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KINETICS AND MECHANISM OF RAFT POLYMERIZATION

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Over the last 10 years, a considerable effort has been expended to develop free radical processes that display the essential characteristics of living polymerizations.[1-6] In particular, radical polymerizations that provide molecular weights that are predetermined by reagent concentrations and conversion, yield narrow molecular weight distributions, copolymers of controlled composition and, most importantly, polymer products that can be reactivated for chain extension or block copolymer synthesis and enable the construction of complex architectures.

RAFT Polymerization (radical polymerization with Reversible Addition-Fragmentation chain Transfer) is one of the most recent entrants and arguably more effective methods in this field.[7,8] Some of the advantages of RAFT polymerization, over competing technologies [atom transfer radical polymerization (ATRP),[5,6] nitroxide mediated polymerization (NMP)[4]], stem from the fact that it is tolerant of a very wide range of functionality in monomer and solvent (e.g. -OH, -COOH, $CONR_2$, $-NR_2$, SO_3Na). This means that it is applicable to a vast range of monomer types and that polymerizations can be successfully carried out under a wide range of reaction conditions (bulk, solution, emulsion, suspension). The RAFT process has been shown to be effective over a wide temperature range (polymerizations have been successfully performed over the range 20-150ºC). Indeed, with some limitations imposed by the need to limit termination reactions, the reaction conditions employed in RAFT polymerization are typical of those used for conventional free radical polymerization.

Notwithstanding this outstanding versatility there are some limitations on the method. Not all RAFT agents work in all circumstances. In this paper we consider aspects of the kinetics and mechanism of RAFT polymerization with a view to understanding how to choose RAFT agents and polymerization conditions to maximize living characteristics and minimize side reactions and retardation.

We will follow by showing how this knowledge may be applied in using RAFT polymerization synthesize polymers of precisely tailored molecular weight and composition and provide a route to novel architectures (block, graft, star, microgel, etc.). Our recent work in the field is documented in the references.[9-17]

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