

Alkoxyamines as valuable precursors for macromolecular engineering

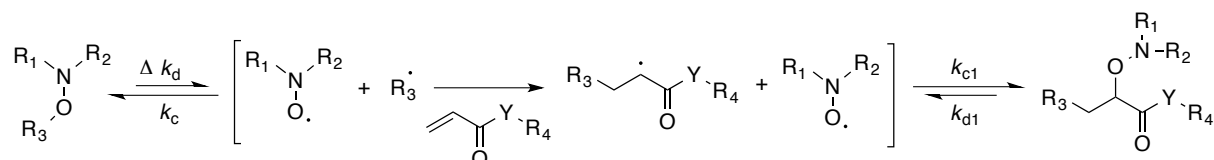
Didier Gigmes

Aix-Marseille Université, CNRS, Institut de Chimie Radicalaire - UMR 7273
13397 Marseille cedex 20, France

didier.gigmes@univ-amu.fr

Alkoxyamines are labile molecules that can undergo homolysis of the C–ON bond under heating or irradiation, to release the corresponding nitroxide and alkyl radical (Scheme 1). Due to this property, alkoxyamines are widely used in Nitroxide Mediated Polymerization (NMP) as initiator/controller agents,¹ but find also valuable applications in radical organic chemistry as a source of alkyl radicals² and even as possible therasnotic agents.³ Moreover, we recently reported that according to their low cleavage temperature, highly labile alkoxyamines can participate in clean intermolecular radical 1,2-addition (IRA) onto various activated olefins in mild condition reactions.⁴

In this lecture we will focus on the potential of this strategy as a key reaction in the preparation of various advanced tri-block copolymers finding applications as solid polymer electrolyte for lithium metal battery technology,⁵ nanoporous membranes for filtration⁶ or guide for spinal cord repairing. The interest of this strategy as promising tool for peptide ligation will be also discussed.⁷ Finally, our latest results on intermolecular radical 1,2-addition initiated from photosensitive alkoxyamines and under a photochemical process will be presented.



Scheme 1. Principle of intermolecular radical 1,2-addition of alkoxyamines onto olefins

References:

1. J. Nicolas; Y. Guillaneuf; C. Lefay; D. Bertin; D. Gigmes; B. Charleux, *Progr. Polym. Sci.*, **2013**, *38*, 63.
2. L. Tebben; A. Studer, *Angew. Chem., Int. Ed.*, **2011**, *50*, 5034
3. G. Audran; P. Bremond; J.-M. Franconi; S. R. A. Marque; P. Massot; P. Mellet; E. Parzy; E. Thiaudière, *Org. Biomol. Chem.*, **2014**, *12*, 719
4. D. Gigmes; P. E. Dufils; D. Gle; D. Bertin; C. Lefay; Y. Guillaneuf, *Polym. Chem.*, **2011**, *2*, 1624
5. R. Bouchet; S. Maria; R. Meziane; A. Aboulaich; L. Lienafa; J.-P. Bonnet; T.N.T. Phan; D. Bertin; D. Gigmes; D. Devaux; R. Denoyel; M. Armand, *Nat. Materials*, **2013**, *12*, 452.
6. P. Tyagi; A. Deratani; D. Bouyer; D. Cot; V. Gence; M. Barboiu; T.N.T. Phan; D. Bertin; D. Gigmes; D. Quemener, *Angew. Chem., Int. Ed.* **2012**, *51*, 7166.
7. T. Trimaille; L. Autissier; M. D. Rakotonirina; Y. Guillaneuf; C. Villard; D. Bertin; D. Gigmes; K. Mabrouk, *Chem. Commun.*, **2014**, *50*, 2744.