

# Enhanced Solubility of Polyvinyl Esters in $scCO_2$ by Means of Vinyl Trifluorobutyrate Monomer

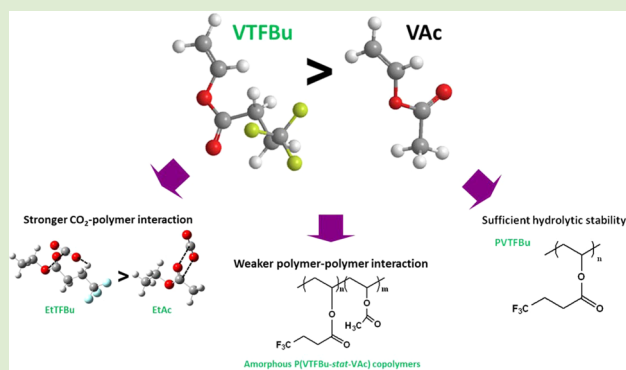
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## Supporting Information

**ABSTRACT:** The novel monomer, vinyl trifluorobutyrate (VTFBu), when polymerized in a controlled fashion by RAFT/MADIX polymerization with a xanthate transfer agent, yields poly(vinyl ester)s with improved solubility in supercritical carbon dioxide. The thermodynamic parameters controlling the solubility of VTFBu/vinyl acetate statistical copolymers are discussed based on ab initio calculations, glass transition temperatures of the copolymers, and surface tension measurements. The enhanced solubility of this new class of  $CO_2$ -philic polymer combined with its good chemical stability render it attractive for the preparation of next-generation macromolecular surfactants for the formation of water- $scCO_2$  emulsions.



The replacement of conventional organic solvents has been identified as a key step in reducing the environmental cost of chemical synthesis, processing, and separations.<sup>1</sup> Supercritical carbon dioxide ( $scCO_2$ ) is a promising environmentally benign solvent that provides low flammability, toxicity, cost, reactivity at an accessible critical temperature, and pressure (31.1 °C, 73 bar). For most compounds, however,  $scCO_2$  is a poor solvent because of its very low dielectric constant and polarizability: only relatively nonpolar low molecular weight compounds and a few fluorinated or silicone polymers show significant solubility. This drawback can be overcome by the use of water-in- $scCO_2$  or  $scCO_2$ -in-water emulsions or microemulsions, which allow high concentrations of polar, ionic, and nonpolar molecules to be solubilized within the dispersed and continuous phases. Surfactants are necessary to stabilize these emulsions. For this application, amphiphilic block copolymers are of interest as they offer better anchoring and steric stabilization at interfaces than low molar mass surfactants.

While fluorinated polyacrylates, perfluoroalkylethers and polysiloxanes are the current  $CO_2$ -philic materials of choice,<sup>2</sup> poly(vinyl ester)s combine moderate  $CO_2$ -philicity with favorable price and toxicity. Low molecular weight ( $M_n = 2060$  g/mol) poly(vinyl acetate) (PVAc) is soluble at 5 wt % in  $CO_2$  at 374 bar and 25 °C. The cloud point pressure and solubility are strongly dependent on the chain length, however, which limits the usefulness of higher molecular-weight PVAc.<sup>3,4</sup> Different strategies have been used to enhance poly(vinyl ester) solubility, such as modification of the chain end with a  $CO_2$ -philic fluorinated segment<sup>4</sup> or copolymerization of vinyl acetate (VAc) with a comonomer. In the latter strategy, incorporation

of repulsive or bulky pendant groups increases  $CO_2$  solubility by enhancing entropic contributions and decreasing polymer-polymer interactions. A large palette of comonomers are available by varying the vinyl ester group, allowing the incorporation of linear aliphatic or branched structures<sup>5-7</sup> and fluorinated moieties.<sup>8-10</sup> Thus, the cloud point pressure ( $P_c$ ) of a 0.2 wt % solution of PVAc ( $M_n = 4000$  g/mol;  $P_c = 280$  bar at 40 °C) falls dramatically to 222 or 177 bar for statistical copolymers containing 1-(trifluoromethyl) vinyl acetate ( $CF_3VAc/VAc$ , 33/67,  $P_c = 222$  bar at 40 °C)<sup>9</sup> or vinyl trifluoroacetate (VTFAc/VAc, 50/50,  $P_c = 177$  bar at 40 °C).<sup>10</sup> While promising, these monomers still present some obstacles to higher solubility enhancement: (i) as determined by DFT calculations, the monomers reduced polymer-polymer interactions but simultaneously decreased polymer- $CO_2$  interactions, (ii) VTFAc-based polymers are chemically unstable, with a particularly high propensity to hydrolysis, which prevents their use as in water/ $CO_2$  systems, and (iii) further increases in the quantity of fluorinated monomers induced a tendency to form semicrystalline polymer (i.e., to increase polymer-polymer interactions) and therefore lowered polymer solubility. Thus, in order to further increase the solubility of poly(vinyl ester) in  $scCO_2$  while retaining its potential as an emulsion stabilizer, comonomers that can increase polymer- $CO_2$  interactions, keep polymer-polymer interactions lower than that of VAc, favor entropy of mixing,

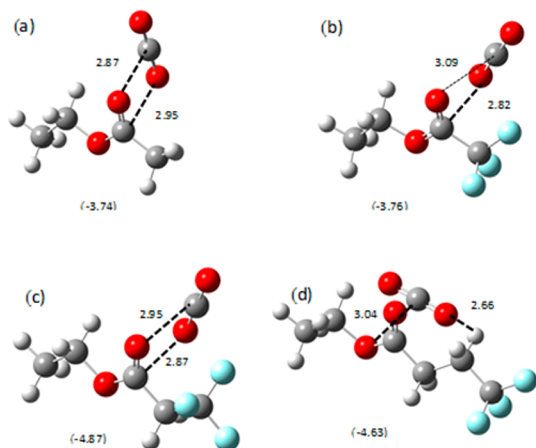
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and resist hydrolysis are needed. These considerations prompted us to investigate the effect of inserting one or two CH<sub>2</sub> groups between the carbonyl and CF<sub>3</sub> groups.

Ab initio calculations were first performed on ethyl acetate (EtAc), ethyl trifluoroacetate (EtTFAC), ethyl 3,3,3-trifluoropropionate (EtTFPr) and ethyl 4,4,4-trifluorobutyrate (EtTFBu) model structures. They are representative of the main functional groups of the backbone of PVAc, PVTFAc, polyvinyl trifluoropropionate (PVTfPr), and polyvinyl trifluorobutyrate (PVTfBu). The optimized equilibrium geometries of these model structures and their complexes with CO<sub>2</sub> are reported in Figure 1. Electron donor–acceptor (EDA) complexes of CO<sub>2</sub>



**Figure 1.** Minimum energy structures at the MP2/aug-cc-pVDZ computational level for (a) EtAc–CO<sub>2</sub>, (b) EtTFAC–CO<sub>2</sub>, (c) EtTFPr–CO<sub>2</sub>, and (d) EtTFBu–CO<sub>2</sub> complexes. The stabilization energies (corrected for zero point energy) for each complex are reported in kcal/mol. Bond lengths of interest are displayed in Ångström (dashed lines).

with carbonyl-containing compounds are mainly stabilized by dispersion interactions that are not well described by density functional theory methods.<sup>11</sup> Thus, ab initio methods have been preferred for these calculations.

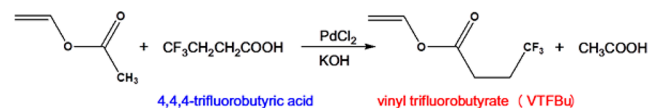
The minimum energy structure of the CO<sub>2</sub>–EtAc complex corresponds to the unconventional cyclic structure reported recently for acetone–CO<sub>2</sub> complexes, where the CO<sub>2</sub> molecule is found to be parallel to the C=O of the acetate group. In this configuration, a reciprocal EDA interaction occurs between CO<sub>2</sub> and the carbonyl group in which each acts simultaneously as electron donor and acceptor. A similar geometry is observed for CO<sub>2</sub>–EtTFAC that is a model for the CO<sub>2</sub>–PVTFAc interaction. In this case, charge transfer mainly occurs from the oxygen atom of CO<sub>2</sub> to the carbon atom of the EtTFAC carbonyl group.

A similar interaction has been reported for fluorinated acetone.<sup>12</sup> Stabilization energies for both complexes are nearly equal at –3.74 and –3.76 kcal/mol, respectively. While the CO<sub>2</sub>–EtTFPr complex representative of CO<sub>2</sub>–PVTfPr also shows a cyclic structure, the stabilization energy of CO<sub>2</sub>–EtTFPr was significantly improved (–4.87 kcal/mol). Finally, for the CO<sub>2</sub>–EtTFBu complex representative of CO<sub>2</sub>–PVTfBu, CO<sub>2</sub> is found beside the carbonyl group where it interacts with the noncarbonyl oxygen atom. There is also evidence for a cooperative hydrogen bond between a hydrogen atom of the methylene in the  $\alpha$ -position of the CF<sub>3</sub> group and an oxygen atom of CO<sub>2</sub>. The stabilization energy of this

complex is found to be –4.63 kcal/mol. Thus, CO<sub>2</sub>–solute interactions were increased significantly by adding one or two CH<sub>2</sub> groups between the carbonyl and CF<sub>3</sub> groups. Therefore, by inserting vinyl trifluoropropionate (VTFPr) or vinyl trifluorobutyrate (VTFBu) units into a PVAc backbone, we expect polymer–solvent interactions to be favored and CO<sub>2</sub> solubility to be enhanced. Furthermore, the addition of one or two methylene spacers separates the electron-withdrawing CF<sub>3</sub> group from the ester group, improving its hydrolytic stability compared to VTFAC.

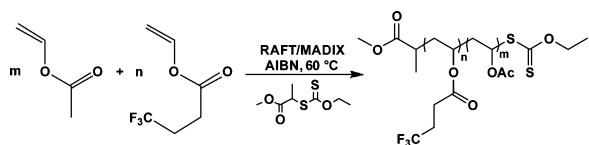
Numerous vinyl esters have been synthesized and studied in free-radical polymerization,<sup>13,22</sup> but surprisingly, the synthesis of VTFPr and VTFBu monomers has never been described. Vinyl esters are prepared through direct addition of carboxylic acids to terminal alkynes catalyzed by mercury salts,<sup>14</sup> Ru, Rh, or Ir complexes,<sup>15</sup> or via transvinylation<sup>16</sup> of carboxylic acids with vinyl donors by using Hg(II)<sup>17</sup> and Pd(II)<sup>18,19</sup> materials. The two novel vinyl fluoroalkylates were prepared through transvinylation of fluorinated carboxylic acid (3,3,3-trifluoropropionic acid for VTFPr or 4,4,4-trifluorobutyric acid for VTFBu, Scheme 1, respectively) with VAc by using palladium

### Scheme 1. Synthetic Procedure for the Synthesis of Vinyl Trifluorobutyrate (VTFBu)



dichloride (PdCl<sub>2</sub>), avoiding the use of toxic mercury salts. When a 2-fold excess of VAc relative 3,3,3-trifluoropropionic acid was used at 60 °C with 5% mol PdCl<sub>2</sub>, VTFPr was obtained (39 wt % relative to the starting acid) after 16 h of reaction, as evidenced by NMR. Unfortunately, our attempts to separate VTFPr from VAc failed because the physicochemical characteristics of the two monomers are too similar for efficient purification by distillation or chromatography. VTFBu was obtained using a similar approach from 4,4,4-trifluorobutyric acid and could be separated from VAc by column chromatography (see SI for experimental details and VTFBu characterization). Prior to the study of the phase behavior of VTFBu-containing polymers in scCO<sub>2</sub>, it was necessary to evaluate its reactivity in free-radical polymerization.

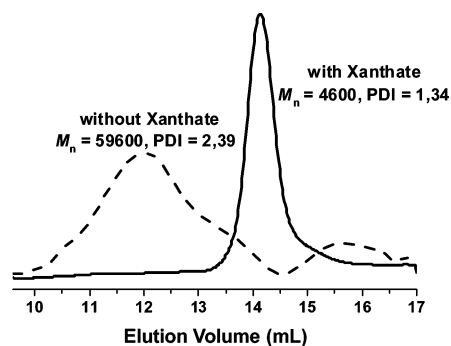
In order to thoroughly study the structure–solubility relationship of polymers in scCO<sub>2</sub>, an access to narrowly dispersed polymer samples with controlled number-average molar masses ( $M_n$ ) is of first importance. Reversible addition–fragmentation chain-transfer (RAFT)<sup>20</sup> macromolecular design via the interchange of xanthates (MADIX)<sup>21</sup> polymerization is undoubtedly the most convenient technique for producing well-defined poly(vinyl esters)<sup>4,8,10</sup> through the introduction of a xanthate chain-transfer agent.<sup>22</sup> Therefore, we considered RAFT/MADIX homopolymerization of VTFBu and its statistical copolymerization with VAc (Scheme 2). The RAFT/MADIX homopolymerization of VTFBu was carried out at 60 °C in ethyl acetate with AIBN initiator, using 2-mercaptopropionic acid methyl ester O-ethyl dithiocarbonate (XA1) as the xanthate transfer agent (Scheme 2 and experimental section of SI) at a concentration corresponding to a theoretical  $M_n$  of 4600 g/mol. A nearly quantitative conversion of 97% was obtained after 24 h of reaction. The experimental  $M_n$  of the resulting PVTfBu was in excellent agreement with the theoretical  $M_n$ , as confirmed by SEC (Table

**Scheme 2. Experimental Procedure for the RAFT/MADIX Synthesis of P(VAc-stat-VTFBu)**


1) and  $^1\text{H}$  NMR spectroscopy (Figure S4 and Table S1), and its dispersity was low ( $\bar{D} = 1.24$ ). The presence of a characteristic  $^1\text{H}$  NMR signal at 4.64 ppm corresponding to two protons of the O-ethyl group of the xanthate and the signal of the methine proton of the terminal VTFBu unit at 6.63 ppm (Figure S5 and Table S3 in SI) provided additional evidence of the successful mediation of the polymerization of VTFBu by XA1.

For comparison, a bulk statistical copolymerization of VAc and VTFBu with a 50:50 molar feed ratio was performed with an AIBN concentration of 1 mol % relative to comonomers, with and without XA1. As shown in Figure 2, very distinct SEC profiles were obtained with high  $M_n$  (59600 g/mol) and broad molar mass distribution ( $\bar{D} = 2.4$ ) without XA1 (see run 8 of Table S1), whereas controlled  $M_n$  and a dispersity of 1.34, characteristic of an efficient RAFT/MADIX process, were obtained when using XA1 (see run 4 of Table S1). Building on this result, a library of VTFBu/VAc statistical copolymers of varying composition, targeting an  $M_n$  close to 4000 g/mol (see runs 2–6 of Table 1), was synthesized. The control of the polymerizations was evidenced by the excellent match between the theoretical  $M_n$  and the experimental  $M_n$  obtained by SEC (Table 1) and also NMR (Table S1 in SI). The dispersity remained relatively low and constant ( $1.31 < \bar{D} < 1.39$ ) between 9 mol % and 100% of VAc in the copolymer (see Table S1).

In order to have an idea of the microstructure of the formed VTFBu/VAc copolymers, the copolymerization of the two monomers was followed by online  $^1\text{H}$  NMR spectroscopy under RAFT/MADIX conditions for two initial comonomer compositions, VTFBu/VAc = 50/50 and 75/25 mol %. The conversion of the two monomers versus time for the two comonomer feeds is represented in Figures S8 and S9 in SI. Then the reactivity ratios were determined by fitting the integrated form of the copolymer composition equation to the



**Figure 2.** Overlays of SEC chromatograms (RI detection, in THF) for the conventional free-radical copolymerization of VAc and VTFBu with a molar ratio of 50:50 (dashed line) and the corresponding RAFT/MADIX copolymerization (solid line).

monomer feed composition versus conversion data using the visualization of the sum of squares method developed by van den Brink et al.,<sup>23</sup> assuming non-negligible errors in both variables. This procedure gave a point estimate of 1.34 for  $r_{\text{VTFBu}}$  and 1.16 for  $r_{\text{VAc}}$  with a 95% joint confidence region spanning the range of 1.21–1.48 for  $r_{\text{VTFBu}}$  and 1.08–1.26 for  $r_{\text{VAc}}$  (see Figure S10). After a long induction period<sup>24</sup> (180 and 320 mn for the 50/50 and 75/25 compositions, respectively), the polymerization reached 90% in 3 h for  $f_{\text{VTFBu}} = 0.5$  and approximately 6 h for  $f_{\text{VTFBu}} = 0.75$ . Most importantly, the two monomers are nearly isoreactive, thereby ensuring that negligible compositional drift is present along the polymer chains.

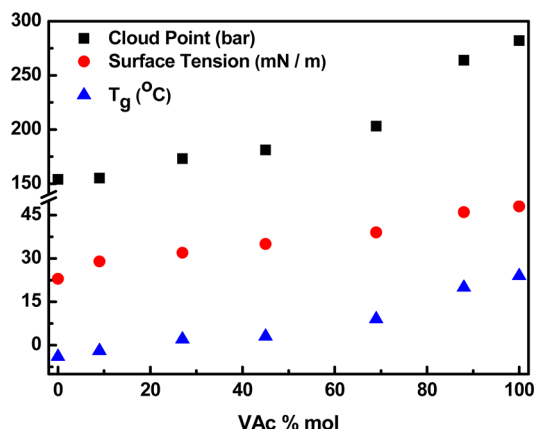
The solubility of the resulting copolymers was evaluated by cloud-point measurement with 0.2 wt % of sample in  $\text{sCO}_2$  at 40 °C in order to allow a comparison with literature results. A PVAc sample of 4600 g/mol exhibited a cloud point at 282 bar (Table 1, run 7). With gradual incorporation of 12–100 mol % of VTFBu units into the polymer chains (runs 1–6),  $P_c$  dramatically decreased from 264 to 154 bar, which means the introduction of VTFBu units into PVAc can greatly improve the solubility of the polymer as expected from the enhanced polymer/ $\text{CO}_2$  interaction. Interestingly the fluorine-free copolymer  $\text{P}(\text{VBu}_{50}\text{-stat-VAc}_{50})$  gave  $P_c = 269$  bar under the same conditions, therefore underlying the positive effect on solubility of the fluorinated counterpart (Table 1, run 8).<sup>25</sup>

**Table 1. Experimental Results for the Solubility and Physical Properties of the Vinyl Ester Statistical Copolymers<sup>a</sup>**

run	sample	$M_n$ (g/mol)		$\bar{D}^c$	$P_{\text{cloud point}}^d$ (bar)	$\Delta P_{\text{cloud}}^e$ (bar)	contact angle <sup>f</sup> (deg)	surface tension (mN m <sup>-1</sup> )	$T_g$ (°C)
		NMR <sup>b</sup>	SEC <sup>c</sup>						
1	PVTFBu	4500	4100	1.24	154	128	99	23	-4
2	P(VTFBu <sub>91</sub> -stat-VAc <sub>9</sub> )	4300	3200	1.37	155	127	91	29	-2
3	P(VTFBu <sub>73</sub> -stat-VAc <sub>27</sub> )	4000	4800	1.31	173	109	86	32	2
4	P(VTFBu <sub>55</sub> -stat-VAc <sub>45</sub> )	3900	4600	1.34	181	101	80	35	3
5	P(VTFBu <sub>31</sub> -stat-VAc <sub>69</sub> )	4500	4800	1.39	203	79	75	39	9
6	P(VTFBu <sub>12</sub> -stat-VAc <sub>88</sub> )	4600	5200	1.34	264	18	63	46	20
7	PVAc	4600	4700	1.39	282	0	59	48	24
8	P(VBu <sub>50</sub> -stat-VAc <sub>50</sub> ) <sup>g</sup>		4000	1.45	269	13			
9	P(VTFBu <sub>75</sub> -stat-VAc <sub>25</sub> )	9900 <sup>b</sup>			213	69			11
10	P(VBu <sub>75</sub> -stat-VAc <sub>25</sub> )	9300 <sup>b</sup>			306	24			-14

<sup>a</sup>See the S1 for experimental details. <sup>b</sup>Determined by  $^1\text{H}$  NMR analysis in acetone- $d_6$ . <sup>c</sup>Determined by SEC in tetrahydrofuran (THF) with polystyrene standards. <sup>d</sup>Cloud-point pressure determined from the onset of turbidity with 0.2 wt % of polymer in  $\text{sCO}_2$  at 40 °C (standard deviation:  $\pm 3$  bar, repeatability  $\pm 5$  bar). <sup>e</sup> $\Delta P_{\text{cloud}} = P_{\text{cloud}}(\text{PVAc, run 7}) - P_{\text{cloud}}(\text{sample})$ . <sup>f</sup>Contact angles, reported as average values of six measurements. <sup>g</sup>From ref 25.

Solubility properties can also be affected by polymer/polymer interactions and entropy of mixing. The contribution of polymer/polymer interactions can be qualitatively estimated from surface tension values (Table 1) obtained from sessile drop experiments. The water contact angle increased from 59° for a pure PVAc sample to 99° for pure PVTFBu. From the empirical formula proposed by Li and Neumann,<sup>26</sup> surface tension values could be extrapolated and are reported in Table 1 and Figure 3.



**Figure 3.** Experimental results for the P(VAc-*stat*-VTFBu) copolymers: cloud points, surface tension measurements, and glass transition temperatures vs VAc mol %.

They followed the same trend as the solubility, starting from 48 mN·m<sup>-1</sup> for pure PVAc and reaching a minimum value at 23 mN·m<sup>-1</sup> for pure PVTFBu. Therefore, weaker polymer/polymer interactions (associated with lower surface tension) are also responsible for the increase of solubility observed. Glass transition temperatures ( $T_g$ ) of the copolymers decreased from 24 °C for homo-PVAc to -4 °C for homo-PVTFBu (Figure 3), suggesting that entropy of mixing is also involved.

An interesting trend can be deduced from the comparison of these results with those obtained for VTFAC/VAc copolymers.<sup>8</sup> Although *ab initio* calculations showed enhanced polymer-CO<sub>2</sub> interactions with VTFBu compared to VTFAC monomer units, cloud point pressures of VTFAC/VAc statistical copolymers were systematically slightly lower than those of their VTFBu counterparts for compositions containing up to 50 mol % fluorinated comonomer:<sup>8</sup> the solubility of P(VTFBu<sub>50</sub>-*stat*-VAc<sub>50</sub>) and P(VTFAC<sub>50</sub>-*stat*-VAc<sub>50</sub>) was thus equal to 181 and 177 bar, respectively. This may be because VTFAC induces lower polymer-polymer interactions compared to VTFBu in the copolymer, as demonstrated by surface tension calculations. For these two polymers surface tensions were 35 and 33 mN·m<sup>-1</sup>, respectively. This effect counterbalances and slightly surpasses other thermodynamic contributions such as polymer-CO<sub>2</sub> interactions and entropy of mixing. Indeed,  $T_g$  of all VTFBu-based copolymers are lower than the corresponding VTFAC-based copolymers, which means the entropy of mixing is not the main feature affecting solubility.<sup>8</sup>

In contrast to VTFAC/VAc copolymers, which become partially insoluble in scCO<sub>2</sub> at about 50% VTFAC due to their semicrystalline character, the amorphous character of VTFBu/VAc copolymers at all compositions allowed the preparation of polyvinyl esters with enhanced solubility (154 bar) in scCO<sub>2</sub> when more than 70% of VTFBu was incorporated in the copolymer. This solubility approaches that of Krytox

perfluoropolyethers of similar  $M_n$  ( $P_c = 110$  bar for  $M_n = 4800$  g/mol)<sup>25</sup> and is similar to that of monomethacrylate-terminated PDMS of  $M_n = 10000$  g/mol.<sup>25</sup> It should be noted that PVBu homopolymer at 3000 g/mol and 50/50 VAc/VBu copolymer at 4000 g/mol give much higher cloud points at 241 and 269 bar, respectively.<sup>25</sup> Furthermore, the effect of increasing molecular weight on the solubility of the VTFBu/VAc copolymers is relatively small, with a cloud point of 213 bar obtained for a 9900 g/mol 75/25 VTFBu/VAc copolymer (c.f. 306 bar for the corresponding VBu/VAc copolymer). Advantageously, like PVAc and PVBu, PVTFBu is much more stable toward methanolysis and hydrolysis (see Figures S11 and S12 in SI) than PVTFAC. Therefore, this new VTFBu monomer is a promising building block for the preparation of macromolecular surfactants with enhanced solubility and chemical stability for heterogeneous processes involving water and scCO<sub>2</sub>.

In summary, VTFBu was synthesized for the first time and polymerized in a controlled manner by RAFT/MADIX using a xanthate reversible transfer agent. PVTFBu homopolymer and random VTFBu/VAc copolymers of controlled  $M_n$  and low dispersities were obtained. The solubility of PVTFBu in scCO<sub>2</sub> was shown to be greatly enhanced compared to PVAc. The 128 bar decrease in cloud point pressure could be rationalized by a decrease of polymer-polymer enthalpic interactions and an increase of both polymer-CO<sub>2</sub> interactions and entropy of mixing. The synthesis of PVTFBu-containing amphiphilic block copolymers and the study of their behavior at water/scCO<sub>2</sub> interfaces will be the subject of forthcoming studies.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Detailed experimental procedures and additional experimental results, including NMR spectra of VTFBu, crude PVTFBu, and P(VTFBu-*stat*-VAc) samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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