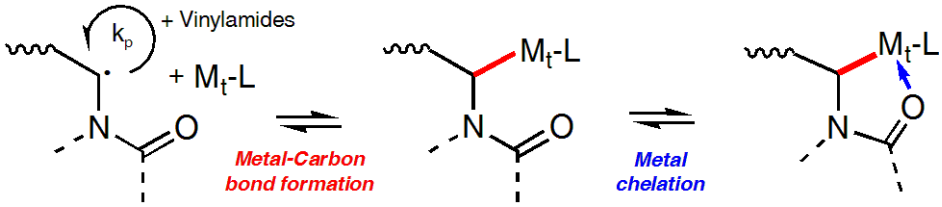
Design of Well-Defined *N*-Vinylamides Based Copolymers via Organometallic-Mediated Radical Polymerization

A. Debuigne[a], *A. Kermagoret*[a], *C.-A. Fustin*[b], *R. Poli*[c], *C. Jérôme*[a], *C. Detrembleur*[a]

[a] Center for Education and Research on Macromolecules (CERM), Chemistry Department, University of Liège (ULg), Belgium.
[b] Institute of Condensed Matter and Nanosciences (IMCN), Bio- and Soft Matter division (BSMA), Université catholique de Louvain, Louvain-la-Neuve, Belgium.
[c] Laboratoire de Chimie de Coordination (LCC), CNRS,Toulouse, France.
Email of corresponding author: **adebuigne@ulg.ac.be**

Poly(*N*-vinylamide)s, like poly(*N*-vinylcaprolactam) (P*N*VCL) or poly(*N*-vinylpyrrolidone) (P*N*VP), represent a major class of polymers which combine valued properties such as water solubility, biocompatibility, thermoresponsiveness. Although *N*-vinylamides can easily be polymerized radically, they are unconjugated monomers whose growing radicals are quite reactive due to the lack of stabilizing groupments. This makes the control of their polymerization and the insertion of well-defined poly(*N*-vinylamide)s segments into complex architectures difficult. This communication aims to present the Organometallic-Mediated Radical Polymerization (OMRP) technique [1] which takes advantage of an intramolecular metal coordination phenomenum in order to control efficiently the polymerization of these monomers [2] (scheme below). The macromolecular engineering potential of this method will be illustrated by the synthesis of new tailor-made *N*-vinylamides-containing statistical, diblock and triblock copolymers, including single and double thermoresponsive polymers with tunable lower critical solution temperatures.[3-5]



[1] M. Hurtgen, C. Detrembleur, C. Jerome, A. Debuigne, *Polym. Rev.*, **2011**, 51, 188-213
[2] A. Debuigne, A. N. Morin, A. Kermagoret, Y. Piette, C. Detrembleur, C. Jerome, R. Poli, *Chem. Eur. J.*, **2012**, *18*, 12834-12844.
[3] A. Debuigne, M. Schoumacher, R. Riva, N. Willet, X. Zhu, S. Ruetten, C. Jérôme and C. Detrembleur, Chem Commun, **2011**, *47*, 12703-12705
[4] M. Hurtgen, J. Liu, A. Debuigne, C. Jerome, C. Detrembleur, *J. Polym. Sci., Part A: Polym. Chem.*, **2012**, *50*, 400-408.
[5] A. Kermagoret, C.-A. Fustin, M. Bourguignon, C. Detrembleur, C. Jérôme, A. Debuigne, *Polym. Chem.*, *submitted*.