Xanthate-mediated thiolactone synthesis and application to macromolecular engineering

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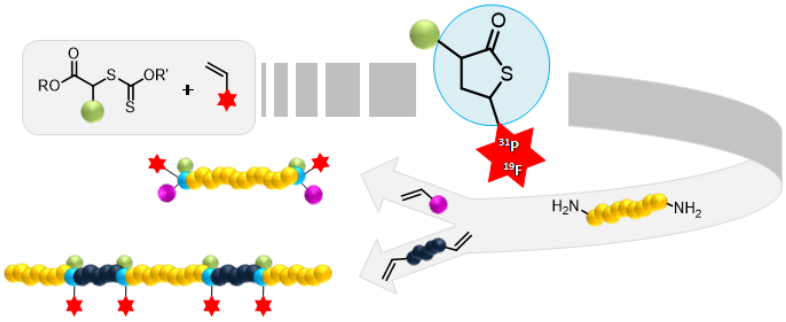
There is an increasing need for simple synthetic procedures that allow catalyst-free polymer synthesis and modification under stoichiometric conditions at mild temperatures, without the need for tedious and costly purification steps. In this regard, Du Prez et *al.* have recently shed a new light on the use of thiolactones, especially 5-membered ring γ-thiolactones, in the field of polymer chemistry.[1]



Scheme 1. Macromolecular engineering from functional γ-thiolactones.

We recently reported the synthesis of a library of new mono- and disubstituted thiolactones using a versatile and robust synthetic procedure based on xanthate chemistry.[2] The method involves free radical-mediated addition of xanthates with appropriate structures to vinyl, allyl or maleimide substrates, followed by thermolysis and cyclization to obtain the corresponding thiolactone in good yields. Due to the wide range of functional alkenes that are available, not only alkyl but also perfluoroalkyl, diethyl phosphonate and N-phenyl succinimide groups could be attached to the thiolactone ring. An amine-thiol-ene conjugation strategy involving these new thiolactone building blocks resulted in successful end-functionalization of amino-terminated polymers and step-growth polymerizations.

We present our last results on the synthesis and use of original functional γ-thiolactones for different strategies of macromolecular engineering.

[1] P. Espeel, F. E. Du Prez. *Eur. Polym. J.* **2015**, *62*, 247-272.
[2] M. Langlais, I. Kulai, O. Coutelier, M. Destarac. *Macromolecules* **2017,** *50*, 3524-3531.

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