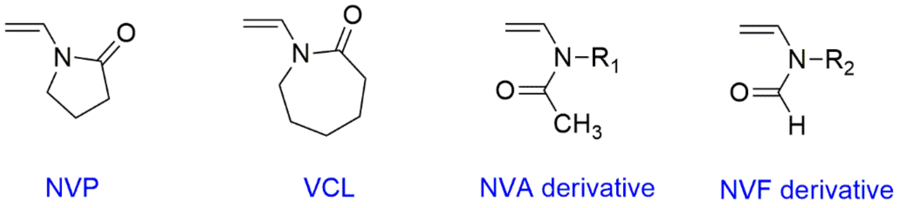
Novel smart poly(*N*-vinylamides): synthesis, physicochemical characterization and applications

Funding: MESR. Joint Doctorate between Université Toulouse III Paul Sabatier and Nara Institute of Science and Technology, Japan.

Keywords: reversible addition-fragmentation chain transfer polymerization, RAFT, N-vinyl monomer, block copolymer, thermoresponsive, gas hydrate inhibitor.

Context

N-vinylamides are vinyl monomers with nitrogen directly attached to the vinyl group (Scheme 1), giving poly(*N*-vinylamides) by free-radical polymerization. This class of polymers exhibit exceptional physicochemical properties which make them highly attractive for various industrial applications.[1] For instance, cyclic *N*-vinylamide-based polymers like poly(*N*-vinylpyrrolidone) (PVP)[2] and poly(*N*-vinylcaprolactam) (PVCL)[3] are not only biocompatible but also blood compatible with good bioadhesive properties. In addition to that, PVCL is thermoresponsive with a lower critical solution temperature (LCST) close to body temperature.[3] *N*-vinylpyrrolidone (NVP) and *N*-vinylcaprolactam (VCL) monomers can be statistically copolymerized in order to obtain thermoresponsive polymers with tunable LCSTs.[4]



Scheme 1: Main N-vinylamide monomers of interest.

Non cyclic *N*-vinylamides like *N*-vinylacetamide (NVA) and *N*-vinylformamide (NVF) lead to cationic poly(*N*-vinylamines) after hydrolysis of the side chain of the corresponding polymers.[5] Assoc. Prof. H. Ajiro (NAIST University, Nara, Japan) developed a series of original non cyclic substituted *N*-vinylamides,[6] some of them showing a LCST behavior and kinetic hydrate inhibition performance.[7]

After a quarter of a century of intensive explorations of reversible-deactivation radical polymerisations (RDRP),[8] it is now possible to synthesize well-controlled polymers (in terms of molar mass, dispersity, end-groups, architecture and microstructure) from most classical monomers. Although RDRP of *N*-vinylamides has been reported by several groups including ours,[2,3,4,9,10] many aspects remain unexplored and deserve consideration.

Thesis subject

In collaboration with Assoc. Prof. H. Ajiro (NAIST, Japan), we propose to study in detail reversible-deactivation radical polymerization (RDRP) of *N*-vinylamides, in particular reversible addition-fragmentation radical (RAFT) polymerization.[2-4] Cyclic and non-cyclic LCST *N*-vinylamide monomers will be incorporated in original LCST polymers of controlled chain lengths, architectures and microstructures. The structure-LCST property relationships will be thoroughly studied prior to exploring their performances as kinetic hydrate inhibitors among other potential applications.

Candidate profile

We are seeking a highly motivated student with a Master of Science or engineering degree. The candidate must be rigorous, autonomous and dynamic with high scientific curiosity. He / she should have very good English skills. The student will be part of *Precision Polymers by Radical Processes* (P3R, http://imrcp.ups-tlse.fr/en/page/p3r-team-m-destarac) team at IMRCP laboratory, and will benefit from the instruments of the laboratory for the synthesis and physicochemical characterization of polymer materials. He / she will have access to the technical platforms of the Toulouse Institute of Chemistry. The student will receive a multidisciplinary training combining organic synthesis, polymer chemistry and characterization, and physico-chemistry of polymers. He / she will spend part (1 year minimum) of his / her thesis at NAIST, Nara, Japan.

Contact: Prof. Mathias Destarac. E-mail : destarac@chimie.ups-tlse.fr

[1] Y.E. Kirsh. Water Soluble Poly-*N*-Vinylamides: Synthesis and Physicochemical Properties. Wiley, Chichester, UK (1998).

[2] Aqueous RAFT/MADIX polymerisation of *N*-vinylpyrrolidone at ambient temperature.
A. Guinaudeau, S. Mazières, D. J. Wilson, M. Destarac, *Polym. Chem.* **2012**, *3*, 81.

[3] Thermoresponsive poly(*N*-vinylcaprolactam)-coated gold nanoparticles: sharp response and easy tunability.
M. Beija, J-D. Marty, M. Destarac. *Chem. Commun.* **2011**, *47*, 2826.

[4] Effect of copolymer composition of RAFT/MADIX-derived *N*-vinylcaprolactam / *N*-vinylpyrrolidone statistical copolymers on their thermoresponsive behavior and hydrogel properties.
X. Zhao, O. Coutelier, H. H. Nguyen, C. Delmas, M. Destarac, J-D. Marty. *Polym. Chem.* **2015**, *6*, 5233.

[5] Novel polyion complex with interpenetrating polymer network of poly(acrylic acid) and partially protected poly(vinylamine) using *N*-vinylacetamide and *N*-vinylformamide.
H. Ajiro, Y. Takemoto, T-A. Asoh, M. Akashi. *Polymer* **2009**, *50*, 3503.

[6] Radical polymerization of novel *N*-substituted-*N*-vinylacetamides and regulated polymer structure by bulky substituents and menthol coordination.
H. Ajiro, M. Akashi. *Macromolecules* **2009**, *42*, 489.

[7] Synthesis of thermosensitive poly(*N*-vinylamide) derivatives bearing oligo ethylene glycol chain for kinetic hydrate inhibitor.
R. Kawatani, Y. Kawata, S-I. Yusa, M. A. Kelland, H. Ajiro, *Macromolecules* **2018**, *51*, 7845.

[8] Industrial development of reversible deactivation radical polymerization: is the induction period over?
M. Destarac. *Polym. Chem.* **2018**, *9*, 4947.

[9] Recent progress in controlled radical polymerization of *N*-vinyl monomers.
K. Nakabayashi, H. Mori. *Eur. Polym. J.* **2013**, *49*, 2808.

[10] Controlled synthesis of poly(vinyl amine)-based copolymers by organometallic-mediated radical polymerization.
M. Drean, P. Guegan, C. Detrembleur, C. Jérôme, J. Rieger, A. Debuigne. *Macromolecules*, **2016**, *49*, 4817.