

COMBINING RAFT POLYMERIZATION AND CLICK CHEMISTRY TO PREPARE  
FUNCTIONALIZED POLYMERS AND NANOPARTICLES

by

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## ABSTRACT

This research focuses on preparing functionalized polymers by combining click chemistry with the reversible addition-fragmentation chain transfer (RAFT) technique.

In the first part of this work, a series of novel monomers with pendent azido moieties were synthesized and polymerized via RAFT polymerization with excellent control over the molecular weight and molecular weight distribution at low-to-high conversions. The subsequent copper-catalyzed Huisgen 1,3-dipolar cycloadditions of the resulting azide polymers with functional alkynes were achieved at room temperature with high efficiency. Complete conversion of the side-chain azide functionalities to triazoles was confirmed by IR and  $^1\text{H}$  NMR analysis. The ability of performing click functionalization at room temperature with high efficiency and fidelity makes this a versatile tool to prepare a wide range of side-functionalized polymers.

In the second part of this work, two novel RAFT agents incorporating clickable R groups were prepared and subsequently employed to mediate the RAFT polymerizations of various monomers, producing polymers with predictable molecular weights and narrow polydispersities. The resulting homopolymers were demonstrated to have retained end group functionality, as evidenced by the successful formation of block copolymers. The alkynyl-terminated and azido-terminated polymers were coupled with high efficiency by click chemistry to functional azides and alkynes, respectively, in the presence of a Cu(I) catalyst, demonstrating the ability to prepare a range of functional telechelics and block copolymers.

Finally, the strategy of combining click chemistry and the RAFT technique was also utilized in prepared functionalized nanoparticles. A functional monomer with a pendant azide moiety, 6-azidohexyl methacrylate (AHMA), was polymerized on the surface of silica nanoparticles via surface-initiated RAFT polymerization with considerable control over the molecular weight and molecular weight distribution. The kinetics of AHMA polymerization mediated by 4-cyanopentanoic acid dithiobenzoate

(CPDB) anchored nanoparticles was investigated and compared with that of AHMA polymerization mediated by free CPDB under similar conditions. The subsequent postfunctionalizations of PAHMA-grafted nanoparticles were demonstrated by reacting with various functional alkynes via click reactions. Kinetic studies showed that the reaction of surface-grafted PAHMA with phenyl acetylene surface-grafted PAHMA was much faster than that of free PAHMA with phenyl acetylene, whereas in the case of high molecular weight alkynes surface-grafted PAHMA showed lower reaction rates as compared to free PAHMA.