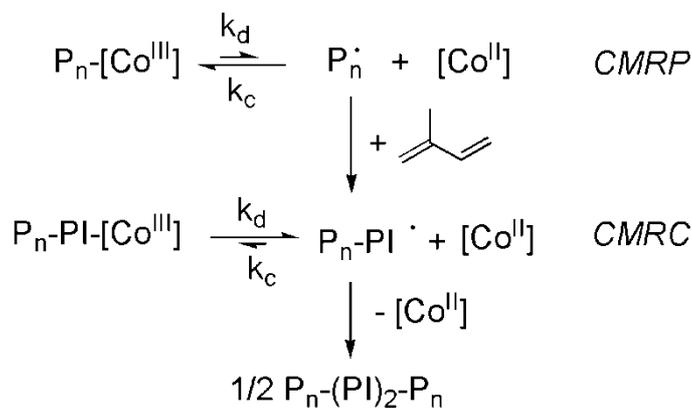


Design of Polymers by Cobalt-Mediated Radical Polymerization and Coupling reaction.

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In the last years, **Cobalt-Mediated Radical Polymerization** (CMRP) emerged as a controlled radical polymerization technique of interest.^[1,2] This method is based on the temporary deactivation of the radical chains by a cobalt complex, which strongly decreases the probability of bimolecular termination reactions and leads to polymers with predictable molecular weights and precise architectures. Until now, CMRP has proved ability to control the polymerization of monomers with different reactivities such as acrylates, acrylonitrile (AN), N-vinylpyrrolidone (NVP) and vinyl acetate (VAc).^[1] Recently, we discovered an unusual radical polymer chain coupling reaction, named **Cobalt-Mediated Radical Coupling** (CMRC),^[3] which is a straightforward approach to the synthesis of symmetrical macromolecules. The latter relies on the addition of 1,3-diene compounds onto polymer precursors preformed by CMRP,^[3,4] and thus capped by a cobalt complex. The CMRC mechanism was established on the basis of mass spectrometry and NMR analyses and corroborated by DFT calculations.^[5] This coupling process was nearly quantitative when using very different 1,3-diene compounds including functional ones.^[5] In all cases, insertion of two diene units was observed in the middle of the coupling product, which is of interest for future use in specific mid-chain functionalization of polymers. Another major interest in CMRC lies in the preparation of highly symmetrical ABA triblock copolymers from tailored diblock precursors.^[3,4]



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