Chem 466
04/01/2014
lecture #19

- no office hours Monday, 04/07/14
- Exam III, Thursday, 04/10/14 (9 days)
  - old Exam III & answer keys to be uploaded today
(6) Controlled Radical Chain-growth Polyg. (contd)

(1) Atom transfer radical Polyg. (ATRP)

- transition metal mediated halogen atom transfer through redox chemistry

Macromolecules 1995, 28, 7901

(2011 ACS Award in Applied Polymer Science)
2011 Wolf Prize from Israel's Wolf Foundation
($100k; shared with 2 other award winners)
(1/3 Wolf prize winner → Nobel Prize)

also M. Sawamoto et al. Macromolecules 1995, 28, 1721

V. Perec et al Macromolecules 1995, 28, 7979

\[ Cu^2+ + \text{R}-\text{S}_2\text{Cl} \]

\[ \text{PMDETA (ligand)} \]

Requires:
- labile halogen
- transition metal (Cu, Ru, Ni, Fe, etc.)
- ligand
- monomer

- redox rxn to mediate reversible transfer of halide
- ligand type & catalyst vs. oxidized catalyst conc. important
- final poly presents on alkyl halide w chain end
Mechanism:

Initiation

[Diagrams of reaction mechanisms involving radicals and chemical symbols]

Reversible termination

Redox

*Swapping of Br* back-and-forth between poly + Cu catalyst system
- ATRP is convenient, w/ many commercially available reagents & good control

- Complication is use of metals + need for their removal, e.g. for biomedical apps (toxicity issues) or microelectronic technologies (conductance issues)

- Matyjaszewski has made several recent advances to limit amt. of Cu catalyst required + to turn polymer "on" + "off" by electrochemical redox of catalyst to "active" (Cu(I)) + "inactive" Cu(II) species, etc.
I. Chain-growth Polym (cont'd)

(a) General Overview
(b) Thermodynamics
(c) Typical monomers + main mechanisms for chain-growth polyms
(d) Anionic Polym
(e) Cationic Polym
(f) Radical Polym
(g) Controlled Radical chain-growth Polym (cont'd)

(1) ATRP

(2) Nitroxide-mediated radical polyn (NMRP)

in mid 1990's, earliest contributions to NMRP development by
Michael George @ Xerox
Craig Hawker @ IBM (now UW)
David Solomon, Graeme Moad, Esio Rizzato +
Sun Han @ CSIRO (Australia)
(Commonwealth Scientific & Industrial
Research Organization)

universal initiator
D. Benoit, U. Chaplinski
I. Braslau, C.J. Hawker
J. Am. Chem. Soc.
1999, 121, 3904-20.
- relies upon alkoxyamine group
- undergoes homolytic cleavage at elevated temp (A)

- one radical is reactive + initiates polymer
- the nitroxide radical is stable

- radical combination terminates the reactive radical chain end reversibly

- propagation

- reversible termination

- reduction of temp. allows for isolation of the reversibly-terminated poly

- the alkoxyamine chain end can be reactivated (by B) in the presence of monomer to give chain extension, block copoly synthesis, etc.
e.g. graft block copoly via sequential

\[ \text{NMCP + ATRP:} \]

- Backbone via NMCP
- Side chains via ATRP

CuBr, PMDETA (grafting-from polymer)

Copolymer:

\[ n, x, 1-x \text{ depend on stoichiometries of initiator + monomers but also on monomer reactivity ratios} \]
(3) Reversible addition–fragmentation chain transfer (RAFT) polymer.

- Introduced in 1998 by Graeme Mood, Esio Rizzarelli, and Sac Thang (CSIRO, Australia) with similarities to earlier (1980s) initiator chemistries (initiator, chain transfer agent, terminator).

- Requires initiator + chain transfer agent + monomer.

We'll discuss just one example from hand-out:

Li, Z.; Ma, J.; Lee, N.S.; Wooley, K.L.

\[ \text{AIBN} + \text{thiol carbonate CT agent} + \text{monomer} \rightarrow \text{RAFT} \]

- The "trile" is for the initiator to produce radicals that undergo an even faster w/ CTA than with monomer so that radicals generated from CTAs initiate polymer:
  - Successful ~80-90% success
  - But 10-20% of chains have initiator-based chain end.
In the article, RAFT of styrene
2) RAFT of methyl acrylate
3) RAFT of tert-butyl acrylate
gave a triblock copolymer containing a norbornyl x-chain end. 
 Macromonomer
see Figure 1(A)