

# DESIGN OF PERFLUORINATED AMINO-MACROLIGANDS FOR THE IMPLEMENTATION OF ATOM TRANSFER RADICAL POLYMERIZATION IN SUPERCRITICAL CARBON DIOXIDE

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## INTRODUCTION

In the 1990's, an explosion of the researches on radical polymerization has been observed in the academic laboratories since the discovery of controlled processes, namely the Nitroxide Mediated Polymerization (NMP) [1,2], the Reversible Addition-Fragmentation chain Transfer (RAFT) [3] and Atom Transfer Radical Polymerization (ATRP) [4]. In each process, the control of the polymerization relies on an equilibrium between active and dormant species. This equilibrium being shifted toward the formation of the dormant species, the radical concentration in the polymerization medium decreases, that favors the propagation step compared to the termination reaction. This characteristic makes the synthesis of polymers with well defined molecular weight, architecture and chain-end functionality easy. Nowadays, because of environmental regulations, green processes are imposing themselves in chemistry, material science and industry. In the past decades, extensive researches have been devoted to the use of supercritical carbon dioxide (scCO<sub>2</sub>) as reaction medium in the field of chemistry. Compared to others supercritical fluids, scCO<sub>2</sub> exhibits many advantages as low critical parameters ( $p_c = 73.8$  bar,  $T_c = 31.1$  °C), low cost, non toxicity, non flammability and easy recyclability. In the field of polymer synthesis, others factors make scCO<sub>2</sub> an attractive medium. Indeed, CO<sub>2</sub> is easily available in high purity on an industrial scale and, more importantly, CO<sub>2</sub> is relatively inert, except towards anionic species, thus eliminating chain transfer to the solvent as side reaction [5], and the low viscosity of scCO<sub>2</sub> removes issues of Tromsdorf effect and autoacceleration [6-8]. As a consequence, scCO<sub>2</sub> is an ideal alternative solvent for polymers to be prepared by free-radical polymerization, cationic polymerization, condensation polymerization, oxidative coupling, transition metal catalysis and in some cases coordination-insertion polymerization [5]. Until recently, conventional free radical polymerization has been extensively studied since it was discovered that amorphous or low crystalline fluoropolymers [9] and silicones [10] exhibit high solubility at easily accessible temperature (< 100°C) and pressure (< 350 bar) in scCO<sub>2</sub>. This observation opened up news areas of research in this medium, mainly in homogeneous as well as in dispersion, suspension and emulsion free radical polymerizations [4]. Nevertheless, only limited attention was paid to the development of controlled radical polymerization, and especially Atom Transfer Radical Polymerization (ATRP) [11-15].

This paper aims at reporting on the controlled homogeneous and heterogeneous Atom Transfer Radical Polymerization of some vinyl monomers, i.e. methyl methacrylate (MMA), 2,2,2-trifluoroethyl methacrylate (FMA) and styrene (Sty) in scCO<sub>2</sub> using a transition metal

salt ligated by a new fluorinated polymeric aminoligand exhibiting high solubility in this medium that leads to the synthesis of polymers with well defined molecular weight and narrow size distribution. In case of MMA or styrene polymerization, it will be also demonstrated that this new CO<sub>2</sub>-philic ATRP catalyst has a dual role, i.e., the complexation of the copper salt and the stabilization of PMMA growing chains that leads to the formation of poly(methyl methacrylate) (PMMA) or polystyrene (PSty) microspheres.

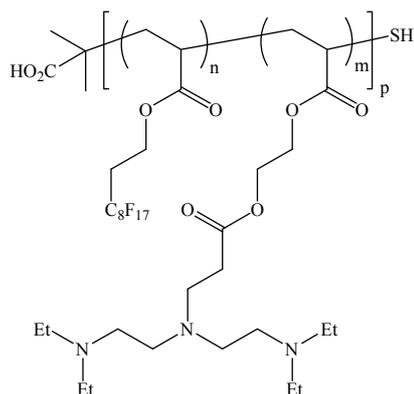
## MATERIALS AND METHODS

CuBr (Aldrich, 98%) was purified by dispersion within glacial acetic acid under stirring for a few hours, filtered, washed with ethanol, dried under reduced pressure at 80°C and stored under nitrogen. Methyl methacrylate (MMA, Aldrich 99%), Styrene (Sty, 99%, Aldrich) and 2,2,2-trifluoroethyl methacrylate (FMA, 99%, Aldrich) were distilled under reduced pressure in order to remove the inhibitor.  $\alpha$ -bromophenylacetate (MBPA, Aldrich,) and 2-bromoethylbenzene (PEBr, Aldrich), N,N,N',N'-tetraethyldiethylenetriamine (TEDETA, Aldrich, 90%) were used as received. Size exclusion chromatography (SEC) was performed in THF at 45°C with a flow rate of 1ml/min using a SDF S5200 autosampler liquid chromatograph equipped with SDF refractometer index detector 2000. Columns (HP PL gel 5 $\mu$ m; 10<sup>5</sup> Å, 10<sup>4</sup> Å, 10<sup>3</sup> Å, 100Å) were calibrated with poly(methyl methacrylate) (PMMA) standards when PMMA are analyzed or with polystyrene (PSty) standards when PSty are analyzed. The fluorinated macroligand was synthesized as reported elsewhere [16].

**ATRP in scCO<sub>2</sub>.** [15] In a typical experiment, the macroligand (15000 g/mol, 3L/chain, 1.56 g, 1.04 10<sup>-4</sup> mol) and copper bromide (0.0402 g, 2.8 10<sup>-4</sup> mol) were introduced in a 35 ml pre-heated high pressure cell at 70°C and deoxygenated by CO<sub>2</sub> purge. Methyl- $\alpha$ -bromophenylacetate (0.1286 g, 5.61 10<sup>-4</sup> mol) and MMA (12ml, 0.112 mol) were introduced in a glass tube and deoxygenated by nitrogen purge before being injected under CO<sub>2</sub> flux in the high pressure cell with the aid of a glass syringe. Pressure was finally equilibrated to 320 bars using an ISCO syringe pump and the reaction medium magnetically stirred at 1000 rpm. After 16h, the reactor was cooled and pressure was rapidly removed. The resulting polymer was dried under vacuo before being analyzed by SEC using THF as eluent. The same procedure was followed for the synthesis of PSty and PFMA.

## RESULTS

The primary requirement for ATRP to be successfully implemented in scCO<sub>2</sub>, relies on the solubility of the organometallic catalyst in this medium [11]. For this reason, perfluorinated macroligands were prepared in a three steps strategy following a procedure described elsewhere [16]. In a first step, random copolymers of heptadecafluorodecyl acrylate and 2-hydroxyethylacrylate were prepared by RAFT polymerization [17], followed by the esterification of the pendant hydroxyl groups with acryloyl chloride. Finally, tetraethyldiethylenetriamine (TEDETA) was grafted onto the acrylic double bonds by Michael addition [16], that leads to the formation of well defined highly CO<sub>2</sub>-soluble macroligands for copper salt (**Scheme 1**). They were then used for the ATRP of vinyl monomers such as methacrylates or styrene in supercritical carbon dioxide [15, 16].



**Scheme 1:** General structure of the fluorinated macroligand

**A. Homogeneous ATRP of 2,2,2-trifluoroethylmethacrylate.** Synthesis of fluorinated poly(meth)acrylates, known for high solubility in supercritical carbon dioxide, was investigated by homogeneous ATRP of 2,2,2-trifluoroethylmethacrylate (FMA). It was initiated by methyl- $\alpha$ -bromophenylacetate (MBPA) in the presence of copper bromide ligated by a fluorinated macroligand ( $M_n = 5000$  g/mol; 2 TEDETA units/chain) at 70°C and 320 bar for 24h ( $[MBPA]/[TEDETA] = 2$ ;  $[CuBr]/[TEDETA] = 1$ ). During the whole polymerization process, the brownish polymerization medium remained homogeneous which attests for the high solubility of the fluoropolymer in supercritical carbon dioxide. Different monomer-to-initiator molar ratios were considered in order to target different molecular weights (**Table 1**). Under identical conditions, the apparent molecular weight increased with the  $[FMA]/[MBPA]$  ratio, and the polydispersity was narrow ( $1.1 \leq M_w/M_n \leq 1.15$ ) until high monomer conversions, that is consistent with a controlled process.

Macroligand		[Cu]/ [MBPA]	[FMA]/ [MBPA]	Conv. (%) [a]	$M_{n, th}$ (g/mol) [b]	$M_{n, exp}$ (g/mol) [c]	PDI
$M_n$ (g/mol)	Nber TEDETA/ chain						
5000	2	0.5	130	78	17400	19000	1.11
5000	2	0.5	240	78	31200	32000	1.14
5000	2	0.5	360	72	43000	45000	1.13

**Table 1:** Experimental conditions for ATRP of FMA in  $scCO_2$

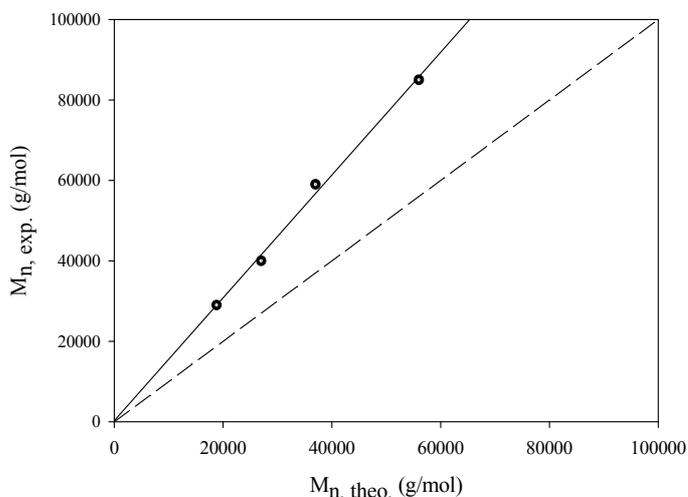
[a] gravimetrically determined

[b]  $M_{n, theoretical} = (\text{weight of monomer}/n \text{ initiator}) \times \text{monomer conversion}$

[c] estimated by SEC with a PMMA calibration

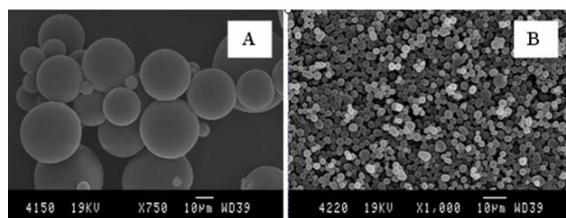
**B. Heterogeneous ATRP of methyl methacrylate.** PMMA is known to be insoluble in  $scCO_2$ , that could render the control of the ATRP of MMA problematic. ATRP of MMA was thus initiated by methyl- $\alpha$ -bromophenylacetate (MBPA) at 70°C and 320 bar, in the presence of copper bromide ligated by an amino-fluorinated macroligand ( $M_n = 15000$  g/mol; 3 TEDETA units/chain;  $[MBPA]/[TEDETA] = 2$ ;  $[CuBr]/[TEDETA] = 1$ ). The monomer-to-initiator molar ratio was changed in order to target different molecular weights. After 24h at 320 bar and 70°C, the reactor was cooled and  $CO_2$  was rapidly vented. The experimental molecular weight increased linearly with the theoretical value until quite high conversion and molecular weight, whereas the polydispersity was low ( $1.15 \leq M_w/M_n \leq 1.20$ ) (**Figure 1**). These observations are consistent with a controlled polymerization. Nevertheless, the initiator

efficiency ( $f = M_{n,th}/M_{n,SEC}$ ) was limited to about 0.65, which is quite comparable to supported ATRP in organic solvents (60%) [18-20].



**Figure 1:** (—)  $M_{n,exp}$  dependence on  $M_{n,theor}$  for ATRP of MMA in  $scCO_2$  initiated by MBPA and catalyzed by the CuBr/macroligand (15000 g/mol, 3 TEDETA/chain) system at 320 bar, 70°C during 16h; (---)  $M_{n,theo}$ .

Interestingly enough, PMMA microspheres with a diameter in the 5 to 30  $\mu m$  range were collected as a white powder after the reactor depressurization (**Figure 2A** and **2B**). Because of the dual structure consisting of  $CO_2$ -phobic Cu complexes and  $CO_2$ -philic fluorinated segments, the macroligand would not only serve to complex copper bromide but also to stabilize the PMMA particles as result of a steric barrier built up at their surface. For sake of comparison, ATRP of MMA was repeated under the same experimental conditions, except that the TEDETA amino ligand was used as a free molecule rather than attached to the fluorinated copolymer (320 bar, 70°C,  $[MBPA]/[TEDETA] = 2$ ;  $[CuBr]/[TEDETA] = 1$ ,  $[MMA]/[MBPA] = 400$ ). Although the polymerization occurred, it was uncontrolled as assessed by a broad and multimodal molecular weight distribution ( $M_w/M_n = 1.9$ ). This loss of control might result from the poor solubility of the non fluorinated catalyst in  $scCO_2$ . Moreover, gross precipitation of PMMA was observed and no microsphere was formed. The fluorinated macroligand has thus a pivotal role in both the polymerization control and the dispersion of the insoluble PMMA chains. Solubility of the catalyst is thus essential as well as the amphiphilicity of the macroligand. An additional evidence that the macroligand is the actual stabilizer of the PMMA particles was found in the conventional free-radical polymerization of MMA initiated by azobisisobutyronitrile (AIBN) in  $scCO_2$  added with a non-complexed macroligand (12.5 wt% compared to the monomer, 15000 g/mol, 3 TEDETA/chain). After 7h under 280 bar at 65°C, the monomer conversion was high (95%) and PMMA ( $M_n = 77000$  g/mol;  $M_w/M_n = 1.8$ ) was recovered as small size microspheres (2 to 3  $\mu m$ ) with a narrow size distribution (**Figure 2B**) instead of a bulk material [15]. The macroligand has thus the capacity to convert a precipitation polymerization into a dispersion one.



**Figure 2:** (A) SEM pictures of PMMA particles prepared by dispersion ATRP of MMA (macroligand: 3 TEDETA/chain, 15000 g/mol, [MMA]/[MBPA] = 400), (B) PMMA particles obtained by conventional free-radical polymerization

**C. Heterogeneous ATRP of styrene.** Dispersion ATRP of styrene was also investigated in  $scCO_2$  using the macroligand/copper (I) bromide catalytic system. ATRP of styrene was first initiated by 1-phenylethyl bromide (PEBr) at 70°C and 340 bar, in the presence of copper bromide ligated by an amino-fluorinated macroligand exhibiting a  $M_n = 15000$  g/mol and bearing 3 TEDETA units/chain ([PEBr]/[CuBr] = 1; [CuBr]:[TEDETA] = 1:1). About 6 days are however required at this temperature in order to reach a total monomer conversion and to collect the polystyrene as a powder (**Table 2**, entry 1 and 2). The experimental molecular weight of PSty was in good agreement with the theoretical value, and the polydispersity index was low (**Table 2**, entries 1 and 2). **Figure 3B** shows the coexistence of particles of undefined morphology and microspheres with a diameter between 10 and 20  $\mu m$ .

For sake of comparison, when styrene is polymerized in  $scCO_2$  by conventional free-radical polymerization using azobisisobutyronitrile (AIBN) as an initiator using a non-complexed macroligand (12.5 wt% compared to the monomer, 15000 g/mol, 3 TEDETA/chain), the monomer conversion was high (95%) after 7h at 65°C and 340 bar, and PSty ( $M_n = 90000$  g/mol;  $M_w/M_n = 1.95$ ) was recovered as small size microspheres ( $\sim 1 \mu m$ ) with a narrow size distribution (**Figure 3A**). This experiment confirms that the macroligand acts as an efficient stabilizer of the growing PSty chains in  $scCO_2$ .

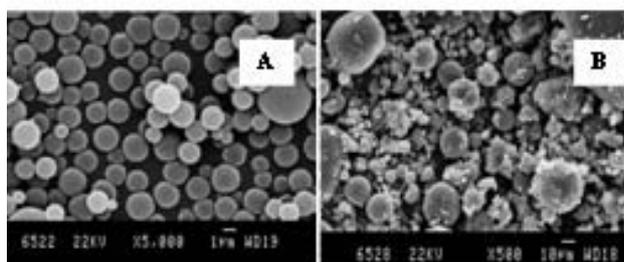
entry	Macroligand		[PEBr]/[Cu]	[Sty]/[PEBr]	T° (°C)	Conv. (%) [a]	M <sub>n, th</sub> (g/mol) [b]	M <sub>n, exp</sub> (g/mol) [c]	PDI
	M <sub>n</sub> (g/mol)	Nber TEDETA/chain							
1	15000	3	1	385	70	96	39000	43000	1.23
2	15000	3	1	190	70	97	19000	22000	1.15

**Table 2:** Experimental conditions for ATRP of styrene in  $scCO_2$

[a] gravimetrically determined

[b]  $M_{n, theoretical} = (\text{weight of monomer}/n \text{ initiator}) \times \text{monomer conversion}$

[c] estimated by SEC with a PSty calibration



**Figure 3:** SEM pictures of PSty particles prepared by conventional free radical dispersion polymerization (A) of and dispersion ATRP of Sty (B)

## CONCLUSION

In this study, we have reported the use of new perfluorinated aminomacroligands for the successful implementation of homogeneous and heterogeneous ATRP of vinyl monomers in scCO<sub>2</sub>. This new catalytic system allows the synthesis of polymers with well defined molecular weight and narrow size distribution. Moreover, in case of styrene or methyl methacrylate polymerization, it was demonstrated that these new macroligands have a dual role, i.e. the complexation of the copper salt and the stabilization of the growing chains. Further developments deal with the synthesis of well-defined block copolymers and the recycling of the catalyst.

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