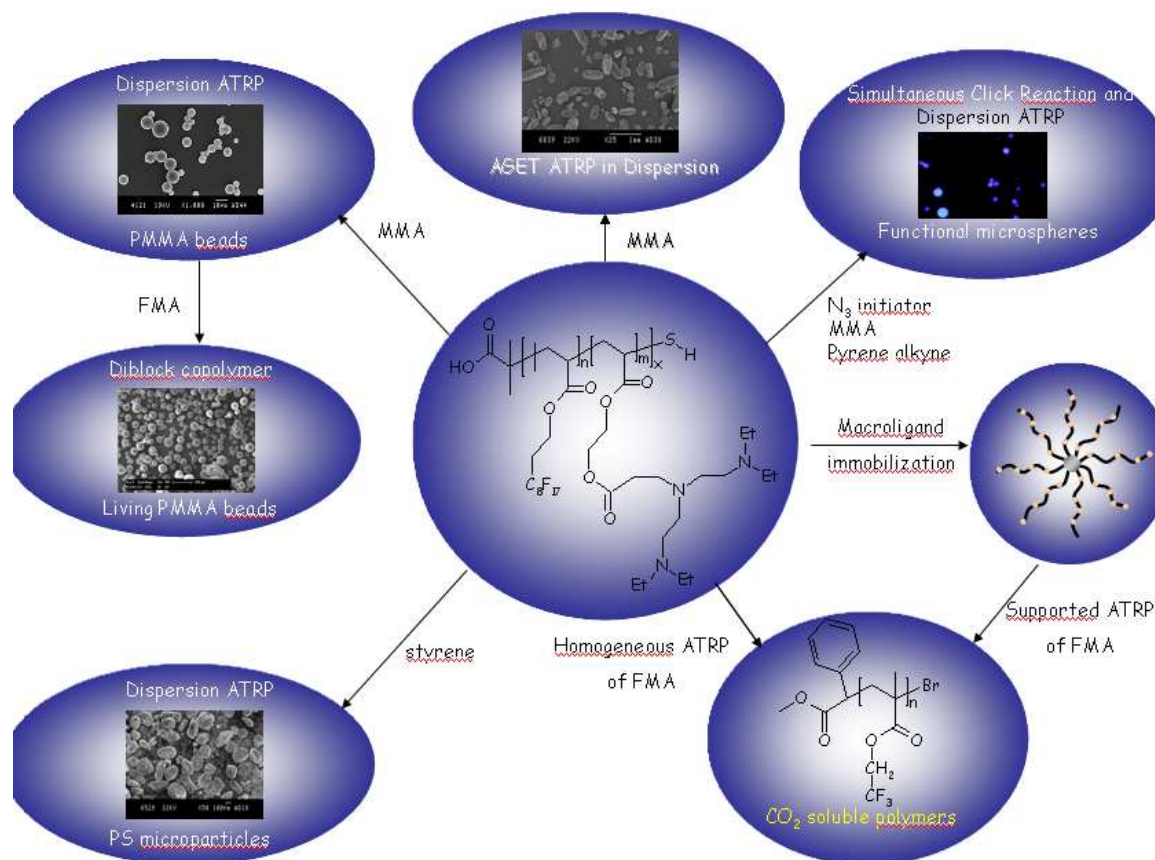


New perfluorinated macroligand for the implementation of dispersion Atom Transfer Radical Polymerization in scCO₂

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Due to an increasing need for polymers with well-defined architecture (diblock-, graft-, star-shaped copolymers), molecular weight and/or functional end-groups, the use of controlled radical polymerization (CRP) in scCO₂ has started to gain attention. Among all the controlled processes, Atom Transfer Radical Polymerization has emerged as a robust tool for the preparation of polymers with well-defined molecular weight, architecture and chain-end functionality. In a very recent paper, we reported the first efficient dispersion ATRP of methyl methacrylate (MMA) in scCO₂ using a fluorinated polymeric ligand that had a dual role, i.e., the complexation of the copper salt and the stabilization of PMMA growing particles^{1,2}. In this contribution, we extended this new system to the dispersion ATRP of styrene², to the synthesis of diblock copolymers beads² or to the preparation of PMMA particles by AGET ATRP. Because both ATRP and alkyne-azide Huisgen's 1,3-dipolar cycloaddition relies on the use of a Cu(I) catalyst, synthesis of pyrene end-functionalized polymers by simultaneous dispersion ATRP and click reaction was also investigated in supercritical carbon dioxide. Finally, the immobilization of these new macroligands onto an inorganic support leads to the formation of pseudo-homogeneous catalyst that were successfully used to prepare CO₂-soluble perfluorinated methacrylate and depending on the molecular weight and TEDETA composition of the macroligand, results obtained by supported ATRP without addition of Cu(II) as deactivator are identical to those obtained by homogeneous ATRP.



- 1) Grignard B., Calberg C., Jérôme C., Jérôme R., Wang W., Howdle S., Detrembleur C., *Chem. Commun.*, 2008, 3, 314
- 2) Grignard B., Calberg C., Jérôme C., Jérôme R., Wang W., Howdle S., Detrembleur C., *Macromolecules*, 2008, 41(22), 8575
- 3) Grignard B., Calberg C., Jérôme C., Jérôme R., Wang W., Howdle S., Detrembleur C., *Chem. Commun.*, 2008, 44, 5803