

**Cobalt Mediated Radical Polymerization (CMRP) using bis(acetylacetonato)cobalt(II) (Co(acac)<sub>2</sub>):  
a tunable reactivity for the precision design of novel copolymers and nanohybrids**

**Christophe Detrembleur**

**Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman B6a, 4000  
Liège, Belgium  
christophe.detrembleur@ulg.ac.be**

Organometallic-Mediated Radical Polymerization (OMRP)<sup>1</sup> techniques belong to an emerging class of controlled radical polymerization (CRP) process that become more and more important in the polymer field, especially for the design of unprecedented macromolecular architectures. OMRP is based on the temporary deactivation of the growing radical species by a transition metal complex with the reversible formation of a carbon-metal covalent bond. Various metals have been used such as titanium, chromium, molybdenum, iron, osmium, vanadium and cobalt. So far, OMRP involving cobalt complexes, also referred as cobalt-mediated radical polymerization (CMRP),<sup>2</sup> is the most investigated and prolific OMRP system. CMRP using bis(acetylacetonato)cobalt(II) (Co(acac)<sub>2</sub>) is the most efficient technique for controlling the radical polymerization of vinyl acetate until high molar masses and low polydispersity.<sup>2-5</sup> In this process the cobalt complex (Co(acac)<sub>2</sub>) reversibly forms a Co-C bond at the chain-end of the polymer. 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 (n-butyl acrylate (nBuA)<sup>6</sup>, acrylonitrile (AN)<sup>7</sup>) and non-conjugated monomers (vinyl acetate (VAc)<sup>2-5</sup>, N-vinyl pyrrolidone (NVP)<sup>8</sup>) using the same cobalt complex. Block copolymerization between these two monomers families is also possible by the fine-tuning of the Co-C bond at the polymer chain-end by metal coordination, giving access to novel copolymers.<sup>1</sup> The importance of this system in the field of the macromolecular engineering is best illustrated by the recent development of a fast, efficient and quantitative radical polymer chain coupling reaction called Cobalt Mediated Radical Coupling (CMRC)<sup>9-11</sup>. Treatment of well-defined polymers prepared by CMRP by a conjugated diene such as isoprene exclusively leads to the coupling product with high coupling efficiencies (~95%) even when the molecular weight of the precursor is high (about 25000g/mol)<sup>9-11</sup>. This Cobalt-Mediated Radical Coupling (CMRC) method also proved efficiency for preparing symmetrical triblock copolymers when applied to a diblock precursor and for the efficient mid-chain functionalization of polymers.

This presentation aims at discussing the important parameters governing the CMRP process and at explaining why this system is so versatile and allows polymerizing monomers than cannot be (co)polymerized efficiently by any other CRP techniques. The high versatility and tunability of the CMRP process will then be illustrated by reporting on the precision design of novel copolymers for advanced

applications. As selected examples, we will discuss (i) how novel diblock graft copolymers can be prepared in a one-pot one-step process; (ii) how polymer ionic liquid based block copolymers can be synthesized, and (iii) how CMRP can be implemented for the preparation of well-defined nanohybrids of fullerene and carbon nanotubes for photodynamic cancer therapy and electromagnetic protection purposes, respectively.

**References.** <sup>1</sup>Hurtgen M.; Detrembleur C.; Jerome C.; Debuigne A. *Polym. Rev.* 2011, 51, 188-213. <sup>2</sup>Debuigne, A.; Poli, R.; Jerome, C.; Jerome, R.; Detrembleur, C. *Prog. Polym. Sci* **2009**, 34, 211-239; and references therein. <sup>3</sup>Debuigne A., Caille J.-R., Detrembleur C., Jerome R. *Angew. Chem., Int. Ed.* **2005**, 44, 3439-3442. <sup>4</sup>Debuigne, A.; Caille, J.-R.; Jerome, R. *Angew. Chem.* **2005**, 44, 1101-1104. <sup>5</sup>Debuigne, A.; Champouret, Y.; Jerome, R.; Poli, R.; Detrembleur, C. *Chem. Eur. J.* **2008**, 14, 4046-4059. <sup>6</sup>Hurtgen M., Debuigne A., Jerome C., Detrembleur C. *Macromolecules* **2010**, 43, 886-894. <sup>7</sup>Debuigne, A.; Michaux, C.; Jerome, C.; Jerome, R.; Poli, R.; Detrembleur, C. *Chem. Eur. J.* **2008**, 14, 7623-7637. <sup>8</sup>Debuigne A., Willet N., Jerome R., Detrembleur C. *Macromolecules* **2007**, 40, 7111-7118. <sup>9</sup>Debuigne, A.; Jerome, C.; Detrembleur, C. *Angew. Chem., Int. Ed.* **2009**, 48, 1422-1424. <sup>10</sup>Debuigne A., Poli, R., De Winter J., Laurent P., Gerbaux, P., Dubois P., Wathélet J.-P., Jérôme C., Detrembleur C. *Chem. Eur. J.* **2010**, 16, 1799-1811. <sup>11</sup>Debuigne A., Poli R., De Winter J., Laurent P., Gerbaux P., Wathélet J.-P., Jerome C., Detrembleur C. *Macromolecules* **2010**, 43, 2801-2813.