A Radical Journey

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In the late eighties and early nineties the prevailing opinion was that free radical polymerization was a mature technology, and there was not much more new to develop. Ten years later, thanks to the introduction of living-radical polymerization, free radical polymerization is one of the fastest growing research areas of polymer chemistry and one indication is the increasing number of publications since 1993 when it was demonstrated that narrow polydispersity polystyrene could be prepared by a stable free radical polymerization (SFRP) process. The SFRP process is a radical polymerization that is conducted in the presence of nitroxide, which reversibly caps the propagating radical chain. This results in a controlled living system and gives polymers with low polydispersity.

The majority of the early work was performed in the bulk and while this was a great system to develop the chemistry and understand the mechanism and kinetics, there is little chance that it will be used for large-scale manufacturing. Therefore, in the last few years attention has turned to developing an emulsion system in the belief that this will facilitate the commercialization of these living-free radical systems. The history of the SFRP will be presented starting from the bulk polymerizations to the current semi-miniemulsion system being developed at XRCC. Successes and issues will be presented that highlight some of the interesting chemistry that was developed.