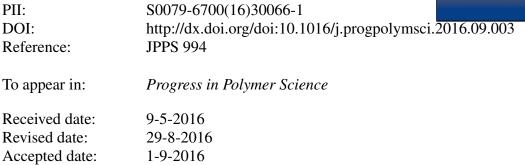
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## ACCEPTED MANUSCRIPT

### Protected Thiol Strategies in Macromolecular Design

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#### Abstract

Reactions involving thiols have been extensively applied in numerous polymeric systems thanks to the reactive nature of the mercapto group, causing these reactions to be efficient and high-yielding. The amount of publications and reviews on the topic of thiol-related reactions in polymer science during the last decade illustrates the rising importance of nucleophilic and radical thiol-ene, thiol-yne and other thiol-X chemistries. In view of orthogonality conflicts and considering their instability towards oxidation and incompatibility with many polymerization processes, several strategies to protect thiols and thus prevent unwanted reactions have been developed and optimized. Generally, a distinction can be made based on the release of byproducts (atom efficiency) of the reactions as well as on the mechanism triggering the thiol release. This review aims to provide an overview of the advances in the use of protected thiols for macromolecular synthesis, with applications in polymerization or post-polymerization modification reactions, but also for the design of more complex structures. In all cases, it is essential that processes must not interfere with the latent thiol function until release is required.

#### Keywords

Thiol-X chemistry, Thiol protection strategy, Disulfide, Polymer functionalization, Thiolactone, Click chemistry

#### Abbreviations

AcSEMA 2-(acetylthio)ethyl methacrylate; AIBN azobisisobutyronitrile; ATRP: atom-transfer radical polymerization; BSA: bovine serum albumin; CANs: covalent adaptable networks; CuAAC: Cu(I)-catalyzed azide-alkyne
cycloaddition; CRP: controlled radical polymerization; CTA: chain transfer agent; DMA: N,N-dimethylacrylamide; DMPA: 2,2-dimethoxy-2-phenylacetophenone; DTT: dithiothreitol; LCST: lower critical solution temperature; MA: methacrylate; MEO<sub>2</sub>MA: 2-(2-methoxyethoxy)ethyl methacrylate; Na-

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