

Preparation of living polymer microspheres by dispersion Atom Transfer Radical Polymerization in scCO₂ using fluorinated macroligands

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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. In this contribution, we extended this new system to the dispersion ATRP of styrene, to the synthesis of diblock copolymers beads and the controlled synthesis of hyperbranched copolymers. Finally, 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.