

# Solubility of Homopolymers and Copolymers in Carbon Dioxide

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The cloud points of various amorphous polyether, polyacrylate, and polysiloxane homopolymers, and a variety of commercially available block copolymers, were measured in CO<sub>2</sub> at temperatures from 25 to 65 °C and pressures of ca. 1000–6000 psia. Almost without exception, the solubility of amorphous polymers increases with a decrease in the cohesive energy density, or likewise, the surface tension of the polymer. With this decrease in surface tension, the polymer cohesive energy density becomes closer to that of CO<sub>2</sub>. Consequently, solubility is governed primarily by polymer–polymer interactions, while polymer–CO<sub>2</sub> interactions play a secondary role. The solubility is strongly dependent upon molecular weight for the less CO<sub>2</sub>-philic polymers. The solubilities of high-molecular-weight poly(fluoroalkoxyphosphazenes) in CO<sub>2</sub> were comparable to those of poly(1,1-dihydroperfluorooctylacrylate), one of the most CO<sub>2</sub>-soluble polymers known.

## Introduction

Supercritical or near-critical fluids, especially CO<sub>2</sub>, may be used as environmentally benign substitutes for organic solvents. A unique feature of these fluids is the ability to tune the solvent strength by varying pressure and/or temperature. CO<sub>2</sub>-based solvents offer new opportunities in chemical manufacturing involving polymer processing,<sup>1,2</sup> heterogeneous reactions including polymerization<sup>3–5</sup> protein chemistry,<sup>6,7</sup> complexation of organic acids<sup>8</sup> and heavy metals,<sup>9</sup> and separations processes including cleaning and purification. A knowledge of phase behavior of polymers in supercritical fluids is emerging primarily from studies of solvents such as ethylene and light hydrocarbons.<sup>1,10–15</sup> Systems with an upper-critical-solution temperature (UCST), lower-critical-solution temperature (LCST), and both an UCST and LCST either as distinct or merged curves have been analyzed in terms of the polymer structure and interactions with the supercritical fluid.

Polymers in general have very limited solubility in supercritical fluid (SF) CO<sub>2</sub> at temperatures below 80 °C,<sup>1,16–22</sup> although solubilities can increase significantly at higher temperatures.<sup>1,23,24</sup> Therefore, oligomers rather than polymers are examined for many of the systems in this study. Efforts are underway to relate the solubility of amorphous polymers in CO<sub>2</sub> to polymer structure and the relevant physical and chemical interactions. To date, little is known about the relative contributions to solubility from the van der Waals interactions, polar interactions, particularly quadrupole–dipole and quadrupole–quadrupole interactions, and Lewis acid–base interactions for various classes of polymers. For crystalline polymers with high melting points, solubility in CO<sub>2</sub> at near ambient temperatures may be expected to be very small, unless CO<sub>2</sub> produces a large depression in the melting point. For low-molecular-weight crystalline solutes, these depressions are typically less than 50 °C.<sup>1</sup>

According to lattice fluid theory, three primary factors which affect solubility of amorphous polymers in CO<sub>2</sub> include the following: solute–solute (2–2) interactions, solute–solvent (1–2) interactions, and solvent–solvent interactions (1–1).<sup>25</sup> Experimental cloud point curves have been modeled quantitatively with this theory for poly(dimethylsiloxane) in CO<sub>2</sub> for temperatures down to 30 °C.<sup>22</sup> A difference in characteristic pressures,  $P_i^*$ s (cohesive energy densities) for these interactions, which is equivalent to the Flory  $\chi$  parameter, may be expressed as  $\Delta P_{12}^* = P_1^* + P_2^* - 2P_{12}^*$ . It is often assumed that the unlike pair size and energy of solute–solvent interactions are simply the geometric mean of the pure component interactions, with the result  $\Delta P_{12}^* = [(P_1^*)^{1/2} - (P_2^*)^{1/2}]^2$ , where  $(P_i^*)^{1/2}$  is the solubility parameter of component  $i$ . With this assumption, solubilities increase as the difference between the solubility parameters decreases. We wish to determine if this type of model describes the trends in solubilities for various classes of polymers in CO<sub>2</sub>. If so, this would provide useful insight into polymer solubility, and help explain why solubilities are so low in CO<sub>2</sub>.

Carbon dioxide and ethane are poor solvents for water and for nonvolatile lipophilic compounds. Thus, either hydrophilic or lipophilic phases (which may both be considered to be CO<sub>2</sub>-phobic) may be dispersed in a supercritical fluid continuous phase in the form of micelles, microemulsions, and emulsions. The design of a suitable polymeric surfactant for these heterogeneous systems in CO<sub>2</sub> is challenging as relatively little is known about the fundamental nature of solvation and solubility of polymers in CO<sub>2</sub>.

In the first studies of organized molecular assemblies in supercritical fluids, thermodynamically stable micelles and microemulsions were formed in supercritical fluids such as ethane and propane, as reviewed elsewhere.<sup>26,27</sup> It is unclear how differently ethane and CO<sub>2</sub> behave as solvents for surfactant tails, although ethane

is a better solvent for sodium di-2-ethylhexyl sulfosuccinate. The solubility of more than 130 commercial surfactants, including homopolymers and block copolymers, in CO<sub>2</sub> have been measured.<sup>28</sup> Many surfactants are insoluble or only slightly soluble in CO<sub>2</sub> because they were designed for aqueous or organic continuous phases. Fluoroethers, fluoroalkanes, fluoroacrylates, and siloxanes are considerably more soluble than hydrocarbons.<sup>1,16–21</sup> For example, it was shown that a ionic hybrid fluorocarbon/hydrocarbon surfactant can dissolve 32 mol of water/mol of surfactant.<sup>29</sup> Recently, we demonstrated with several spectroscopic techniques that microemulsion droplets with “bulk-like” water properties may be formed in CO<sub>2</sub> with a relatively nontoxic ammonium carboxylate perfluoroether surfactant.<sup>6,30</sup>

The objectives of this work were to extend the currently sparse database for polymer cloud points in CO<sub>2</sub> at temperatures below 75 °C and to use the database to determine if trends in polymer solubility can be described in terms of polymer cohesive energy density, that is polymer–polymer interactions. Due to polydispersity, the cloud point is only an approximate measure of the solubility, but this approximation will be shown to be accurate enough to test our hypothesis for the trends in solubility. A key step was to identify a pure component polymer parameter, in our case the surface tension, to describe the strength of the polymer–polymer interactions. We chose to focus on the solubility of an array of nonionic, nonfluorinated homopolymers and block copolymers in CO<sub>2</sub> including various polyethers, polyacrylates, and polysiloxanes to complement earlier studies of fluorinated polymers.<sup>17,21,23</sup> The cloud points of various block copolymers of various molecular weights, block ratios, and molecular structures were measured. For the polydisperse polymers studied, the cloud point is only an approximate measure of the solubility, but in a companion paper, we present a lattice fluid hydrogen bonding (LFHB) model to predict the details of the phase behavior of homopolymers and block copolymers composed of poly(ethylene oxides) and poly(propylene oxides).<sup>31</sup>

## Review of Solvation in CO<sub>2</sub>

We begin with a summary of the properties of CO<sub>2</sub>. In previous studies, we have emphasized that the most useful single property to describe the solvent strength of CO<sub>2</sub> (with regard to solubility behavior) is the polarizability/volume.<sup>32–35</sup> The molecular polarizability, a constant for a molecule, divided by the molar volume is a measure of the number and strength of van der Waals interactions in a given volume. This function has been compared for several fluids versus pressure.<sup>33</sup> The van der Waals forces for CO<sub>2</sub> are considerably weaker than those of ethane and ethylene and are more like those of fluoroform. Consequently, the energy interaction parameters between nonpolar aromatic or aliphatic hydrocarbons and CO<sub>2</sub> may be expected to be weaker than those for ethylene. This behavior had been shown earlier for the solutes naphthalene, hexamethylbenzene, fluorene, anthracene, phenanthrene, and pyrene.<sup>36</sup>

The thermodynamic calculation of the solubility parameter of a pure fluid, as a function of the enthalpy and molar volume at a given temperature and pressure, is rigorous and requires no assumptions.<sup>37</sup> The solubility parameters,  $\delta$ 's, of ethane, propane, and CO<sub>2</sub> have been compared.<sup>34</sup> The  $\delta$  of CO<sub>2</sub> is the largest of the three and approaches that of hexane. However, the

solubilities of polymers considered in this study are extremely different in CO<sub>2</sub> versus hexane. Polymers such as atactic polypropylene and polybutadiene are all quite soluble in hexane, but are insoluble in CO<sub>2</sub>. Conversely, poly(1,1-dihydroperfluorooctyl acrylate), PFOA, is quite soluble in CO<sub>2</sub> to very high molecular weights yet insoluble in hexane. This apparent paradox between these solubilities and solubility parameters may be overcome. A substantial contribution to the CO<sub>2</sub> solubility parameter, possibly as much as 20%,<sup>38</sup> is due to its large quadrupole moment. The quadrupole moment is the main reason that CO<sub>2</sub> has a much higher critical pressure than ethane, 74 versus 49 bar, respectively. It is also the reason for the relatively large value of  $P^*$  in lattice fluid theory.<sup>39</sup> Because the high  $P^*$  or  $\delta$  of CO<sub>2</sub> can be misleading, we have chosen to describe the nonspecific interactions in terms of the polarizability per volume instead of  $\delta$ .

Because the quadrupole moment influences the properties of pure CO<sub>2</sub>, it is of interest to determine how much quadrupole–dipole and quadrupole–quadrupole interactions between CO<sub>2</sub> and various solutes influence solvation and solubilities. These interactions may be expected to be insignificant for hydrocarbons, small for ethers, which have dipole moments of only 1.3 D, but become stronger for esters with dipole moments of 1.8 D. The role of the quadrupole moment in determining polymer solubility in CO<sub>2</sub> has been studied for certain polymers.<sup>24</sup>

Spectroscopic probes have been used to characterize the solvent polarizability/dipolarity of CO<sub>2</sub>.<sup>32,40</sup> Weak van der Waals forces between CO<sub>2</sub> and the solute phenol blue were characterized on the basis of solvatochromic shifts.<sup>32</sup> At a given reduced temperature the maximum transition energy of phenol blue is comparable in ethylene and CO<sub>2</sub>. The van der Waals contribution from CO<sub>2</sub> is actually weaker than that of ethane. The reason that the transition energies are the same is that the Lewis acidity of CO<sub>2</sub> causes some shift, since phenol blue is a Lewis base.

Hyatt<sup>41</sup> measured the shifts in IR frequencies of several probe compounds in both liquid and supercritical fluid (SF) CO<sub>2</sub>. Shifts in the  $\nu(\text{C}=\text{O})$  of acetone and cyclohexanone were slightly greater than those in the solvent *n*-hexane and slightly less than those in aromatic solvents, indicating a low tendency for CO<sub>2</sub> to interact with basic carbonyl groups. For the probe pyrrole, large shifts in the  $\nu(\text{N}-\text{H})$  stretching frequency indicated hydrogen bonding between pyrrole and CO<sub>2</sub>. Consequently, CO<sub>2</sub> was considered to be a stronger Lewis base than acid. Sigman et al.<sup>42</sup> measured  $\pi^*$  dipolarity–polarizability values for 10 solvatochromic indicators in SF CO<sub>2</sub>. They found  $\beta$ , the hydrogen-bonding basicity parameter, to be near zero in supercritical and liquid CO<sub>2</sub>, indicating a low tendency to donate electrons, in contrast to Hyatt. O'Shea et al.<sup>33</sup> found that the Lewis acidity of CO<sub>2</sub> has a large effect on the azo–hydrazone equilibrium of 4-(phenylazo)-1-naphthol relative to ethane. Yee et al.<sup>43</sup> used Fourier transform infrared spectroscopy to examine molecular interactions of CO<sub>2</sub> dissolved in C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>F<sub>6</sub>. From shifts in the  $\nu_2$  frequency of CO<sub>2</sub> and a semiempirical dielectric continuum model, they concluded that CO<sub>2</sub> is more repulsive to C<sub>2</sub>F<sub>6</sub> than C<sub>2</sub>H<sub>6</sub> and that no specific attractive interactions exist between CO<sub>2</sub> and perfluorinated molecules. FTIR spectroscopy has been used to show that CO<sub>2</sub> interacts as an electron acceptor

toward carbonyl groups in polymers, based upon splitting of the  $\nu_2$  bending mode of  $\text{CO}_2$ .<sup>44</sup> It also interacts with polystyrene and fluorine atoms on polymers, but these interactions are weaker than those with a carbonyl group.

Recently, quantitative thermodynamic studies of Lewis acid–base interactions involving  $\text{CO}_2$  have been measured with FTIR spectroscopy.<sup>45</sup> Equilibrium constants have been measured from the  $\nu_2$  bending mode of  $\text{CO}_2$  by FTIR spectroscopy for the electron donor–acceptor interactions of  $\text{CO}_2$  with three Lewis bases: triethylamine, pyridine, and tributyl phosphate (TBP). The equilibrium constants were relatively weak, compared to those between these bases and Lewis acids such as methanol, water, or phenol. For the strongest interaction,  $\text{CO}_2$ –TBP, the solubility of  $\text{CO}_2$  in TBP is increased by up to 28% due to specific interactions. Given that solubilities of various polymers in  $\text{CO}_2$  can differ by many orders of magnitude, this level of enhancement due to acid–base interactions may be relatively minor.

Specific interactions between  $\text{CO}_2$  and hexafluoroethane have been studied by ab initio calculations.<sup>46</sup> The interactions between four  $\text{CO}_2$  molecules and hexafluoroethane is 3 kcal/mol in the optimized geometry. This interaction will be smaller when averaging over all geometries; it is unknown whether it is strong enough to have much influence on the solubility compared with the nonspecific interactions. Specific interactions between  $\text{CO}_2$  and fluorinated molecules have been characterized in detail by  $^{19}\text{F}$  NMR.<sup>47</sup> Future work would be useful to obtain thermodynamic parameters (e.g., equilibrium constants) from NMR data which may be used to determine whether these interactions have a significant influence on solubility, relative to nonspecific interactions.

## Theory

The solubilities of nonpolymeric solutes in supercritical fluids such as  $\text{CO}_2$  can be predicted if the properties which describe the solute–solvent interactions are chosen properly.<sup>36,48</sup> For polynuclear aromatic hydrocarbons, examples of appropriate solute properties include the enthalpy of vaporization<sup>36</sup> and the solute molecular volume.<sup>49</sup> To further understand the role of solute–solvent interactions on solubilities and selectivities, it is instructive to define an enhancement factor  $E$  as the actual solubility,  $y_2$ , divided by the solubility in an ideal gas, with the result  $E = y_2 P/P_2^{\text{sat}}$ . This factor is a normalized solubility, because it removes the effect of the vapor pressure, providing a means to focus on interactions in the SCF phase. In carbon dioxide at 35 °C and 200 bar,  $E$  is about 7 for the similar tetracyclic sterols: cholesterol, stigmasterol, and ergosterol, each of which contains a single OH group. In fact, enhancement factors typically vary by only about 1–2 orders of magnitude for many types of organic solids in  $\text{CO}_2$ , even though the actual solubilities vary by many orders of magnitude. This means that solubilities in carbon dioxide are governed primarily by vapor pressures, a solute–solvent interaction, and only secondarily by solute–solvent interactions in the SCF phase. An exception is strong bases such as ammonia that can react with carbon dioxide to form covalent bonds.

We wish to determine if solute–solvent interactions play a secondary role for many polymer systems as well. The concept of an enhancement factor does not appear to be applicable to polymers because vapor pressures

are typically too small to be measurable. Furthermore, heats of vaporization are unavailable. A pure component polymer property related in some way to a solubility parameter is needed to quantify polymer–polymer interactions and their role on solubility in  $\text{CO}_2$ . For nonvolatile polymers, the characteristic pressure or cohesive energy density,  $P^*$ , is known from lattice fluid theory.<sup>50</sup> For carbon dioxide  $P^*$  is typically much larger than that of most hydrocarbon polymers. It is difficult to rationalize this physically, as solubility behavior suggests the opposite. The large  $P^*$  for  $\text{CO}_2$  obtained from regressing  $PVT$  properties reflects its large critical pressure due to its large quadrupole moment and is not a useful measure of van der Waals forces.

For polymers, extensive compilations of solubility parameters and component solubility parameters, describing van der Waals, polar, and hydrogen-bonding interactions, have been regressed from turbidimetric titrations of solubility in solvents and from swelling of polymers by solvents. Often the solvent is described by component solubility parameters as well. Consequently, a significant degree of the character of the solvents is likely to end up in the solubility parameter of the polymer. Since the solvation properties of carbon dioxide are so different than those of the solvents used in these studies, we do not expect that these solubility parameters will describe solubilities in  $\text{CO}_2$ .

To describe the cohesive energy density of a polymer, it would be useful to use an experimental property of a pure polymer that is not contaminated by polymer–solvent interactions. The surface tension of a polymer melt,  $\gamma$ , is an example of such a property; furthermore, it is widely available. Unlike solubility parameter determined from cloud points or swelling, this property is a pure component property and is not biased by the solvent. The surface tension may be extrapolated very reliably from above the melting point down to 20 °C by using the following relationship:

$$-d\gamma/dT = (11/9)(\gamma_0/T_0)(1 - T/T_0)^{2/9}$$

where  $T_0$  is the value of the surface tension at 0 K.<sup>51</sup> Since  $T_c$  would be very large for most polymers (if they did not first degrade),  $-d\gamma/dT$  is practically constant at ordinary temperatures, making temperature extrapolations reliable.

The surface tension is related to the work of cohesion, which is in turn related to the cohesion energy. The cohesion energy is the difference between the internal energy of an ideal gas and the actual fluid at the same temperature,  $\Delta u = u^{\text{ig}} - u$ .<sup>51</sup> The molar work of cohesion is given by

$$W = 2\gamma N_{\text{Avog}}^{1/3} V^{2/3}$$

where  $V$  is the volume. The ratio of  $W$  to  $\Delta u$  is a dimensionless constant ranging from about 3.5 for nonpolar liquid to between 4 and 8 for hydrogen-bonded liquids. Therefore, the cohesive energy density is related to the surface tension by

$$c = \Delta u/v = A\gamma V^{-1/3}$$

where  $A$  is a constant which varies only between certain limits according to the type of molecule. This equation is for spherical molecules where the area/molecule is related to  $V^{2/3}$ , so that for a polymer,  $c$  is for a polymer repeat unit.  $\gamma$  is approximately proportional to the



cohesive energy density of a polymer at a given temperature. The variation in  $V^{-1/3}$  for the polymers in this study is small compared to the variations in  $\gamma$  and will be neglected. Thus,  $\gamma$  should be a reliable measure of the cohesive energy density for polymer-polymer interactions, without any uncertainty arising from polymer-solvent interactions.

## Experimental Section

Poly(ethylene oxide) (PEO; 600 g/mol), PEO with methoxy end caps (PEODME; 400 and 1000 g/mol), and poly(propylene oxide) (PPO; 400, 1025, and 2000 g/mol) were obtained from Polysciences, Inc. Pluronic and Tetronics (block copolymers of PEO and PPO) were donated by BASF Corp. Polyethylene sulfide was obtained from Aldrich. Surfynol (substituted acetylenic diols or alcohols) commercial surfactants were supplied by Air Products and Chemicals. Polybutylene glycol monol, which we will designate poly(butylene oxide) (PBO; 800 g/mol), is composed of an ethylene oxide backbone with an ethyl side group. It was supplied by Air Products.

Poly(butyl acrylate), poly(2-ethylhexyl acrylate), and poly(*n*-butyl acrylate/acrylic acid) were supplied by Air Products. For the synthesis of trifluoroacetate end-capped Pluronic, the EO/PO surfactant of choice was added to a two-necked round-bottom flask and the mixture and apparatus purged thoroughly with nitrogen for several hours. The mixture was stirred and excess trifluoroacetic anhydride and triethylamine (ratio of 10:1) were added to the flask via syringe. The mixture was stirred overnight and filtered twice. Excess reagent was removed under vacuum for several hours. The removal of hydroxyl functionality with the appearance of trifluoroacetate groups was shown with FTIR.

Jeffamine samples (amine-terminated PEO/PPO random copolymers) were donated by the Huntsman Corp. SAM copolymer samples (PEO/PBO block copolymers) were obtained from Pittsburgh Paint and Glass. PDMS (13 000 g/mol, low polydispersity) was provided by J. M. DeSimone at the University of North Carolina. PDMS-monomethacrylate was obtained from Aldrich. Copolymer samples of PDMS-*g*-PEO/PPO, designated as DABCO DC 5357 and DC 5384, were supplied by Dow Corning, PDMS(20)-*g*-EO(20) and PDMS(13)-*g*-EO(10) were synthesized by Unilever Research, and the commercial Abil surfactants were from Goldschmidt. The ammonium carboxylate perfluoropolyether (PFPE) surfactants,  $\text{CF}_3\text{O}(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})_3\text{CF}_2\text{COO}^-\text{NH}_4^+$ , were provided by Ausimont.<sup>52</sup> PFPEs are also commercially available in the COOH form. All samples were used as received unless otherwise specified.

Krytox FSL-*b*-poly(ethylene oxide) (PEG600) and Krytox FSL-*b*-tetra(ethylene oxide) (TEG) were prepared as follows. Krytox FSL (100 g; DuPont), perfluoromethylcyclohexane (100 g; Aldrich), thionyl chloride (9.51 g; Aldrich) were added to a three-necked flask equipped with a stirrer nitrogen purge and a dry ice coldfinger. Dimethyl formamide (2.92 g; Aldrich) was added to the mixture which was stirred under reflux overnight. The solution was filtered and PEG (~5 M excess) in a trichlorotrifluoroethane:THF mixture (4:1) was added to the acid chloride solution. The reaction mixture was heated to 35 °C for 24 h and the solvent removed under vacuum. The product was washed with a large excess of water and dried overnight in a vacuum

oven. FTIR indicates a carboxylic acid stretch at 1776  $\text{cm}^{-1}$ . The loss of this stretch and the appearance of the PEG at 1725  $\text{cm}^{-1}$  indicates the product had been prepared. The tetraethyleneglycol end-capped perfluorinated polyether was prepared in a similar manner.

The surfactant DABCO DC5357 was encapped with acetate groups as follows. DABCO 5357 (48.5 g; Air Products) was added to a two-necked round-bottom flask. Acetic anhydride (10 g) and triethylamine (1 g) were added to the reagent after a thorough nitrogen purge for 1 h. The mixture was stirred overnight after which the product was filtered and excess acetic anhydride removed under vacuum. The product was washed with ether and dried once more under vacuum. FTIR of the DC5357 starting compound exhibits a hydroxyl stretch at 3478  $\text{cm}^{-1}$ . The acetate-modified product provided an FTIR spectrum with carbonyl functionality (1741  $\text{cm}^{-1}$ ) and a methyl group at 456  $\text{cm}^{-1}$ .

A 28-mL high-pressure variable volume view cell, as described previously,<sup>53</sup> was used to determine the phase boundaries of the solutions. The cell contains a piston to control the volume (and consequently the pressure) of the sample portion of the cell. A water bath was used to control the temperature of the cell and its contents. The temperature and pressure may be varied independently while keeping the composition constant. The phase behavior was measured in SF CO<sub>2</sub> at temperatures ranging from 25 to 65 °C, and from 1000 to 6000 psig.

The high-pressure cell was filled with a known amount of CO<sub>2</sub> using a HIP manual syringe pump. The syringe pump was also connected to the backside of the cell to generate the desired pressures. Solid samples were weighed accurately to within  $\pm 10^{-4}$  g and placed in the high-pressure cell before pressurization. For liquid samples a six-port rotary valve, a sample loop of known volume, and a motor-driven injection pump<sup>53</sup> were used to introduce the samples into a known amount of CO<sub>2</sub>. Sample loops of various sizes were used depending on the solubility of the sample. All samples were stirred rapidly until a single phase was obtained. The phase boundaries were obtained by visual observation of the onset of turbidity (i.e., cloud point) upon slow depressurization of a single-phase solution at constant temperature.

The polymers in this study were used as received. In some cases, especially for poly(alkylene oxides), polydispersities can be relatively high. An enormous amount of time would have been required to fractionate the polymers, which was beyond the scope of this study, as well as the majority of similar studies in the literature. A potential limitation of this method is that high-molecular-weight fractions will precipitate first as the pressure is lowered. As pressure is reduced further, lower-molecular-weight fractions will precipitate. The assignment of the cloud point for a polydisperse system can be done reliably by careful visual observation if the high-molecular-weight fraction is small. In our study the cloud point was not chosen as the onset of turbidity. It was chosen as the point where the turbidity changed markedly with pressure. In this way, turbidity due to small amounts of the highest molecular weight material could be neglected, and the cloud point pressure could be assigned closer to the average molecular weight. The difference between the pressure where turbidity was first observed and the pressure where the majority of the polymer precipitated typically ranged from 1 to 20

**Table 1. Surface Tensions and Solubilities in CO<sub>2</sub> for Various Homopolymers**

polymer	surface tension (mN/m), 20 °C	solubility, wt % (MW) @ 3000 psia, 35 °C
poly(1,1-dihydrodecafluorooctyl acrylate)	10	≥10 (1 × 10 <sup>6</sup> g/mol) <sup>17</sup>
poly(1,1-dihydroheptafluorobutyl acrylate)	15	
poly(heptafluorooctyl methacrylate)	15.3	
poly(fluoroalkoxyphosphazene)	n/a	≥4 (high MW)
perfluoropolyether ammonium carboxylate	n/a	≥5 (740 g/mol)
		≥2.5 (940 g/mol)
poly(dimethylsiloxane)		
1272 g/mol	19.9	4 (13 000 g/mol)
75 000 g/mol	20	
poly(tetrafluoroethylene)	23.9	insoluble (high MW)
poly(isobutylene oxide)		
30 000 g/mol	27.5	n/a
poly(propylene), atactic	29.4	insoluble
poly(2-ethylhexyl acrylate)		≤0.1 (4 233 g/mol)
34 000 g/mol	30.2	insoluble (92 514 g/mol)
poly(propylene oxide) dimethyl ether		
3 000 g/mol	30.7	
poly(propylene oxide)		
2025 g/mol	31.5	≥10 (400 g/mol)
		10 (1025 g/mol)
		0.5 (2000 g/mol)
		insoluble (500 000 g/mol)
poly(vinylidene fluoride)	33.2	
polyethylene, branched		
2000 g/mol	33.7	
poly( <i>n</i> -butyl acrylate)		0.1 (5 600 g/mol)
32 000 g/mol	33.7	insoluble (37 419 g/mol)
paraffin wax	34.7	
(mp 65 °C)		
polyethylene, linear		
67 000 g/mol	35.7	insoluble
poly(vinyl acetate)	36.5	
poly(butylene oxide) (poly(ethylene oxide))	n/a	>0.5 (800 g/mol)
poly( <i>n</i> -butylene oxide) (poly(tetrahydrofuran))	38.2	insoluble (1000 g/mol)
poly(ethylene oxide) dimethyl ether		
114 g/mol	28.6	≥3.5 (400 g/mol)
600 g/mol	37.5	0.43 (1000 g/mol)
100 000 g/mol	44.2	
polystyrene	39.3	insoluble (1700 g/mol)
poly(methyl methacrylate)	41.1	insoluble (3000 g/mol)
poly(ethylene oxide)		
6000 g/mol	42.9	0.4 (600 g/mol)
poly(acrylonitrile)	50	insoluble
poly(acrylamide)	52.3	insoluble

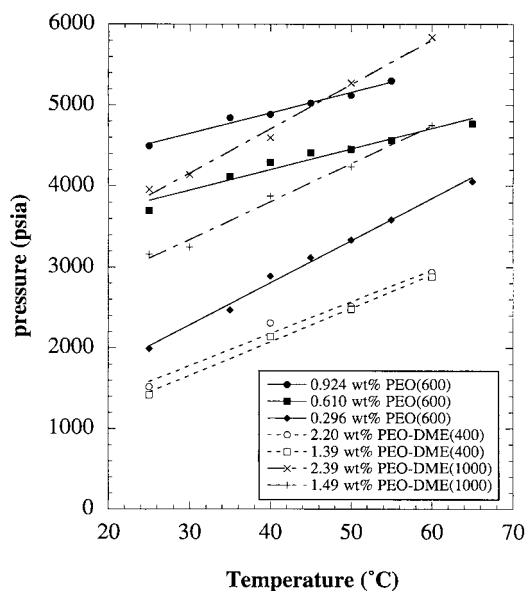
bar depending upon the molecular weight distribution. Thus, the reported cloud point pressures may be expected to be a little too large, but become more accurate for polymers with lower polydispersities. At pressures above the onset of turbidity, the polymer solutions appeared to be very clear. In this study, important trends were observed in cloud points, despite an uncertainty of up to 20 bar. The vast majority of polymer–supercritical fluid data have been obtained by the cloud point technique.<sup>1,12</sup>

## Results and Discussion

The polymer structure and surface tension for each homopolymer or copolymer is listed in Table 1 from the lowest surface tension to the highest, along with the approximate solubility at an arbitrary reference condition, 35 °C and 3000 psia. Given the extremely small polarizability of CO<sub>2</sub>, the dispersion contribution to the cohesive energy density of CO<sub>2</sub> may be expected to be smaller than that of every polymer in this study. Therefore, we expect that the solubility will increase as the surface tension of the polymer decreases. Both the solubility and surface tension change with molecular weight, even for molecular weights above 1000 g/mol, although the molecular weight dependence is not often studied for solubilities. Notice that one of the only polymers known to be highly soluble in CO<sub>2</sub> for high

molecular weights, poly(1,1-dihydrodecafluorooctyl acrylate),<sup>21</sup> has the lowest surface tension of any of the polymers listed. The solubility data for all the polymers in this study in CO<sub>2</sub> are listed in detail in a table in the Supporting Information.

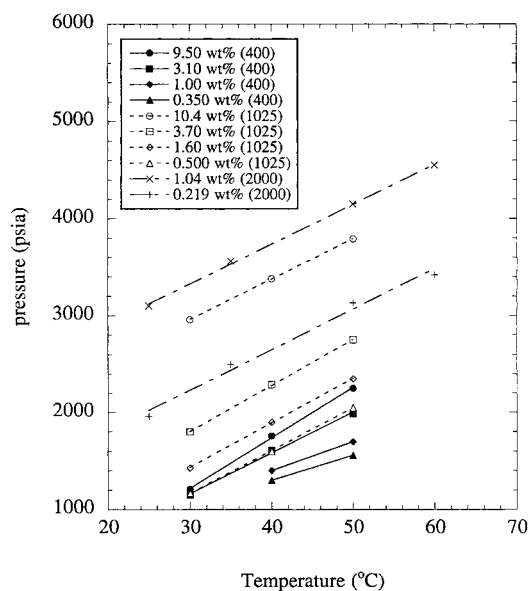
**Polyether Homopolymers.** *Poly(ethylene oxide) (PEO).* The phase-behavior data for PEO are shown in Figure 1. The polydispersity is large for all of the polyethers in this study due to the nature of the polymerizations. A consistent dissolution time of 1 h with stirring was used for all experiments unless stated otherwise. It was observed for longer dissolution times (≥1 h) that higher cloud points were obtained, in a few cases by up to 1000 psia. The longer time period allows more of the high-molecular-weight portion of the sample to be solubilized by CO<sub>2</sub>. A small very high molecular weight fraction can have a large effect on the cloud point. After 1 h, the volume of the undissolved material was very small, typically less than 5%. The goal was to measure the solubility closest to the average molecular weight and not for the small fraction of highest-molecular-weight oligomers. In the measurements of Daneshvar<sup>16</sup> for PEO(600), a more accurate and time-consuming technique was used. Samples were withdrawn and analyzed by GC. At 50 °C, our measurements at the two lowest pressures overlap the pressure range of Daneshvar.



**Figure 1.** Cloud point pressures for hydroxy- and methoxy-terminated PEO homopolymers in CO<sub>2</sub> for various molecular weights and concentrations.

For systems which exhibit lower-critical-solution-temperature (LCST) phase behavior, solubility decreases with increasing temperature at constant pressure. This trend is due to the decrease in solvent density with temperature. Density, not pressure, is the natural variable for understanding solvation in supercritical fluids. Density describes free volume which plays a central role in LCST phase separation. When a solvent such as CO<sub>2</sub> expands, it gains free volume, resulting in an increase in the polymer–polymer segmental interactions due to localized densification. By leaving the polymer segments, CO<sub>2</sub> expands into a new phase, increasing the volume and entropy of the mixture. In all cases shown in this study, the cloud point pressure increases with temperature for a given concentration of polymer, indicative of LCST-type phase separation.

Samples of dimethoxy end-capped PEO (PEO-DME) were tested to assess the effects of hydrogen bonding on the phase behavior of PEO in CO<sub>2</sub>. Although exact matches of molecular weights were not available, it can be seen that 1000 g/mol of methoxy end-capped PEO (PEO-DME) had higher solubilities versus 600 g/mol of PEO at a given *T* and *P* (Figure 1). PEO-DME(400) has approximately an order of magnitude higher solubility than PEO(600) in CO<sub>2</sub> at similar conditions. The hydrogen bonding between primary alcohol groups of PEO dramatically increases the pressures required to solubilize a given molecular weight sample (Figure 1). These trends are very consistent with the large decrease in surface tension with the addition of methoxy end caps, from 42.9 to 37.5 mN/m. The high degree of self-association for PEO is the result of strong hydrogen bonds. Because of hydrogen bonding, PEO is water soluble. The decrease in solubility due to polymer self-association through hydrogen bonds has been modeled quantitatively with the LFHB model.<sup>31</sup> It does not appear likely that CO<sub>2</sub> participates in specific acid–base interactions with the hydroxyl groups. If such specific interactions were significant, cloud point pressures would not have decreased so dramatically when OH end groups were replaced with non-hydrogen-bonding methoxy end groups.



**Figure 2.** Cloud point pressures for hydroxy-terminated PPO homopolymers in CO<sub>2</sub> for various molecular weights and concentrations.

*Poly(propylene oxide) (PPO).* The phase behavior data for PPO of various molecular weights in CO<sub>2</sub> are shown in Figure 2. The PPO(400) and PPO(1025) samples are quite soluble in CO<sub>2</sub>, up to about 10 wt % at 30 °C and 1310 psia. PPO(2000) is significantly less soluble than PPO(1025), only 1.0 wt % at 30 °C and 3100 psia, indicating a rapid decrease in solubility with molecular weight.

PPO is much more soluble than PEO for a given molecular weight. Clearly, the methyl substitution on each monomer unit in the chain has a large effect on solubility. The solubilities of PEO(600), PEO-DME(400), and PPO(400) in CO<sub>2</sub> may be compared at 50 °C for a constant molecular weight. PEO is the least soluble among the three due to the strongest physical and chemical interactions between polymer segments. The PEO-DME, which may be assumed to have about the same van der Waals interactions as PEO, is more soluble than PEO due to the absence of self-association. However, even though PPO can self-associate, it is more soluble than PEO-DME for two reasons:<sup>31</sup> (1) the acid–base interactions for PPO are much less prevalent than for PEO and (2) the physical segment–segment interactions are weaker for PPO than those for PEO due to steric effects. The first reason is demonstrated by the fact that methoxy end capping produces a much greater reduction in the surface tension of PEO than that of PPO, leading to a large loss in acid–base interactions for PEO. In summary, the higher solubility of PPO versus PEO is due to both the weaker segment–segment interactions and the weaker self-association. The trend in solubility for these three polyethers in CO<sub>2</sub>, PPO > PEO-DME > PEO, follows the order of surface tensions for the molecular weights studied at 25 °C. The surface tensions<sup>54</sup> of PPO are 31.4 and 30.7 mN/m at 400 and 4100 g/mol, respectively. For PEO-DME it is 37.7 mN/m at a molecular weight (MW) of 600. For PEO it is 42.7 mN/m at 600 MW and 42.4 at 3800 and 17 000 MW. The surface tension appears to be influenced by the same physical and specific polymer–polymer interactions as the solubility. On the basis of all of these arguments, trends in solubility in CO<sub>2</sub> may



**Table 2. Copolymer Structure and Polymer Solubility in CO<sub>2</sub> at 4000 psi and 35 °C**

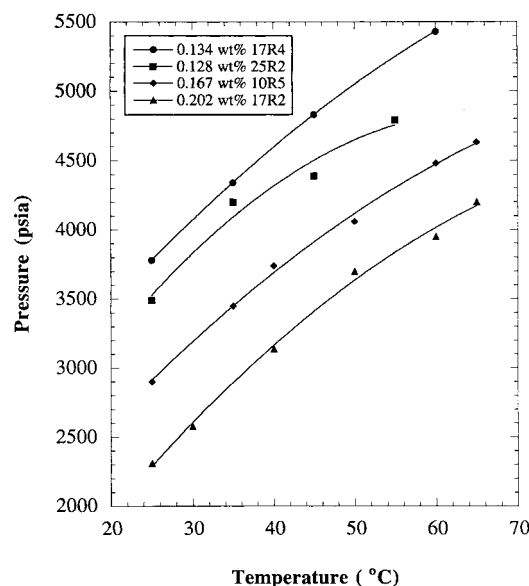
name	structure	PEO (g/mol)	PPO (g/mol)	est. solubility (wt %)
Pluronic 17R2	(PPO) <sub>14.7</sub> - <i>b</i> -(PEO) <sub>9.7</sub> - <i>b</i> -(PPO) <sub>14.7</sub>	425	1700	0.7
Pluronic 10R5	(PPO) <sub>8.6</sub> - <i>b</i> -(PEO) <sub>22.7</sub> - <i>b</i> -(PPO) <sub>8.6</sub>	1000	1000	0.3
Pluronic 17R4	(PPO) <sub>14.7</sub> - <i>b</i> -(PEO) <sub>25.8</sub> - <i>b</i> -(PPO) <sub>14.7</sub>	1133	1700	0.1
Pluronic 25R2	(PPO) <sub>21.6</sub> - <i>b</i> -(PEO) <sub>14.2</sub> - <i>b</i> -(PPO) <sub>21.6</sub>	625	2500	0.1
Pluronic L31	(PEO) <sub>1.1</sub> - <i>b</i> -(PPO) <sub>16.5</sub> - <i>b</i> -(PEO) <sub>1.1</sub>	100	950	3.0
Pluronic L61	(PEO) <sub>2.7</sub> - <i>b</i> -(PPO) <sub>34.0</sub> - <i>b</i> -(PEO) <sub>2.7</sub>	240	1970	0.8
Pluronic L43	(PEO) <sub>6.3</sub> - <i>b</i> -(PPO) <sub>22.2</sub> - <i>b</i> -(PEO) <sub>6.3</sub>	554	1290	0.3
Pluronic L62	(PEO) <sub>5.6</sub> - <i>b</i> -(PPO) <sub>34.0</sub> - <i>b</i> -(PEO) <sub>5.6</sub>	490	1970	0.2
Pluronic L81	(PEO) <sub>3.3</sub> - <i>b</i> -(PPO) <sub>45.7</sub> - <i>b</i> -(PEO) <sub>3.3</sub>	294	2650	0.2
Pluronic L92	(PEO) <sub>8.5</sub> - <i>b</i> -(PPO) <sub>51.6</sub> - <i>b</i> -(PEO) <sub>8.5</sub>	748	2990	0.1
Tetronic 150R1	((PPO) <sub>28.9</sub> - <i>b</i> -(PEO) <sub>4.2</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> N((PEO) <sub>4.2</sub> - <i>b</i> -(PPO) <sub>28.9</sub> ) <sub>2</sub>	744	6700	insol.
Tetronic 90R4	((PPO) <sub>17.0</sub> - <i>b</i> -(PEO) <sub>14.9</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> N((PEO) <sub>14.9</sub> - <i>b</i> -(PPO) <sub>17.0</sub> ) <sub>2</sub>	2628	3940	insol.
Tetronic 701	((PEO) <sub>1.7</sub> - <i>b</i> -(PPO) <sub>11.5</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> N((PPO) <sub>11.5</sub> - <i>b</i> -(PEO) <sub>1.7</sub> ) <sub>2</sub>	300	2668	insol.
Jeffamine M-600	(PEO) <sub>1</sub> - <i>b</i> -(PPO) <sub>9</sub> NH <sub>2</sub>	44	522	0.7
Jeffamine M-2000	(PEO) <sub>3</sub> - <i>b</i> -(PPO) <sub>32</sub> NH <sub>2</sub>	132	1856	0.1
Surfynol 61	3,5-dimethyl-3-hydroxy-1-hexyne	126 (total)		> 10
Surfynol 104	2,4,7,9-tetramethyl-4,7-dihydroxy-5-decyne	227 (total)		> 10
Surfynol 420	2,4,7,9-tetramethyl-4,7-di(ethylene oxide) <sub>0.65</sub> -5-decyne	57	283 total	> 5
Surfynol 440	2,4,7,9-tetramethyl-4,7-di(ethylene oxide) <sub>1.7</sub> -5-decyne	151	377 total	5
Surfynol 465	2,4,7,9-tetramethyl-4,7-di(ethylene oxide) <sub>4.8</sub> -5-decyne	420	646 total	0.9
Surfynol 485	2,4,7,9-tetramethyl-4,7-di(ethylene oxide) <sub>14.6</sub> -5-decyne	1281	1507 total	0.3
SAM 185	(PBO) <sub>12</sub> - <i>b</i> -(PEO) <sub>15</sub>	660	960 (PBO)	0.1
SAM 187	(PBO) <sub>12</sub> - <i>b</i> -(PEO) <sub>35</sub>	1540	960 (PBO)	insol.
Dabco DC5384	PDMS with grafted PEO			> 1
Dabco DC5357	PDMS with grafted PEO			0.1
PDMS(20)- <i>g</i> -EO(20)	MD <sub>20</sub> D <sub>2</sub> *M, D* = grafted EO <sub>10</sub> , M = trimethylsilyl end group, D = dimethyl siloxyl monomer	2758 total		0.2
PDMS(13)- <i>g</i> -EO(10)	MD <sub>13</sub> D <sub>1</sub> *M, D* = grafted EO <sub>10</sub>	1660 total		1
Abil B-8851	MD <sub>22</sub> D <sub>4</sub> *M, D* = 75/25: PEO/PPO	6000 total		0.1
Abil B-88184	MD <sub>73</sub> D <sub>4</sub> *M, D* = 75/25: PEO/PPO	13 000 total		0.5
Zonyl TM				> 0.7
Zonyl FSN-100	F(CF <sub>2</sub> CF <sub>2</sub> ) <sub>3-8</sub> CH <sub>2</sub> CH <sub>2</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>n</sub> H, <i>n</i> = 10–15			> 0.4
Zonyl FSO-100	F(CF <sub>2</sub> CF <sub>2</sub> ) <sub>3-8</sub> CH <sub>2</sub> CH <sub>2</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>n</sub> H, <i>n</i> = 10–15			> 0.4
Krytox FSL-TEG	(C <sub>3</sub> F <sub>7</sub> O) <sub>13.5</sub> CH <sub>3</sub> COO(EO) <sub>4.0</sub>			> 0.5
Krytox FSL-PEG(600)	(C <sub>3</sub> F <sub>7</sub> O) <sub>13.5</sub> CH <sub>3</sub> COO(EO) <sub>13.6</sub>			0.5

be described quite well without even considering polymer–CO<sub>2</sub> interactions.

**Poly(butylene oxide) (PBO).** Phase-behavior data for 800 g/mol of poly(butylene oxide) (PBO) are shown in Table 1; this isomer of PBO is ethyl-substituted PEO. The ethyl substitution to the PEO backbone increases the solubility significantly compared with that of PEO, yet PBO is less soluble than PPO. The solubility of PBO in CO<sub>2</sub> with respect to PPO is smaller as demonstrated by higher cloud point pressures. This solubility reduction may be due in part to the fact that the ethyl substitution adds a larger surface tension increment than the methyl substitution. Steric factors may also be important. The surface tension for this isomer of PBO could not be found, but this species is ranked in Table 1 based on phase equilibria data. In comparison, the dimethyl-substituted PEO, or poly(isobutylene oxide), has an even lower surface tension than PPO despite the significantly higher molecular weight of the former. This polymer was not available for phase-behavior tests, but it is expected to be even more soluble in CO<sub>2</sub> than PPO.

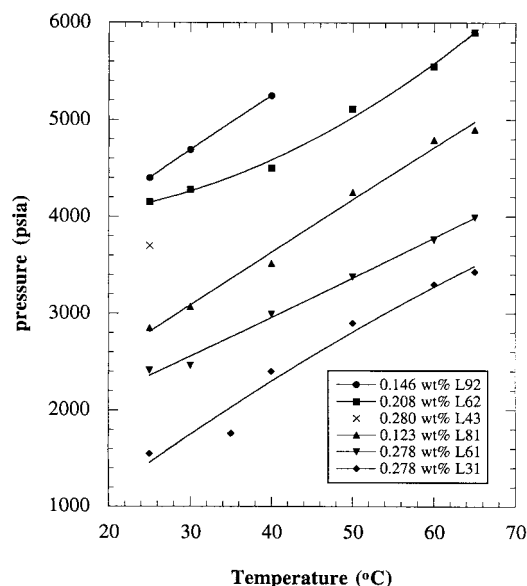
**Polytetrahydrofuran (P(n-BO)).** Terathane, or poly(*n*-butylene oxide) (P(*n*-BO)), is the linear isomer of PBO without any branching. The lack of branching and the lipophilic nature of this polymer, due to the large number of methylene groups, are likely the causes of its negligible solubility in CO<sub>2</sub>. P(*n*-BO) was only slightly soluble in supercritical CO<sub>2</sub> (<1 wt % at 25 °C and 5000 psia) based on the partial dissolution of a small sample loading of a 1000 g/mol sample.

**Polyether Copolymers.** PEO–PPO Block Copolymers (*Pluronics*). The phase behavior of a variety of

**Figure 3.** Cloud point pressures for Pluronic R (PPO-*b*-PEO-*b*-PPO) copolymers in CO<sub>2</sub> at similar concentrations.

commercially available polyether block copolymers was measured in CO<sub>2</sub>. These included Pluronic R (PPO-*b*-PEO-*b*-PPO), Pluronic L (PEO-*b*-PPO-*b*-PEO), Tetronic R (tetrafunctional), SAM (PEO-*b*-PBO), and Jeffamine PEO–PPO amine-terminated block copolymers (Table 2).

The phase behavior of Pluronic R copolymers is shown in Figure 3. The relative order of solubilities 17R2 > 10R5 > 25R2 > 17R4 indicates that solubility depends on PEO block length and the total copolymer molecular



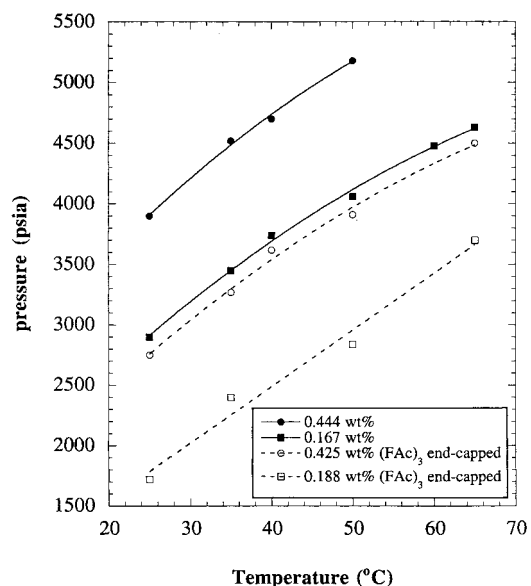
**Figure 4.** Cloud point pressures for Pluronic L (PEO-*b*-PPO-*b*-PEO) copolymers in CO<sub>2</sub> at similar concentrations.

weight. Pluronic 17R2 has the smallest PEO block length and is the most soluble in CO<sub>2</sub>, while the least soluble, 17R4, has the largest PEO block length. The copolymers with intermediate solubilities did not follow this trend though, as 10R5 (PEO block = 1000 g/mol) was more soluble than 25R2 (PEO block = 625 g/mol). The solubility in this case decreases because of the increase in the overall molecular weight.

The phase behavior of the six Pluronic L copolymers tested is shown for similar polymer concentrations in Figure 4. The trend in increasing solubility for Pluronic L's in CO<sub>2</sub> almost exactly follows decreasing PEO content (see Table 2). It should be noted, however, with only one major exception (L81), this order also corresponds to increasing PPO molecular weight. For these copolymers the ratio of the PEO to total molecular weight varies much less than for the Pluronic R copolymers described above. The solubilities of each of the Pluronic R and L block copolymers is intermediate between those of PPO and PEO homopolymers of the same overall molecular weight, as is also the case for the surface tensions.

In a companion study,<sup>31</sup> the phase behavior of PEO-PPO copolymers was modeled with a modified SAFT equation of state. The predictions of the model were quite reasonable, especially since the interaction parameters in the model were fit only to homopolymer solubility data and not to any data for block copolymers. The model provided a means to explore the effects of the PEO/PPO ratio, molecular weight, and molecular structure on the solubility in CO<sub>2</sub> in a systematic fashion. Overall, the solubilities of Pluronic block copolymers, for a given molecular weight, decrease with an increase in the PEO/PPO ratio. For a given PEO/PPO ratio, solubility increases with increasing molecular weight as expected.

A comparison of Pluronic L62 and 17R2 copolymers with similar molecular weights and PEO/PPO ratios indicates that the location of the blocks can influence solubility. The cloud point pressure of 17R2 is about 2000 psia lower than that of L62 at a concentration of close to 0.20 wt %. The terminal hydroxyl groups on the PPO outer blocks form much weaker hydrogen bonds than the hydroxyl group on PEO blocks on the



**Figure 5.** Effect of trifluoroacetate end capping on the cloud point pressures for Pluronic 10R5 in CO<sub>2</sub>.

basis of the surface tension data as discussed above. Thus, 17R2 with outer PPO blocks is more soluble than L62, as was predicted by the SAFT model. However, the effect of block position is modest compared with that of the PEO/PPO ratio (for a series of either Pluronic L or R copolymers), according to the SAFT equation of state.

The effect of hydrogen bonding was determined by replacing the terminal hydroxyl groups with non-hydrogen-bonding species. With trifluoroacetate end caps, the cloud point pressure for Pluronic 10R5 decreased by 1200–1500 psia in each case, as shown in Figure 5. Similar reductions in cloud point pressure were observed for all trifluoroacetate end-capped Pluronics when compared to their hydroxylated analogues. However, this decrease in cloud point was similar to that obtained with methoxy end caps. As will be discussed later, even for polymers without any self-association, the incorporation of fluorinated groups enhances polymer solubility in CO<sub>2</sub> due to a reduction in cohesive energy and surface tension. In these cases the fluorinated groups act as "in-chain" cosolvents. The amount of fluorine incorporated into the above copolymer via trifluoroacetate end capping is too small to influence surface tension and thus solubility, beyond what is observed for methoxy end caps. The reduction in cloud point pressure by end capping in these cases mainly results from the loss of hydrogen bonding with the elimination of the hydroxyl end caps.

**PEO-PPO Block Copolymers (Tetronics).** The molecular weights of the Tetronic copolymers are typically higher than those of the Pluronic copolymers as shown in Table 2. Tetronics are X-shaped; the central unit is a tetra-substituted ethylenediamine group with the amino hydrogens replaced with diblock copolymer "arms" of PEO and PPO. Tetronic R copolymers have arms with PEO groups proximal to the ethylenediamine and PPO groups in the terminal position, while those with PPO proximal to the central group and PEO in the terminal position are simply called Tetronic copolymers.

The two Tetronic R samples tested, 150R1 and 90R4, were only slightly soluble in CO<sub>2</sub> (<0.10 wt % at 25 °C and 5000 psia), as was the Tetronic 701 sample (<0.10 wt % at 3600 psia and 25 °C). After the sample was



stirred in excess of 1 h, large amounts of the sample were still visible on the walls and window of the view cell. The molecular weight of the Tetronic 150R1 was 7444 g/mol total, with 744 g/mol distributed between four proximal PEO groups and 6700 g/mol distributed between four terminal PPO groups. If an even distribution of molecular weights is assumed, then each arm of Tetronic 150R1 is  $\sim 1700$  g/mol PPO and  $\sim 200$  g/mol PEO. On the basis of phase-behavior data for homopolymers and Pluronics, each of these arms would be soluble in CO<sub>2</sub> at 0.1 wt % were it not bonded to the central ethylenediamine group. Thus, the high overall molecular weight greatly limits solubility for the Tetronic R and Tetronic 701 samples, relative to the Pluronic samples.

**Surfynols.** Air Product's Surfynol series constitute a variety of hydroxide or ethylene-oxide-substituted unsaturated hydrocarbons, as shown in Table 2. The Surfynol 400 series is composed of 4,6-di(PEO)-substituted 2,4,7,9-tetramethyl-5-decyne. The last two digits of the series notation refer to the relative weight percent of PEO in the molecule (i.e., Surfynol 420 contains approximately 20 wt % PEO). Of the seven Surfynol surfactants tested, Surfynol 420 was the most soluble (3.8 wt % at 25 °C and 1870 psia) and Surfynol 485 was the least soluble (0.24 wt % at 25 °C and 2350 psia) (Table 2). The solubility decreases as the ethylene oxide molecular weight increases as was demonstrated above for Pluronic surfactants. In comparison to Pluronics and Tetronics, Surfynol solubilities were generally much higher due to the significantly lower overall molecular weights and PEO block molecular weights. The exception was Surfynol 485 because of its large PEO content.

**Jeffamines.** Jeffamine M random EO/PO copolymers are terminated at one end with a primary amine. M-600 has a molecular weight of about 600 g/mol and a PEO/PPO ratio of 9/1. This sample was soluble in CO<sub>2</sub> to 0.79 wt % at 25 °C and 3970 psia. As with Pluronics, the cloud point pressure increased after equilibration for longer periods of time, likely indicating a significant polydispersity. Upon depressurization, a white solid, likely a carbamate, was visible in the cell. This solid was not visible before depressurization, suggesting it was soluble in CO<sub>2</sub>. Jeffamine M-2005 had a molecular weight of about 2000 g/mol and a PPO/PEO ratio of 32/3. A concentration of 0.38 wt %, this sample would not fully dissolve in CO<sub>2</sub> at 25 °C and 5000 psia. Formation of the white solid was not as pronounced with M-2005 relative to M-600. In neither case was the solid stable for greater than 15 min after depressurization.

**Polyacrylates.** Low- and high-molecular-weight samples of poly(*n*-butyl acrylate) (PBA,  $37.4 \times 10^3$  and  $5.6 \times 10^3$  g/mol, respectively) and poly(2-ethylhexyl acrylate) (PEHA,  $92.5 \times 10^3$  and  $4.2 \times 10^3$  g/mol, respectively) were tested for solubility in CO<sub>2</sub>. The high-molecular-weight samples for both acrylates were only very slightly soluble in CO<sub>2</sub> at 25 °C and 5000 psia. Only a small fraction of the sample dissolved (i.e., solubility of PBA  $\ll 0.33$  wt % and PEHA  $\ll 0.12$  wt %). The low-molecular-weight PEHA was also only very slightly soluble ( $\ll 0.09$  wt %). Low-molecular-weight PBA ( $5.6 \times 10^3$  g/mol) was the only sample to be completely solubilized by CO<sub>2</sub>, having a solubility of 0.11 wt % in CO<sub>2</sub> at 25 °C and 3190 psia. It is known that CO<sub>2</sub> solubility in acrylates is enhanced by interactions between the carbonyl moieties of each species.<sup>44,45</sup> The greater solubility of PBA in CO<sub>2</sub> versus PEHA may be

due to a smaller hydrocarbon functionality on the ester group. This result is inconsistent with the lower surface tension for PEHA (Table 1), although the surface tensions were not very different. This modest discrepancy possibly suggests that the polydispersities for the acrylates were different.

**Polystyrene.** Samples of very low molecular weight polystyrene (PS) were only slightly soluble in CO<sub>2</sub>; PS-(500) was slightly soluble ( $\ll 0.1$  wt %), while the slightly higher molecular weight PS(1850) was insoluble in CO<sub>2</sub>. The higher surface tension for PS versus polyacrylates is consistent with its much lower solubility of PS. The high cohesive energy density of the aromatic phenyl ring is unfavorable for solubility in CO<sub>2</sub>. Unlike acrylates, PS does not have any functionalities, such as carbonyl groups, which interact well with CO<sub>2</sub>.

**Poly(dimethylsiloxane).** *PDMS Homopolymer.* Poly(dimethylsiloxane) (PDMS) has a relatively low surface tension, and consequently is highly soluble in CO<sub>2</sub>, compared with nearly all polymers tested besides fluorinated polymers and polyphosphazenes. The solubility of poly(dimethylsiloxane) (PDMS) (13 000 g/mol) was relatively high ( $> 10$  wt %) at pressures under 5000 psia over a temperature range from 25–60 °C. Solubilities were significantly higher than those of any polyacrylate or polyether samples measured in this study, and of polyolefins.<sup>24</sup> The data have been modeled successfully with lattice fluid and SAFT equations of state.<sup>55</sup> The solubility of PDMS monomethacrylate (PDMS-MMA;  $1 \times 10^4$  g/mol) was similar to that of the above 13 000 g/mol PDMS homopolymer. Because MMA interacts reasonably well with CO<sub>2</sub>, it did not lower the solubility significantly.

A recent SANS study has shown that PDMS has a negative second virial coefficient in CO<sub>2</sub>, unlike the case for PFOA which has a positive second virial coefficient.<sup>56</sup> The greater chain extension for PFOA in CO<sub>2</sub> is consistent with its much lower surface tension.

*PDMS-PEO Copolymers.* PDMS(13)-*g*-EO(10), synthesized at Unilever Research, was highly soluble in carbon dioxide, much more so than Pluronic surfactants with a similar number of EO segments. For a given number of EO segments, a smaller amount of PDMS is required for solubility compared with that of PPO. PDMS(20)-*g*-EO(20) had a similar solubility to Pluronic 17R4, which has 26 EO groups. The two OH groups on a terminal EO group in the case of PDMS(20)-*g*-EO(20) lower the solubility more than the two OH groups do on a terminal PPO for Pluronic 17R4. The stronger hydrogen bonding for an OH terminal group on EO versus PO has been quantified.<sup>31</sup>

*PDMS-PEO/PPO Copolymers.* The DABCO surfactants contain PDMS backbones with (EO-*b*-PO) copolymer grafts. DABCO DC5357 (0.11 wt % at 25 °C and 3000 psia) and DC5384 (1.1 wt % at 25 °C and 2450 psia) both showed limited solubility in CO<sub>2</sub>, between that of PDMS and PPO/PEO block copolymers (Table 2). The higher solubility for DC5384 as compared to that of DC5357 is due to a significantly lower molecular weight. For DC 5384, essentially all of the graft is PEO. Its phase behavior is therefore not unlike that observed for PEO(600). It is likely that the CO<sub>2</sub>-insoluble PEO fraction of both copolymers dominates their phase behavior. As with polyether samples, trifluoroacetate end capping of the PEO functionality of DC5357 further enhanced its solubility in CO<sub>2</sub>.

The Abil surfactants were quite soluble because of the

high ratio of PDMS to poly(alkylene oxides) and the presence of PPO with PEO.

**Fluorinated Polymers.** Fluoroacrylates<sup>21</sup> and fluoroethers<sup>9</sup> can be extremely soluble in CO<sub>2</sub>. It is the weak van der Waals forces between fluorinated moieties which can make them compatible with CO<sub>2</sub>. Certain fluorinated polymers also have very low surface tensions, indicative of weak polymer–polymer interactions and a low cohesive energy density.

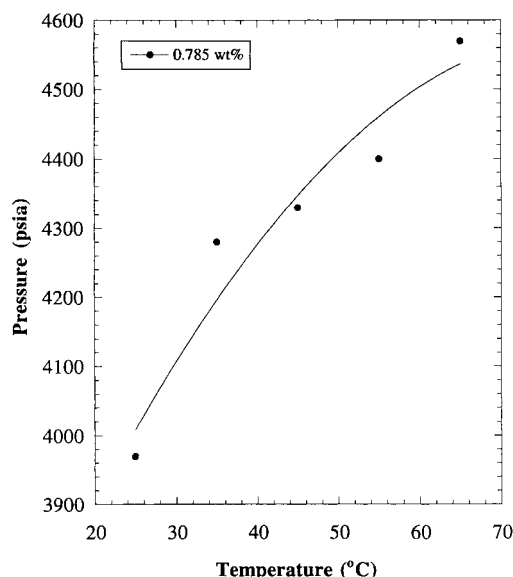
**Perfluoropolyethers.** Two low-molecular-weight samples (740 and 940 g/mol) of an ammonium carboxylate perfluoropolyether (PFPE) were found to be significantly soluble in CO<sub>2</sub> at relatively low pressures. The CO<sub>2</sub>-philic fluoroether tail and low molecular weight contribute to the high solubility of this surfactant, despite its ionic nature (Table 1). Again, low surface tension fluoroether materials allow for significant solubilities due to the relatively weak polymer–polymer interactions. Poly(tetrafluoroethylene) is insoluble in CO<sub>2</sub> at ambient temperature because of its higher surface tension (stronger polymer–polymer interactions) and its high melting point and degree of crystallinity.

Krytox is the DuPont trade name for perfluorinated PPO terminated at one end with a carboxylic acid group. Two samples, Krytox FSL/PEO(600) and Krytox FSL/tetraethylene glycol (TEG), were tested. The FSL notation refers to a fluoroether group having a molecular weight of 2500 g/mol. The solubility of Krytox FSL/PEO(600) (0.52 wt % at 25 °C and 3980 psia) was slightly lower than that of PEO(600) (0.61 wt % at 25 °C and 3700 psia). Because the fluoroether group did not aid solubilization of PEO, it is likely that the molecular weight of the fluoroether group was somewhat too large according to previous studies<sup>17</sup> and the results above for ammonium carboxylate fluoroethers. Krytox FSL/TEG was soluble to 0.55 wt % at 25 °C and 1360 psia. The higher solubility for the copolymer with the smaller PEO block is consistent with the results for Pluronic copolymers. Unlike the case for fluoroacrylates, fluorinated polyethers have been found to have negative second virial coefficients in CO<sub>2</sub>, indicating limited chain extension.<sup>56</sup> This is consistent with the higher solubilities for fluoroacrylates.

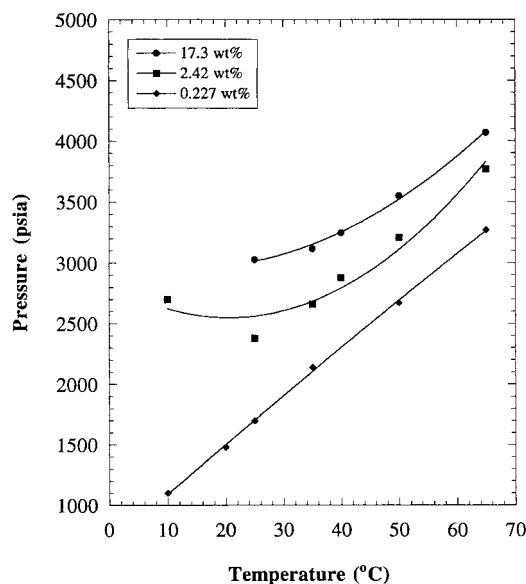
**Poly(vinylidene fluoride) (PVF).** A 500 000 g/mol sample, in the morphology of a powder, was found to be insoluble in CO<sub>2</sub> at 25 °C and 5000 psia. After attempts to dissolve the sample for > 1 h was completed, the system pressure was lowered and no cloud point was seen, indicative of negligible solubility. Despite its partially fluorinated chemical character, PVF has a reasonably high surface tension (Table 1) and melting point of 160 °C, and therefore its insolubility in CO<sub>2</sub> is expected.

**Zonyl (DuPont).** The trade name Zonyl refers to a group of fluorinated alkanes with ethylene oxide headgroups. Three samples, Zonyl FSO-100, Zonyl FSN-100, and Zonyl TM, were tested. Zonyl FSO-100 was the least soluble of the three (0.40 wt % at 25 °C and 2000 psia). The most soluble was Zonyl TM (1.4 wt % at 35 °C and 1480 psia). These samples all appeared to be some type of mixture and would separate into multiple phases at ambient conditions.

**Polyphosphazene.** Polyphosphazene is an inorganic polymer with an alternating P and N backbone (i.e.,  $(-PX_2=N-)_n$ ). The samples tested for solubility in CO<sub>2</sub> were a poly(fluoroalkoxyphosphazene) (EYPEL-F



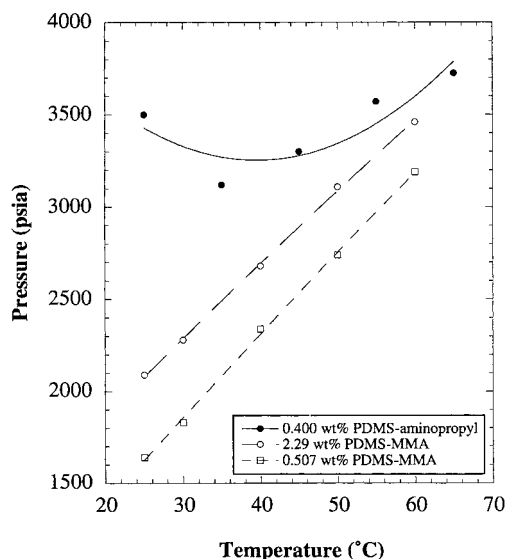
**Figure 6.** Cloud point pressures for Jeffamine M-600 copolymer in CO<sub>2</sub>.



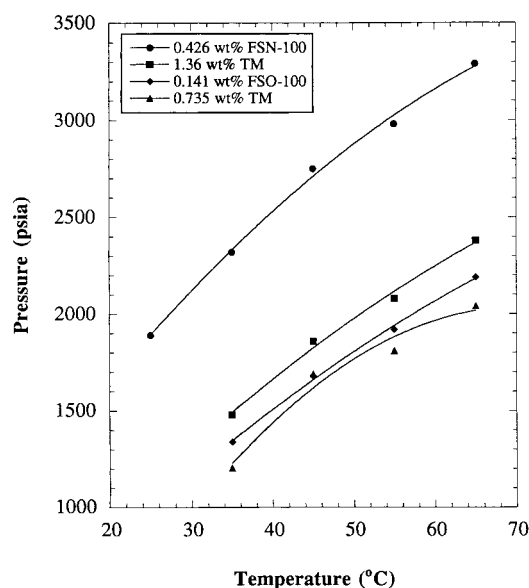
**Figure 7.** Cloud point pressures for PDMS (13 000 g/mol) in CO<sub>2</sub> at various concentrations.

gum, exact MW unknown) and poly[*P*-tris(trifluoroethoxy)-*N*-trimethylsilyl]phosphazene ( $M_w = 96$ ,  $M_n = 62$  kg/mol). As can be seen in Figure 11, both polymers are quite soluble in CO<sub>2</sub> to > 4 wt % at 3000 psia and 35 °C even at these relatively high molecular weights. The poly(fluoroalkoxyphosphazenes) sample had similar cloud point pressures to  $1.3 \times 10^4$  g/mol of PDMS (monodisperse) at similar loadings, while the other polyphosphazene was even more soluble, having cloud point pressures ~500 psia lower than the unmodified sample at similar conditions and concentrations. In comparison, another highly soluble organic fluoropolymer, poly(1,1-dihydroperfluorooctyl acrylate) or PFOA, has a cloud point pressure similar to the modified polyphosphazene. Aside from PDMS, this is the only other example of a CO<sub>2</sub>-soluble inorganic polymer that we are aware of.

One significant characteristic of fluorinated acrylates is their resistance to a wide variety of solvents, with the exception of fluorinated solvents (e.g., Freons). In the case of block copolymers of fluorinated acrylates



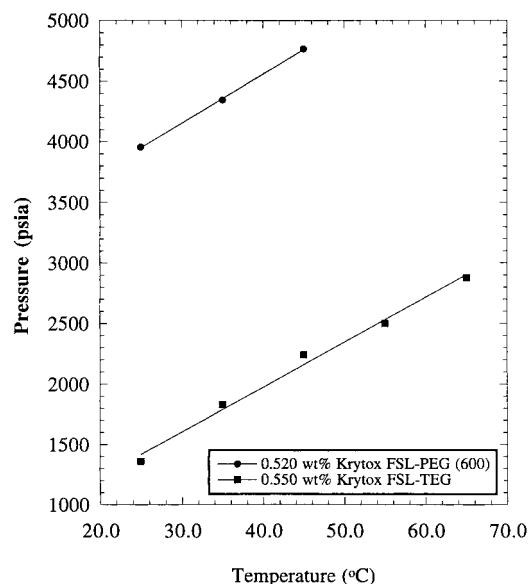
**Figure 8.** Cloud point pressures for aminopropyl- and mono-methacrylate-terminated PDMS in CO<sub>2</sub>.



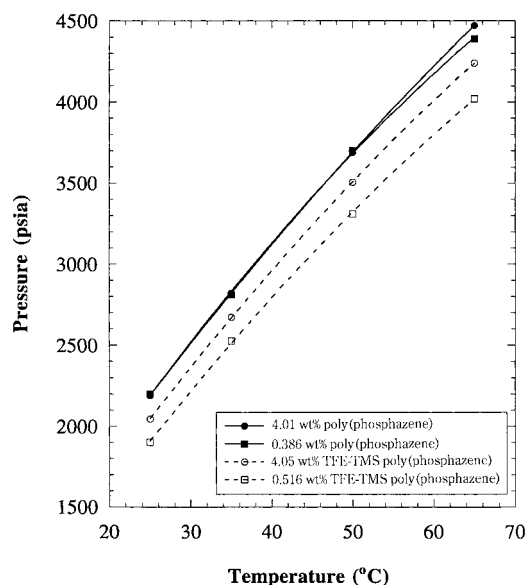
**Figure 9.** Cloud point pressures for various DuPont Zonyl polymers in CO<sub>2</sub> at similar concentrations.

with other more common polymers, it is difficult to find any solvent in which they are fully solubilized with the exception of CO<sub>2</sub>. In contrast, the poly(fluoroalkoxyphosphazene) samples tested were also found to be miscible in acetone and several other solvents. This again shows the uniqueness of poly(fluoroalkoxyphosphazenes) which, unlike PDMS, are soluble in CO<sub>2</sub> at very high molecular weights and are the only fluorinated polymers we are aware of that are also highly soluble in common, nonhalogenated liquid solvents.

**Miscellaneous.** *Poly(ethylene sulfide).* Poly(ethylene sulfide), or Thiokol, showed negligible solubility in CO<sub>2</sub> ( $\ll 0.17$  wt % at 25 °C and 5000 psia). Sulfur has a very high surface tension ( $>60$  mN/m), and as such will likely dramatically increase the surface tension when incorporated into polymers, such as poly(ethylene sulfide). The insolubility of this polymer in CO<sub>2</sub> follows the general trend relationship between increasing surface tensions and decreasing solubility in CO<sub>2</sub>.



**Figure 10.** Cloud point pressures for ethylene-glycol-modified Krytox polymers in CO<sub>2</sub> at similar concentrations.



**Figure 11.** Cloud point pressures for poly(fluoroalkoxyphosphazene) and poly[*P*-tris(trifluoroethoxy)-*N*-trimethylsilyl]phosphazene in CO<sub>2</sub> at similar concentrations.

## Conclusions

On the basis of cloud point measurements, polymer solubility in carbon dioxide at temperatures below 80 °C increases with a decrease in the surface tension of the polymer, a pure component property. Consequently, solubility is governed primarily by polymer–polymer interactions, while polymer–CO<sub>2</sub> interactions play a secondary role. The trend in decreasing solubility with surface tension is observed in the following order for the series: poly(fluorooctyl acrylate), poly(fluoroalkoxyphosphazene) > PDMS > poly(propylene oxide) > polyacrylates > poly(ethylene oxide). The change in solubility for these polymers (and oligomers) is enormous as shown in Table 1. Therefore, uncertainty due to determination of solubility from cloud points is not be large enough to question the relationship between solubility and surface tension. Future work would be useful to determine how much the secondary role of specific interactions increases solubility over the amount



expected from the surface tension, especially for functional groups with stronger specific interactions with CO<sub>2</sub> than those considered in this study.

The branching on a poly(ethylene oxide) backbone has a large effect on the surface tension and thus the solubility. The solubility of PPO oligomers is significantly greater than that of PEO oligomers due to the steric and chemical effects of the added methyl substituent to the PEO backbone. The increased lipophilic nature of the ethyl-substituted PEO (i.e., PBO) results in a reduction in solubility when compared to that of PPO. The solubilities of block copolymers follow expectations on the basis of the solubilities and surface tensions of the homopolymer constituents. The correlation between solubility and surface tension in Table 1 is clearly evident due to the enormous variation in solubility and molecular weight of the various polymers and oligomers. The modest uncertainty in the cloud points due to polydispersity is not nearly enough to question this conclusion.

Methoxy or trifluoroacetate end-capped polyethers showed substantially higher solubility in CO<sub>2</sub> than hydroxyl-terminated PEO due to the reduction of hydrogen bonding by the terminal alcohols. The incorporation of a primary amine group in a random PEO/PPO copolymer did not significantly enhance solubility; however, carbamate compound formation was seen as solid residues for short periods after depressurization of the mixture.

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**Supporting Information Available:** Experimental cloud point pressures are presented in table form for numerous polymers as a function of temperature and concentration (5 pages). Ordering information is given on any current masthead page.

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