

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-dihydroperfluorooctyl 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.

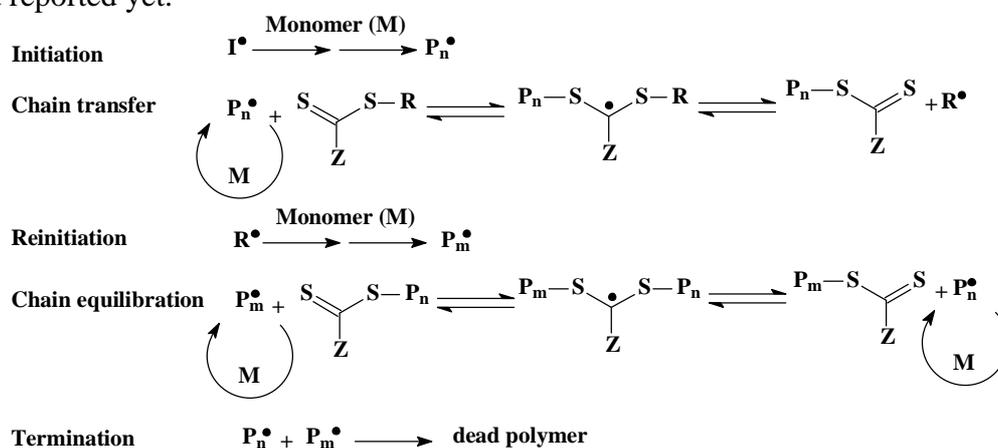
INTRODUCTION

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 $M_n=1000$ or lower have a substantial solubility in neat CO₂ whereas PEOs of $M_n=2000$ and higher are essentially insoluble (CO₂-phobic) at moderate pressure and temperature (P<400 bar, T<100°C). A poly(1,1-dihydroperfluorooctyl 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].

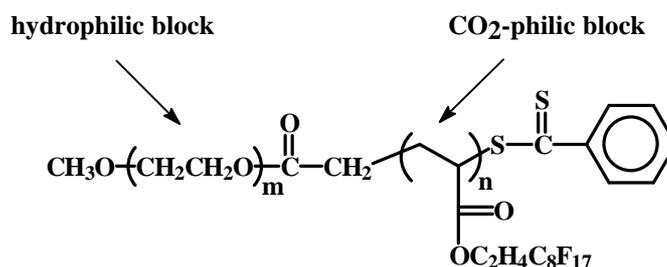
The recent development of various living radical polymerization processes permits the synthesis of a wide range of well-defined polymers (predetermined molecular weight, narrow distribution) with complex architectures (such as block, graft, and star copolymers) [7]. Such polymers with controlled structures 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-dihydroperfluorooctyl 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



Scheme 2 : Structure of the PEO-*b*-PFDA block copolymers prepared by RAFT

I - MATERIALS AND METHODS

Materials 1,1,2,2-tetrahydroperfluorodecyl acrylate (FDA, Elf Atochem) and 1,1-dihydroperfluorooctyl 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, $M_n=2000 \text{ g}\cdot\text{mol}^{-1}$), 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 ($\text{PhCS}_2\text{CH}_2\text{Ph}$, **Bz-CTA 2**), *tert*-butyl dithiobenzoate ($\text{PhCS}_2\text{C}(\text{CH}_3)_3$, **tBu-CTA 3**) and 1-(ethoxycarbonyl)-ethyl dithiobenzoate ($\text{PhCS}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{Et}$, **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 ($M_{n,SEC}=2218 \text{ g}\cdot\text{mol}^{-1}$ 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_6D_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_6D_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_6D_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 α,α,α -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 CO₂. Most of the product was solubilized by pressurizing the cell with CO₂ 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 CO₂ 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 (PhCS₂- 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 $M_{n,theo}$ determined by H-NMR analysis. So, the block copolymers possess living characteristics in accordance with the RAFT process.

Table 1. Synthesis and characterization of PEO-*b*-PFDA block copolymers

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

^a [AIBN]₀/[PEO-CTA 1]₀ = 0.298; ^b [AIBN]₀/[PEO-CTA 1]₀ = 0.197; ^c [AIBN]₀/[PEO-CTA 1]₀ = 0.306; ^d By H-NMR after precipitation; ^e By H-NMR after Soxhlet extraction; ^f $M_{n,theo} = ([FDA]/[PEO])_e \cdot M_{FDA} + M_{PEO-CTA1}$; ^g According to UV analysis of PhCS₂- end group using a calibration with **EtA-CTA 4**.

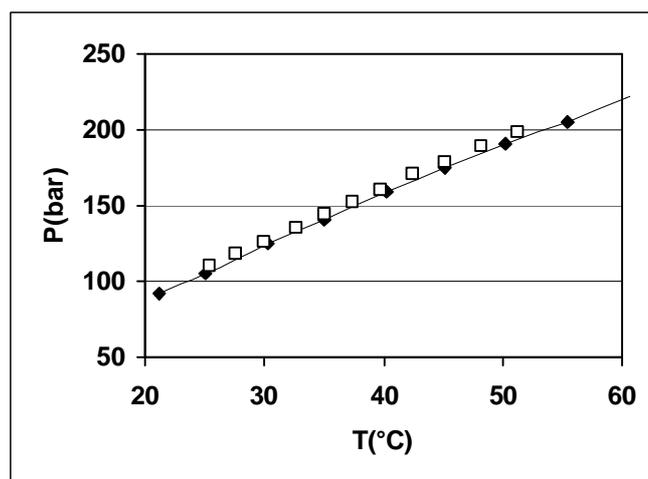


Figure 2. Cloud point curves of *PEO-b-PFDA 3* diblock copolymer (□) and a *PFDA* homopolymer (◆) in neat CO_2 (at 3.8 wt% versus CO_2).

RAFT Polymerization of FOA in Supercritical CO_2

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 PhCS_2 - 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 $M_{n,theo}$ calculated from the monomer conversion. These preliminary results indicate that RAFT polymerization is compatible with supercritical CO_2 as reaction medium. It opens the door to the preparation of smart macromolecular architectures (intelligent polymers) by RAFT in supercritical CO_2 . This could be considered as a new step towards the development of integrated processes in supercritical CO_2 .

Table 2. Synthesis and characterization of PFOA homopolymers

Run	Feed ratio $[FOA]_0/[CTA]_0$	Time (h)	CTA	Monomer conversion (%)	$M_{n,theo}^a$ ($\text{g}\cdot\text{mol}^{-1}$)	$M_{n,SEC}^b$ ($\text{g}\cdot\text{mol}^{-1}$) $[I_p]$	$M_{n,UV}^c$ ($\text{g}\cdot\text{mol}^{-1}$)
PFOA 1	136.2	44h00	Bz-CTA 2	76.6	47623	33857 1.24	67356
PFOA 2	137.1	45h23	tBu-CTA 3	89.2	55747	39617 1.14	60980
PFOA 3	137.7	44h50	EtA-CTA 4	86.9	54596	41009 1.13	75257

^a $M_{n,theo} = ([FOA]/[CTA])_0 \cdot (\text{monomer conversion}) \cdot M_{FOA} + M_{CTA}$; ^b SEC in trifluorotoluene with PS calibration; ^c According to UV analysis of PhCS_2 - 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/CO₂-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 CO₂ 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 CO₂. Furthermore, RAFT polymerization of 1,1-dihydroperfluorooctyl acrylate (FOA) in supercritical CO₂ was performed successfully. So, the preparation of smart macromolecular architectures by RAFT polymerization in supercritical CO₂ can now be envisaged.

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