In situ Formation of Stabilizers for the Implementation of Dispersion Nitroxide Mediated Polymerization of MMA in Supercritical Carbon Dioxide

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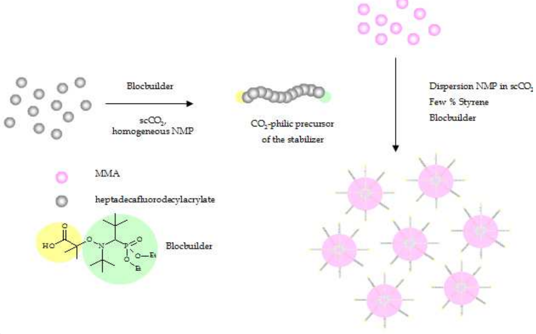
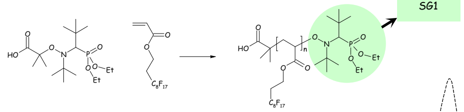
1. Introduction. Nitroxide Mediated Polymerization is a very attractive metal-free controlled radical process that allows the polymerization of a broad range of monomers, including the functional ones. In NMP, a relatively weak C-ON bond is homolytically and reversibly cleaved under thermal stimuli to generate a growing radical (active species) and a less reactive radical also known as persistent or stable free radical (nitroxide). Until now, NMP in organic solvents or water as polymerization medium was extensively studied. In this contribution, we would like to report on the first ***dispersion NMP of MMA in*** an ***environmentally friendly*** medium, i.e. ***supercritical carbon dioxide*** using CO_2-philic perfluorinated polymers as precursors of the stabilizer that was generated "in situ" during the MMA polymerization.

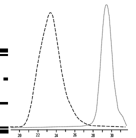
2. Strategy. The control of the MMA polymerization relies on the strategy developed by Charleux et al. that consists of using a SG1-based alkoxyamine, i.e. the blocbuilder, in the presence of small amount of styrene. In a first step, CO2 soluble polyheptadecafluorodecylacrylate was prepared by homogeneous NMP in scCO2 using blocbuilder as an alkoxyamine. In a second step, nitroxide SG1 mediated dispersion polymerization of MMA was conducted at 70°C in the presence of 5 wt% of polyheptadecafluorodecylacrylate end-capped by SG1.



3. Homogeneous NMP of heptadecafluorodecyl acrylate (FDA) in $scCO_2$. Homogeneous NMP of FDA was conducted at 100°C for 24h at 300 bar in the presence of blocbuilder as alkoxyamine. Livingness of the polymerization was evidenced by the synthesis of PFDA-b-PnBuA diblock copolymer in $scCO_2$.



Entry	Initiator	Monomer	Conv (%)	Mn theo (g/mol)	Mn ^{1}H RMN (g/mol)	Mn Maldi Tof (g/mol)	PDI [a]
1	blocbuilder	FDA	92	4600	3800	3700	1.09
2			90	9000	/	10000	/
3	PAC8-SG1 Mn = 3800g/mol	nBuA	91	48000	45000	/	1.40



Livingness of the PFDA-SG1 chains

4. NMP of MMA in $scCO_2$: evidence of the control. NMP of MMA was conducted at 300 bars and 70°C for 114h in the presence of 8.8 mol% of styrene in order to observe control of the polymerisation and 5 w% of PFDA-SG1 as precursor of the stabilizer that will be generated "in situ". Whatever the MMA/alkoxyamine molar ratio, Mn exp. was in good agreement with Mn theo. and PMMA with narrow polydispersity was produced.

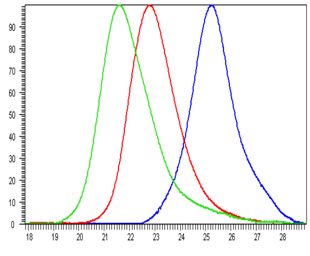
Entry	T (°C)	Time (h)	PFDA-SG1 loading (w%)	Conv (%) [a]	Mn theo (g/mol) [b]	Mn exp (g/mol) [c]	PDI
1	70	114	5	94	52000	57000	1.26
2	70	114	5	89	17800	18500	1.29
3	70	114	5	90	90000	94000	1.31
4	70	114	5	98	54000	60000	1.22

Overlay of SEC traces recorded for PMMA prepared by dispersion NMP in $scCO_2$

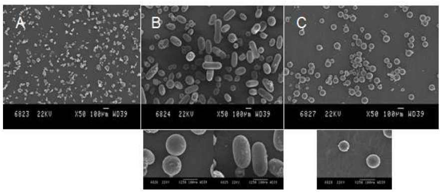
-- PMMA, Mn = 18500 g/mol, PDI = 1.29, entry 2

-- PMMA, Mn = 57000 g/mol, PDI = 1.26, entry 1

-- PMMA, Mn = 94000 g/mol, PDI = 1.31, entry 3

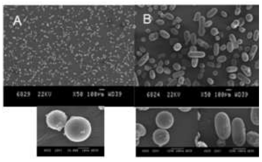


5. PMMA stabilization. After depressurisation of the cell, PMMA was collected as a free flowing powder. Depending on the molecular weight of PMMA prepared by dispersion NMP, ill-stabilized particules (A), well defined microspheres with an average diameter of 91 +/- 7 µm (C) or microspheres/elongated particles mixtures (B) are produced.



SEM characterization of PMMA particles obtained by dispersion NMP in scCO2 at 70°C in the presence of 5 w% of PDFA-SG1 surfactant
A : PMMA, Mn = 18500 g/mol, PDI = 1.29
B : PMMA, Mn = 57000 g/mol, PDI = 1.26
C : PMMA, Mn = 94000 g/mol, PDI = 1.31

6. PMMA stabilization: effect of the stabilizer precursor loading. PFDA-SG1 loading was changed in order to improve the stabilization of PMMA growing particles. A same experiment was then repeated in the previously reported conditions in the presence of 5%, 10% or without precursor of the stabilizer. Without stabilizer, PMMA was collected as a single chunk of polymer whereas powders consisting of micropsheres with a mean diameter of 16 +/- 2 µm or microspheres/elongated particles mixtures were obtained in the presence of 10 and 5% of the stabilizer precursor respectively



SEM characterization of PMMA particles obtained by dispersion NMP in scCO2 at 70°C: effect of the surfactant loading

A : PMMA, Mn = 57000 g/mol, PDI = 1.26, 10 w% of PFDA-SG1
B : PMMA, Mn = 60000 g/mol, PDI = 1.22, 5 w% of PFDA-SG1

7. Effect of the styrene loading on the polymerization control . Charleux demonstrated that the control of the NMP of MMA using SG1 based alkoxyamine was due to the presence of a styryl-SG1 moiety at the ω chain-end. So, a decrease of the styrene content was expected to influence the polymerization control. A same experiment was then repeated (70°C, 300 bar, 5w% of PFDA-SG1) in the presence of decreasing amount of styrene. At higher styrene loading (8.8 or 4.4 mol%), NMP of MMA is controlled whereas at low styrene loading of 2.2% or without styrene, the control is lost.

Entry	T (°C)	Time (h)	PFDA-SG1 loading (w%)	Styrene loading (%)	Conv (%) [a]	Mn theo (g/mol) [b]	Mn exp (g/mol) [c]	PDI
1	70	114	5	8.8	94	53000	55000	1.23
2	70	114	5	4.4	95	52000	56000	1.26
3	70	114	5	2.2	85	47000	25000	1.55
4	70	114	5	0	91	50000	29000	1.44

8. Conclusion. The synthesis of PMMA microspheres by dispersion NMP was successfully achieved in supercritical carbon dioxide using a fluorinated polyacrylate terminated by SG1, prepared by homogeneous NMP in this medium, as precursor of the stabilizer that was generated "in situ". Polymers with well defined molecular weight and narrow polydispersities (Mw/Mn ~1.2) were produced when small amount of styrene were added in the polymerization medium.

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