

From cobalt-mediated radical polymerization (CMRP) to cobalt-mediated radical coupling (CMRC): a unique strategy for the preparation of novel precise polymer architectures

Christophe Detrembleur,* Christine Jérôme, Antoine Debuigne

Allée de la chimie, 3, Bld B6a, Sart-Tilman, Liege.
Center for Education and Research on Macromolecules, University of Liege.
Liege, Belgium
christophe.detrembleur@ulg.ac.be

Nowadays, controlled radical polymerization (CRP) techniques are powerful tools for the preparation of a large range of polymeric materials with low molar mass distributions, predictable molar masses and precise architectures.

This communication aims at presenting synthetic and mechanistic features of two recent macromolecular engineering tools based on a cobalt complex, $\text{Co}(\text{acac})_2$. The first one is a controlled radical polymerization technique called Cobalt Mediated Radical Polymerization (CMRP)¹⁻⁵. And the second one is an efficient radical polymer chain coupling reaction called Cobalt Mediated Radical Coupling (CMRC)⁶.

In the case of CMRP mediated by $\text{Co}(\text{acac})_2$, the controlling agent is a cobalt complex ($\text{Co}(\text{acac})_2$) which reversibly forms a Co-C bond at the chain-end of the polymer.¹ At any time, a large number of polymer chains capped by a cobalt complex are in equilibrium with a tiny amount of propagating species such that irreversible termination reactions that occur between radicals by coupling or dismutation are avoided. The reversibility of the deactivation is ensured by homolytic cleavage of the Co-C bond by thermal treatment or radical exchange. By carefully adjusting the polymerization conditions, this CMRP process allows to control efficiently both conjugated (acrylates, acrylonitrile (AN)) and non-conjugated monomers (vinyl acetate (VAc), N-vinyl pyrrolidone (NVP)). More importantly, by the fine-tuning of the Co-C bond at the polymer chain-end by metal coordination, block copolymerization between these two monomers families is now possible, giving access to new copolymers that are not available by any other existing CRP techniques.¹

Recently, we reported on a new radical coupling method⁶ which consists in the addition of isoprene to polymer precursors formed by CMRP using $\text{Co}(\text{acac})_2$ as controlling agent. Treatment of well-defined PAN precursors, capped by bis(acetylacetonato)cobalt complexes, exclusively lead to the coupling product (PAN-b-PAN)⁶. In this case, the extent of coupling was above 95% even for PAN precursors with molar mass as high as 25000 g/mol and the coupling reaction is very fast. This Cobalt-Mediated Radical Coupling (CMRC) method also proved efficiency for preparing symmetrical triblock copolymers when applied to a diblock precursor. For example, well-defined PVAc-b-PAN-b-PVAc copolymers have been prepared starting from PVAc-b-PAN- $\text{Co}(\text{acac})_2$ diblock precursors.⁶ Recent mechanistic advances in Cobalt-Mediated Radical Polymerization Coupling (CMRC) reaction as well as expected impact of this technique in macromolecular engineering will be discussed in this talk.

References

¹ Debuigne, A.; Poli, R.; Jerome, C.; Jerome, R.; Detrembleur, C. *Prog. Polym. Sci* **2009**, *34*, 211-239 ; and references therein. ² Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943-7944. ³ Debuigne, A.; Caille, J.-R.; Jerome, R. *Angew. Chem.* **2005**, *44*, 1101-1104. ⁴ Debuigne, A.; Michaux, C.; Jerome, C.; Jerome, R.; Poli, R.; Detrembleur, C. *Chem. Eur. J.* **2008**, *14*, 7623- 7637. ⁵ Debuigne, A.; Champouret, Y.; Jerome, R.; Poli, R.; Detrembleur, C. *Chem. Eur. J.* **2008**, *14*, 4046-4059. ⁶ Debuigne, A.; Jerome, C.; Detrembleur, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 1422-1424.