RAFT POLYMERIZATION AND SUPERCritical CARBON DIOXIDE

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ABSTRACT

First, reversible addition-fragmentation chain transfer (RAFT) polymerization of
1,1,2,2-tetrahydroperfluorodecyl acrylate (FDA) has been performed in trifluorotoluene in the
presence of a dithioester based on poly(ethylene oxide) (PEO) as reversible chain transfer
agent to prepare PEO-b-PFDA (hydrophilic/CO2-philic) block copolymers. The solubility
behavior of such macromolecular surfactants has been studied by determination of the cloud
point curve in neat supercritical CO2. Second, supercritical CO2 has been used as the reaction
medium for RAFT polymerization of 1,1-dihydroperfluoroctyl acrylate (FOA) (solvent free
high pressure living radical polymerization). For both PEO-b-PFDA block copolymers and
PFOA homopolymers, high yields were obtained and the living character was checked by
quantitative UV analysis of the dithiobenzoyl end group of the polymer chains.

INTRODUCTION

Supercritical carbon dioxide is of interest in many industrial areas, as an
environmentally benign medium, but it sometimes suffers from the low solubility of polar
molecules [1-2]. This limitation could be advantageously overcome by using appropriate
surfactants. Some macromolecular surfactants with hydrophilic/CO2-philic structures have
already been studied [2]. For instance, DeSimone et al. have reported the synthesis of sugar-
containing diblock fluorocopolymers by sequential living anionic polymerization in THF at –
78°C and its application in CO2 emulsion polymerization [3-4]. Another interesting class of
hydrophilic polymer is poly(ethylene oxide) (PEO). The solubility of PEO in supercritical
CO2 strongly depends on the molecular weight and the nature of the end-groups of the
polymer chains [5]. Roughly, PEOs of Mn=1000 or lower have a substantial solubility in neat
CO2 whereas PEOs of Mn=2000 and higher are essentially insoluble (CO2-phobic) at
moderate pressure and temperature (P<400 bar, T<100°C). A poly(1,1-dihydroperfluoroctyl
acrylate)-g-PEO graft copolymer was shown to aggregate in supercritical CO2, forming a core
domain rich in PEO that is able to stabilize small amounts of water [6].

The recent development of various living radical polymerization processes permits the
synthesis of a wide range of well-defined polymers (predetermined molecular weight, narrow
distribution) with complex architectures (such as block, graft, and star copolymers) [7]. Such
copolymers with controlled structures find many applications as surfactants, adhesives, and
compatibilizers to name a few. In a previous paper, we reported the synthesis of
hydrophobic/CO2-philic polystyrene-b-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) block
copolymers by nitroxide-mediated radical polymerization (NMP) and their use in CO2
dispersion polymerization [8]. Recently, PEO and poly(fluorooctyl methacrylates) containing
block copolymers were prepared by atom transfer radical polymerization (ATRP) using PEO
macroinitiators [9-10], and such block copolymers were shown to lower the interfacial tension
between water and supercritical CO₂ [10], but their solubility behavior in neat supercritical CO₂ was not reported. Besides NMP and ATRP, reversible addition-fragmentation chain transfer (RAFT) polymerization, which was invented in the late nineties [11], is one of the most promising techniques of living radical polymerization because it proceeds in smooth conditions (scheme 1) [12]. RAFT is compatible with a wide range of temperature, solvents, and monomers.

In this paper, we investigate the RAFT polymerization of 1,1,2,2-tetrahydroperfluorodecyl acrylate (FDA) in the presence of a chain transfer agent based on poly(ethylene oxide) (PEO-CTA 1) to prepare PEO-b-PFDA (hydrophilic/CO₂-philic) block copolymers (Scheme 2). Furthermore, the solubility behavior of such copolymers in supercritical CO₂ will be reported. Finally, in our effort to design smart and high purity polymers by sustainable processes (solvent free), we have studied the RAFT polymerization of 1,1-dihydroperfluoroocetyl acrylate (FOA) in supercritical CO₂ in the presence of various molecular transfer agents to check the living character of the polymerization in this environmentally friendly medium. Living radical polymerization techniques were already attempted in CO₂ [13], with some success by ATRP [14], but to our knowledge RAFT in CO₂ was not reported yet.

![Scheme 1: General principle of RAFT polymerization](image1)

![Scheme 2: Structure of the PEO-b-PFDA block copolymers prepared by RAFT](image2)

**I - MATERIALS AND METHODS**

**Materials** 1,1,2,2-tetrahydroperfluorodecyl acrylate (FDA, Elf Atochem) and 1,1-dihydroperfluoroocetyl acrylate (FOA, 3M) were distilled under reduced pressure and passed through alumina. 2,2'-Azobis(isobutyronitrile) (AIBN, 98%, Fluka) was recrystallized from
methanol. α,α,α-trifluorotoluene (99%, Lancaster) was distilled under reduced pressure. S-(thiobenzoyl)thioglycolic acid (Aldrich, 99%), poly(ethylene glycol) methyl ether (Aldrich, \( M_n = 2000 \text{ g mol}^{-1} \)), carbon dioxide (purity > 99.9992%, supercritical grade 5.2, AGA, France) (or SFE/SFC grade by Air Products, Allentown, PA, USA), 1,1,2-trichlorotrifluoroethane (F113, 99%, Aldrich) and solvents were used as received. Benzyl dithiobenzoate (PhCS\(_2\)CH\(_2\)Ph, Bz-CTA 2), tert-butyl dithiobenzoate (PhCS\(_2\)C(CH\(_3\)_3), tBu-CTA 3) and 1-(ethoxycarbonyl)-ethyl dithiobenzoate (PhCS\(_2\)CH(CH\(_3\))CO\(_2\)Et, EtA-CTA 4) RAFT chain transfer agents were synthesized as reported elsewhere [12].

**Equipment**
ISCO model no. 260D automatic syringe pump was used to deliver CO\(_2\). Montpellier (France): Cloud point measurements were carried out in a 15 mL high pressure variable-volume view cell equipped with a sapphire window on the end for visual observations. Chapel Hill (USA): CO\(_2\) solution polymerization of FOA was carried out in a 10 mL stainless steel reactor equipped with two sapphire windows, and fitted with a pressure transducer. The reactor was heated with a heating tape monitored by a temperature controller with a thermocouple (type K) inside the reaction medium.

**Synthesis of the Poly(ethylene oxide)-Based RAFT Agent (PEO-CTA 1)**
PEO-CTA 1 was synthesized by a conventional esterification technique, reacting a two-fold excess of dithiobenzoic acetic acid with poly(ethylene oxide) methyl ether in benzene (oil bath at 100°C) with a Dean Stark apparatus, in the presence of methane sulfonic acid as catalyst. The final product was purified by precipitation in diethyl ether, dried under vacuum at 35°C (yield 90%) and characterized by H-NMR in CDCl\(_3\) (spectrum conforms to the expected structure) and size exclusion chromatography in tetrahydrofuran (\( M_n,SEC = 2218 \text{ g mol}^{-1} \) and polydispersity index \( I_p = 1.05 \), versus poly(ethylene oxide) standards).

**RAFT Polymerization of FDA in α,α,α-Trifluorotoluene with PEO-CTA 1**
Typically, 2.3584 g (1.074 mmoles) of PEO-CTA 1 and 38 g of α,α,α-trifluorotoluene were introduced in a 100 mL Schlenk flask and the solution was thoroughly purged with argon. 10 g (19.32 mmoles) of FDA purged with argon was added to the Schlenk under positive argon flow. Then, a solution of 52.6 mg (0.32 mmoles) of AIBN in 2 g of trifluorotoluene was added, the schlenk was sealed with a septum, and placed in an oil bath at 65°C with magnetic stirring. Aliquots were withdrawn and analyzed by H-NMR with C\(_6\)D\(_6\) capillaries to determine the monomer conversion. After 51h (82% monomer conversion), the polymer solution was poured in diethyl ether at ambient temperature, stirred overnight, and filtered to recover a slightly pink powder which was dried under vacuum at 35°C. Composition of the copolymer was determined by H-NMR in trifluorotoluene/F113 mixture with C\(_6\)D\(_6\) capillaries. Block copolymers were purified by Soxhlet extraction with refluxing acetone to remove any PEO homopolymer.

**RAFT Polymerization of FOA in Supercritical CO\(_2\) with Bz-CTA 2, tBu-CTA 3, and EtA-CTA 4**
Typically, the high pressure cell was charged with 9.4 mg (0.057 mmoles) of AIBN and 16.9 mg (0.080 mmoles) of chain transfer agent tBu-CTA 3 and purged with argon. Then, 5.0 g (11.01 mmoles) of FOA monomer stored under argon was added, the cell was sealed and pressurized with CO\(_2\) to about 80 bar. Under magnetic stirring, the temperature was raised to 65°C. If necessary, more CO\(_2\) was added to reach the desired pressure (275 bar). The polymerization was allowed to proceed with stirring for two days. At the end of the reaction, the reactor was cooled, the CO\(_2\) was very slowly vented in methanol to collect any residual reactants or sprayed out polymer. The sticky pink PFOA was recovered by adding F113 in the cell, purified by precipitation in methanol, and dried under vacuum at 35°C. Monomer conversion was determined by H-NMR on crude product (before precipitation) in F113 with C\(_6\)D\(_6\) capillaries.
Characterization  Size exclusion chromatography (SEC) was performed with a Spectra Physics Instruments SP8810 pump and a Shodex RIse-61 refractometer detector (30°C, two 300 mm columns PL gel mixed C from Polymer Laboratories). The eluent was either tetrahydrofuran (flow rate 1 mL.min\(^{-1}\)) for PEO-CTA 1 or \(\alpha,\alpha,\alpha\)-trifluorotoluene (flow rate 0.9 mL.min\(^{-1}\)) for FOA homopolymers. H-NMR analyses were conducted on a Bruker spectrometer at 200 MHz. UV-VIS analyses were performed on a Shimadzu 1205 UV-VIS spectrophotometer in F113 (for PFOA) or trifluorotoluene/F113 mixtures (for PEO-b-PFDA).

II - RESULTS AND DISCUSSION

Synthesis and Characterization of PEO-b-PFDA Block Copolymers

Three block copolymers were prepared with different targeted copolymer compositions (Table 1). In all cases, high yields were obtained and essentially no polymer fractionation was observed by precipitation in diethyl ether. The cloud point curve of a reference PFDA sample, synthesized in the absence of PEO-CTA 1, is shown in Figure 2. The solubility of copolymer PEO-b-PFDA 3 before Soxhlet extraction was investigated in neat CO\(_2\). Most of the product was solubilized by pressurizing the cell with CO\(_2\) at 108 bar and 23.0 °C, although the solution became turbid under stirring. However, cloud points were clearly identified without stirring and were shown to be close to those of the reference PFDA homopolymer (Figure 2). The turbidity of the solution under stirring can be ascribed to the dispersion of a minor amount of residual PEO-CTA 1 (and/or insoluble PEO-rich block copolymers) stabilized by PEO-b-PFDA block copolymers acting as efficient macromolecular surfactants. All copolymers were extracted with acetone to remove PEO homopolymer, resulting in purified PEO-b-PFDA samples. Alternatively, the block copolymers could be purified by CO\(_2\) extraction. Comparison of cloud point curves of the copolymers is under investigation and will be presented elsewhere. In addition, UV analysis of the purified block copolymers shows a strong absorption at about 298-301 nm, confirming the presence of the dithiobenzoyl moiety (PhCS\(_2\)- end group). Furthermore, the quantitative UV analysis using a calibration curve based on EtA-CTA 4 indicates a molecular weight value \(M_{n,UV}\) in good agreement with the theoretical value \(M_{n,\text{theo}}\) determined by H-NMR analysis. So, the block copolymers possess living characteristics in accordance with the RAFT process.

<table>
<thead>
<tr>
<th>Run</th>
<th>Feed ratio [FDA]/[PEO] (_{0})</th>
<th>Time (h)</th>
<th>Monomer conversion (%)</th>
<th>([FDA]/[PEO])(_{0}) (d)</th>
<th>([FDA]/[PEO])(_{e})</th>
<th>(M_{n, \text{theo}}) (f) (g.mol(^{-1}))</th>
<th>(M_{n, \text{UV}}) (g) (g.mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-b-PFDA 1 (^a)</td>
<td>18.0</td>
<td>51</td>
<td>82.0</td>
<td>13.8</td>
<td>18.5</td>
<td>11781</td>
<td>16572</td>
</tr>
<tr>
<td>PEO-b-PFDA 2 (^b)</td>
<td>36.0</td>
<td>168</td>
<td>70.0</td>
<td>22.4</td>
<td>39.0</td>
<td>22403</td>
<td>22288</td>
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<tr>
<td>PEO-b-PFDA 3 (^c)</td>
<td>91.5</td>
<td>54</td>
<td>76.7</td>
<td>67.7</td>
<td>68.8</td>
<td>37845</td>
<td>44983</td>
</tr>
</tbody>
</table>

\(^a\) \([\text{AIBN}]/[\text{PEO-CTA} 1]_{0} = 0.298;\) \(^b\) \([\text{AIBN}]/[\text{PEO-CTA} 1]_{0} = 0.197;\) \(^c\) \([\text{AIBN}]/[\text{PEO-CTA} 1]_{0} = 0.306;\) \(d\) By H-NMR after precipitation; \(e\) By H-NMR after Soxhlet extraction; \(f\) \(M_{n, \text{theo}} = ([\text{FDA}]/[\text{PEO}]) \times M_{\text{FDA}} + M_{\text{PEO-CTA}};\) \(g\) According to UV analysis of PhCS\(_2\)- end group using a calibration with EtA-CTA 4.
RAFT Polymerization of FOA in Supercritical CO₂

RAFT polymerization proceeded homogeneously (solution polymerization) and polymers were recovered in high yields (Table 2). Polymers were purified by precipitation in methanol to remove any residual chain transfer agent. SEC of the polymers is difficult due to their limited solubility in conventional solvents, so the reported values of $M_{n,SEC}$ and $I_p$ should be considered with caution due to some possible fractionation/aggregation undesirable effects. UV analysis was performed on precipitated polymers and showed strong absorption at 301 nm, typical of the PhCS₂⁻ moiety. The quantitative UV analysis of the end-group gives a molecular weight value $M_{n,UV}$ which is slightly higher but in the same range as the theoretical molecular weight $M_{n,tho}$ calculated from the monomer conversion. These preliminary results indicate that RAFT polymerization is compatible with supercritical CO₂ as reaction medium. It opens the door to the preparation of smart macromolecular architectures (intelligent polymers) by RAFT in supercritical CO₂. This could be considered as a new step towards the development of integrated processes in supercritical CO₂.

Table 2. Synthesis and characterization of PFOA homopolymers

<table>
<thead>
<tr>
<th>Run</th>
<th>Feed ratio [FOA]/[CTA]₀</th>
<th>Time (h)</th>
<th>CTA</th>
<th>Monomer conversion (%)</th>
<th>$M_{n,tho}$ a (g.mol⁻¹)</th>
<th>$M_{n,SEC}$ b (g.mol⁻¹/$I_p$)</th>
<th>$M_{n,UV}$ c (g.mol⁻¹)</th>
</tr>
</thead>
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<tr>
<td>PFOA 1</td>
<td>136.2</td>
<td>44h00</td>
<td>Bz-CTA 2</td>
<td>76.6</td>
<td>47623</td>
<td>33857/1.24</td>
<td>67356</td>
</tr>
<tr>
<td>PFOA 2</td>
<td>137.1</td>
<td>45h23</td>
<td>tBu-CTA 3</td>
<td>89.2</td>
<td>55747</td>
<td>39617/1.14</td>
<td>60980</td>
</tr>
<tr>
<td>PFOA 3</td>
<td>137.7</td>
<td>44h50</td>
<td>EtA-CTA 4</td>
<td>86.9</td>
<td>54596</td>
<td>41009/1.13</td>
<td>75257</td>
</tr>
</tbody>
</table>

* $M_{n,tho}=([FOA]/[CTA]₀)₀×(monomer conversion)×M_{FOA} + M_{CTA};$  
 * SEC in trifluorotoluene with PS calibration;  
 * According to UV analysis of PhCS₂⁻ end group using a calibration with EtA-CTA 4.

CONCLUSION
Poly(ethylene oxide)-b-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) PEO-b-PFDA hydrophilic/CO$_2$-philic block copolymers have been synthesized in high yields by reversible addition-fragmentation chain transfer (RAFT) polymerization in trifluorotoluene in the presence of a poly(ethylene oxide)-based reversible chain transfer agent. Cloud point curve in neat CO$_2$ shows a substantial solubility at moderate pressure and temperature, indicating potential surface active properties which could be beneficial for processes involving polar molecules in supercritical CO$_2$. Furthermore, RAFT polymerization of 1,1-dihydroperfluorooctyl acrylate (FOA) in supercritical CO$_2$ was performed successfully. So, the preparation of smart macromolecular architectures by RAFT polymerization in supercritical CO$_2$ can now be envisaged.

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REFERENCES: