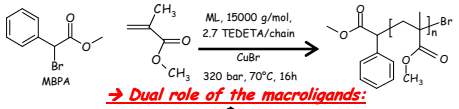
New perfluorinated macroligand for the implementation of dispersion Atom Transfer Radical Polymerization in $scCO_2$

Grignard Bruno, Cedric Calberg, Jerome Christine, Christophe Detrembleur*
University of Liège,Sart-Tilman, B6a, B-4000 Liège

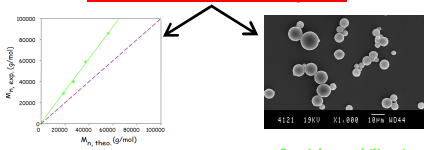
Center for Education and Research on Macromolecules

1. Introduction: Atom Transfer Radical Polymerization (ATRP) has emerged as one of the most robust tool for the synthesis of polymers with well defined characteristics. ATRP mechanism is based on the reversible transfer of a radically transferable atom, typically a halogen atom, from a monomeric or polymeric alkyl (pseudo)halide to a transition metal complex in a lower oxidation state with formation of an organic radical, generated through the reversible redox process, and a transition metal complex in a higher oxidation state. The chain control that makes molecular weight predictable and polydispersity possibly low, relies on an equilibrium between active and dormant species as result of the halogen transfer, lowering the instantaneous radical concentration during the polymerization and so limiting the termination reactions by disproportionation or recombination. In this contribution, we report on the use of *new perfluorinated aminomacroligands for the implementation of ATRP in $scCO_2$.*

2. Dispersion ATRP of MMA: Using the MBPA/Cu(I)Br/macroligand catalytic system, ATRP of MMA was controlled at 300 bar and 70°C as evidenced by the linear increase of Mn exp with the theoretical values and the narrow polydispersity (MwMn ~ 1.2). Moreover, at the end of the polymerization, PMMA was collected as microspheres.



→ Dual role of the macroligands:

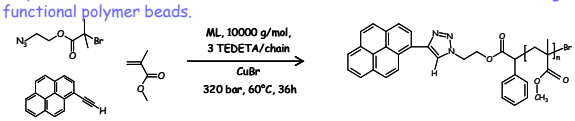


Complexation (and solubilization) of the Cu(I) catalyst in $scCO_2$

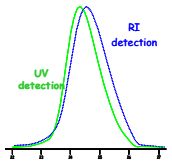
Particles stabilization

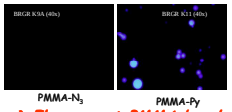
Grignard et al., Chem. Commun., 2008, 314

5. Polymer functionalization by combination of Huisgen's cycloaddition and dispersion ATRP: Because both ATRP and copper catalyzed cycloaddition of Huisgen, that consists of the reaction between alkyne and azide, relies on the use of a Cu(I) catalyst, polymers end-functionalization by combining click reaction and dispersion ATRP was investigated in a one-pot process. Dispersion ATRP of MMA was controlled at 60°C and 300 bar leading to functional polymer beads.



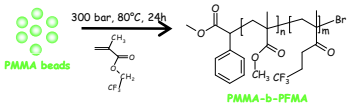
MMA/ N_3-initiator	T° (°C)	P (bar)	Time (h)	Conv. (%)	Mn theo	Mn exp GPC	Mn exp RMN	PDI
400	60	300	36	96	38000	62000	65000	1.16
100	60	300	36	94	9400	27000	29000	1.18



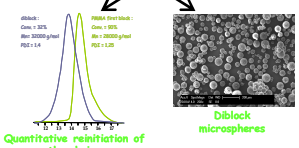


→ Fluorescent PMMA beads

3. Livingness of the PMMA beads: The livingness of the ATRP was demonstrated by the synthesis of diblock copolymer in a one-pot two-step process using PMMA beads as macroinitiator.



→ Living PMMA beads:

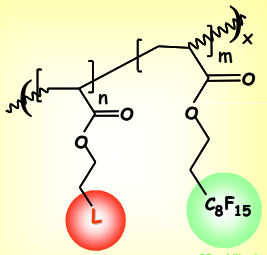


Quantitative reinitiation of the chains

Diblock microspheres

Grignard et al., Macromolecules, 2008, 41(22), 8575

New perfluorinated amino-macroligands



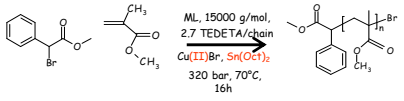
CO_2-phobic Complexation of the copper salt

CO_2-philic → solubilization of the ATRP catalyst (Cu(I))

L = TEDETA =

Grignard et al., Eur. Polym. J., 2008, 44, 861

6.AGET ATRP. AGET ATRP was implemented in $scCO_2$ using Tin(II) 2-ethylhexanoate ($Sn(EH)_2$) in order to reduce Cu(II) and generate "in situ" the catalyst onto its active form (Cu(I)). This concept was introduced with the hope to improve the poor catalytic activity of the recycled catalyst. Indeed, more than 98% of the catalyst can be removed by SFE with 400 ml of CO_2 at 50°C and 300 bar (5ml/min).

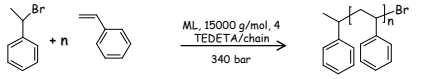


[MMA]/ [MBPA]	MBPA/Cu^0/Sn^{II}	Conv (%)	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol)	Mw/Mn
400	1/1/0.5	92	37000	36000	1.49
400	1/1/0.25	90	36000	27000	2
400	1/0.4/0.18	25	10000	11600	1.33

→ Control of the AGET ATRP and particles stabilization

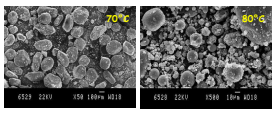
Grignard et al., Macromolecules, 2008, 41(22), 8575

4. Dispersion ATRP of styrene: Using the PEBr/Cu(I)Br/macroligand catalytic system, ATRP of styrene was controlled at 300 bar and 70°C, 80°C or 100°C as evidenced by the good agreement between the experimental and theoretical Mn values and the narrow polydispersity. After depressurisation of the cell, PS was collected as a powder.



[sty]/[PEBr]	[PEBr]/[Cu]	Time (h)	T, (°C)	Conv. (%)	Mn, theo (g/mol)	Mn, exp (g/mol)	PDI
385	1	24	70	15	6000	7000	1.21
385	1	48	70	38	15000	18000	1.19
385	1	144	70	98	39000	43000	1.22
190	1	144	70	97	19000	22000	1.15
575	1	144	70	20	12000	11000	1.32
385	1	72	80	96	38000	39000	1.23
385	1	48	100	89	36000	38000	1.15

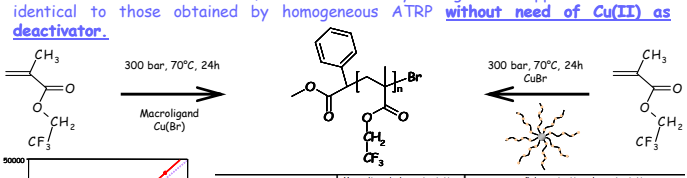
→ evidence of the control

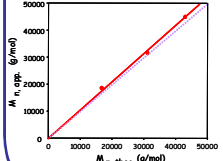


→Stabilization of PS growing particles

Grignard et al., Macromolecules, 2008, 41(22), 8575

7. Homogeneous and supported ATRP of fluorinated methacrylate: The MBPA/Cu(I)Br/macroligand catalytic system was successfully used for preparing perfluorinated methacrylate by homogeneous ATRP in $scCO_2$. Because both the polymer and the catalyst exhibit high solubility in this medium, the concept of supported ATRP was introduced in order to produce polymers with low catalytic residues. Depending on the molecular weight and TEDETA composition of the macroligand that were immobilized onto Cab-O-Sil EH5, results obtained by homogeneous supported ATRP are identical to those obtained by homogeneous ATRP without need of Cu(II) as deactivator.





Evidence of the control for homogeneous ATRP of FMA

Entry		Macroligand characteristics M_n (g/mol)	Nr TEDETA /chain	Polymerization characteristics [FMA]/ [MBPA]	Conv (%)	$M_{n,GPC}$ (g/mol) PS	PDI
1	Free TEDETA	/	/	240	20	9200	5.6
2	Supported TEDETA	/	0.25 TEDETA/nm²	240	82	36000	1.4
3	Homogeneous ATRP	5000	2	240	78	32000	1.14
4	Supported ATRP	5000	2	240	77	33000	1.10
5	Homogeneous ATRP	15000	4	240	90	37000	1.15
6	Supported ATRP	15000	4	240	78	31000	1.35

Immobilization of the macroligand
→Pseudo homogeneous catalyst
→ Low catalytic residues after extraction of the catalyst

Grignard et al., Chem. Commun., 2008, 5803

8. Conclusions: We reported on the use of new perfluorinated macroligands for controlling the ATRP of vinyl monomers in $scCO_2$. When the polymerization of fluorinated methacrylate is concerned, polymers with well defined molecular weight and narrow polydispersity were produced by homogeneous or supported ATRP (without need of Cu(II). In case of heterogeneous ATRP of styrene or MMA in $scCO_2$, we showed a dual role of these new ligands, i.e. the catalyst complexation and the stabilization of polymers growing chains leading to the formation of microspheres in the case of PMMA. Livingness of the PMMA beads was demonstrated by the synthesis of diblock copolymer that were collected as microspheres. Finally, we introduced the concept of dispersion AGET ATRP in order to improve the catalytic activity of the recycled catalyst and end-functionalized PMMA were prepared by combining Huisgen's cycloaddtion and dispersion ATRP in a one-pot process.

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