

Living ATRP Polymerization of Acrylamide and N-Isopropylacrylamide

Living polymerization (http://en.wikipedia.org/wiki/Living_polymerization) is a polymerization with no termination and no chain transfer. Typically living polymerization is characterized by an extremely low polydispersity since the chains are initiated in a single step and grow at close to identical rates. A living polymerization will proceed until all monomer is consumed. If more monomer is added the polymerization will continue. It is possible to add a different monomer to produce a block copolymer using living polymerization. Prior to the 1990's living polymerization was usually conducted using anionic polymerization under extremely controlled conditions, no oxygen, water. Anionic polymerization can only proceed with monomers that can maintain an anion so the choice of monomers is limited, styrene, butadiene, acrylonitrile, methylmethacrylate.

In the 1990's a group in Poland that later moved to Carnegie-Mellon University in Pittsburgh developed a polymerization technique that could produce living polymerization in a free radical system opening a wide range of monomers and the ability to conduct living polymerization in aqueous systems. Atom transfer radical polymerization (ATRP) involves protection of the growing free radical by transfer of the radical between the growing chain and an organometallic molecule that can protect the radical. ATRP can be used in the conventional free radical systems, bulk, solution, suspension and emulsion polymerizations.

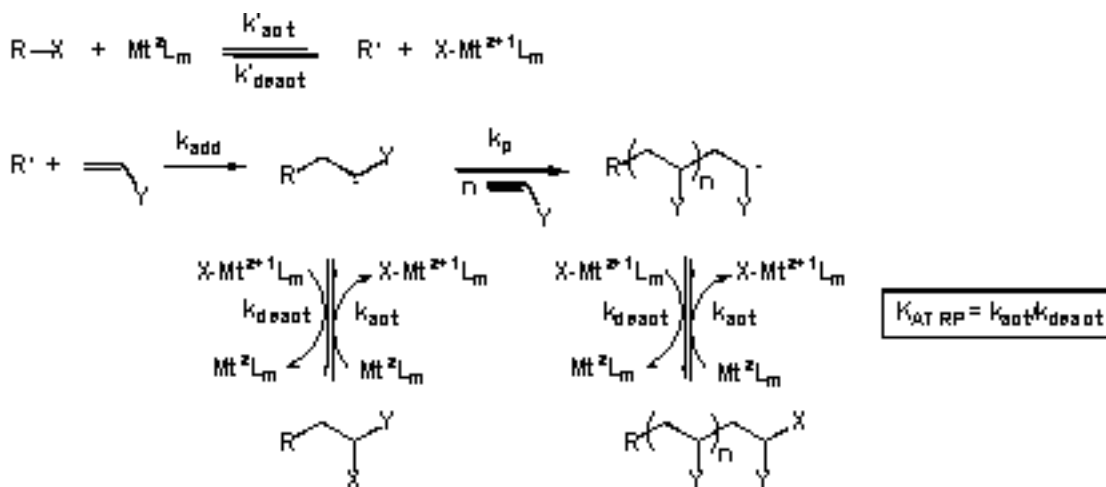
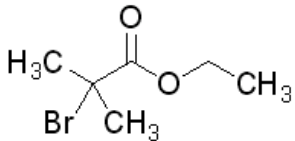
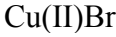
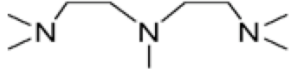
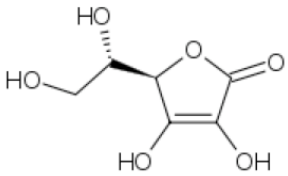
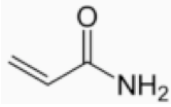
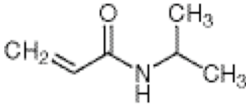
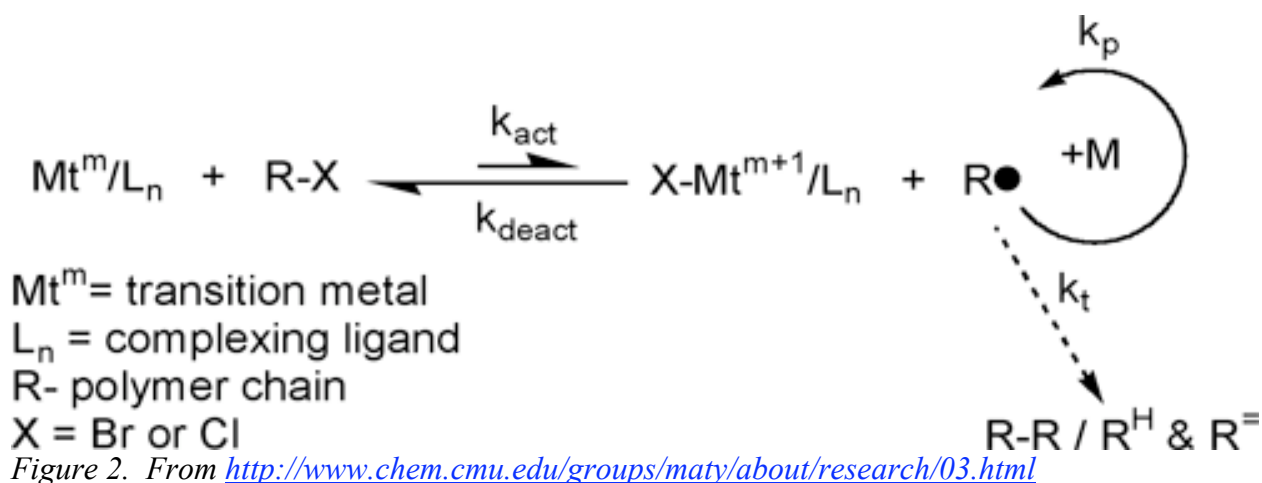


Figure 1. From <http://www.chem.cmu.edu/groups/maty/about/research/03.html>

In ATRP an organohalide (RX) and a transition metal (Mt)/ligand complex (Lm) are in equilibrium with a radical R•. The radical initiator reacts with a monomer to produce a propagating polymeric species. The halide/radical equilibrium serves to protect the radical from recombination since the radical is only present a small amount of the time in an unprotected, propagating form and spends most of the time protected by the organohalide group.

| | | | |
|--------------------------------|--------|---|---|
| R-X | EBIB | Ethyl Bromo isobutyrate |  |
| Mt ² | | Cupric Bromide |  |
| L _m | PMDETA | N,n,n',n',n-Pentamethyldiethylenetriamine |  |
| O ₂ Reduction Agent | | Ascorbic Acid |  |
| Monomer 1 | | Acrylamide |  |
| Monomer 2 | | n-isopropylacrylamide |  |



Procedure:

Use a 100 ml beaker with a magnetic stir bar.

- 1) Dissolve the monomer in water. (Best results are found for degassed water since O₂ reacts with the radical but it is possible to use even tap water as a solvent). Both monomers dissolve rapidly in water but heating can be used if needed. Use a significant amount of monomer for a rapid reaction (< 30 minutes).
- 2) Add ethyl bromo isobutyrate. This does not dissolve but has some solubility in water so you need to stir the suspension to maintain good dispersion of this ester. The ester has an odor but is nontoxic.

- 3) Add CuBr_2 . This may need heat to dissolve.
- 4) Add the PMDTA ligand. This dissolves easily. The Cu PMDTA complex turns the suspension a vibrant blue.
- 5) Finally add the reducing agent, ascorbic acid and the suspension will turn dark blue/black/ or green depending on the amount of reducing agent. This is conversion of Cu^{+2} to Cu^{+} with formation of the protected free radical in the activated state. The color is determined by the equilibrium between activated and deactivated state in Figure 1. Oxygen in air gradually dissolves in the solution from the air and oxidizes Cu^{+} to Cu^{+2} . You will notice a gradual color change. Adding more ascorbic acid will oppose this oxidation. (*Alternatively the water can be degassed and the reaction run in an oxygen free atmosphere.*)
- 6) Polyacrylamide can be separated from water by precipitation in toluene. Use 200 ml of toluene, stir and slowly add the reaction mixture after about 30 minutes. Polyacrylamide will precipitate out of the solution. The polymer can be further washed with propanol.
- 7) Poly(n-isopropylacrylamide) PNIPAM can be separated from the aqueous suspension by heating since it phase separates from water at about 30°C . It can also be precipitated by pouring the reaction mixture into hot water.

Note: Acrylamide has a primary amine that can interfere with the ligand/Cu complex. PNIPAM should be easier to synthesize compared to polyacrylamide.