

Emulsion Polymers Consulting and Education, LLC

Did you know?

The “*Did you know?*” series is a quarterly note from EPCEd that is intended to present simple questions about topics that are important to those working in the emulsion polymers area. Short and concise answers to those questions are presented to educate readers and to elicit comments and further discussion. Some readers will already know the answers and be familiar with the topic while others, especially those newer to the field, will benefit from the answers and discussion. Experienced practitioners may also find new insights in the discussion.

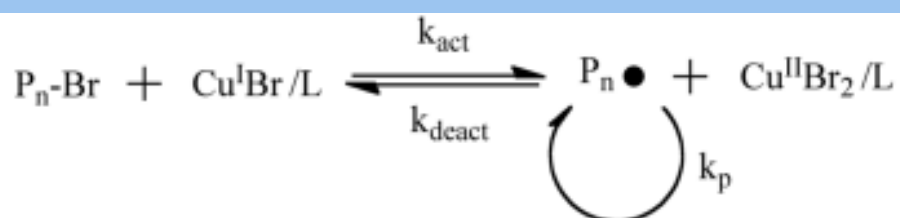
Did you know? series for October - December 2024

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 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. ***This second article describes ATRP.***

Atom Transfer Radical Polymerization (ATRP)

ATRP employs a Cu (or Ru) catalyst complex in its lower oxidation state to abstract a halide (usually Br) from an alkyl halide initiator thereby generating a radical that can add monomer and begin growing a polymer chain. Like NMP, growing chains are *reversibly* terminated (by the higher oxidation state form of the catalyst) to give a dormant chain that can be continually reactivated, 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. ATRP mechanism showing chain activation and deactivation.

Polymers made by ATRP typically have well controlled molecular weights ranging from ~2-100k, with dispersities (M/Ma)~1.1-1.4. Because the end of each polymer chain has a halide, once the monomer is consumed a second monomer can be added to make a di-block copolymer. Multi-functional ATRP initiators easily yield star-shaped polymers, as well as a variety of other chain microstructures. ATRP requires typical free radical polymerization temperatures of ~50-90 °C, and works with a wide range of monomer (e.g. acrylates, methacrylates, styrenics) although functional monomers (e.g. acrylic acid) can be problematic. The final product may contain color if the Cu concentration is too high but recent developments have enabled ATRP to be carried out with very low Cu levels, and even in air. Like NMP, ATRP has been mostly studied in solution and bulk but can also be performed in emulsion polymerization.

As always, we invite your questions and comments by going to our [website](http://www.epced.com) www.epced.com or via email at info@epced.com.