Preparation of End-Functional Polymers via Thiol-Click Chemistry
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Reversible addition-fragmentation chain transfer (RAFT) radical polymerization lends itself to the preparation of (co)polymers with thiol terminal functional groups located commonly, but not necessarily exclusively, at the \(\omega\)-termini. This is a direct consequence of the RAFT mechanism and the fact that (co)polymers prepared via this technique bear thiocarbonylthio end-groups that are readily cleaved to thiol species via a number of different, often facile, routes. Importantly, given the high reactivity of the –SH functional group, to a wide range of electrophilic species, allows for the straightforward synthesis of \(\omega\)-functional (co)polymers via this reactive handle. For example, thiol-terminal RAFT-prepared polymers have been shown to react readily with both activated and non-activated enes, via thiol-ene chemistry, a range of isocyanates, and oxiranes yielding novel telechelic (co)polymers, Scheme 1.

![Scheme 1](image)

General protocols for effecting these transformations are presented employing both polystyrene (PS) and poly\((N,N\text{-diethylacrylamide})\) (PDEA) as model substrates. Reactions are demonstrated to be high yielding and, generally, executed under facile conditions. In several instances the effect of hydrophilic and hydrophobic end-groups on the lower critical solution temperature (LCST) of modified PDEA homopolymers is demonstrated. Finally, the ability to use such end-modified polymers in further high yielding chemical transformations is shown with an emphasis on sequential thiol-ene/thiol-yne and thiol-oxirane/thiol-ene processes.


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Research interests: RAFT, ROMP, water-soluble polymers, applications of thio-click chemistry