

# Fluorinated Block Copolymer as Steric Stabilizer for the Formation of Ionic Liquid-in-Compressed Carbon Dioxide Emulsions

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## ABSTRACT

A block copolymer poly(ethylene oxide)-*b*-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) PEO-*b*-PFDA of  $M_n=22800 \text{ g}\cdot\text{mol}^{-1}$  has been synthesized by living free-radical polymerization from a PEO-based trithiocarbonate chain transfer agent of  $M_n=2300 \text{ g}\cdot\text{mol}^{-1}$ . As this fluorinated block copolymer was shown to be soluble in mild conditions of pressure and temperature in both liquid and supercritical  $\text{CO}_2$ , it was investigated as surfactant in 1-butyl-3-methyl imidazolium hexafluorophosphate/ $\text{CO}_2$  system (bmim-PF<sub>6</sub>/ $\text{CO}_2$ ). In contrast to macroscopic phase separation in the absence of surfactant, the copolymer acted as an efficient steric stabilizer and allowed the formation of ionic liquid-in- $\text{CO}_2$  emulsions, which are of considerable interest as microreactors in green or sustainable chemistry.

## INTRODUCTION

Environmentally benign solvents are of considerable interest for various applications including organometallic catalysis, enzymatic synthesis or nanoparticle synthesis[1,2]. Emulsions combining such solvents are expected to offer additional advantages for their industrial implementation. It has been established that block copolymers containing fluorinated segments are efficient surfactants for the preparation of water-in- $\text{CO}_2$  emulsions[3]. Here, we describe the synthesis and the utilization of this type of macromolecular surfactant for the preparation of ionic liquid-in- $\text{CO}_2$  emulsions which have not been reported yet.

## EXPERIMENTAL

**Materials.** The trithiocarbonate chain transfer agent PEO-CTA for reversible addition-fragmentation chain transfer (RAFT) polymerization was prepared by esterification of S-1-dodecyl-S'-( $\alpha,\alpha'$ -dimethyl- $\alpha''$ -acetic acid) trithiocarbonate (Noveon Inc., 91%) with poly(ethylene glycol) methyl ether (PEO2000, Aldrich,  $M_n=2000 \text{ g}\cdot\text{mol}^{-1}$ ) as previously described [4].  $\alpha,\alpha,\alpha$ -trifluorotoluene (TFT, Lancaster, 99%) was vacuum distilled. 1,1,2,2-Tetrahydroperfluorodecyl acrylate (FDA, Atofina) was distilled under reduced pressure and passed through alumina to remove inhibitor before use. 2,2'-Azobis(isobutyronitrile) (AIBN, Fluka, 98%) was recrystallized from methanol. 1,1,2-Trichlorotrifluoroethane (F113, Aldrich, 99%), methyl imidazole, 1-chlorobutane, potassium hexafluorophosphate and other solvents of A.R. grade for synthesis and analysis were all used without further purification unless

otherwise indicated. Carbon dioxide (purity>99.9992%, supercritical grade 5.2, AGA, France) was used as received.

**Synthesis of block copolymers.** 0.537 mmoles of PEO-CTA was dissolved in 38 g of TFT in a 100 mL Schlenk flask. This solution and 19.32 mmoles of FDA (targeted molar ratio of FDA and PEO in copolymer ( $n([FDA]/[PEO])$  is 36) in another flask were both purged with argon for 30 min. After the addition of the monomer and a solution of 0.108 mmoles (0.0177 g) AIBN in 2 g of TFT under positive argon flow, the Schlenk flask was sealed with a septum and placed in an oil bath at 65°C with magnetic stirring for 48 h. At the end of the reaction, an aliquot was taken and analyzed by <sup>1</sup>H-NMR spectroscopy in F113/TFT with C<sub>6</sub>D<sub>6</sub> capillaries to determine the monomer conversion. Then, the reaction mixture was precipitated dropwise in Et<sub>2</sub>O at room temperature and stirred overnight. The product was isolated by filtration and dried under vacuum at 35°C. Yield=97.8%.

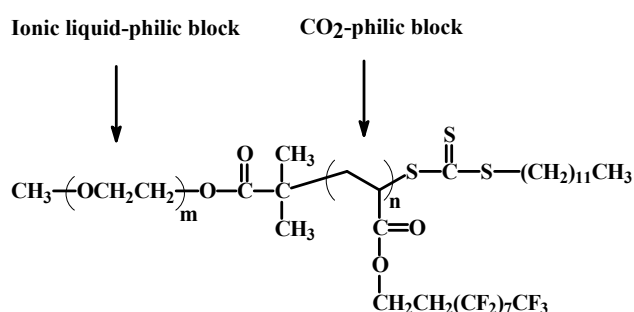
**Synthesis of ionic liquid 1-butyl-3-methyl imidazolium hexafluorophosphate (bmim PF<sub>6</sub>)[5].** *First step: synthesis of bmim Cl.* A three-necked round bottomed flask, equipped with a condenser was loaded with methylimidazole (1 mole, 82.11 g) and of *n*-chlorobutane (1 mole, 92.57 g). The mixture was stirred under argon for 48 h at 70°C, until appearance of a pale yellow viscous mixture. It was then transferred into a flask and stored at 3-5°C under argon until quantitative precipitation ( $\approx$  12 h). White crystals were obtained which were washed several times with ethyl acetate and filtered each time on a Büchner apparatus. They were transferred into a dry box containing phosphorus pentoxide and set under vacuum. BmimCl was obtained as a fine white powder. Yield: 80%. *Second step : Synthesis of bmim PF<sub>6</sub>.* A solution of bmimCl (110 g, 0.63mol) in water (150 mL) was added to a solution of potassium hexafluorophosphate (129 g, 0.7 mol) in water (300 mL). The resulting mixture was stirred at 60°C for 1 h. After cooling to r.t., the bottom phase (bmim PF<sub>6</sub>) was washed several times with de-ionized water (10×350 mL) and purified by flash chromatography using SiO<sub>2</sub> as stationary phase. The pure product was obtained as a transparent, slightly viscous liquid. It was stored in a dry box under argon. Yield: 80%.

**Formation of ionic liquid-in-CO<sub>2</sub> emulsions.** The formation of ionic liquid-in-CO<sub>2</sub> (IL/CO<sub>2</sub>) emulsions was carried out in a 16 mL stainless steel cell equipped with two sapphire windows, a magnetic stir bar, a rupture disk, and a pressure transducer. The cell was heated with a heating cartridge monitored by a temperature controller with a thermocouple (type K) inside the reaction medium. 593 mg of PEO-*b*-PFDA and 5.78 g of bmim-PF<sub>6</sub> ionic liquid were introduced into the dry cell under a small positive CO<sub>2</sub> purge. Then the cell was sealed tightly and pressurized with CO<sub>2</sub> by ISCO model no. 260D automatic syringe pump. CO<sub>2</sub> pressure in the cell was adjusted according to experimental requirements (*i.e.* either in the liquid or the scCO<sub>2</sub> region, and below or above the cloud point curve of the PEO-*b*-PFDA block copolymer) in order to observe the emulsion formation. Digital photography was employed to depict the emulsion formation.

## RESULTS AND DISCUSSION

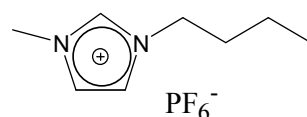
**Synthesis and characterization of the fluorinated block copolymer.** The fluorinated block copolymer PEO-*b*-PFDA (**Figure 1**) was synthesized by living free-radical polymerization (RAFT method) in order to control the molecular weight of the PFDA block and ensure a narrow molecular weight distribution[6]. The block copolymer was characterized

by  $^1\text{H-NMR}$  and UV-VIS spectroscopy (absorbency of the  $-\text{S-C(S)-S-C}_{12}\text{H}_{25}$  end group of the polymer chains at 306 nm) in fluorinated solvents due to the low solubility of PFDA in common solvents[7]. The PEO block is polar and has a much better affinity with the ionic liquid (**Figure 2**) than with  $\text{CO}_2$ . For instance, a solubility test showed that the PEO homopolymer (PEO2000) is soluble in  $\text{bmim-PF}_6$  whereas it is known to be insoluble in  $\text{CO}_2$  at moderate pressure and temperature [8]. In contrast, PFDA homopolymer is known to be soluble in  $\text{CO}_2$  in mild conditions ( $\text{CO}_2$ -philic polymer)[9,10] whereas a solubility test with a PFDA homopolymer of about  $20000 \text{ g}\cdot\text{mol}^{-1}$  showed that it is not soluble in  $\text{bmim-PF}_6$ . The rather high targeted molecular weight ratio between the two blocks  $M_{n,\text{PFDA}}/M_{n,\text{PEO}}\approx 10$  was chosen in order to favor the solubility of the block copolymer in  $\text{CO}_2$ .

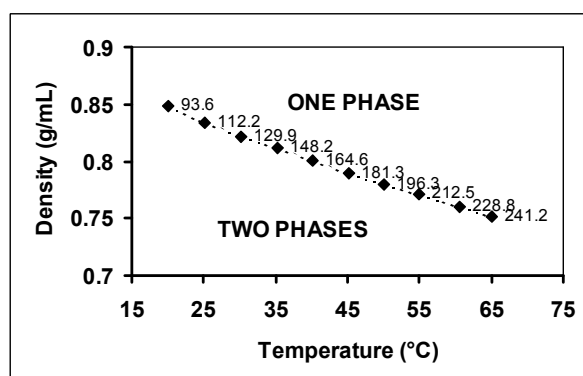


**Figure 1.** Structure of the PEO-*b*-PFDA diblock copolymer used as steric stabilizer ( $M_n=22800 \text{ g}\cdot\text{mol}^{-1}$ ).

The cloud point curve of the block copolymer in  $\text{CO}_2$  defines the region of density and temperature at which the copolymer is soluble in  $\text{CO}_2$  (**Figure 3**). Above the cloud point curve (one phase region), the polymer is soluble in  $\text{CO}_2$ [11]. This characterization is a prerequisite since the copolymer needs to be soluble to act as a steric stabilizer. Therefore, the cloud point curve is extremely useful to choose the conditions of density and temperature to favor the formation of emulsions in  $\text{CO}_2$ .

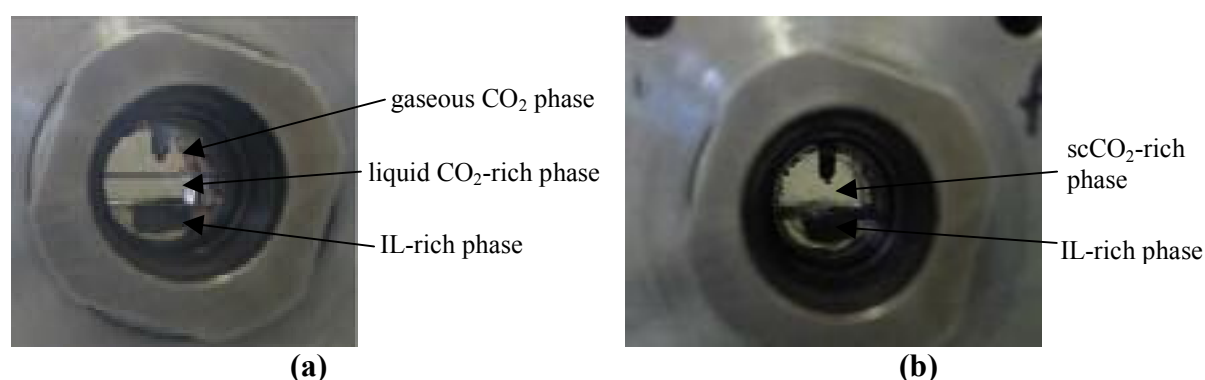


**Figure 2.** Structure of the ionic liquid 1-butyl-3-methyl-imidazolium hexafluorophosphate (*bmim-PF*<sub>6</sub>).



**Figure 3.** Cloud point curve of the PEO-*b*-PFDA in  $\text{CO}_2$  (at 4 w/w % copolymer versus  $\text{CO}_2$ ) (cloud point pressures are indicated as labels, in bar).

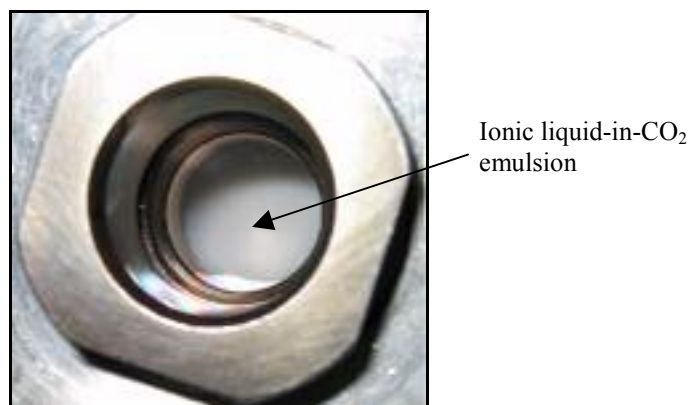
**Formation of ionic liquid in CO<sub>2</sub> emulsions.** At first, the bicomponent system of ionic liquid and CO<sub>2</sub> was observed in the absence of the block copolymer. At T=22°C and P=57 bar ( $m_{\text{CO}_2}$ =6.11 g), a three-phases system is formed (upper gaseous CO<sub>2</sub> phase, medium liquid CO<sub>2</sub> rich phase, lower IL rich phase) and the stir bar is inoperative because the IL rich phase is too viscous (**Figure 4a**). By increasing the amount of CO<sub>2</sub> in the cell (T=22°C, P=74 bar,  $m_{\text{CO}_2}$ =10.93 g), the gaseous CO<sub>2</sub> phase is no longer visible: the medium is biphasic (upper liquid CO<sub>2</sub> rich phase and lower IL rich phase). The stir bar now operates, indicating that CO<sub>2</sub> increasingly swells the IL rich phase [12] and lowers the viscosity of this phase. At T=22°C, the amount of CO<sub>2</sub> was increased up to a pressure of 187 bar ( $m_{\text{CO}_2}$ =12.74 g) and the medium remained biphasic under stirring. The small expansion volume of the IL rich phase due to the swelling by CO<sub>2</sub> was visible through the rise of the meniscus between the two phases, although it was not quantified. Then, at a constant CO<sub>2</sub> loading, the temperature was increased up to T=42°C (P=295 bar) to reach the supercritical region: the medium still remains biphasic (upper supercritical CO<sub>2</sub> rich phase) while the stirring becomes more efficient indicating a further decrease of the viscosity of the lower IL rich phase which is more swollen by CO<sub>2</sub> (**Figure 4b**). Therefore, in this range of pressure and temperature, the system is clearly biphasic under stirring with a macroscopic phase separation between the upper light CO<sub>2</sub> rich phase and the lower heavy IL rich phase.



**Figure 4.** Digital photographs depicting the multiphasic nature of the IL/CO<sub>2</sub> mixture under stirring: (a)  $m_{\text{IL}}=5.78$  g,  $m_{\text{CO}_2}=6.11$  g, T=22°C, P=57 bar (three phases from up to bottom of the cell: gaseous CO<sub>2</sub> / liquid CO<sub>2</sub> / IL); (b)  $m_{\text{IL}}=5.78$  g,  $m_{\text{CO}_2}=12.74$  g, T=42°C, P=295 bar (two phases: scCO<sub>2</sub> / IL).

In a second stage, we studied the ternary system of ionic liquid and CO<sub>2</sub> in the presence of the block copolymer POE-*b*-PFDA. The IL and the block copolymer were placed in the cell: the block copolymer appears to be insoluble in the IL. Then, the cell was pressurized with CO<sub>2</sub>. Under stirring at T=21°C and P=92 bar ( $m_{\text{CO}_2}$ =11.35 g) (*i.e.* below the cloud point of the block copolymer in CO<sub>2</sub>), the copolymer had no macroscopic effect on the phase behavior of IL in liquid CO<sub>2</sub>. At higher pressure (T=23°C, P=187 bar,  $m_{\text{CO}_2}$ =12.46 g) (*i.e.* above the cloud point curve of the block copolymer in CO<sub>2</sub>), the IL phase was partly emulsified in the liquid CO<sub>2</sub> phase upon stirring, showing that the block copolymer effectively acts as a surfactant. Then, at a constant CO<sub>2</sub> loading, the temperature was increased up to T=43°C to reach the supercritical region (P=259 bar): under stirring, the macroscopic phase separation between the two phases was non longer visible and a milky-like emulsion of IL-in-scCO<sub>2</sub> filled the entire

volume of the cell (**Figure 5**). The better results in the supercritical region might be ascribed to the decreased viscosity of the IL rich phase: the stirring becomes more efficient and facilitates the dispersion process. In addition, the droplet size of the macro-emulsion can be calculated from the rate of settling of a settling front when the agitation is stopped (Stoke's law): a rough estimation gives a diameter size in the range of 30 micrometers although much smaller droplets were also present as evidenced by the persistence of a white upper phase. Lastly, when the pressure was decreased by slowly venting the cell at  $T=40^{\circ}\text{C}$ , the loss of stability of the emulsion was clearly noticed around  $P=145$  bar which is close to the cloud point pressure of the PFDA homopolymer ( $P=134$  bar at  $T=40^{\circ}\text{C}$ ). All these findings indicate that the PEO-*b*-PFDA block copolymer is an efficient steric stabilizer to form emulsions of IL in  $\text{CO}_2$ , re-emphasizing the key role of fluorinated polymers in the potential applications of  $\text{CO}_2$ -based technologies. To our knowledge, this is the first example of IL-in- $\text{CO}_2$  emulsion reported in the literature. Such emulsions of neoteric solvents are of interest for the future development of green or sustainable chemistry [13]. Indeed, they can be used as microreactors with a high specific area and they also open the route to continuous processes in tubular reactor for instance.



**Figure 5.** Digital photograph depicting the IL-in- $\text{CO}_2$  emulsion under stirring ( $m_{\text{IL}}=5.78$  g,  $m_{\text{CO}_2}=12.46$  g,  $m_{\text{PEO-}b\text{-PFDA}}=593$  mg,  $T=43^{\circ}\text{C}$ ,  $P=259$  bar).

## Conclusions

A block copolymer PEO-*b*-PFDA has been successfully synthesized by living radical polymerization (RAFT) and was shown to be soluble in  $\text{CO}_2$  in mild conditions of pressure and temperature ( $P<250$  bar,  $T<65^{\circ}\text{C}$ ). This block copolymer interacts both with bmim- $\text{PF}_6$  ionic liquid through the polar PEO block and with  $\text{CO}_2$  through the fluorinated PFDA block, thus exhibiting surface active properties. Bmim- $\text{PF}_6$ , which is insoluble in  $\text{CO}_2$ , was efficiently emulsified in the presence of the block copolymer under gentle stirring. This is the first report on IL-in- $\text{CO}_2$  emulsions. Such emulsions involving two neoteric solvents are of considerable interest as microreactors.

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