

# SELF-ORGANIZATION OF GRADIENT AND BLOCK COPOLYMERS WITH COMPLEXING PROPERTIES IN SUPERCRITICAL CO<sub>2</sub>

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## ABSTRACT

We report the synthesis of new gradient and block fluorinated copolymers, which have complexing properties and are soluble in supercritical carbon dioxide. Poly(1,1,2,2-tetrahydroperfluorodecyl acrylate-co-acetoacetoxyethyl methacrylate) (poly(FDA-co-AAEM)) and poly(1,1,2,2-tetrahydroperfluorodecyl acrylate-co-vinylbenzylphosphonic acid diethylester) (poly(FDA-co-VBPDE)) were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization in solvent medium. The cloud points of the copolymers in CO<sub>2</sub> were measured in a variable volume view cell at temperatures between 25~65°C. It was found that the gradient copolymers are soluble in very mild conditions of pressure and temperature. Their self-organization was studied by small-angle neutron scattering (SANS) measurements.

## 1. INTRODUCTION

More and more techniques are developed to reduce liquid waste in nuclear decontamination processes. A promising solution is the use of supercritical carbon dioxide (scCO<sub>2</sub>) as a green extraction solvent. Metal ions, oxides and hydroxides are not soluble in scCO<sub>2</sub>. Therefore, researches focus on the way to transport these contaminants in scCO<sub>2</sub>. Water/scCO<sub>2</sub> microemulsions<sup>1,2</sup> and molecular chelating agents<sup>2-5</sup> soluble in scCO<sub>2</sub> were mainly studied. Finding out the most suitable ligand for a particular contaminant is a scientific challenge. Surfactants were also investigated for metal oxide extraction<sup>6,7</sup>. The combination of surfactant and ligand is possible by synthesizing a surfactant with complexing moieties. DeSimone et al. synthesized by conventional radical polymerization different statistical copolymers with multiple ligand sites randomly distributed along the polymer chain and studied their solubility in scCO<sub>2</sub><sup>8</sup>.

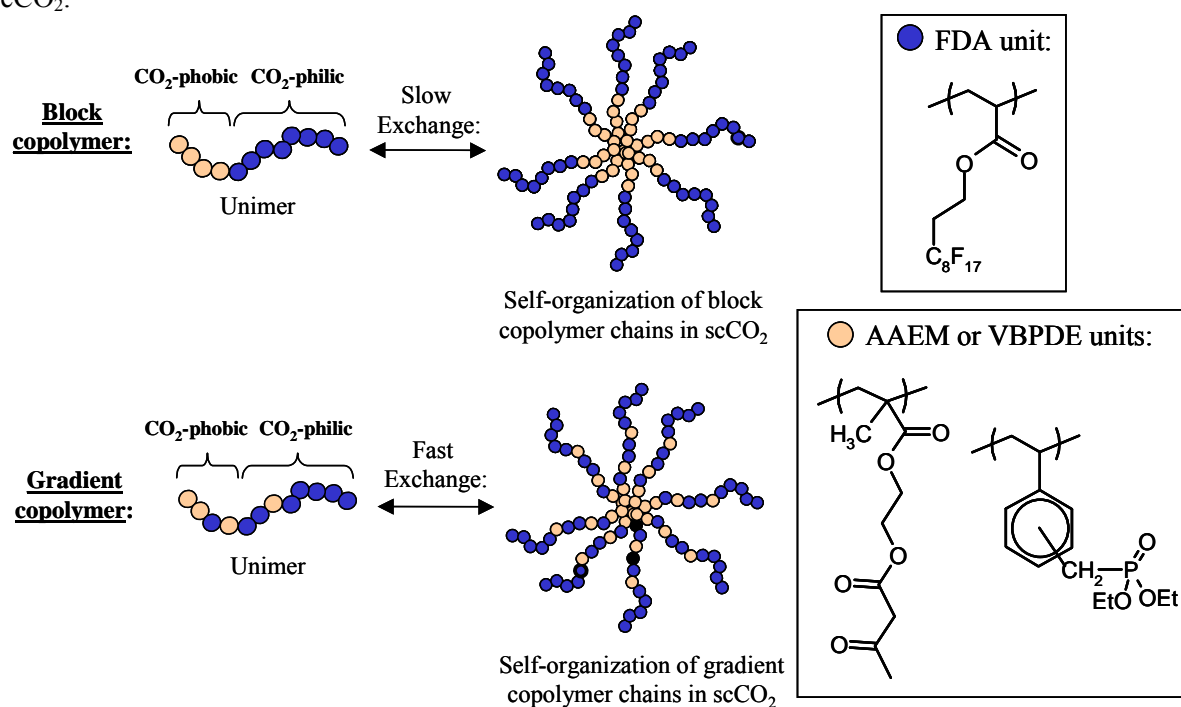
In our approach, the extraction of cobalt derivatives will be realized by amphiphilic controlled-architected copolymers bearing complexing moieties and able to self-assemble in scCO<sub>2</sub> (Scheme 1). These copolymers are gradient copolymers. Termed gradient copolymers constitute a promising new class of copolymers, characterized by a controlled gradient composition along the polymer chain. Unlike random copolymers synthesized by conventional radical polymerization, all chains of gradient copolymers have similar length and composition. And unlike block copolymers, their synthesis only requires one step. Several experimental and theoretical studies proved that gradient copolymers exhibit special interfacial behaviors<sup>9-12</sup>. They form a monolayer which has a larger interfacial width than that

of block copolymers<sup>13</sup>. Furthermore, contrary to amphiphilic diblock copolymers, which tend to form frozen aggregates, some gradient copolymers are at equilibrium and able to exchange free chains in reasonable time scales. They consequently have a better surface activity<sup>14</sup>.

Block and gradient copolymers are attainable by controlled radical polymerization. Reversible addition-fragmentation chain transfer polymerization (RAFT) is a reliable controlled radical polymerization method, due to the versatility of monomers which can be polymerized and the mildness of the reaction conditions.

The gradient copolymers synthesized herein are new and contain a CO<sub>2</sub>-philic part and complexing moieties. 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><sup>15</sup> and the complexing groups are poly(AAEM) or poly(VBPDE) which can afford the phosphonic diacid moiety after hydrolysis (poly(VBPDA)).

Aggregation in scCO<sub>2</sub> has been studied by SANS for several kinds of polymers (homopolymers, graft and block copolymers)<sup>16-19</sup>, but gradient copolymers were rarely studied by SANS<sup>20</sup> and never in scCO<sub>2</sub>.



Scheme 1: Self-organization of copolymer chains in scCO<sub>2</sub>.

## 2. EXPERIMENTAL

### Materials

1,1,2,2-tetrahydroperfluorodecylacrylate (FDA, Atofina) and acetoacetoxyethylmethacrylate (AAEM, Eastman, 97 %) were purified by passing through activated basic aluminum oxide and neutral aluminum oxide respectively. Azobis(isobutyronitrile) (AIBN) was recrystallized from cold methanol and dried in vacuum.  $\alpha,\alpha,\alpha$ -trifluorotoluene (TFT, Lancaster, 99 %) was distilled before use. VBPDE was synthesized as described in the literature<sup>21</sup>. The chain transfer agent (CTA) 1-(ethoxycarbonyl)-ethyl dithiobenzoate was synthesized as described elsewhere<sup>22</sup>. 1,1,2 Trichlorotrifluoroethane (F113, Aldrich, 99%), CO<sub>2</sub> (99.99992 %, SFE 5.2, Linde Gas SA, France) and all other chemicals were used as received unless otherwise stated.

### Synthesis of polymers by RAFT polymerization

All polymerizations were carried out with a molar ratio [AIBN]/[CTA]=0.3 and an initial concentration in monomer of 0.8 g per mL of solvent. AIBN, CTA, the monomers and TFT were

introduced along with a stir bar in a Schlenk flask. After three freeze-pump-thaw cycles, the polymerization was performed at 65 °C under argon. After solvent evaporation, the polymer was washed with n-pentane 95 %, and then dried under vacuum.

### Characterization

<sup>1</sup>H NMR spectra were recorded at room temperature on a Bruker 400 Ultra Shield spectrometer (400 MHz). Conversions of monomers were determined by <sup>1</sup>H NMR analysis of the crude reaction medium with deuterated benzene (C<sub>6</sub>D<sub>6</sub>) capillaries. The composition of the purified copolymers was determined by <sup>1</sup>H NMR spectroscopy in F113 with deuterated benzene (C<sub>6</sub>D<sub>6</sub>) capillaries. Molecular weights were calculated according to <sup>1</sup>H NMR chain-end analysis.

### Cloud-points measurements

Cloud-points measurements were carried out in a high-pressure, variable volume view cell according to a procedure previously reported<sup>23,24</sup>.

### 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>).

## 3. RESULTS AND DISCUSSION

### Synthesis of well-defined copolymers

Because of the controlled character of the RAFT polymerization, the architecture of gradient copolymers only depends on the reactivity ratios ( $r_1=k_{11}/k_{12}$  and  $r_2=k_{22}/k_{21}$ ) of the monomers M1 and M2. Since the reactivity ratio  $r_1$  of an acrylate monomer is less than the reactivity ratio  $r_2$  of the methacrylate and styrenic monomers<sup>25</sup>, AAEM (M2) thus reacts faster than FDA (M1) and the obtained copolymer is a gradient copolymer. The same holds for VBPDE (M2) (Table 1).

Table 1: Characterization of the synthesized polymers

Run	Monomer M <sub>2</sub>	Type	Monomer conversion (%)	Overall weight Conversion (%)	M <sub>n</sub> (g/mol)		Molar fraction of M <sub>2</sub> (%)	
					Theoretical	( <sup>1</sup> H NMR chain-end analysis)	Theoretical	( <sup>1</sup> H NMR (washed polymer))
1	None	Homo-Poly(FDA)	76.5		14300	17300	None	
2	AAEM	Gradient Copolymer	AAEM: 96.0 FDA: 83.8	84.6	16000	19000	16.8	14.3
3	AAEM	Gradient Copolymer	AAEM: 99.4 FDA: 87.6	89.0	16300	22000	27.5	24.2
4	AAEM	Gradient Copolymer	AAEM: 98.8 FDA: 76.7	87.2	15400	16200	45.8	47.5
5	VBPDE	Gradient Copolymer	VBPDE: 90.8 FDA: 68.3	70.1	13200	12500	18.9	18
6	VBPDE	Block Copolymer	VBPDE: 56.5 FDA: 79.1	-	20600	23300	23.5	17.6

### Solubility in scCO<sub>2</sub>

Gradient copolymers poly(FDA-co-AAEM) are very soluble and their cloud point curves are logically above the poly(FDA) homopolymer curve (figure 1). As predicted, the phase behavior of these

gradient copolymers depends on the amount of non-fluorinated units in the chain, that is the CO<sub>2</sub>-philic/CO<sub>2</sub>-phobic balance: incorporation of AAEM units increases the cloud point pressure at a given temperature. But very interestingly, they are soluble at much lower pressures than random copolymers poly(FDA-co-AAEM) synthesized by conventional radical polymerization and having nearly the same molar percentages of AAEM units<sup>8,26</sup>.

The gradient copolymer poly(FDA-co-VBPDE) 18 % mol VBPDE is also very soluble. Its cloud point values are equivalent to those of poly(FDA-co-AAEM) 14 % mol AAEM. In contrast, cloud point values of the block copolymer poly(VBPDE)-*b*-poly(FDA) 18 % mol VBPDE are much higher (25<T<65 °C, 260<P<360 bars). Thus, gradient copolymers seem to be soluble at much lower pressure than block copolymers.

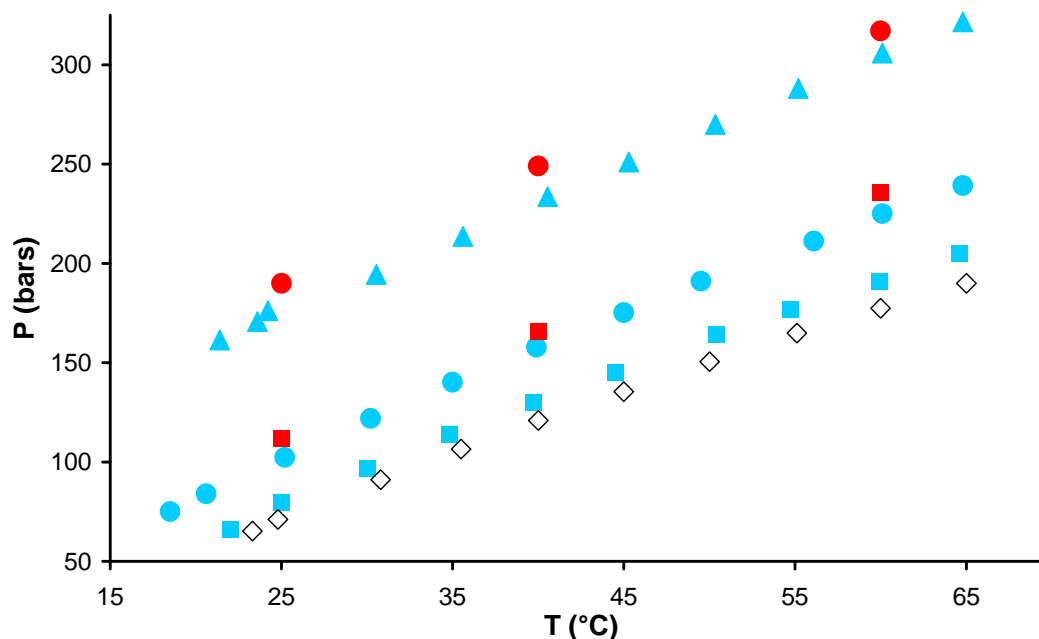


Figure 1: Cloud points (4 % wt of polymer versus CO<sub>2</sub>) of poly(FDA-co-AAEM) gradient copolymers 14 % mol AAEM (■), 24 % mol AAEM (●), 48 % mol AAEM (▲), and poly(FDA) homopolymer (◇) all synthesized by RAFT polymerization (this work), in comparison with poly(FDA-co-AAEM) random copolymers 15 % mol AAEM (■) and 25 % mol AAEM (●) synthesized by conventional radical polymerization (DeSimone et al.<sup>8,26</sup>).

### SANS study of the self-organization of poly(FDA-co-AAEM) with AAEM 15 % mol

Self-organization of this gradient copolymer was studied at 40 °C and at two pressures (140 bar, 210 bar) by SANS. The scattered intensities are shown in Figure 2. Despite the high concentration of polymer (8 % wt of polymer versus CO<sub>2</sub>), low absolute intensities were measured and pure form factor scattering was observed. The absence of a structure factor peak implied that scattering reflected the structure of isolated objects. Low intensities indicated that these objects had rather low mass and are due to the low contrasts (T=40 °C; P=140 bar,  $\rho(\text{CO}_2)=1.91 \cdot 10^{10} \text{ cm}^{-2}$  and  $\rho(\text{copolymer})=3.18 \cdot 10^{10} \text{ cm}^{-2}$ ; P=210 bar,  $\rho(\text{CO}_2)=2.12 \cdot 10^{10} \text{ cm}^{-2}$  and  $\rho(\text{copolymer})=3.18 \cdot 10^{10} \text{ cm}^{-2}$ ).

More specifically, the low-angle intensity limit was used to extract the average aggregation number. By changing the pressure from 140 to 210 bar, changes of aggregation can be noticed in Figure 2: the aggregation number decreased from 5 to 2. For finite q-vectors, the scattered intensity decreased, as one would expect for form factors. This decay can be described at small angles by a Guinier law ( $I=I_0 \cdot \exp(-q^2 R_g^2/3)$ ). As shown in Figure 2, we determined the radii of gyration  $R_g$  of the copolymers: 47 and 22 Å, at 140 and 210 bar, respectively. These values can be compared with the theoretical estimation of the  $R_g$  of a single copolymer chain in CO<sub>2</sub> (15 Å). Thus, the size of aggregates decreased with increasing pressure. This phenomenon was already observed for solutions of block copolymers in scCO<sub>2</sub><sup>17,19,27,28</sup>: the increase in the surface area of block copolymer in contact with the solvent was

explained by the higher solubility of polymers when CO<sub>2</sub> density increases. The solvent quality of CO<sub>2</sub> for poly(FDA) homopolymer was indeed shown to increase with CO<sub>2</sub> pressure<sup>15</sup>. Gradient copolymers seem thus to be as able to pressure-induced micellization as block copolymers.

The difference between the volume deduced from Guinier approximation, and the dry volume of the gradient copolymer aggregate deduced from I<sub>0</sub>, showed an important solvation of the copolymer chains: V(CO<sub>2</sub>)/V(polymer)=11.1 at 140 bar and 1.9 at 210 bar. If we consider the weights: m(CO<sub>2</sub>)/m(polymer)=5.1 at 140 bar and 1 at 210 bar. From these calculations, each gradient copolymer chain is surrounded by 1850 molecules of CO<sub>2</sub> at 140 bar and 360 molecules of CO<sub>2</sub> at 210 bar.

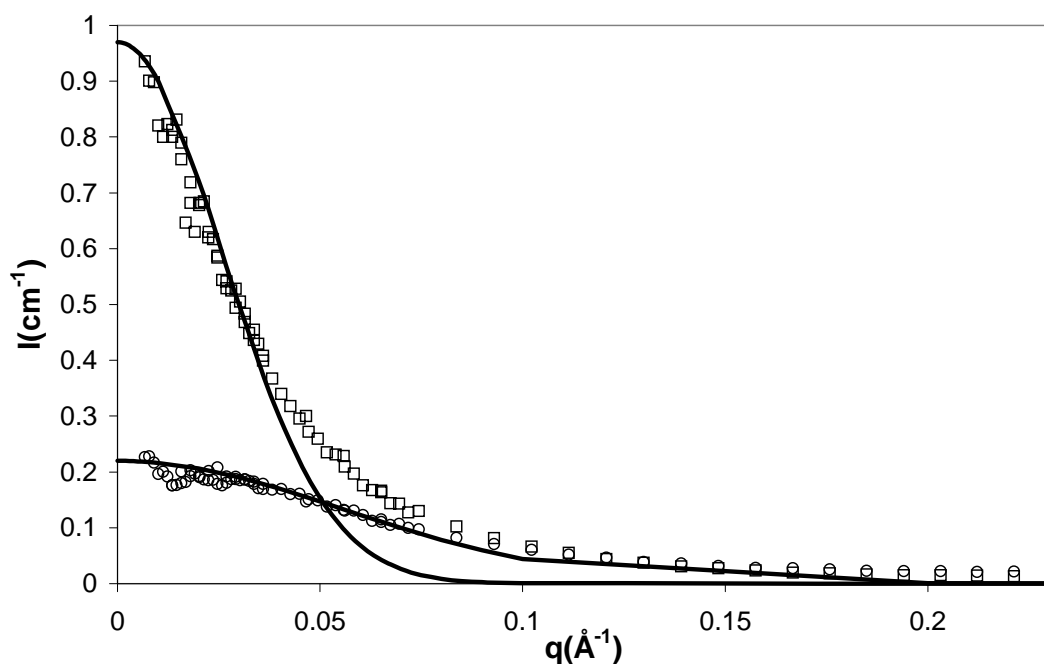


Figure 2: SANS data for poly(FDA-co-AAEM) gradient copolymer 15 % mol AAEM ( $T=40^{\circ}\text{C}$ ,  $P=140$  bar ( $\square$ ) or  $P=210$  bar ( $\circ$ )) (8 % wt of polymer versus CO<sub>2</sub>) and the corresponding Guinier plots.

#### Extraction of cobalt derivatives

Gradient copolymers were shown to increase the sedimentation time of cobalt hydroxide (Co(OH)<sub>2</sub>) dispersions in scCO<sub>2</sub>. This enhanced stability indicates a favored interaction between the polymer and the contaminant.

#### 4. CONCLUSION

This work confirmed that RAFT polymerization is an appropriate method to obtain semifluorinated well-architected copolymers. Poly(FDA-co-AAEM) and poly(FDA-co-VBPDE) gradient copolymers, as well as poly(VBPDE)-*b*-poly(FDA) block copolymer, were synthesized with good conversions. The gradient copolymers exhibit remarkable CO<sub>2</sub> solubility that will allow using them as complexing surfactants for extraction of metallic derivatives in scCO<sub>2</sub>. Furthermore, SANS study of the gradient copolymer poly(FDA-co-AAEM) shows that its self-organization depends on the CO<sub>2</sub> pressure. Our aim is now to use such pressure-sensitive supramolecular self-assemblies of complexing polymers in applications such as sustainable decontamination processes.

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