SUPERCRITICAL CO_2-SOLUBLE FUNCTIONAL AMPHIPHILIC FLUORINATED COPOLYMERS AND THEIR PALLADIUM COMPLEXES : SYNTHESIS AND THEIR USE AS CATALYST

energie atomique • energies alternatives

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➢Introduction

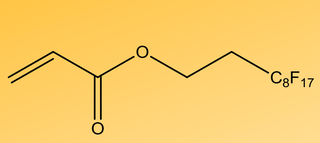
Poly(fluoroalkyl acrylate)s exhibit excellent solubility properties in supercritical carbon dioxide ($scCO_2$). In the literature, a lot of work[1,2,3] in $scCO_2$ has been performed using this type of polymers. We synthesized by RAFT polymerization gradient copolymers from fluoroalkylacrylate and functional monomers to obtain copolymers with special abilities for applications in $scCO_2$ (extraction, catalysis…).

- ✓ Copolymer architecture[4] : gradient > block
- ✓ CO_2-philic unit: fluoroalkyl acrylate → best solubility in CO_2
- ✓ Functional units : acetoacetoxy or phosphonic acid groups for metal complexation

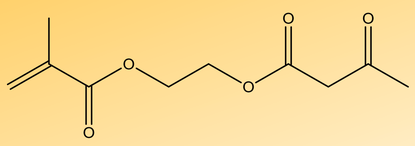
➢Monomers

The CO_2-philic monomer is composed of a C_8 fluorinated pendant chain. The functional monomers are a commercial methacrylate bearing an acetoacetoxy group and a synthesized styrenic with phosphonic diester group.

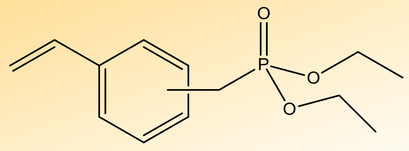
● CO_2-philic unit ● CO_2-phobic units



1,1,1,2,2-Tetrahydroperfluorodecylacrylate (FDA)



Acetoacetoxyethyl methacrylate (AAEM)

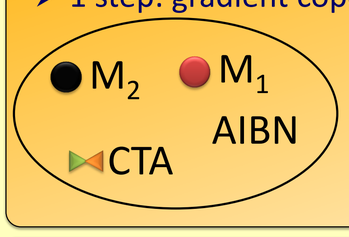


Vinylbenzylphosphonic acid diethyl ester (VBPDE)

➢Copolymerization

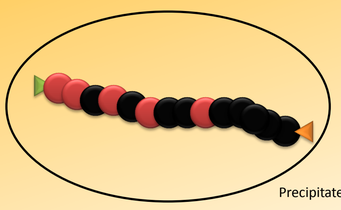
Controlled free radical polymerization RAFT was used to synthesize the copolymers with gradient architecture[4].

➢ 1 step: gradient copolymers



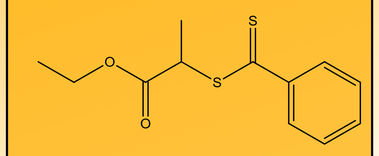
48h 65°C

TFT



Precipitated in pentane

Control transfer agent (CTA)

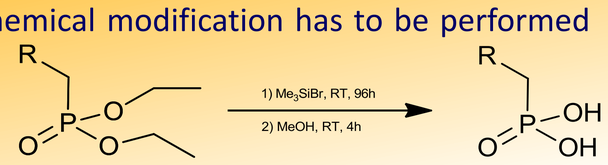


1-(ethoxycarbonyl)-ethyldithiobenzoate *(CTA)*

➢Copolymer modification

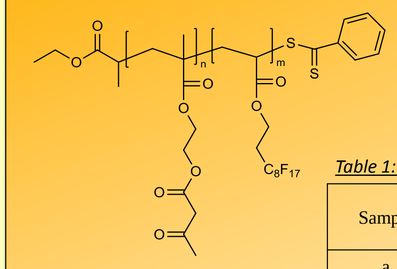
To obtain the phosphonic acid group, a chemical modification has to be performed on the phosphonic diester[4].

Phosphonic diester → Phosphonic diacid

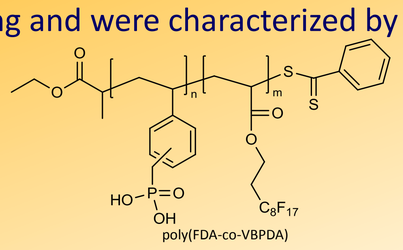


➢Copolymers

The copolymers used in the experiments are the following and were characterized by ^1H NMR (using TFT or F113 as solvent and C_6D_6 capillaries for locking).



poly(FDA-co-AAEM)



poly(FDA-co-VBPDA)

Table 1: characteristics of copolymers

Sample	Polymer type	M_n (g/mol)		Molar composition of AAEM or VBPDA (%)	
		Theor.	^1H NMR	Theor.	^1H NMR
a	Poly(FDA-*co*-AAEM)	18250	25700	15.1	12.9
b	Poly(FDA-*co*-VBPDA)	15080	19840	17.4	18.9

The molecular weight determined by ^1H NMR is calculated using the aromatic characteristic peak of the chain-end

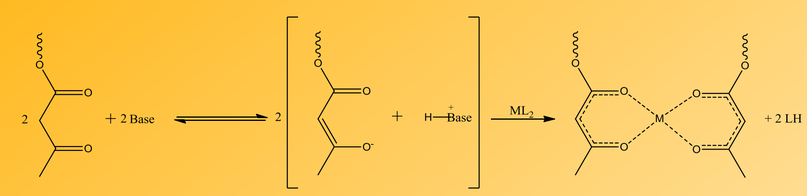
➢Copolymer-metal complexes

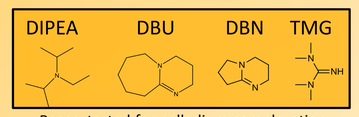
Copolymers and metals were mixed together to study the complexation properties of the copolymers

- **Poly(FDA-co-AAEM)-metal complexes**

poly(FDA-co-AAEM) + Pd^{II} precursor —(complexation, F113 or CO_2 SC)→ poly(FDA-co-AAEM)-Pd^{II} complex

- **Complexation of Pd by AAEM with base**





Bases tested for palladium complexation

- **Copolymer-Pd^{II} complexes**

The products were analyzed by ICP-AES to measure the metal content.

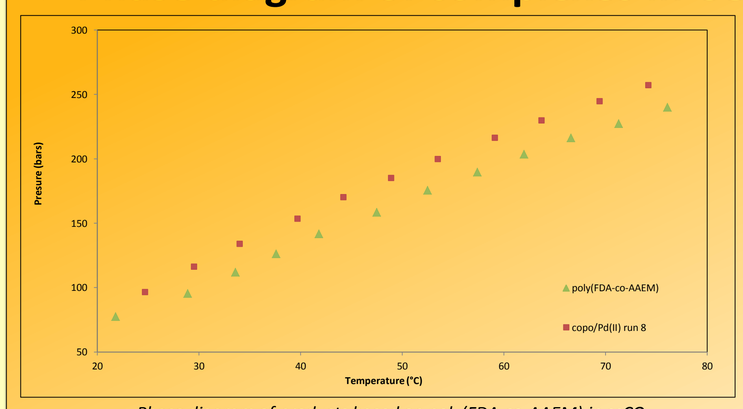
Best results were obtained with the use of 1,1,3,3-tetramethylguanidine (TMG) as base :

$Pd(OAc)_2$ + AAEM + TMG → AAEM-Pd^{II}

Table 2: characteristics of copolymer-Pd complexes

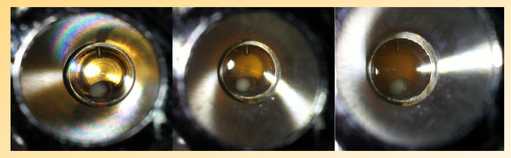
Run	Polymer	base	Solvent	[Pd]/[AAEM]	wt% Pd_{th}	wt% Pd_{exp}
1	poly(FDA-co-AAEM)	-	F113	1/2	1.6	0.9
2	poly(FDA-co-AAEM)	DBN	F113	1/2	1.6	1.5
3	poly(FDA-co-AAEM)	DIPEA	F113	1/2	1.6	1.6
4	poly(FDA-co-AAEM)	-	**CO2 SC**	1/2	1.4	0.3
5	poly(FDA-co-AAEM)	DBN	**CO2 SC**	1/2	1.4	0.3
6	poly(FDA-co-AAEM)	DBU	**CO2 SC**	1/2	1.4	0.4
7	poly(FDA-co-AAEM)	DIPEA	**CO2 SC**	1/2	1.4	0.4
8	poly(FDA-co-AAEM)	TMG	**CO2 SC**	1/2	1.5	1.1

➢Phase diagram of complexes in CO_2



Phase diagram of products based on poly(FDA-co-AAEM) in $scCO_2$

Phase diagrams of products in CO_2 were determined by cloud point pressure measurement at different temperatures at a polymer weight fraction of 4wt% using a setup described in the literature[5].

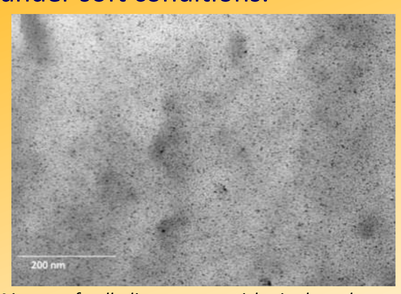


A small increase of cloud point pressure is observed when the metal is incorporated to the copolymers.

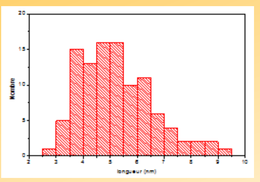
➢Reduction of copolymer-Pd^{II} complexes

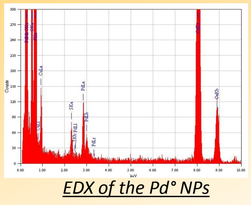
Pd^0 nanoparticles incorporated into the copolymer can be obtained by reduction of the copolymer-Pd^{II} complex under soft conditions.

poly(FDA-co-AAEM)-**Pd^{II}** complex —(H_2)→ poly(FDA-co-AAEM)-**Pd^0** complex



TEM image of palladium nanoparticles in the polymer matrix





EDX of the Pd^0 NPs

→ Monodisperse nanoparticles of Pd^0 (3-6 nm)

➢ Applications

- **Catalytic activity of copolymer-Pd complexes:**

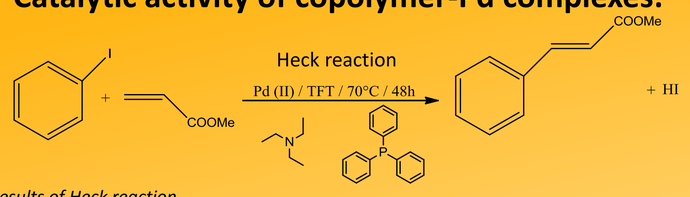


Table 3: results of Heck reaction

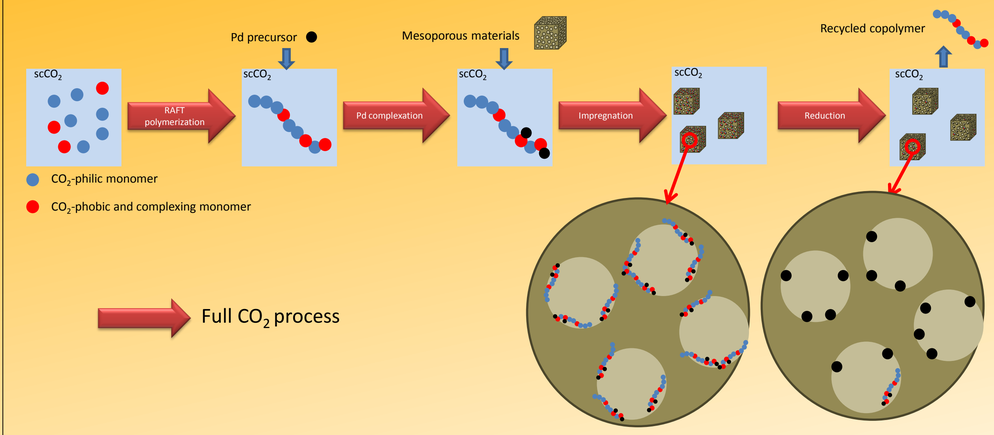
Run	Catalyst	%w Pd_{exp} [a]	conv t24h (%)	conv t96h (%)
0	$Pd(OAc)_2$	47.4	27	100
4	Poly(FDA-co-AAEM)/Pd(II)	0.3	0	0
8	Poly(FDA-co-AAEM)/Pd(II)	1.1	0	78

(a): Pd mass percentage into the catalyst

→ The product copolymer-Pd^{II} is catalytically active for Heck reaction

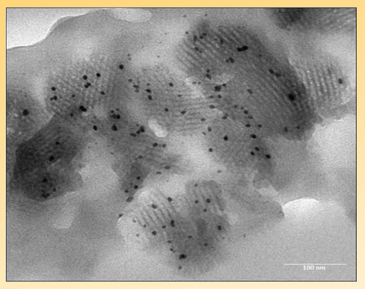
→ 78% of reaction yield for the product (run 8) copolymer-Pd Similar to standard catalyst ($Pd(OAc)_2$)

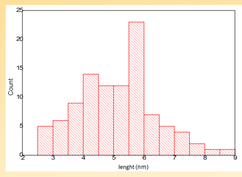
- **Heterogeneous supported catalyst:**



→ Full CO_2 process

Copolymer-Pd^{II} complex (run 8) is impregnated into commercial mesoporous silica in $scCO_2$ media, then reduction is performed under soft conditions.





TEM image of entrapped palladium nanoparticles

→ Monodisperse nanoparticles of Pd^0 are obtained into mesoporous silica and this supported catalyst (0.8 wt% Pd) was found to be active in Heck reaction (95% conversion after 48h)

➢Acknowledgments and references

Laboratoire de métallographie et d'analyses chimiques DEN/DTEC/SGCS/LMAC at CEA Marcoule for ICP-AES and ICP-MS analyses
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➢Conclusion

CO_2-soluble complexing fluorinated gradient copolymers have been successfully synthesized by RAFT polymerization. **Pd** (1.1 wt%) can be **incorporated** in these **copolymers** without a significant change in the solubility properties. The applications of those CO_2-soluble copolymers can be the preparation of innovative materials for catalysis by using these supramolecular systems in a bottom-up approach fully performed in $scCO_2$ and/or simply by reducing the metal to its zerovalent oxidation state. This type of materials are active in catalysis for the Heck reaction.