# On the Cleavage of Alkoxyamines: Prospects of "Smart" Mediation Systems for Radical Polymerization Reactions

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Alkoxyamines have attracted scientific interest due to their ability to decompose into radicals under mild and controllable conditions. The involved fragmentation pathways can however be complex and are highly dependent on the reaction conditions. While oxidation of the parent alkoxyamine yields radicals by mesolysis of a radical cation intermediate[1], photochemical and thermal decomposition proceeds directly via C-O homolysis[2]. Proton transfer reactions on substituents may introduce further fragmentation pathways. Decomposition however often yields nitroxide radicals. If released in a controlled and selective way, they can serve as "smart" mediators for radical polymerization reactions. For such applications, it is crucial to get a holistic view on alkoxyamine reactivity.

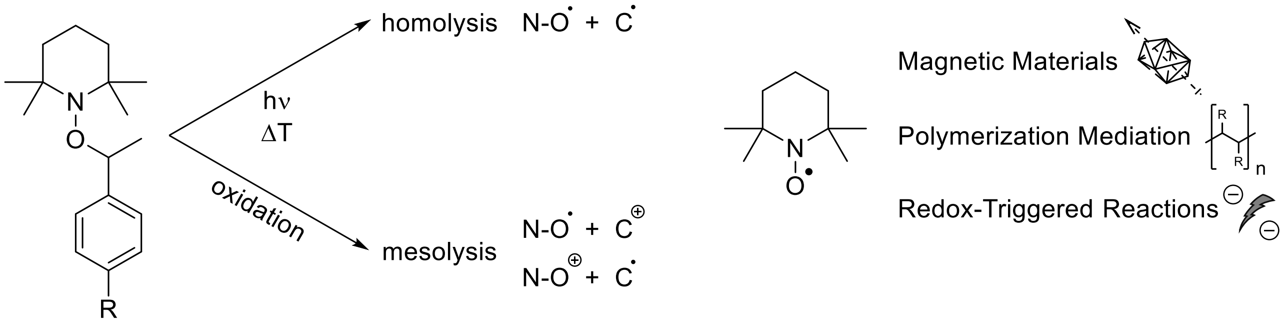

**Figure 1:** General decomposition pathways of an alkoxyamine (left) and possible applications of released nitroxide radicals (right).

Following a mechanistic approach, we will elaborate on the reactivity of selected alkoxyamines and the influence of substituents on their cleavage pathways. In doing so, we will illustrate how synergistically employing theoretical, electrochemical and spectroscopic (EPR/CIDNP) methods can shine light on the underlying fragmentation processes.

References

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