USE OF FLUORINATED AND SILICONE-BASED COPOLYMERS WITH COMPLEXING GROUPS FOR APPLICATIONS IN SUPERCRITICAL CO_2

Mathieu CHIRAT[1,2a], Sebastien CLERC[1], Tiphaine RIBAUT[1,2a,3], Frédéric CHARTON[2a], Jérémy CAUSSE[2c], Bruno FOURNEL[2b] and Patrick LACROIX-DESMAZES*[1]

[1] Institut Charles Gerhardt – UMR 5253 CNRS, Ingénierie et Architectures Macromoléculaires (IAM), ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France.
[2] CEA Marcoule, [a] DEN/DTCD/SPDE/Laboratoire des Fluides Supercritiques et Membranes (LFSM), [b] DEN/DTCD/DIR, [c] DEN/DTCD/SPDE/Laboratoire des procédés avancés de décontamination (LPAD) BP17171, 30207 Bagnols Sur Cèze, France
[3] Institut de Chimie Séparative de Marcoule, UMR 5257, ICSM Site de Marcoule, BP 17171, 30207 Bagnols Sur Ceze Cedex, France
Correspondence: fax: (+33)467147220; E-mail address: patrick.lacroix-desmazes@enscm.fr.

ABSTRACT
Copolymers of either 1,1,2,2-tetrahydroperfluorodecylacrylate (FDA) or α-monomethacryloxypropyl polydimethylsiloxane (PDMS-MA) have been synthesized by Reversible Addition-Fragmentation chain Transfer (RAFT) copolymerization with acetoacetoxyethylmethacrylate (AAEM) or vinylbenzylphosphonic acid diethylester (VBPDE) as functional comonomers. The resulting copolymers are soluble in carbon dioxide (CO_2) and exhibit controlled and amphiphilic architecture. Hydrophilic moieties can be obtained by modification of VBPDE groups. The phase diagrams of these copolymers in liquid and supercritical CO_2 have been investigated and showed a larger dependence in terms of concentration and molecular weight for the silicone-based copolymers compared to the fluorinated ones. Two applications for these CO_2-soluble functional copolymers are studied. First, the copolymers aim to be used for nuclear decontamination in compressed CO_2. The nuclear contamination being radioactive cobalt, its complexation with the copolymers has been checked by ICP-AES. Thus, extraction tests of cobalt nitrate from textile in scCO_2 give an extraction yield of 66% without optimization. Second, the copolymers are used for the preparation of innovative materials for heterogeneous catalysis using a bottom-up approach fully performed in dense CO_2.

INTRODUCTION
Among the variety of polymers, only a few types exhibit a relatively good solubility in compressed carbon dioxide (CO_2). To the best of our knowledge [1-4], poly(fluoroalkylacrylate)s and poly(siloxane)s require the lowest CO_2 pressures to be soluble at moderate temperature, which make them extremely interesting for CO_2 applications. Therefore, to synthesize functional copolymers, FDA or PDMS-MA have been selected to play the role of CO_2-philic units whereas AAEM, VBPDE or vinylbenzylphosphonic acid (VBPDA) are the functional units. Several copolymers have been synthesized to study the effect of different parameters on CO_2 solubility or complexing ability.

MATERIALS AND METHODS

Materials

1,1,2,2-Tetrahydroperfluorodecylacrylate (FDA, Atofina, distilled), α-monomethacryloxypropyl polydimethylsiloxane (PDMS-MA) (viscosity 6-9 cSt., MCR-M07, abcr) (M_n = 736 g/mol determined by ^{1}H NMR) and acetoacetoxyethylmethacrylate (AAEM, Eastman, 97 %) were purified by passing through activated basic aluminum oxide (Aldrich, 150 mesh - 58Å) and filtered on PTFE 0.2 µm filter. Vinylbenzylphosphonic acid diethylester (VBPDE) was synthesized as described in the literature [1,5]. Azobis(isobutyronitrile) (AIBN, Fluka 98%) was recrystallized in methanol and dried under vacuum. α,α,α-Trifluorotoluene (TFT, Sigma-Aldrich, anhydrous, ≥99 %) and methyl acrylate (Aldrich, 99%) were distilled before use. The chain transfer agents (CTA) 1-(ethoxycarbonyl)-ethyl dithiobenzoate (ECEDB) and 2-cyanoprop-2-yl dithiobenzoate (CPDB) were prepared as previously described [6,7]. All metal precursors were used as received: cobalt(II) nitrate hexahydrate ($Co(NO_3)_2$, $6H_2O$) (Aldrich, 99.999%), cobalt(II) chloride hexahydrate ($Co(Cl)_2$, $6H_2O$) (Aldrich, analysis grade), cobalt(II) acetate anhydrous ($Co(C_2H_3O_2)_2$) (Aldrich, 99.995%), cobalt(II) acetate tetrahydrate ($Co(C_2H_3O_2)_2$, $4H_2O$) (Acros Organics, 98+%), palladium(II) acetate ($Pd(C_2H_3O_2)_2$) (Aldrich, 99.9%). 1,1,2 Trichlorotrifluoroethane (F113, Aldrich, 99%), 1,1,3,3-tetramethylguanidine (TMG) (Aldrich, 99%), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (Fluka, 98%), iodobenzene (Aldrich, 98%), triphenylphosphine (Aldrich, 99%), triethylamine (SDS, 99.5%), CO_2 (99.99992 %, SFE 5.2, Linde Gas SA, France) and all other chemicals were used as received unless otherwise stated.

Instrumentation

Size Exclusion chromatography (SEC) was used to determine the molecular weight distributions of silicone-based copolymers with respect to polystyrene standards (Polymer Laboratories). The apparatus is a PL-GPC 50 plus equipped with two columns (mixed-C PL-gel 5 µm columns: $2×10^2$ - $2×10^6$ g/mol) thermostated at 35°C with THF as eluent at a flow rate of 1.0 mL/min and a refractometer detector.

^{1}H NMR spectra of the polymers were obtained at room temperature on a Bruker 400 Ultra Shield spectrometer (400 MHz) using 5 mm o.d. tubes and $CDCl_3$ as deuterated solvent for silicone-based copolymers or C_6D_6 capillaries in TFT or F113 for fluorinated copolymers.

Cloud-point measurements were carried out in a high-pressure view cell with variable volume according to a procedure previously reported [8].

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) or inductively coupled plasma mass spectroscopy (ICP-MS) were used to determine the cobalt or palladium composition of samples.

Copolymer syntheses

Fluorinated copolymers

Fluorinated gradient copolymers, poly(FDA-*co*-VBPDA) and poly(FDA-*co*-AAEM) (**Figure 1**) were synthesized by RAFT copolymerization using ECEDB or CPDB as chain transfer agent following the procedure described elsewhere [1]. **Table 1** sums up the copolymers prepared for this study. A relatively good agreement between theoretical and experimental values was obtained for the molecular weight and composition of the copolymers, confirming the controlled behavior of the copolymerization.
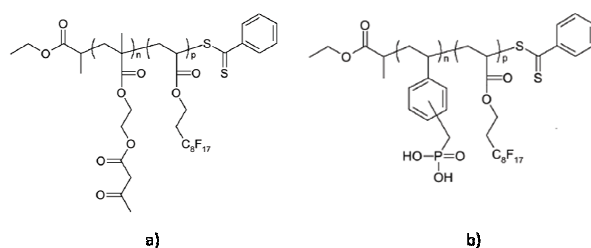
Figure 1. Structures of a) poly(FDA-*co*-AAEM) and b) poly(FDA-*co*-VBPDA).

Table 1. Characteristics of the fluorinated gradient copolymers

Sample	Polymer type	M_n (g/mol)		Molar composition of AAEM or VBPDA (%)	
		Theor.	^{1}H NMR	Theor.	^{1}H NMR
a	Poly(FDA-*co*-AAEM)	15760	22950	16.6	14.6
b	Poly(FDA-*co*-VBPDA)	15080	19840	17.4	18.9

Silicone-based copolymers

Silicone-based statistical/gradient and block copolymers (**Figure 2**), poly(PDMS-MA-*co*-AAEM), poly(PDMS-MA-*co*-VBPDE), poly(AAEM)-*block*-poly(PDMS-MA), poly(PDMS-MA-*co*-AAEM)-*block*-poly(PDMS-MA) were synthesized by RAFT polymerization using CPDB as chain transfer agent. All polymerizations were carried out with a molar ratio [AIBN]/[CTA]=0.3 and an initial concentration in monomer of 0.8 g/mL of solvent. AIBN, CPDB, the monomers and TFT or ethyl acetate were introduced along with a stir bar in a Schlenk flask. After three freeze-thaw-pump cycles, the polymerization was performed for 15 to 28 hours at 65 °C under argon. In the case of block copolymer, an additional step was then performed: a thoroughly deoxygenated (freeze-thaw pump) solution of solvent containing PDMS-MA (0.35 to 1.5 g/mL of solvent) and AIBN ([AIBN]/[CTA]$_0$=0.1) was carefully introduced in the reaction mixture under argon and the polymerization was left to proceed for 1 day. Finally, the reaction mixture was precipitated in methanol, then washed twice with methanol and put under vacuum (5×10^{-2} mbar at room temperature) for the removal of solvent traces. The product was stored in the freezer (T = −20°C).
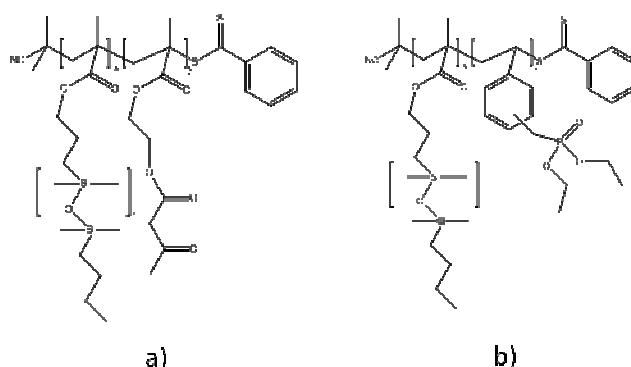

Figure 2. Structures of a) poly(PDMS-MA-*co*-AAEM) and b) poly(PDMS-MA-*co*-VBPDE).

Table 2 sums up the characteristics of the silicone-based copolymers. The conversions of the copolymerization are high. Molecular weights determined by SEC are close to the theoretical values and the compositions obtained by ^{1}H NMR are in agreement with the theoretical ones.

Table 2. Characterization of silicone-based copolymers synthesized by RAFT polymerization

Run	Polymer type	Conversion (%)		M_n (g/mol)		Molar composition of AAEM or VBPDE (%)	
		PDMS-MA	AAEM or VBPDE	Theor.	SEC *precipitated* (PDI)	Theor.	^{1}H NMR
1	poly(PDMS-MA-*co*-AAEM)	92.7	94.9	9,450	9,900 (1.17)	20.5	20.6
2	poly(PDMS-MA-*co*-AAEM)	99.5	94.1	17,980	15,150 (1.17)	20.5	17.5
3	poly(PDMS-MA-*co*-AAEM)	90.0	97.9	36,860	27,450 (1.22)	20.2	20.4
4	poly(PDMS-MA-*co*-AAEM)	97.3	100	9,760	10,600 (1.14)	10.0	10.6
5	poly(PDMS-MA-*co*-AAEM)	97.7	99.7	10,070	9,950 (1.16)	30.5	30.0
6	poly(PDMS-MA-*co*-AAEM) 1st part	80	100	2,800	5,750* (1.15)	81.8	n.d.
	poly(PDMS-MA-*co*-AAEM)-*block*-poly(PDMS-MA)	64.3	100	16,510	11,700 (1.23)	26.5	25.4
7	poly(AAEM) 1st part	n.a.	93.2	1,540	3,400* (1.08)	100	n.d.
	poly(AAEM)-*block*-poly(PDMS-MA)	95.2	100	16,210	10,900 (1.14)	21.8	19.9
8	poly(PDMS-MA-*co*-VBPDE)	84.6	100	7,360	10,900 (1.31)	22.7	23.2
9	poly(PDMS-MA-*co*-VBPDE)	87.5	100	8,650	9,850 (1.41)	21.7	15.6
10	poly(PDMS-MA-*co*-VBPDE)	97	100	17,900	14,700 (1.41)	20.3	18.2

* From the crude mixture (not precipitated); n.d.: not determined; n.a.: not applicable.

Heck reaction

Iodobenzene (1.0 eq.), methyl acrylate (1.0 eq.), triethylamine (6.0 eq.) and triphenylphosphine (0.08 eq.) were mixed in TFT ([reactant] = 0.1 M) and introduced with the Pd-based catalyst (0.024 eq. of Pd (theoretical values)) in 20 ml tubes for Radley Carrousel 12. The reaction was performed under inert gas (Argon), at 70°C, in absence of light, for 46 h. Conversion was determined on the crude reaction mixture by ^{1}H NMR.

RESULTS AND DISCUSSION
Phase diagrams of copolymers in carbon dioxide

The working pressure is a key point for pressurized carbon dioxide processes. When the use of polymer is required in the process, the working pressure (that usually you want as low as possible) is often limited by the cloud point pressure of the polymer. Poly(FDA) has been shown to have excellent solubility properties in CO_2 and it has been extensively studied [3]. Poly(PDMS-MA) has been selected as an alternative to fluorinated polymers. For applications, functionality is introduced in the polymer with a comonomer during the polymerization. Previous studies [1] have shown the effect of molecular weight, nature and proportion of the CO_2-phobic part for FDA-based copolymers. **Figure 3** compares the solubility of different poly(PDMS-MA-co-AAEM)s. An increase of molecular weight has a

huge impact on the cloud pressure whereas a variation in the CO_2-phobic unit proportion does not affect a lot the solubility. The solubility of a poly(FDA-co-AAEM) with same molecular weight and proportion of AAEM is presented on Figure 3: the cloud pressures are lower verifying the better solubility of poly(FDA). It is also important to notice that the poly(FDA-co-AAEM) is at a weight percentage in CO_2 of 4% whereas the poly(PDMS-MA-co-AAEM)s are at 0.2%. Solubility of fluorinated copolymers based on FDA is not really affected by the concentration. It is not the case for silicone-based copolymer: as **Figure 4** shows, the cloud pressure increases dramatically with the concentration. Consequently, applications with silicone-based copolymer are therefore restricted to applications using low concentration of copolymers.
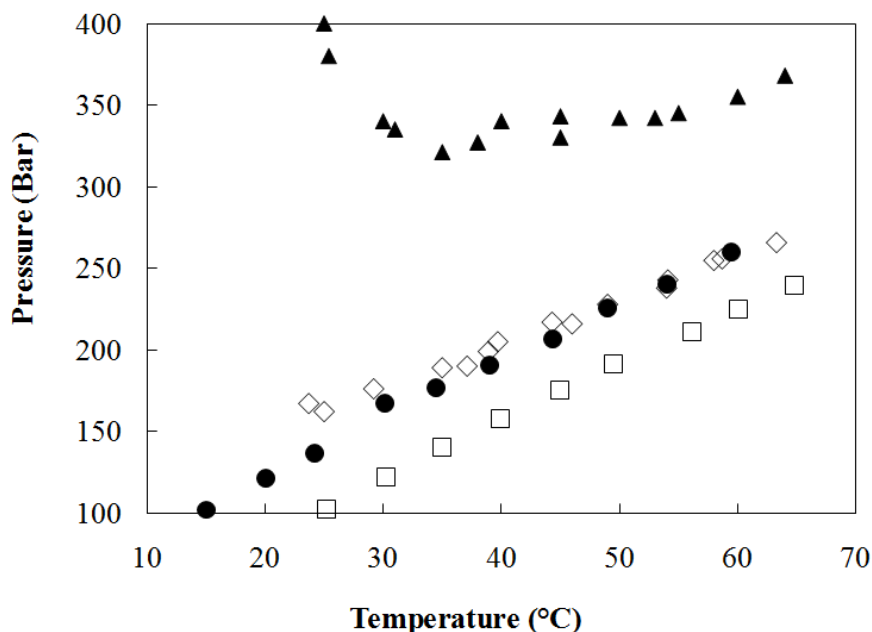

Figure 3. Comparison of the cloud point pressures in CO_2 versus temperature of the poly(PDMS-MA-co-AAEM) gradient copolymers ($\Diamond$) : (M_n=9900 g/mol / 20.6 mol% AAEM / 0.2wt% in CO_2), ($\bullet$) : (M_n=10600 g/mol / 10.6 mol% AAEM / 0.2wt%), g/mol), ($\blacktriangle$) (M_n=27450 g/mol / 20.4 mol% AAEM / 0.2wt%) and poly(FDA-co-AAEM) ($\square$): (M_n=16300 g/mol / 24.2 mol% AAEM / 4wt%).
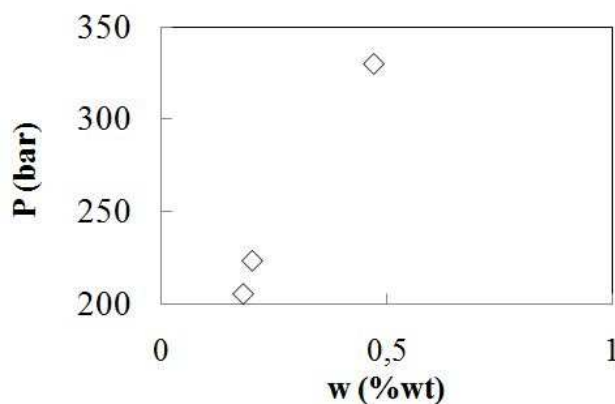

Figure 4. Evolution of the cloud point pressure versus weight concentration of the poly(PDMS-MA-co-AAEM) gradient copolymer in CO_2 ($\Diamond$) :(M_n =9900 g/mol / 20.6 mol% AAEM).

Application 1 : Nuclear decontamination
Nuclear decontamination of textile is currently performed in aqueous medium. A large amount of contaminated water is thus produced and has to be treated in a further process. The use of CO_2 as medium for the decontamination avoids the production of the aqueous effluent. As in aqueous medium, an additive is required for the removal of radioactive contaminant in CO_2. Radioactive cobalt is our targeted contamination. The additives are the copolymers bearing complexing groups: poly(FDA-co-AAEM) and poly(FDA-co-VBPDA).

Complexation of cobalt by copolymers
Complexation of cobalt with the copolymers was studied in Freon 113 (F113) (for convenience). The cobalt precursor and complexing groups were varied. The cobalt precursors were introduced in a solution of copolymer in F113. The incorporation of cobalt in the copolymers was analyzed by ICP-AES.
For poly(FDA-co-AAEM)s, a base was added to activate the complexing properties of the acetoacetoxy moiety. **Table 3** shows the results of these experiments in term of Co incorporation. A correlation between the type of precursor and the type of complexing unit is found. For poly(FDA-*co*-AAEM), the highest incorporation is found with cobalt acetate hydrate whereas with cobalt nitrate the incorporation is almost null in the copolymer. For poly(FDA-*co*-VBPDA), we can observe a good incorporation with cobalt nitrate and an inefficient incorporation with cobalt acetate. These opposite results can find their explanations in the differences in terms of binding forces between the ligands (from the precursors or from the copolymers) and cobalt and their solubility in solvents (F113 or water).

Table 3. Cobalt uptake of poly(FDA-*co*-AEEM) and poly(FDA-*co*-VBPDA)

Run	Polymer	Base	Precursor *(0.5 eq / AAEM or VBPDA)*	Theo. Co content (%)	ICP-AES Co content (%)
I	Poly(FDA-*co*-AAEM)	TMG	Co(acetate)$_2$	0.92	0.33
II	Poly(FDA-*co*-AAEM)	TMG	Co(acetate)$_2$, 4H$_2$O	0.92	0.72
III	Poly(FDA-*co*-AAEM)	TMG	Co(Cl)$_2$, 6H$_2$O	0.94	0.32
IV	Poly(FDA-*co*-AAEM)	TMG	Co(NO$_3$)$_2$, 6H$_2$O	0.88	0.06
V	Poly(FDA-*co*-VBPDA)	None	Co(acetate)$_2$	1.32	0.06
VI	Poly(FDA-*co*-VBPDA)	None	Co(acetate)$_2$, 4H$_2$O	1.43	0.03
VII	Poly(FDA-*co*-VBPDA)	None	Co(NO$_3$)$_2$, 6H$_2$O	1.32	1.36

CO_2 solubility of some of the products cobalt-copolymers were checked in dense CO_2. For example, the product of the run II has cloud pressures 30 to 40 bar higher than the starting copolymer (sample a). This is reasonable for the potential applications.

Extraction test
Cobalt nitrate is deposited on a textile piece of 50/50 cotton/polyester from an aqueous solution. The piece is introduced in a pressurized cell with additives: copolymers, water or other. The decontamination process is performed in CO_2 at 160 bar and 40°C for 1h30min and the piece is rinsed in CO_2. Residual cobalt is analyzed by ICP-MS. The full procedure will be described elsewhere. A extraction yield of 66% is found when using poly(FDA-co-VBPDA)

in the presence of a water. All reference trials confirmed that the extracting agent has to be a surfactant in CO_2 bearing VBPDA complexing groups for a contamination of cobalt nitrate.

Application 2: Catalytic materials
The copolymers have abilities to complex metals, therefore they can be used to synthesize catalytic materials in carbon dioxide. We aim to produce heterogeneous supported catalyst using a full CO_2 process starting from the synthesis of the copolymers to the impregnation of the support (**Figure 4**).
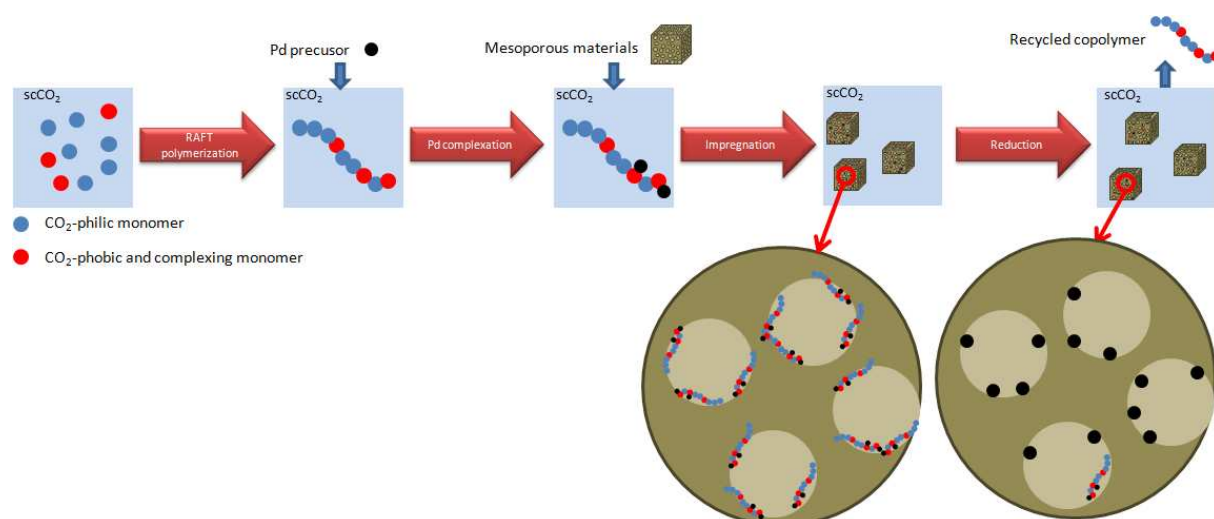

Figure 4. Schematic process of the heterogeneous supported catalyst synthesis

The synthesis of the fluorinated copolymers in CO_2 has been already reported [1]. The incorporation of Pd (from palladium acetate) in the copolymer poly(FDA-co-AAEM) using TMG for activation in F113 provides a product with a palladium content of 3.13% for 3.10% theoretically. Incorporation of palladium in CO_2 was performed as well with DBN for activation. The product has 0.86% of Pd for 1.8% theoretically in CO_2.

To check the catalytic activity of our Pd-polymer complex, Heck reaction was performed between iodobenzene and methyl acrylate. A reaction yield of 50% in 46 hours is found to be similar to the standard catalyst palladium acetate for a Pd-poly(FDA-co-AAEM) containing 1.50% of Pd. This confirms the presence of palladium in active form for catalysis in the copolymer.

Impregnation experiments of mesoporous materials by Pd-polymer complexes in dense CO_2 are in progress and promising results have been obtained. They will eventually lead to heterogeneous supported catalysts after reduction of Pd^{II} to Pd^0.

CONCLUSIONS

We successfully synthesized different types of copolymers starting from a silicone-based macromonomer or fluorinated acrylate and functional comonomers with statistical/gradient, blocky and block architectures using RAFT polymerization. Silicone-based copolymers have lower solubility and higher dependence in terms of molecular weight and concentration than fluorinated copolymers. Fluorinated copolymers show complexing properties with cobalt and

palladium allowing their use in different applications. For nuclear decontamination, copolymers with VBPDA groups obtain 66% of extraction yield. Since the required concentration of copolymer is not too high, silicone-based copolymers represent a good alternative for this application where the use of fluorinated compounds is unwanted or difficult regarding the nuclear waste processing system. We have also started to demonstrate the possibility of producing materials (in this case: heterogeneous supported catalyst) using a clean process fully developed in dense CO_2.

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