Free Radical Polymerization

Free radical is most versatile type of chain growth
  → Most monomers are available
  → Can be done in
    • emulsion
    • suspension
    • bulk
  → Most robust method: less sensitive to
    • solvent
    • impurity
    • atmospheric conditions
  → Limitations
    • broad
    • lack of control over PDI
    • difficult to make well defined block copolymers
  → Methods to improve upon traditional free radical
    • Stable Free Radical Polymerization (SFRP)
    • Atom Transfer Radical Polymerization (ATRP)

"Controlled Free Radical Polymerization"

Stable Free Radical Polymerization

TEMPO → stable nitroxy free radical
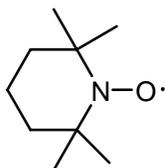
Use with initiator that has a fast half life
Benzoyl peroxide (BPO) half life $\lesssim$ 3 minutes

Requirements for SFRP
  • Stable free radical must NOT initiate polymerization
  • $R_{SFRcomb} > R_p$

    rate of free radical combination
  • Need $R_i >> R_p$
  • $R_t << R_p, R_{SFR}$

This system first described by
  Georges, Veregin, Kazmeier, Homer

Macromolecules, 26, 5316 (1993)

Results

- PDI's as low as 1.1 − 1.5
- Can form diblocks and triblocks with acrylates and co-monomers (styrene) regardless of addition order!!
- Slow reaction times (30-70 hours)
        - rate can be increased with camphor sulfonic acid (~6 hours)
- High MWs achievable
- PDI's narrower for higher ratios of
        TEMPO:BPO $\Rightarrow$ R$_{SFRcomp}$ ↗
- Initiation at high temps lowers PDI
        Ri ↗   (complete ~ 15 min)
- Higher temps $\Rightarrow \dfrac{R_p}{R_t} = \dfrac{k_p[M][M\cdot]}{k_t[M\cdot]^2}$

- Reaction has 2 stages
        1) TEMPO catalyzed decomposition of BPO
        2) Propagation through reversible TEMPO activation/deactivation

Disadvantages

        - variability in PDI, MW
        - different TEMPO/initiator/monomer combinations can yield different results

Kinetics for SFRP

$$P_n\cdot + \cdot T \xleftarrow{\ K_L\ } L_n \qquad \text{(trapping)}$$

Propagating   dissociated   trapped "living" chain
polymer chain   TEMPO   or P+T
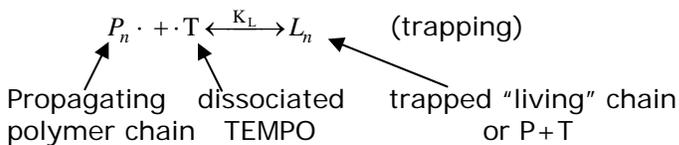
$$K_L = \frac{k_{L,t}}{k_{L,rev}} = \frac{[L_n]}{[P_n\cdot][\cdot T]}$$

$$[P_n\cdot] = \frac{[L_n]}{K_L[\cdot T]} \cong \text{constant}$$

        much lower than in traditional free radical

generally $[\cdot T] \approx 5\%[T_o]$

$$R_{trap} = k_{L,t}[\cdot T][P_n\cdot] \gg R_p$$

termination rate is much lower

        as $R_t \propto [P_n\cdot]^2$ and $R_p \propto [P_n\cdot]$

Probability of untrapped living chains meeting is very low (termination by combination is negligible).

Atom Transfer Radical Polymerization (ATRP)

Kinetics same as previously described.

Requirements for Trapping Process to Work

1. $K_L = \dfrac{k_{L.f}}{k_{L,r}} >> 1.0$ ⇒ forward rate is much faster

2. Rate of free radical trapping >> propagation rate

3. $R_p >> R_t$ (if [M·] is low, usually true)

ATRP Mechanism

Initiation

1. $R - X + LiM_t^{z+} \Leftrightarrow R \cdot + LiM_t^{(z+1)+} X$

    alkyl   metal

    halide   ligand   oxidized complex

           complex

     X = Cl, Br   M = Cu, Ni, Pd, Ru, Fe

               most common

2. $R \cdot + $ ⟍⟍R' $\xrightarrow{k_p} P_1 \cdot$

Propagation

$$P_N - X + LiM_t^{z+} \xleftrightarrow{k_{eq}} P_N \cdot + LiM_t^{(z+1)+} X$$

$$P_N \cdot + \text{⟍⟍R'} \xrightarrow{k_p} P_{N+1} \cdot$$
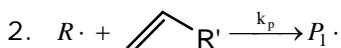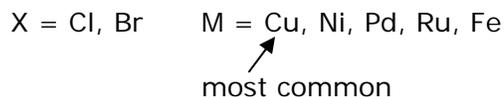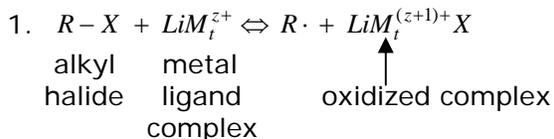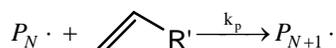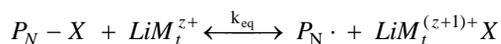
Can use a broad range of catalytic systems.

Synthesis of Custom Polymers using Controlled Radical Polymerization

⇒ Grow a linear polymer from a dendrimer.

⇒ Create a graft copolymer.
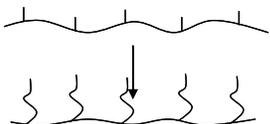
⇒ Transfer from ionic polymerization to controlled radical to create block copolymers otherwise inaccessible.

J. Am. Chem. Soc., Vol 118, No 45, 1996
    Pg 11112

Dendrimer Block Copolymer
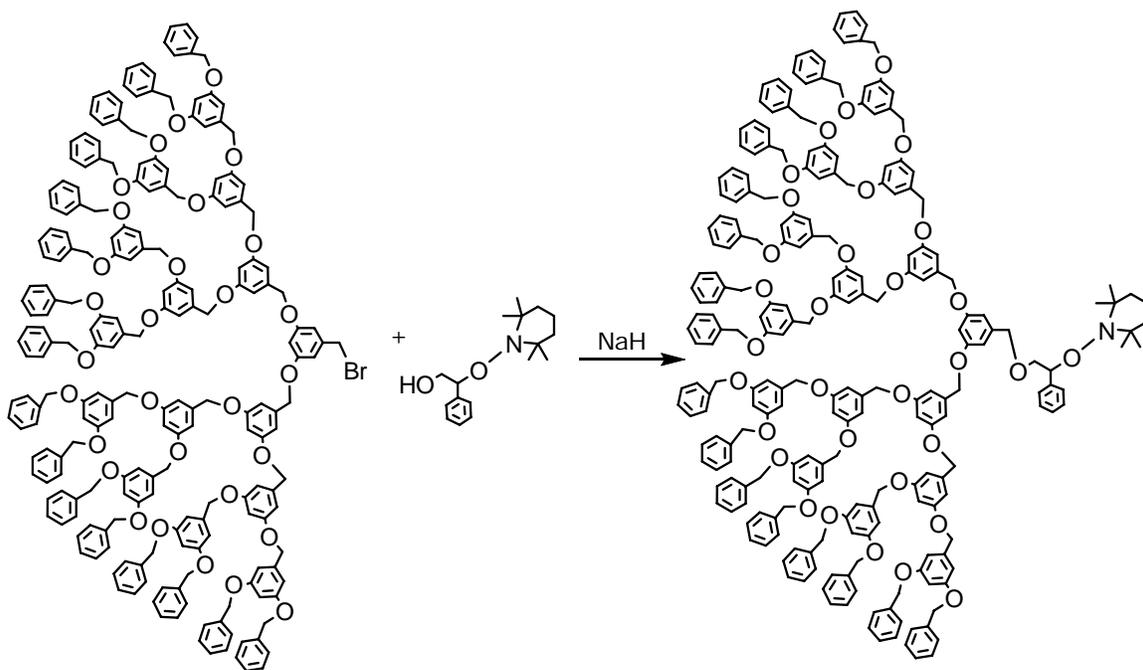
Use of Aluminum Alkyls
⇒ low PDI's, promising approach
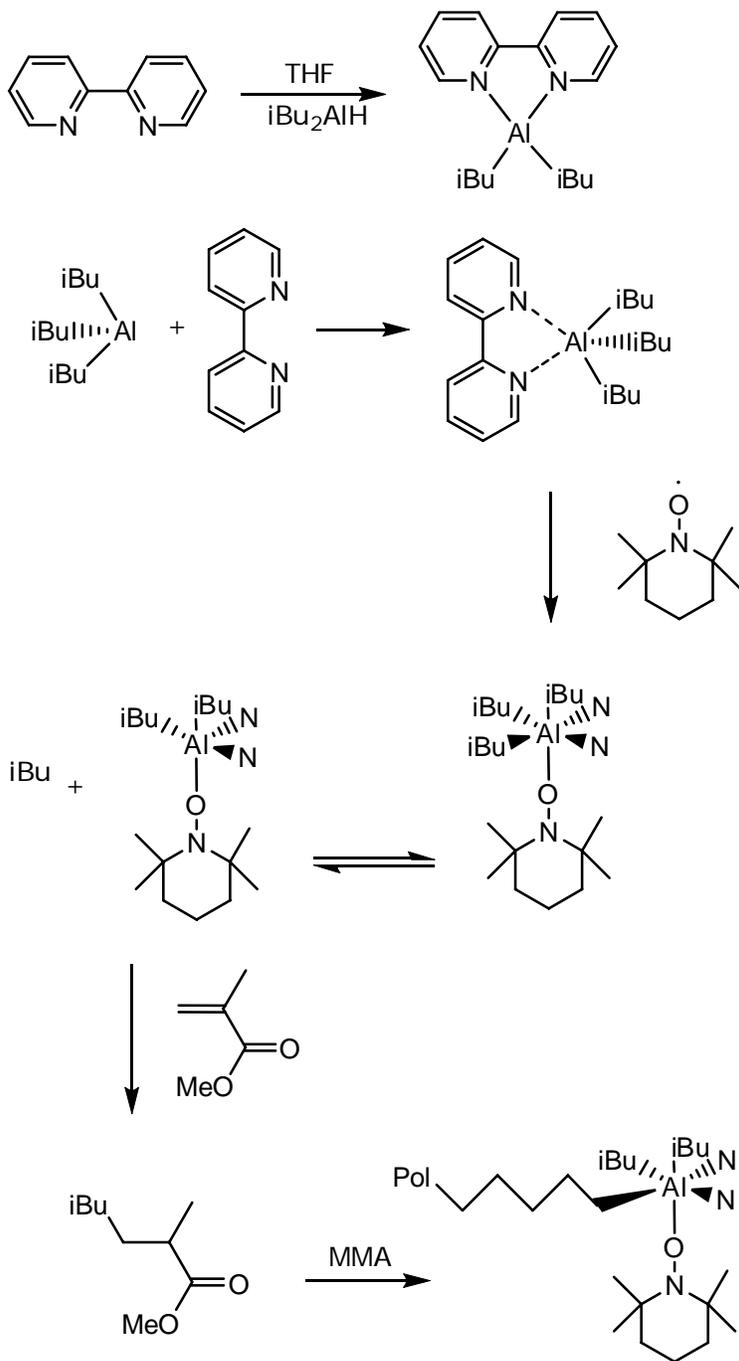
Table 1. Initiating and Terminating Species for Living Radical Polymerizations

	I·		X·	
1	$(C_2H_5)_2NCS \cdot$ with $\Vert S$	1	$\cdot SCN(C_2H_5)_2$ with $\Vert S$	← iniferter
2	$(CH_3)_2C \cdot$ | CN	7	nitroxide structure (isoindoline)	
3	$(C_6H_5)CO \cdot$ || O			
4	$C_6H_5 \cdot$	8	$\cdot ON = N - C_6H_5$	
5	$CH_3 \cdot$	9	Al complexes	
6	succinimidyl radical	10	nitroxide structure (TEMPO)	
		11	nitroxide structure (pyrrolidine, CO_2H)	

Nitroxide Stable Free Radicals (brace spanning structures 7–11)

Scheme 2. Living Polymerization of Acrylates and Methacrylates

R=H or alkyl

10.569, Synthesis of Polymers, Fall 2006
Prof. Paula Hammond

Lecture 32
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Here is an example involving an anionic polymerization that is then end capped with an initiator for ATRP,
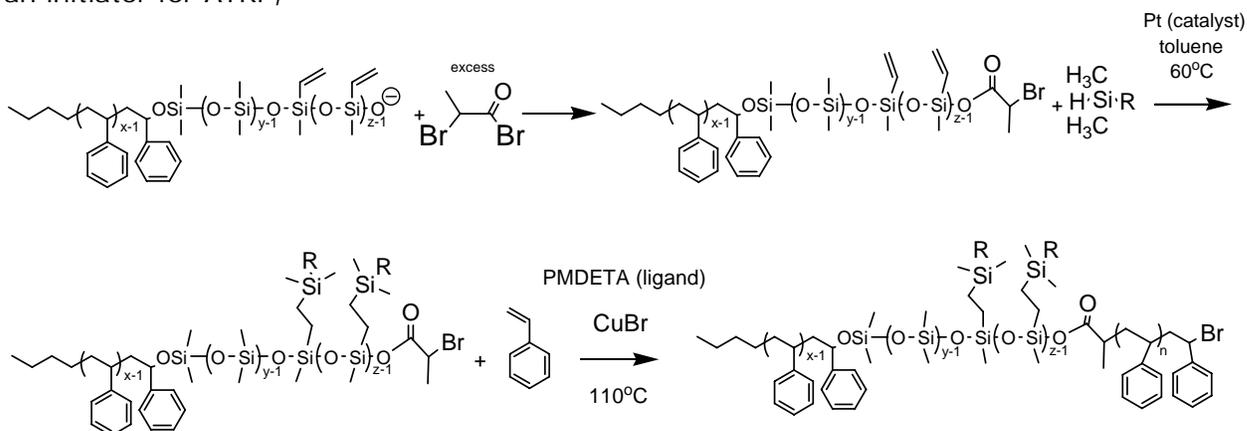
the additional step of hydrosilation of the vinyl groups on the siloxane is not needed for a simple PDMS and would look like:
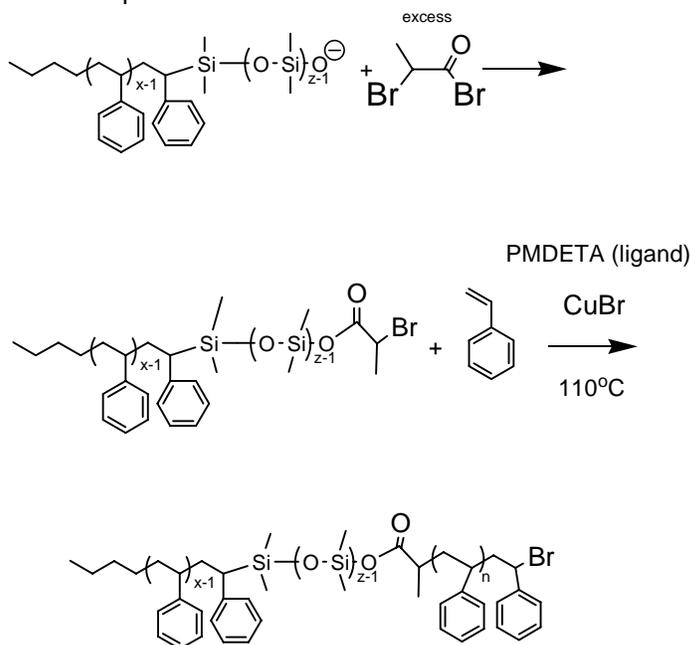
The details for the catalyst and ligand are in the review articles listed below.

Patten, Timothy E., and Krzysztof Matyjaszewski. "Atom Transfer Radical Polymerization and Synthesis of Polymeric Materials." *Advanced Materials* 10, no. 12 (1998): 901-915.

Pyun, Jeffrey, Shijun Jia, Tomasz Kowalewski, and Krzysztof Matyjaszewski. "Synthesis and Surface Attachment of ABC Triblock Copolymers Containing Glassy and Rubbery Segments." *Macromol. Chem. Phys.* 205 (2004): 411-417.