

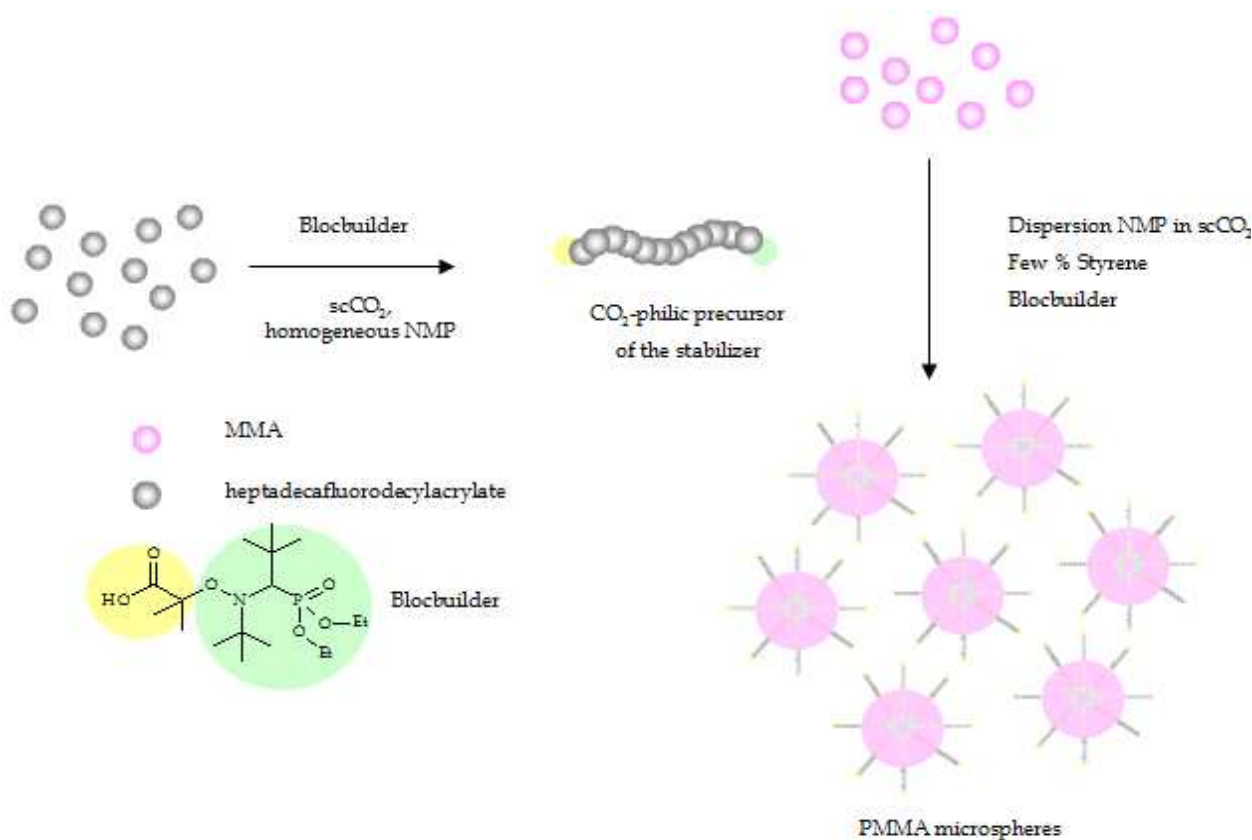
In situ Formation of Stabilizers for the Implementation of Dispersion Nitroxide Mediated Polymerization of MMA in Supercritical Carbon Dioxide

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Abstract. Controlled dispersion Nitroxide Mediated Polymerization (NMP) of methyl methacrylate (MMA) was successfully carried out for the first time in supercritical carbon dioxide (scCO₂) in the presence of CO₂-philic perfluorinated surfactant that was generated "in situ". The control of the MMA polymerization relies on the strategy developed by Charleux et al.¹ that consists of using a SG1-based alkoxyamine, i.e. the block-builder, in the presence of small amount of styrene. In a first step, CO₂ soluble polyheptadecafluorodecylacrylate was prepared in scCO₂ using block-builder as an alkoxyamine. In a second step, nitroxide SG1 mediated dispersion polymerization of MMA was conducted at 70°C and 300 bar in the presence of 5 w% of SG1 terminated surfactant compared to the monomer. Different monomer to alkoxyamine molar ratios were investigated in order to target different molecular weights. In each case, the monomer conversion was high (>90 %), the experimental molecular weight was in good agreement with the theoretical value and the polydispersity was narrow (Mw/Mn ~1.2). Moreover, after depressurisation of the cell, PMMA was collected as a free flowing powder consisting of small sized microspheres.



1) J. Nicolas, C. Dire, L. Mueller, J. Belleney, B. Charleux, S. R. A. Marque, D. Bertin, S. Magnet, L. Couvreur, *Macromolecules*, 2006, 39(24), 8274-8282