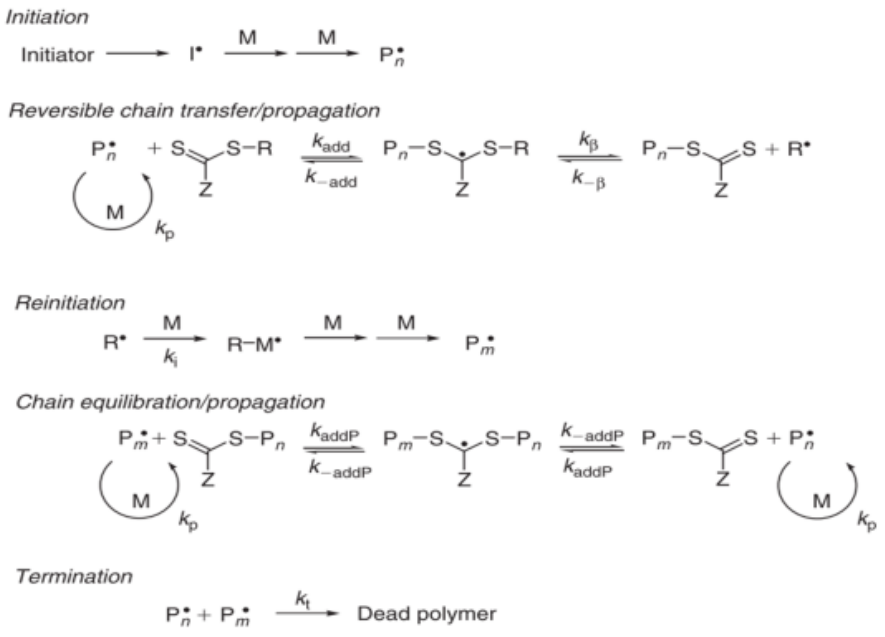
Did you know? series for January - March 2025

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 nay find 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. The first two articles covered NMP and ATRP. ***This final article about RDRP describes RAFT.***

Reversible Addition Fragmentation Transfer (RAFT)

RAFT employs a sulfur containing compound (e.g.dithioester, trithiocarbonate) which acts as a chain transfer agent. Unlike NMP and ATRP, which have reversible termination mechanisms, in RAFT the growing chains undergo *reversible chain transfer* where a propagating chain reversibly transfers to a RAFT agent and a previously dormant chain now becomes active (Scheme 1). Selection of the RAFT agent is critical and must be done to ensure compatibility of the monomer(s) with the chosen agent.



Scheme 1. RAFT mechanism showing reversible addition, fragmentation, and chain transfer steps.

Polymers made by RAFT typically have well controlled molecular weights ranging from ~2-100k, with dispersities (Mw/Mn) ~1.1-1.4. Because the end of each polymer chain has a RAFT agent, once the monomer is consumed a second monomer can be added to make a di-block copolymer. Star-shaped polymers and other chain microstructures can alco be made. RAFT requires typical free radical polymerization temperatures of ~50-90 C, and works with a wide range of monomers (e.g. acrylates, methacrylates, styrenics) including functional monomers (e.g. acrylic acid). The final product may contain color and have odor if the RAFT agents are not removed from the chain ends in a separate step. Like MNP and ATRP, RAFT has been mostly studied in solution and bulk but can also be easily 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.