Chem 466

04/01/2014

Lecture #19

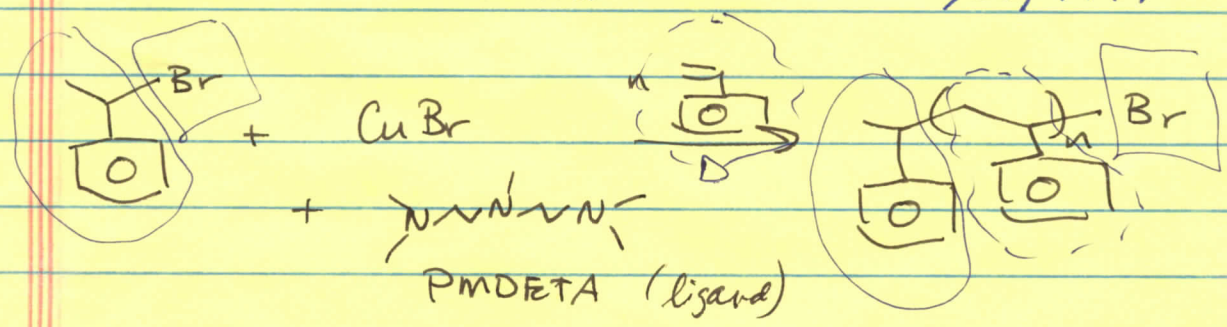
- no office hours Monday, 04/07/14
- Exam III, Thursday, 04/10/14 (9 days)
  - old Exam III + answer keys to be uploaded today

(6) Controlled Radical Chain-growth Polym (cont'd)

(1) Atom transfer radical Polym. (ATRP)

- transition metal mediated halogen atom transfer through redox chemistry

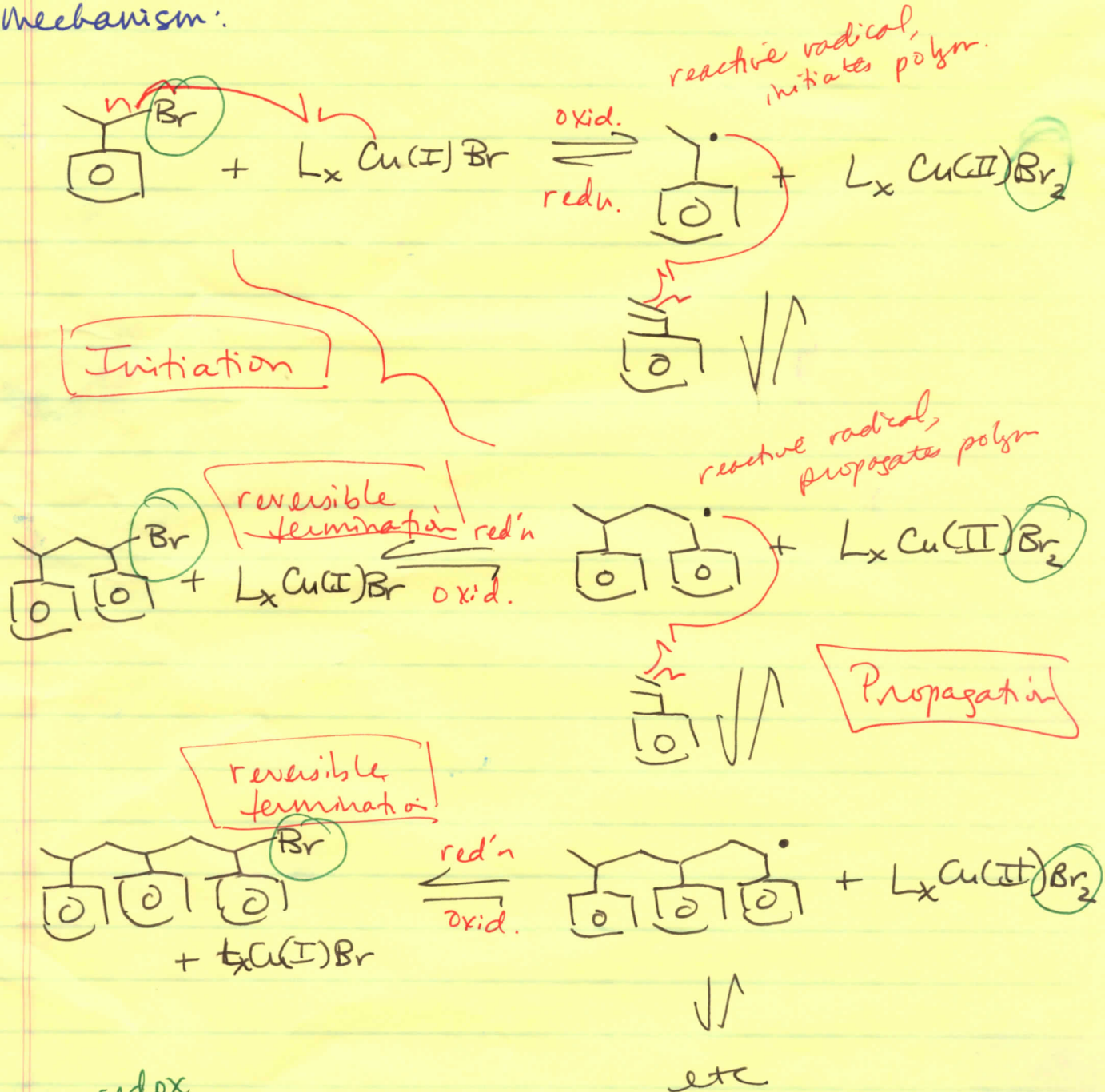
K. Matyjaszewski et al. J. Am. Chem Soc. 1995, 117, 5614
alkyl halides + Cu^{I} Macromolecules 1995, 28, 7901
(2011 ACS Award in Applied Polymer Science
2011 Wolf Prize from Israel's Wolf Foundation
($100k; shared w/2 other award winners)
(~1/3 Wolf prize winners → Nobel Prize)
also M. Sawamoto et al. Macromolecules 1995, 28, 1721 Ru^{II}, Ni^{0}
e.g. V. Percec et al Macromolecules 1995, 28, 7979 Cu^{I} + R-SO_2Cl



Requires: (initiating system)
- labile halogen
- Transition metal (Cu, Ru, Ni, Fe, etc)
- ligand
- monomer

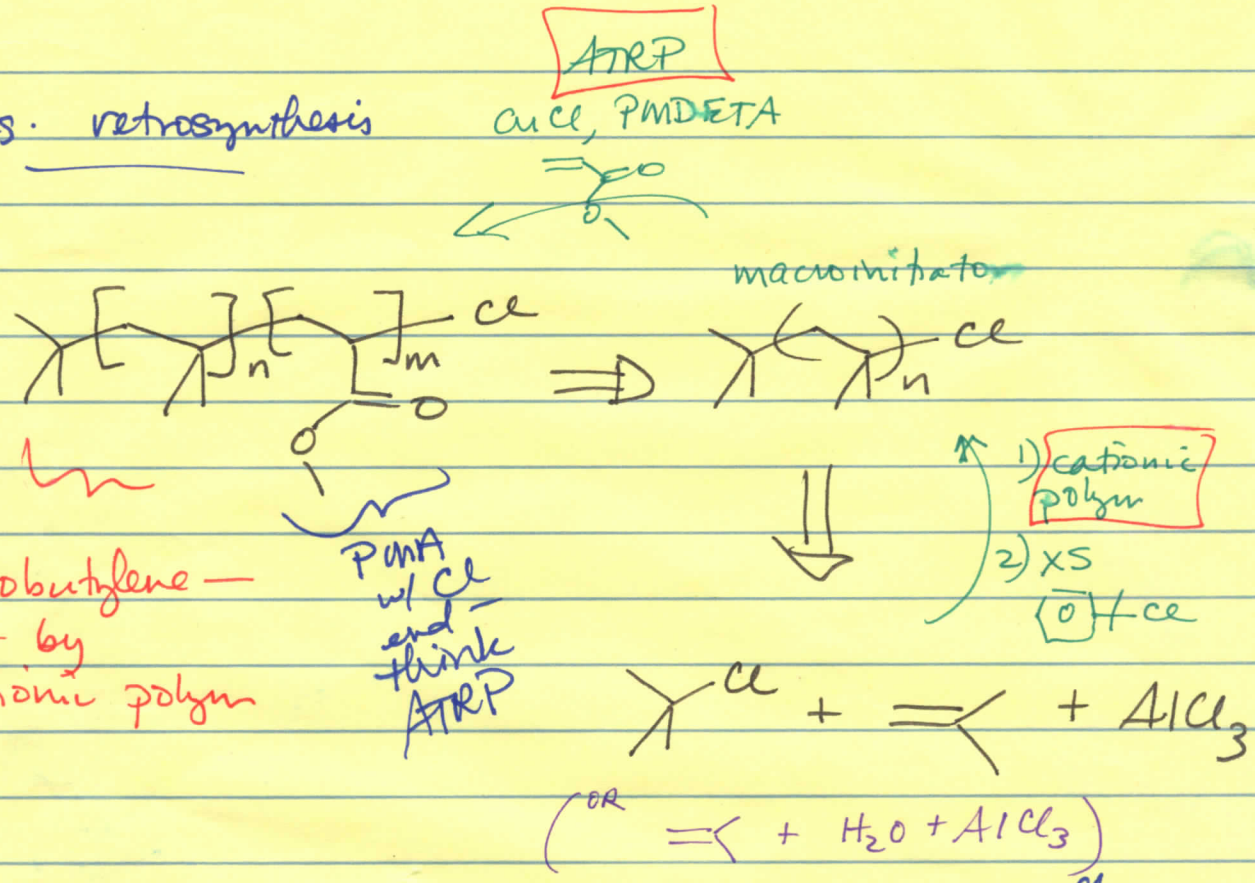
- redox rxns mediate reversible transfer of halide
- ligand type + catalyst vs. oxidized catalyst conc. important
- final poly presents an alkyl halide w chain end

Mechanism:



• redox swapping of $Br^{\bullet}$ back-and-forth between poly + Cu catalyst system

e.g. retrosynthesis



polyisobutylene — best by cationic polym

- 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)

  - for instance, computer chip production by negative-tone + positive-tone photoresist technology

- Matyjaszewski has made several recent advances to limit amt. of Cu catalyst required + to turn polym "on" + "off" by electrochem redox of catalyst to "active" (Cu^{I}) + "inactive" Cu^{II} species, etc.

V 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

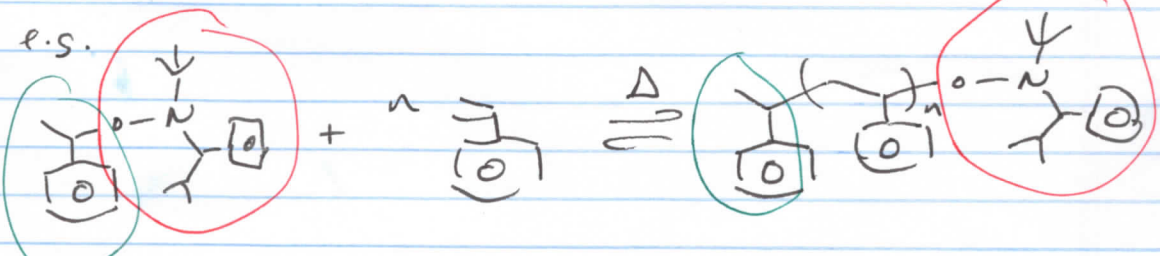
(2) Nitroxide-mediated radical polym (NMRP)

- in mid 1990's, earliest contributions to NMRP development by
  Michael Georges @ Xerox
  Craig Hawker @ IBM (now UCSB)
  David Solomon, Graeme Moad, Ezio Rizzardo + San Thang @ CSIRO (Australia)
  (Commonwealth Scientific + Industrial Research Organization)

see history in D.H. Solomon J. Polym. Sci., Part A: Polym. Chem. 2005, 43, 5748-64.

e.g.

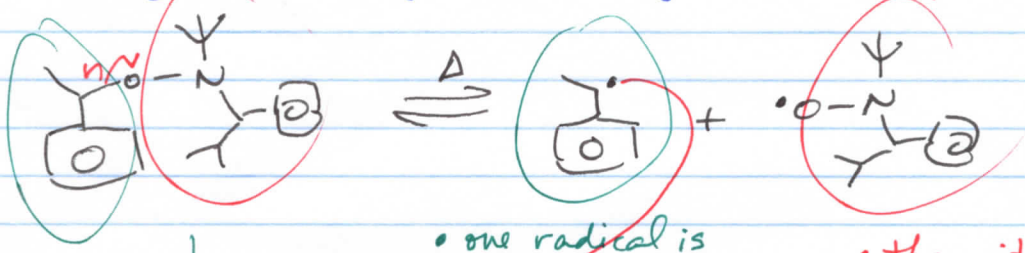
alkoxy-amino initiator



alkoxy-amino chain end

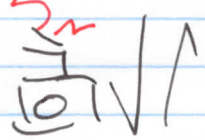
universal initiator
D. Benoit, V. Chaplinski, R. Braslau, C.J. Hawker
J. Am. Chem. Soc. 1999, 121, 3904-20.

- relies upon alkoxyamino group
- undergoes homolytic cleavage at elevated temp (Δ)

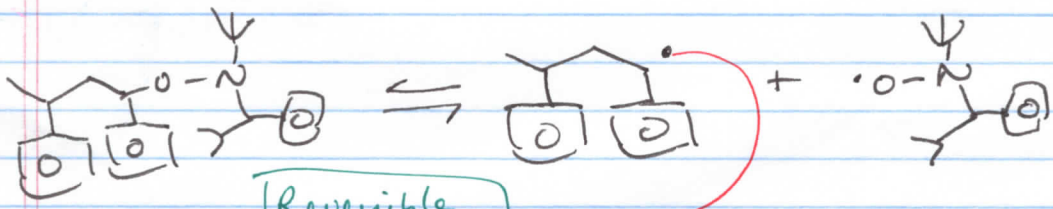


- one radical is reactive + initiates polym
- the nitroxide radical is stable

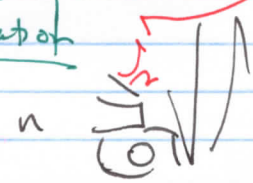
Initiation



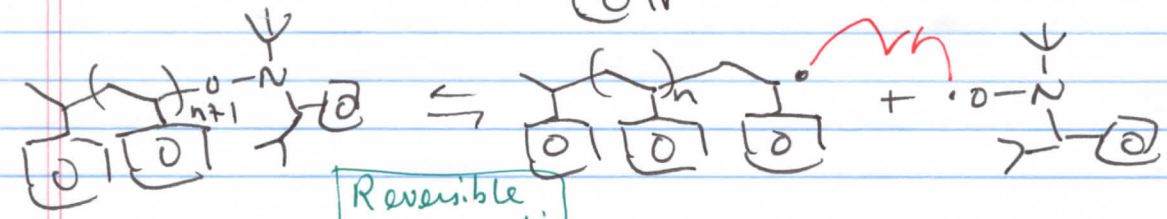
- radical combination terminates the reactive radical chain end reversibly



Reversible Termination



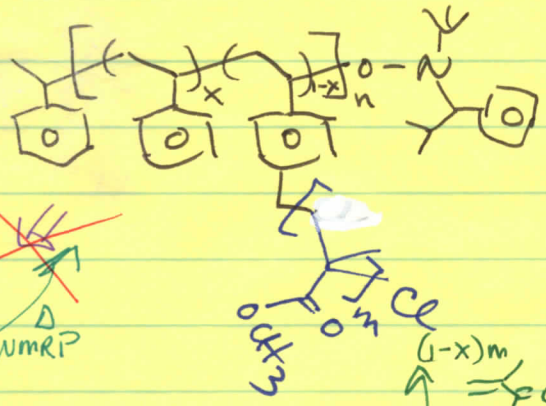
Propagation



Reversible Termination

- reduction of temp. allows for isolation of the reversibly-terminated poly
- the alkoxyamine chain end can be reactivated (by Δ) in the presence of monomer to give chain extension, block copoly synthesis, etc.

e.g. graft block copoly via sequential NMRP + ATRP:



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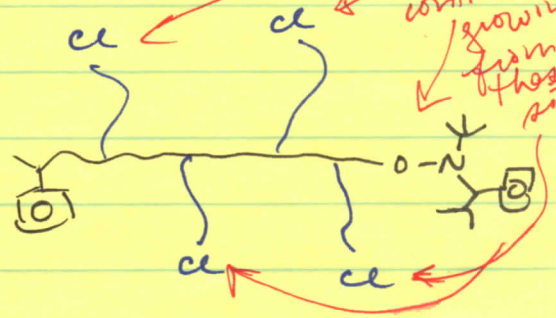
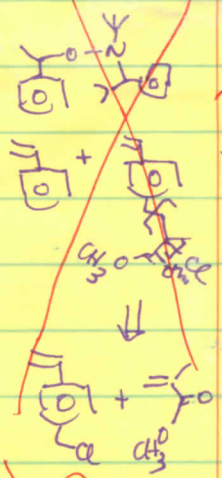


AND could continue growing from those sites

- backbone via NMRP
- side chains via ATRP

alternate, grafting through:

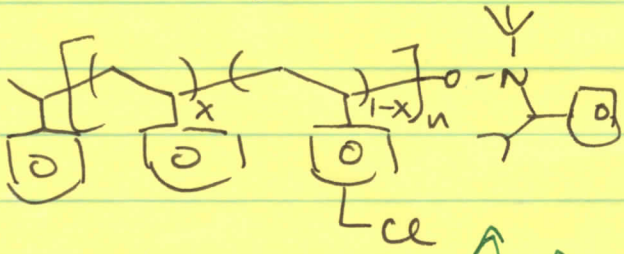


problem, cannot polym MMA w/ styrenyl group present

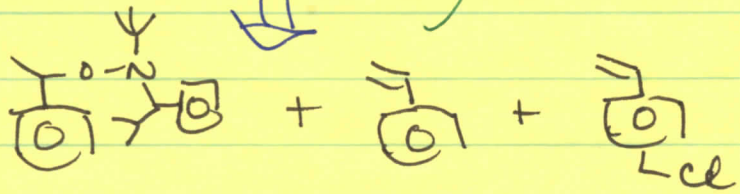
Δ NMRP

ATRP

CuBr, PMDETA (grafting-from polym)



NMRP Δ



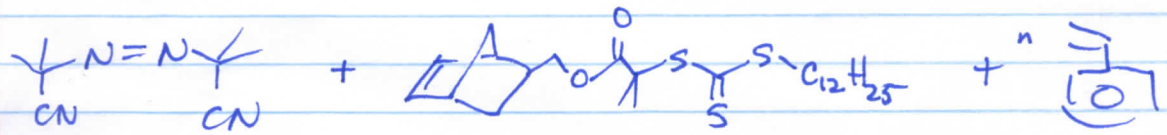
copolym:
n, x, 1−x depend on stoichiometries of initiator + monomers but also on monomer reactivity ratios

(3) reversible addition-fragmentation chain transfer (RAFT) polym.

- introduced in 1998 by Graeme Moad, Ezio Rizzardo, + San Thang (CSIRO, Australia) with similarities to earlier (1980's) iniferter chemistries (initiator, chain transfer agent, terminator)

- requires initiator + chain transfer agent + monomer

- will discuss just one example from hand-out
  Li, Z.; Ma, J.; Lee, N.S.; Wooley, K.L. J. Am. Chem. Soc. 2011, 133, 1228-31



AIBN radical source | trithiocarbonate CT agent + monomer for ROMP | monomer for RAFT

- the "trick" is for the initiator (radical source) to produce radicals that undergo rxn faster w/ CTA than with monomer so that radicals generated from CTAs initiate polym.
  - successful ~80-90 %
  - but 10-20 % of chains have initiator (radical source) based α chain end

(radical source-based)

- In the article, 1) RAFT of styrene
  2) RAFT of methyl acrylate
  3) RAFT of tert-butyl acrylate

  gave a triblock copolymer, containing a norbornenyl α-chain end ⇒ macromonomer
  see Figure 1(A)