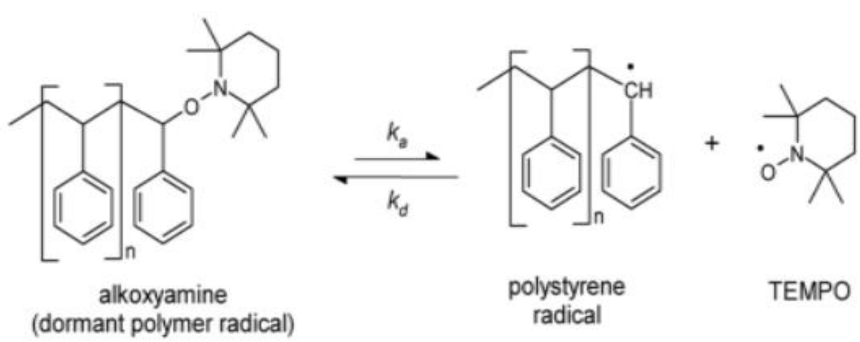
Did you know? series for July-September 2024

Did you know....that Reversible Deactivation Radical Polymerization (RDRP) can be a useful tool for those working with latexes and emulsion polymerization? RDRP is the IUPAC-recommended term for what used to be known as living/controlled radical polymerization, and includes different types of chemistries including Nitroxide-Mediated Polymerization (NMP), Atom Transfer Radical Polymerization (ATRP) and Reversible Addition Fragmentation Transfer (RAFT). Other less common types of RDRP include Iodine Transfer Polymerization (RITP) and Tellurium mediated Radical Polymerization (TERP). RDRP can be used to make a variety of valuable polymer structures that are not achievable using conventional radical polymerization, including for example di- and tri-block copolymers which may finds use as dispersants and stabilizers, and low molecular weight functional materials with star-like structures that can be used as rheology modifiers. These techniques, first developed in the 1990's, used to be considered somewhat exotic but they should now be considered as routine tools to provide polymers with controlled microstructure at a much lower cost and ease of synthesis than anionic polymerization (formerly the only way to synthesize such materials). We are featuring a three part series on the most popular types of RDRP (NMP, ATRP, RAFT) that will describe for each system the most important features, advantages and potential concerns. This first article describes NMP.

Nitroxide-Mediated Polymerization (NMP)
NMP uses a nitroxide to reversibly terminate a growing polymer chain to give a dormant chain that can be continually re-activated, so that the chain retains the ability to grow by adding more monomer (propagating) throughout the entire polymerization (Scheme 1). In contrast, in a conventional radical polymerization, newly initiated chains rapidly add monomer units and then terminate with another growing chain, all within ~0.1-1 second.



Scheme 1. NMP of styrene using TEMPO as the nitroxide.

Polymers made by RDRP, including NMP, typically have molecular weights ranging from ~2-100k, with dispersities (M/Ma)~1.1-1.4. Because the end of each polymer chain has a mediating agent, once the monomer is consumed a second monomer can be added to make a di- block copolymer. To make a tri-block, such as those used as thermoplastic elastomers (TPEs), a difunctional middle block is first made (i.e. with a nitroxide at both ends), and then a second monomer is added to grow new blocks from both ends of the first block, thereby giving an A-B-A triblock structure. NMP requires temperatures of ~115-125 °C for acrylates and styrenics, and ~90 °C for methacrylates (a small amount of styrene monomer is also needed with methacrylates). The final product is odorless and colorless. NMP has been mostly studied in solution and bulk but is also readily performed in emulsion polymerization.

As always, we invite your questions and comments by going to our website www.epced.com or via email at info@epced.com.