

Nitroxide-Mediated Controlled/Living Dispersion and Precipitation Polymerizations in Supercritical Carbon Dioxide

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Supercritical carbon dioxide (scCO₂) has attracted attention as a benign, inexpensive, non-flammable and widely available alternative to volatile organic solvents.¹ Most monomers and polymers are, respectively, soluble and insoluble in scCO₂ making the medium suitable for precipitation and dispersion polymerizations. Dispersion polymerizations in scCO₂ are carried out in the presence of an appropriate polymeric stabilizer, which usually consists of a CO₂-philic segment such as a fluorocarbon² or siloxane,³ as well as a polymer-philic segment. The addition of such a stabilizer allows for the formation of colloiddally stabilized sub-micron sized particles. In contrast, precipitation polymerizations⁴ are conducted in the absence of such a stabilizer with the advantage that polymer free from stabilizer is formed upon venting of the CO₂.

Recently we reported the first successful nitroxide mediated dispersion polymerizations in scCO₂.⁵⁻⁷ Two separate protocols were used to perform successful controlled/living polymerizations of styrene (St) to high conversion in the presence of the *N*-tert-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1); a) a combined initiation and stabilization system (*inistab*³ - poly(dimethylsiloxane-*b*-polystyrene)-SG1; PDMS-*b*-PSt-SG1)⁶ and b) separate initiation (AIBN) and stabilization (poly(dimethylsiloxane-*b*-methyl methacrylate; PDMS-*b*-PMMA).⁷ Molecular weight distributions (MWDs) were narrow ($M_w/M_n \sim 1.1-1.4$) and the products were recovered as colloidal powders (number-average particle diameter < 200 nm) at high conversion.

Since the above breakthroughs, we have shown that it is also possible to conduct nitroxide-mediated precipitation polymerizations of St in a controlled/living manner in scCO₂. Importantly, high conversion is also possible, despite the absence of colloidal stabilization. SG1-mediated polymerizations of St initiated by AIBN were conducted in a 25 ml stainless steel reactor at 110°C and approx. 42 MPa using 44 vol% St. A relatively high excess of SG1 (100% rel. to the low molecular weight alkoxyamine formed in situ) was employed. High conversion (92% in 72 h) was reached and the polymer was recovered as a white powder. The molecular weight distributions shifted to higher molecular weight with increasing conversion and remained narrow ($M_w/M_n < 1.33$), consistent with a controlled/living process. Bulk chain extensions (with St) of the isolated polymer also indicated living character. Further optimization of the polymerization conditions revealed that virtually full conversion could be achieved at 66 vol% St and 30% excess SG1 in 48 h, in contrast to the previously reported problem of low limiting conversions in conventional (non-living) precipitation polymerization of St in scCO₂.⁸ The critical factor in reaching high conversions was found to be the high temperature employed rather than the controlled/living nature of the system.

References

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