Correlation of Cloud Points in CO_2 + Fluorinated Polymer Systems[†]

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We demonstrate the application of a compressible lattice model to the correlation of cloud point behavior in CO_2 + fluorinated polymer systems. The model uses two adjustable parameters that are temperature, pressure, and molecular weight independent and is able to correlate cloud point behavior within experimental uncertainty (AAD of ~2 %). We infer from the values of the parameters obtained that weak complexes exist in these systems, and these complexes have an appreciable effect on cloud point behavior. However, the model cannot separate the effects of complex formation from free volume effects since the enthalpy of association apparently follows the same trends as the free volume of the polymer in these systems.

Introduction

It is well-known that some polymers are soluble in supercritical CO_2, and this solubility can be exploited in the processing of such polymers.[1,2] However, most polymers exhibit only very limited solubility in CO_2 unless very high pressures are applied. This has led to significant interest in synthesizing polymers that contain CO_2-philic functional groups.[3,4] It has been suggested that these functional groups interact with CO_2 via an acid−base mechanism since CO_2 acts as a Lewis acid in the presence of Bronsted and Lewis bases.[5−8] This has been demonstrated by Kazarian et al.[9] in the case of interactions between CO_2 and the C═O oxygen in the backbone of polymers such as PMMA. Weak acid−base interactions between CO_2 and the lone pair of electrons in fluorine in a C−F bond have also been proposed to account for the solubility of fluoropolymers[10−12] in CO_2. However, quantitative estimates of the strength of these interactions in fluorinated polymers are still lacking. Not surprisingly, thermodynamic models such as the Flory−Huggins equation or the Sanchez−Lacombe equation of state do not explicitly account for these weak interactions.[13,14] This can sometimes lead to poor predictions of phase equilibria in systems containing fluorinated polymers.[15]

Recently, we have proposed a compressible lattice model that is able to correlate cloud points and sorption equilibria in CO_2 + polymer systems when the polymer incorporates carbonyl functional groups.[16,17] The model contains two parameters that do not depend on temperature or molecular weight, and furthermore, we have shown that it is possible to obtain one of the parameters from independent measurements (such as FTIR spectra). This has allowed us to predict CO_2 sorption in carbonyl polymers using a single parameter obtained from high-pressure cloud point data.[17] In the present study, we apply the model to systems containing fluorinated polymers to infer the existence of specific interactions in these systems and the role that such interactions might play in phase equilibria in these systems. Ultimately, we hope to quantify the interactions between CO_2 and polymers containing CF_2 groups and relate this information to phase equilibria and other macroscopic properties.

Compressible Lattice Model for Solutions

The model is based on lattice theory and accounts explicitly for complex formation between a polymer segment A and μ molecules of solvent B according to the reaction

$$A + \mu B \Leftrightarrow A...B_{\mu} \qquad (1)$$

Furthermore, the solution is assumed to consist of polymer−solvent complexes, unassociated solvent molecules, and unassociated polymer molecules. The formation of complexes restricts a certain number of solvent molecules to specific positions on the lattice, with the remaining solvent molecules being distributed randomly. The entropy of mixing $\Delta_{\text{mix}}S$ for such a formulation has been calculated by Sukhadia et al.[18] and is given by

$$\frac{\Delta_{\text{mix}}S}{nR} = -\frac{\phi_2}{\xi}\ln\phi_2 - \left(\frac{1-\phi_2(1+\mu\alpha)}{(1+\mu\alpha)}\right)\ln\{1-\phi_2(1+\mu\alpha)\} + \phi_1\ln\frac{\phi_1}{\phi_1-\mu\alpha\phi_2} - \mu\alpha\phi_2\ln\frac{\mu\alpha\phi_2}{\phi_1-\mu\alpha\phi_2} - \phi_2(1-\alpha)\ln(1-\alpha) - \alpha\phi_2\ln\alpha \qquad (2)$$

where ϕ_1 and ϕ_2 are the volume fractions of CO_2 and polymer; n is the total number of moles; μ is the solvent−solute binding ratio; α is the association ratio; and ξ represents the number of segments in a polymer molecule. For each polymer chain, there are $\alpha\xi$ associated segments and $(1-\alpha)\xi$ unassociated segments. The associated segments have $(z - 2 - \mu)$ neighbors of the unbound solvent, and unassociated segments have $(z - 2)$ neighbors of the unbound solvent (z is the lattice coordination number and is generally assumed to be equal to 10). The enthalpy change of mixing can be calculated by multiplying the number of associated and unassociated contacts with their energies. Thus

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[†] Part of the "Sir John S. Rowlinson Festschrift".

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10.1021/je100565h © 2010 American Chemical Society
Published on Web 08/25/2010

$$\Delta_{\mathrm{mix}}H = \alpha\mu\phi_2\chi_{\mathrm{a}} + \phi_2\{1 - \phi_2(1 + \alpha\mu)\}[(z - 2 - \mu)\alpha + (1 - \alpha)(z - 2)]\chi_{\mathrm{u}} \quad (3)$$

where χ_{a} is the interaction parameter for association and χ_{u} is the interaction parameter for dispersion. The Gibbs free energy of mixing is then given by

$$\begin{aligned}\frac{\Delta_{\mathrm{mix}}G}{nRT} = {} & \alpha\mu\phi_2\chi_{\mathrm{a}} + \phi_2\{1 - \phi_2(1 + \alpha\mu)\} \times [(z - 2 - \mu)\alpha + (1 - \alpha)(z - 2)]\chi_{\mathrm{u}} \\ & + \frac{\phi_2}{\xi}\ln\phi_2 + \left(\frac{1 - \phi_2(1 + \mu\alpha)}{(1 + \mu\alpha)}\right) \times \ln\{1 - \phi_2(1 + \mu\alpha)\} - \phi_1\ln\frac{\phi_1}{\phi_1 - \mu\alpha\phi_2} \\ & + \mu\alpha\phi_2\ln\frac{\mu\alpha\phi_2}{\phi_1 - \mu\alpha\phi_2} + \phi_2(1 - \alpha)\ln(1 - \alpha) + \alpha\phi_2\ln\alpha\end{aligned} \quad (4)$$

where R is the gas constant; T is the temperature; and the other symbols have been described previously. There are five characteristic quantities in this expression: χ_{a}, χ_{u}, μ, α, and ξ. Two of these quantities take on constant values in the systems of interest in this work. Thus, the binding ratio μ assumes a value of 1 because only one CO_2 molecule is able to associate with a functional group in the polymer segment. The dispersion parameter χ_{u} also has a constant value in a particular CO_2 + polymer system because χ_{u} is estimated from the solubility parameter δ_1 of CO_2 and δ_2 of the homomorph as follows

$$\chi_{\mathrm{u}} = \frac{V_1(\delta_1 - \delta_2)^2}{RT(z - \mu\alpha - 2)} \quad (5)$$

where the functional group in the polymer molecule which interacts with CO_2 is substituted with a nonpolar group to obtain the homomorph. In eq 5, V_1 is the molar volume of CO_2, and the other quantities have been defined previously.

The remaining three quantities (χ_{a}, α, and ξ) can be expressed in terms of independently measurable quantities. The interaction parameter χ_{a} is related to the enthalpy of association ΔH_{a} via

$$\chi_{\mathrm{a}} = \frac{\Delta H_{\mathrm{a}}}{RT} \quad (6)$$

In turn, ΔH_{a} can be expressed in terms of the equilibrium constant K for the binding reaction (eq 1) via

$$\ln\frac{K}{K_0} = \frac{-\Delta H_{\mathrm{a}}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \quad (7)$$

where K_0 is the equilibrium constant for association at a reference temperature T_0 (280 K in this work). In the above expression, ΔH_{a} has been assumed to be independent of T over the range of temperatures of interest. The equilibrium constant K is related to the association ratio α or the fraction of associated segments per molecule, as follows

$$\alpha = \frac{(1 + K) - \sqrt{(1 + K)^2 - 4\phi_1\phi_2K(1 + K)}}{2\phi_2(1 + K)} \quad (8)$$

χ_{a} and α can therefore be replaced by ΔH_{a} and K_0 in the model.

The segment number ξ is related to the ratio of molar volumes of the polymer and the solvent at ambient conditions in the Flory–Huggins theory.[13] However, to account for the compressibility of the lattice, Ozkan and Teja[16] allowed the segment number to vary with temperature and pressure. In their model

$$\xi = \frac{V_2[T, P]}{V_1[T, P]} \quad (9)$$

where V_2 is the volume of the polymer and V_1 is the molar volume of CO_2. Equation 9 implies that the entropy of mixing changes with temperature and pressure, or the number of possible lattice configurations changes with the temperature and pressure to allow for flexibility of the polymer chain. The use of eq 9 allowed Ozkan and Teja to calculate both cloud point and sorption behavior using the same set of parameters. However, agreement with experiment was only qualitative when sorption behavior was predicted using parameters obtained from cloud point data. Further, the model failed to correlate CO_2 + fluoropolymer phase behavior.

In our previous work,[17] we have modified eq 9 to account for the dependence of the entropy of mixing (and therefore the segment number) on the free volume as follows

$$\xi = \frac{V_2[T, P] - 1.2V_2^{\mathrm{vdW}}}{V_1[T, P] - V_1^{\mathrm{vdW}}} \quad (10)$$

where V_1^{vdW} is the van der Waals volume of CO_2 and V_2^{vdW} that of the polymer. In our work, we were able to correlate both cloud point behavior and sorption behavior of CO_2 + carbonyl polymer systems using one adjustable parameter (K_0) and one parameter obtained from FTIR measurements (ΔH_{a}). In the present work, we extend the model to the calculation of phase behavior in CO_2 + fluorinated polymer systems.

Cloud Point Calculations

For equilibrium between two phases l and h we may write

$$[a_i(\phi_i, T, P)]^{(l)} = [a_i(\phi_i, T, P)]^{(h)} \quad (11)$$

where a_i is the activity of component i in the phase indicated by the superscript. The activity depends on the temperature, pressure, and composition as indicated by the variables in the brackets. For convenience, we have chosen the standard state of each component to be the same in both phases. These two equations (with $i = 1$ or 2) may be solved for any two of the quantities T, P, $\phi_2^{(l)}$, and $\phi_2^{(h)}$ if the other two quantities are known. Therefore, given the polymer composition in one of the phases at any temperature, we can calculate the corresponding cloud point pressure and concentration in the other phase by solving eq 11 with $i = 1$ and 2. Cloud point curves at constant concentration (isopleths) can also be calculated by repeating the calculations at different temperatures. In the results discussed below, the activities were obtained by differentiation of eq 4 to obtain

$$\begin{aligned}\ln a_1 = {} & \beta\phi_2\chi_a + \phi_2[(-\phi_2\beta + \phi_2(1+\alpha))(z-3) - \\ & \beta(1-\phi_2(1+\alpha))]\chi_u - \frac{\phi_2}{\xi} + \\ & \left(\frac{1}{1+\alpha} - \frac{\beta}{(1+\alpha)^2}\right)\ln(1-\phi_2(1+\alpha)) + \\ & \left(\frac{1-\phi_2(1+\alpha)}{(1+\alpha)}\right)\left(\frac{1-\beta\phi_2}{1-\phi_2(1+\alpha)} - 1\right) - \ln\left(\frac{\phi_1}{\phi_1-\alpha\phi_2}\right) - \\ & 1 + \phi_1\left(\frac{1-\beta\phi_2}{\phi_1-\alpha\phi_2}\right) + \beta\phi_2\ln\frac{\alpha\phi_2}{\phi_1-\alpha\phi_2} + \\ & \alpha\phi_2\left(\frac{\beta}{\alpha} - \frac{1-\beta\phi_2}{\phi_1-\alpha\phi_2}\right) + \beta\phi_2\ln\frac{\alpha}{1-\alpha}\end{aligned} \qquad (13)$$

with

$$\beta = \frac{\alpha(K+1) - K}{(2\alpha\phi_2 - 1)(1+K)} \qquad (14)$$

Molar volumes V_2 of the polymers of interest were calculated using the group contribution modified cell model of Sato et al.[19] CO_2 volumes V_1 were obtained using the Patel−Teja equation of state.[20]

Results

CO_2 + Poly(alkyl methacrylate) (PAMA) and CO_2 + Poly(fluoroalkyl methacrylate) (PFAMA) Systems. We have calculated cloud point curves in CO_2 + poly(alkyl methacrylate) (PAMA) systems which contain a C═O group in each segment, with the corresponding cloud point curves in CO_2 + poly(fluoroalkyl methacrylates) (PFAMA) which contain both C═O and CF_2 groups in each segment. Table 1 presents the results of our calculations for three CO_2 + PAMA systems (CO_2 + PHMA, CO_2 + POMA, and CO_2 + PDMA with the alkyl side chain containing 6, 8, or 10 carbon atoms), as well as for the corresponding CO_2 + PFAMA systems (CO_2 + PFHMA, CO_2 + PFOMA, and CO_2 + PFDMA). Experimental data are from McHugh et al.[21] We have listed the two fitted parameters that we obtained for each system in Table 1 together with average absolute deviations (AAD) between calculated and experimental cloud points. AADs were generally less than 2.4 % which is probably within experimental uncertainty in these systems. As mentioned previously, we have shown elsewhere[17] that it is possible to obtain one of these parameters from FTIR measurements. However, such measurements were not available for the systems studied in the present work. The two parameters were found to change monotonically with the number of carbon atoms in the side chain in both the PAMA and PFAMA systems. Thus, K_o increased with the number of carbon atoms in the side chain in the PAMA systems (PHMA > POMA > PDMA) and decreased with the number of carbon atoms in the corresponding PFAMA systems (PFHMA < PFOMA < PFDMA). Note however that K_0 values were larger in PFAMA systems than in PAMA systems, indicating that a larger number of PFAMA molecules form complexes with CO_2 than is the case for PAMA molecules. Nevertheless, the magnitude of K_0 and hence the number of complexes was very small in all these systems. This also suggests that the contribution from association is probably very small in these systems, which agrees with McHugh et al.[21] who concluded that dispersive interactions dominate in CO_2 + PAMA systems. The enthalpy of interaction ΔH_a is about the same in both types of systems (approximately $-6\ \mathrm{kJ \cdot mol^{-1}}$ in PFAMA systems and about $-7\ \mathrm{kJ \cdot mol^{-1}}$ in the PAMA systems), which suggests that complex formation is predominantly with the C═O group in both PAMA and PFAMA systems.

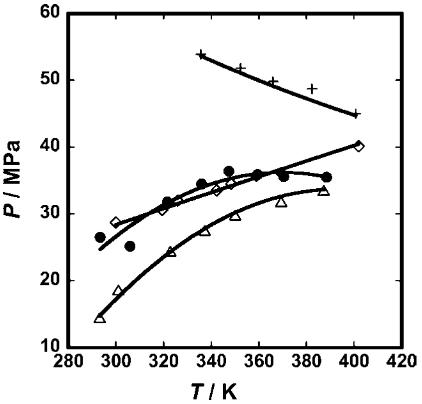

Figure 1. Cloud point behavior of CO_2 + PFMIT$_m$ systems. Experimental data of Li et al.[22] for systems in which +, $m = 3$; ●, $m = 5$; △, $m = 7$; and ◇, $m = 9$. Solid lines represent calculations for polymer $w \sim 0.01$ and $M_W \sim 150\,000$.

CO_2 + Poly(perfluoro monoitaconate) (PFMIT) and CO_2 + Poly(perfluoro diitaconate) (PFDIT) Systems. We have also correlated the phase behavior in CO_2 + poly(perfluoro monoitaconate) (PFMIT) and CO_2 + poly(perfluoro diitaconate) (PFDIT) systems to investigate the effect of chain branching (both the length and number of branches) on polymer solubility. We will use PFMIT$_m$ to represent poly(di-1*H*,1*H*,2*H*,2*H*-perfluoro monoitaconate) in which *m* represents the number of CF_2 groups in the single fluorinated alkyl side chain. Also PFDIT$_m$ will be used to denote poly(di-1H,1*H*,2*H*,2*H*-perfluoro diitaconate) in which there are *m* CF_2 groups in both fluorinated alkyl side chains. Figure 1 and Table 2 present the results of our calculations of cloud point curves in CO_2 + PFMIT$_3$, CO_2 + PFMIT$_5$, CO_2 + PFMIT$_7$, and CO_2 + PFMIT$_9$. Figure 2 and Table 3 present corresponding results for the CO_2 + PFDIT systems. The average molecular weights of the polymers in these studies[22] was about 150 000 $\mathrm{g \cdot mol^{-1}}$. We see that the model is able to correlate data in these systems with an AAD of about 2 % which is probably within experimental uncertainty. The addition of CF_2 groups to the side chain leads to an increase in the polymer free volume and reduces the entropic mismatch between supercritical CO_2 and the polymer. Furthermore, polymer−polymer interactions become weaker as the dipole

Table 1. Cloud Point Calculations in CO_2 + Poly(alkyl methacrylate) (PAMA) and CO_2 + Poly(fluoroalkyl methacrylate) (PFAMA) Systems

polymer	M_W / $\mathrm{g \cdot mol^{-1}}$	K_0	$-\Delta H_a$ / $\mathrm{kJ \cdot mol^{-1}}$	AAD %
PHMA poly(hexyl methacrylate)	230 000	0.058	6.9	2.4
POMA poly(octyl methacrylate)	163 000	0.026	7.3	1.3
PDMA poly(decyl methacrylate)	157 000	0.017	7.6	0.2
PFHMA poly(1*H*,1*H*,2*H*,2*H*-tetrahydroperfluorohexyl methacrylate)	200 000	0.139	6.0	0.5
PFOMA poly(1*H*, 1*H*, 2*H*, 2*H*-tetrahydroperfluorooctyl methacrylate)	292 000	0.156	6.0	1.0
PFDMA poly(1*H*,1*H*,2*H*,2*H*-tetrahydroperfluorodecyl methacrylate)	196 000	0.161	6.0	0.8

Table 2. Cloud Point Calculations in CO_2 + Poly(di-1*H*,1*H*,2*H*,2*H*-perfluoro monoitaconate) $PFMIT_m$ Systems[a]

polymer	$-\Delta H_\mathrm{a}$ / $\mathrm{kJ \cdot mol^{-1}}$	K_0	AAD %
$PFMIT_3$	8.6	0.026	2.1
$PFMIT_5$	7.9	0.060	0.9
$PFMIT_7$	7.9	0.0875	1.4
$PFMIT_9$	8.1	0.043	1.0

[a] *m* represents the number of CF_2 groups in the single fluorinated alkyl side chain.

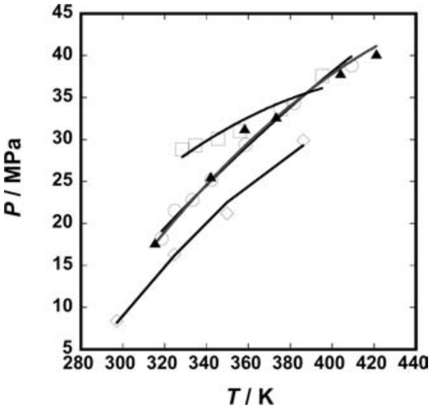

Figure 2. Cloud point behavior of CO_2 + $PFDIT_m$ systems. Experimental data of Li et al.[22] for systems in which □, $m = 3$; ▼, $m = 5$; ○, $m = 7$; and ◇, $m = 9$. Solid lines represent model calculations for polymer $w \sim 0.01$ and $M_W \sim 150\,000$.

Table 3. Cloud Point Calculations in CO_2 + Poly(di-1*H*,1*H*,2*H*,2*H*-perfluoro diitaconate) $PFDIT_m$ Systems[a]

system	$-\Delta H_\mathrm{a}$ / $\mathrm{kJ \cdot mol^{-1}}$	K_0	AAD %
$PFDIT_3$	7.8	0.056	1.4
$PFDIT_5$	7.8	0.058	2.3
$PFDIT_7$	7.9	0.064	2.6
$PFDIT_9$	7.2	0.138	2.2

[a] *m* represents the number of CF_2 groups in both fluorinated alkyl side chains.

moment of the ester groups is distributed over larger volumes.[23] Hence, the pressures required to form a single phase decrease with increasing side chain length. As seen in Figure 2, this trend holds up to a side chain length of 7 for PFMITs. Further addition of CF_2 groups adversely affects complex formation (K_o drops for $PFMIT_9$), and there is a corresponding increase in pressure required to form a single phase. Therefore, there is an optimum side-chain length for PFMITs although no such optimum exists for the PFDITs in the range of side-chain lengths investigated here. Addition of CF_2 groups aids complex formation as indicated by increasing K_0 in the order $PFMIT_3 < PFMIT_5 < PFMIT_7 < PFMIT_9$. It is possible that above a certain chain length shielding of the functional group in the polymer by the alkyl chain or competition between individual F atoms leads to decreasing interaction with CO_2.

Figure 3 shows that higher pressures are required to dissolve $PFMIT_9$ in CO_2 than to dissolve $PFDIT_9$. Note that K_0 for $PFDIT_9$ (= 0.138) is significantly larger than K_0 for $PFMIT_9$ (= 0.043) which implies that increasing the number of branches in the polymer backbone favors interaction with CO_2, as branching increases the free volume of the polymer and makes it more accessible to CO_2. Also, branching reduces interactions between polymer segments due to short-range molecular orientation offered by a high content of linear segments without pendant groups.

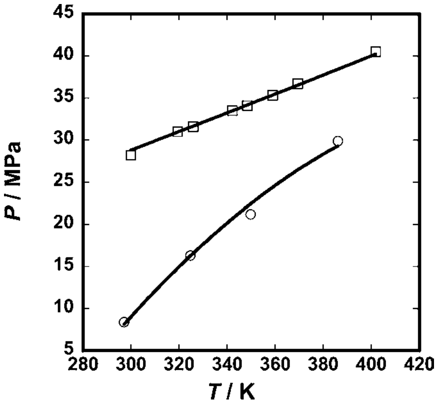

Figure 3. Cloud point behavior in CO_2 + $PFMIT_9$ and CO_2 + $PFDIT_9$. Experimental data from Li et al.[22] for □, CO_2 + $PFMIT_9$ and ○, CO_2 + $PFDIT_9$. Solid lines represent model calculations for polymer $w \sim 0.01$ and $M_W \sim 150\,000$.

Most of the CO_2 + poly(fluoroalkyl itaconates) systems exhibit a positive slope with respect to temperature. The only exception is the $PFMIT_3$ chain which has the lowest amount of complex formation of all the systems studied. This is a strong indicator that phase equilibria in these systems are affected by specific interactions between CO_2 and functional groups in the polymer segments.

Conclusions

We have demonstrated that the compressible lattice model is able to correlate cloud point behavior in CO_2 + fluorinated polymer systems within experimental error (AAD of ∼2 %) using two adjustable parameters. The calculations suggest that weak complexes exist in these systems, although the number of complexes formed is probably very small. Phase equilibria in these systems are affected by association (as indicated by nonzero values of $-\Delta H_\mathrm{a}$ and K_0), as well as the free volume of the polymer. The enthalpy of association ($-\Delta H_\mathrm{a}$) increases with increasing side chain length and with greater polymer free volume but is not significantly affected by the location of the interacting group in either the side chain or the main chain. Even when the enthalpy of association is significant, the extent of complex formation may be small due to limited accessibility of the interacting group (since K_0 values increase with increasing branching).

Acknowledgment

This paper is dedicated to Professor John Rowlinson, who served as the PhD advisor of one of the authors (AST). Professor Rowlinson's writings have greatly influenced this work as well as the author's research over the past forty years.

Literature Cited

(1) Cooper, A. I. Polymer synthesis and processing using supercritical carbon dioxide. *J. Mater. Chem.* **2000**, *10*, 207–34.
(2) Tomasko, D. L.; Li, H.; Liu, D.; Han, X.; Wingert, M. J.; Lee, J.; Koelling, K. W. A review of CO_2 applications in the processing of polymers. *Ind. Eng. Chem. Res.* **2003**, *42*, 6431–56.
(3) Sarbu, T.; Styranec, T. J.; Beckman, E. J. Design and synthesis of low cost, sustainable CO_2-philes. *Ind. Eng. Chem. Res.* **2000**, *39*, 4678–83.
(4) Drohman, C.; Beckman, E. J. Phase behavior of polymers containing ether groups in carbon dioxide. *J. Supercrit. Fluids* **2002**, *22*, 103–10.
(5) Dobrowolski, J. C.; Jamroz, M. H. Infrared evidence for carbon dioxide electron donor-acceptor complexes. *J. Mol. Struct.* **1992**, *275*, 211–19.

(6) Shieh, Y.; Liu, K.-H. Solubility of CO_2 in glassy PMMA and PS over a wide pressure range: the effect of carbonyl groups. *J. Polym. Res.* **2002**, *9*, 107–13.

(7) Raveendran, P.; Wallen, S. L. Cooperative C−H···O hydrogen bonding in CO_2-lewis base complexes: implications for solvation in supercritical CO_2. *J. Am. Chem. Soc.* **2002**, *124*, 12590–99.

(8) Fowkes, F. M.; Tischler, D. O.; Wolfe, J. A.; Lannigan, L. A.; Ademu-John, C. M.; Halliwell, M. J. Acid-base complexes of polymers. *J. Polym. Sci., Part A: Polym. Chem.* **1984**, *22*, 547–66.

(9) Kazarian, S. G.; Vincent, M. F.; Bright, F. V.; Liotta, C. L.; Eckert, C. A. Specific intermolecular interaction of carbon dioxide with polymers. *J. Am. Chem. Soc.* **1996**, *118*, 1729–36.

(10) Yonker, C. R.; Palmer, B. J. Investigation of CO_2/Fluorine interactions through the intermolecular effects on the ^{1}H and ^{19}F shielding of CH_3F and CHF_3 at various temperatures and pressures. *J. Phys. Chem. A* **2001**, *105*, 308–14.

(11) Dardin, A.; DeSimone, J. M.; Samulski, E. T. Fluorocarbons dissolved in supercritical carbon dioxide. NMR Evidence for specific solute-solvent interactions. *J. Phys. Chem. B* **1998**, *102*, 1775–80.

(12) Raveendran, P.; Wallen, S. L. Exploring CO_2-philicity: effects of stepwise fluorination. *J. Phys. Chem. B* **2003**, *107*, 1473–77.

(13) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(14) Sanchez, I.; Lacombe, R. Statistical thermodynamics of polymer solutions. *Macromolecules* **1978**, *11*, 1145–56.

(15) Kiszka, M. B.; Meilchen, M. A.; McHugh, M. A. Modeling high-pressure gas-polymer mixtures using the Sanchez-Lacombe equation of state. *J. Appl. Polym. Sci.* **1988**, *36*, 583–97.

(16) Ozkan, I.; Teja, A. S. Phase equilibria in systems with specific CO_2 - polymer interactions. *Fluid Phase Equilib.* **2005**, *228−229*, 487–91.

(17) Kasturirangan, A.; Grant, C.; Teja, A. S. Compressible lattice model for phase equilibria in CO_2 + polymer systems. *Ind. Eng. Chem. Res.* **2008**, *47*, 645–649.

(18) Sukhadia, T. Ph.D. Dissertation, Georgia Institute of Technology, Atlanta, GA, 1999.

(19) Sato, Y.; Hashigucji, H.; Takishima, S.; Masuoka, H. Prediction of PVT properties of polymer melts with a new group-contribution equation of state. *Fluid Phase Equilib.* **1998**, *144*, 427–40.

(20) Patel, N. C.; Teja, A. S. A new cubic equation of state for fluids and fluid mixtures. *Chem. Eng. Sci.* **1982**, *37*, 463–468.

(21) McHugh, M. A.; Garach-Domech, A.; Park, I.; Li, D.; Barbu, E.; Graham, P.; Tsibouklis, J. Impact of fluorination and side chain length on poly methyl propenoxy alkyl siloxane and poly alkyl methacrylate solubility in supercritical carbon dioxide. *Macromolecules* **2002**, *35*, 6479–82.

(22) Li, D.; Shen, Z.; McHugh, M. A.; Tsibouklis, J.; Barbu, E. Solubility of poly(perfluoromonoitaconates) and poly(perfluorodiitaconates) in supercritical CO_2. *Ind. Eng. Chem. Res.* **2003**, *42*, 6499–6504.

(23) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1986.

Received for review May 27, 2010. Accepted August 12, 2010.

JE100565H