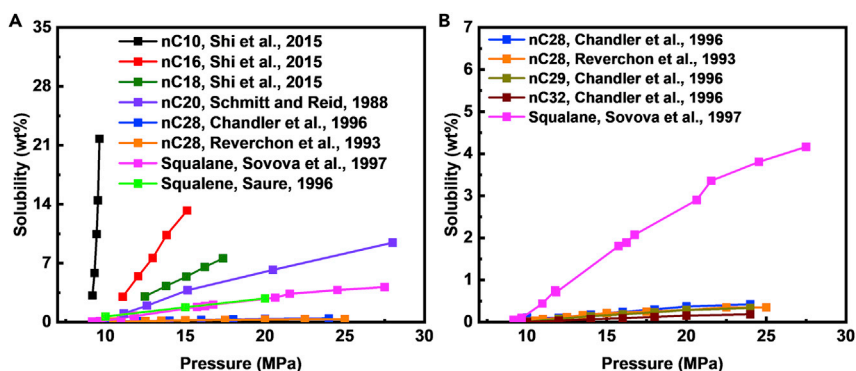
**Figure 4.** Solubility of 1-decene and poly-1-decene (P1D) molecules in supercritical CO<sub>2</sub> at T = 308 K and 323 K and p = 24 MPa

We are not aware of a discussion on the solubility of hydrocarbons of different molecular structures in CO<sub>2</sub> in the literature. In 1-decene and in normal decane, both with a molecular weight of about 140, there is huge difference in CO<sub>2</sub> solubility (Figures 3 and 6). The solubility of nC<sub>20</sub> is about 3 folds higher than P1D with two repeating units; besides, both have a molecular weight of around 280. The trend in CO<sub>2</sub> solubility completely reverses in P1D with six repeating units of about 910 molecular weight of g/mole, which is 10 times higher than nC<sub>32</sub> that has a molecular weight of around 450 g/mole. The main difference between normal alkanes and P1D molecules is the number of methyl functionalities and branching. The single double-bond in P1D is not likely to contribute to the solubility in CO<sub>2</sub>. The number of methyl functionalities may have a significant effect on CO<sub>2</sub> solubility. 1-decene has one methyl group, whereas nC<sub>10</sub> has two methyl groups. P1D with six repeating units has 7 methyl groups; however, nC<sub>32</sub> has only two methyl groups. It may be the combined contribution of molecular size (i.e., molecular weight), orientation, branching, and the number of methyl groups that determine CO<sub>2</sub> solubility. In normal alkanes, the number of methyl groups is two irrespective of size. A decreasing solubility trend with size is observed. In P1D, as the molecular size increases, the number of methyl groups also increases. We observe a non-monotonic trend with size at 17 MPa and 24 MPa. In methyl groups, there are three hydrogen atoms. Methylene groups have two hydrogen



**Figure 5.** Solubility data of P1D (with 6 repeating units) from various sources





**Figure 6. Solubility of: (A) normal and branched alkanes and alkene, and (B) magnified data in supercritical CO<sub>2</sub> at 318 K. [nC<sub>20</sub> data at 320 K, squalene data at 313 K]**

Solubility of: (A) n-alkanes (C<sub>10</sub>, C<sub>16</sub>, C<sub>18</sub>, and C<sub>28</sub>), branched alkane (C<sub>30</sub>: squalane), and branched alkene (C<sub>30</sub>: squalene), and (B) magnified solubility data of n-alkanes (C<sub>28</sub>, C<sub>29</sub>, and C<sub>32</sub>), branched alkane (C<sub>30</sub>: squalane) in supercritical CO<sub>2</sub>. nC<sub>20</sub> data is at 320 K and C<sub>30</sub> squalene data at 313 K, all the other data are at 318 K.

atoms. The solubilization of P1D in CO<sub>2</sub> may be assisted by hydrogen bonding between oxygen in CO<sub>2</sub> and hydrogen in P1D (Goicochea and Firoozabadi, 2019b). Apart from the number of methyl groups, the molecular orientation, and position of the side chains, among other features, may affect solubility efficiency of these hydrocarbons in supercritical CO<sub>2</sub>. In our molecular simulations, we find that the number of CO<sub>2</sub> molecules around a methyl group is higher than in the methylene group in normal alkanes. The number of CO<sub>2</sub> molecules around a methyl group in P1D is consistently higher than in methyl groups in normal alkanes.

Functional groups such as fluorine increase solubility (Besnard et al., 2009); fluorine is environmentally undesirable and expensive. Fluorinated molecules promote adsorption to rock surfaces which rules them out for many applications. One main conclusion of our work is that P1D polymers without additional functional groups may be the best choice in achieving the desired solubility. The purpose of our work is to assess the contribution of structural features of P1D to solubility in CO<sub>2</sub> and eventual viscosification without additional functional groups.

Based on Figure 3 and the aforementioned analysis on the effectiveness of methyl groups in enhancing solubility, we next present the viscosification data. The effect of water on relative viscosity is also examined to ensure the viability of polymer-viscosified CO<sub>2</sub> to maintain its rheology in aquifers.

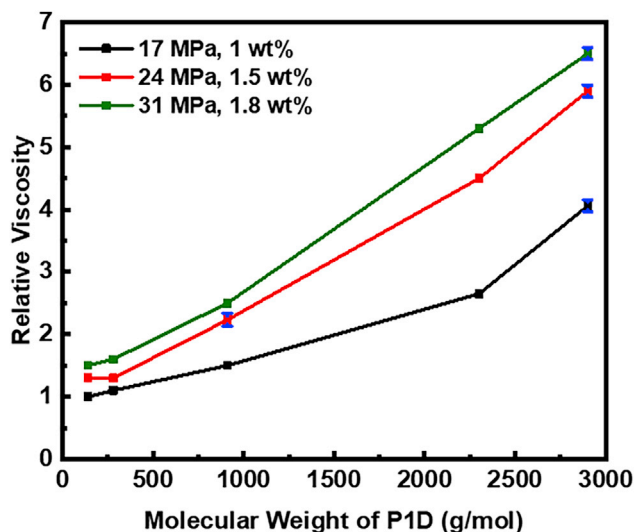
### Viscosity measurements

The soluble concentration of polymers in CO<sub>2</sub> is examined for viscosification at 308 K and pressures of 17, 24, and 31 MPa. Increase in molecular weight of a polymer is expected to result in higher viscosification of CO<sub>2</sub>, provided the molecule is soluble in CO<sub>2</sub>. Our measured viscosity and relative viscosity for P1D polymers (with respect to the viscosity of base CO<sub>2</sub> at the same conditions) are portrayed in Figure 7. We observe an increasing trend of relative viscosity, which is approximately exponential. This trend for hydrocarbons without introduction of heteroatoms such as O or N is being reported for the first time and is the most important observation in our work and perhaps in CO<sub>2</sub> viscosification. The trend is opposite to that of solubility presented in Figure 3.

Viscosity data for P1D molecules of approximately 4000 and 4200 molecular weight in g/mol are not shown in Figure 7 because of differences in soluble concentrations but included in Table 2. P1D of molecular weight of 4000 gives a relative viscosity of 3.2 at 0.5 wt% concentration at 31 MPa. Because of higher molecular weight, even a significantly lower polymer concentration gives a moderate relative viscosity increase.

The effect of increase in temperature on viscosification of 1-decene and P1D molecules is presented in Figure 8 from 308 to 323 K at pressure of 24 MPa. There is less than 10% reduction in relative viscosity with increase in temperature by 15 K. Temperature does not have a significant effect on the viscosity in the conditions examined. One reason for the mild effect of temperature on viscosity may be because of the fact that P1D molecules do not associate in CO<sub>2</sub>. Viscosifier molecules with oxygen functionality associate,





**Figure 7. Relative viscosity of 1-decene and poly-1-decene (P1D) molecules in supercritical CO<sub>2</sub> (compared to base case viscosity of CO<sub>2</sub>) at temperature of 308 K and pressures of 17, 24, and 31 MPa. Blue bars show the standard deviation of duplicate measurements**

and therefore as temperature increases, the viscosity may decrease significantly. The association characteristics have been shown by molecular simulations (Goicochea and Firoozabadi, 2019a).

### Effect of side chain length

We measure the viscosity of 2.5 wt% squalane dissolved in supercritical CO<sub>2</sub> at pressure and temperature of 24 MPa and 308 K. There is only a 10–20% increase in viscosity. On evaluating the data with Figure 8, a comparable molecular weight of P1D (obtained through interpolation) provides a relative viscosity close to 1.5 at a lower concentration (1.5 wt% in CO<sub>2</sub>). One may interpret the difference as being in the chain length. P1D has considerably longer side chains compared to squalane. According to Graessley (1977), the solution viscosity of branched polymers may exceed that of linear polymers of comparable molecular weight at the same concentration of polymer in solvent, depending on branched structure and length of the branches.

We further compare the viscosification effect of P1D (molecular weight 2,300 g/mol) with PIB (molecular weight 2,250 g/mol) of considerably higher number of methyl groups than P1D but shorter branch lengths. Comparable molecular weight of the two polymers provides similar viscosification. P1D results in a relative viscosity of 3.6, whereas PIB, with more than four times the number of methyl groups than P1D, gives a relative viscosity of 3.5 at 1 wt% polymer concentration at  $T = 308$  K and  $P = 24$  MPa.

### Effect of water on CO<sub>2</sub> viscosification

We have examined the effect of water dissolved in CO<sub>2</sub> in relation to viscosification at 308 K and 17 MPa. We add 0.15 wt% water to CO<sub>2</sub>, which is below the solubility limit. Addition of water to the polymer mixture in CO<sub>2</sub> is not found to affect the viscosity significantly for P1D (MW 2900 g/mol). Presence of water lowers the relative viscosity from 4.1 to 3.9 for 1 wt% of polymer measured at 308 K and 17 MPa.

### Conclusions

In this work we have found polymers of 1-decene with an unusual solubility characteristic. At supercritical pressure conditions of 17 MPa and 24 MPa, the solubility in CO<sub>2</sub> is not monotonic. At 31 MPa, also a supercritical condition, there is a slow reduction in CO<sub>2</sub> solubility with molecular weight followed by a sharp drop. Viscosification has the expected trend. For the same concentration, there is increase in viscosity from increase in molecular size. The trend is exponential. The P1D oligomers do not adsorb onto the rock and have very low solubility in the aqueous phase. They have all the desirable features to make CO<sub>2</sub> sequestration safe. For most CO<sub>2</sub> sequestration conditions, a five-to-six-fold increase in CO<sub>2</sub> viscosity will allow significant sweep improvement and make CO<sub>2</sub> storage safe.

**Table 2. Relative Viscosity of 1-decene and poly-1-decene (P1D) molecules in supercritical CO<sub>2</sub> (compared to base case viscosity of CO<sub>2</sub>) at temperatures of 308 and 323 K and pressures of 17, 24, and 31 MPa**

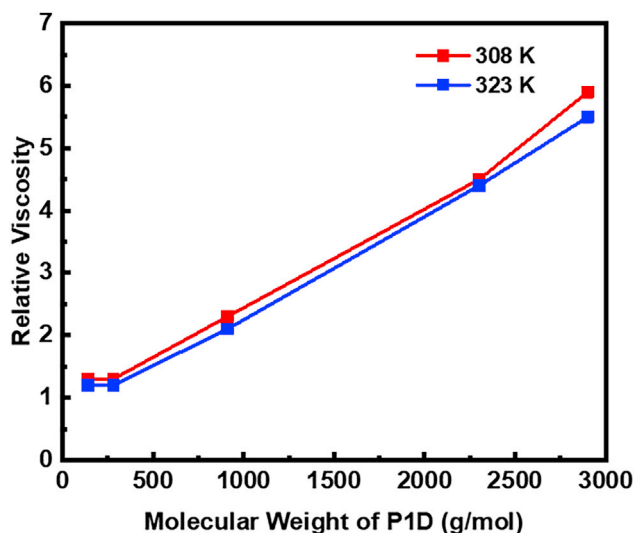
No.	Source	Polymer mol wt (g/mol)	Relative viscosity at 308 K		
			17 MPa, 1 wt %	24 MPa, 1.5 wt%	31 MPa, 1.8 wt%
1	Sa	140	1.0	1.3	1.5
2	Lb	280	1.1	1.3	1.6
3	Sa	910	1.5	2.3	2.5
4	Lb	2300	2.7	4.5	5.3
5	Lb	2900	4.1	5.9	6.5
6	Lb	4000	1.6 (0.2 wt%)	2.8 (0.4 wt%)	3.2 (0.5 wt%)
7	Br	4200	1.6 (0.15 wt%)	2.0 (0.25 wt%)	3.0 (0.4 wt%)

Sa- Sigma Aldrich, Lb- Lubrizol, Br- Brookfield.

In the past, only P1D with six repeating units, which has a moderate enhanced viscosifying effect, has been studied. There is a large difference in solubility and especially viscosification reports in the literature. In this study, we provide definitive measurements for both solubility and viscosity. We also report on a P1D molecule with about twenty repeating units which can provide a six-fold increase in CO<sub>2</sub> viscosity at 31 MPa and 308 K. At higher pressure applications, P1D of high molecular weight at low concentration is an excellent candidate to provide much higher viscosification of CO<sub>2</sub> for a broad range of applications. Our findings relate to the effect of methyl functionality and branching in relation to solubility and branching in viscosification.

The essence of our findings is summarized below:

1. Polymers of P1D have a non-monotonic trend in solubility with increase in molecular size at moderate pressures, which turns to a monotonic trend at higher pressures.
2. Presence of methyl groups enhances solubilization in CO<sub>2</sub>.
3. An exponential clear-cut trend is observed for relative viscosity, with P1D (MW 2900 g/mol) providing the highest relative viscosity of 6.5, at 1.8 wt% concentration, 308 K and 31 MPa.



**Figure 8. Relative viscosity of 1.5 wt% concentration of 1-decene and poly-1-decene (P1D) molecules in supercritical CO<sub>2</sub> (to base case viscosity of CO<sub>2</sub>) at pressure of 24 MPa, and temperatures of 308 K, and 323 K**

The sweep efficiency improvement of viscosified CO<sub>2</sub> by P1D of approximately 2,900 g/mol molecular weight is significant (related data and results are being prepared for submission). The effectiveness is because of negligible adsorption onto the rock surface and very low solubility in brine.

### Limitations of the study

Based on the solubility and viscosity measurements from this work, extensive coreflooding tests have been successfully conducted to gauge the polymer efficiency for sequestration and IOR applications. The findings have been submitted for publication. Ongoing studies are focused on synthesizing and testing polymers with higher relative viscosification at lower polymer concentrations. Systematic measurements conducted up to temperature of 90°C indicate a mild effect of temperature on relative viscosity of the polymer-CO<sub>2</sub> mixture. This observation points toward an efficient polymer performance at subsurface conditions. Continuing studies in this direction are being carried out to consolidate our findings at higher temperature conditions. Molecular simulations are being conducted to gain molecular insight to methyl functionality on solubility.

### STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

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### AUTHOR CONTRIBUTIONS

Conceptualization, T.K. and A.F.; Experimental work, T.K.; Writing – Review & Editing, T.K. and A.F.; Supervision, A.F.; Funding Acquisition, A.F.

### DECLARATION OF INTERESTS

The authors declare no competing interests.

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## STAR★METHODS

## KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
1-decene	Sigma-Aldrich	Product#30650
Poly-1-decene (Approx MW 280)	Lubrizol	N/A
Poly-1-decene (Approx MW 910)	Sigma-Aldrich	Product#462349
Poly-1-decene (Approx MW 2300)	Lubrizol	N/A
Poly-1-decene (Approx MW 2900)	Lubrizol	N/A
Poly-1-decene (Approx MW 4000)	Lubrizol	N/A
Poly-1-decene (Approx MW 4200)	Brookfield	Part#B1060
Polyisobutylene	Brookfield	Part#B10200

## RESOURCE AVAILABILITY

## Lead contact

Further information and queries will be directed to the lead contact, Abbas Firoozabadi ([abbas.firoozabadi@rice.edu](mailto:abbas.firoozabadi@rice.edu)).

## Materials availability

This study did not generate new unique reagents.

## Data and code availability

- All data generated in this study is included in the manuscript.
- This study did not generate custom code.
- Any additional information required to analyze the data reported in this paper is available from the [lead contact](#) upon request.

## METHOD DETAILS

P1D oligomers of varying molecular weights are sourced from Lubrizol, Sigma Aldrich, and Brookfield. 1-decene and P1D molecules are listed in [Table 1](#). Viscosification of P1D in CO<sub>2</sub> is compared with that of squalane (branched alkane C<sub>30</sub> from Sigma Aldrich). Poly isobutylene (PIB) of approximate molecular weight 2,250, from Brookfield has been also investigated for viscosification of CO<sub>2</sub>. We have compared solubility and viscosification effects for equivalent molecular weight P1D and PIB, which differ in the length of branching, and number of methyl groups in the structures.

**Table A. List of 1-decene, poly-1-decene, and polyisobutylene in our study**

No.	Sample	Source	Approximate molecular weight (g/mol)
1	1-decene	Sigma Aldrich	140
2	Poly-1-decene	Lubrizol	280
3	Poly-1-decene	Sigma Aldrich	910
4	Poly-1-decene	Lubrizol	2300
5	Poly-1-decene	Lubrizol	2900
6	Poly-1-decene	Lubrizol	4000
7	Poly-1-decene	Brookfield	4200
8	Polyisobutylene	Brookfield	2250

All the polymers listed above have a low solubility in deionized (DI) water, approximately about 0.05 wt%. pH measurements are conducted using 0.5 wt% concentration of polymers in DI water to measure pH of aqueous phase, without and with exposure to CO<sub>2</sub>. No change in pH is observed with addition of polymers to DI water compared to base case of DI water. Exposure to CO<sub>2</sub> causes a pH reduction from 6.4 to 5.6; but no significant difference in pH is observed by adding polymer. The pH measurements are conducted at atmospheric conditions.

There have been significant differences in solubility and viscosity measurements reported by various authors as mentioned above. We have verified our measurements using different methods. In the following, we will first describe the equipment used in solubility and viscosity determination.

### Solubility measurements

Solubility measurements are performed using a sapphire rocking cell setup from PSL Systemtechnik (RCS 2). A steel ball is placed inside each cell. The polymers are introduced into the cell after purge with CO<sub>2</sub>. Pressurized CO<sub>2</sub> is then fed into the two cells, which are periodically rocked through  $-45^{\circ}$  to  $45^{\circ}$  via an in-built motor system, at 4-second intervals. During rocking, the cells are also turned axially, ensuring that the steel balls are in contact with the polymer spread on the walls of the cells. Temperature of the system and pressure in the two cells are continuously recorded by data acquisition. For the experiments at 17 and 24 MPa, Teledyne ISCO 500 D syringe pumps are used to pressurize the cells with CO<sub>2</sub>, while a Vindum Engineering 6K piston displacement pump is used for the 31 MPa experiments.

Initially, the pressure is maintained between 6 and 7 MPa as temperature is increased from 297 to 308 K (297–323 K, for experiments at higher temperature), at a rate of 0.122 K/min. After stabilizing at the final desired temperature, the cells are further pressurized with CO<sub>2</sub> to the final pressure. The temperature and pressure conditions are maintained, along with periodic rocking of the cells, for a duration of five hours. The solubility of the polymers at the final stabilized pressure and temperature are visually observed.

Careful visual measurements are conducted to determine the concentration of polymer solubility in CO<sub>2</sub> at desired pressure and temperature. We first use two different concentrations of the polymer (one at a low value and the other at significantly higher value, likely above the solubility limit) in the two sapphire cells. If single phase is observed with no visible polymer remaining in the cell, that concentration is determined to be fully soluble. Once an approximate range is established (lower concentration limit - soluble, upper concentration limit - insoluble), we perform additional runs by increasing lower limit concentration and decreasing upper limit, to determine the solubility limit for the polymer at the given pressure and temperature. The difference between concentrations in the two cells is less than 5% in all the tests with low molecular weight polymers. It is less than 10% for the heavier polymers (molecular weight greater than 4000) due to low solubility. The method takes many iterations but provides a high degree of confidence in all measurements. The method also embeds repeatability.

### Viscosity measurements

A moving piston viscometer is used for viscosity measurements. The viscometer unit is connected in line with the rocking cell setup. The Visco Pro 2,100 viscometer (from Cambridge Viscosity Inc) consists of a sensor in which a piston is moved from one end of the sensor to the other with electromagnetic coils. The sensor also includes a temperature probe. This system is highly accurate for our experiments as viscosity measurements can be performed directly after the solubility measurements, thereby requiring less fluid; the time is also saved. Less than 4 mL of fluid is required in the sensor to determine the viscosity. The sensor is initially purged with CO<sub>2</sub>, and then connected to the outlet of the solubility setup. By opening the outlet valves for the two sapphire cells, the mixture of CO<sub>2</sub> and polymer flows into the viscometer. During flow of fluid into the viscometer, we stabilize flow by CO<sub>2</sub> injection pump at one end of the system to stabilize the pressure at the desired value. Temperature control in the lines connecting the viscometer and rocking cell setup is through heating bands. Real-time readings of viscosity and temperature of the fluid in the sensor are recorded.

A second measurement setup is used for viscosity measurements of selected polymers at 24 MPa for comparison and all the measurements at 31 MPa. The setup is a custom-built accumulator with volume of 500 mL, maximum pressure of 48 MPa, and maximum temperature of 393 K. The accumulator consists of a magnetic drive mixer equipped with four turbine impellers, which facilitate rigorous mixing of the



polymer with CO<sub>2</sub>. A speed of 1,500 rpm is employed for mixing. We allow several hours for complete mixing and stabilization based on periodic viscosity measurements. Once the mixture is prepared, the viscometer is connected to the accumulator. Very close viscosity results are obtained from the two independent setups, which confirm the measurement accuracy. The accumulator has also a piston; this setup is used for core flooding experiments, to investigate the efficiency of viscosified CO<sub>2</sub> in sequestration in saline aquifers. Pressure drop across the rock is in agreement with the CO<sub>2</sub> viscosification factor. The core flooding results are being prepared for submission.