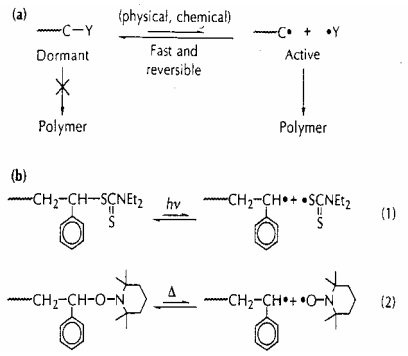
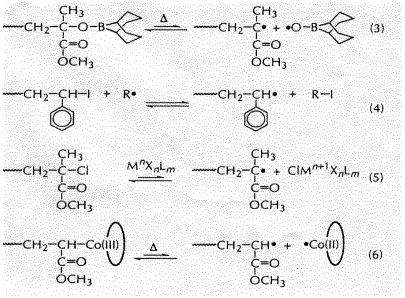
Controlled Radical Polymerization

ATRP and RAFT Processes

Controlled Radical Polymerization



Controlled Radical Polymerization



Nitroxide (SFR) Controlled Radical Polymerizations

Scope and Limitations

Controllable Monomers

Styrene, Butadiene, Methyl Methacrylate, Styrene Sulfonate(Aq)

Problem Monomers

Alkyl Acrylates, Vinyl Acetate, Vinyl Chloride

Initiator Structure

Initiator formed *in situ* using commercial initiators

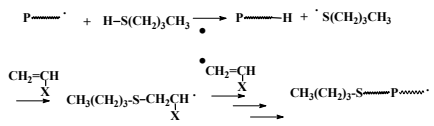
SFR adduct can be introduced to preformed structures including dendrimers, functionalized polymers and telechelics

Useful Additives

Camphorsulfonic acid - deactivates styrene dimer

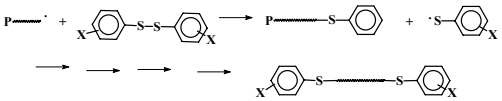
Chain Transfer Chemistry

- 1. Thiols:



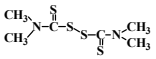
•To produce monofunctional polymers, use functionalized thiols:

2. Disulfides

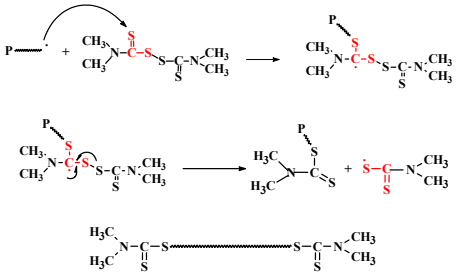


Can lead to difunctional telechelics

Dithiauram disulfide extremely efficient



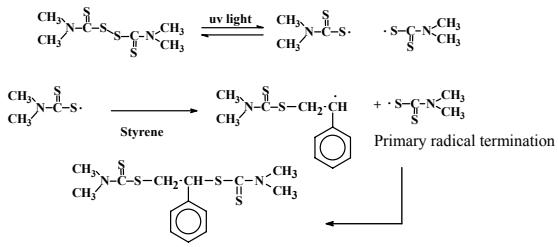
Dithiauram Chain Transfer Process



Resultant polymer is difunctional iniferter, Useful in controlled free radical polymerization

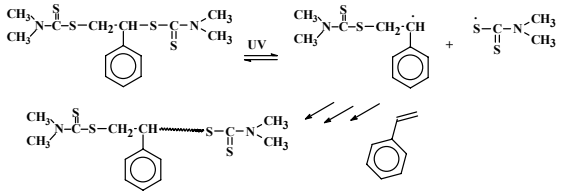
Iniferter Polymerization Technique

Initiator Transfer Terminator = Iniferter

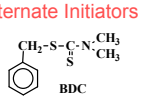


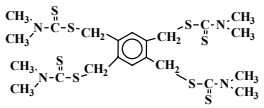
Otsu, et. al. Makromol. Chem., Rapid Commun., 1982. **3**: 127-132; 133-140.

Formation of Carbon Centered Radicals



Alternate Initiators

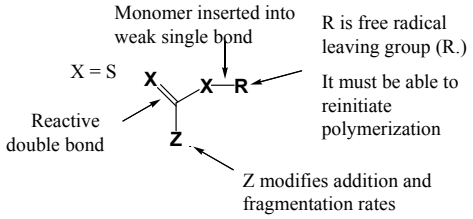




Durene tetrakis (N,N-diethyldithiocarbamate (DDC)

Generic RAFT Agent

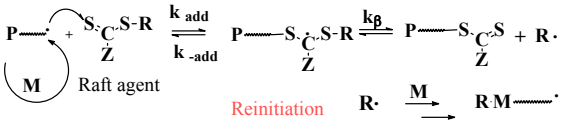
Chain transfer agent that acts by fragmentation



Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT)

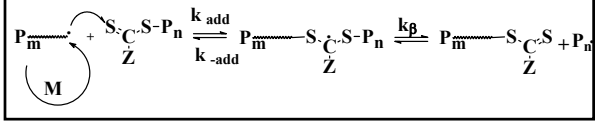
Controlled with designed chain transfer agents (RAFT agents)

Chain transfer



Reinitiation

Chain Equilibration

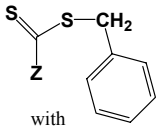


Apparent Chain Transfer Constants

$C_{tr} = k_{tr}/k_p$ where $k_{tr} = k_{add} \frac{k_\beta}{k_{-add} + k_\beta}$

Useful Raft agents have Ctr > 2

Impact of Z substituents on reactivity



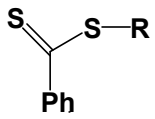
with

Styrene monomer

Raft agent	C_{tr} at 80 C
Z = Ph	26
Z = CH_3	10
Z = OC_6F_6	2.3
Z = OPh	0.72
Z = NEt_2	0.01

Apparent Chain Transfer Constants

- Impact of R substituents on reactivity



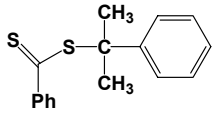
with

Styrene monomer

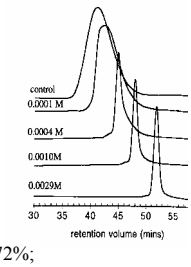
Raft agent	C_{tr} at 80 C
R = $C(CH_3)_2CN$*	13
R = $C(CH_3)_2Ph$*	10
R = $C(CH_3)_2CO_2Et$	2
R=$C(CH_3)_2CH_2C(CH_3)_3$	0.4
R = $CH(CH_3)Ph$	0.16
R = $C(CH_3)_3$	0.03
R = CH_2Ph	0.03

* Dependent upon initial concentration of RAFT agent

Concentration effect of RAFT agent



Thermal initiated polymerization of styrene at 110C for 16 hr



Mn, PDI, conv: control, 324K, 1.74, 72%;

0.0001RA, 189K, 1.59, 59%; 0.0004RA, 107K, 1.21, 60%

0.0010 RA, 48K, 1.07, 55%; 0.0029RA, 14.4K, 1.04, 55%

Factors responsible for retardation

- Slow fragmentation of initiator adduct

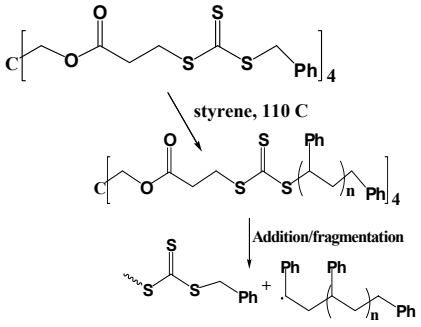
Slow fragmentation of polymer adducts during propagation

Slow reinitiation by expelled radicals

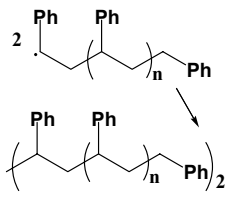
Selectivity for the expelled radical ($R\cdot$) to add to the RAFT agent rather than to monomer

Selectivity for the propagating radical ($Pn\cdot$) to add to the RAFT agent rather than to monomer, (i.e. transfer constant to high)

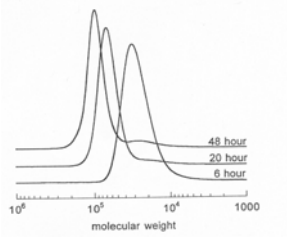
Star Polystyrene Synthesis



Byproduct formation during star synthesis



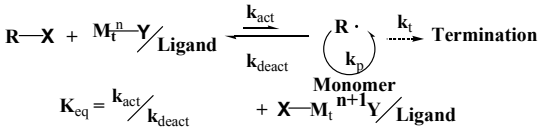
+ Disproportionation



RI and LS detectors

Using UV detector, no shoulder detected

General Mechanism for Atom Transfer Radical Polymerization (ATRP)



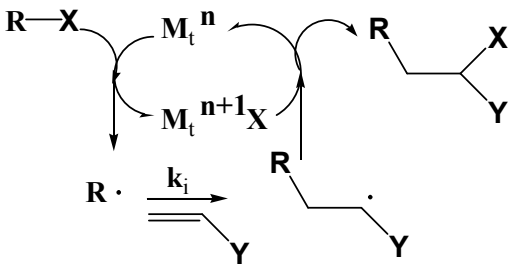
$K_{eq} = k_{act} / k_{deact}$

Keq determines polymerization rate

$Rp = kp[M][P^*] = kpKeq[M][I]_o \times [Cu^I/[X\text{-}Cu^{II}]$

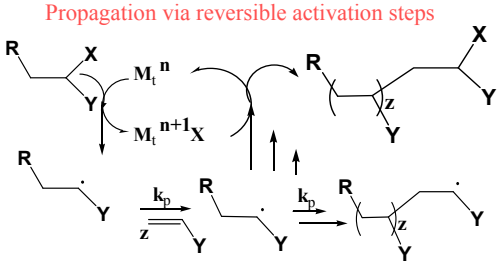
Mechanism of ATRP Process

Initiation via Redox activation of alkyl halide



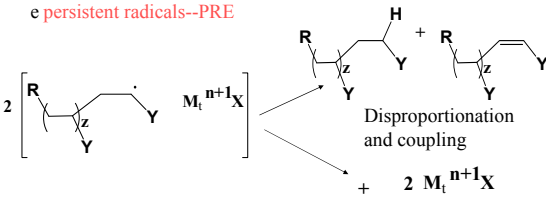
Mechanism of ATRP Process

Propagation via reversible activation steps



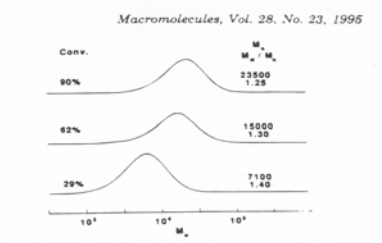
Mechanism of ATRP Process

TTermination reactions lead to enhanced concentration of e persistent radicals--PRE



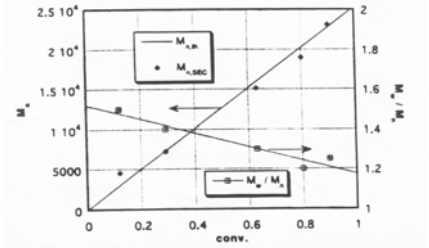
Persistent radicals shift equilibrium and lower concentration of propagating radicals

Polymerization of Methyl Acrylate (MA)



Evolution of Mn and MWD, Mw/Mn with monomer conversion for bulk polymerization of MA at 130 C[1-(PE)Cl]= [CuCl] = 0.038; [bpy] = 0.11

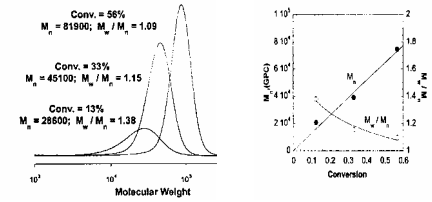
Polymerization of Methyl Acrylate (MA)



Mn and MWD, Mw/Mn on monomer conversion for bulk polymerization of MA at 130 C

[1-(PE)Cl]= [CuCl] = 0.038; [bpy] = 0.11

Optimized MA Polymerization



Evolution of molecular weight and polydispersity in the ATRP of MA,

T = 90 C,[MA] = 11.2 M; [MA]/[MBP]= 1513; [MBP/[CuBr]/[dtbpy] = 1/1/2

MBP = methyl 2-bromoporpionate, dTbpy = 4,4'-di-tert-butyl-2,2'-bypyidine

Components of ATRP

- 1. Monomers—Stabilizing groups (phenyl or carbonyl) adjacent to carbon radicals

2. Initiators-- Alkyl halides or psuedohalides
   Structure should be similar to propagating halide

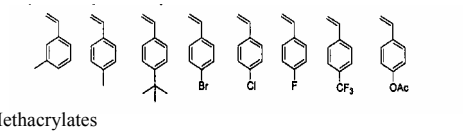
3. Catalysts-- Transition metal with two readily available oxidation states
   Ligands control solubility and dynamics of ATRP equilibrium

4. Solvents—inert to chain transfer, non-poison to catalysts but solvate catalyst initiator complex

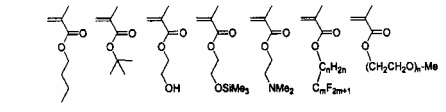
5. Temperature—high temperature better but side reactions and catalyst stability limit choice

ATRP Monomers

- Styrenes

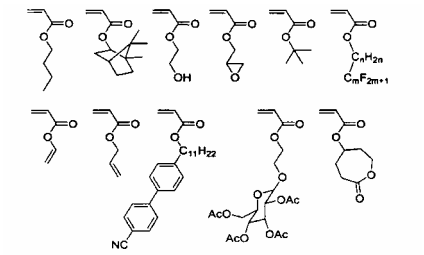


Methacrylates



ATRP Monomers

- Acrylates



ATRP Monomers

- Acrylonitrile—need solvent like ethylene carbonate

(Meth)acrylamides—tend to deactivate catalysts

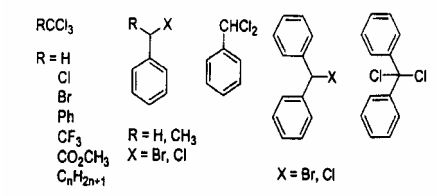
Acrylamide not successful

Methacrylic acids --poison catalysts

Can polymerize protected monomers

Initiators

- Halogenated Alkanes and Benzylic Halides

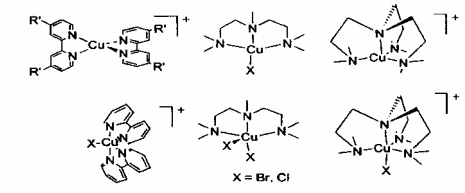


α-Haloesters, a-Haloketones, Alkyl and Aryl Sulfonyl Chlorides

Catalysts

- Transition metal complexes of:
- Rhenium,
- Ruthenium and Iron
- Rhodium,
- Nickel and Palladium
- **Copper**

Ligands for Copper Complexes

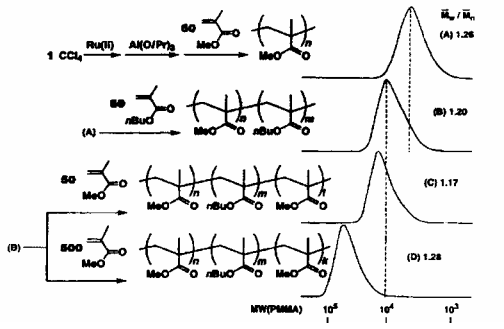


Reactivity

Bipyridines << Me_5DETA < Me_6TREN

Block Copolymers

Best results with monomers in same class (i.e. acrylates)



Block Copolymers

- Sequence of addition critical for monomers from different classes

  Methyl acrylate then methyl methacrylate

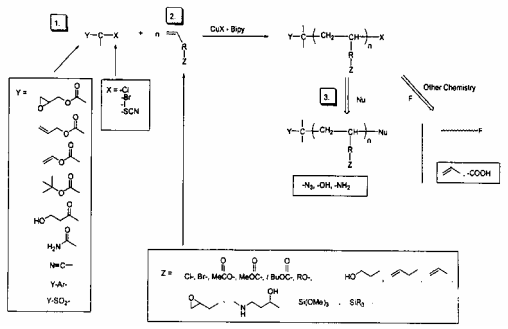
  poor transfer, broad PDI

  Methyl methacrylate then methyl acrylate

  good transfer, narrow PDI

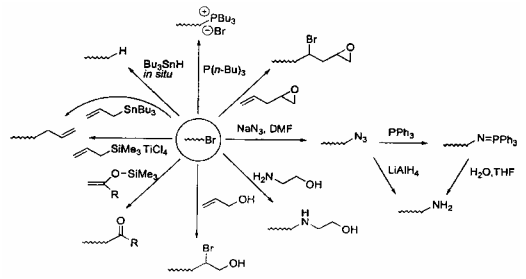
Crosspropagation activity AN > MMA > Sty ~~MA

Functionalized Polymers via ATRP

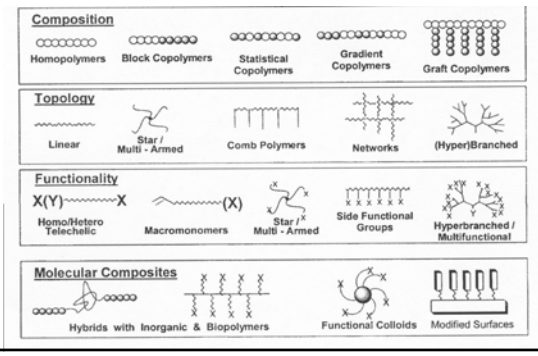


Functionalized Polymers via ATRP

Nucleophilic modification of active halide end group



Molecular Architecture via ATRP



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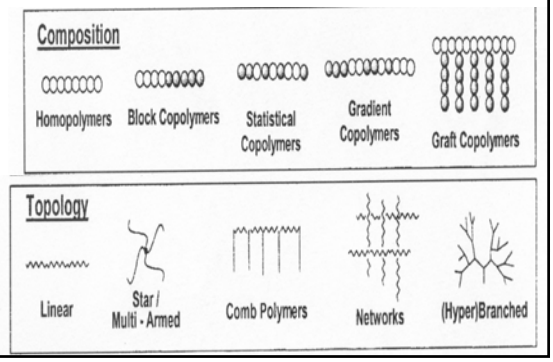

Molecular Architecture via ATRP