The Solubility of Low Molecular Weight Poly(Dimethyl siloxane) in Dense CO₂ and its Use as a CO₂-philic Segment

Jason J. Lee^a, Stephen D. Cummings^a, Eric J. Beckman^a, Robert M. Enick^{a*}, Ward A. Burgess^b, Mark D. Doherty^c, Michael J. O'Brien^c, Robert J. Perry^c

^aDepartment of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15261, United States

^bAECOM, Pittsburgh, Pennsylvania 15236, United States

^cGE Global Research, Niskayuna, NY 12309, United States

*Corresponding author *e-mail address*: rme@pitt.edu

1. Introduction

Supercritical carbon dioxide is considered to be more environmentally benign than conventional organic solvents and hence many chemical and petroleum engineering processes utilizing high pressure CO₂ have been documented [1]. Despite its pressure-adjustable solvent strength, relatively mild critical conditions, and its ability to dissolve a wide array of low molecular weight hydrocarbons, CO₂ is a notoriously feeble solvent for polar, ionic and high molecular weight compounds [2]. Therefore, most conventional ionic surfactants, dispersants, chelating agents, self-assembling thickeners and polymers are essentially insoluble in CO₂.

Numerous investigators have tailored novel molecules with highly CO₂-philic moieties to enhance their solubility in liquid or supercritical CO₂. CO₂-philes composed of fluoroalkane [3–7], polyfluoroacrylate [8–12] and polyfluoroethers [13–15] have been particularly effective, however their expense and the environmental persistence of some of these fluorinated compounds and their degradation products have limited their widespread commercial use. Highly oxygenated amorphous hydrocarbon polymers, such as polypropylene glycol, polyvinyl acetate or amorphous polylactic acid, exploit Lewis acid-base interactions between the CO₂ carbon and ether/carbonyl oxygens along with weak solute hydrogen-CO₂ oxygen interactions to impart CO₂-philicity [16–22]. However, the pressure required to attain solubility in CO₂ with these oxygenated hydrocarbon oligomers and polymers can be unacceptably high (40–120 MPa). Low molecular weight sugar acetates [23] and oligomers of cellulose triacetate exhibit a high degree of CO₂-philicity, although high molecular weight cellulose triacetate polymers are CO₂-insoluble due to their crystallinity and consequent high melting temperatures [24].

Polydimethyl siloxane (PDMS) has emerged as a compromise CO₂-philic segment between the previously mentioned fluorinated materials and oxygenated hydrocarbons. Although it is not as CO₂-philic as a polyfluoroacrylate, it has a relatively low surface tension, higher backbone flexibility and consequently higher CO₂-solubility than oxygenated hydrocarbon polymers of comparable molecular weight [16,25]. PDMS is an inexpensive, environmentally benign polymer that is commercially available in large amounts over an extremely wide molecular weight range. Although PDMS is most commonly

found in a trimethylsilyl-terminated product, it is also available in a hydroxy-terminated form that is also CO₂ soluble [26]. Commercially available forms of PDMS are typically polydisperse, although a narrow molecular weight distribution can be obtained via supercritical CO₂ fractionation [27]. Extremely high molecular weight PDMS has even been suggested as a CO₂-thickener for improved mobility control during CO₂ enhanced oil recovery (EOR), although the large amount of toluene (e.g. 20 vol.% toluene + 80 vol.% CO₂) that is required as a co-solvent is problematic [28]. CO₂ dissolves readily in PDMS, therefore PDMS has been suggested as a pre-combustion CO₂-selective solvent for the extraction of CO₂ from a warm, gaseous post-water-gas shift reactor stream that also contains hydrogen and water [29,30].

Phase behavior of mixtures of CO₂ and high molecular weight hydroxy-terminated [26] and trimethylsilyl-terminated [25,31,32] PDMS (38000 < Mw < 170000) have been thoroughly examined at concentrations below ~10wt% PDMS in CO₂ over the 25-180°C temperature range. For example, at 50°C, the cloud point pressure of a 5wt% solution of PDMS (Mw 38900) in CO₂ is approximately 27 MPa. However, phase behavior data for mixtures of CO₂ and lower molecular weight (<10000 g/mol) trimethylsilyl-terminated PDMS are not plentiful. Alessi et al. [33] have studied the solubility of low molecular weight PDMS (5970 and 2000) samples over a temperature range of 40-60°C at dilute concentrations (<0.1wt%) using a gravimetric method. Our group considered PDMS as a pre-combustion CO₂ solvent and presented the entire bubble point curve (0 - 100% PDMS) of the two-phase CO₂-rich vapor – PDMS-rich liquid region (V-L) for mixtures of very low molecular weight PDMS (Mn = 237) and CO₂ at 25 °C [29], Figure 1. Our group also measured the CO₂-rich vapor – PDMS-rich liquid bubble point boundary in the 60 – 100% PDMS range for low molecular weight PDMS (Mn = 550) at 25°C, Figure 1, along with the bubble point locus of the CO₂-rich fluid – PDMS-rich liquid region (F-L) at 40°C [30], Figure 2. There remains a substantial gap in the literature for two-phase boundary pressures for mixtures of CO₂ with low molecular weight PDMS (410 – 10000 g/mol), especially at dilute polymer concentrations. Therefore, the first objective of this study was to determine the phase behavior of a series of trimethylsilyl-terminated PDMS samples (Mw 410 - 10000 g/mol) at dilute concentrations of 1-4wt% in CO₂ at 23 °C and 40 °C, Figures 1-4. It is expected that mixtures of CO₂ and the lowest molecular

weight PDMS will exhibit the greatest degree of miscibility, as evidenced by a single two-phase region, Figures 1 and 2, with low bubble point pressures, while mixtures containing higher molecular weight PDMS will exhibit CO₂-rich liquid - PDMS-rich liquid (L₂-L₁) equilibrium (Figure 3) or CO₂-rich fluid-PDMS-rich liquid (F-L) equilibrium and higher pressure two-phase pressure boundaries. In addition to defining these two-phase pressure loci experimentally, an effort was made to correlate experimental PVT results with the PC-SAFT equation of state.

PDMS is of particular interest in the generation of CO₂-soluble amphiphiles because this silicone polymer is relatively easy to end-functionalize. Therefore PDMS has been used as a CO₂-philic segment in conjunction with CO₂-phobic functional groups in the design of novel CO₂-soluble dispersants [34], surfactants [35–39], chelating agents [40], and post-combustion CO₂ capture solvents [41], as shown in Table 1. However, the effect of varying the molecular weight of the PDMS segment on the CO₂-solubility of an end-functionalized PDMS has not been systematically documented in these prior studies. Therefore, the second objective of this study was to determine an optimum PDMS molecular weight for enhancing the CO₂-solubility of a compound composed of a CO₂-philic PDMS segment that is decorated with a CO₂-phobic group (e.g. ionic, polar, hydrogen-bonding, chelating, associating or aromatic). It should be noted that functional groups deemed CO₂-phobic are referred to as such due to their CO₂-phobicity in relation to highly CO₂-philic PDMS and are not necessarily incapable of interacting with CO₂ or dissolving in CO₂. Based on our prior studies of fluoroether-functionalized surfactants [15], it is unlikely that the greatest CO₂ solubility will be attained for the lowest molecular weight PDMS segment. If the molecular weight of the PDMS is too low, the unfavorable interaction potentials between CO₂ and the CO₂-phobic groups will dominate the free energy of mixing, rendering the compound CO₂-insoluble. However, if the molecular weight of the PDMS is increased too much, the compound may become CO₂-insoluble due to both the previously mentioned unfavorable enthalpic interactions associated with the CO₂-phobic functionalities and the entropic penalty associated with the large disparity in the molecular weights of CO₂ and the PDMS segment. It is therefore likely that an optimal PDMS molecular weight exists between these two extremes at which the end-functionalized PDMS exhibits the greatest solubility

in CO₂ at low concentrations despite the occurrence of a L₂-L₁ immiscibility gap at higher concentrations, Figure 5.

Table 1. Novel CO₂-soluble compounds composed of a CO₂-philic PDMS segment and CO₂-phobic functional groups.

Ref.	PDMS MW	No. of DMS Units	Head group; CO ₂ -phobe	Application
[34]	9900	131	pyrrolidone carboxylic acid, monomethylmethacrylate (required cosolvent)	dispersant
[35]	5000- 20000	70-270	poly(methyl acrylate), poly(acrylic acid)	surfactant
[36]	8280	110	pyrrolidone carboxylic acid, poly(ethylene glycol-co-propylene glycol)	surfactant
[37]	1900	26	allyl glycidyl ether, ammonium chloride	surfactant
[38]	9623	130	methacryloxy	surfactant
[39]	890- 13000	12-175	sulfonate, carboxysulfonate, poly(propylene glycol), poly(ethylene glycol)	surfactant
[40]	150-220	2-3	diphosphate	ligand
[41]	70-670	1-9	alkyl primary and secondary amines	post-combustion CO ₂ capture solvent

The third objective of this study was to synthesize numerous other end-functionalized CO₂-soluble PDMS-based compounds based on these principles and rank the CO₂-phobicity of the functional groups based on acquired cloud point data.

2. Materials and Methods

2.1 Materials

Seven oligomers and polymers of dimethylsiloxane were received from Gelest and used as received. Table 2 provides a list of the average molecular weight and number of repeat units for these compounds. The average molecular weights and corresponding number of repeat units of five α,ω -bis(2-ethylnaphthyl)polydimethylsiloxane (PDMS-NAP) materials prepared according to the procedure which follows are also included in Table 2.

Table 2. Polydimethylsiloxane (PDMS) and α,ω -bis(2-ethylnaphthyl)polydimethylsiloxane (PDMS-NAP) samples.

Composition	Avg. MW Of compound	No. of Repeat DMS Units n of Fig 2.	Mw of PDMS segment
PDMS	237	1	237
PDMS	410	3.3	410
PDMS	1250	14.7	1250
PDMS	2000	24.8	2000
PDMS	3780	48.8	3780
PDMS	5970	78.3	5970
PDMS	9430	125	9430
PDMS-NAP	454	0	132
PDMS-NAP	1181	9.8	859
PDMS-NAP	1530	14.5	1207
PDMS-NAP	2679	30.0	2357
PDMS-NAP	5986	74.6	5664

2.2 General hydrosilylation procedure for vinyl compounds

Hydride terminated siloxane was dissolved in toluene in a three neck flask containing a magnetic stir bar and fitted with a N₂ inlet, thermometer and addition funnel. Approximately 0.1 molar equivalents of olefin were added to the stirring solution followed by 3-5 drops of a 4 mol% xylene solution of Karstedt's Pt⁰ catalyst resulting in a light yellow solution. The remaining olefin (10% molar excess

relative to number of silicon hydrides) was introduced to the addition funnel and added dropwise (neat or as a toluene solution) to the stirring siloxane solution over the course of 5 minutes so as to manage the reaction exotherm and maintain a reaction temperature at or below 80°C. When the reaction was complete as determined by ^1H NMR spectroscopy, the reaction mixture was concentrated by rotary evaporation. For siloxanes containing three or less silicon atoms, products were isolated by vacuum distillation while siloxanes containing more than three silicon atoms were stripped under high vacuum (35 – 45 mTorr) at 125°C for several hours. Synthesis and characterization details for each of the compounds employed in this study are shown in the Supplementary Material.

2.3 Phase Behavior Measurement

The solubility of the silicone solutes in CO_2 were determined via a standard, non-sampling technique using a high pressure, windowed, agitated, variable-volume view cell [DB Robinson – Schlumberger] rated to 69 MPa and 180°C with a constant temperature air bath (-20°C to 180°C, $\pm 0.5^\circ\text{C}$) [30], Figure 6. A stainless steel phase behavior cell with two thick borosilicate opposing windows retains a thick-walled Pyrex tube (3.175 cm I.D.). This tube contains a sliding (i.e. floating) piston with an O-ring around its perimeter that separates the (CO_2 + solute) sample volume above the seal from the transparent overburden liquid below. Because ~ 0.03 MPa is required to move the piston, the pressure in the sample volume is about the same as the pressure of the overburden fluid. The overburden fluid also surrounds the Pyrex tube and a short length of tubing ensures that the pressure of the overburden fluid below the sample volume and the pressure around the Pyrex tube are equivalent; therefore there is no pressure drop across the Pyrex tube wall.

Initially, a specified amount of solute is weighed out on the piston before insertion into the Pyrex tube. Overburden fluid is pumped around and then into the bottom of the tube (below the floating piston) to displace the floating piston upward, thereby minimizing the sample volume. The small vapor space in the sample volume is purged of air with CO_2 . A known amount of CO_2 is then added to the sample from a positive displacement pump to obtain the desired composition. Typically this is accomplished by injecting

compressed liquid CO₂ into the sample volume at the same volumetric flow rate (± 0.1 cm³/hr) as the overburden fluid is withdrawn, which results in a well-controlled, isothermal, isobaric addition of CO₂ into the sample volume. The volume of CO₂ (± 0.01 cm³) that is introduced is determined by the graduations on the positive displacement pump. The mass of CO₂ is determined as the product of the added CO₂ volume and the CO₂ density as estimated with the NIST web book correlation [42]. The valve at the top of the sample volume is closed after the desired amount of CO₂ has been introduced, which isolates the mixture.

The mixture of invariant overall composition is then compressed and stirred using a magnetically driven slotted fin impeller spinning at 2500 rpm at elevated pressure as high as 69 MPa at the temperature of interest until a transparent, single-phase solution was attained. A light source behind the cell allows the observer to look through the flat windows of the high pressure vessel, the overburden fluid, and the wall of the Pyrex tube to view the single phase residing within the entire sample volume.

The mixture is then expanded very slowly via the withdrawal of the overburden fluid situated below the floating piston, as shown in Figure 6, until a second phase appears. For example at the conditions encountered in this study we report bubble points of a rapidly rising CO₂-rich vapor phase V at sub-critical temperatures (Figure 1), bubble points of a rising CO₂-rich fluid phase F at supercritical temperature or cloud/dew points for sinking PDMS-rich liquid droplets (Figure 2), and cloud/dew points of sinking PDMS-rich liquid droplets, L₁ or L, at sub-critical temperatures (Figures 3 and 5) and supercritical temperatures (Figures 4). At pressures slightly below the cloud point, a thin liquid layer accumulates slowly at the bottom of the sample volume under quiescent conditions (because the PDMS-rich liquid is higher in density than the dense CO₂-rich phase at the pressures encountered in this study). In order to provide a reproducible and conservative measure of solubility (i.e. so as to not overestimate the solubility at the cloud point), the cloud point pressure is reported as the pressure at which the extremely fine suspended droplets prevent one from seeing clearly through the solution (i.e. the outlines of objects behind the sample volume could not be discerned). This cloud pressure value is typically 0.5 MPa greater than the lower cloud point pressure at which a greater proportion of the solute comes out of

solution and the sample volume becomes opaque. The measurement was repeated at least three times with a reproducibility of ± 0.7 MPa.

2.4 Modelling methods

The PC-SAFT equation [43] was used to model the phase equilibrium for the PDMS-CO₂ mixtures at 23°C and 40°C. Pure-component PC-SAFT parameters for CO₂ suggested by Gross and Sadowski were used [43]. Parameters for the PDMS of varying molecular weight were determined using the group contribution method of Tihic et. al [44] and the group contribution parameters of Tihic et. al [45]. The binary interaction parameter (k_{ij}) was initially set equal to 0 to determine if accurate predictions of the phase behavior could be obtained. The k_{ij} value was then adjusted to minimize the mean absolute percent deviation (MAPD) for the entire set of PDMS/CO₂ two-phase boundary pressures between 1-4wt% PDMS in CO₂ for all PDMS molecular weights. No attempts were made to make k_{ij} a function of temperature and/or PDMS molecular weight or polydispersity.

3. Results and Discussion

Because of our on-going interest in the design of CO₂-thickeners for EOR, we selected a CO₂-phobe (CO₂-phobic relative to PDMS) composed of an aromatic associating group for this study. Naphthalene and anthracene groups have been used frequently in the design of simple organogelators due to their ability to promote self-assembly via π - π interactions [46,47]. Therefore, we selected the ethyl naphthalene functionality as a model terminal associating group on PDMS segments of varying molecular weight to assess the affect phase behavior of a potential self-assembling small molecule CO₂ thickener architecture. Pressure-composition data at 35°C, Figure 7, confirms our hypothesis that naphthalene (M_w 128) is indeed much less CO₂-philic [48] than PDMS (i.e. naphthalene is more CO₂-phobic), even though the molecular weight of the PDMS is 237. The limiting solubility of naphthalene in CO₂ at 35°C and extremely high pressures is ~ 6.5 wt%, whereas the bubble point locus of the PDMS (M_w 237) – CO₂ mixtures (see Figure 2), remains flat at about 7 MPa. At higher concentrations of PDMS, the bubble point

curve would extend to even lower pressures, reaching the vapor pressure of PDMS as its concentration approaches unity [30,49].

Once the choice of terminal CO₂-phobe was made, model end-terminal PDMS compounds were synthesized as described above and their phase behavior in CO₂ compared to that of un-functionalized PDMS materials. The molecular structures of the compounds used in this study are shown in Figure 8.

3.1 Experimental CO₂ – PDMS Two Phase Boundaries

Pseudo-binary pressure-composition (P-x) diagrams for mixtures of dilute amounts of the PDMS in CO₂ have been determined at 23°C and 40°C, Figures 9 and 10, respectively, for the PDMS samples listed in Table 2. All of these trimethylsilyl-terminated linear silicones formed homogenous one phase solutions at elevated pressure at concentrations up to 4wt% PDMS. As expected, the two-phase boundary pressure loci increase with increasing concentration and PDMS chain length.

For mixtures containing PDMS with an average molecular weight of 410 or 1250 at a sub-critical temperature of 23°C (the critical temperature of CO₂ is 31.1°C), Figure 9, the bubble point pressure data is fairly flat and can be extended to the vapor pressure of CO₂ (y-intercept in Figures 1, 9). A CO₂-rich vapor phase and a PDMS-rich liquid phase co-exist below these bubble point loci (V-L region of Figure 1). At higher PDMS concentrations (not shown in Figure 9), the bubble point curves would decrease until the vapor pressure of the silicone oil was attained at a concentration of 100% PDMS (Figure 1), as shown in our prior studies for a mixture of CO₂ and low molecular weight PDMS at 25°C [30,49]. For mixtures containing PDMS with an average molecular weight of 2000 or more at 23°C, a CO₂-rich liquid and a PDMS-rich liquid are in equilibrium (L₂-L₁) at pressures below the cloud point loci, Figures 3 and 9. These cloud point curves are therefore not extended to the vapor pressure of CO₂ because a small CO₂-rich vapor – CO₂-rich liquid (V-L₂) region occurs at very low concentrations of PDMS as shown in Figure 3; the precise location of this V-L₂ region on the P-x diagram was not experimentally determined in this study.

For mixtures containing 1-4wt% PDMS with an average molecular weight of 410, 1250, 2000 and 3780 at a supercritical temperature of 40°C, Figure 10, a CO₂-rich fluid and a PDMS-rich fluid are in equilibrium at pressures below the cloud point loci as shown by the F-L region in Figure 2. For mixtures containing 1-4wt% PDMS with an average molecular weight of 5970 or 9430 at a supercritical temperature of 40°C, Figure 10, a CO₂-rich fluid and a PDMS-rich fluid are in equilibrium at pressures below the cloud point loci as shown by the F-L region in Figure 4.

The loci found in Figures 9 and 10 represent the lowest possible cloud point pressures that a compound containing a PDMS oligomer or polymer of average molecular weight up to 9430 and one or more CO₂-phobic functional groups can be expected to exhibit at 23°C or 40°C, respectively. For example, if one desires to design a CO₂-soluble surfactant with a polar or ionic head group that is soluble at 1wt% in CO₂ at 40°C at a pressure less than 13 MPa, the average molecular weight of the PDMS would have to be less than 3780. Figure 10 shows that a pressure of 13 MPa is required to dissolve 1wt% unfunctionalized PDMS Mw 3780, therefore pressures greater than 13 MPa would be required to dissolve the same PDMS after a CO₂-phobic group is incorporated into its structure.

3.2 PC SAFT correlated CO₂ – PDMS Two-Phase Boundaries

Predictions of the two-phase boundaries were obtained by using PC SAFT with the binary interaction parameter set equal to zero ($k_{ij} = 0$). The PC SAFT predictions and the experimental data are shown in Figures 11 and 12. The mean absolute percent deviation (MAPD) at 23°C was 16.4%, with a standard deviation (SD) of 14.5%. The MAPD at 40°C was 21.0%, with a SD of 15.9%. At 23°C, good agreement was realized for PDMS 410 and 1250, overestimations occurred for PDMS M_w 2000 and 3780, and the PDMS M_w 5970 and 9430 results were underestimated. At 40°C, good agreement was again attained for PDMS Mw 410, the two-phase boundaries for mixtures containing PDMS Mw 1250, 2000, 3780 and 5970 were overestimated, while the two-phase boundary for PDMS Mw 9430 was underestimated. We were unable to attain smaller MAPD values by varying the value of k_{ij} . These results indicate that while it may be possible to provide reasonable estimates of the order-of-magnitude of cloud

point and dew point pressures of the CO₂-PDMS system using PC SAFT, accurate fits of all of the two-phase boundaries may require accounting for the polydispersity of PDMS and correlating k_{ij} to temperature and polymer molecular weight.

3.3 CO₂ – PDMS-NAP Two Phase Boundaries

The two-phase liquid-liquid (CO₂-rich liquid – PDMS-NAP-rich liquid) boundaries for mixtures of PDMS-NAP and CO₂ at 23°C are found in Figures 5 and 13. Results for PDMS-NAP 443 and 5974, the lowest and highest molecular weight versions of PDMS-NAP, are not illustrated because each is CO₂-insoluble up to 69 MPa. It is likely that the lowest molecular weight PDMS-NAP was insoluble because the CO₂-phobicity (i.e. unfavorable enthalpic interactions between CO₂ and ethyl naphthalene) of the two terminal ethyl-naphthalene groups could not be compensated for by the favorable CO₂-PDMS interactions of the very short PDMS chain. The highest molecular weight PDMS-NAP was likely insoluble because of the combined effects of the unfavorable enthalpic interactions between the terminal groups and CO₂ along with the entropic mixing energy penalty associated with the increased molecular weight of the PDMS.

The optimal PDMS backbone molecular weight (of those listed in Table 2) for enhancing the CO₂ solubility of PDMS terminated at each end with ethyl naphthalene is represented by the PDMS content of the compound that exhibited the lowest cloud point pressures. The lowest pressures were observed in the CO₂ - PDMS-NAP 2679 mixture ranging from 18-28 MPa over the 1-4wt% concentration range at 23°C. The cloud point pressure for an un-functionalized PDMS with a comparable backbone molecular weight, about 2357, can be estimated from Figure 9 as roughly 7 MPa indicating that the CO₂-phobicity of the terminal ethyl-naphthalene groups is responsible for the higher cloud point pressure values of the CO₂ - PDMS-NAP 2679 mixture.

3.4 CO₂-solubility of Other End-functionalized PDMS Compounds

In section 3.3, a PDMS-based compound with an average of 9.8 repeat units functionalized on both ends with ethylnaphthalene (PDMS-NAP 1181) was determined to be soluble at 1 wt% in CO₂ at 23°C

but CO₂-insoluble at 69 MPa at 2-4wt%. Two examples of PDMS end-functionalized with ethyl naphthalene moieties that were 1-4wt% soluble in CO₂ were generated by incorporating either 14.5 or 30.0 DMS repeat units (PDMS-NAP 1530 and 2679, respectively). In order to demonstrate that a wide variety of CO₂-soluble end-functionalized PDMS compounds could be generated in a similar manner, many other end groups were selected. In most cases, these functionalities were selected because they had the potential to associate in solution, therefore the resultant molecule would have the potential to not only dissolve in CO₂, but to also associate in solution and thicken the CO₂-rich phase. The general structure is shown in Figure 14. The ethylnaphthalene-terminated result is also provided in Table 3.

Table 3. End-functionalized Polydimethylsiloxane (PDMS) samples.

Compound	Ar	Two-phase boundary type	Two-phase Pressure (1 wt%, 23 °C) MPa
A		Bubble Point	6.0
B		Bubble Point	6.0
C		Cloud Point	6.6
D		Cloud Point	8.3
E		Cloud Point	9.2
F		Cloud Point	16.6
PDMS-NAP 1530		Cloud Point	23.4
G			Insoluble

A simple phenyl group was also examined as a comparison to the naphthyl group to determine if the number of aromatic rings played an important role in CO₂ solubility. Several different chain lengths were tested for solubility that ranged from 0 to 14.5 repeat units (Table 4). The general structure is shown in Figure 15.

Table 4. Bubble Point Pressures of CO₂-(Ethylphenyl-functionalized Polydimethylsiloxane (PDMS)) mixtures.

Compound	X	Bubble Point Pressure (1wt%, 23 °C) MPa
H	0	5.9
I	1	6.1
J	7.4	6.0
A	14.5	6.0

In general, PDMS containing 10-40 repeat units proved to be effective segment length for generating a CO₂-soluble compound. Table 3 lists the results in order of increasing cloud point pressure values for equivalent PDMS chain lengths therefore it provides an approximate ranking of the CO₂-phobicity of the R group, with the least CO₂-phobic group on top and the most CO₂-phobic group on the bottom. For example, if the R-PDMS_n-R compound has a low cloud point pressure as for compound A with ethylbenzene end groups, then the R group is only mildly CO₂-phobic. Similarly, 4-methoxyphenethyl, 4-cyanophenethyl, ethyl pyridine and ethyl biphenyl groups are also shown to be mildly CO₂-phobic functionalities. Conversely, a higher cloud point pressure classifies the R functionality as CO₂-phobic. For example, the benzoic acid, ethyl naphthalene and aniline R groups exhibit high cloud points or insolubility as a result of strong intermolecular interactions such as hydrogen bonding (benzoic acid, aniline), rigid π - π stacking (naphthalene), and carbamate formation (aniline). One caveat related to anilines is that although primary and secondary amines may quickly form insoluble ammonium carbamates upon exposure to CO₂ [41], the aniline groups in compound F have a much higher pK_b than their aliphatic analogs resulting in much slower reaction kinetics. This is due to the aniline nitrogen's lone pair electrons contributing to the adjacent aromatic resonance structures rendering the amine less reactive. Given enough time, the anilines may form completely insoluble ammonium carbamate salts but we did not observe this in our experimental timeframe of less than 4 hours.

Table 4 shows the two-phase boundary pressures resulting from slow expansion of 1wt% single phase mixtures consisting of CO₂ and one of the four ethylbenzene functional compounds H, I, J, and A.

Upon expansion, all mixtures exhibited bubble point pressures below which a CO₂-rich vapor phase and a PDMS-rich liquid phase co-exist (V-L₁ equilibrium). These relatively low two phase boundary pressures in relation to their ethylnaphthalene functional PDMS counterparts indicates that the ethylbenzene groups are more CO₂-philic than ethylnaphthalene. Interestingly, the length of the PDMS portion had very little bearing on bubble point pressure in the range of molecular weight included in this study indicating the feeble strength of benzene-benzene interactions. The comparable bubble point pressures of compounds H, I, J, A, PDMS 410 and PDMS 1250 provide further evidence that the ethylbenzenes contribute minimally to solute-solute interactions.

Although the number of aromatic rings plays a role in CO₂-solubility, rigidity of the functional group must also be considered. Clearly, two ringed aromatics as seen in molecule E and PDMS-NAP 1530 raise the two-phase boundary pressure compared to the single ring as seen in molecule A. It appears that the biphenyl group used in molecule E is more CO₂-philic than the naphthyl group used in PDMS-NAP 1530 based on the trend in cloud point pressures. This may be due to the ability of the biphenyl rings to rotate around the central phenyl-phenyl linkage, potentially allowing the biphenyl group to adopt more favorable geometric conformations which can interact favorably with each other or with CO₂.

Unfortunately, our falling ball viscometry results indicated that none of the compounds presented in this study yielded significant viscosity increases when dissolved in CO₂ at dilute concentration [50,51].

4. Conclusions

Pressure-composition diagrams for mixtures of 1-4wt% trimethylsilyl-terminated PDMS of Mw < 10000 and CO₂ systems have been determined at 23°C and 40°C. The two-phase pressure loci of the PDMS in CO₂ are fairly flat and increase to higher pressure values with longer polymer chain lengths. PC-SAFT used in conjunction with binary interaction parameter k_{ij} set equal to zero provided rough approximations for cloud point pressures for CO₂-PDMS mixtures containing dilute concentrations of lower molecular weight PDMS, however it was not possible to match all of the two-phase boundary pressure values by manipulating the k_{ij} value. These two-phase boundaries represent the lowest possible

pressure at 23°C and 40°C required to dissolve a PDMS-based compound with $410 < \text{PDMS Mw} < 10000$ that is functionalized with one or more CO₂-phobic functionalities.

To illustrate this concept, the solubility of five ethylnaphthalene-terminated PDMS compounds has been determined at 23°C. The solubility of the ethylnaphthalene-terminated PDMS in CO₂ reaches a maximum value at a molecular weight of 2679 as evidenced by its low cloud point pressure values (increasing from 18-28 MPa over the 1-4wt% concentration range). The cloud point pressure for an unfunctionalized (i.e. TMS-terminated) PDMS with a comparable PDMS molecular weight is approximately 7 MPa. Ethylnaphthalene-terminated PDMS compounds with lower molecular weights are less CO₂ soluble because increasingly weaker favorable interactions between CO₂ and the shorter CO₂-philic PDMS polymer chain cannot compensate for the unfavorable enthalpic interactions between CO₂ and the CO₂-phobic ethylnaphthalene groups. For higher molecular weight ethylnaphthalene-terminated PDMS, the unfavorable enthalpic interactions between the ethylnaphthalene groups and CO₂, coupled with the unfavorable entropic effects associated with the increased molecular weight of the PDMS, render the compound much less CO₂ soluble.

Seven other end groups were assessed by incorporating them into molecules that contained 14.5 DMS repeat units and comparing their two phase boundary pressures. General ranking of terminal group CO₂-phobicity was determined by comparing the molecules' two phase boundary pressures to each other; a highly CO₂-phobic group would exhibit a higher boundary pressure than a less CO₂-phobic group. Generally, end groups with a high propensity to self-interact through mechanisms such as hydrogen bonding, π - π stacking and ammonium carbamate formation were most CO₂-phobic. It was also concluded that two ringed aromatic functionalities like naphthalene and biphenyl groups were more CO₂-phobic than benzene based groups but rigidity of the systems may also play a role as seen in the differing cloud point pressures of PDMS-NAP 1530 and compound A.

Acknowledgements

This work was funded by the US Department of Energy, Advanced Research Project Agency - Energy under award number DE-AR0000292 and by the National Energy Technology Laboratory under cooperative agreement DE-FE0010799.

References

- [1] E.J. Beckman, Supercritical and near-critical CO₂ in green chemical synthesis and processing, *J. Supercrit. Fluids*. 28 (2004) 121–191. doi:10.1016/S0896-8446(03)00029-9.
- [2] J.P. Heller, D.K. Dandge, R.J. Card, L.G. Donaruma, Direct thickeners for mobility control of CO₂ floods, *Soc. Pet. Eng. J.* 25 (1985) 679–686. doi:10.2118/11789-PA.
- [3] F. Rindfleisch, T.P. DiNoia, M.A. McHugh, Solubility of Polymers and Copolymers in Supercritical CO₂, *J. Phys. Chem.* 100 (1996) 15581–15587. doi:10.1021/jp9615823.
- [4] A. Galia, P. Pierro, G. Filardo, Dispersion polymerization of methyl methacrylate in supercritical carbon dioxide stabilized with poly(ethylene glycol)-b-perfluoroalkyl compounds, *J. Supercrit. Fluids*. 32 (2004) 255–263. doi:10.1016/j.supflu.2003.12.017.
- [5] A. Mohamed, M. Sagisaka, F. Guittard, S. Cummings, A. Paul, S.E. Rogers, et al., Low fluorine content CO₂-philic surfactants., *Langmuir*. 27 (2011) 10562–9. doi:10.1021/la2021885.
- [6] J. Eastoe, S. Gold, D.C. Steytler, Surfactants for CO₂., *Langmuir*. 22 (2006) 9832–42. doi:10.1021/la060764d.
- [7] J.B. McClain, D. Londono, J.R. Combes, T.J. Romack, D.A. Canelas, D.E. Betts, et al., Solution Properties of a CO₂-Soluble Fluoropolymer via Small Angle Neutron Scattering, *J. Am. Chem. Soc.* 118 (1996) 917–918. doi:10.1021/ja952750s.
- [8] G. Luna-Bárcenas, S. Mawson, S. Takishima, J.M. DeSimone, I.C. Sanchez, K.P. Johnston, Phase behavior of poly(1,1-dihydroperfluorooctylacrylate) in supercritical carbon dioxide, *Fluid Phase Equilib.* 146 (1998) 325–337. doi:10.1016/S0378-3812(98)00215-5.
- [9] P. André, P. Lacroix-Desmazes, D.K. Taylor, B. Boutevin, Solubility of fluorinated homopolymer and block copolymer in compressed CO₂, *J. Supercrit. Fluids*. 37 (2006) 263–270. doi:10.1016/j.supflu.2005.08.007.
- [10] M. Chirat, T. Ribaut, S. Clerc, F. Charton, B. Fournel, P. Lacroix-Desmazes, Extraction of Cobalt Ion from Textile Using a Complexing Macromolecular Surfactant in Supercritical Carbon Dioxide, *Ind. Eng. Chem. Res.* 52 (2012) 121219151443008. doi:10.1021/ie301754v.

- [11] L. Du, J.Y. Kelly, G.W. Roberts, J.M. DeSimone, Fluoropolymer synthesis in supercritical carbon dioxide, *J. Supercrit. Fluids*. 47 (2009) 447–457. doi:10.1016/j.supflu.2008.11.011.
- [12] Z. Huang, C. Shi, J. Xu, S. Kilic, R.M. Enick, E.J. Beckman, Enhancement of the Viscosity of Carbon Dioxide Using Styrene/Fluoroacrylate Copolymers, *Macromolecules*. 33 (2000) 5437–5442. doi:10.1021/ma992043+.
- [13] R. Enick, E. Beckman, A. Yazdi, V. Krukonis, H. Schonemann, J. Howell, Phase behavior of CO₂–perfluoropolyether oil mixtures and CO₂–perfluoropolyether chelating agent mixtures, *J. Supercrit. Fluids*. 13 (1998) 121–126. doi:10.1016/S0896-8446(98)00043-6.
- [14] R.P. Nielsen, R. Valsecchi, M. Strandgaard, M. Maschietti, Experimental study on fluid phase equilibria of hydroxyl-terminated perfluoropolyether oligomers and supercritical carbon dioxide, *J. Supercrit. Fluids*. 101 (2015) 124–130. doi:10.1016/j.supflu.2015.03.011.
- [15] D.A. Newman, T.A. Hoefling, R.R. Beitle, E.J. Beckman, R.M. Enick, Phase behavior of fluoroether-functional amphiphiles in supercritical carbon dioxide, *J. Supercrit. Fluids*. 6 (1993) 205–210. doi:10.1016/0896-8446(93)90028-V.
- [16] Y. Wang, L. Hong, D. Tapriyal, I.C. Kim, I.-H. Paik, J.M. Crosthwaite, et al., Design and evaluation of nonfluorous CO₂-soluble oligomers and polymers., *J. Phys. Chem. B*. 113 (2009) 14971–80. doi:10.1021/jp9073812.
- [17] L. Hong, D. Tapriyal, R.M. Enick, Phase Behavior of Poly(propylene glycol) Monobutyl Ethers in Dense CO₂, *J. Chem. Eng. Data*. 53 (2008) 1342–1345. doi:10.1021/jc800068v.
- [18] P.J.M. Stals, J.F. Haveman, R. Martín-Rapún, C.F.C. Fitié, A.R.A. Palmans, E.W. Meijer, The influence of oligo(ethylene glycol) side chains on the self-assembly of benzene-1,3,5-tricarboxamides in the solid state and in solution, *J. Mater. Chem*. 19 (2009) 124–130. doi:10.1039/B816418E.
- [19] D. Tapriyal, Y. Wang, R.M. Enick, J.K. Johnson, J. Crosthwaite, M.C. Thies, et al., Poly(vinyl acetate), poly((1-O-(vinyl-oxy) ethyl-2,3,4,6-tetra-O-acetyl- β -D-glucopyranoside) and amorphous poly(lactic acid) are the most CO₂-soluble oxygenated hydrocarbon-based polymers, *J. Supercrit.*

- Fluids. 46 (2008) 252–257. doi:10.1016/j.supflu.2008.05.001.
- [20] D. Tapriyal, DESIGN OF NON-FLUOROUS CO₂ SOLUBLE COMPOUNDS, University of Pittsburgh, 2009. <http://d-scholarship.pitt.edu/6565/>.
- [21] T. Sarbu, T. Styranec, E. Beckman, Non-fluorous polymers with very high solubility in supercritical CO₂ down to low pressures, *Nature*. 405 (2000) 165–8. doi:10.1038/35012040.
- [22] C. Drohmann, E.J. Beckman, Phase behavior of polymers containing ether groups in carbon dioxide, *J. Supercrit. Fluids*. 22 (2002) 103–110. doi:10.1016/S0896-8446(01)00111-5.
- [23] P. Raveendran, S.L. Wallen, Sugar Acetates as Novel, Renewable CO₂-philic, *J. Am. Chem. Soc.* 124 (2002) 7274–7275. doi:10.1021/ja025508b.
- [24] V.K. Potluri, J. Xu, R. Enick, E. Beckman, A.D. Hamilton, Peracetylated sugar derivatives show high solubility in liquid and supercritical carbon dioxide., *Org. Lett.* 4 (2002) 2333–5. <http://www.ncbi.nlm.nih.gov/pubmed/12098240> (accessed April 25, 2014).
- [25] M.L. O'Neill, Q. Cao, M. Fang, K.P. Johnston, Solubility of Homopolymers and Copolymers in Carbon Dioxide, 5885 (1998) 3067–3079.
- [26] D. Sanli, C. Erkey, Demixing pressures of hydroxy-terminated poly(dimethylsiloxane)–carbon dioxide binary mixtures at 313.2K, 323.2K and 333.2K, *J. Supercrit. Fluids*. 92 (2014) 264–271. doi:10.1016/j.supflu.2014.05.014.
- [27] S. Kim, Y.-S. Kim, S.-B. Lee, Phase behaviors and fractionation of polymer solutions in supercritical carbon dioxide, *J. Supercrit. Fluids*. 13 (1998) 99–106. doi:10.1016/S0896-8446(98)00040-0.
- [28] J.H. Bae, C.A. Irani, A laboratory investigation of viscosified CO₂ process, *SPE Adv. Technol. Ser.* 1 (1993) 166–171. <https://www.onepetro.org/journal-paper/SPE-20467-PA>.
- [29] M.B. Miller, D.R. Luebke, R.M. Enick, CO₂-philic Oligomers as Novel Solvents for CO₂ Absorption, *Energy & Fuels*. 24 (2010) 6214–6219. doi:10.1021/ef101123e.
- [30] M.B. Miller, D.-L. Chen, H.-B. Xie, D.R. Luebke, J. Karl Johnson, R.M. Enick, Solubility of CO₂ in CO₂-philic oligomers; COSMOtherm predictions and experimental results, *Fluid Phase Equilib.*

- 287 (2009) 26–32. doi:10.1016/j.fluid.2009.08.022.
- [31] Z. Bayraktar, E. Kiran, Miscibility, phase separation, and volumetric properties in solutions of poly(dimethylsiloxane) in supercritical carbon dioxide, *J. Appl. Polym. Sci.* 75 (2000) 1397–1403. doi:10.1002/(SICI)1097-4628(20000314)75:11<1397::AID-APP12>3.0.CO;2-F.
- [32] Y. Xiong, E. Kiran, Miscibility, density and viscosity of poly(dimethylsiloxane) in supercritical carbon dioxide, *Polymer (Guildf)*. 36 (1995) 4817–4826. doi:10.1016/0032-3861(95)99298-9.
- [33] P. Alessi, K. Ireneo, C. Angelo, F. Alessia, M. Mariarosa, Polydimethylsiloxanes in supercritical solvent impregnation (SSI) of polymers, *J. Supercrit. Fluids*. 27 (2003) 309–315. doi:10.1016/S0896-8446(02)00267-X.
- [34] M. Yates, P. Shah, K. Johnston, K. Lim, S. Webber, Steric Stabilization of Colloids by Poly(dimethylsiloxane) in Carbon Dioxide: Effect of Cosolvents., *J. Colloid Interface Sci.* 227 (2000) 176–184. doi:10.1006/jcis.2000.6850.
- [35] P.A. Psathas, S.R.P. da Rocha, C.T. Lee, K.P. Johnston, K.T. Lim, S. Webber, Water-in-Carbon Dioxide Emulsions with Poly(dimethylsiloxane)-Based Block Copolymer Ionomers, *Ind. Eng. Chem. Res.* 39 (2000) 2655–2664. doi:10.1021/ie990779p.
- [36] S. Kwon, K. Lee, W. Bae, H. Kim, Synthesis of a biocompatible polymer using siloxane-based surfactants in supercritical carbon dioxide, *J. Supercrit. Fluids*. 45 (2008) 391–399. doi:10.1016/j.supflu.2008.01.021.
- [37] T.A. Hoefling, D.A. Newman, R.M. Enick, E.J. Beckman, Effect of structure on the cloud-point curves of silicone-based amphiphiles in supercritical carbon dioxide, *J. Supercrit. Fluids*. 6 (1993) 165–171. doi:10.1016/0896-8446(93)90015-P.
- [38] K.A. Shaffer, T.A. Jones, D.A. Canelas, J.M. DeSimone, S.P. Wilkinson, Dispersion Polymerizations in Carbon Dioxide Using Siloxane-Based Stabilizers, *Macromolecules*. 29 (1996) 2704–2706. doi:10.1021/ma9516798.
- [39] R. Fink, E.J. Beckman, Phase behavior of siloxane-based amphiphiles in supercritical carbon dioxide, *J. Supercrit. Fluids*. 18 (2000) 101–110. doi:10.1016/S0896-8446(00)00052-8.

- [40] J.A. Dzielawa, A. V. Rubas, C. Lubbers, D.C. Stepinski, A.M. Scurto, R.E. Barrans, et al., Carbon Dioxide Solubility Enhancement through Silicone Functionalization: “CO₂ -philic” Oligo(dimethylsiloxane)-substituted Diphosphonates*, Sep. Sci. Technol. 43 (2008) 2520–2536. doi:10.1080/01496390802122063.
- [41] R.J. Perry, T.A. Grocela-Rocha, M.J. O’Brien, S. Genovese, B.R. Wood, L.N. Lewis, et al., Aminosilicone solvents for CO₂ capture., ChemSusChem. 3 (2010) 919–30. doi:10.1002/cssc.201000077.
- [42] D.G. Lemmon, E.W. , McLinden, M.O., Friend, Thermophysical Properties of Fluid Systems, NIST Chem. WebBook, NIST Stand. Ref. Database Number 69. (n.d.). <http://webbook.nist.gov/chemistry/fluid/> (accessed December 14, 2015).
- [43] J.G. and, G. Sadowski*, Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules, (2001).
- [44] A. Tihic, G.M. Kontogeorgis, N. von Solms, M.L. Michelsen, L. Constantinou, A Predictive Group-Contribution Simplified PC-SAFT Equation of State: Application to Polymer Systems, Ind. Eng. Chem. Res. 47 (2008) 5092–5101. doi:10.1021/ie0710768.
- [45] A. Tihic, N. von Solms, M.L. Michelsen, G.M. Kontogeorgis, L. Constantinou, Application of sPC-SAFT and group contribution sPC-SAFT to polymer systems—Capabilities and limitations, Fluid Phase Equilib. 281 (2009) 70–77. doi:10.1016/j.fluid.2009.04.002.
- [46] G. Clavier, M. Mistry, F. Fages, J.-L. Pozzo, Remarkably simple small organogelators: di-n-alkoxy-benzene derivatives, Tetrahedron Lett. 40 (1999) 9021–9024. doi:10.1016/S0040-4039(99)01918-8.
- [47] P. Terech, G. Clavier, H. Bouas-Laurent, J.-P. Desvergne, B. Demé, J.-L. Pozzo, Structural variations in a family of orthodialkoxyarenes organogelators., J. Colloid Interface Sci. 302 (2006) 633–42. doi:10.1016/j.jcis.2006.06.056.
- [48] M. McHugh, M.E. Paulaitis, Solid solubilities of naphthalene and biphenyl in supercritical carbon dioxide, J. Chem. Eng. Data. 25 (1980) 326–329. doi:10.1021/je60087a018.

- [49] R.M. Enick, P. Koronaios, C. Stevenson, S. Warman, B. Morsi, H. Nulwala, et al., Hydrophobic Polymeric Solvents for the Selective Absorption of CO₂ from Warm Gas Streams that also Contain H₂ and H₂O, *Energy & Fuels*. 27 (2013) 6913–6920. doi:10.1021/ef401740w.
- [50] M.D. Doherty, J.J. Lee, A. Dhuwe, M.J. O'Brien, R.J. Perry, E.J. Beckman, et al., Small Molecule Cyclic Amide and Urea Based Thickeners for Organic and sc-CO₂/Organic Solutions, (2016).
- [51] M.J. O'Brien, R.J. Perry, M.D. Doherty, J.J. Lee, A. Dhuwe, E.J. Beckman, et al., Anthraquinone Siloxanes as Thickening Agents for Supercritical CO₂, (2016).

Figure 1. Qualitative P - x diagram illustrating the V-L region for sub-critical ($T < 31^\circ\text{C}$) mixtures of CO_2 with lower molecular weight PDMS (410 and 1250). The dashed ellipse indicates region where V-L bubble points were measured. V.P. = vapor pressure

Figure 2. Qualitative P - x diagram illustrating the two-phase region for supercritical ($T > 31^{\circ}\text{C}$) mixtures of CO_2 with low molecular weight PDMS (237) dotted ellipse F-L bubble points; PDMS (410, 1250, 2000, 3780) dashed ellipse F-L cloud/dew points. V.P. = vapor pressure

Figure 3. Qualitative P-x diagram illustrating the three two-phase regions and three-phase line for sub-critical ($T < 31^{\circ}\text{C}$) mixtures of CO_2 with higher molecular weight PDMS (2000, 3780, 5970, 9430). The dashed ellipse indicates region where L₂-L₁ cloud/dew points were measured. V.P. = vapor pressure

Figure 4. Qualitative P - x diagram illustrating the three two-phase regions and three-phase line for supercritical ($T > 31^\circ C$) mixtures of CO_2 with higher molecular weight PDMS (5970, 9430). The dashed ellipse indicates region where F-L cloud/dew points were measured. V.P. = vapor pressure

Figure 5. Qualitative P - x diagram illustrating the three two-phase regions and three-phase line for sub-critical ($T < 31^\circ\text{C}$) mixtures of CO_2 with PDMS-NAP. The dashed ellipse indicates region where L_2-L_1 cloud/dew points were measured for PDMS-NAP of intermediate molecular weight. V.P. = vapor pressure

Figure 6. Experimental apparatus used to conduct phase behavior experiments using a variable-volume, windowed, agitated, high pressure cell. o.b. = overburden, P = pressure transducer. Arrows indicate direction of movement or flow during isothermal expansion of sample volume (black valves are closed, white valve is open).

Figure 7. A comparison of the solubility of CO₂-phobic naphthalene (Mw 128.17) (triangles, reference [45]) and CO₂-philic PDMS (Mw 237) (stars, this work) in CO₂ at 35°C. Naphthalene cloud point pressures indicate a limiting solubility of 6.5wt% at extreme pressure. The PDMS-CO₂ mixture bubble point data are indicative of a high degree of miscibility between PDMS 237 and CO₂.

Figure 8. Structures of PDMS (top) and ethylnaphthalene-terminated PDMS (PDMS-NAP) (bottom). The two possible end groups shown on the ethylnaphthalene-terminated PDMS illustrate that this compound is a mixture of isomers.

Figure 9. Two-phase boundaries of trimethylsilyl-terminated PDMS in CO₂ at 23°C. Mixtures containing PDMS 410 or 1250 exhibited V-L bubble points (refer to Figure 1); mixtures containing PDMS 2000, 3780, 5970 or 9430 exhibited cloud points (refer to Figure 3). The curves are guides to the eye; they are not model results.

Figure 10. Solubility of trimethylsilyl-terminated PDMS in CO₂ at 40°C. Mixtures containing PDMS 410, 1250, 2000, or 3780 exhibited F-L cloud points (refer to Figure 2); mixtures containing PDMS 5970 or 9430 exhibited F-L cloud points (refer to Figure 4). The curves are guides to the eye; they are not model results.

Figure 11. PC-SAFT results at 23°C with $k_{ij} = 0$. Experimental data depicted by markers while PC-SAFT predictions are labeled above plotlines.

Figure 12. PC-SAFT results at 40°C with $k_{ij} = 0$. Experimental data depicted by markers while PC-SAFT predictions are labeled above plotlines.

Figure 13. Solubility of the PDMS-NAP compounds in CO₂ at 23°C, as represented by cloud point data. PDMS-NAP 1181 is soluble at 1wt%, but is insoluble at 2wt%. The curves are guides to the eye; they are not model results. PDMS-NAP 454 and PDMS-NAP 5986 are not shown because they are insoluble up to 69 MPa.

Figure 14. Phenyl-R-functionalized Polydimethylsiloxane (PDMS)

Figure 15. Ethylphenyl-functionalized Polydimethylsiloxane (PDMS)

Graphical Abstract