

Controlled Radical Polymerization

Concepts

CRP = A radical polymerization that can be stopped and re-initiated under external control

Controlled Radical Polymerization

Concepts

Living Polymerization = A chain growth polymerization which proceeds without termination or chain transfer steps. The molecular weight is a linear function of conversion (if initiation is competitive with propagation)

Criteria for Living Polymerizations

1. Polymerization proceeds until all monomer has been consumed. Further addition of monomer results in continued polymerization.
2. Molecular weight (Mn) is a linear function of conversion. Requires that all chains are initiated and grow uniformly.

Controlled Radical Polymerization

Concepts

Conventional Radical Polymerization

$$I \xrightarrow{k_d} 2 R^\bullet$$

$$R^\bullet + M \xrightarrow{k_i} P_1^\bullet$$

$$P_n^\bullet + M \xrightarrow{k_p} P_{n+1}^\bullet$$

$$P_n^\bullet + P_m^\bullet \xrightarrow{k_t} P_nH + P_m^\bullet$$

I: RO-OR, RN=NR
 $T \sim 80 \pm 20^\circ C$
 $k_{dec} \sim 10^{10} s^{-1}$
 $k_p \sim 10^{3 \pm 1} M^{-1} s^{-1}$
 $k_t \sim 10^{7 \pm 1} M^{-1} s^{-1}$

Controlled/Living Radical Polymerization

$$R-X \xrightleftharpoons[k_d]{k_a} R^\bullet + X^\bullet$$

$$R^\bullet + M \xrightarrow{k_i} P_1^\bullet$$

$$P_n^\bullet + M \xrightarrow{k_p} P_{n+1}^\bullet$$

$$P_n^\bullet + P_m^\bullet \xrightarrow{k_t} P_nH + P_m^\bullet$$

$$P_n-X \xrightleftharpoons[k_d]{k_a} P_n^\bullet + X^\bullet$$

R-X: P1-ONR2, P1-CoIII Lx,
 $P_1-X + Cu^I L_x$
 $T \sim 120 \pm 20^\circ C$
 $k_a \sim 10^{10 \pm 2} s^{-1}$
 $k_d \sim 10^{6 \pm 1} s^{-1}$
 $k_p \sim 10^{4 \pm 1} M^{-1} s^{-1}$
 $k_t \sim 10^{7 \pm 1} M^{-1} s^{-1}$
 $K \sim 10^{-8 \pm 1}$

Controlled Radical Polymerization

Concepts

How CRP is Different from Living Polymerization

Ionic Living Polymerization: Rate of initiation faster or comparable to rate of propagation, i.e. $R_i \geq R_p$. That way, all chains start at the same time and propagate at the same time, and give the same DP

R (kp/ki)	Xw/Xn for Xn = 100
0.1	1.008
0.5	1.01
10	1.019
100	1.242 (Xn = 60) not all initiator used

CRP: Rate of initiation faster or comparable to rate of propagation, i.e. $R_i \leq R_p$. This keeps a low level of radicals (almost at "0") to prevent side reactions, terminations, etc. If $R_i \geq R_p$, then all the radicals would be present, and there would be no control over polymerization. Instead, you would get $DP \geq 1.5$ just like ordinary radical polymerization.

Controlled Radical Polymerization

Concepts

Effect (and Advantages) of Being able to Control Polymerization

1. Molecular weight is a function of conversion.
2. Constant number of polymer molecules that is independent of conversion.
3. Narrow molecular weight distribution (as long as all chains grow uniformly, which is not the case at higher molecular weight).
4. Can make end functionalized (telechelic) polymers
5. Can control polymer architecture

Controlled Radical Polymerization

Concepts

Types of Living Polymerization

1. Anionic
2. Cationic
3. Radical

Advantages of Using Radicals

1. Tolerance to other functional groups
2. Do not need pure reagents, not water sensitive
3. Relatively easy and simple
4. Can control copolymerization: new life from commodity polymers

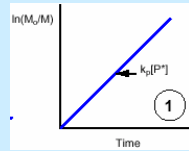
Controlled Radical Polymerization

Concepts

Things to keep in mind about CRP

0. R_i and $R_w \ll R_p$; & $R_t \leq R_p$

1. $[P_n^*] = \text{constant}$
 a. Only sensitive to termination

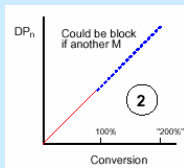


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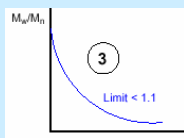
Concepts

Things to keep in mind about CRP

2. $DP_n = \Delta[M_0]/[I_0]$
 a. Constant # of chains
 b. Only sensitive to transfer



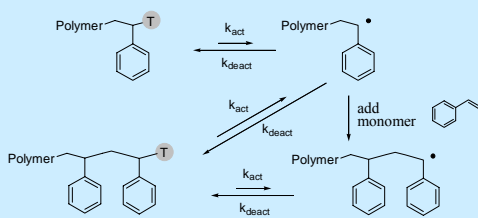
3. $M_w/M_n = 1 + (1/DP)$

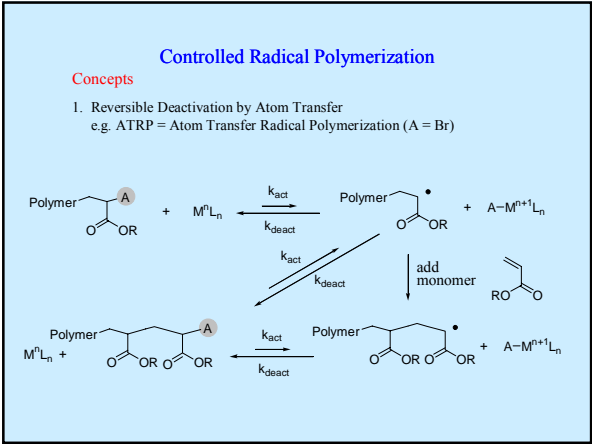


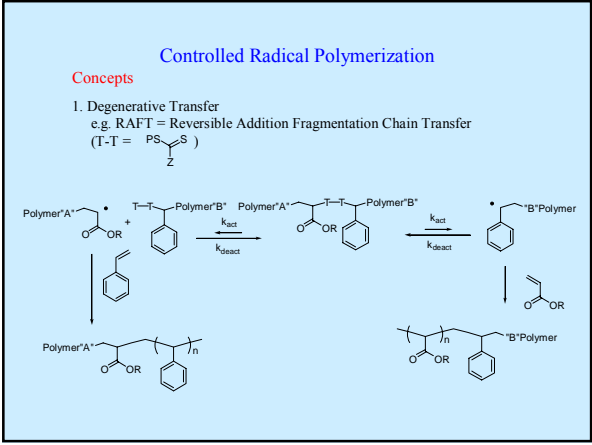
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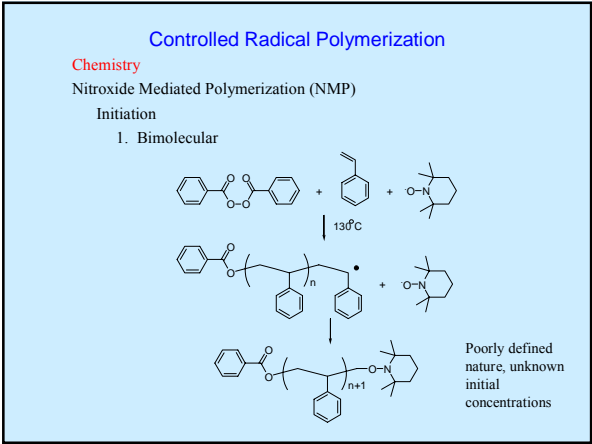
Concepts

1. Reversible Deactivation by Coupling
 e.g. NMP = Nitroxide mediated polymerization ($T = \text{R}^1 \text{N}^{\text{R}2}$)









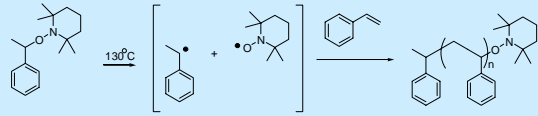
Controlled Radical Polymerization

Mechanism

Nitroxide Mediated Polymerization (NMP)

Initiation

2. Unimolecular – Better control over initiation

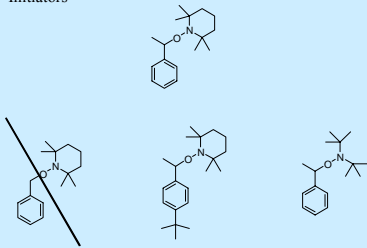


Controlled Radical Polymerization

Mechanism

Nitroxide Mediated Polymerization (NMP)

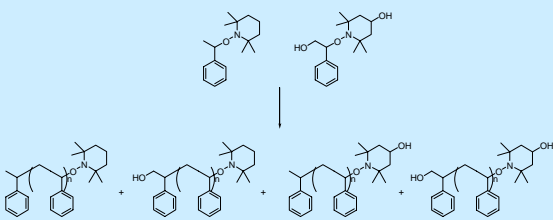
Initiators

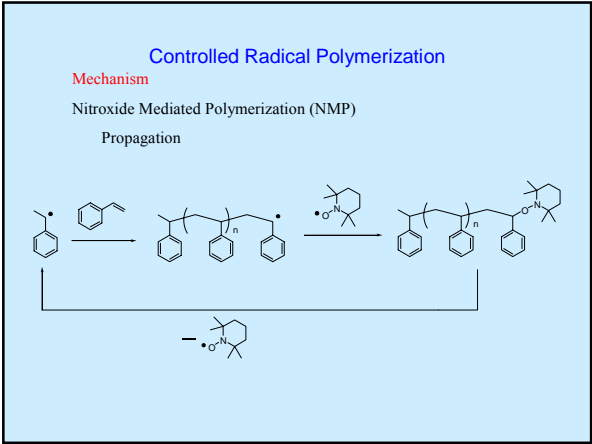


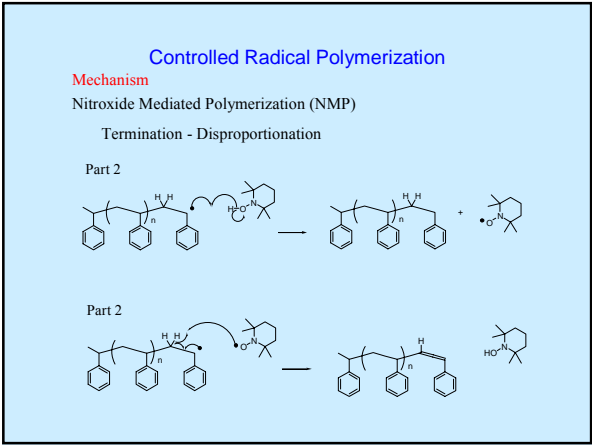
Controlled Radical Polymerization

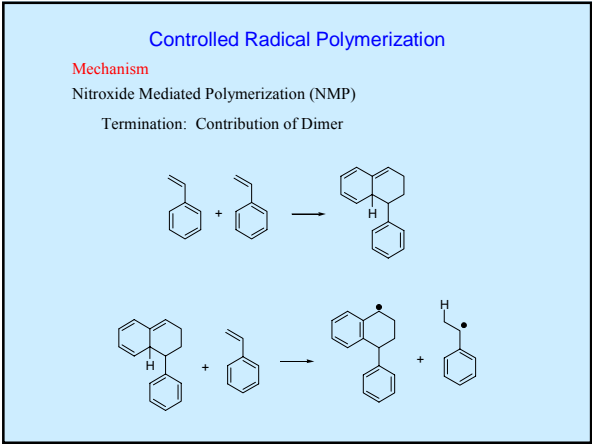
Mechanism

Crossover Experiment









Controlled Radical Polymerization

Kinetics

$$R-X \xrightleftharpoons[k_d]{k_a} R^\bullet + X^\bullet$$

Rate = $k_p/k_d [RX] = [R^\bullet]$

$$R^\bullet + M \xrightarrow{k_i} P_1^\bullet$$

Rate = $k_i [R^\bullet][M]$

Overall Initiation Rate = $R_i = (k_p/k_d)k_i[RX][M]$

$$P_1^\bullet + M \xrightarrow{k_p} P_{n+1}^\bullet$$

Rate = $k_p [P_1^\bullet][M]$

$$P_n^\bullet + P_m^\bullet \xrightarrow{k_t} P_n^H + P_m^H$$

$$R-X \xrightleftharpoons[k_d]{k_a} P_n^\bullet + X^\bullet$$

Controlled Radical Polymerization

Kinetics

For system with: [P-N] and M with no extra [N*] added

$$\frac{d[P^*]}{dt} = R_i - k_t[P^*]^2 + k_d[P-N] - k_c[P^*][N^*]$$

$$\frac{d[N^*]}{dt} = k_d[P-N] - k_c[P^*][N^*]$$

At steady state, $d[P^*]/dt = d[N^*]/dt = 0$

$$R_p = k_p [P^*] [M]$$

$$= (k_p^2 R_i / k_t)^{1/2} [M]$$

Therefore polymerization rate is independent of SFR conc.

Controlled Radical Polymerization

Concepts

Persistent Radical Effect

Controlled Radical Polymerization

Concepts

NMP 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

Process Advantages

Narrow molecular weight distribution up to moderate conversions
No Trommsdorff (Gel) effect

Process Disadvantages

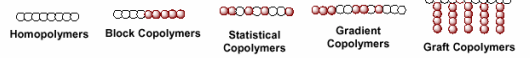
Loss of molecular weight control at high conversions
Very slow rates of polymerization

Controlled Radical Polymerization

Architecture

What can you do with CRP?

Compositions



Architecture



Controlled Radical Polymerization

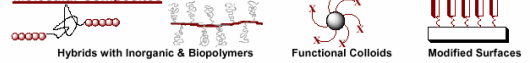
Architecture

What can you do with CRP?

Functionality



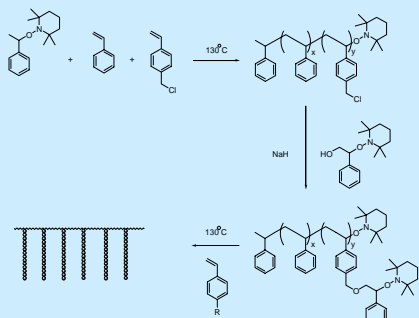
Molecular Composites



Controlled Radical Polymerization

Architecture

Graft Copolymerization



Controlled Radical Polymerization

Selected Reading

1. Controlled/living radical polymerization : progress in ATRP, NMP, and RAFT Matyjaszewski, K. Washington, DC : American Chemical Society : Distributed by Oxford University Press, c2000. (On reserve in the Chemistry Library)
2. Hawker, C.J., et. al.; "New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations." *Chem. Rev.* **2001**, *101*, 3661-3688.
3. Hawker, C.J.; " "Living" Free Radical Polymerization: A Unique Technique for the Preparation of Controlled Macromolecular Architectures." *Acc. Chem. Res.* **1997**, *30*, 373-382
4. Greszia, D., Matyjaszewski, K.; "Mechanism of Controlled / "Living" Radical Polymerization of Styrene in the Presence of Nitroxyl Radicals. Kinetics and Simulations." *Macromolecules* **1996**, 297661-7670.

Controlled Radical Polymerization

Selected Reading

5. Matyjaszewski, KI, Xia, J.; "Atom Transfer Radical Polymerization." *Chem. Rev.* **2001**, *101*, 2921-2990.
6. Kamigaito, M., et. al.; "Metal-Catalyzed Living Radical Polymerization." *Chem. Rev.* **2001**, *101*, 3689-3745.
