Single addition of an allylamine monomer enables access to end-functionalized RAFT polymers for Native Chemical Ligation

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Integration of biomolecules such as peptides or proteins into the architecture of polymer scaffolds and nanoparticles affords biomaterials that display the functionality of both components. Such modifications of polymers enable researchers to enhance and optimize the existing properties of a biologically inert structure. For example, polymer–peptide conjugates have been utilized to increase targeted cellular uptake of therapeutics and improve cell adhesion and growth in scaffold applications. Equally, the modification of biological molecules with polymeric groups, e.g. polyethylene glycol (PEG), has been successfully employed to alter the physicochemical properties of numerous therapeutic proteins providing improved *in vivo* stability.

Access to polymer conjugates has been greatly expedited by advances in both synthetic polymer and bioconjugation chemistry. Specifically, developments in living radical polymerization (LRP) techniques, such as reversible addition fragment chain-transfer (RAFT) polymerization, make it possible to synthesize well defined polymers with control over a number of variables, including composition, molecular shape, chain length and α- and ω-functionalities. Furthermore, chemoselective bioconjugation methods have enabled a range of functionalities to be appended to polymers in high yield *via* a range of different chemical linkages.

In this study[1] we were interested in expanding the repertoire of chemistry that can be used to generate polymer–peptide conjugates through the use of native chemical ligation (NCL) to functionalize the end group of RAFT polymers. NCL is the most robust and widely used ligation technology employed to assemble proteins from peptide fragments yet, surprisingly, has rarely been employed in the assembly of functional polymers. Here, we report the use of NCL chemistry, in combination with RAFT polymerization technologies, to generate end-functionalized peptide–polymer conjugates which can be applied to the design of bioactive surfaces.

1. Isahak, N., et al., *Single addition of an allylamine monomer enables access to end-functionalized RAFT polymers for native chemical ligation.* Chemical Communications, 2016. **52**(88): p. 12952-12955.