

# Impact of Hexafluoroisopropylidene on the Solubility of Aromatic-Based Polymers in Supercritical Fluids

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**ABSTRACT:** Three different supercritical fluids (SCF), CO<sub>2</sub>, dimethyl ether (DME), and propane, are investigated as potential solvents for processing two lactide-based terpolymers and two perfluorocyclobutyl (PFCB) aryl ether polymers. The repeat unit of the lactide-based terpolymers consists of a 1:1:1 ratio of L-lactide, diglycidyl ether of bisphenol A (DGEBA), and, in one case, 4,4'-hexafluoroisopropylidenediphenol (6F-Bis-A) and, in the other case, 4,4'-isopropylidenediphenol (6H-Bis-A). The PFCB-based polymers are synthesized from 1,1-bis[4-[(trifluorovinyl)oxy]phenyl]hexafluoroisopropylidene (6FVE) and from bis(trifluorovinyl)oxybiphenyl (BPVE). For both classes of polymer the steric effect of the hexafluoroisopropylidene (6F) group reduces chain-chain interactions, disrupts electronic resonance between adjacent aromatic groups, and improves solubility. The two lactide-based terpolymers do

not dissolve in CO<sub>2</sub> or propane, but dissolve in DME. At room temperature the poly(lactide 6F-BisA DGEBA) terpolymer dissolves at 700 bar lower pressure in DME compared to the poly(lactide 6H-Bis-A DGEBA) terpolymer. Although the 6FVE polymer dissolves in all three SCF solvents, pressures in excess of 800 bar are needed to dissolve this polymer in CO<sub>2</sub> and propane while 6FVE dissolves in DME at pressure below 150 bar. The other PFCB-based polymer (BPVE) only dissolves in DME, again at low pressure, although BPVE drops out of solution as the system temperature is raised above ~40°C, whereas 6FVE remains in solution in DME for temperatures up to 90°C. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1736–1743, 2005

**Key words:** supercritical fluids; phase behavior; fluoropolymers; biodegradable; hexafluoroisopropylidene

## INTRODUCTION

There is a continued interest in using supercritical fluid (SCF) solvents to process polymers for a variety of potential market applications.<sup>1–3</sup> Typically, it takes kilobar pressures to dissolve a polymer in an SCF solvent, although many SCF solvents exhibit high solubility in the polymer-rich phase at pressures in the hundreds-of-bar range. Several research groups have applied a molecular approach to design polymer architectures that exhibit enhanced solubility in SCF solvents with special attention given to polymer solubility in CO<sub>2</sub>. Partially or fully fluorinating a hydrocarbon polymer lowers the pressures and temperatures needed to dissolve a given polymer in CO<sub>2</sub> due to specific interactions between CO<sub>2</sub> and the fluorine atoms. For example, high-pressure fluorine NMR has been used to elucidate specific CO<sub>2</sub>-fluorocarbon interactions in mixtures of low-molecular-weight fluorocarbons with CO<sub>2</sub><sup>4</sup> and in mixtures of fluorinated polymers and copolymers with CO<sub>2</sub>.<sup>5</sup> Ab initio molecular orbital energy calculations have been used to predict the formation of a favorable CO<sub>2</sub>-fluorine qua-

drupole-dipole interaction with a magnitude less than that typically observed for hydrogen bonding but greater than that found with dispersion type interactions.<sup>6</sup> Experimental studies have shown that partially or fully fluorinating a hydrocarbon polymer, such as poly(ethylene-co-propylene) (EP), does indeed make the resultant fluorinated EP polymer soluble in CO<sub>2</sub>. Hence, fluorinating a polymer enhances its solubility in supercritical CO<sub>2</sub> although the polymer also must have a measurable polar moment to ensure that the polymer dissolves at low pressures and at low temperatures.<sup>7–10</sup> In fact, Sarbu and co-workers synthesized poly(ether-carbonate) copolymers containing carbonyl groups to demonstrate that polymer polarity can be a controlling factor that determines whether the polymer dissolves in CO<sub>2</sub>.<sup>11</sup> Kazarian et al. used FTIR spectroscopy to show that carbonyl groups in the polymer exhibit specific interactions with CO<sub>2</sub> that result in reduced pressures needed to solubilize these polymers in CO<sub>2</sub>.<sup>12</sup> Shen et al. reported phase behavior measurements to confirm the favorable impact carbonyl groups have on polymer solubility in CO<sub>2</sub>.<sup>13</sup>

A different synthetic and phase behavior approach is taken in the present study to demonstrate the impact of polymer polarity, backbone architecture, and extent of fluorination on polymer solubility in CO<sub>2</sub>. The polymers of interest in the present study are

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**TABLE I**  
Structures of the Polymers Investigated in This Study

Sample	Chemical structure of the repeat unit
Poly(lactide 6F-Bis-A DGEBA)	
Poly(lactide 6H-Bis-A DGEBA)	
6FVE	
BPVE	

based on the ring-opening polymerization of lactide as this type of polymer can be created from renewable resources and biodegradable materials<sup>14,15</sup> and the lactides can be copolymerized to create a desired polymer architecture.<sup>16–21</sup> In the present study the synthesis strategy is to introduce aromatic moieties into the backbone of lactide-based polymers to create polyesters with enhanced hydrolytic and thermal characteristics. In an alternative synthesis approach, perfluorocyclobutyl (PFCB) aryl ether polymers are prepared by cyclodimerization of trifluorovinylether monomers that have potential applications in photonics.<sup>22</sup> PFCB polymers combine the engineering thermoplastics nature of polyaryl ethers with fluorinated segments and therefore exhibit excellent processability, optical transparency, high temperature performance, and low dielectric constants.<sup>23</sup> These synthetic schemes provide the opportunity to study the impact of different architectures on polymer solubility in SCF solvents.

The terpolymers are synthesized from 4,4'-hexafluoroisopropylidenediphenol (6F-Bis-A) or isopropylidenediphenol (6H-Bis-A) with lactide and diglycidyl

ether of bisphenol-A (DGEBA) to create 1:1:1 poly(lactide 6F-Bis-A DGEBA) or poly(lactide 6H-Bis-A DGEBA) terpolymers.<sup>20–21</sup> The synthesis of PFCB polymers 1,1-bis[4-[(trifluorovinyletheroxy)phenyl]hexafluoroisopropylidene(6FVE) and bis(trifluorovinyletheroxy)-biphenyl (BPVE) were described in previous papers.<sup>24,25</sup> Table I shows the structures of the terpolymers and the PFCB polymers (6FVE and BPVE) synthesized for the phase behavior studies presented here.<sup>43</sup> Table II lists the physical properties of the polymers used in this study.

The fluorinated methyl groups in the backbone of the poly(lactide 6F-Bis-A DGEBA) terpolymer and the PFCB polymers are expected to have a large effect on chain conformation caused by the trifluoromethyl groups. The bulky trifluoromethyl (CF<sub>3</sub>) groups also disrupt any electronic resonance that may exist between adjacent aromatic groups. In addition, the CF<sub>3</sub> groups are expected to create local dipole moments in this part of the repeat group. It should also be noted

**TABLE II**  
Physical Properties of the Polymers Used in This Study

	Poly(lactide 6F-Bis-A DGEBA)	Poly(lactide 6H-Bis-A DGEBA)	6FVE	BPVE
$M_w$ (g/mol)	32,100	16,000	62,600	78,800
Polydispersity ( $M_w/M_n$ )	1.9	1.8	2.0	2.1
$T_g$ (°C)	85	76 <sup>21</sup>	113	144
$T_m$ (°C)	—	—	190	—

**TABLE III**  
Physical Properties of Solvents Used in This Study.<sup>40,41</sup>

Solvent	$T_c$ (°C)	$P_c$ (bar)	Polarizability (Å <sup>3</sup> )	Dipole moment (D)
CO <sub>2</sub>	31.0	73.8	2.65	—
Propane	96.7	42.5	6.26	0.1
Dimethyl ether	126.8	53.0	5.22	1.3

Note. CO<sub>2</sub> has a quadrupole moment of  $-4.3 \times 10^{-26}$  erg<sup>1/2</sup> cm<sup>5/2</sup>.

that partially fluorinating a hydrocarbon polymer can have a large effect on the solubility of the polymer in CO<sub>2</sub>. For example, McHugh et al.<sup>9</sup> showed that incorporating difluorocarbene (CF<sub>2</sub>) into a polybutadiene or polyisoprene repeat group yields a gemdifluorocyclopropane repeat group that contains fluorine and has a significant dipole moment. Both the fluorinated isoprene and the butadiene polymers dissolve in CO<sub>2</sub>, but pressures in excess of 1000 bar are needed to obtain a single phase. The cloud-point curves for these fluorinated polymers shift to lower pressures and temperatures as the number of CF<sub>2</sub> groups increases in a repeat unit.

Table III shows the properties of CO<sub>2</sub>, propane, and dimethyl ether (DME) which are the three representative SCF solvents used in this study. Although CO<sub>2</sub> is the preferred SCF solvent for most applications, CO<sub>2</sub> is a very poor quality solvent for lactide-derived polymers.<sup>26</sup> More polar SCF solvents readily dissolve lactide-derived polymers;<sup>26,27</sup> hence the solvent quality of DME, which has a dipole moment, is compared to that of CO<sub>2</sub> for the same polymers. Nonpolar propane is used as a reference SCF solvent since it is an excellent solvent for nonpolar hydrocarbon polymers.<sup>1,8</sup>

## EXPERIMENTAL

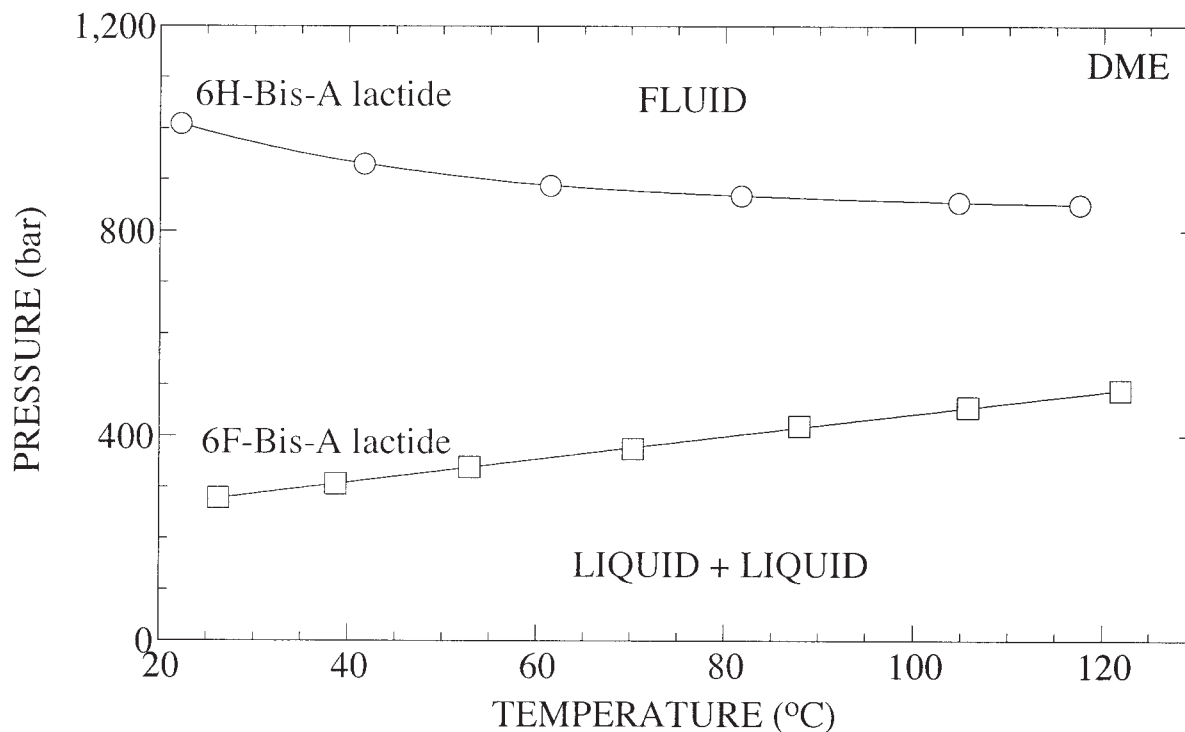
Described elsewhere are the equipment and techniques used to obtain cloud points.<sup>7,28</sup> Fixed polymer concentrations of approximately 2 to 5 wt % are used for each cloud-point curve since this concentration range is expected to be close to the maximum in the pressure-composition isotherms.<sup>7,29-31</sup> The cloud-point pressure is defined as the point at which the solution becomes so opaque that it is no longer possible to see the stir bar in solution. These cloud points have been compared in our laboratories to those obtained using a laser light set-up where the phase transition is identified with a 90% drop in light transmitted through the solution. Both methods gave identical results within the reproducibility of the data. Cloud points with a scatter of approximately  $\pm 5.0$  bar are reproduced two to three times at each temperature that is held to within  $\pm 0.3^\circ\text{C}$ . Solution density data are also determined at the phase transition using a piston

displacement technique.<sup>32-34</sup> Solution densities are calculated knowing the amount of material loaded into the cell and the volume of the cell at a given pressure and temperature by detecting the location of the internal piston with an LVDT coil (Lucas Schaevitz Co., Model 2000-HR) that fits around a 1.43-cm high-pressure tube and tracks the magnetic tip of a steel rod connected to the piston. The solution densities have an accumulated uncertainty of  $\pm 1.5\%$ .<sup>34</sup>

## RESULTS AND DISCUSSION

Both poly(lactide 6F-Bis-A DGEBA) and poly(lactide 6H-Bis-A DGEBA) terpolymers dissolve in acetone, but neither one dissolves in CO<sub>2</sub> to temperatures as high as 150°C and pressures of 2000 bar. The semifluorinated terpolymer, poly(lactide 6F-Bis-A DGEBA), does not dissolve in CO<sub>2</sub> when  $\sim 10$  wt % acetone is used as a cosolvent even at 170°C and 2275 bar. Although it has been argued that the carbonyl group promotes polymer solubility in CO<sub>2</sub>, it is likely that lactide carbonyl-CO<sub>2</sub> interactions, favorable for dissolving the polymer, do not compensate for interpolymer hydrogen bonding among hydroxyl, ether, and carbonyl groups. The nonfluorinated, hydrocarbon poly(lactide 6H-Bis-A DGEBA) terpolymer does not dissolve in pure propane to temperatures as high as 150°C and pressures of 1900 bar. Likewise, the semifluorinated poly(lactide 6F-Bis-A DGEBA) terpolymer does not dissolve in pure propane even at 150°C and 1900 bar. However, both terpolymers dissolve in DME.

Figure 1 shows that the poly(lactide 6H-Bis-A DGEBA) terpolymer dissolves in DME at pressures greater than 1000 bar at room temperature. The cloud-point pressure for this mixture decreases slightly as the temperature is increased to 120°C and as polymer polar-polar interactions are reduced. The semifluorinated poly(lactide 6F-Bis-A DGEBA) terpolymer also dissolves in DME but at much lower pressures than the poly(lactide 6H-Bis-A DGEBA)-DME mixture. It is interesting that the cloud-point curve for the poly(lactide 6F-Bis-A DGEBA)-DME mixture has a slightly positive slope, which suggests that increasing the temperature reduces favorable poly(lactide 6H-Bis-A DGEBA)-DME interactions. The difference in cloud-point pressures for these polymers is  $\sim 700$  bar at room temperature and  $\sim 350$  bar at 120°C, which is quite impressive considering that the only difference in polymer architecture is the fluorination of the methyl groups on the isopropylidene phenol portion of the repeat group. The difference in cloud-point pressures for these two binary mixtures is not caused by a molecular weight effect since the semifluorinated polymer has a higher molecular weight than the nonfluorinated polymer. The steric hindrance caused by the CF<sub>3</sub> groups reduces longer-range interactions similar



**Figure 1** Comparison of the phase behavior of poly(lactide 6H-Bis-A DGEBA) (open circles) and poly(lactide 6F-Bis-A DGEBA) (open squares) in dimethyl ether (DME) at ~3 wt % polymer concentration for each solution.

to those found with polymers that form liquid crystals.<sup>35–37</sup> The bulky  $\text{CF}_3$  groups in the semifluorinated polymer reduce chain–chain interactions more than the  $\text{CH}_3$  groups, resulting in better solubility of this polymer in DME. This is not altogether surprising given that the steric size of a  $\text{CF}_3$  group is similar to that of a hydrocarbon isopropyl group.<sup>38</sup> The solution densities at the cloud points for these two systems are given in Table IV along with cloud-point data. In both cases the density decreases with increasing temperature although the density of the hydrocarbon polymer–DME solution is greater than that of the semifluorinated polymer–DME solution, likely due to the higher transition pressures.

Table V lists the cloud-points, bubble points, three-phase liquid + liquid + vapor (LLV) points, and solution densities at these points for the 6FVE–SCF and BPVE–SCF solvent mixtures considered in this study. Figure 2 shows a comparison of the phase behavior of the 6FVE– $\text{CO}_2$  system with two other polymer– $\text{CO}_2$  mixtures: fluorinated poly(isoprene) (FPI) with 90% of the repeat groups containing a gem-difluorocyclopropane repeat unit and poly(tetrafluoroethylene-*co*-65 mol % 4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole) (Teflon AF 1600,  $T_g = 160^\circ\text{C}$ ). The 6FVE– $\text{CO}_2$  curve exhibits a modest pressure minimum at approximately  $62^\circ\text{C}$  at a pressure of ~825 bar. At temperatures less than  $62^\circ\text{C}$  the cloud-point curve begins to increase slightly in pressure due to

strong copolymer self interactions that do not favor solubility, compared to copolymer– $\text{CO}_2$  cross interactions that favor polymer solubility. The higher pressure needed to dissolve 6FVE in  $\text{CO}_2$  relative to Teflon AF 1600 is likely due to the stiffer backbone of 6FVE, which promotes longer-range chain–chain interactions. Note that the Teflon AF– $\text{CO}_2$  cloud-point curve exhibits a sharp pressure minimum at  $\sim 67^\circ\text{C}$  whereas

**TABLE IV**  
Cloud-Point (CP) Data for the 3.0 wt % Poly(lactide 6H-Bis-A DGEBA)–DME and 2.8 wt% poly(lactide 6F-Bis-A DGEBA)–DME Mixtures

System	$T$ (°C)	$P$ (bar)	Density (g/cm <sup>3</sup> )
Poly(lactide 6H-Bis-A DGEBA)–DME	22.2	1009.2	0.767
	41.6	931.2	0.749
	61.4	888.9	0.733
	81.7	869.0	0.719
	104.7	856.1	0.703
	117.5	851.6	0.694
Poly(lactide 6F-Bis-A DGEBA)–DME	26.3	279.0	0.713
	38.7	306.9	0.702
	52.9	339.3	0.690
	70.3	375.2	0.675
	88.0	419.7	0.663
	105.8	455.9	0.650
	121.9	489.4	0.640

TABLE V  
Cloud-Point (CP), Bubble-Point (BP), and Liquid  
+ Liquid + Vapor (LLV) Data for the 2.8 wt % 6FVE-  
CO<sub>2</sub>, 5.1 wt% 6FVE-DME, 3.6 wt% 6FVE-propane,  
and 4.7 wt% BPVE-DME Mixtures

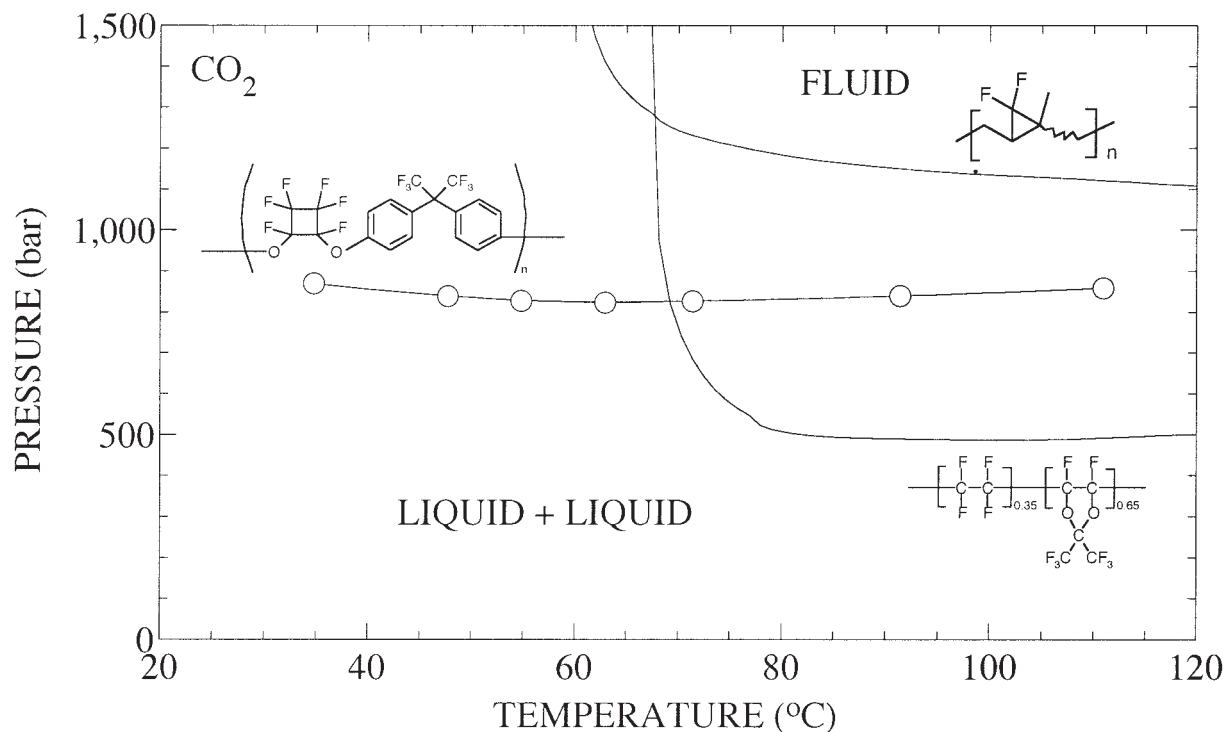
System	<i>T</i> (°C)	<i>P</i> (bar)	Transition	Density (g/cm <sup>3</sup> )	
6FVE-CO <sub>2</sub>	34.8	870.0	CP	1.110	
	47.7	839.7	CP	1.088	
	54.8	828.3	CP	1.065	
	62.9	824.1	CP	1.055	
	71.4	826.9	CP	1.032	
	91.4	840.0	CP	0.998	
	110.9	859.3	CP	0.967	
	6FVE-DME	54.1	13.6	BP	0.649
		67.0	18.1	BP	0.629
83.4		25.2	BP	0.591	
90.5		28.6	BP	0.574	
93.1		30.0	CP	0.568	
95.9		35.5	CP	0.571	
99.8		49.9	CP	0.568	
102.1		53.1	CP	0.568	
112.7		83.4	CP	0.560	
126.5		113.6	CP	0.555	
133.8		129.3	CP	0.553	
96.7		32.8	LLV	0.519	
103.7		36.2	LLV	0.503	
110.7		41.7	LLV	0.501	
120.2	48.6	LLV	0.428		
128.6	55.2	LLV	0.354		
6FVE-propane	104.6	1,291.8	CP	0.624	
	107.2	1,220.3	CP	0.617	
	113.1	1,096.3	CP	0.606	
	126.4	849.2	CP	0.577	
	136.1	759.9	CP	0.562	
BPVE-DME	22.2	5.5	BP	0.673	
	38.7	9.0	BP	0.654	
	41.4	9.7	BP	0.656	
	43.0	15.2	CP	0.658	
	53.5	58.8	CP	0.655	
	70.0	119.3	CP	0.641	
	84.5	173.7	CP	0.638	
	109.4	252.4	CP	0.625	
	131.0	311.0	CP	0.613	
	42.7	9.7	LLV	0.546	
	53.6	12.8	LLV	0.556	
	87.3	25.9	LLV	0.505	
	111.0	39.7	LLV	0.489	
128.8	53.8	LLV	0.355		

the 6FVE curve exhibits only a very modest pressure minimum at roughly the same temperature. Teflon AF 1600 has a  $T_g$  of 160°C, which suggests that at temperatures near 65°C the energy penalty to adopt many chain conformations now dominates polymer-CO<sub>2</sub> enthalpic interactions so that the polymer drops out of solution due to an unfavorable entropy of mixing.

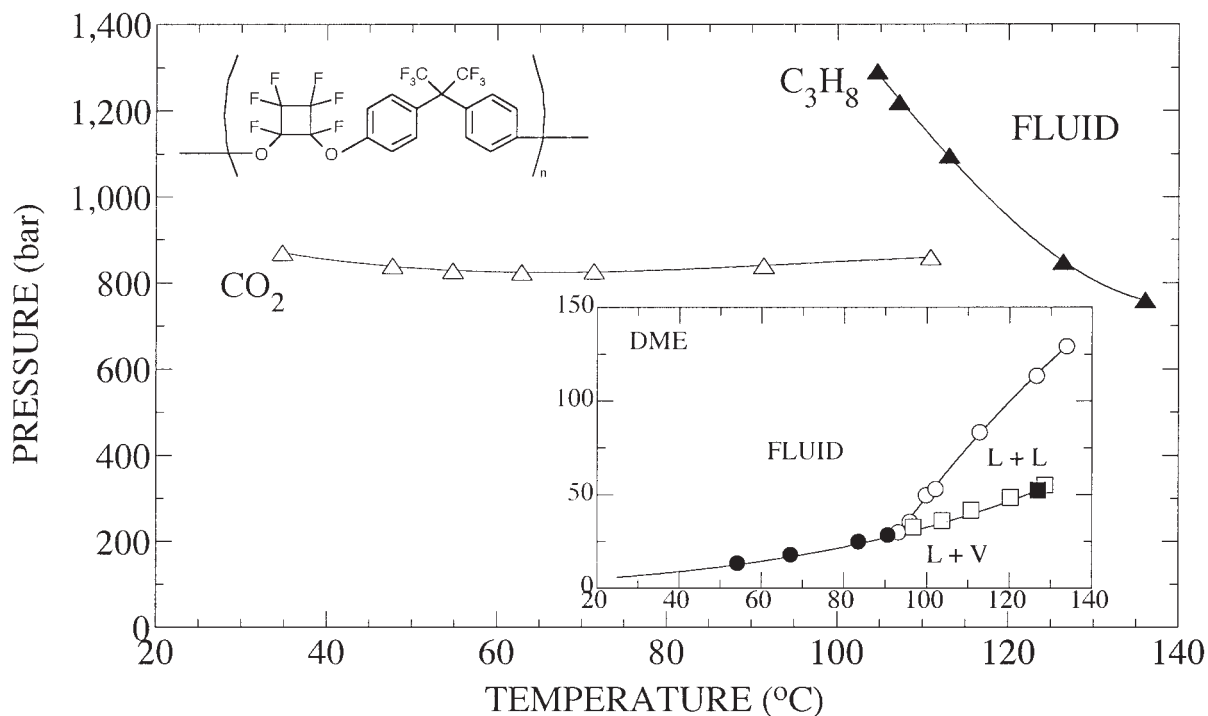
The impact of solvent quality is demonstrated in Figure 3, which shows a comparison of the phase behavior of 6FVE in propane, CO<sub>2</sub>, and DME. Note that 6FVE dissolves in nonpolar propane at temperatures in excess of ~100°C where polymer-polymer

polar interactions are reduced. The cloud-point pressure increases with decreasing temperature for this mixture and, in fact, it is not possible to obtain a single phase at temperatures below 100°C even for pressures in excess of 2000 bar. Polar interactions scale with inverse temperature; hence the interchange energy<sup>39</sup> favors polymer-polymer interactions rather than polymer-solvent interactions as the temperature is lowered, which results in a sharp rise in pressure to maintain a single phase. The shape of the 6FVE-propane cloud-point curve is consistent with the curves exhibited for binary polymer-SCF solvent mixtures where one component is polar and the other component is nonpolar.<sup>8</sup> The impact of solvent polarity is evident for the 6FVE-CO<sub>2</sub> curve, which is essentially flat over a temperature range of 30 to 110°C, which suggests that polymer-polymer polar interactions and CO<sub>2</sub>-CO<sub>2</sub> quadrupolar interactions are balanced with polymer-CO<sub>2</sub>, polar-quadrupolar interactions as the temperature is lowered. The inset diagram in Figure 3 shows that the 6FVE-DME phase behavior is at much lower pressures than that observed with propane or CO<sub>2</sub>. It is not surprising that 6FVE readily dissolves in DME, which is a polar solvent with a dipole moment of 1.3 D, since 6FVE dissolves in liquid acetone, which has a dipole moment of 2.8 D. DME is such a good solvent that the cloud-point curve is actually a bubble-point curve at temperatures below 54°C where the bubble-point curve superposes onto the vapor pressure curve of pure DME. The cloud-point curve for the 6FVE-DME system exhibits a positive slope as the temperature is increased from 90 to 140°C although the cloud-point pressures remain below 138 bar. This mixture also exhibits three-phase, LLV equilibria at temperatures from 40 to 130°C where the LLV curve superposes onto the vapor pressure curve for pure DME.

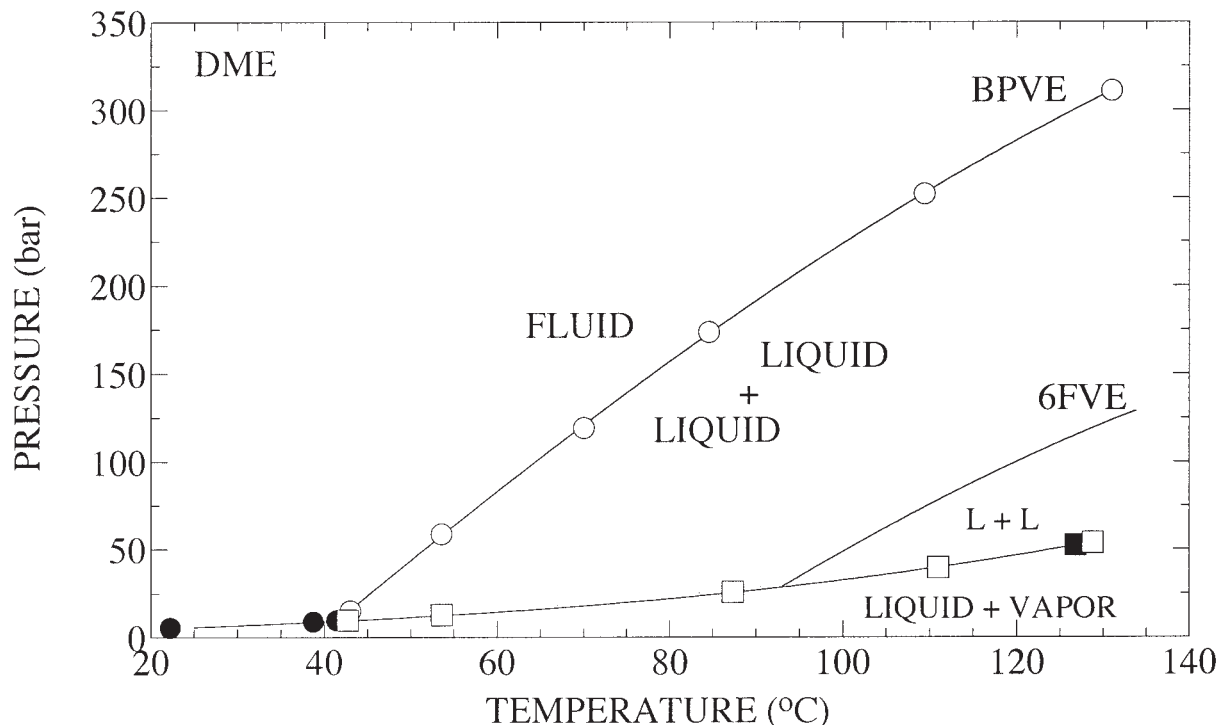
BPVE does not dissolve in CO<sub>2</sub> or in propane even to temperatures in excess of 150°C and pressures of 2000 bar. It is important to note that 6FVE melts at ~190°C whereas BPVE does not exhibit a melting point. However, BPVE does dissolve in DME. Figure 4 shows that the BPVE cloud-point curve is parallel to the 6FVE curve. Also, the BPVE cloud-point curve intersects the bubble-point curve at ~40°C, which is 60°C lower than that observed for the 6FVE system. Hence, the BPVE-DME system exhibits a much larger region of immiscibility than the 6FVE-DME system. The addition of the 4,4'-hexafluoroisopropylidene group affects the types and strengths of intermolecular interactions between DME and a polymer repeat group as well as affecting the conformation of the polymer chain due to steric hindrance. As noted earlier, the CF<sub>3</sub> groups reduce longer-range interactions.<sup>35-37</sup> Once again, the bubble points and LLV points for the mixture essentially superposes onto the vapor pressure curve of DME.



**Figure 2** Comparison of the phase behavior of the 2.8 wt % 6FVE-CO<sub>2</sub> system (open circles) with the 2.0 wt % FPI (M<sub>w</sub> = 48,000; 90 mol % CF<sub>2</sub> in the backbone)-CO<sub>2</sub><sup>9</sup> and 5.0 wt % Teflon AF 1600 (M<sub>w</sub> ~ 400,000; T<sub>g</sub> ~ 160°C)-CO<sub>2</sub><sup>42</sup> systems. Smooth curves are used to represent the FPI and Teflon AF data.



**Figure 3** Comparison of the phase behavior of 6FVE in propane (filled triangles), CO<sub>2</sub> (open triangles), and DME. The DME data are given in the inset graph where open circles are cloud-point transitions, filled circles are fluid → liquid + vapor bubble-point transitions, open squares are liquid + liquid → liquid + liquid + vapor transitions, and the filled square is the critical point of DME. The vapor pressure curve of pure DME is the solid line through the bubble-point and three-phase transitions.



**Figure 4** Comparison of the phase behavior of 6FVE (curves only) and BPVE (open circles are cloud-point transitions, filled circles are fluid  $\rightarrow$  liquid + vapor bubble-point transitions, open squares are liquid + liquid  $\rightarrow$  liquid + liquid + vapor transitions, and the filled square is the critical point of DME.) The vapor pressure curve of pure DME is the solid line through the BPVE-DME bubble-points and the DME critical point.

## CONCLUSIONS

It is now well documented that partially or fully fluorinating a hydrocarbon polymer lowers the pressures and temperatures needed to dissolve a given polymer in  $\text{CO}_2$  due to specific interactions between  $\text{CO}_2$  and the fluorine atoms. However, the experimental evidence also strongly suggests that the polymer must exhibit some polar character to make it soluble in supercritical  $\text{CO}_2$ , especially at low temperatures. The polymers considered in the present study, poly(lactide 6F-Bis-A DGEBA), poly(lactide 6H-Bis-A DGEBA), 6FVE, and BPVE, have rather stiff backbones that make them difficult to dissolve in any SCF solvent. However, the addition of 6F groups in the chain backbone imposes an important conformational effect on the polymer that enhances solubility. The steric hindrance caused by the 6F groups minimizes chain-chain interactions and reduces longer-range interactions similar to those found with polymers that form liquid crystals. It is interesting that the steric size of a  $\text{CF}_3$  group is similar to that of a hydrocarbon isopropyl group, which means that the addition of a  $\text{CF}_3$  group can have a significant effect on solubility. The steric hindrance of the  $\text{CF}_3$  groups also disrupts any electronic resonance that might occur between adjacent aromatic groups, which will increase poly-

mer solubility levels in a given solvent. Further work is in progress to determine the most efficacious combination of repeat groups to lower the pressures needed to dissolve a polymer in supercritical  $\text{CO}_2$ .

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43. The PCFB Polymers and Intermediates are now commercially available from Tetramer Technologies, and are distributed by Oakwood Chemicals, Inc., Columbia, SC.