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ORGANOMETALLIC-MEDIATED RADICAL POLYMERIZATION OF VINYL AMIDES: EFFECT OF METAL COORDINATION.

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Organometallic-Mediated Radical Polymerization (OMRP) is an emerging class of controlled radical polymerization which permits the synthesis of precise macromolecular architectures with predictable molecular weights.[1] This technique is based on the reversible deactivation of the growing radical chains by a metal complex, which strongly decreases the probability of irreversible termination reactions, abundant in a free radical polymerization. The OMRP based on cobalt is very efficient for important classes of non-conjugated and reactive monomers such as vinyl esters or vinyl amides.[2] Recent kinetics and theoretical investigations revealed the preponderance of an intramolecular cobalt chelation phenomenon in the CMRP mechanism.[3,4] The latter reinforces the cobalt-polymer bond at the polymer chain-end.[3] Such a double linkage between the controlling agent and the polymer, via a covalent bond and a dative one, represents a unique opportunity to improve the control of the polymerizations, especially for the synthesis of well-defined poly(N-vinyl amide)s which sustain numerous applications. A controlled radical polymerization of N-vinylcaprolactame and N-methyl-N-vinylacetamide has been achieved for the first time. [4] The effects of the carbonyl donor power in the formation of the chelated structure, of the ring strain for the cyclic amides (lactams) and of hydrogen bonding for secondary vs tertiary amides have been rationalized with help of DFT calculations.

[1] M. Hurtgen, C. Detrembleur, C. Jérôme, A. Debuigne, Polym. Rev. 2011, 51, 188.[2] A. Debuigne, R. Poli, C. Jérôme, R. Jérôme, C. Detrembleur Prog. Polym. Sci. 2009, 34, 211.[3] A. Debuigne, Y. Champouret, R. Jérôme, R. Poli, C. Detrembleur Chem. Eur. J. 2008, 14, 4046.[4] A. Debuigne, A. Morin, A. Kermagoret, Y. Piette, C. Jérôme, C. Detrembleur, R. Poli 2012, submitted.

