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# Atom transfer radical polymerization of MMA with a macromolecular ligand in a fluorinated solvent and in supercritical carbon dioxide

Bruno Grignard, Christine Jérôme, Cédric Calberg, Robert Jérôme, Christophe Detrembleur

*Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6a, B-4000 Liège, Belgium*

**Abstract**

Macromolecular fluorinated ligands were prepared according to a three-step strategy that consists of the random copolymerization of heptadecafluorodecyl acrylate and 2-hydroxyethylacrylate, followed by the esterification of the pendant hydroxyl groups with acryloyl chloride and the Michael-type addition of tetraethyldiethylenetriamine onto the acrylic double bonds of the polymeric chains. These fluorinated macroligands were successfully used in the atom transfer radical polymerization of MMA catalyzed by a copper salt in a fluorinated solvent. The polymerization control was analyzed in relation to the copper salt, the initiator and the molecular weight and composition of the macroligand before being extended to the heterogeneous ATRP of MMA in $scCO_2$.

**Keywords:** atom transfer radical polymerization (ATRP) ; controlled radical polymerization ; fluoropolymers ; fluorinated ligand ; macromolecular ligand ; supercritical carbon dioxide

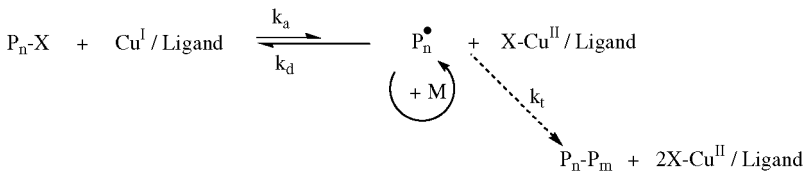
## 1. Introduction

Transition-metal mediated radical polymerization, also known as atom transfer radical polymerization (ATRP) (Scheme 1), has emerged as a powerful tool for the controlled radical polymerization of vinylic monomers, such as styrene, acrylates and methacrylates [1]. This control that makes molecular weight predictable and polydispersity possibly low, relies on an equilibrium between active and dormant species as result of an halogen transfer (Scheme 1). Whenever the equilibrium is too much shifted towards the dormant species, the polymerization is very slow if not inhibited. In contrast, any excess of active species is self-regulated by irreversible termination reaction. This self-regulation of the radical concentration was discussed by Fischer as the "Persistent Radical Effect" [2].

The position of this equilibrium depends on several parameters, including monomer, ligand, solvent, temperature and catalyst [3-7]. Among these parameters, the structure of the ligand has great impact on the solubility of the transition-metal salt in the organic solvent and on the redox potential of the metal, thus on the position and dynamics of the atom transfer equilibrium.

Due to environmental regulations, the development of green processes is an ongoing effort in chemistry, material science and industry. The term "green" refers to the use of environmentally friendly, non-toxic and reusable reagents and solvents in order to minimize the environmental pollution [8-11]. In the field of synthetic polymers, considerable effort is devoted to polymerization processes in aqueous media and in supercritical fluids. Whereas conventional free-radical polymerization of vinyl monomers in supercritical carbon dioxide is largely discussed [12-14], only few publications deal with controlled polymerization in this medium [15-22]. This paper aims at reporting on the controlled homogeneous atom transfer radical polymerization of methyl methacrylate (MMA) in a fluorinated solvent (benzotrifluoride) using transition-metal salt ligated by new fluorinated polymeric aminoligands. This is a preliminary step to the ATRP of MMA in $scCO_2$, which is a typical heterogeneous process, because PMMA is insoluble in this medium and thus precipitates during polymerization. In contrast fluorinated polymers, amorphous or of low crystallinity, are soluble in $scCO_2$ [23-26], which justifies the choice of the fluorinated aminoligands.

***Scheme 1.*** *General mechanism of ATRP.*



## 2. Experimental part

### *2.1. Materials*

CuBr (Aldrich, 98%) and CuCl (Aldrich, 99+%) were dispersed 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. Anhydrous benzotrifluoride (TFT, Aldrich, 99%) was degassed by nitrogen bubbling for 20 min. Methyl methacrylate (MMA, Aldrich 99%), lH,lH,2H,2H-heptadecafluorodecyl acrylate (AC8, Aldrich, 96%) and 2-hydroxyethyl acrylate (HEA, Aldrich, 96%) were distilled under reduced pressure in order to remove the inhibitor. Ethyl-2-chloropropionate (ECP, Aldrich, 99%), ethyl-2-bromopropionate (EBP, Aldrich, 99%) and α-bromophenylacetate (Aldrich,), acryloyl chloride (Aldrich, 96%), 4-methylmorpholine (Aldrich, 99.5%), *N,N,N',N'*-tetraethyldiethylenetriamine (TEDETA, Aldrich, 90%), 2,2'-azo-bis(2-methylpropionitrile) (AIBN, Fluka) and 1,1,2-trichlorotrinuoroethane (CFC 113, Aldrich, 99,8%) were used as received.

### *2.2. Characterization*

$^1$H NMR spectra were recorded in $CDCl_3$ with a Brucker AN 400 spectrometer (400 MHz) at 25 °C.

Size exclusion chromatography (SEC) was performed in THF at 45 °C with a flow rate of 1 ml/ min using a SDF S5200 autosampler liquid chromatograph equipped with SDF refractometer index detector 2000. Columns (HP PL gel 5 µm; $10^5$ Å, $10^4$ Å, $10^3$ Å, 100 Å) were calibrated with poly(methyl methacrylate) standards.

### *2.3. Synthesis of PAC8-co-PHEA random copolymers and esterification by acryloyl chloride*

Copolymerization of AC8 and HEA by RAFT was reported elsewhere [27]. In a typical copolymerization experiment, the RAFT initiator (S-l-dodecyl-S-(α,α'-dimethyl-α''-acetic acid)trithiocarbonate, 0.259 g, 7.1 x $10^{-4}$ mol) and AIBN (0.0024 g, 1.4 x $10^{-5}$mol) were added into a glass tube degassed by three vacuum/nitrogen cycles. Then, TFT (4 ml), AC8 (4 ml, 0.0125 mol), DMF (1.2 ml) and HEA (0.6 ml, 0.0052 mol) were added under nitrogen with a syringe. The mixture was heated at 60 °C for 6 h. The copolymer was repeatedly precipitated into methanol, dried at 40 °C in vacuo overnight, and finally characterized by $^1$H NMR spectroscopy and SEC.

Purified PAC8-co-PHEA copolymer (10 g, $M_n$ = 15,000 g/mol, 2 OH/chain, 6.66 x $10^{-4}$ mol) was added in a round bottom flask and dissolved in 50 ml of dry benzotrifluoride (1.33 mol/l). Three milliliters of 4-methylmorpholine (2.7 x $10^{-2}$ mol) was added, and the reaction mixture was cooled down to 0 °C in ice. Acryloyl chloride (2.2 ml, 2.7 x $10^{-2}$ mol) was then added dropwise at 0 °C under vigorous stirring over 15 min. The flask was then warmed up to room temperature and maintained under stirring for 1 day. The modified copolymer was purified by repeated precipitation in methanol and dried in vacuo at room temperature for 1 day. $^1$H NMR spectra of the copolymer were recorded in a CFC C113/$CDCl_3$ mixture (50/50; v/v).

### *2.4. Michael-type addition of TEDETA*

Ten grams of the esterified PAC8-co-PHEA copolymer ($M_n$ = 15,000 g/mol, 6.66 x $10^{-4}$ mol) was dissolved in 30 ml of benzotrifluoride. TEDETA (6.8 ml, 0.0266 mol) was added to the solution, and the mixture was stirred at room temperature for 3 days. After reaction, the copolymer was purified by repeated precipitation in methanol, dried in vacuo at 40 °C for 1 day and analyzed by $^1$H NMR in a CFC C113/$CDCl_3$ mixture (50/50; v/v).

### *2.5. Homopolymerization of MMA in benzo trifluoride*

In a typical experiment, the initiator (ethylchloropropionate, ethylbromopropionate or methyl-α-bromophenylacetate), CuCl or CuBr, the polymeric ligand, the solvent (benzotrifluoride) and a magnetic stirrer were added into a glass flask that was closed by a three-way stopcock. This solution was degassed by bubbling of nitrogen for 10 min and mixed for 30 min in order to complex the copper salt. The monomer was added with a syringe, and the reactor was heated in an oil bath thermostated at 70 °C. MMA conversion was monitored by $^1$H NMR spectroscopy on the basis of the relative intensity of the peaks at 5.5 and 6.1 ppm for MMA protons and at 3.6 ppm for the peak characteristic of the methyl protons of the pendant methacrylate groups. Each sample picked out from the polymerization medium was also dissolved in THF for analysis by size exclusion chromatography (calibrated with PMMA standards). The macroligand that was insoluble in THF, was separated by filtration (0.2 µm filter) before analysis.

### *2.6. Homopolymerization of MMA in supercritical carbon dioxide*

As a typical example, the catalyst (CuBr, 0.0201 g, 1.4 x $10^{-4}$ mol) and the macroligand ($M_n$ = 15,000 g/mol, 3 TEDETA/chain, 0.7017 g, 1.04 x $10^{-4}$ mol of TEDETA) were added into a 35 ml high pressure reactor equipped with a stirring bar. Oxygen was eliminated by $CO_2$ venting for 15 min. Temperature was increased by an oil bath pre-heated at 70 °C. A mixture of MMA (12 ml, 0.1123 mol) and methyl α-bromophenylacetate (0.0643 g, 2.8 x $10^{-4}$ mol) was prepared in a glass tube and deoxygenated by a 5 min nitrogen purge. It was then

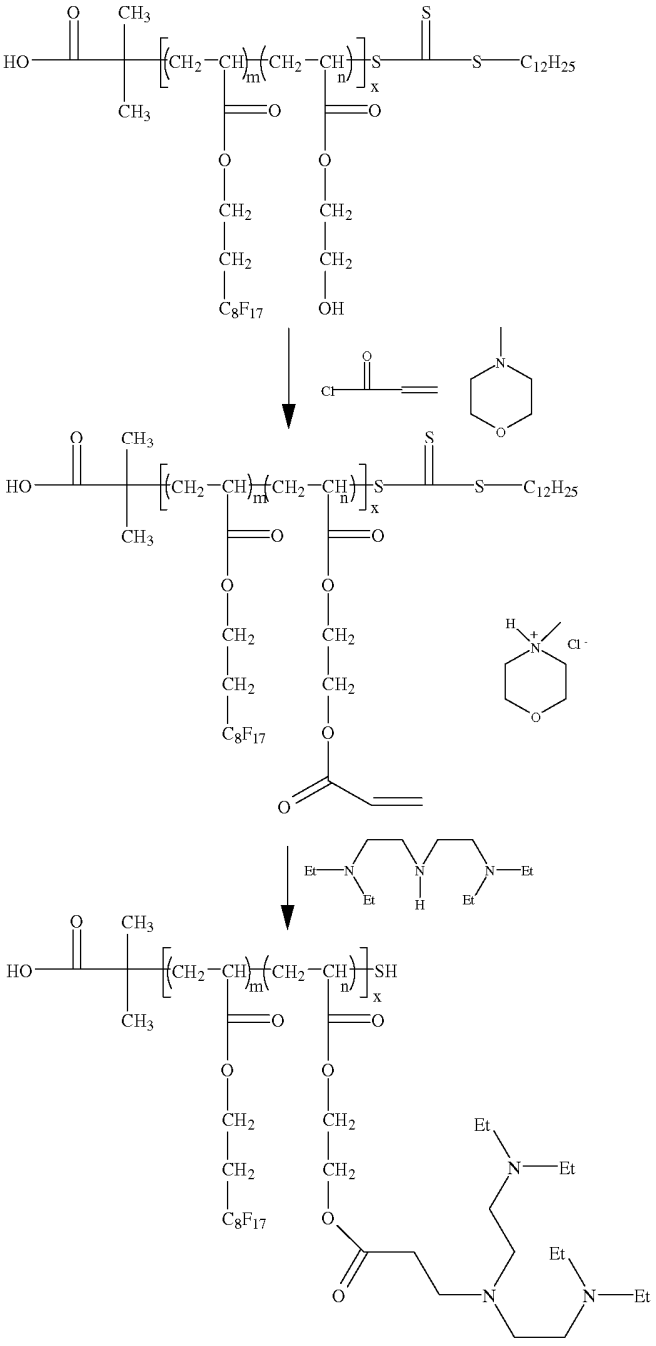
injected into the pre-heated high pressure reactor under $CO_2$ flow with a glass syringe. The $CO_2$ pressure was finally fixed at 320 bar.

## 3. Results and discussion

### *3.1. Synthesis of the macroligand*

The grafting of the ligand onto PAC8-co-PHEA chains is illustrated in Scheme 2. The three-step strategy consists of the synthesis of random copolymers of heptadecafluorodecyl acrylate and 2-hydroxyethyl acrylate with predeterminated molar composition and molecular weight, by RAFT polymerization in the presence of S-l-dodecyl-S-(α,α'-dimethyl-α"-acetic acid)trithiocarbonate as a chain transfer agent. This copolymerization was conducted in benzotrifluoride at 80 °C for 4 h, as reported elsewhere [27]. The second step was the esterification of the pendant hydroxyl groups of the copolymer with acryloyl chloride. Finally, tetraethyldiethylenetriamine was added onto the acrylate double bonds by a Michael-type addition, so making well defined binding sites available to copper complexation.

***Scheme 2.*** *Synthesis of aminated macroligand.*



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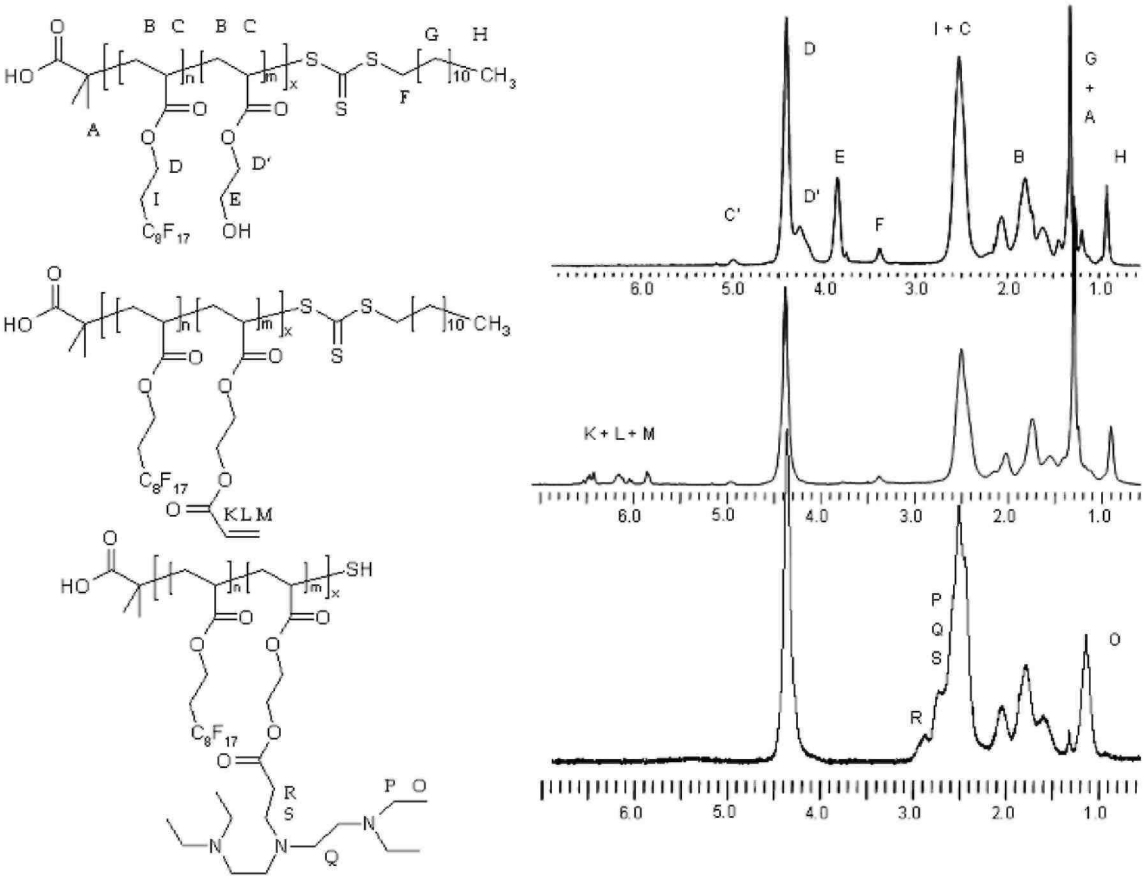
For being successful, the hydroxyl groups of random PAC8-co-PHEA copolymers were esterified with an excess of acryloyl chloride (20 eq) in dry benzotrifluoride in the presence of *N*-methylmorpholine. The copolymer solution was diluted (6 wt%) in order to avoid precipitation of the copolymer during reaction at room temperature for 1 day. The esterified copolymer was purified by repeated precipitation in methanol before analysis by $^1$H NMR spectroscopy. Expectedly, the peak characteristic of the methylene protons of the primary alcohol (PHEA co-units, C$H_2$-OH, $\delta$ = 3.85 ppm) disappeared, whereas new resonances characteristic of the olefinic protons of the pendant acrylate groups ($\delta$ = 5.85 ppm, $\delta$ = 6.15 ppm, $\delta$ = 6.45 ppm) were observed (Fig. 1).

***Fig. 1.*** *Structure and $^1$H NMR spectra for a PAC8-co-PHEA random copolymer before esterification (1) ($M_n$ = 5000 g/mol, 2 OH/chain); after esterification by acryloyl chloride (2) ($M_n$ = 5000 g/mol, 2 $CH_2$=CH-C(O)-O-/chain) and after addition of TEDETA (3) ($M_n$ = 5000 g/mol, 2 TEDETA/chain). C corresponds to the CH group of the last acrylate unit bearing the trithiocarbonate group.*




The Michael-type addition of a large excess of tetraethyldiethylenetriamine (TEDETA) onto the pendant acrylate was conducted in benzotrifluoride at room temperature and monitored by $^1$H NMR spectroscopy. After 3 days, the peaks characteristic of the olefinic protons ($\delta$ = 5.85 ppm, $\delta$ = 6.15 ppm, $\delta$ = 6.45 ppm) were no longer observed in agreement with the complete conversion of the acrylate groups into amines. It must be noted that the trithiocarbonate end-group of the original PAC8-co-PHEA copolymer was released during the Michael addition. Indeed, primary and secondary amines are known to react with these groups with formation of thiols. The complete disappearance of the CH resonance of the last monomer unit of the chains ($\delta_{HC'}$ = 4.95 ppm), of the methylene protons ($\delta_{HF}$ = 3.45 ppm and $\delta_{HG}$ = l.2ppm) and the methyl protons ($\delta_{HH}$ = 0.9 ppm) of the RAFT residue was in favour of the quantitative release of the trithiocarbonate end-group [28-32]. Quantitative removal of the trithiocarbonate end-group was also evidenced by UV-analysis. Indeed, as reported by Lacroix-Desmazes, the RAFT agent used to prepare such kind of polymers exhibits in benzotrifluoride a strong UV absorption at 309 nm corresponding to the -S-C(S)-S- group [33]. After random copolymerization of HEA and AC8, this absorption is shifted to a wavelength higher value of 320 nm. This absorption completely disappeared after fixation of TEDETA onto the pendant acrylate groups. These UV experiments are additional evidences of the removal of the trithiocarbonate group by reaction of the copolymer with TEDETA and confirm the NMR data.

Macroligands with different molecular weights and contents of TEDETA were successfully prepared by this methodology (Table 1). It should be mentioned that copolymers with low TEDETA content were prepared and studied in this paper. The three main reasons for this low TEDETA content are the following. First, it is important to keep in mind that for extending such catalytic system in $scCO_2$, the catalyst has to be soluble in this medium. Thus, by increasing the amount of $CO_2$-phobic TEDETA groups in the copolymer, the solubility of the catalyst in $scCO_2$ will decrease. The second reason relies on the stability of the copolymer formed after esterification with acryloyl chloride (first reaction step, Scheme 2). At too high HEA content, after esterification with acryloyl chloride, the copolymers rapidly crosslinked due to the presence of a too high local concentration of the pendant acrylate functions. The third reason relies on the proximity effects. At too high TEDETA content, while keeping the molecular weight of the macroligands constant, the probability for the proximity effect [34] to be observed is increased, that could lead to deleterious kinetic consequences.

***Table 1*** *Experimental data for the derivatization of PAC8-co-PHEA copolymers*

| $M_n$ PAC8-co-PHEA | PAC8-co-PHEA average number of OH/chain[a] | Average number of $CH_2$=CH-C(O)-O-/ chain after esterification[b] | Average number of TEDETA/chain[c] |
|---|---|---|---|
| 15,000 | 2 | 1.85 | ~2 |
| 16,000 | 3 | 2.9 | ~3 |
| 15,000 | 4.2 | 3.95 | ~4 |
| 5000 | 2 | 1.95 | ~2 |

[a] Determined from the relative intensity of the $^1$H NMR resonances for one proton of the HEA co-unit ($CH_2$, $\delta$ = 3.8 ppm) and one proton of the chain-end (CH, $\delta$ = 4.95 ppm).
[b] Determined from the relative intensity of the $^1$H NMR resonances of one proton of the olefinic group ($CH_2$=CH, $\delta$ = 5.85 ppm, $\delta$ = 6.15 ppm, $\delta$ = 6.45 ppm) and one proton of the chain-end (CH, $\delta$ = 4.95 ppm).
[c] Estimated on the basis of the complete disappearance of the $^1$H NMR resonances of the olefinic protons.

### *3.2. Polymerization of MMA by ATRP*

ATRP of MMA was investigated in benzotrifluoride in the presence of the aminated macroligands listed in Table 1. This reaction was used as a model in order to optimize the experimental parameters, i.e., choice of both the metal salt and the initiator; and molecular weight and composition of the macroligand.

### *3.3. Effect of the initiator*

One major role of the initiator is to control the number of growing chains. Whenever transfer and termination reactions are negligible, the degree of polymerization (DP) is predicted by the DP = $[M]_0/[initiator]_0$ x conversion relationship. Moreover, if initiation is fast compared to propagation, the molecular weight distribution is narrow.

Three α-haloesters, i.e., ethylchloropropionate, ethylbromopropionate and methyl-α-bromophenylacetate, were investigated as possible initiators for the ATRP of MMA (Scheme 3) catalyzed by CuCl ligated by a macroligand ($M_n$ = 15,000 g/mol, 2 TEDETA/chain).

The polymerization was homogeneously conducted in TFT at 70 °C with an initial monomer concentration of 3.12 mol/l. At higher MMA concentrations, the fluorinated macroligand was no longer soluble. The semi-logarithmic plot of $\ln([M]_0/[M])$ vs time was linear for each initiator, consistent with a first-order polymerization with respect to the monomer and a constant concentration of the growing radicals (Fig. 2). The monomer conversion was estimated by $^1$H NMR spectroscopy from the relative intensity of the proton resonances at 5.5 and 6.1 ppm typical of the monomer and at 3.6 ppm characteristic of the monomer units of the chains.
The conversion dependence of $M_n$ showed that the initiator has a deep effect on the molecular weight control. According to Fig. 3, the MMA polymerization was uncontrolled when ethylchloropropionate (ECP) was the initiator. A substantial improvement was observed when ethylbromopropionate (EBP) was substituted for ECP. Except for a limited burst effect, dependence of $M_n$ on the monomer conversion was indeed linear. This burst, emphasized by a finite extrapolation at zero conversion, results from the initial formation of an excess of active species and thus an exceedingly high monomer conversion at the early stage of the polymerization, followed by the self-regulation of the radical concentration by the "persistent radical effect" [2]. Finally, the burst effect disappeared when the polymerization was initiated by methyl-α-bromophe-nylacetate (MBP). The linear dependence of molecular weight on the MMA conversion and $\ln([M]_0/[M])$ on time were consistent with a controlled polymerization even though the molecular weight distribution is rather high (~1.4).

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***Scheme 3.*** *Structure of the tested initiators.*

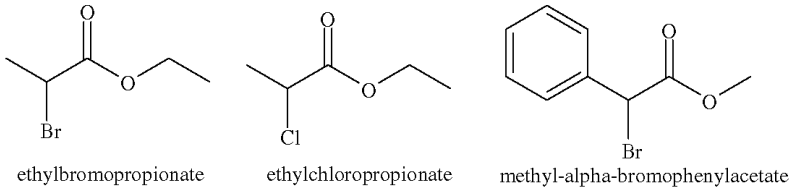



***Fig. 2.*** *Time dependence of ln($[M]_0$/[M]) for ATRP of MMA initiated by EBP (▼), ECP (▲) or MBP (●) and catalyzed by CuCl/ macroligand (15,000 g/mol, 2 TEDETA/chain) in TFT at 70 °C. $[MMA]_0$ = 3.12 M, $[initiator]_0/2 = [CuCl]_0 = [macroligand]_0$ = 15.71 mM.*

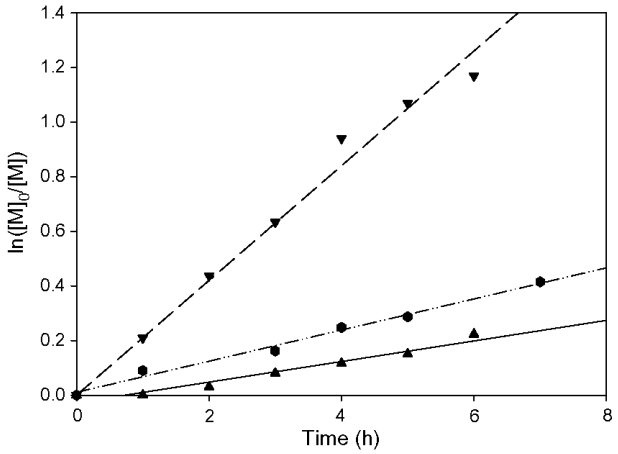
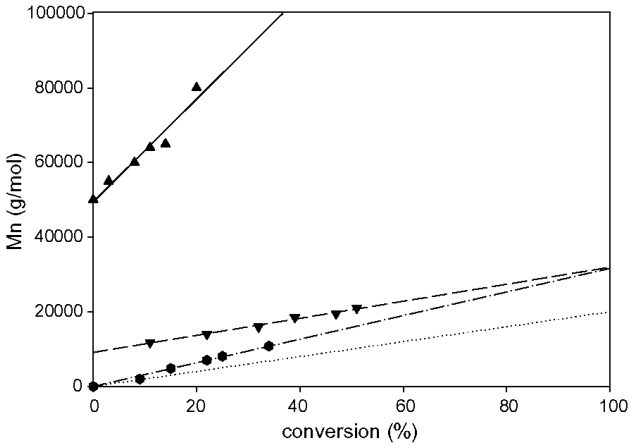



***Fig. 3.*** *Conversion dependence of theoretical $M_n$ for ATRP of MMA initiated by EBP (▼), ECP (▲) or MBP (●) and catalyzed by CuCl/macroligand (15,000 g/mol, 2 TEDETA/chain) in TFT at 70 °C; $[MMA]_0$ = 3.12 M, $[initiator]_0/2 = [CuCl]_0 = [macroligand]_0$ = 15.71 mM.*




*3.4. Effect of the macroligand composition*

The TEDETA content of the macroligand is expected to impact the control of the ATRP polymerization. At high TEDETA content, a proximity effect may be noted, as reported by van Koten and co-workers in atom transfer radical addition [33]. Indeed, the probability for two radicals to be in very close vicinity is increased and so is the chance for irreversible termination. As a result, the amount of oxidized catalyst ($M_t^{n+1}$) must increase in the polymerization medium and the equilibrium of the reaction must be shifted towards formation of the dormant species which slows down the polymerization.

In order to optimize the macroligand composition, ATRP of MMA was initiated by methyl-α-bromophenylacetate in trifluorotoluene ([MMA]/ TFT = 3.12 mol/l) at 70 °C in the presence of copper chloride

ligated by chains of the same molecular weight (15,000 g/mol) and containing 2, 3 and 4 TEDETA units, respectively. As a rule, the time dependence of $\ln([M]_0/[M])$ and the conversion dependence of the molecular weight were linear in agreement with a controlled polymerization. Nevertheless, the experimental molecular weight at comparable monomer conversion and the polymerization rate changed with the macroligand composition. Figs. 4 and 5 show that the macroligand with 3 TEDETA units is the best compromise in terms of high polymerization rate and high initiation efficiency ($f$ = 0.8, $f = M_{n,theor.}/M_{n,exp.}$). Indeed, when the macroligand contains 2 TEDETA units, the initiating efficiency decreases ($f$ = 0.6), whereas the polymerization is very slow when there are 4 TEDETA units per macroligand. This slowing down of the polymerization is a consequence of the proximity effect of the catalytic sites (cfr supra).

***Fig. 4.*** *Time dependence of $\ln([M]_0/[M])$ for ATRP of MMA initiated by MBP and catalyzed by CuCl/macroligand (15,000 g/ mol, 2 TEDETA/chain, ▼), CuCl/macroligand (15,000 g/mol, 3 TEDETA/chain, ▲) and CuCl/macroligand (15,000 g/mol, 4 TEDETA/ chain, ●) in TFT at 70 °C. $[MMA]_0$ = 3.12 M, $[initiator]_0/2 = [CuCl]_0 = [macroligand]_0$ = 15.71 mM.*

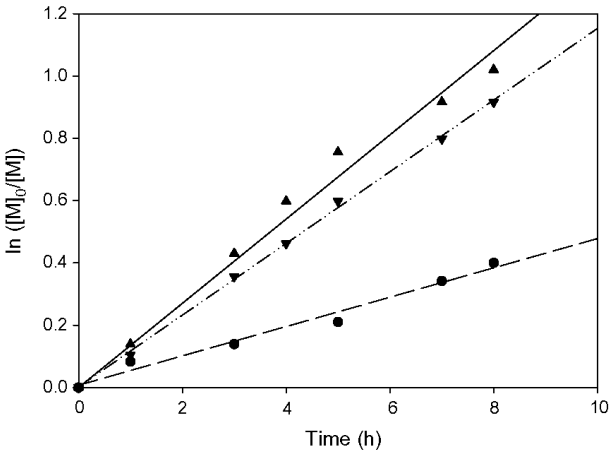
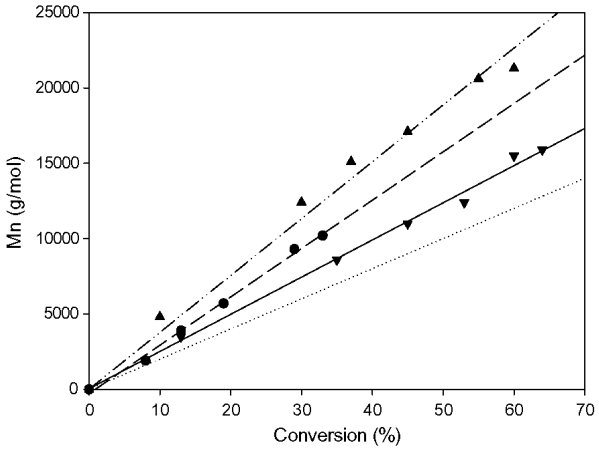



***Fig. 5.*** *Conversion dependence of $M_n$ for ATRP of MMA initiated by MBP and catalyzed by CuCl/macroligand (15,000 g/ mol, 2 TEDETA/chain, ▼), CuCl/macroligand (15,000 g/mol, 3 TEDETA/chain, ▲) and CuCl/macroligand (15,000 g/mol, 4 TEDETA/chain, ●) in TFT at 70 °C. $[MMA]_0$ = 3.12 M, $[initiator]_0/2 = [CuCl]_0 = [macroligand]_0$ =15.71 mM.*




### *3.5. Effect of the copper salt*

Until now, a brominated initiator was used in combination with CuCl, such that C-Br bonds were involved in the initiation step, whereas less reactive C-Cl bonds participated to propagation. For sake of comparison, CuBr was substituted for CuCl in ATRP of MMA in trifluorotoluene at 70 °C, in the presence of methyl-α-bromophenylacetate as the initiator, and a fluorinated macroligand ($M_n$ = 15,000 g/mol) with 3 TEDETA units per chain. Both the time dependence of $\ln([M]_0/[M])$ and the conversion dependence of $M_n$ were linear whatever the copper catalyst, as illustrated in Figs. 6 and 7. Nevertheless, the polymerization rate is higher when copper

bromide is the catalyst, which is consistent with the lower strength of the carbon-bromide bond compared to the carbon-chloride one. Although substitution of CuCl by CuBr has no substantial effect on the control of molecular weight, the polydispersity index of PMMA is significantly and reproducibly lower when copper bromide is the catalyst ($M_w/M_n$ ~ 1.2 for CuBr, compared to ~ 1.4 for CuCl) (Fig. 8). The reason for this effect is not understood yet.

***Fig. 6.*** *Time dependence of $ln([M]_0/[M])$ for the ATRP of MMA initiated by MBP and catalyzed by CuCl/macroligand (15,000 g/ mol, 3 TEDETA/chain, ■) and CuBr/macroligand (15,000 g/ mol, 3 TEDETA/chain, ▲) in TFT at 70 °C. $[MMA]_0$ = 3.12 M, $[initiator]_0/2 = [CuCl]_0 = [macroligand]_0$ = 15.71 mM*

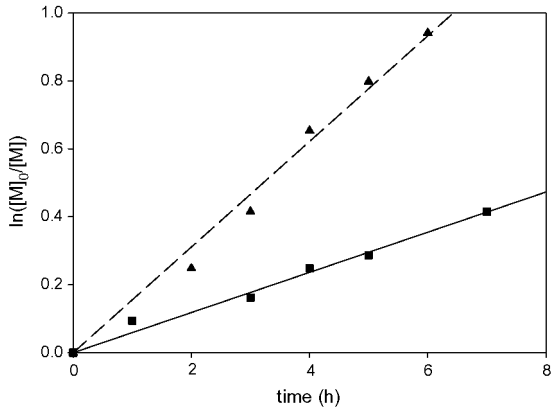



***Fig. 7.*** *Conversion dependence of $M_n$ for the ATRP of MMA initiated by MBP and catalyzed by CuCl/macroligand (15,000 g/ mol, 3 TEDETA/chain, ■) and CuBr/macroligand (15,000 g/ mol, 3 TEDETA/chain, Δ) in TFT at 70 °C. $[MMA]_0$ = 3.12 M, $[initiator]_0/2 = [CuCl]_0 = [macroligand]_0$ = 15.71 mM.*

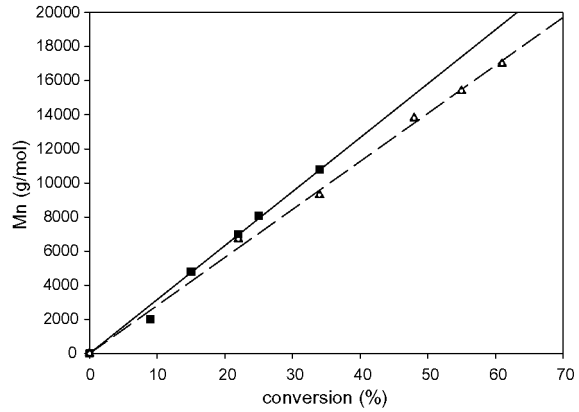



***Fig. 8.*** *Polydispersity index as a function of the monomer conversion with CuCl (▲) and CuBr (■) as the catalyst, respectively.*

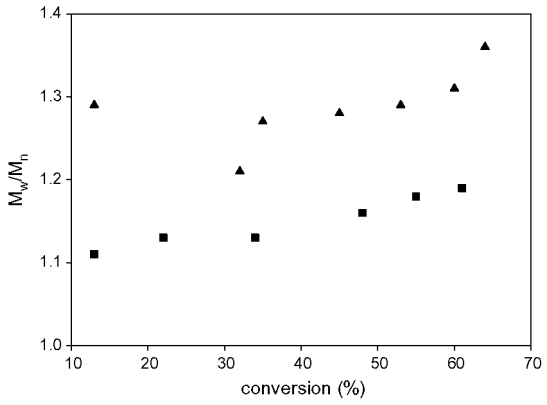


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***Table 2*** *Homogeneous ATRP of MMA initiated by MBP and catalyzed by CuBr/macroligand systems (15,000 g/mol, 3 and 4 TEDETA/chain) in benzotrifluoride at 70 °C ($[MMA]_0$ = 3.12 M, $[initiator]_0/2 = [CuBr]_0 = [macroligand]_0$ = 15.71 mM, for 7 h) and heterogeneous ATRP of MMA initiated by MBP and catalyzed by CuBr/macroligand systems (15,000 g/mol, 3 and 4 TEDETA/chain) in $scCO_2$; $[initiator]_0/2 = [CuBr]_0 = [macroligand]_0$, P = 320 bar at 70 °C for 24 h)*

| Macroligand | | Homogeneous ATRP of MMA in benzotrifluoride | | | | | | Heterogeneous ATRP of MMA in $scCO_2$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (g/mol) | Nber TEDETA/chains | [MMA]/[MBPA] | Conv. (%) | $M_{n,theor.}$ (g/mol) | $M_{n,exp.}$ (g/mol) | $f$ | PDI | [MMA]/[MBPA] | Conv. (%) | $M_{n,theor.}$ (g/mol) | $M_{n,exp.}$ (g/mol) | $f$ | PDI |
| 15,000 | 3 | 200 | 61 | 12,000 | 18,000 | 0.66 | 1.2 | 200 | 94 | 19,000 | 29,000 | 0.65 | 1.15 |
| 15,000 | 3 | 400 | 63 | 25,000 | 39,000 | 0.64 | 1.2 | 400 | 93 | 37,000 | 59,000 | 0.63 | 1.20 |
| 15,000 | 4 | 200 | 61 | 12,000 | 17,000 | 0.70 | 1.2 | 200 | 85 | 17,000 | 24,000 | 0.71 | 1.20 |
| 15,000 | 4 | 400 | 72 | 29,000 | 38,000 | 0.75 | 1.2 | 400 | 78 | 31,000 | 41,000 | 0.75 | 1.20 |

### *3.6. Heterogeneous ATRP of MMA in $scCO_2$*

ATRP of MMA was initiated by methyl-α-bromophenylacetate (MBPA) in $scCO_2$ at 70 °C and 320 bar, in the presence of copper bromide ligated by different amino-fluorinated macroligands ($M_n$ = 15,000 g/mol; 3 and 4 TEDETA units/chain; [MBP]/[TEDETA] = 2; [CuBr]/[TEDETA] = 1). Under these experimental conditions, all the components are soluble in $scCO_2$ and the ATRP of MMA starts under homogeneous conditions. During the polymerization, heterogeneity appears as a result of the precipitation of PMMA during its formation. A detailed study on the solubility of this new catalytic system in $scCO_2$ will be reported in a forthcoming paper [35]. Preliminary experiments were conducted in $scCO_2$ at the same temperature (70 °C) and for the same time (7 h) as in TFT. Although the MMA conversion was at least 60% in TFT (Table 2), it was comparatively low in $scCO_2$ (~10%). The reason might be the slow complexation of copper bromide in $scCO_2$. Consistently, high MMA conversions were observed when the reaction time was increased from 7 h to 24 h (Table 2). Comparison of PMMA prepared in TFT and $scCO_2$ at the same temperature and falling in the same range of molecular weight shows a remarkable agreement at least for two characteristic features, (i) the polydispersity index of PMMA which is low (1.2) whatever the macroligand (3 or 4 TEDETA/chain) and the monomer over initiator molar ratio (200 vs 400), (ii) the initiator efficiency that increases from ~0.65 to 0.70-0.75 when the number of TEDETA per fluorinated chain is increased from 3 to 4. These preliminary results are very encouraging because the behavior of the fluorinated macroligand does not seem to be perturbed by the change of solvent -excepted for the complexation rate of the copper salt - and, above all, by the precipitation of the growing chains. Although not obvious a priori, TFT allows the ATRP of MMA to be foreshadowed in $scCO_2$, which is a substantial advantage because of time saving when series of experiments have to be conducted for testing macroligands and/or experimental conditions. The origin of the low initiator efficiency is not understood yet but needs to be optimized in the future.

## 4. Conclusions

The ATRP of MMA was successfully conducted in a fluorinated solvent at 70 °C with a copper salt as a catalyst ligated by a fluorinated macroligand. A series of aminated macroligands were prepared in three steps. Heptadecafluorodecyl acrylate and 2-hydroxyethyl acrylate were first randomly copolymerized by RAFT, followed by the esterification of the pendant hydroxyl groups by acryloyl chloride and the Michael-type addition of tetraethyldiethylenetriamine onto the acrylic double bonds. The effect of the initiator, the copper salt and the composition of the macroligand on the polymerization control and kinetics was investigated in benzotrifluoride at 70 °C. The best compromise was found for the polymerization initiated by methyl-α-bromophenylacetate and catalyzed by copper bromide ligated by a macroligand of 15,000 g/mol with 3 TEDETA units per chain. The use of such system was successfully extended to the heterogeneous ATRP of MMA in $scCO_2$. These results pave the way to the ATRP of MMA in supercritical carbon dioxide, with the prospect of recovering (by supercritical fluid extraction) and recycling the catalyst. These results will be discussed in a forthcoming paper.

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