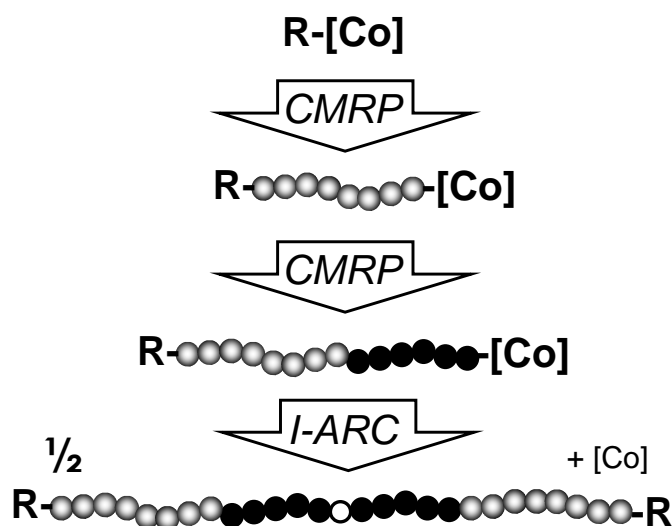


# Unusual quantitative (co)polymer chain coupling reaction based on isoprene and cobalt complexes

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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. In this context, we designed an innovative and very promising tool for macromolecular engineering.<sup>1</sup> This technique, called **Isoprene-Assisted Radical Coupling** (I-ARC)<sup>1</sup>, allows to couple quantitatively polymer chains preformed by **Cobalt-Mediated Radical Polymerization** (CMRP)<sup>2</sup>, an efficient controlled radical polymerization system for vinyl acetate (VAc)<sup>3,4</sup> and acrylonitrile (AN)<sup>4</sup>. Typically, addition of isoprene to well-defined polymers prepared by CMRP invariably leads to the quantitative coupling reaction of the chains, as assessed by the perfect doubling of the molar mass of the polymer. Importantly, the I-ARC reaction is not limited to macromolecules with low molar masses and homopolymers,



contrary to the previously reported radical chains coupling methods. Indeed, when applied to diblock copolymers<sup>5</sup>, I-ARC constitutes a straightforward approach for the synthesis of telechelic symmetrical ABA triblock copolymers, as illustrated by the preparation of poly(vinyl acetate)-*b*-poly(acrylonitrile)-*b*-poly(vinyl acetate) triblock copolymers and their derivatives.

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<sup>2</sup> Debuigne, A.; Poli, R.; Jérôme, C.; Jérôme, R.; Detrembleur, C. *Prog. Polym. Sci.* **2009**, doi:10.1016/j.progpolymsci.2008.11.003

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<sup>4</sup> Debuigne, A.; Michaux, C.; Jérôme, C.; Jérôme, R.; Poli, R.; Detrembleur, C. *Chem. Eur. J.* **2008**, 14, 7623-7637.

<sup>5</sup> Debuigne, A.; Warnant, J.; Jérôme, R.; Voets, I.; de Keizer, A.; Cohen Stuart, M. A.; Detrembleur, C. *Macromolecules* **2008**, 41, 2353-2360.