THIOLACTONE GROUPS AS FUNCTIONAL HANDLES: FROM DOUBLE END GROUP MODIFICATION TO MACROMOLECULAR LINEUPS

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ABSTRACT

The design and synthesis of tailor-made polymers for different applications requires a variety of synthetic methodologies to fine-tune the polymer structure and adjust its final properties. Introducing reactive functional handles in a post-polymerization modification step, often via 'click'-type reactions, became a popular tool. Moreover, insertion of multiple functional groups per reactive handle can be a quite attractive feature.

This presentation will focus, first, on the one-pot double modification of a variety of different polymers containing a thiolactone end group. For this purpose, a functional amine opens the five-membered ring, releasing a thiol group. This thiol reacts orthogonally with an acrylate already present in the reaction medium, enabling the quantitative introduction of two distinct functionalities at the same reactive site. A series of different polymers containing a thiolactone end group were synthesized through RDRP of a thiolactone-containing initiator or modification of commercial hydroxyl-functionalized polymers with an isocyanate-containing thiolactone. Libraries of functionalities were introduced by reaction with different amine/acrylate combinations.[1]

This strategy was extended to the synthesis of a thiolactone-acrylate hetero-telechelic macromonomer. Upon addition of a functional amine, a multisegmented block copolymer was created with selected functionalities positioned at each segment connection and thus equally spaced along the polymeric backbone.[2] Finally, these materials were applied in the design of glyco- and amphiphilic polymers.

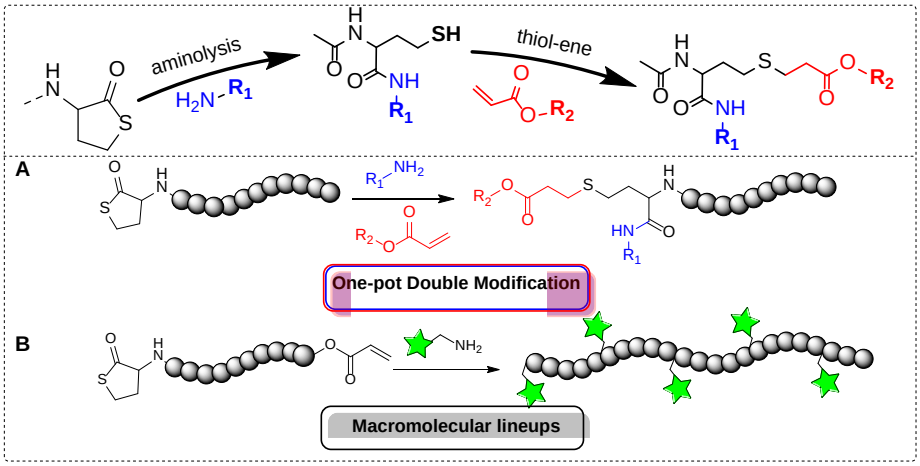

Fig. 1: Amine-thiolactone-ene conjugation for (A) the double modification of polymer end groups and (B) the synthesis of macromolecular lineups**.**

References:

[1] Driessen, F.; Martens, S.; De Meyer, B.; Du Prez, F.E.; Espeel, P. *Macromol. Rapid Commun.* **2016**, *37*, 947.
[2] Driessen, F.; Du Prez, F.E., Espeel, P. *ACS Macro Lett.*, **2015**, *4*. 616.