Toward the Development of "CO_2-philic" Hydrocarbons. 1. Use of Side-Chain Functionalization to Lower the Miscibility Pressure of Polydimethylsiloxanes in CO_2

R. Fink, D. Hancu, R. Valentine, and E. J. Beckman*

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

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Previous fundamental work on the solvent properties of carbon dioxide by the research groups of McHugh, DeSimone, Johnston, and Eckert has been used as a road map for the design of materials that will be miscible with CO_2 at relatively moderate pressures. In this initial work, judicious side chain functionalization of an oligomeric silicone has been shown to produce a material whose phase behavior in CO_2 resembles that of a fluorinated polyether. The phase behavior results are quite dramatic in that addition of only five ester-functional side chains to the silicone polymer lowers the cloud point curve at 22 °C by 2500 psi. It was also observed that addition of simple alkyl side chains raises the cloud point pressures of the silicone in CO_2. This latter observation is consistent with results on the phase behavior of poly(*n*-alkyl acrylates) in CO_2 that showed that increasing alkyl content (i.e., increasing alkyl chain length) also raises cloud point pressures.

Introduction

The feasibility for use of carbon dioxide as a process solvent has been extensively investigated in both academic and industrial circles because CO_2 is generally considered to be an environmentally benign solvent. Conventional wisdom at one time held that the solvent power of CO_2 was similar to that of short *n*-alkanes, given that solubility parameter calculations using CO_2's equation of state behavior suggested this. Although such solubility parameter values precluded the use of CO_2 for processing of polar materials, it was believed then that use of conventional alkyl-functional surfactants could effectively deal with the problem. However, early attempts to employ conventional surfactants in CO_2 failed owing to poor solubility of the amphiphiles, despite the fact that these same molecules exhibited adequate solubility in ethane and propane.[1] As the 1980s drew to a close, a number of research groups began to explore the design of CO_2-philic materials, i.e., compounds that dissolve in CO_2 at significantly lower pressures than do alkyl functional materials of equivalent molecular size. For example, Harrison et al.[2] generated a hybrid alkyl−fluoroalkyl surfactant that both dissolved in CO_2 and solubilized significant amounts of water. DeSimone and co-workers generated homo- and copolymers of fluorinated acrylates, which exhibit extraordinary solubility in CO_2 at moderate pressures.[3] Block copolymers featuring fluorinated acrylate monomers were used to support dispersion polymerization in CO_2,[4] allowing generation of micrometer-size monodisperse spheres. Fluoroether-functional amphiphiles have been used to support emulsion polymerization,[5] to solubilize proteins,[6,7] and to extract heavy metals from soil and water.[8]

Despite success in development of fluorinated CO_2-philic amphiphiles, the cost (on a mass basis) of these fluorinated materials renders the economics of a process generally unfavorable unless the amphiphile can be recycled. Whereas in-process recycling of a "CO_2-phile" is at times straightforward, this is not true in all cases where CO_2 has been proposed as a replacement for organic solvents. Thus, design and development of a hydrocarbon "CO_2-phile" would greatly expand the potential applications for CO_2 as a process solvent. The question becomes, given the extensive previous work, "Can a hydrocarbon be 'CO_2-philic'?"

Clearly, for a material to be CO_2-philic, the free energy of mixing between the compound and CO_2 must be favorable (negative). Although the entropy and enthalpy of mixing are mathematically coupled, as a first approximation we treat the two factors separately. In the case of the entropy of mixing, well-known theories such as that due to Flory and Huggins[9] would say that chain length is the most significant factor involved, where mixing of shorter chains with solvents produce the greater entropy of mixing and thus more favorable conditions for mixing. However, early variations of the Flory−Huggins entropy of mixing due to Huggins included a material constant describing chain flexibility, where more flexible chains produce a greater entropy of mixing. A similar concept was also employed by Flory in his description of the phase behavior of mixtures of stiff and flexible molecules, where increasing chain stiffness decreased the entropy of mixing, tending to favor phase separation. We conclude from this previous work that use of flexible chains favors mixing, particularly in systems where solute−solvent interactions may not be favorable or particularly strong, such as mixtures of materials with CO_2. Highly flexible chains often exhibit relatively low glass transition temperatures (T_g's), and hence, we use low T_g as a marker for chain flexibility. Many (although notably not all) of the fluorinated compounds and silicones considered to be CO_2-philic exhibit relatively low T_g's.

With regards to the enthalpy of mixing, we treat this factor in the first approximation as a sum of contributions from all solvent−solute interactions, minus the contribution of those solute−solute and solvent−solvent interactions lost during the process of mixing. We have found a number of differing approaches in the literature describing the major contributors to the energy of mixing of CO_2-philic materials with CO_2. For example, O'Neill and colleagues[10] correlate the solubility of a variety of polymers and oligomers in CO_2 to the interfacial tension, itself a function of the cohesive energy density. The

* Corresponding author.

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O'Neill work concludes that weak solute−solute interactions promote good solubility in CO_2, and hence, materials with low interfacial tension (low cohesive energy density and thus weak solute−solute interactions) would tend to be more CO_2-philic. It is certainly true that many of the fluorinated and silicone materials described as CO_2-philic exhibit weak solute−solute interactions, as evidenced by low values of the solubility parameter (and hence, low cohesive energy density).

Although CO_2 is a low-dielectric fluid, it is also a Lewis acid, and thus there is the potential that CO_2 could exhibit specific interactions with Lewis bases. Work by DeSimone and colleagues[11] using ^{19}F NMR shows, for example, evidence of specific interactions between F atoms on perfluoroalkanes and CO_2 (possibly at the carbon atom) in mixtures at high pressure. Further, work by Meredith[12] on tertiary amine−CO_2 mixtures and by Kazarian[13] on mixtures of carbonyl-containing compounds and CO_2 (each using FT-IR to examine interactions) shows that CO_2 exhibits measurable, albeit weak, interactions with these types of Lewis bases.

Finally, work by McHugh and colleagues [refs 14 and 15, for example] on the phase behavior of polymers in CO_2 at elevated pressure and temperature suggests that although CO_2 is a low-dielectric fluid, it can exhibit "polar" interactions with certain types of functional groups. Such interactions are attributed to dipole−quadropole or quadropole−quadropole interactions and are used to explain why CO_2 is typically a poor solvent for hydrocarbon polymers yet a somewhat better solvent for polymers that include polar functional groups, such as esters and ethers (and also certain types of hydrofluorocarbon groups). In an extremely interesting result, it appears that the position of the polar groups in the molecule (relative to the polymer backbone) plays a significant role in the phase behavior. For example, the phase behavior of poly(vinyl acetate) differs appreciably from that of poly(methyl acrylate), despite the fact that these materials are simply isomers.

We conclude that the design of a CO_2-philic moiety can be performed that is consistent with all of the background work described above. We start with polydimethylsiloxane as our base material, given that silicones are often considered to be CO_2-philic, yet are clearly not as useful as fluorocarbons in this regard. Silicones exhibit one of the lowest T_g's observed for polymeric materials, suggesting high chain flexibility, and also a low solubility parameter, suggesting weak solute−solute interactions. However, silicones are known to exhibit upper critical solution temperature (UCST) type behavior in CO_2 in temperature−concentration space, where the miscibility gap shrinks as temperature increases. Traditional polymer thermodynamic theories would suggest that a UCST phase envelope derives from less than adequate solute−solvent interactions, the magnitude of which decreases with increasing temperature (ultimately allowing complete miscibility at the UCST). This suggests to us that while parts of the free energy of mixing are already optimal for the case of mixing CO_2 and silicones, improvements can be made regarding specific interactions. Hence, we have explored the use of side chain functionalization to improve the enthalpy of mixing of a silicone with CO_2, where we use lower cloud point pressures at constant temperature to signify improvements.

There are two other issues that should be mentioned briefly. First, the topology of a molecule will affect its phase behavior, as shown both experimentally and theoretically. Kleintjens,[16] in a study of the phase behavior of polyethylenes in supercritical hydrocarbons, showed that branching in a polymer can reduce cloud point pressures by 10's to 100's of bar at constant temperature and molecular weight. This experimental result is supported by the theoretical work by Madden and Freed,[17] which suggests that both the entropy and enthalpy of mixing are affected by topology. Finally, we have found that increasing the degree of branching at constant composition and molecular weight and temperature can reduce cloud point pressures by 10's of bar in hydrocarbon−fluorocarbon graft copolymers.[18] Hence, we would expect side chain functionalization to be a more effective strategy than functionalization of the backbone of the oligomer.

Finally, although we have treated the entropy and enthalpy of mixing as separate entities, it is clear that these factors are coupled in a full description of the free energy of mixing. Increasing the number of specific interactions renders the enthalpy more favorable yet reduces the entropy of mixing, as has been described extensively in the literature. Thus, it is likely that any strategy to render the enthalpy of mixing between a model compound and CO_2 more favorable through use of functional groups that allow for specific interactions with CO_2 will reach a point of diminishing returns.

Given this background, we have explored the use of side chain functionalization to "improve" the phase behavior of silicone oligomers in CO_2 at 22 °C. In this paper we compare the phase behavior of silicones with side chain acetate groups to those without and to those with an equal number of simple alkyl side chains.

Experimental Section

Synthesis of Model Oligomers. *Materials.* Copolymers of dimethylsiloxane and methylhydrosiloxane, as well as platinum vinyltetramethyldisiloxane complex in xylene, were obtained from Gelest and used as received. Solvents were obtained from Aldrich Chemical Co. and purified using conventional techniques.[19] Other materials were obtained from Aldrich Chemical and used as received unless otherwise specified. Glassware was flame-dried and purged with a stream of dry argon (ultrahigh purity grade) prior to use. Argon was also used as an inert atmosphere during synthesis. Liquid carbon dioxide (Liquid Carbonic, 99.9%) was used as received.

Synthesis of Polydimethylsiloxane-g-Propyl Acetate. To 10 g of (a) poly([3.5%]-methylhydro-[96.5%]-dimethyl)siloxane copolymer ((b) 6.5%; (c)16.5%) and 0.584 g allyl acetate (1.08 g; 2.75 g) in 60 mL of toluene, 100 mg of platinum divinyltetramethyldisiloxane complex in xylene (low color) was added. The solution was kept for ca. 3−4 h at room temperature and then heated to 50 °C for an additional 12 h. The color of the mixture turned slightly yellow during heating. In all cases FT-IR was used to monitor the reaction, following the disappearance of the Si−H absorption at ca. 2150 cm^{-1}. After cooling to room temperature the solvent was removed by evaporation under reduced pressure, producing a yellow-brown oil. The product was purified by column chromatography on aluminum oxide (basic surface) using toluene as eluent, giving a colorless to pale-yellow oil. Yield: 55−60%. FT-IR (cm^{-1}): 2962, 2904, 1744, 1442, 1412, 1369, 1258, 1068, 808. ^1H NMR (300 MHz, $CDCl_3$): δ 0.09 (s, Si−CH_3), 0.52 (broad, Si-CH_2−CH_2), 1.40 (broad, Si−CH_2-CH_2−CH_2−), 1.61 (broad, −Si−O−CH_3), 2.06 (s, −O−OC−CH_3), 4.01 (t, −CH_2−O−CO).

Synthesis of Hexyl-Functional Polydimethylsiloxane (PDMS). The procedure employed is similar to that used above for the propyl acetate functional PDMS except that 1-hexene is use in place of allyl acetate. In a typical experiment, a three-neck, 250 mL flask is flushed with argon and preheated to 65 °C. The flask is then charged with 15.30 g (7.8 mmol) of poly([3.5%]-

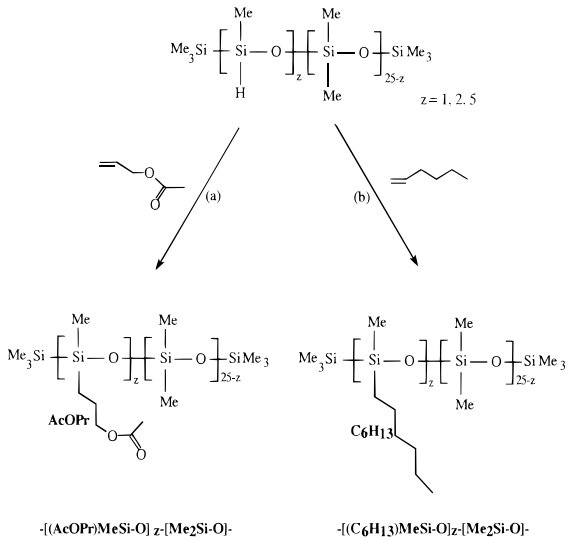

Figure 1. Synthetic scheme for preparation of functionalized silicone oligomers.

methylhydro-[96.5%]-dimethyl)siloxane copolymer, 1.9 mL (15.5 mmol) of 1-hexene, 50 mL of dry toluene, and 100 mg of platinum complex. The solution was left with vigorous stirring overnight. The color of the mixture changed from a pale-yellow solution to that of a dark-brown. The progress of the reaction was monitored using FT-IR. The disappearance of the Si−H peak at 2152 cm^{-1} indicated completion of the reaction. After cooling to room temperature, the solution was concentrated under vacuum to produce a dark-yellow oil. The product was purified by column chromatography using aluminum oxide (activated, basic) as the stationary phase and toluene as the mobile phase. The fractions were again analyzed by FT-IR for 1-hexene contamination, concentrated, and refluxed with decolorizing activated carbon (powder) for 4 h. The product was filtered with 0.2 μm Millipore filter and the remaining solvent removed under vacuum to yield a colorless oil. Yield = 11.32 g (74%). The same procedure was followed for 15.03 g (7.7 mmol) of poly([6.5%]-methylhydro-[93.5%]-dimethyl)siloxane copolymer and 15.04 g (7.7 mmol) of poly([16.5%]-methylhydro-[83.5.5%]-dimethyl)siloxane copolymer, with 3.9 mL (31 mmol) and 11.0 mL (78.8 mmol) of 1-hexene, respectively, and 100 mg of platinum complex in 50 mL of dry toluene. Yield = 6.7 g (45%) and 1.4 g (9.3%). FT-IR (cm^{-1}): 2959, 1410, 1256, 1094, 1020, 804. ^{1}H NMR (300 MHz, $CdCl_3$) δ 0.09 (s, Si−CH_3), 0.52 (broad, Si−CH_2−CH_2), 1.40 (broad, Si−CH_2−CH_2−CH_2−), 1.61 (broad, −Si−O−CH_3).

Phase Behavior of Model Oligomers in Carbon Dioxide. The phase behavior of the model oligomers in CO_2 was measured using a variable volume view cell, as described previously.[20]

Results and Discussion

Functionalized silicones were prepared via the hydrosilylation of model dimethylsiloxane (DMS)−hydromethylsiloxane (HMS) oligomers over a platinum catalyst (see Figure 1). We employed both allyl acetate and 1-hexene to generate side chains in order to examine the effect of the ester group on the phase behavior of the oligomers in CO_2. Note also that the ester group is separated from the main chain of the silicone by a propyl spacer, a move suggested by Rindfleisch's previous work.[14,15] The model silicone oligomers obtained from Gelest contain 25 total repeat units, with three different hydromethyl content such that

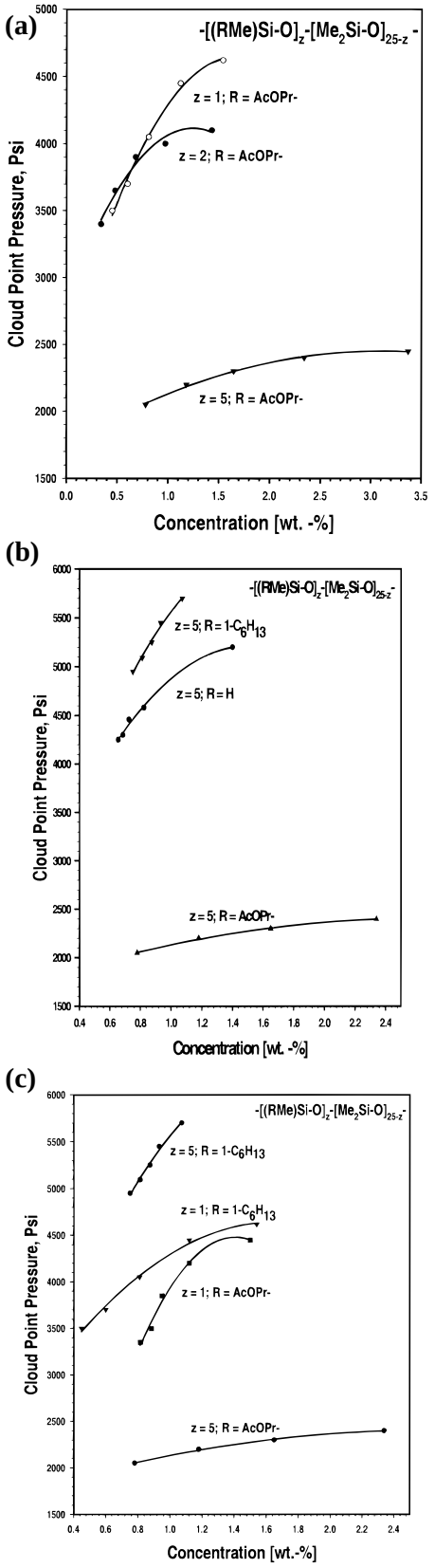

Figure 2. (a) Cloud point curves of model siloxane oligomers (25 repeat units total) where *z* is the number of repeats containing propyl acetate groups. (b) Cloud point curves of model siloxane oligomers (25 repeat units total) where five repeats are other than dimethylsiloxane; curves for −H, propyl acetate, and *n*-hexyl analogues are shown. (c) Cloud point curves of model siloxane oligomers (25 repeat units total) where *z* is the number of repeats containing either propyl acetate or *n*-hexyl groups.

we could prepare model oligomers with one, two, or five side chains. Characterization using both FT-IR and ^{1}H NMR suggested nearly complete conversion during the hydrosilylation reaction.

The phase behavior results (see Figure 2) are quite dramatic in that addition of only five ester-functional side chains to the silicone polymer lowers the cloud point curve at 22 °C by 2500 psi. By comparison, the cloud point curve of a perfluoropolyether with the equivalent number of repeat units (molecular weight, therefore, of 5000) lies at 1000−1400 psi,[21] and thus, we have succeeded in generating a silicone material whose phase behavior begins to approach that of a fluoroether.

In addition to the dramatic reduction in the phase separation pressure observed as a result of functionalization with acetate-terminal side chains, we also observed that addition of simple alkyl side chains raises the cloud point pressures (Figure 2b). This is what one would expect given the previous work of Rindfleisch and colleagues,[14] who showed that increases to the length of the side chain in acrylate and methacrylate polymers render the polymer less CO_2-philic, despite a decrease in the glass transition and thus presumably a more favorable entropy of mixing. As shown in Figure 2c, the magnitude of the effect of side chain functionalization is proportional to the number of side chains, as one would expect.

Given these results, we conclude at this time that addition of side chains containing terminal carbonyl groups does indeed improve the phase behavior of a model silicone oligomer in CO_2, presumably owing to specific interactions between the side chain carbonyl and CO_2. Could we further improve the phase behavior via addition of more side chains? Although it is not clear at this time what the optimum extent of side chain functionalization is, we suspect that a point of diminishing returns will ultimately be reached, particularly if we consider side chain functionalization as a form of "bound" cosolvent addition. McHugh and colleagues found, in a study of the ternary phase behavior of polymer−CO_2−cosolvent mixtures, that a point of diminishing returns was reached during addition of increasing amounts of cosolvent.[15]

In summary, we have employed the previous fundamental work by various research groups as a road map for the design of materials that will be miscible with CO_2 at relatively moderate pressures. In this initial work, we have shown that judicious side chain functionalization of a typical silicone material will produce an oligomer whose phase behavior in CO_2 resembles that of the more expensive fluorinated materials. At this point, we would propose that the next step in the development of a CO_2-philic hydrocarbon would involve the replacement of the silicone backbone of the model materials with one containing only C, H, and O. We would propose polyethers as potentially useful candidates, given that the T_g's of poly(alkylene ethers) tend to be low, often near 200 K. This work will be the subject of a future paper.

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