

## Precision design of novel copolymers and nanohybrids by Cobalt Mediated Radical Polymerization (CMRP)

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**Introduction.** Cobalt Mediated Radical Polymerization (CMRP) using bis(acetylacetonato)cobalt(II) ( $\text{Co}(\text{acac})_2$ ) is the most efficient technique for controlling the radical polymerization of vinyl acetate until high molar masses and low polydispersity.<sup>1-4</sup> In this process the cobalt complex ( $\text{Co}(\text{acac})_2$ ) reversibly forms a Co-C bond at the chain-end of the polymer. 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 (n-butyl acrylate (nBuA)<sup>5</sup>, acrylonitrile (AN)<sup>6</sup>) and non-conjugated monomers (vinyl acetate (VAc)<sup>1-4</sup>, N-vinyl pyrrolidone (NVP)<sup>7</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>8-10</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>8-10</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.

**Results and discussion.** This communication aims at presenting recent advances in the field of CMRP, more particularly in the precision design of novel copolymers for advanced applications. Recent developments in our laboratory have demonstrated the possibility to promote the n-butyl acrylate homopolymerization with control until high molar masses (~  $6 \cdot 10^5$  g/mol) in mild conditions using  $\text{Co}(\text{acac})_2$  as controlling agent.<sup>5</sup> In the frame of synthesizing novel materials useful for bio-applications, we were interested in controlling the polymerization of poly(ethylene oxide) methyl ether acrylate (APEO) and in copolymerizing this monomer with vinyl acetate. We will show that controlling the APEO polymerization is not trivial and the reactivity of the CMRP system for APEO is different than that of

nBuA. After discussing the optimal conditions for control, we will describe the synthesis of poly(vinyl acetate)-b-poly(poly(ethylene oxide) methyl ether acrylate) (PVAc-b-PAPEO), a novel block copolymer of interest in the field of drug delivery systems and surfactants.

Conditions for controlling the vinyl chloride (VC) homopolymerization and for synthesizing poly(vinyl chloride)-b-poly(vinyl acetate) (PVC-b-PVAc) block copolymers in mild conditions by CMRP will also be described. These new results open new avenues in the design of novel PVC based block copolymers.

In the last part of the talk, we will report on the preparation of novel well-defined nanohybrids of fullerene and carbon nanotubes grafted by poly(vinyl alcohol) based copolymers for photodynamic cancer therapy and electromagnetic protection purposes, respectively. A universal radical grafting onto approach of poly(vinyl acetate) based copolymers prepared by CMRP in mild conditions is used for the formation of the nanohybrids.

**Conclusions.** This talk will therefore emphasize the versatility of the CMRP process for the precise design of unprecedented copolymers and nanohybrids of interest using a cheap and commercially available cobalt complex ( $\text{Co}(\text{acac})_2$ ). Ways for adjusting the reactivity of the system in regards to the polymerized monomers will be highlighted.

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