

# Potential of Novel Gradient Copolymers for Applications in Supercritical Carbon Dioxide: a New Step Towards Surface Decontamination in Nuclear Industry

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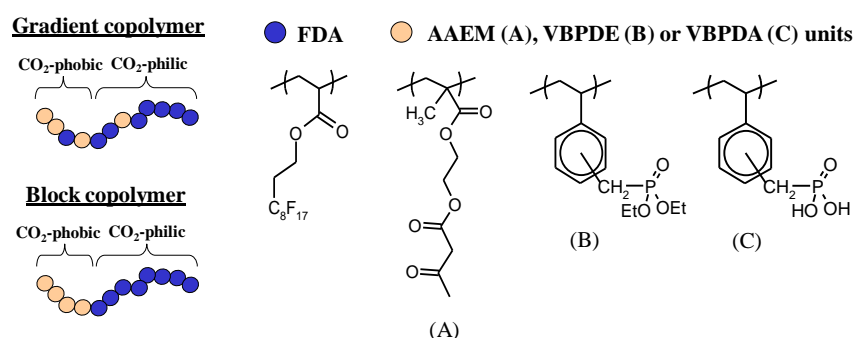
## ABSTRACT

Amphiphilic gradient copolymers with complexing moieties have been studied to evaluate their applicability for surface decontamination in supercritical carbon dioxide (scCO<sub>2</sub>). Based on poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) (poly(FDA)) as CO<sub>2</sub>-philic part, poly(FDA-co-acetoacetoxyethyl methacrylate) (poly(FDA-co-AAEM)), poly(FDA-co-vinylbenzylphosphonic acid diethylester) (poly(FDA-co-VBPDE)) and poly(FDA-co-vinylbenzylphosphonic diacid) (poly(FDA-co-VBPDA)) are tailor-made copolymers. Their cloud point curves have been determined experimentally and the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state was used for modeling in view to determine the main parameters affecting the solubility of the copolymers in scCO<sub>2</sub>. Gradient copolymers appear very advantageous compared to block copolymers due to their solubility in much milder conditions of pressure and temperature. Small angle neutron scattering (SANS) allowed us to evidence the pressure-responsive self-organization of the copolymers in CO<sub>2</sub>. Lastly, the surface active properties of the copolymers have been demonstrated by water/scCO<sub>2</sub> interfacial tension and turbidity measurements on cobalt hydroxide/CO<sub>2</sub> dispersions.

## INTRODUCTION

Extraction processes in supercritical carbon dioxide (scCO<sub>2</sub>) are generally investigated to avoid the use of organic solvents. Performing nuclear decontamination in scCO<sub>2</sub> can also reduce the amount of radioactive wastes. But metal ions and metal particles (oxides and hydroxides) are not soluble in this solvent. Therefore, researches focus on the way to transport these contaminants in scCO<sub>2</sub>: water/scCO<sub>2</sub> microemulsions [1] and molecular chelating agents [1-4] soluble in scCO<sub>2</sub> are mainly studied, while surfactants are also investigated for particle extraction [5]. We propose to combine surface active and chelating properties by using a surfactant containing complexing moieties. In our approach, amphiphilic controlled-architected gradient copolymers bearing complexing sites will perform the extraction of cobalt derivatives in CO<sub>2</sub>. Gradient copolymers are particularly interesting due to their easy

synthesis and it was shown in conventional solvents that they have special interfacial properties [6]. Several works concern the self-organization of block copolymers in scCO<sub>2</sub> [7] but gradient copolymers were never studied. In our work, it is fundamental to know the conditions where aggregation occurs because polymers can extract contaminants more efficiently as aggregate than as unimer. The tailor-made gradient and block copolymers studied herein are new and contain a CO<sub>2</sub>-philic part and complexing moieties, as shown in Figure 1. The CO<sub>2</sub>-philic polymer is poly(1,1,2,2-tetrahydroperfluorodecylacrylate) (poly(FDA)) which was already proved to be extremely soluble in scCO<sub>2</sub> [8] and the complexing groups are poly(acetoacetoxyethyl methacrylate) (poly(AAEM)), poly(vinylbenzylphosphonic acid diethylester) (poly(VBPDE)) or poly(vinylbenzylphosphonic diacid) (poly(VBPDA)). Their self-organization in scCO<sub>2</sub> is studied by small-angle neutron scattering (SANS). The ability to stabilize microemulsions is demonstrated by interfacial tension measurements and SANS. Turbidity measurements in scCO<sub>2</sub> [9], which relate to dispersed volume fraction of the particles, are used to assess the stability of dispersions of cobalt hydroxide particles in the presence of the copolymers.



**Figure 1:** Nature and structure of gradient and block copolymers

## MATERIALS AND METHODS

### Materials

Cobalt hydroxide (Co(OH)<sub>2</sub>) powder (99.9 % purity) was purchased from Alfa Aesar. Specific surface area of 20 m<sup>2</sup>/g was measured by BET method. MEB pictures show a particle size of 100-200 nm. All studied polymers were synthesized by RAFT polymerization. Poly(FDA) homopolymer [10], poly(FDA-co-AAEM), poly(FDA-co-VBPDE) and poly(FDA-co-VBPDA) gradient copolymers [10] as well as poly(ethylene oxide)-*b*-poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) (poly(EO)-*b*-poly(FDA)) [11] were synthesized as described previously. The synthesis of the other block copolymers will be described in a following paper. The characteristics of the polymers studied herein are given in Table 1.

### Characterization

**Cloud-points investigations:** cloud-points measurements were carried out in a high-pressure variable volume view cell according to a procedure previously reported [11].

**Small-Angle Neutron Scattering:** SANS data were collected at the Laboratoire Leon Brillouin (LLB), CEA Saclay, France, on beam line PACE. Experimental procedures will be described in a following paper. Data presented here have been corrected for empty cell scattering and converted to absolute units (cm<sup>-1</sup>).

**Interfacial tension measurements:** these studies were performed thanks to the pendant drop method in a cell of 270 ml equipped with two sapphire windows disposed at 90° and an internal stainless steel capillary coupled to a manual water pump filled with deionized water

(18 M $\Omega$ ). A CCD camera connected to a computer equipped with real time interfacial tension acquisition software (WinDrop v.1.8) is placed in front of a window. Measurements consist to create a drop of water at the end of the capillary and then to measure the variations of volume of the drop and interfacial tension versus time.

Turbidimetry by UV transmission measurements: these studies were performed on an experimental setup comprising two high pressure cells. In the first cell of 270 mL, 40 mg of Co(OH)<sub>2</sub> are dispersed at 313.15 K and 310 bar with or without polymer. The reactor is stirred mechanically at a rate of 300 rpm for 20 minutes. Then, the dispersion is transferred thanks to the difference of pressure to a second cell of 30 ml prefilled at 90 bar (313.15 K) where the turbidity measurements take place. This reactor is equipped with two optical probes (disposed at 180°) connected to a spectrophotometer PerkinElmer Lambda 40 through two optical fibers. The distance from the center of the probes to the top of the cell is 65 mm. After the transfer, the pressure in both cells is equalized at 210±10 bar (313.15 K). The transmission is measured in function of time and converted to turbidity  $\tau$  as given in equation 1:

$$\tau = \frac{1}{l} \times \ln \frac{I_0}{I_t} \quad (1)$$

Where  $l$  is the optical length in cm ( $l=1$  cm here),  $I_0$  and  $I_t$  are the intensities of the incident and transmitted beams, respectively.

**Table 1:** Structure and composition of polymers

Polymer	Type	M <sub>n</sub> (g/mol)	Molar fraction of CO <sub>2</sub> -phobic monomer (%)
Poly(FDA)	Homopolymer	14300	0
Poly(FDA)	Homopolymer	30000	0
Poly(FDA)	Homopolymer	56200	0
Poly(FDA-co-AAEM)	Gradient copolymer	16300	27.5
Poly(FDA-co-VBPDE)	Gradient copolymer	34100	16.9
Poly(FDA-co-VBPDA)	Gradient copolymer	33400	16.9
Poly(FDA-co-VBPDA)	Gradient copolymer	11000	23.0
Poly(VBPDE)- <i>b</i> -poly(FDA)	Block copolymer	31000	13.2
Poly(VBPDA)- <i>b</i> -poly(FDA)	Block copolymer	30500	13.2
Poly(EO)- <i>b</i> -poly(FDA)	Block copolymer	22800	54.0

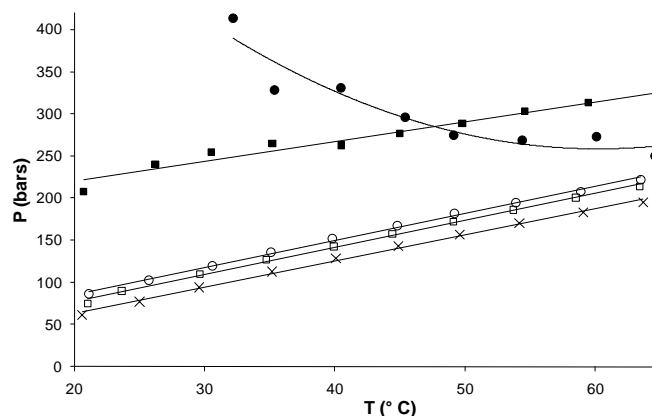
## RESULTS AND DISCUSSION

### Solubility in scCO<sub>2</sub> and PC-SAFT modeling of the phase diagram of polymers

Nuclear decontamination processes require low working pressures. To this aim, gradient copolymers studied herein are particularly interesting. Indeed, cloud point measurements show that the gradient copolymers exhibit very good solubility in compressed CO<sub>2</sub> with the decreasing order: poly(FDA-co-AAEM)≈poly(FDA-co-VBPDE)>poly(FDA-co-VBPDA). They are soluble at much lower pressures than the block copolymers of same molecular weight and composition (Figure 2). Contrary to gradient copolymers, phase diagrams of block copolymers in scCO<sub>2</sub> are very different in function of the nature of the CO<sub>2</sub>-phobic part. Poly(AAEM)-*b*-poly(FDA) is much more soluble than both poly(VBPDE)-*b*-poly(FDA) and poly(VBPDA)-*b*-poly(FDA), and the cloud point pressures of these last two copolymers evolves differently with the temperature, as shown in Figure 2.

To predict the phase diagram of copolymers in scCO<sub>2</sub>, Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state [12] is used for modeling in view to determine the main parameters affecting the solubility of the copolymers in scCO<sub>2</sub>. First, pure component

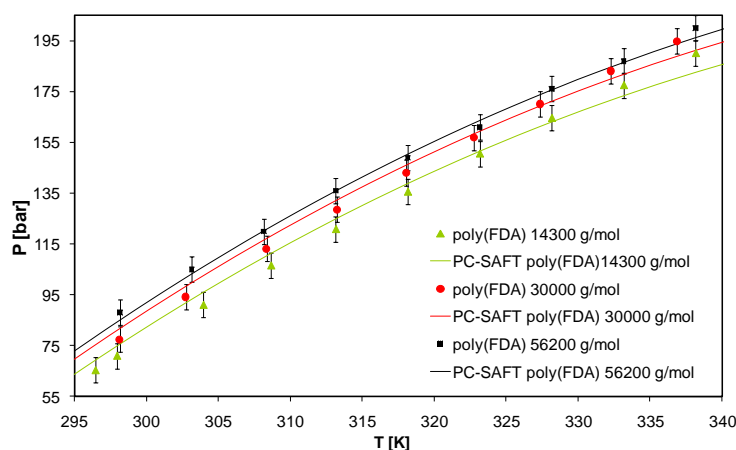
parameters of poly(FDA) homopolymer given in Table 2 were determined to model its behavior in scCO<sub>2</sub>, as shown in Figure 3. Completion for modeling the copolymers will be detailed in a forthcoming paper.



**Figure 2:** Comparison of the cloud points at a concentration of 4.0 w/w% polymer versus CO<sub>2</sub> of the poly(FDA) homopolymer (x) ( $M_n = 30000$  g/mol), the gradient copolymers poly(FDA-co-VBPDE) 16.9 % mol VBPDE (□) ( $M_n = 34100$  g/mol) and poly(FDA-co-VBPDA) 16.9 % mol VBPDA (○) ( $M_n = 33400$  g/mol); the block copolymers poly(VBPDE)-b-poly(FDA) 13.2 % mol VBPDE (■) ( $M_n = 31000$  g/mol) and poly(VBPDA)-b-poly(FDA) 13.2 % mol VBPDA (●) ( $M_n = 30500$  g/mol).

**Table 2:** Pure component parameters of poly(FDA) and binary interaction parameter with CO<sub>2</sub>

Polymer	m/M (mol.g <sup>-1</sup> )	$\sigma$ (Å)	e/k (K)	$k_{ij}$ (Poly(FDA)-CO <sub>2</sub> )
Poly(FDA)	$4.2 \times 10^{-2}$	2.65	120	-0.005

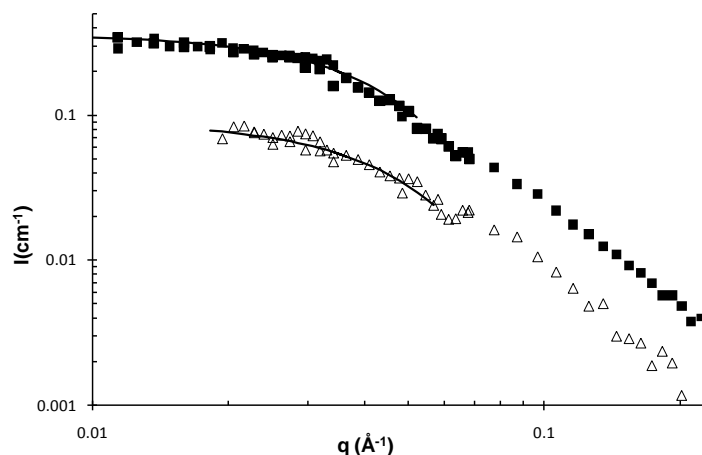


**Figure 3:** Experimental cloud-point pressures (symbols) with an error bar of  $\pm 5\%$  and PC-SAFT calculations (lines) at a concentration of 4.0 w/w% of poly(FDA) versus CO<sub>2</sub>.

### SANS study of gradient copolymers in scCO<sub>2</sub>

The self-organization in scCO<sub>2</sub> of the gradient copolymers was studied by SANS in function of several parameters (concentration, pressure and molecular weight). Pressure was shown to be the most important parameter. For poly(FDA-co-VBPDE), the size of the micellar

aggregate decreases to tend to an unimer when the pressure is increased. For poly(FDA-*co*-VBPDE) with 16.9 % mol VBPDE ( $M_n=34100$  g/mol) at a concentration of 8 w/w% versus CO<sub>2</sub>, the number of aggregation  $N_{agg}$  and the radius of gyration  $R_g$  change from 4.1 and 38 Å at 155 bar to 1.9 and 35 Å at 350 bar respectively, as shown in Figure 4. In the same time, the volume fraction of CO<sub>2</sub> in the aggregate is twice more.



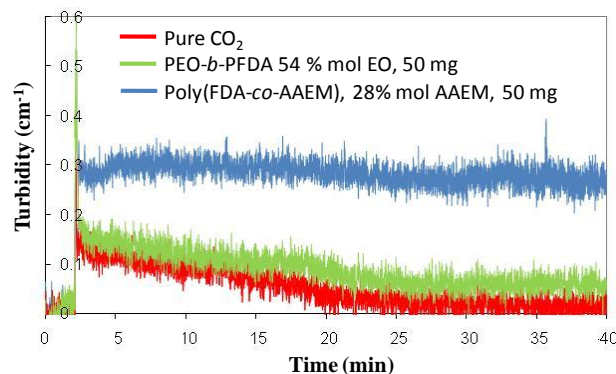
**Figure 4:** SANS data for poly(FDA-*co*-VBPDE) gradient copolymer 16.9% mol VBPDE  $M_n=34100$  g/mol at a concentration of 8 w/w% versus CO<sub>2</sub>, at  $T=40$  °C and  $P=155$  bar (■) or  $P=350$  bar (Δ), and the corresponding Guinier plots (lines) in the domain  $q \times R_g < 2$  for readability reasons.

### Microemulsion water-in-scCO<sub>2</sub>

The phosphonic diacid moiety VBPDA is polar and hydrophilic. For this reason, the gradient copolymer with VBPDA was expected to be active at the interface water/CO<sub>2</sub>. Indeed, at 40°C and 160 bar, just above the cloud point, a small concentration (0.0067 % wt) of poly(FDA-*co*-VBPDA) with 23% mol VBPDA ( $M_n=11000$  g/mol) is sufficient to reduce the interfacial tension between water and CO<sub>2</sub> down to 1 mN/m. Actually, the water drop is rapidly dissolved, indicating that this gradient copolymer can potentially stabilize some microemulsions. This was confirmed by SANS. A microemulsion was formed with a higher polymer concentration of 4.6 w/w% versus CO<sub>2</sub> (required for contrast) and a very low amount of water (0.37 % wt D<sub>2</sub>O) at 40°C and 350 bar. The microemulsion was stable during eight hours with a corrected molar ratio [water]/[polymer] of 13. The results indicate a swollen aggregate of small size ( $R_g=22.5$  Å,  $N_{agg}=8$ ) without penetration of CO<sub>2</sub>.

### Transfer and stabilization of dispersions of Co(OH)<sub>2</sub>

The addition of a gradient copolymer has a noticeable effect on the evolution of turbidity with time. As shown in Figure 5, the poly(FDA-*co*-AAEM) gradient copolymer ( $M_n=16300$  g/mol, 27.5 % mol AAEM) is more efficient than the poly(EO)-*b*-poly(FDA) block copolymer ( $M_n=22800$  g/mol, 54 % mol EO). The higher turbidity indicates that more particles are transferred and the longer sedimentation time confirms that the copolymer stabilizes sterically the particles. Interestingly, when the mechanical stirring is replaced by an ultrasound field, the turbidity is increased. This is consistent with the formation of smaller aggregates of particles which are easier to transport than in the case of the dispersion created with mechanical stirring.



**Figure 5:** Turbidity of  $\text{Co}(\text{OH})_2$  dispersions in  $\text{CO}_2$  versus time (mechanical stirring of 300 rpm before transfer, 40 mg  $\text{Co}(\text{OH})_2$ , 50 mg copolymer)

## CONCLUSION

This work confirmed that gradient copolymers are interesting in comparison with block copolymers for their use as complexing surfactants in  $\text{scCO}_2$ . Poly(FDA-co-AAEM), poly(FDA-co-VBPDE) and poly(FDA-co-VBPDA) gradient copolymers exhibit remarkable  $\text{CO}_2$  solubility. Furthermore, SANS study of the gradient copolymers has shown that they can form micellar aggregates and that their self-organization depends principally on the  $\text{CO}_2$  pressure. In addition, poly(FDA-co-VBPDA) is able to stabilize water-in- $\text{CO}_2$  microemulsions. All these properties will allow us to use them as complexing surfactants for extraction of metallic derivatives in  $\text{scCO}_2$ , as assessed by the results obtained on the transfer and stabilization of dispersions of cobalt hydroxide.

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