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Influence of tert-amine groups on the solubility of polymers in CO_2

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ABSTRACT

There is a need to develop new, non-fluorous polymers that are highly soluble in CO_2. Experimental evidence indicates that tertiary amine and pyridine groups may exhibit favorable Lewis acid–Lewis base type interactions with CO_2. It is therefore reasonable to assume that incorporation of tertiary amines into the side chain or backbone of non-fluorous polymers may impart a degree of CO_2-solubility to the polymer. We present experimental results for eight different tert-amine-containing polymers. Of these polymers, only propyl dimethylamine-functionalized poly(dimethylsiloxane) is soluble in CO_2 at temperatures and pressures accessible in our experiments, but even this polymer is less soluble than non-functionalized poly(dimethylsiloxane) at the same chain length. We have performed *ab initio* calculations on tertiary amine-containing moieties representative of some of the polymers examined experimentally. Our calculations confirm that amine–CO_2 interactions are indeed energetically favorable. However, we also find that the moiety self-interactions are typically more favorable than the CO_2-moiety interactions. This indicates that the lack of solubility of amine-containing polymers in CO_2 is a direct result of strong polymer–polymer interactions.

1. Introduction

Polyfluoroacrylates and polyfluorophosphazines are among the most CO_2-soluble polymers that have been identified to date [1]. Perfluoropolyethers are also quite miscible with CO_2, although the cloud point pressures associated with these polymers increase dramatically as molecular weight increases above 10,000 [2]. Poly(dimethylsiloxane) (PDMS) has the highest solubility of any known non-fluorinated polymers [3–6]. Spectroscopic [7–10] and theoretical [11–13] investigations have provided insight related to the favorable thermodynamic interactions between dense CO_2 and the fluorinated and siloxane-based polymers. There is a general consensus that the ability of these polymers to dissolve in CO_2 is related to their low glass transition temperature, low cohesive energy density [14,15], and Lewis acid–Lewis base interactions between the polymers and CO_2 [3,16].

There has been recent interest in identifying hydrocarbon-based polymers that also exhibit solubility in CO_2 comparable to that of the fluorinated and siloxane-based polymers. Hydrocarbon-based polymers would likely have the advantages of being more environmentally benign and less expensive. Although no polymers composed solely of carbon and hydrogen were found to be remarkably CO_2-soluble, theoretical and experimental studies led to a handful of CO_2-soluble oxygenated hydrocarbon polymers being identified [14]. Enhanced solubility of these polymers in CO_2 was attributed to a specific interaction between the carbon atom of CO_2 and the lone pairs on the oxygen of a carbonyl group, in which CO_2 acts as a Lewis acid and the carbonyl group as a Lewis base [17]. This, in turn, led to studies [18–20] aimed at the inclusion of a carbonyl or acetate group in polymers to promote solubility in CO_2 [21–26]. Subsequently, Raveendran and Wallen's *ab initio* calculations indicated that a second interaction, a cooperative interaction between oxygen atoms of CO_2 and hydrogen atoms attached directly to the carbonyl carbon or the α-carbon atom [27], was responsible for the superior CO_2-philicity of carbonyl-based groups. Our group employed *ab initio* calculations to reveal that the carbon of CO_2 can interact to a comparable degree with the ether-like ester oxygen in the acetate group [6,14], confirming earlier reports that interactions of CO_2 with this oxygen could occur [28,29]. The occurrence of multiple binding sites in an amorphous polymer with a low glass transition temperature is thought to be responsible for poly(vinyl acetate) displaying a greater degree of solubility in CO_2 than any other high molecular weight oxygenated hydrocarbon [26]. We recently designed novel oligomers that dissolved in CO_2, including polyvinyl methoxymethylether and poly(3-acetoxyoxetane) [30] and also demonstrated that

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poly(1-O-(vinyloxy)ethyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside) (a polymer with pendant sugar acetate groups) and amorphous polylactic acid are CO_2-soluble over a wide range of molecular weight [31]. Nevertheless, poly(vinyl acetate) (PVAc) remains the most CO_2-soluble polymer composed solely of carbon, hydrogen and oxygen that has yet been identified. Unfortunately, the pressure required to dissolve ~5 wt% of PVAc in CO_2 at 298 K is on the order of 50–70 MPa [26], which is substantially higher than the pressure required to dissolve perfluoroacrylates or poly(dimethylsiloxane) (PDMS).

In an attempt to design other non-fluorous, non-silicone polymers that were soluble in CO_2, we considered moieties composed of atoms other than C, H, O, N, S and P while retaining the fundamental strategy of exploiting CO_2 behavior as a Lewis acid in the presence of a Lewis base [18,19,20,32]. While others have shown that trialkyl phosphate, trialkyl phosphite [33] and sulfonyls [27] may provide favorable interaction sites with CO_2, we focused our efforts on aminated polymers. We note in passing that despite the *ab initio* calculations by Raveendran and Wallen showing that the binding energy between CO_2 and the S=O sulfonyl group is much higher than that between CO_2 and the carbonyl group, we found that sulfonyl functionalized poly(propylene glycol) exhibits much poorer miscibility with CO_2 than the acetate-functionalized analogue [34].

Meredith et al. measured equilibrium constants by FT-IR spectroscopy for electron donor–acceptor interactions of CO_2 with three Lewis bases: triethylamine, pyridine, and tributyl phosphate [35]. Their FT-IR spectroscopy results indicated that tributyl phosphate exhibits the strongest interactions with CO_2—followed by pyridine and triethylamine. The authors stated that their density functional theory calculations, carried out to compare the relative stabilities and geometries of the CO_2–triethylamine and CO_2–pyridine complexes, also confirmed that CO_2 interacts more strongly with pyridine than with triethylamine. They concluded that steric repulsion of the ethyl groups in triethylamine causes the binding energy of the CO_2–triethylamine complex to be weaker than that of the CO_2–pyridine complex, whereas the planar structure of pyridine leads to less steric hindrance, allowing the nitrogen atom to be closer to the carbon of CO_2. The density functional theory formalism used by Meredith et al. to compute the CO_2–amine interactions [35] lacks an accurate description of electron correlation effects that give rise to van der Waals interactions [36], which are expected to dominate the CO_2–amine interaction; therefore the binding energies and perhaps even the geometries they report may be substantially in error. Furthermore, contrary to the results by Meredith et al., our *ab initio* calculations, reported in this paper, indicate that interactions between CO_2 and tert-amines are highly favorable—even stronger than CO_2–carbonyl interactions. Therefore, one might expect that the tert-amine moiety incorporated into a polymer would have favorable Lewis acid–Lewis base type interactions with CO_2, leading to miscibility of the tert-amine functionalized polymers with CO_2.

Another indication that the amine group might enhance the solubility of a polymer in CO_2 was associated with the electron donating capacity (donor number) of the compounds [37], which is a qualitative measure of Lewis basicity. Kachi et al. observed a linear relationship between electron donating capacity (donor number) of a molecule and the red-shift of the Raman bands of supercritical CO_2, and suggested that the extent of the shift of the CO_2 band can be used as a measure of CO_2-philicity of solutes in supercritical CO_2 [38]. According to the tabulated data, triethylamine has a donor number of DN = 61 (units of kcal/mol), which is very large compared to acetone (DN = 17), diethyl ether (DN = 19.2), ethyl acetate (DN = 17.1), methyl acetate (DN = 16.5), pyridine (DN = 33.1), and tributyl phosphate (DN = 23.7) [37,39]. It is important to note that unlike primary and secondary amines, tert-amines do not form carbamate salts with CO_2 in the absence of water [40]. While such reactions may be desirable for the formation of surfactants upon reaction with CO_2, our objective is the design of a polymer that dissolves in CO_2 *without* reacting with the CO_2. Therefore, we evaluated the CO_2-solubility of several (polyethyleneimines) composed of C, H, O and N. In addition to the requisite Lewis acid–Lewis base types of interactions likely to occur between poly(ethyleneimines) and CO_2, poly(ethyleneimine)s are reported to exhibit weak self-interactions and relatively low glass transition temperature [41], and have a surface tension comparable to that of PDMS. For example, poly(hexanoyliminoethylene) and PDMS have surface tension values of 23 and 21 mN/m at 293 K respectively [41], and glass transition temperatures of 283 K and 150 K, respectively, while fluoroacrylates have a glass transition temperature of 263 K and surface tension of 10 mN/m [41].

In summary, there are several indications that polymers containing tert-amines may show solubility in CO_2. In order to test this hypothesis, we measured the CO_2-solubility of seven hydrocarbon-based polymers possessing tert-amine groups either in the backbone or in the pendant chain. The hydrocarbon-based polymers we tested are listed in Table 1. We also carried out complementary quantum mechanical calculations that are used to explore the atomic-level interactions in model polymer/CO_2 systems. We note that quantum chemical calculations alone cannot provide a complete description of the CO_2-polymer system, but in this case it successfully explains our results where our design strategy fails.

2. Experimental procedure

The following section provides a description of the source or synthesis of the polymers investigated in this work.

2.1. Materials

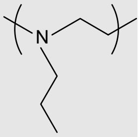
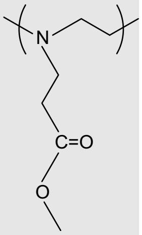
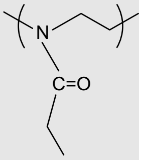
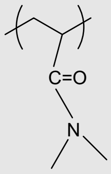
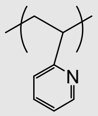
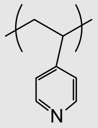
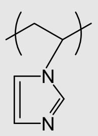
Linear poly(ethyleneimine) hydrochloric salt (Mn ≅ 2000) was a gift from Polymer Chemistry Innovations, Inc. N,N-dimethylacryl amide, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 99%), anhydrous toluene, 2,2′-azobis(isobutyronitrile) (AIBN, 98%) anhydrous 1 M BH_3. THF (tetrahydrofuran) complex and methyl acrylate were obtained from Aldrich. N,N-dimethylacrylamide was purified by distillation under reduced pressure, and AIBN was purified by crystallization from ethanol prior to use.

Poly(2-ethyl-2-oxazoline) (PEOX) with a number average molecular weight of 5000 (50 repeat units) was purchased from Scientific Polymer Products, Inc. Poly(4-vinyl pyridine) (P4VP) (Mn = 3000, PDI = 1.50), poly(2-vinyl pyridine) (P2VP) (Mn = 3000, PDI = 1.12), and poly(N-vinyl imidazole) (PVIZ) (Mn = 9500, PDI = 3.00) were purchased from Polymer Source, Inc. All materials were used as received.

2.2. Synthesis of poly(N,N-dimethylacrylamide) PDMAA

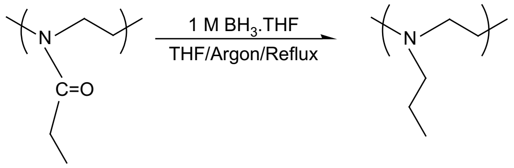
N,N-dimethylacrylamide was polymerized following a procedure given by Li and Brittain [42]. 0.50 g (3.04 mmol) AIBN and 0.47 g (3.01 mmol) TEMPO, such that [AIBN]/[TEMPO] = 1, were charged into a 250 ml round-bottomed, three-neck flask equipped with a condenser and argon feed. 25.0 g (0.25 mol) N,N-dimethylacrylamide and 100 ml anhydrous toluene were then added to the flask. The flask was then placed in an oil bath at 371 K. Initially, the solution exhibited the orange color of TEMPO, but the color disappeared in less than 30 min. After 14 h of polymerization, the product was precipitated into hexane. The polymer was re-dissolved in toluene and re-precipitated into hexane twice, followed by vacuum drying overnight. White, hygroscopic, polymer

Table 1
Structure of nitrogen-containing hydrocarbon-based polymers.

Name of the polymer	Structure
Poly(propylethyleneimine) (PPEI)	
Poly(propylmethylacrylate ethyleneimine) (PPMAEI)	
Poly(2-ethyl-2-oxazoline) (PEOX); precursor of PPEI	
Poly(N,N-dimethylacrylamide) (PDMAA)	
Poly(2-vinyl pyridine) (P2VP)	
Poly(4-vinyl pyridine) (P4VP)	
Poly(N-vinyl imidazole) (PVIZ)	

powder was recovered at 99% yield. The molecular weight of poly(N,N-dimethylacrylamide) was determined via gel permeation chromatography using toluene as eluent (Mn = 1298, Mw = 1672, PI = 1.29). ^{1}H NMR (300 MHz, C_6D_6): δ 2.7–2.9 (broad, 1H, –CH–CO–N–$(CH_3)_2$), δ 2.9–3.0 (broad, 6H, –N–$(CH_3)_2$), δ 1.5–1.9 (broad, 2H, –CH_2–CH–CO).

2.3. Synthesis of poly(propylethyleneimine) PPEI



Scheme 1. Synthetic route for preparation of poly(propylethylenimine).

Poly(propylethyleneimine) was synthesized via the reduction of poly(2-ethyl-2-oxazoline) by borane (Scheme 1). The glassware was oven-dried overnight and purged with ultra-high purity argon before use. 9.4 g of polymer was charged into a 500-ml three-neck, round-bottomed flask. The system was equipped with a magnetic stir-bar, a condenser, addition funnel, and an argon feed. 25 ml of anhydrous THF were added to completely dissolve the polymer. After dissolution, 430 ml 1 M $BH_3 \cdot THF$ complex (4.2 equivalent) were added to the flask drop-wise over 180 min. The solution temperature was raised to reflux, and the solution was stirred for 4 days. After cooling, the excess borane was eliminated by drop-wise addition of methanol until hydrogen gas ceased evolving. The THF/methanol mixture was evaporated under reduced pressure, and the sample was dissolved in 144 ml of methanol. An aqueous solution of HCl (6 N, 48 ml, 3 times excess) was added and to the sample and the solution heated to 338 K and stirred for 40 h. Upon cooling the green solution, NaOH aqueous solution (6 N, 50 ml) was added to neutralize the mixture. Methanol was removed with a rotary evaporator under reduced pressure, and water by azeotropic distillation with toluene. The salt was removed by filtration after re-dissolving the polymer in methanol. In the event that some salt remained dissolved in the residual water after azeotropic distillation with toluene, the methanol was removed, and the polymer was dissolved in chloroform. The solution was dried over $MgSO_4$. Upon removal of chloroform, a viscous, brown polymer was obtained (47% yield). Disappearance of the peak at 1647 cm^{-1} (corresponding to C=O stretching in poly(2-ethyl-2-oxazoline)) was a sign of complete reduction of the amide. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (broad, 3H, (–N–CH_2–CH_2–CH_3), δ 1.5 (broad, 4H, –N–CH_2–CH_2–CH_3), δ 2.3–2.5 (broad, 4H, N–CH_2).

2.4. Synthesis of poly(propylmethylacrylate ethyleneimine) PPMAEI

Poly(propylmethylacrylate ethyleneimine) was prepared via reaction of poly(ethyleneimine) with methyl acrylate (known as 'Michael addition' reaction) [43–45]. Prior to the reaction, poly(ethyleneimine) hydrochloric salt was first neutralized with aqueous NaOH solution. For this, 11.0 g poly(ethyleneimine) hydrochloric salt was allowed to dissolve in 60 ml water, then 5 g NaOH dissolved in 20 ml water was added slowly to the polymer solution until the pH of the solution was 8.0–8.5, as determined by pH paper. The solution was stirred overnight. Upon precipitation of the polymer into acetone (twice), a yellowish viscous, oily polymer precipitated at the bottom of the flask. In case some salt remained dissolved in the residual water, the polymer was dissolved in methanol and dried over K_2CO_3. Upon filtration, excess methanol was removed with a rotary evaporator as needed. The Michael addition reaction was then employed. The solution (~75 ml) was transferred to a 250-ml 3-neck, round bottom flask equipped with a condenser, and 18.5 g (0.22 mol) of methyl acrylate was then added. Initially, the solution was opaque and yellow in appearance, but after 72 h of stirring, the color turned to orange. After filtration, the solution was concentrated under vacuum to remove unreacted methyl acrylate and methanol. A very viscous, red-brownish polymer was obtained (92% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.5 (broad, 2H, –N–CH_2–CH_2),

δ 2.3–2.5 (broad, 4H, $-N-CH_2$), δ 2.5–2.9 (broad, 2H, $N-CH_2-CH_2-CO$), δ 3.7 (s, 3H, $CO-O-CH_3$).

2.5. *Synthesis of functional siloxane copolymers*

In addition to the seven hydrocarbon-based polymers containing tert-amine groups discussed above, dimethylsiloxane polymer was functionalized via the addition of acetate- or tert-amine-containing groups in order to assess the influence of these two CO_2-philic groups on the cloud point pressure of a highly CO_2-soluble siloxane polymer.

Propyl acetate (PA) and propyl dimethylamine (PDMA) functional siloxane copolymers were prepared according to the procedure described earlier [6].

2.6. *Phase behavior measurements*

Phase behavior measurements of the polymers were performed in the same way as described earlier [6]. Typical variability in the cloud point measurement is less than ±0.7 MPa.

3. Simulation methods

We used Møller–Plesset second order perturbation theory (MP2) and the 6-31 + G(d) basis set to perform geometry optimization calculations, as implemented within the Gaussian 03 suite of programs [46]. We have found that the MP2 level of theory gives results in fairly good agreement with coupled-cluster with single, double, and perturbative triple excitations calculations on similar systems [6]. A larger basis set, aug-cc-pVDZ, was used for single point energy calculations on the 6-31 + G(d) optimized structures. The counterpoise (CP) method [47] was used to correct for basis set superposition errors. We used the average of the CP-corrected and uncorrected energies to approximate the energy at complete basis set limit. This approach is less computationally expensive than basis set extrapolation and has been shown to be accurate in our previous calculations [6]. Feller and Jordan have also used this method for approximating complete basis set energies [48].

It is not currently feasible to carry out extensive MP2 calculations on molecules containing more than about 10 heavy atoms. We have therefore used three moderately sized tertiary amine molecules to approximate the interactions of CO_2 with poly(propylethyleneimine), poly(2-vinyl pyridine), and poly(4-vinyl pyridine). The representative molecules we have chosen are trimethylamine, 4-methyl pyridine, and 2-methyl pyridine; the structures of these molecules are shown in Fig. 1.

4. Results and discussion

Interactions of CO_2 with the functional groups in Fig. 1 have been computed, along with the self-interactions for each of the three moieties. These calculations alone are not capable of predicting the solubilities of polymers in CO_2 because self- and cross-interaction energies are only part of the picture. Entropic and cooperative effects must be considered within the framework of statistical mechanics. Thus, our quantum mechanical calculations can only serve as a guide to understanding solubility trends.

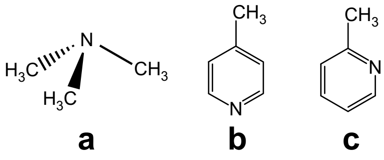


Fig. 1. Structures of three polymer moieties used in our *ab initio* calculations. (a) Trimethylamine, a surrogate for poly(propylethyleneimine). (b) 4-Methyl pyridine, a surrogate for poly(4-vinyl pyridine). (c) 2-Methyl pyridine, a surrogate for poly(2-vinyl pyridine).

Only one binding mode has been identified for the trimethylamine/CO_2 complex (see Fig. 2). The calculated interaction energy is −19 kJ/mol. To put this binding energy in context, we note that interaction of CO_2 with the carbonyl oxygen of isopropyl acetate (IPA) is −15.9 kJ/mol[16] and that IPA is a surrogate for poly(vinyl acetate), a polymer that has been identified as having the highest CO_2-solubility of any known oxygenated hydrocarbon polymer (a polymer containing only carbon, oxygen, and hydrogen) [16].

The results of the binding energy calculations for trimethylamine/CO_2 indicate that poly(propylethyleneimine) may be soluble in CO_2. However, one must also take into account the polymer–polymer interactions, which we approximate by computing the dimer energies for trimethylamine. We have found two binding modes for the trimethylamine dimer, which we identify as modes A and B. These modes are illustrated in Fig. 3.

The two binding modes both show strong self-interactions of −14.0 kJ/mol and −21.1 kJ/mol for configuration A and B, respectively. The interaction energy of binding mode B is stronger than the interaction energy between trimethylamine and CO_2. We also note that the existence of these two binding modes will sterically hinder the CO_2–trimethylamine interaction. Note that a third trimethylamine molecule can be added symmetrically to the molecule on the right side in the binding mode B and this will completely block the CO_2 binding site of the molecule on the left side. Hence, it is likely that the self-interactions among the amine side chains in poly(propylethyleneimine) will weaken their interactions with CO_2 molecules, in turn leading to reduced CO_2-solubility.

We have optimized the pyridine/CO_2 systems and have identified a single minimum for each of the pyridine structures. The binding modes are shown in Fig. 4. The interaction energies are computed to be −19.1 and −21.2 kJ/mol for 4-methyl pyridine/CO_2 and 2-methyl pyridine/CO_2, respectively. These energies are comparable to the interaction energy of trimethylamine/CO_2 complex and stronger than those of IPA/CO_2 system [14].

We have also investigated the self-interactions between two pyridine molecules. We have carried out calculations with dimers of the 4-methyl pyridine molecule. The dimer energies of the 2-methyl pyridine molecule are expected to be very similar to those for 4-methyl pyridine and so are not calculated here. Two optimized binding structures have been found for 4-methyl pyridine self-interaction (see Fig. 5), which we identify as modes A and B. The two pyridine rings are parallel to each other for mode A, and are perpendicular to each other for mode B. The binding energy for

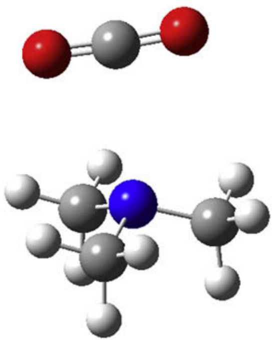


Fig. 2. Optimized binding structure for trimethylamine/CO_2 complex. Interaction energy = −19 kJ/mol.

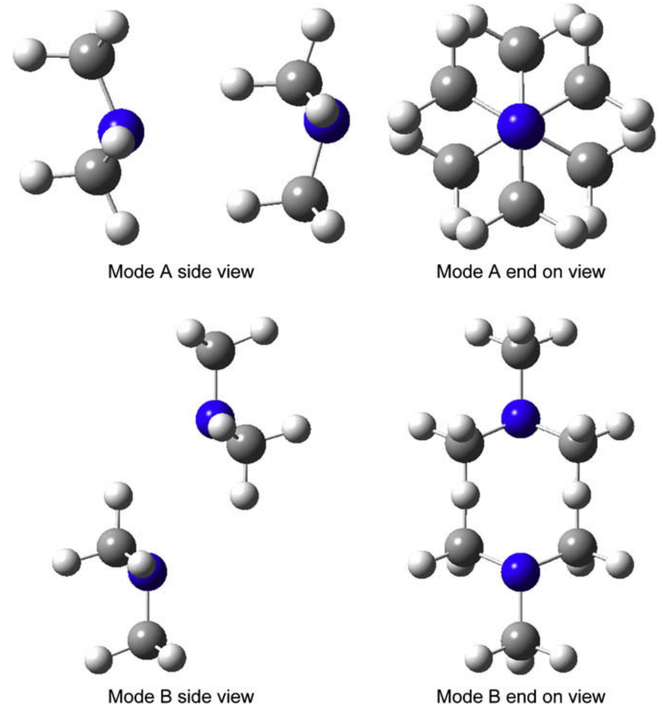


Fig. 3. Side views and end on views of two different optimized binding structures, denoted A and B, for the trimethylamine dimer. Binding mode A has an interaction energy of −14.0 kJ/mol; Binding mode B has an interaction energy of −21.1 kJ/mol.

the parallel ring configuration was calculated to be −42.8 kJ/mol. The interaction energy of the perpendicular ring configuration has a value of −18.1 kJ/mol.

Note that the perpendicular configuration has a binding energy that is comparable to the pyridine/CO_2 interaction energies, whereas the parallel structure binding is about a factor of two more strongly bound than the pyridine/CO_2 dimers. This result suggests that the polymer/polymer interactions are dominant over the polymer/CO_2 interactions. Hence, we would expect that polymers with pyridine-like side groups would not exhibit high solubility in CO_2, since the very strong polymer–polymer interactions would likely prohibit CO_2 from solubilizing the polymer.

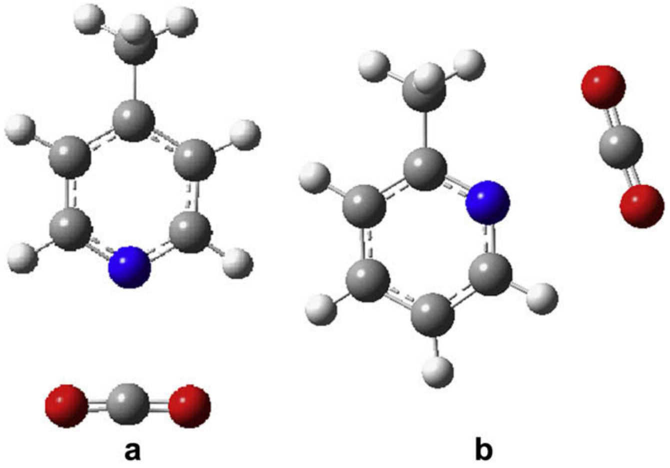


Fig. 4. Optimized binding structures for 4-methyl pyridine/CO_2 (a) and 2-methyl pyridine/CO_2 (b) systems. The interaction energies are −19.1 and −21.2 kJ/mol, respectively.

A summary of our *ab initio* calculation results for the interaction energies of the systems investigated is presented in Table 2.

We have evaluated CO_2-solubility of seven hydrocarbon-based polymers containing nitrogen, either in the backbone or in the side chain, (see Table 1 for structures) as well as that of propyl dimethyamine (PDMA) and propyl acetate (PA) functionalized siloxane polymers (see Fig. 7 for structures). We evaluated their solubility in CO_2 at conditions where CO_2 is a dense liquid at 295 K and in some cases at supercritical conditions.

We have tested the solubility of the three ethyleneimine polymers: poly(propylethyleneimine) (PPEI), poly(propylmethylacrylate ethyleneimine) (PPMAEI) and poly(2-ethyl-2-oxazoline) (PEOX). The number of repeat units for all these three polymers is about the same (∼47–50 repeat units). The structures of these polymers are shown in Table 1. None of these polymers were soluble in CO_2 at 295 K down to 1 wt% and pressures up to 45 MPa. The result for PPEI is consistent with our *ab initio* calculations summarized in Table 2, showing that trimethylamine self-interactions dominate over trimethylamine–CO_2 cross interactions. Moreover, only one binding mode was found for the CO_2/trimethylamine system shown in Fig. 2. This implies that even if the site is not blocked by amine self-interactions, only a single CO_2-amine bond per repeat unit is probably insufficient to induce solubility of the polymer. PPMAEI and PEOX have CO_2-philic acrylate and carbonyl side groups, respectively. We had postulated that these groups would induce CO_2-solubility of the polymers [14]. Unfortunately, even the addition of these groups failed to achieve any measurable solubility. The lack of solubility is not entirely unexpected for PPMAEI for two reasons. Firstly, an ethylene group separates the acrylate group from the backbone and we know that insertion of a methylene group between the backbone and the acetate group of poly(vinyl acetate), resulting in poly(allyl acetate), has a remarkable deleterious effect on miscibility of poly(allyl acetate) in CO_2 [14]. Secondly, the acrylate group is known to be much less effective than an acetate group at imparting CO_2-solubility from the comparison of poly(vinyl acetate) versus poly(methyl acrylate) [26]. For PEOX the lack of an oxygen atom between the backbone and the carbonyl group diminishes side chain rotational motion, and hence the free volume of the polymer, leading to less favorable interactions between CO_2 and the polymer side chain [6].

In order to test whether steric hindrance plays a role in the CO_2-solubility of tert-amine-containing polymers (the N is in the backbone of PPEI, PPMAEI, and PEOX), we measured the solubility of PDMAA in CO_2. PDMAA was synthesized with a mole cular weight of 1298 (13 repeat units). PDMAA, unfortunately, was found to be immiscible with CO_2 at pressures of 45 MPa and concentrations as low as 0.7 wt% at 295 K. The polymer was swollen to some degree by CO_2. This may be an indication for the formation of a polymeric network structure as a result of self-interactions between the polymer chains, with the CO_2 molecules having been encapsulated within, possibly via carbonyl–CO_2 and tert-amine–CO_2 interactions. Increasing the temperature to 353 K failed to produce a single phase solution. The immiscibility of PDMAA can be attributed to the very high cohesive energy density of the polymer (surface tension: ∼52 mN/m at 293 K) and very high T_g (362 K) [41], meaning that entropic and enthalpic factors favor immiscibility. Here again, Lewis acid–Lewis base interactions of CO_2 with the carbonyl or the tert-amine group were insufficient to overcome the self-interactions between polymer chains.

We hypothesized that the tert-amine group strengthens the Lewis basicity of the carbonyl group through its electron donor character, and thereby increases carbonyl CO_2-philicity while weakening its own CO_2-philicity. Indeed, our *ab initio* calculations for the natural bond order charge distributions of N,N-dimethyl

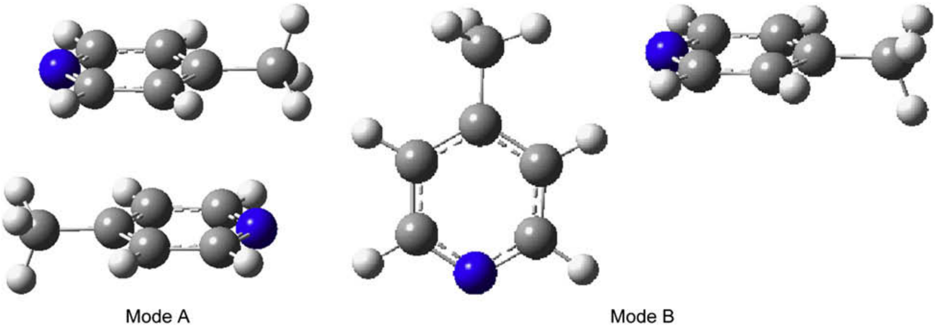


Fig. 5. Optimized binding structures for 4-methyl pyridine dimer. For mode A the interaction energy is −42.8 kJ/mol. For mode B the interaction energy is −18.1 kJ/mol.

acetamide support this hypothesis. The nitrogen atom is less electron rich, having a charge of −0.526 e, compared with −0.571 in trimethylamine. The oxygen atom in N,N-dimethyl acetamide is a stronger Lewis base (−0.616) compared with the carbonyl oxygen (−0.534) in methyl-isobutyl-ketone.

The polymers we have considered so far have all been tertiary amines. Meredith and coworkers[35] reported that interactions between CO_2 and triethylamine are not as favorable as between CO_2 and pyridine, because the ethyl groups in triethylamine sterically hinder the CO_2 molecule from getting as close to the nitrogen atom in triethylamine as in pyridine [35]. This observation was based on gas-phase density functional theory (DFT) calculations. The DFT calculations utilized the B3LYP generalized gradient approximation [49]. They reported that the C atom in CO_2 was 0.27 Å closer to the nitrogen in CO_2/pyridine than in CO_2/triethylamine. Moreover, they reported that the CO_2/pyridine complex was more strongly bound by 5.6 kJ/mol than the CO_2/triethylamine complex [35]. However, the calculations performed by Meredith et al. may be in error because DFT is known not to be accurate for weakly bound systems because the electron correlation treatment in B3LYP has the wrong long-range behavior, and therefore cannot capture the correct van der Waals dispersion interactions [36]. Hence, for supramolecular systems in which the binding is dominated by dispersive interactions, both the geometries and binding energies may be in error. Our *ab initio* calculations using the MP2 level of theory show that the interaction energy for CO_2/trimethylamine is about the same as that for CO_2/4-methyl pyridine, and only 2.2 kJ/mol less than the interaction between CO_2 and 2-methyl pyridine (see Table 2). We also have optimized the geometry and computed the binding energy for the CO_2/triethylamine system in order to compare with the DFT calculations of Meredith et al. [35]. We found that the carbon-nitrogen distance is only 0.012 Å larger for the CO_2–triethylamine complex (shown in Fig. 6) compared with the CO_2–4-methyl pyridine complex.

In further contrast to the DFT calculations of Meredith et al., the CO_2–triethylamine binding energy is −23.6 kJ/mol and is therefore slightly more favorable than that between CO_2 and either 4-methyl pyridine or 2-methyl pyridine. The slightly more favorable binding for the CO_2–triethylamine complex compared with the pyridines or the trimethylamine is likely due to van der Waals interactions between CO_2 and the adjacent ethylene groups. In other words, the primary Lewis acid–Lewis base interactions are about the same for all of these molecules and hence there is no evidence of steric hindrance decreasing the binding between CO_2 and triethylamine. The larger distance and weaker interaction energy Meredith et al. [35] observed is very likely an artifact of using DFT to compute the interaction energies. Our previous calculations indicate that B3LYP DFT can be even worse than Hartree–Fock theory (which lacks electron correlation) for computing binding energies between CO_2 and small molecules [6].

Our *ab initio* calculations for the CO_2/pyridine systems predict that self-interactions between the pyridine groups will dominate over the Lewis acid–Lewis base interactions between CO_2 and the nitrogen and therefore polymers that contain pyridine-like groups should not show high solubility in CO_2. In order to test this hypothesis we tested the solubilities of poly(2-vinyl pyridine) (P2VP), poly(4-vinyl pyridine) (P4VP) and poly(N-vinyl imidazole) (PVIZ) in CO_2. None of these polymers were found to be miscible with CO_2 at a temperature of 295 K and pressures up to 55 MPa and at concentrations down to 0.7 wt%. Elevated temperature (343 K) did not result in a single phase solution. The surface tensions of P2VP and P4VP were reported as 45 and 71.5 mN/m at 293 K, respectively [50]. Hence, the polymer–polymer interactions appear to be too strong for the polymer to be soluble in CO_2, in agreement with our *ab initio* calculations.

We have tested a total of seven polymers containing only the elements C, H, O, and N, with the nitrogen atoms forming tertiary amine groups either in the backbone or in the side chain. None of these polymers were found to be soluble in CO_2. In order to establish whether tert-amine groups increase or decrease the cloud point pressure of polymers known to be highly CO_2-soluble, we have functionalized the backbone of PDMS with PDMA (Fig. 7). We also synthesized propyl acetate (PA) functionalized PDMS to compare the CO_2-solubility of acetate-functionalized siloxane

Table 2
Summary of interaction energies for amine/CO_2 systems and amine self-interactions.

	System	Interaction energy (kJ/mol)
Trialkylamine	trimethylamine/CO_2	−19.0
	triethylamine/CO_2	−23.6
	trimethylamine self-interactions mode A	−14.0
	trimethylamine self-interactions mode B	−21.1
Cyclic amine	4-methyl pyridine/CO_2	−19.1
	2-methyl pyridine/CO_2	−21.2
	4-methyl pyridine self-interaction mode A	−42.8
	4-methyl pyridine self-interaction mode B	−18.1

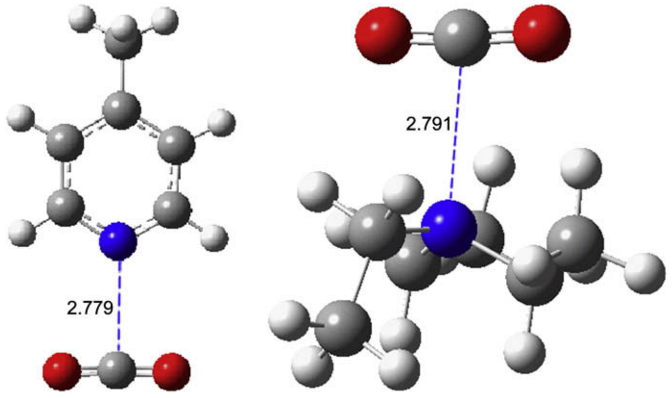


Fig. 6. The distances between the carbon and nitrogen atoms for CO_2–4-methyl pyridine and CO_2–triethylamine are 2.779 and 2.791 Å, respectively.

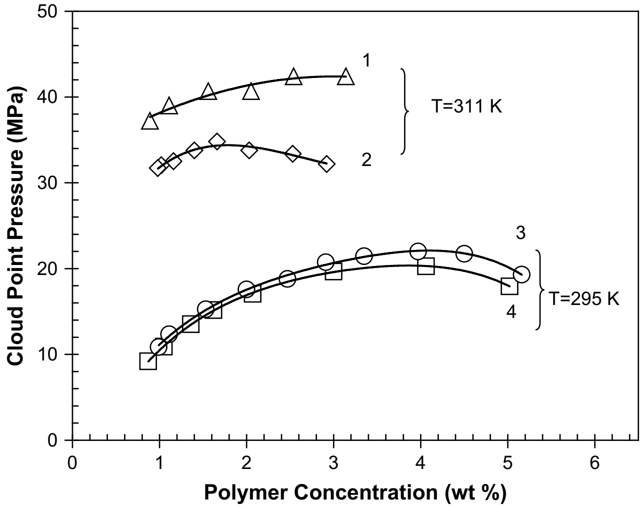


Fig. 8. Phase behavior of propyl dimethylamine (PDMA)-functional siloxane copolymers at different degrees of substitution and temperatures. 1) $z = 11$, $T = 311$ K, 2) $z = 5$, $T = 311$ K, 3) $z = 2$, $T = 295$ K, 4) $z = 1$, $T = 295$ K. The polymers with $z = 5$ or 11 did not dissolve in CO_2 at $T = 295$ K.

polymers with tert-amine-functionalized siloxane polymers, both having the same chain length, and the PA-functionalized PDMS having a slightly higher molecular weight at the same degree of substitution. We have previously shown that Lewis base functionalized (e.g., ether, ketone, carbonate, acetate, acrylate) siloxane polymers can be synthesized that have higher solubility in CO_2 than PDMS at their optimum substitution [6]. Typically, we found that an optimum degree of functionalization exists as a result of a balance between factors suppressing miscibility (increased molecular weight, increased cohesive energy density) and factors promoting miscibility (Lewis acid–Lewis base interactions, free volume, chain flexibility, configuration entropy, etc.) [6]. We therefore synthesized siloxane polymers functionalized with either PDMA or PA side chains, having varying degrees of functionalization, as shown in Fig. 7. The siloxane polymers have a total of 25 repeat units with the degree of substitution (z) varying from 1 to 25. Thus, we investigated the effect of varying amounts of PDMA and PA side chains on constant chain length siloxane polymers on CO_2-solubility. We have also examined the phase behavior of the non-functionalized polymer ($z = 0$). The phase behavior data for PDMA-functional siloxane polymers shown in Fig. 8 illustrate that $z = 1$ is the optimum degree of substitution, with $z = 2$ being very close to the $z = 1$ result. The $z = 5$ and $z = 11$ PDMA-functional copolymers were immiscible up to the pressure of 45 MPa at 295 K, but became miscible with CO_2 at a temperature of 311 K (Fig. 8). This implies that PDMA-functionalized siloxane becomes increasingly less CO_2-soluble with increasing degree of substitution. Moreover, these polymers exhibit UCST (upper critical solution temperature) behavior (the miscibility pressure shifts to lower values as the temperature increases). UCST behavior in turn implies that the heat of mixing is positive, $\Delta H_m > 0$, and that at high temperature the $T\Delta S_m$ term becomes large enough for the Gibbs free energy of mixing to become negative, $\Delta G_m = \Delta H_m - T\Delta S_m$. The positive heat of mixing, arising from strong polymer–polymer interactions, is consistent with our *ab initio* calculations showing strong self-interactions between the trimethylamine moieties (Table 2). We note that the fully PDMA-functional siloxane polymer ($z = 25$) was immiscible with CO_2 at 295 K and 311 K at pressures lower than 45 MPa.

Our previous experimental work identified the optimum degree of substitution for PA-functionalized siloxane as $z = 5$ [6]. We plot the cloud point pressures for the optimum PDMA ($z = 1$) and PA ($z = 5$) substituted siloxanes in Fig. 9. The cloud point curve for the PDMA-functional siloxane polymer lies above that for the PA-functional siloxane polymer, even though the latter has a larger molecular weight, due to the higher degree of substitution of the

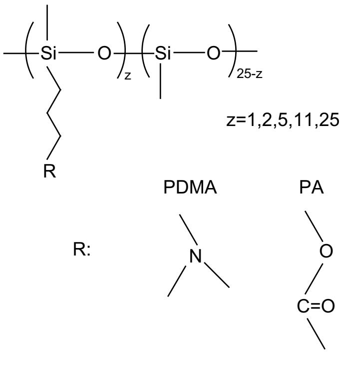


Fig. 7. Structure of propyl dimethylamine (PDMA)- and propyl acetate (PA)-functionalized siloxane copolymers.

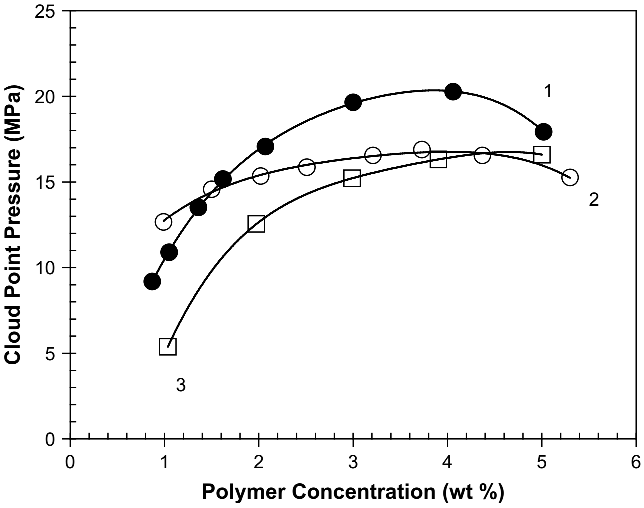


Fig. 9. Comparison of phase behavior of propyl dimethylamine-functional (PDMA) and propyl acetate (PA)-functional siloxane copolymers at their optimum number of substitution with the PDMS base polymer at 295 K. 1) ($z = 1$) Propyl dimethylamine-functional (PDMA), 2) ($z = 5$) propyl acetate (PA)-functional siloxane copolymers, 3) ($z = 0$) PDMS base polymer.

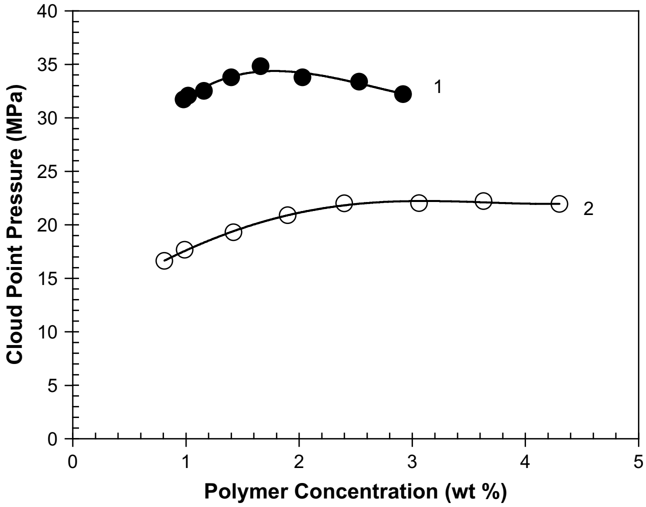


Fig. 10. Comparison of phase behavior of ($z = 5$)-functional siloxane copolymers at 311 K, 1) propyl dimethylamine (PDMA) 2) propyl acetate (PA).

acetates. Also, the PDMA- and PA-functional polymers are miscible at higher pressures than the PDMS base polymer ($z = 0$), especially at low polymer concentrations. These results lend credence to the hypothesis that the self-interactions between functional groups in the side chains have a larger impact on the miscibility of polymers with CO_2 than the CO_2–polymer cross interactions. The crossover in miscibility pressures between PDMA and PA substituted siloxanes seen in Fig. 9 at about 1.5 wt% is due to the increased importance of molecular weight at low concentrations, where polymer self-interactions are mitigated.

We now compare the change in cloud point pressures as a function of temperature for ($z = 5$) PDMA-functional and the ($z = 5$) PA-functional siloxane copolymers. The cloud point curves for the ($z = 5$) PA-functional siloxane copolymers at 295 K and 311 K are plotted in Figs. 9 and 10, respectively. We note that the cloud point curve for the PA-functional PDMS is shifted to higher pressures at 311 K, indicating LCST (lower critical solution temperature) behavior. This implies that $\Delta H_m < 0$ and becomes less negative with increasing temperature. The decrease in solubility (increase in cloud point pressure) with increasing temperature is a result of a decrease in the density of CO_2 as one goes from a liquid (295 K) to a supercritical fluid (311 K, pressure > 7.4 MPa).

The cloud point curves at 311 K for both PDMA- and PA-functionalized polymers, both with $z = 5$, are plotted in Fig. 10. We see that the PA-functionalized siloxane has significantly lower miscibility pressures than PDMA-functionalized siloxane at the same degree of substitution and about the same molecular weight.

These results of the modified PDMS oligomers confirm the findings associated with the insolubility of the aminated hydrocarbon polymers; despite the favorable thermodynamic Lewis acid–Lewis base interactions between CO_2 and tertiary amine or pyridine groups, amine–amine self-interactions are responsible for *diminished* CO_2-solubility of amine-containing hydrocarbon polymers relative the oxygenated hydrocarbon polymer PVAc.

5. Conclusions

In an attempt to identify a Lewis base group capable of inducing CO_2-solubility to a hydrocarbon-based polymer, seven hydrocarbon-based polymers possessing tertiary amine groups either in the backbone or in the pendant chain were designed. All of the polymers were insoluble in CO_2 despite the highly "CO_2-philic" nature of the tert-amine group. We also carried out complementary quantum mechanical calculations to explain the results at an atomic-level. Although our *ab initio* calculations suggest that CO_2–amine interactions are even stronger than CO_2–carbonyl interactions (known to promote the CO_2-solubility of oxygen-rich polymers such as polyvinyl acetate), tert-amine groups do not impart any CO_2-solubility to the polymers. The calculations reveal that self-interactions between the amine moieties are energetically more favorable than the CO_2-moiety interactions. Hence, dominance of polymer-polymer self-interactions over polymer–CO_2 cross interactions is most likely responsible for the tert-amine group not imparting solubility to the hydrocarbon-based polymers. Phase behavior of PDMA-functional siloxane polymers also demonstrated that inclusion of tert-amine moieties in the polymer increases the cohesive energy density of PDMS polymers (even more than does the acetate moiety), resulting in the diminished solubility of tert-aminated PDMS in CO_2.

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