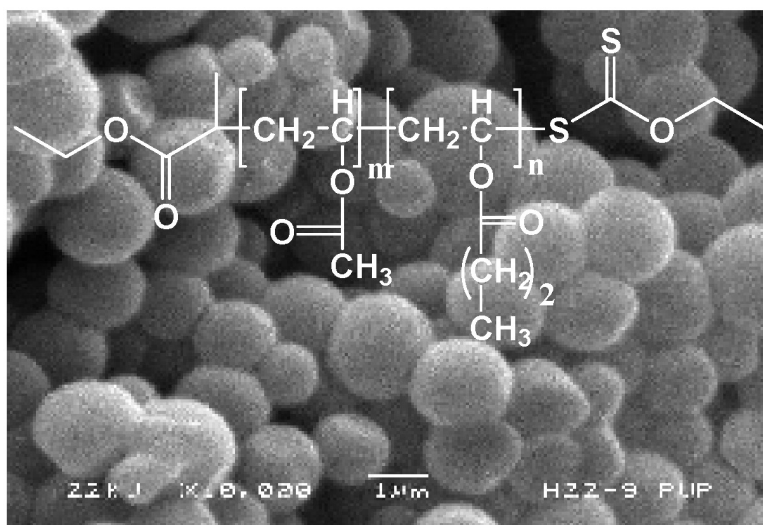


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## Successful Dispersion Polymerization in Supercritical CO<sub>2</sub> Using Polyvinylalkylate Hydrocarbon Surfactants Synthesized and Anchored via RAFT

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In recent years the chemical industry has come under increasing pressure to respond to environmental issues concerning the use of volatile organic solvents. Supercritical carbon dioxide (scCO<sub>2</sub>) is one environmentally friendly alternative, particularly for polymer synthesis.<sup>1,2</sup> Most polymers are insoluble in scCO<sub>2</sub>, and hence heterogeneous polymerizations have proved successful. However, soluble surfactants are required to stabilize the growing polymer particles in scCO<sub>2</sub>, and out of necessity these have been limited to costly fluorinated or siloxane based polymers<sup>3</sup> that have good CO<sub>2</sub>-philicity.<sup>2,4</sup> In this paper we report the facile synthesis of highly soluble hydrocarbon based copolymers, prepared with good control via controlled free radical polymerization from readily accessible commercially available monomers. Moreover, we demonstrate that these new hydrocarbons act as very effective stabilizers for dispersion polymerization reactions in scCO<sub>2</sub>.

These new CO<sub>2</sub>-philic hydrocarbon molecules are synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization of vinylalkylate comonomers (Table 1).

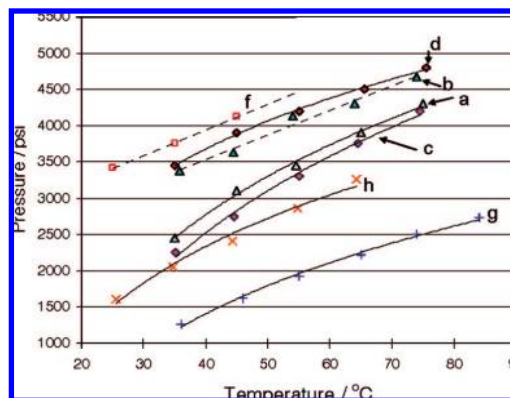
Poly(vinyl acetate) is known to have good solubility in scCO<sub>2</sub>,<sup>5</sup> and we have demonstrated that by increasing the side-chain length using vinyl butyrate there is an increase in solubility in scCO<sub>2</sub> and this is likely attributable to the increase in free volume of the polymer. Indeed, a 50:50 random copolymer of vinyl acetate and vinyl butyrate (PVAc-PVB) yielded the highest solubility (lowest cloud point) of all polymers synthesized in this study (Figure 1). A RAFT agent (*S*-(1-ethoxycarbonyl)ethyl *O*-ethyl xanthate) was chosen to provide a controlled route to the well-defined vinyl alkylate polymers<sup>6,7</sup> providing good control over the surfactant molecular weight and polydispersity. This in turn provides a facile route to controlling both the comonomer ratios and the chain length, both of which are crucial in determining solubility and stabilizer activity.

The solubility of the polymers in scCO<sub>2</sub> was measured using a variable volume view cell with a fixed polymer concentration of 0.2 wt %. The most soluble hydrocarbon surfactants are the random copolymers of PVAc and PVB (c, d, and e in Table 1), and these show the greatest solubility of any hydrocarbon oligomers in scCO<sub>2</sub> reported to date. For comparison, we show the cloud point data for CO<sub>2</sub>-propylene oxide copolymers (the current hydrocarbon benchmark<sup>8</sup>) and also PDMS-MA (10 kDa) and hydroxyl-terminated Krytox (4800 Da), two of the most common types of CO<sub>2</sub>-philic surfactants used in scCO<sub>2</sub>. While the cloud points of the PVAc and PVB hydrocarbon polymers are higher than these commercially available materials (based on absolute molecular weight comparisons), we have now

**Table 1.** Properties of Polyvinylalkylate Polymers

entry	structure	$M_n^a$ /kDa	PDI	cloud point pressure at 40 °C/psi <sup>b</sup> (MPa)
a	PVAc	2.3	1.40	2700 (18.6)
b	PVB	3.0	1.45	3500 (24.1)
c	PVAc-PVB <sup>f</sup>	2.4	1.29	2500 (17.2)
d	PVAc-PVB	3.6	1.43	3750 (25.9)
e	PVAc-PVB	4.0	1.45	3900 (26.9)
f	PEC-PPG <sup>c</sup>	3.0	na	3800 (26.2)
g	Krytox <sup>d</sup>	4.8	na	1600 (11.0)
h	PDMS-MA <sup>e</sup>	10.0	na	2400 (16.5)

<sup>a</sup> Measured by RI GPC using polystyrene standards in THF. <sup>b</sup> Onset of turbidity. <sup>c</sup> Polyethercarbonate/polypropylene oxide from ref 8. <sup>d</sup> Monohydroxy terminated Krytox (Dupont). <sup>e</sup> Monomethacrylate terminated polydimethylsiloxane (Itticha Co. Japan). <sup>f</sup> Copolymer ratio 50:50.



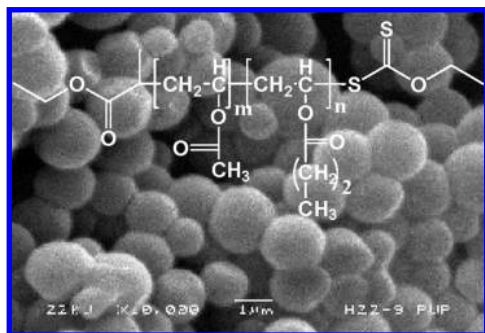
**Figure 1.** Cloud points for series of polyvinylalkylates and commercially available polymers in pure CO<sub>2</sub>. Each point is the average of three measurements. Labels refer to entries in Table 1.

produced hydrocarbons with cloud points well below 5000 psi at temperatures that are appropriate for free radical polymerization. The effect of the xanthate end group on the solubility of the copolymers was also investigated. RAFT terminated polyvinylalkylates were shown to be only slightly less soluble in scCO<sub>2</sub> than the equivalent polymer formed by conventional free-radical polymerization (see Supporting Information).

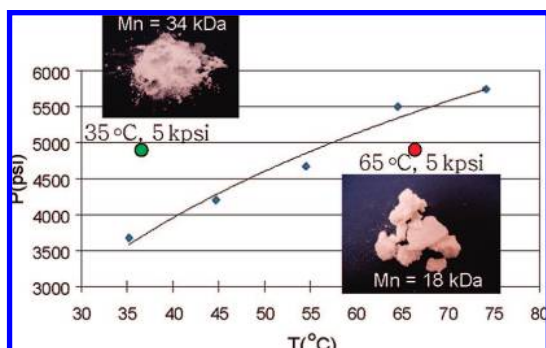
These new materials (Table 1) were tested for activity as stabilizers for dispersion polymerization of *N*-vinylpyrrolidone (NVP) in scCO<sub>2</sub>. PVAc-based stabilizers have been shown to be effective for dispersion polymerization in fluorinated solvents.<sup>9,10</sup> Initial experiments in scCO<sub>2</sub> were not successful, and this was ascribed to insufficient length of these chains to force steric stabilization of the dispersion. However, on increasing the PVAc-co-PVB copolymers to molecular weights greater than 8 kDa, we achieved excellent dispersion stability. Polymerizations resulted in

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**Figure 2.** Scanning electron micrograph of PVP particles formed in  $sc\text{CO}_2$  using RAFT-terminated PVAc-PVB as surfactant ( $M_n = 10$  kDa). The structure of the surfactant is overlaid in the figure.



**Figure 3.** Cloud points for RAFT terminated PVAc-PVB ( $M_n = 10$  kDa, 5 wt %) in  $sc\text{CO}_2$ /monomer mixture (15% N-VP). Above the cloud point using V-70 as initiator (35 °C, 5 kpsi) the surfactant dissolves and works effectively. For AIBN (65 °C, 5 kpsi) as initiator, the surfactant is not soluble and the PVP is a rock-like agglomerated solid.

high monomer conversion and well stabilized polymeric microspheres. We even extended the PVAc-co-PVB copolymer surfactant molecular weights up to 15 kDa and demonstrated polymer yields >99% (Figure 2). Interestingly, these longer surfactant chains are not soluble in pure  $sc\text{CO}_2$  at pressures below 5000 psi, but they are soluble in the  $sc\text{CO}_2$ /monomer mixture that is required for dispersion polymerization. Thus, the monomer acts as a cosolvent, and under these conditions, the PVAc-PVB copolymer (50:50,  $M_n = 10$  kDa) shows a cloud point of less than 5000 psi in the  $sc\text{CO}_2$ /N-VP mixture (15 wt % N-VP) at temperatures less than 58 °C. Dispersion polymerizations were carried out at 35 °C using VA-070 as initiator ( $t_{1/2} = 10$  h at 30 °C, 1 wt %) along with monomer (8.4 g) and the hydrocarbon surfactant (typically 5 wt %) in a 60 mL autoclave. Following quantitative conversion after 48 h, the resulting polymer was collected directly as a free flowing powder ( $M_n = 34$  kDa, PDI = 6.0) with a well-defined spherical morphology (Figure 3), the first time that successful hydrocarbon stabilization has been achieved in  $sc\text{CO}_2$ . However, when the polymerization was performed at 65 °C and 5000 psi using alternative initiator AIBN ( $t_{1/2} = 10$  h at 65 °C) the resulting polymer product was an agglomerated mass with an ill-defined morphology ( $M_n = 18$  kDa, PDI = 4.9). This difference can be fully explained by the stabilizer solubility: At the higher temperature (lower density) the surfactant shows poor solubility in the continuous phase (Figure 3) leading to precipitation polymerization, rather than dispersion.

Xanthates are known to be active for polymerization of N-VP.<sup>6</sup> Clearly, our results demonstrate broad polydispersities, so these RAFT terminated stabilizers are not exerting control on the

poly(vinyl pyrrolidone) (PVP) polymerizations. However, the RAFT mechanism is providing a route to good anchoring to the growing polymer. To test this, we converted the RAFT end group to a thiol via reduction using hexylamine.<sup>6</sup> The cloud point of the thiol product was very similar, but the thiol terminated hydrocarbon surfactant does not effectively anchor to the growing PVP, and no successful dispersion polymerization was observed. For good stabilization, a  $\text{CO}_2$ -philic surfactant must have a reactive, or strongly polymer-philic end group, as has been widely reported for successful PDMS and fluorinated surfactants.<sup>2</sup> We have also recently reported that RAFT-mediated dispersion polymerization works effectively in  $sc\text{CO}_2$  with a free RAFT agent, but again, this only works well when there is effective anchoring; in that case, a PDMS-MA macromonomer provided the stabilization.<sup>11</sup> To further prove the requirement for effective anchoring, we undertook the dispersion polymerization of methyl methacrylate (MMA) in  $sc\text{CO}_2$  using the same xanthate functionalized stabilizers. However, the low reactivity of the C=S bond toward radical addition of methacrylate radicals is known to limit the incorporation of the xanthate end group in the growing PMMA chains,<sup>6</sup> and we would predict that this lack of anchoring would reduce stabilizer activity. The same RAFT terminated PVAc-PVB copolymer surfactants were soluble in the  $sc\text{CO}_2$ /MMA solution, but the dispersion polymerization was unsuccessful; only very low conversion to polymer was observed. This further demonstrates that effective anchoring and good steric stabilization in addition to surfactant solubility are all required for dispersion polymerization in  $sc\text{CO}_2$ .

In conclusion, we report the synthesis of new hydrocarbon surfactants showing the highest solubility of any previously reported hydrocarbon polymers in  $sc\text{CO}_2$ . By utilizing the cosolvency effect, RAFT-terminated polyvinylalkylate copolymers ( $M_n > 8$  kDa) prove to be very effective stabilizers for dispersion polymerization in  $sc\text{CO}_2$ . Our studies are now focused on extending the strategy to a wider range of vinyl polymerizations in  $sc\text{CO}_2$  and investigating the application of this approach to areas such as surfactant synthesis or homogeneous catalysis.

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**Supporting Information Available:** Surfactant synthesis, polymerization results for MMA in  $sc\text{CO}_2$ , additional SEMs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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