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NOVEL POLYMER LATEXES BY PHOTOACTIVATED RING-OPENING METATHESIS POLYMERIZATION IN MINIEMULSION VIA THE IN SITU GENERATION OF RUTHENIUM-ARENE CATALYST THROUGH PHOTOLATENT N-HETEROCYCLIC CARBENE LIGAND

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Many useful polymers as polynorbornene (PNb) or polydicyclopentadiene (PDCPD), having interesting applications as optical components, high impact thermosets or shock absorbers, are prepared by ring-opening metathesis polymerization (ROMP). However, the air sensitivity and the lack of processability of the metal-based catalysts used for ROMP is a drag for their implementation at industrial scale. Nevertheless, *in situ* generation/activation of ROMP catalysts employing stimuli like temperature, pH or UV irradiation can palliate this drawback. Among them, photoactivable ROMP catalysts are certainly the most interesting and have often relied on a ligand dissociation/rearrangement under UV light. In this project, we propose an alternative pathway to generate active ruthenium complexes under UV light. The latter employs photosensitive imidazolium salts to generate N-heterocyclic carbene (NHC) under irradiation that can be subsequently employed as ligands. As such, when associated with the inactive [RuCl₂(p-cymene)]₂ dimer, the system allows the formation of the Noels' catalyst RuCl₂(p-cymene)(NHC) *in situ* under UV light. Polymer latexes, commonly synthesized by emulsion polymerization, have high industrial interest. However, few contributions have been reported regarding polymer latexes obtained by ROMP, first due to the high sensitivity of the active species involved and also because of difficulties to mix ROMP initiators and monomers without causing a premature polymerization. The use of photolabile catalytic systems permit to let go off these drawbacks and can afford a new range of polymer latex by ROMP which cannot be prepared by other routes. In this contribution, the synthesis of PNb by ROMP with two photolabile catalytic systems will be first presented. Then this strategy will be transferred in miniemulsion conditions to prove the ability of this system to form PNb latexes.

Recent Publications

1. Pichavant, L., López-González, M.J., Favereaux, A., Héroguez, V. (2018) Thermosensitive polynorbornene poly(ethylene oxide) nanoparticles loaded with oligoDNAs: An innovative approach for acting on cancer-associated pain. *Polymer Chemistry* 9(3): 362-371

2. Pinaud J., Trinh T.K.H., Sauvanier D., Placet E., Songsee S., Lacroix-Desmazes P., Becht J.M., Tarablsi B., Lalevée J., Pichavant L., Héroguez V., Chemtob A. (2018) *In Situ* Generated Ruthenium-Arene Catalyst for Photoactivated Ring-Opening Metathesis Polymerization Through Photolabile N-Heterocyclic Carbene Ligand. *Chemistry A European Journal* 24(2): 337-341
3. Pichavant, L., Carrié, H., Durrieu, M.C., Héroguez, V. (2016) Nanoparticles highly loaded with gentamicin sulfate by a combination of polyhydroxylated macromonomers and ROMP for the synthesis of bioactive biomaterials. *Polymer Chemistry* 7(45): 7019-7028
4. Cao, E., Pichavant, L., Prouzet, E., Héroguez, V. (2016) The formation and study of poly(ethylene oxide)-poly(norbornene) block-copolymers on the surface of titanium-dioxide particles: A novel approach towards application of si-ROMP to larger surface modification. *Polymer Chemistry* 7(15):2751-2758
5. Pichavant, L., Carrié, H., Nguyen, M.N., Plawinski, L., Durrieu, M.C., Héroguez, V. (2016) Vancomycin Functionalized Nanoparticles for Bactericidal Biomaterial Surfaces. *Biomacromolecules* 17(4):1339-1346

Biography

Loïc Pichavant is a Post-doctoral Researcher at the Laboratoire de Chimie des Polymères Organiques (LCPPO) at the University of Bordeaux (France) since 2010. His research interests deal with the formation of nano-objects by ring-opening metathesis polymerization in dispersed media (dispersion; miniemulsion) of cyclo-olefins and their use in biomedical applications (nano-carriers; drug delivery systems). He obtained a PhD Degree in 2009 from the University of Reims Champagnes-Ardenne, working on the synthesis of new biosourced monomers and their polymerization by photoinitiated free radical polymerization.

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