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-O 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 CO₂-phlic 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 Charles et al. that consists of using a SGI-based alkoxamine, i.e. the blockbuilding, in the presence of small amount of styrene. In a first step, CO₂ soluble polyheptadecafluoradoacrylate was prepared by homogenous NMP in scCO₂ using blockbuilding as an alkoxamine. In a second step, nitroxide SGI mediated dispersion polymerization of MMA was conducted at 70°C in the presence of 5 wt% of polyheptadecafluoradoacrylate end-capped by SGI.

3. Homogenous NMP of heptadecafluoroacrylate (PFA) in scCO₂. Homogenous NMP of PFA was conducted at 100°C for 24h at 300 bar in the presence of blockbuilding as alkoxamine. Livingness of the polymerization was evidenced by the synthesis of PFDAA-b-PFDBA diblock copolymer in scCO₂.

4. NMP of MMA in scCO₂ evidence of the control. NMP of MMA was conducted at 300 bars and 70°C for 114h in the presence of 8.5 mol% of styrene in order to observe control of the polymerization and 5 wt% of PFDAA-SGI as precursor of stabilizer that will be generated “in situ”. Whatever the MMA/alkoxamine molar ratio, Mn exp. was in good agreement with Mn theor. and PMMA with narrow polydispersity was produced.

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 particles (A), well defined microspheres with an average diameter of 91 +/- 7 μm (C) or microspheres/elargated particles mixtures (B) are produced.

6. PMMA stabilization: effect of the stabilizer precursor loading. PFDAA-SGI 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 microspheres with a mean diameter of 16 +/- 2 μm or microspheres/elargated particles mixtures were obtained in the presence of 10 and 5% of the stabilizer precursor respectively.

7. Effect of the styrene loading on the polymerization control. Charles et al. demonstrated that the control of the NMP of MMA using SGI based alkoxamine was due to the presence of a styryl-SGI moiety at the a 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, 5% of PFDAA-SGI) 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.

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

Acknowledgements. The authors are thankful to the Belgian Science Policy for general support to CERM in the frame of the “Strategic Research Projects” (PSP) - Functional Supramolecular Systems – B.G. Elsaffy is the “Bourses Nationale pour la Recherche Scientifique” (FNS) for financial support. C.D. is a chercheur de la Région Wallonne.