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CO_2-solubility of oligomers and polymers that contain the carbonyl group

Z. Shen[a,*], M.A. McHugh[a], J. Xu[b], J. Belardi[b], S. Kilic[b], A. Mesiano[b], S. Bane[b], C. Karnikas[b], E. Beckman[b], R. Enick[b]

[a]*Department of Chemical Engineering, Virginia Commonwealth University, 601 West Main Street, Richmond, VA 23284, USA*
[b]*Department of Chemical and Petroleum Engineering, 1249 Benedum Engineering Hall, University of Pittsburgh, Pittsburgh, PA 15261, USA*

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Abstract

Poly(vinyl acetate) (PVAc) is miscible with CO_2 over a broad range of molecular weights at 298 K. The cloud-point pressures needed to dissolve ~5 wt% poly(methyl acrylate) (PMA) at 298 K are significantly greater than those needed to dissolve PVAc, even though a PMA repeat group has the same number of carbon, hydrogen, and oxygen atoms as in PVAc. This large difference in dissolution pressures is attributed to the lack of accessibility of the carbon dioxide to the carbonyl group in PMA. In addition, experimental data for poly(dimethyl siloxane) (PDMS) copolymers with readily accessible side groups suggest that an acetate group is slightly more CO_2-philic than an acrylate group. PVAc is more CO_2-soluble than other hydrocarbon homopolymers, including poly(propylene oxide) (PPO) and poly(lactide) (PLA). However, PVAc is significantly less miscible with CO_2 than PDMS and poly(fluoroalkyl acrylate) (PFA).

Keywords: Carbon dioxide; Phase behavior; Carbonyl

1. Introduction

The identification of highly CO_2-soluble polymers composed of only carbon, hydrogen, and oxygen could facilitate the design of safe, inexpensive, environmentally benign 'CO_2-philes'. These compounds could enhance the performance and economics of CO_2-based technologies that require the dissolution of amphiphiles, such as surfactants, chelating agents, thickeners, and dispersants and homopolymers or copolymers for foam, fiber, and film applications. Heller, et al. [1] performed an extensive review of polymer solubility in dense carbon dioxide to identify a thickener that would reduce the mobility of supercritical CO_2 flowing through porous media. Although no viscosity-enhancing polymer was identified, hydrocarbon-based polymers that exhibited slight solubility in CO_2 (0.1–1.0 wt%) were water-insoluble, atactic, amorphous, and had solubility parameters less than 8 $(cal/cm^3)^{0.5}$. For reference, the solubility parameter of liquid CO_2 is calculated to be in the range of 4–5 $(cal/cm^3)^{0.5}$ at 298 K and pressures above 10 MPa [2].

Subsequent published solubility studies were more successful in identifying polymers capable of dissolving at much higher concentrations in CO_2. In one particular study, cloud-point data at a concentration of approximately 5 wt% polymer, which is expected to be the maximum of a pressure-concentration isotherm, were reported for a series of polyacrylates along with poly(vinyl acetate) (PVAc) [3]. PVAc ($M_w = 125{,}000$) was much more soluble in CO_2 at 298 K than poly(methyl acrylate) (PMA) ($M_w = 31{,}000$) even though PMA had a much lower molecular weight. The PVAc cloud-point pressures increased with temperature over the 295–423 K range while the PMA cloud-point pressures decreased over approximately the same temperature range. Nevertheless, the PVAc two-phase locus remained lower than that of PMA by approximately 150–100 MPa. It should be noted that the pressure required to dissolve PVAc increased from 60 MPa at 295 K to 100 MPa at 423 K, which is high relative to most proposed CO_2-based technologies. The glass transition temperature of PVAc is 21 K higher than that of PMA, indicative of the stronger polar interactions between acetate groups relative to methyl acrylate groups. PVAc was therefore considered to be more polar than PMA, facilitating the formation of a weak complex between CO_2 and vinyl acetate especially at low to

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[*] Corresponding author. Tel.: +1-804-827-7000x460; fax: +1-804-828-3846.

E-mail address: zshen@vcu.edu (Z. Shen).

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moderate temperatures. McHugh and coworkers concluded that a slight degree of polarity is required to establish CO_2 solubility, and the solubility-enhancing weak complex between CO_2 and a carbonyl group in the polymer was more readily formed in the CO_2–PVAc system [3].

Polymer solubility studies of amorphous polyether and polyacrylate homopolymers in CO_2 suggested that polymer solubility increased as the surface tension of the polymer decreased [4]. The lower surface tension is correlated with a lower polymer cohesive energy density which is now closer to the value for CO_2. Low molecular weight poly(propylene oxide) (PPO) exhibited substantial solubility in dense CO_2. For example, 10 wt% PPO, with a molecular weight of 400, dissolved in CO_2 at 303 K and 8.3 MPa. PPO was significantly more soluble than poly(ethylene oxide) (PEO) each at the same molecular weight.

Poly(lactide) (PLA) has been previously shown to dissolve at high concentrations in neat CO_2 [5]. The pressure required to attain a single-phase exceeded that needed for PVAc, however. For example, at 308 K the cloud-point pressures of PVAc and PLA ($M_w = 128,500$) at ~5 wt% in carbon dioxide were 70 and 140 MPa, respectively. Copolymers of lactide and glycolide were even more difficult to dissolve, indicating that polymers rich in the glycolide functionality are less CO_2-philic than PLA.

PMA, PVAc, and PLA contain a carbonyl group in the repeat unit either in the main chain or in the short side chain. The solubility of these polymers in CO_2 is undoubtedly attributable to favorable interactions between the oxygen of the carbonyl group and the carbon of CO_2. Results from ab initio calculations [6], Fourier transform IR spectroscopy [7], and the design of ether-carbonate copolymers [8] all suggest that the electron-donating carbonyl group promotes Lewis acid–Lewis base interactions that enhance CO_2-philicity of a polymer, if the carbonyl is accessible to CO_2. Further studies with low molecular weight solutes and with polymers also support this conjecture. For example, the cloud-point locus of polydimethylsiloxane (PDMS) can be reduced via the incorporation of pendant acetate groups [9]. Small sugar molecules, such as 1,2,3,4,6-pentaacetyl α-D-glucose, 1,2,3,4,6-pentaacetyl β-D-glucose, and 1,2,3,4,6-pentaacetyl β-D-galactose, have been functionalized with acetate groups to dramatically enhance CO_2-solubility [10]. The enhancement in CO_2 solubility was attributed to a two-point interaction of the methyl acetate with CO_2, including the Lewis acid–Lewis base interaction and a weak cooperative hydrogen bond between a proton on the methyl group and an oxygen of the CO_2 [10]. Subsequently, sorbitol, β-cyclodextrin, and small hydrogen-bonding compounds were acetylated to promote CO_2 solubility [11]. Interestingly, cellulose triacetate remains insoluble in CO_2, however, at temperatures up to 373 K and pressures of 70 MPa. It is also noted that the carbonyl-CO_2 interaction contributes to the high solubility of CO_2 in a polymer-rich phase. For example, both PVAc [12] and PMA [13,14] exhibit very high sorption of CO_2.

The objective of this work was to identify the most CO_2-soluble homopolymer composed solely of hydrogen, carbon, and oxygen, and to identify the structure characteristics that promote CO_2 philicity. Solubility measurements were primarily performed at near room temperature. Solubility was determined over a wide range of molecular weights, and, where possible, comparisons were made for polymers with an equivalent number of repeat units. The solubility of PVAc, PMA, poly(vinyl formate) (PVF), and PPO in CO_2 was determined and compared with previously published data for PLA [5]. The repeat unit structure of each of these non-fluorous homopolymers is presented in Fig. 1. Finally, the conditions needed to dissolve the most CO_2 soluble hydrocarbon-based homopolymer were compared to those needed to dissolve two expensive CO_2-soluble polymers, poly(fluoroalkyl acrylate) (PFA) and PDMS.

2. Experimental

2.1. Materials

PPO, PVAc ($M_w > 10,000$), and PMA ($M_w > 10,000$) were obtained from Aldrich Chemical Company. PVF,

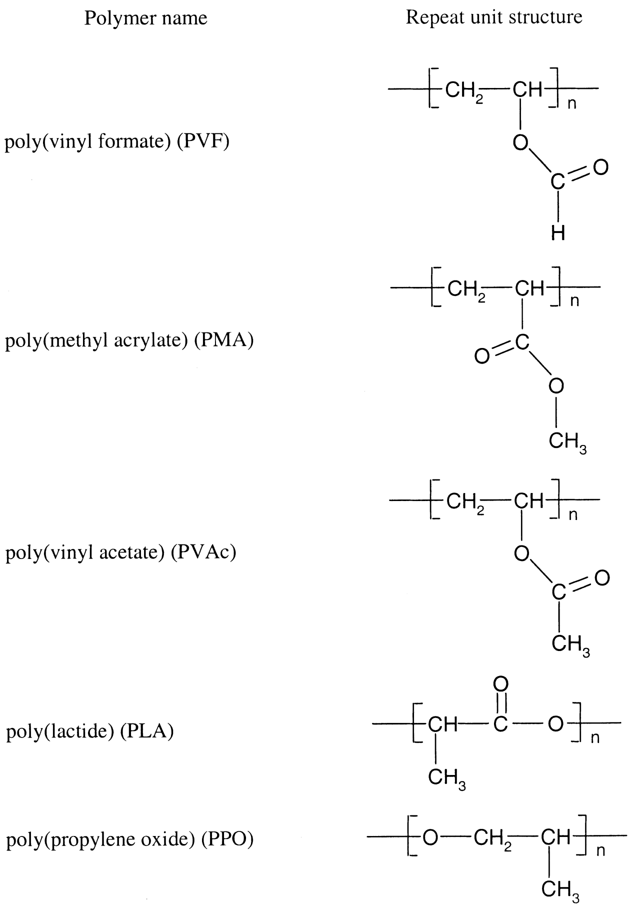

Fig. 1. Repeat unit structures of the non-fluorous polymers, poly(vinyl formate) (PVF), poly(methyl acrylate) (PMA), poly(vinyl acetate) (PVAc), poly(lactide) (PLA), and poly(propylene oxide) (PPO) used in this study.

PVAc ($M_w = 1700$), and PMA ($M_w = 1390$) were synthesized by Scientific Polymer Products. Low molecular weight PVAc ($4000 < M_w < 10,000$) and PMA ($M_w = 2850$) were synthesized at the University of Pittsburgh using vinyl acetate or methyl acrylate, methyl 2-bromopropionate, CuBr, 2,2′-bipyridine, CCl_4, $Fe(CH_3CO_2)_2$, and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMETA), and tetrahydrofuran (THF) obtained from Aldrich Chemical Company. The shortest PVAc oligomer ($M_w = 980$) was synthesized at the University of Pittsburgh using vinyl acetate, isopropanol, and di-*tert*-butylperoxide obtained from Aldrich Chemical Company. Methyl isobutyrate and dimethyl 2,4-dimethylglutarate, the monomer and dimer models of PMA, were obtained from Aldrich Chemical Company. Isopropyl acetate, which served as the monomer model of PVAc, was obtained from Aldrich Chemical Company.

Methylhydrosiloxane (16.5 mol%)–dimethylsiloxane (83.5 mol%) copolymer and platinum–vinyl tetramethyldisiloxane complex in xylene (low color) purchased from Gelest were used as received. Anhydrous toluene, allyl acetate, and methyl-3-butenoate were obtained from Aldrich Chemical Company and used without further purification.

2.2. Polymer synthesis

Atom transfer radical polymerization (ATRP) was employed to synthesize low molecular weight PVAc ($4000 < M_w < 10,000$) and PMA ($M_w = 2850$) following the general procedures described in literature [15]. In a typical experiment, the vinyl acetate monomer was combined with the carbon tetrachloride initiator, iron (II) acetate catalyst, and PMETA ligand in a monomer/initiator/catalyst/ligand molar ratio of R:1:1:2, where R was varied to alter the polymer chain length. For example, when $R = 30$ the resulting M_n of PVAc was 2060. The mixture was exposed to a freeze-thaw-pump cycle three times and then degassed for 10 min with nitrogen. The flask was placed in an oil bath maintained at 333 K for 12 h. The contents of the flask were poured through an alumina packed-column and subsequently washed twice with 100 ml of THF. Most of the THF was then removed using a rotovap and hexane was subsequently employed as an anti-solvent to precipitate the PVAc. The polymer was dried overnight in a vacuum oven. The PVAc yield was 40%.

The lowest molecular weight PVAc ($M_w = 980$) was synthesized following a recently described polymerization procedure [16].

Propyl acetate- and methyl butyrate-grafted methylhydrosiloxane–dimethylsiloxane copolymers were each prepared via a hydrosilylation reaction between the methylhydrosiloxane–dimethylsiloxane copolymer and the corresponding allyl compound according to the procedure described earlier [9], where only the methylhydro (CH_3–Si–H) groups can react with the allyl compound. The same starting copolymer (with the 16.5 mol% methylhydro group) was used for the preparation of each polymer. Periodically during the reaction, 0.5 ml of reaction solution was placed between NaCl crystal windows, and an FT-IR spectrum was taken on a Madison Instruments Inc. Research Series FT-IR. Reaction progress was monitored by observing the disappearance of the Si–H absorption at 2157 cm^{-1} to judge the point at which the hydrosilylation reaction had gone to completion.

2.3. Molecular weight determination

The molecular weight of each polymer synthesized in our laboratories (or not reported by the manufacturer) was determined using a Waters 150CV gel permeation chromatograph equipped with a refractive index detector. THF was used as the mobile phase at a flow rate of 1.0 ml/min and 308 K. Three columns in series were installed in the instrument to achieve sufficient separation for the molecular weight range of 500–30,000 Da. The first two columns, PL-gel Mixed-E columns from Polymer Laboratories, had mixed porosity. The third column, a Waters Ultrastyragel column, had a uniform pore size of 500 Å. A calibration curve, which plotted the log of the molecular weight versus the retention time, was constructed using 11 polystyrene standards in the molecular weight range of 580–66,000 Da.

2.4. Phase behavior procedures

Low pressure (<50 MPa) data were determined at the University of Pittsburgh. A known amount of the polymer and six stainless steel mixing balls were introduced to the sample volume to within ±0.001 g of a high pressure, windowed, variable-volume view cell (DB Robinson and Assoc., 3.18 cm ID, ~100 cm^3 working volume). After the sample volume was purged with carbon dioxide at 0.2 MPa, the volume of the cell was minimized. High pressure liquid carbon dioxide (295 K, 13.78 MPa) was then introduced to the sample volume as the silicone oil overburden fluid was withdrawn at the equivalent flow rate using a dual-proportioning positive displacement pump (Ruska, Inc.). This technique facilitated the isothermal, isobaric addition of a known volume of CO_2 to within ± 0.001 cm^3 into the sample volume. The mass of CO_2 was determined from the displaced volume, temperature, and pressure using an equation of state for carbon dioxide [17]. The polymer-CO_2 mixture was then compressed and mixed via rocking until a single, transparent phase was attained. Cloud-points were determined by slowly expanding the sample volume until it was no longer possible to see through the solution. Cloud points are reproduced two to three times to within approximately ±0.5 MPa, as measured with a Heise pressure gauge accurate to within ±0.07 MPa for data to 70 MPa, at each temperature held to within ±0.2 K, as measured with a type K thermocouple.

Cloud-point pressures greater than 50 MPa were determined at Virginia Commonwealth University. The apparatus and techniques used to obtain CO_2—polymer cloud-points are described elsewhere [18,19]. The main component of the apparatus was a high-pressure, variable-volume cell (Nitronic 50, 7.0 cm OD × 1.6 cm ID, ~30 cm^3 working volume). The cell was first loaded with a measured amount of polymer to within ±0.002 g. The cell was then flushed very slowly with gaseous CO_2, at pressures less than 0.3 MPa, to remove entrapped air. CO_2 was then transferred into the cell gravimetrically to within ±0.02 g using a high-pressure bomb. The mixture in the cell was viewed with a borescope (Olympus Corporation, model F100-024-000-55) placed against a sapphire window secured at one end of the cell. A stir bar activated by a magnet located below the cell mixed the contents of the cell. The cloud-point pressure was defined as the point at which the solution becomes so opaque that it is no longer possible to see the stir bar in solution. These cloud points have been compared in our laboratories to those obtained using a laser light set-up where the phase transition is the condition of 90% drop-off in light transmitted through the solution. Both methods gave identical results within the reproducibility of the data. Cloud points are reproduced two to three times to within approximately ±0.4 MPa, as measured with a digital pressure transducer (Viatran Corporation, Model 245, accurate to within ±0.35 MPa) for data to 300 MPa. The system temperature is held to within ±0.3 K, as measured with a type K thermocouple (Omega Corporation) calibrated in-house using a silicone oil bath and a thermometer (Fisher Scientific, catalog #15-000C) calibrated against NIST-traceable standards.

3. Results and discussion

PVAc. Isopropyl acetate served as the model of the PVAc monomer. The CO_2–isopropyl acetate binary exhibits Type I phase behavior. The bubble-point locus at 298 K decreases steadily from its maximum value at the vapor pressure of CO_2 to its minimum value at the vapor pressure of isopropyl acetate. Therefore, the vapor pressure of CO_2 is the maximum pressure bounding the two-phase region. For a longer oligomer of PVAc, Fig. 2 shows that the two-phase locus of PVAc–CO_2 mixtures exhibits a relatively flat profile over the 1–12 wt% region at 298 K with the cloud-point pressure maximum occurring near 5 wt% concentration. The cloud-point pressure increases with PVAc chain length. Table 1 presents the cloud-point pressure data at ~5 wt% concentration of these loci and other PVAc samples. Even the highest molecular weight PVAc ($M_w = 585{,}000$) is soluble in CO_2 at 298 K at a pressure of 67.6 MPa. The strength of the CO_2–acetate interactions is apparently great enough to overcome repeat group-repeat group interactions, and entropic effects associated with polymer conformation do not have a dramatic effect on the cloud-point pressure. The temperature-dependence of the cloud-point pressure is illustrated in Fig. 3 for two high molecular weight PVAc samples ($M_w = 125{,}000$ and 585,000). Not surprisingly, higher pressures are required for the dissolution of the higher molecular weight PVAc.

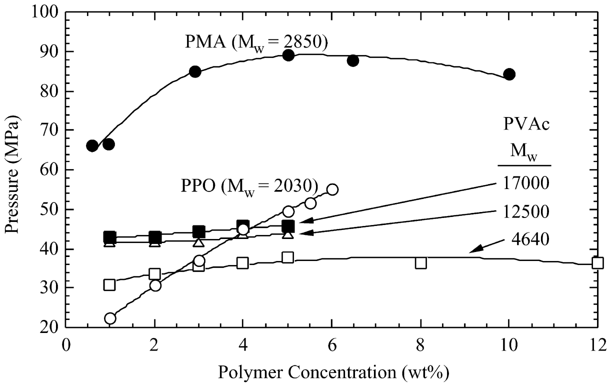

Fig. 2. Pressure-composition isotherms at 298 K for binary mixtures of carbon dioxide with poly(propylene oxide) (PPO—open circles), poly(methyl acrylate) (PMA—filled circles), and poly(vinyl acetate) (PVAc—filled squares, open triangles, and open squares). Molecular weights are given for each polymer in the figure. More physical property information is available in Table 1.

PVF. PVF was insoluble in CO_2 at temperatures up to 484 K and pressures up to 240 MPa. This result is consistent with the previous observations [3,20], which concluded that very polar or hydrogen bonded polymers do not dissolve in carbon dioxide. Formate will interact with itself more

Table 1

Molecular weight information, including number averaged molecular weight (M_n), weight averaged molecular weight (M_w), polydispersity (M_w/M_n), number of repeat units based on M_n ($N_{RU,n}$), and number of repeat units based on M_w ($N_{RU,w}$), for poly(methyl acrylate) (PMA), poly(vinyl acetate) (PVAc), poly(propylene oxide) (PPO), and poly(vinyl formate) (PVF) and cloud-point pressures (P_{cp}) for their binary mixtures with CO_2 at ~5 wt% and 298 K

Polymer	M_n	M_w	M_w/M_n	$N_{RU,n}$	$N_{RU,w}$	P_{cp} (MPa)
PMA	780	1390	1.78	9	16	34.6
	2080	2850	1.37	24	33	89.1
	10,600	30,700	2.90	123	357	225.0[a]
PVAc	780	980	1.25	9	11	13.6
	850	1700	2.00	10	20	20.8
	2060	4150	2.01	24	48	37.4
	3090	4640	1.5	36	54	37.6
	5680	8380	1.47	66	97	42.0
	7700	12,500	1.62	89	145	43.6
		12,800			149	45.7
	13,000	17,000	1.31	151	198	45.7
	52,700	124,800	2.37	612	1451	60.2[a]
		167,000			1941	62.5
	61,600	182,000	2.95	716	2116	63.7
	193,000	585,000	3.02	2244	6802	67.6
PPO	1640	2030	1.24	28	35	43.6
		3500			60	Insoluble
PVF	1070	2327	2.18	15	27	Insoluble

[a] Data from Ref. [3].

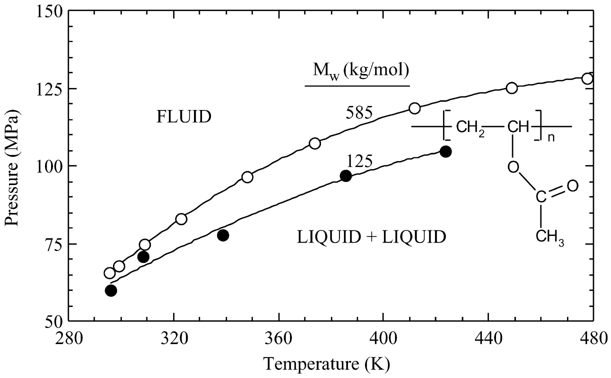

Fig. 3. Effect of polymer molecular weight on the cloud-point curves for ~5 wt% poly(vinyl acetate) (PVAc)–CO_2 mixtures. (Filled circles—data from Ref. [3]; open circles—data from this study.)

strongly than acetate, even though the formate proton is not highly acidic. Nonetheless, this interaction is much stronger than the CO_2–formate interaction, causing PVF to be CO_2-insoluble.

PPO. Table 1 shows that low molecular weight PPO ($M_w = 2030$) was soluble in CO_2 at 298 K, especially at low concentration. The result at 1 wt% is in very good agreement with previously reported solubility results at low concentrations [4,21]. The cloud-point pressure is strongly related to the polymer concentration at 298 K, increasing from 22 to 55 MPa as the PPO concentration increased from 1 to 6 wt%. PPO ($M_w = 3500$) could not dissolve in CO_2 at 298 K, but cloud-point pressure data were obtained at higher temperatures as seen in Fig. 4. Although the upper critical solution temperature (UCST) behavior of the CO_2–PPO ($M_w = 3500$) system inhibited miscibility at temperatures in the 298–322 K range, the cloud-point pressures decreased over the 323–343 K temperature range.

Low molecular weight PPO oligomers may be promising non-fluorous, CO_2-philic tails in the design of CO_2-soluble surfactants, dispersants, and chelating agents because these amphiphiles are typically used in dilute concentration. High molecular weight PVAc is more CO_2 soluble than PPO, even though the surface tension of PVAc, 36.5 mN/m, is greater than that of PPO, 31.5 mN/m. The relatively high solubility of PVAc in CO_2 may therefore be attributed to the acetate–CO_2 interaction being more favorable than the ether–CO_2 interaction associated with the PPO–CO_2 system.

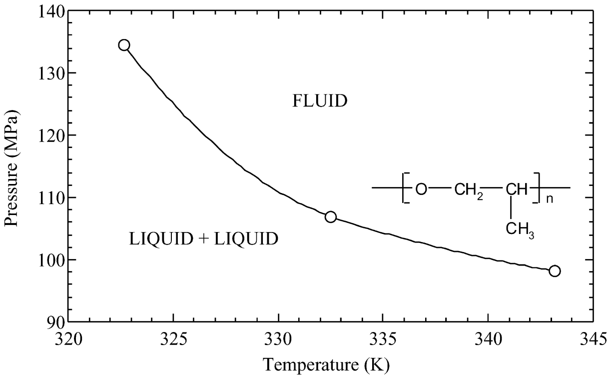

Fig. 4. Cloud-point curve for ~5 wt% poly(propylene oxide) (PPO, $M_w = 3500$)–CO_2 mixture.

PMA. The monomer and dimer results ($n = 1$ and 2) for PMA at 298 K were obtained by measuring the bubble-point pressures of methyl isobutyrate and dimethyl 2,4-dimethylglutarate in CO_2, respectively. These binaries exhibit Type I phase behavior. Therefore, the vapor pressure of CO_2 is the maximum pressure bounding the two-phase region at 298 K. The PMA oligomer ($M_w = 1390$) dissolves in CO_2 at 298 K and 34.6 MPa. A higher molecular weight PMA oligomer ($M_w = 2850$) dissolves in CO_2 at 298 K at a much higher pressure (see Table 1 and Fig. 2), and also remains CO_2-soluble at slightly higher pressures in the 298–323 K temperature range as shown in Fig. 5. The PMA isotherms exhibit a maximum value at about 5 wt% PMA at each temperature, which has been previously observed for other polymer–solvent mixtures [3,18,19,22–24]. PMA is also characterized by a steep increase in cloud-point pressure with increasing polymer chain length (see Table 1). PMA is much less soluble in CO_2 than PVAc even though the repeat groups for both polymers contain the same functional group that is slightly rearranged. Fig. 6 shows that the cloud-point pressure of PMA increases dramatically with molecular weight relative to PVAc. Note that the PMA carbonyl group is closer to the polymer backbone, while the PVAc carbonyl group can rotate more freely due to the ether linkage between the polymer backbone and the acetate. Therefore, the PVAc carbonyl group is more accessible to interact with CO_2. Further, the carbonyl functionality of PVAc is adjacent to a methyl group. Ab initio calculations suggest that a weak but cooperative bond between the hydrogen of the acetate methyl group and the oxygen of the CO_2, along with the stronger Lewis acid–Lewis base interaction of the carbonyl's oxygen and the carbon of CO_2 accounts for the effectiveness of acetylation in enhancing CO_2-philicity [10].

Two graft copolymers were synthesized to assess the influence of carbonyl accessibility and the CO_2-philicity of the acetate and acrylate groups on polymer solubility in CO_2. A 25-repeat unit silicone oligomer was

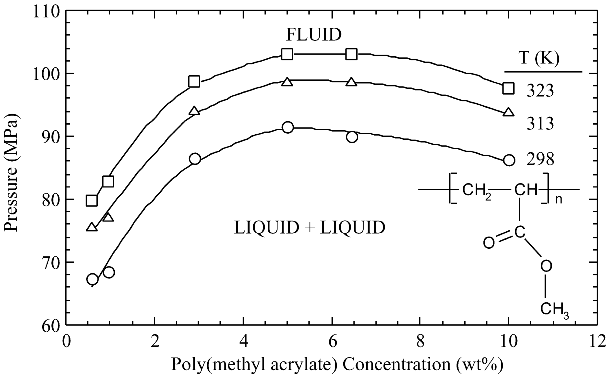

Fig. 5. Pressure-composition isotherms for the system CO_2—poly(methyl acrylate) (PMA) ($M_w = 2850$) at 298, 313, and 323 K.

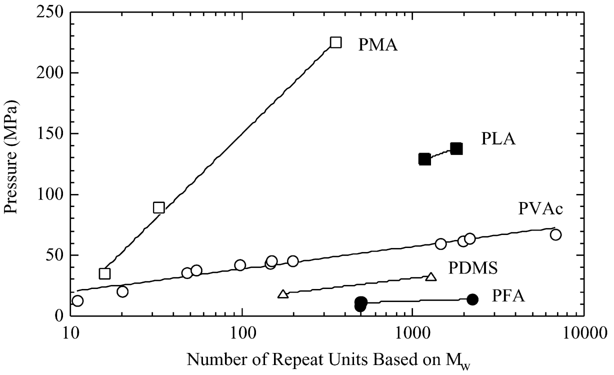

Fig. 6. Cloud-point pressures at ~5 wt% polymer concentration and 298 K for binary mixtures of CO_2 with poly(methyl acrylate) (PMA), poly(lactide) (PLA), poly(vinyl acetate) (PVAc), poly(dimethyl siloxane) (PDMS), and poly(fluoroalkyl acrylate) (PFA) as a function of number of repeat units based on M_w.

functionalized by adding five pendant acetate or acrylate groups separated from the polymer backbone by a linear propyl spacer as depicted in Fig. 7. Note that each of the copolymers was prepared from the same starting siloxane copolymer, and each hydrosilylation reaction was conducted to completion (see IR results in Fig. 8). Therefore, each resulting copolymer has the same graft density. Phase behavior results in Fig. 9 illustrate that the propyl acetate (analog to the PVAc side chain)-functionalized copolymer is slightly more CO_2 soluble than the methyl butyrate (analog to the PMA side chain)-functionalized PDMS. This indicates that the acetate functionality is more CO_2-philic than the methyl acrylate functionality. The difference between the cloud-point pressures shown in Fig. 9 is modest, however, relative to the substantial differences between those for PVAc and PMA shown in Fig. 6. The difference between the methyl acrylate–CO_2 and acetate–CO_2 interactions alone is unlikely to account for the low solubility of PMA relative to PVAc. Therefore, steric effects, which prevent the carbonyl of PMA from being easily accessed by the CO_2, are also responsible for the low solubility of PMA relative to PVAc.

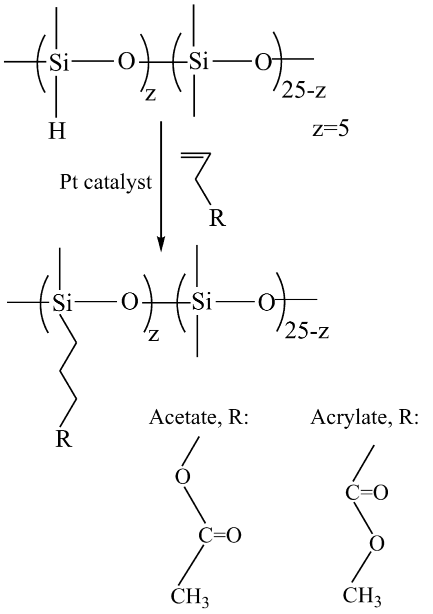

Fig. 7. Structures of the random copolymers of poly(dimethyl siloxane) (PDMS) side-functionalized with propyl acetate and methyl butyrate groups ($z = 5$) to establish effect of accessible acetate and acrylate groups, respectively.

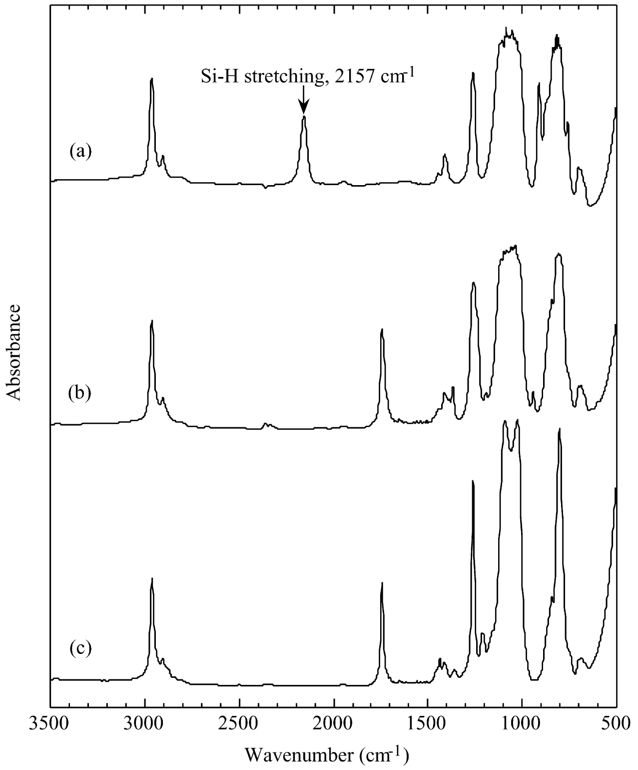

Fig. 8. Infrared (IR) spectrum for: (a) Methylhydrosiloxane (16.5 mol%)–dimethylsiloxane (83.5 mol%) copolymer; (b) Acetate-functionalized silicone copolymer; (c) Acrylate-functionalized silicone copolymer.

PLA. The solubility of PLA in CO_2, as shown in Fig. 6, has been determined previously [5]. PVAc is also more

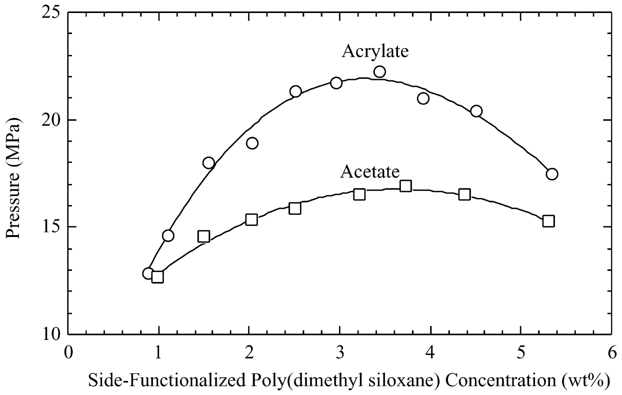

Fig. 9. Pressure-composition isotherms of siloxane random copolymers with pendant propyl acetate and methyl butyrate groups to establish effect of accessible acetate and acrylate groups, respectively, at 298 K.

soluble in CO_2 than PLA, even though the acetate side group of PVAc is similar in chemical composition to the repeat unit of PLA. PVAc is an amorphous polymer with a pendant acetate on each repeat unit, resulting in an entropic advantage for dissolution. However, PLA is a high melting point, crystalline polyester that is likely to exhibit enhanced polymer–polymer interactions that inhibit dissolution in dense CO_2.

PFA. Although PVAc is a promising non-fluorous, CO_2-soluble homopolymer, it is far less CO_2-philic than fluoroalkyl acrylate polymers. PFA typically has a linear side-chain terminated with a long fluorocarbon segment, such as poly(heptadecafluorodecyl acrylate), $-[CH_2\text{-}CHCOOC_2H_4C_8F_{17})_n-$. DeSimone pioneered the incorporation of fluoroalkyl acrylate into a homopolymer or copolymer to attain CO_2-solubility [25]. Fig. 6 shows that the cloud-point pressures of PFA [26–28] are significantly lower than those of PVAc. This difference in solubility in dense CO_2 at relatively low pressures has been exploited in PVAc–PFA copolymers, which have been used to facilitate the emulsion polymerization of vinyl acetate in CO_2 [29] because PVAc is CO_2-phobic relative to PFA at low pressures.

PDMS. The solubility of PDMS, $-[Si(CH_3)_2O]_n-$, in CO_2 has been previously reported at ~298 K [4,30]. Silicone homopolymers are also more CO_2-soluble than PVAc as seen in Fig. 6, although PDMS is not as CO_2-soluble as PFA.

4. Conclusions

PVAc is the most CO_2-soluble vinyl homopolymer composed solely of carbon, hydrogen, and oxygen identified to date, as reflected by the relatively low pressure required to attain dissolution of approximately 5 wt% polymer at 298 K. PVAc exhibits remarkable CO_2 solubility over a wide range of concentration (1–15 wt%) and molecular weight (11–6800 repeat units based on the weight averaged molecular weight) at 298 K and pressures ranging from 13.6 to 67.6 MPa. The highest molecular weight PVAc investigated ($M_w = 585{,}000$) exhibited an increase in cloud-point pressure from 68 to 130 MPa as temperature increased from 298 to 430 K. The CO_2-philic nature of this amorphous, low-melting point polymer was attributed to the accessibility of the acetate group for favorable interactions with the CO_2 solvent. Other carbonyl-rich polymers containing similar functional groups were significantly less soluble or insoluble in CO_2 due to their crystallinity, lack of side chains, or less accessible carbonyl groups. PVAc may serve as a non-fluorous, CO_2-philic tail of polymeric or amphiphilic compounds designed to exhibit CO_2 solubility. Copolymers containing vinyl acetate may even exhibit lower solubility than the PVAc homopolymer [8]. Despite the high degree of CO_2 miscibility attained with PVAc relative to other hydrocarbon homopolymers, PFA and PDMS are CO_2-soluble at markedly lower pressures.

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