

How Can Cobalt Complexes Help Synthetic Polymer Chemists?

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Nowadays, progresses in medicine, biotechnology, microelectronic and many other fields are more and more sustained by the development of novel polymer materials with constantly improved properties and well-defined molecular parameters. This communication aims at presenting synthetic and mechanistic features of two macromolecular engineering tools based on cobalt complexes. The first is a controlled radical polymerization technique called Cobalt Mediated Radical Polymerization (CMRP)¹⁻⁵. The second is an efficient radical polymer chain coupling reaction called Cobalt Mediated Radical Coupling (CMRC)⁶.

Controlled radical polymerization (CRP) techniques give access to a large range of polymeric materials with low molar mass distribution, predictable molar masses and precise architectures. All these processes are based on the temporary deactivation of the growing radical species, which limits the extent of irreversible termination reactions that occur between radicals by coupling or dismutation. In the case of CMRP, the controlling agent is a cobalt complex 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 is in equilibrium with a tiny amount of propagating species. The reversibility of the deactivation is ensured by homolytic cleavage of the Co-C bond by thermal treatment (Figure 1).

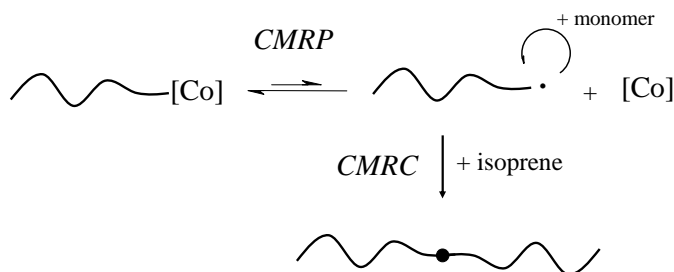


Figure 1 : General scheme for the Cobalt-Mediated Radical Polymerization (CMRP) and Coupling reaction (CMRC).

Temperature and use of ligands have strong influence on the course of the CMRP. These features will be addressed in the presentation. From the synthetic point of view, CMRP is efficient for controlling both conjugated and non-conjugated monomers such as acrylates, vinyl acetate (VAc), N-vinyl pyrrolidone (NVP) and acrylonitrile (AN) but is also a valuable approach for the preparation of well defined block copolymers based on these monomers¹. Main synthetic possibilities of CMRP will be presented.

Occurrence of termination during CRP is detrimental to the control of the molecular parameters and leads to materials with large and/or multimodal molar mass distributions. A notable exception to this rule is the case where termination is fast, quantitative and proceeds specifically by coupling. In that case, a perfect doubling of the polymer molar mass is expected without broadening of the molar mass distribution. Such a quantitative coupling process should be a powerful synthetic tool since α -functional polymers and diblock

copolymers should lead to the corresponding telechelic and triblock copolymers, respectively. Such a radical coupling process, named ATRC (for Atom Transfer Radical Coupling)^{7,8}, is reported in literature. However, high coupling efficiencies are restricted to polymer precursors with relatively low molar masses. Recently, we reported a new radical coupling method⁶ which consists in addition of isoprene to polymer precursors formed by Cobalt Mediated Radical Polymerization (CMRP). This reaction was discovered while attempting to prepare a PAN-b-PIP block copolymer by sequential CMRP of AN and isoprene. However, treatment of well-defined PAN precursors, capped by bis(acetylacetonato)cobalt complexes (Co(acac)₂), 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 (Figure 2). 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-Co(acac)₂ diblock precursors.⁶

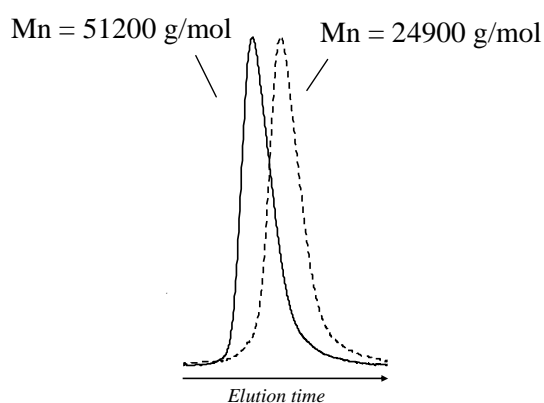


Figure 2: Size-exclusion chromatograms of the PAN-[Co] precursor prepared at 0°C in DMSO (dotted line) and the resulting coupling product upon treatment with isoprene (full line).

Recent mechanistic advances in Cobalt-Mediated Radical Polymerization (CMRP) and Coupling (CMRC) reaction as well as expected impact of these techniques in macromolecular engineering will be discussed in this talk.

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Acknowledgements.

The “Belgian Science Policy” in the frame of the “Interuniversity Attraction Poles Programme” (PAI VI/27), and the “Fonds National de la Recherche Scientifique” (F.N.R.S.) are acknowledged for financial support. A. D. and C. D. are “FNRS Postdoctoral Researcher” and “FNRS Senior Research Associate”, respectively. The authors thank G. Cartigny for assistance. The authors would also like to thank R. Poli (University of Toulouse), J. Dewinter, P. Gerbaux and P. Dubois from UMH (Mons, Belgium), P. Laurent and J-P Wathélet from fsagx (Gembloux, Belgium) for current mechanistic investigations on CMRC.