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. In this context, we designed a controlled radical polymerization (CRP) technique based on cobalt complexes which is able to efficiently control the radical polymerization of challenging monomers such as vinyl acetate (VAc), N-vinyl pyrrolidone (NVP) and acrylonitrile (AN). This so-called Cobalt-Mediated Radical Polymerization (CMRP)\(^1\)\(^2\) also gave access to unique diblock copolymers by sequential polymerization of the above mentioned monomers. However, addition of isoprene to polymer chains preformed by CMRP did not lead to the expected poly(isoprene) containing copolymers. Instead, the quantitative coupling reaction of the polymer chains was observed, as assessed by the perfect doubling of the molar mass of the initial macromolecules. This result is very exciting because this so-called Isoprene-Assisted Radical Coupling (I-ARC)\(^3\) reaction is not limited to polymers with low molar masses and homopolymers, contrary to the existing radical chains coupling methods. Indeed, when applied to diblock copolymers, I-ARC constitutes a straightforward approach for the synthesis of telechelic symmetrical ABA triblock copolymers and is thus a very promising tool for macromolecular engineering.