

Polymerization
“Living”/Controlled Polymerization
Polymerization for Nanotechnology

중합반응에 관한 소개
(나노기술과 관련 있는 중합 방법)

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Polymers with Controlled Architectures

Many Natural Polymeric Materials ← Perfect Monodisperse Macromolecules
Successive condensation of monomers with polymer end-groups activated by enzymes

Synthetic Polymeric Materials
with Controlled Architecture

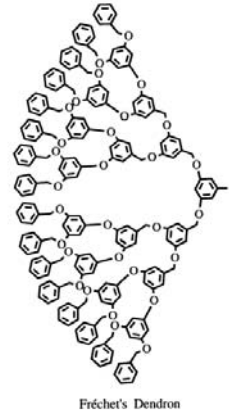
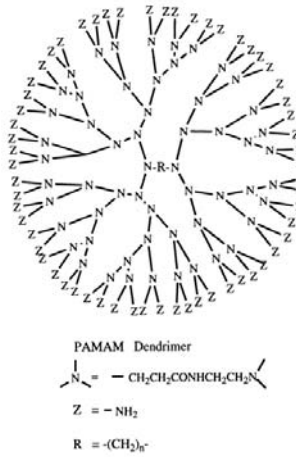
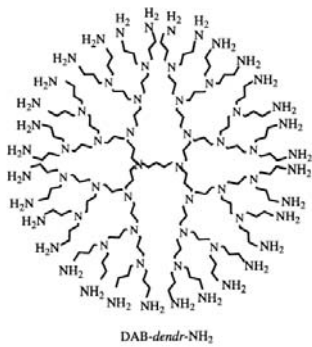
“Living”/Controlled Polymerization
Radical, Cationic, Anionic, ROMP, Coordination
(via Chain-Growth Polycondensation)

Dendritic Macromolecules & Linear Oligomers
(Stepwise synthesis via Step-Growth Condensation)

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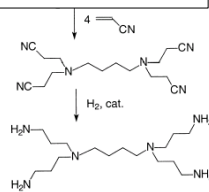
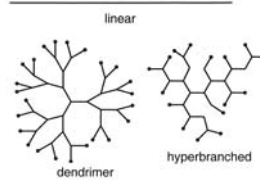
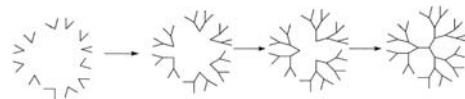
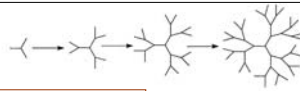
Dendrimers

Commercially Available Dendrimers

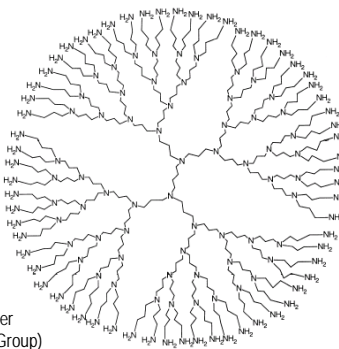


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Synthesis of Dendrimers

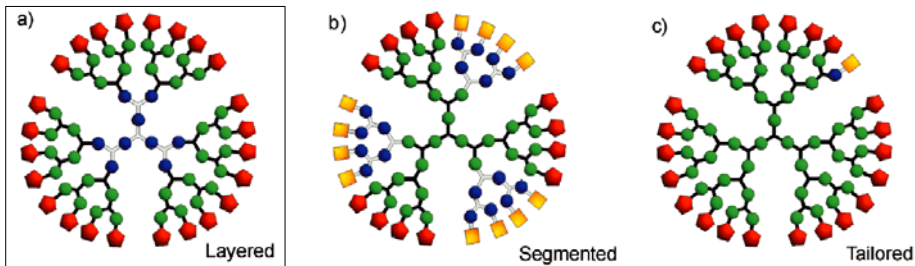


DSM's Poly(propylene imine) Dendrimer
(Fifth Generation - 64 primary amine Group)



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Well-Defined Dendrimers



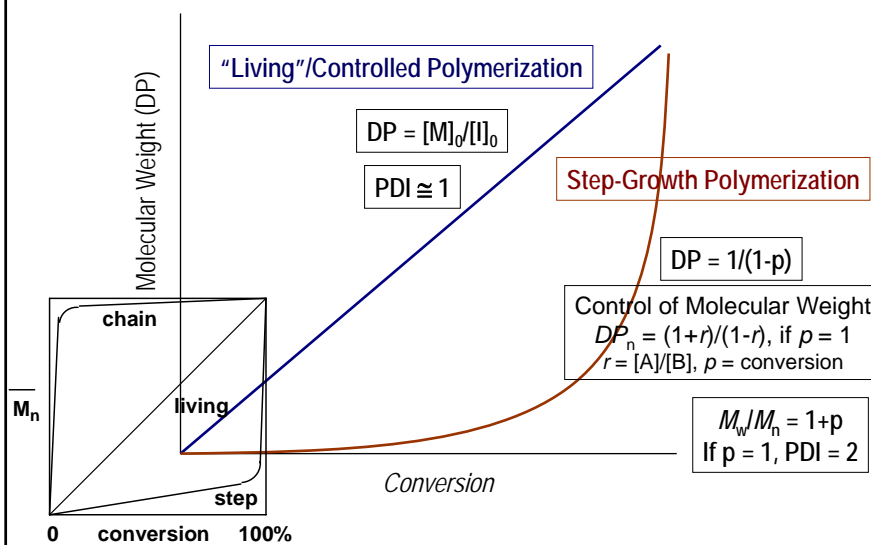
Frechet J. M. J. et al. *Chem. Rev.* 2001, 101, 3855.

Well-Defined (Monodisperse & Controlled)

Branched vs. Linear & Folded

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"Living"/Controlled Polymerization vs. Step-Growth Polymerization

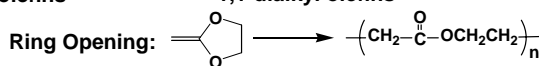
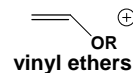
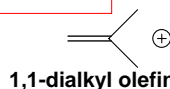
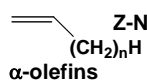


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Types of Chain Polymerizations of Various Unsaturated Monomers

Monomers	Types of Initiation		
	Radical	Cationic	Anionic
Ethylene	+	-	+
1-Alkyl olefins (α -olefins)	-	-	-
1,1-Dialkyl olefins	-	+	-
1,3-Dienes	+	+	+
Styrene, α -methyl styrene	+	+	+
Halogenated olefins	+	-	-
Vinyl esters ($\text{CH}_2=\text{CHOCOR}$)	+	-	-
Acrylates, methacrylates	+	-	+
Acrylonitrile, methacrylonitrile	+	-	+
Acrylamide, methacrylamide	+	-	+
Vinyl ethers	-	+	-
N-Vinyl carbazole	+	+	-
N-Vinyl pyrrolidone	+	+	-
Aldehydes, ketones	-	+	+

Exceptions:

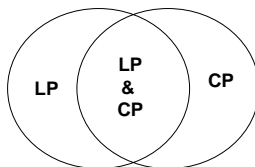


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Living Polymerization (LP) vs. Controlled Polymerization (CP)

Living Polymerization and Polydispersity \rightarrow Weak Correlation

- Chain-breaking reactions: increase of DP_w/DP_n with increasing DP_n and conversion
- Slow initiation and slow exchange: decrease DP_w/DP_n and DP_n with increasing conversion
- Polydispersity alone is a poor criterion for judging the living character of a polymerization
 - Living polymerizations can have $\text{DP}_w/\text{DP}_n > 2$ (slow exchange)
 - Polymers with $\text{DP}_w/\text{DP}_n < 1.1$ can have 50% terminated chain ends



Living Polymerization:
Chain growth
No chain breaking (no transfer/termination)
- *slow initiation* possible
- *slow exchange* possible
- *uncontrolled molecular weights* possible
- high polydispersities possible

Controlled Polymerization:
Chain or Step growth
Limited chain breaking possible
- *fast initiation*
- *fast exchange*
- *controlled molecular weights*
- *low polydispersities*

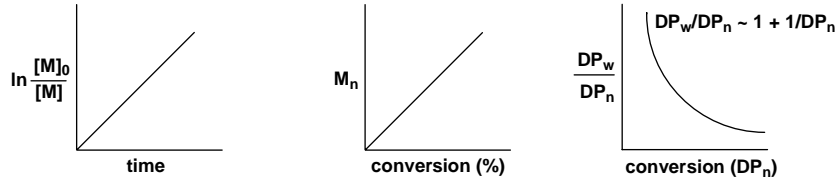
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Experimental Evaluation of "Living"/Controlled System

Necessarily, $R_{tr} = R_t = 0$ (a truly living system)

Ideally, $R_i \geq R_p$, $R_{exch} \geq R_p$, propagation is irreversible

When these conditions hold, the following can be used to experimentally evaluate the livingness of a polymerization:



Real Systems

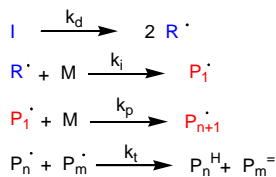
Kinetic characteristic	Overall Effect ^a		
	on R_p	on $M_w/M_{n,th}$	on DP_w
slow initiation (rel. to propagation)	↓	↑	↑↑
slow exchange (rel. to propagation)	∅ / ↓	∅ / ↑	↑↑
transfer (to anything other than polymer)	∅	↓	↑
termination	↓	∅	↑

^a ↑ = increase; ↓ = decrease; ∅ = unaffected

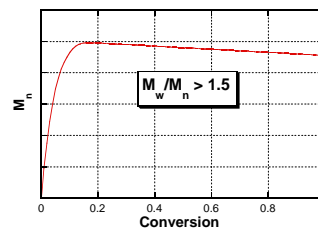
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Conventional vs. Controlled (Radical Polymerization)

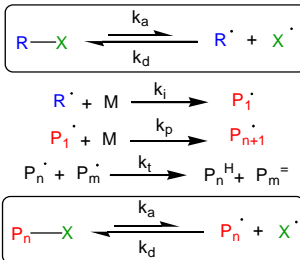
Conventional Radical Polymerization



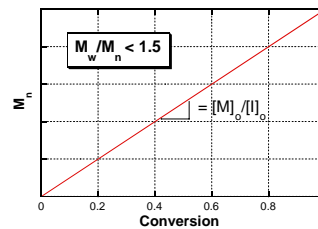
$$\begin{aligned}
 T &\sim 80 \pm 20 \text{ }^\circ\text{C} \\
 k_d &\sim 10^{-5} \text{ s}^{-1} \\
 k_p &\sim 10^{3 \pm 1} \text{ M}^{-1}\text{s}^{-1} \\
 k_t &\sim 10^{7 \pm 1} \text{ M}^{-1}\text{s}^{-1}
 \end{aligned}$$



"Living"/Controlled Radical Polymerization



$$\begin{aligned}
 T &\sim 120 \pm 20 \text{ }^\circ\text{C} \\
 k_a &\sim 10^{0 \pm 2} \text{ s}^{-1} \\
 k_d &\sim 10^8 \pm 1 \text{ s}^{-1} \\
 k_p &\sim 10^4 \pm 1 \text{ M}^{-1}\text{s}^{-1} \\
 k_t &\sim 10^7 \pm 1 \text{ M}^{-1}\text{s}^{-1}
 \end{aligned}$$



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Controlling Radical Polymerizations

a. The problem with conventional radical polymerizations:

1. diffusion-controlled termination ($k_t = 10^7 \text{ M}^{-1} \text{ s}^{-1}$)

termination is bimolecular: $R_t = k_t [M \bullet]^2$

b. The solution: keep $[M \bullet]$ low through slow initiation:

2. slow initiation

$$R_i = 2 f k_d [I] \quad (k_d = 10^5 \text{ M}^{-1} \text{ s}^{-1}; [I]_0 = 10^{-2} \text{ M})$$

Therefore, high polymer is still possible in spite of the high termination rate constant because of slow initiation and termination rate (WARNING! rate \neq rate constant!).

c. Designing a Controlled Radical Polymerization - HOW?

1. By definition, $R_i \geq R_p$ and $[I]_0 =$ concentration of propagating chains.

2. Additionally, for any controlled polymerization:

$$DP_n = \frac{\Delta [M]}{[I]_0} = \frac{[M]_0}{[I]_0} \quad (\text{at full conversion})$$

consider full conversion for $DP_n = 1000$; $[M]_0 = 10 \text{ M}$; $[I]_0 = 10^{-2} \text{ M}$.

3. However, from the definition of DP_n :

$$DP_n = \frac{R_p}{R_t} = \frac{k_p [M] [M \bullet]}{k_t [M \bullet]^2} = \frac{k_p [M]}{k_t [M \bullet]}$$

and:

$$[M \bullet] = \frac{k_p [M]}{k_t DP_n}$$

(instantaneous concentration of radicals)

for $DP_n = 1000$; $[M]_0 = 10 \text{ M}$; $k_p = 10^2 \text{ M}^{-1} \text{ s}^{-1}$; $k_t = 10^7 \text{ M}^{-1} \text{ s}^{-1}$; $[M \bullet] = 10^{-7} \text{ M}$

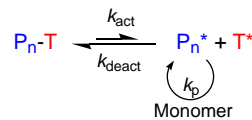
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Control of Radical Polymerization

- Extending life of propagating chains (from $<1\text{s}$ to $>1\text{h}$) (*similar rates?*)
- Enabling quantitative initiation (From $R_i \ll R_p$ to $R_i \gg R_p$)
- Controlling DP_n ($D[M]/[I]_0$), *MWD, Functionality, Composition, Topology*
- BY EQUILIBRIA BETWEEN RADICALS AND DORMANT SPECIES

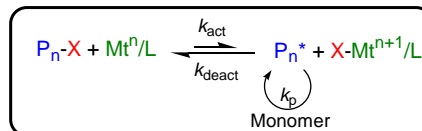
➤ Reversible deactivation by coupling

- Nitroxide-mediated polymerization



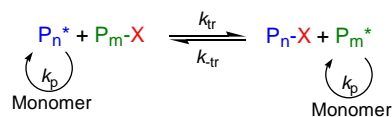
➤ Reversible deactivation by atom transfer

- ATRP



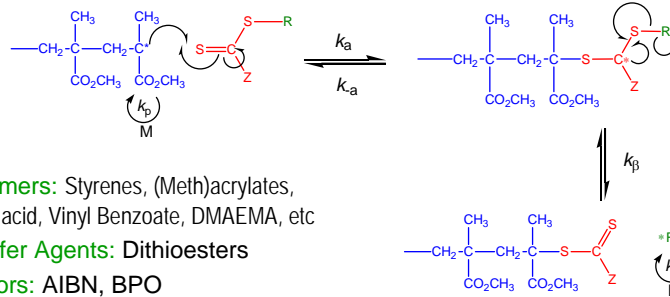
➤ Degenerative transfer

- Alkyl iodides
- Unsaturated polymethacrylates (CCT)
- Dithioesters (RAFT)

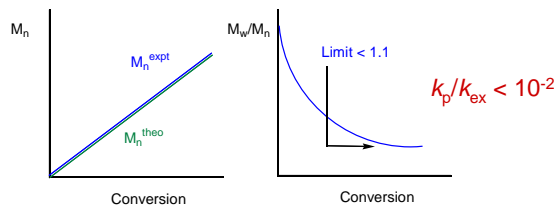


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RAFT: Reversible Addition Fragmentation Chain Transfer

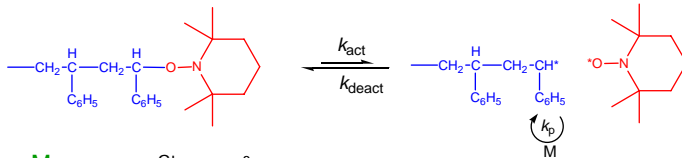


- **Monomers:** Styrenes, (Meth)acrylates, Acrylic acid, Vinyl Benzoate, DMAEMA, etc
- **Transfer Agents:** Dithioesters
- **Initiators:** AIBN, BPO
- **[M]:** bulk, solution
- **[TA]₀:** 10⁻¹ to 10⁻² M
- **[In]₀/[TA]₀:** 0.1 to 0.6
- **Temp:** 60-150 °C
- **Time:** 2-20 hours
- **Blocks:** possible but limits



Moad, G.; Rizzardo, E. et al. *Macromolecules* **1998**, *31*, 5559; **1999**, *32*, 2071
 Le, T.P.; Moad, G.; Rizzardo, E.; Thang, S.H. *PCT Int. Appl. WO 9801478 A1* 980115.
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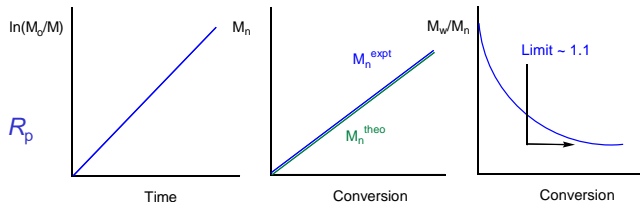
Nitroxide/TEMPO Polymerization



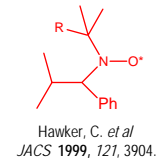
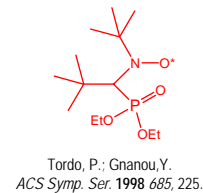
- **Monomers:** Styrenes & comonomers
- **Initiators:** Alkoxyamines or BPO/Nitroxides
- **[M]:** bulk
- **[In]₀:** 10⁻¹ to 10⁻² M
- **Temp:** 120-140 °C
- **Time:** >10 hours

- Self initiation dominates R_p
- $k_{act}/k_{deact} \sim 10^{-11}$ M
- Side reactions (H-abstraction by TEMPO)

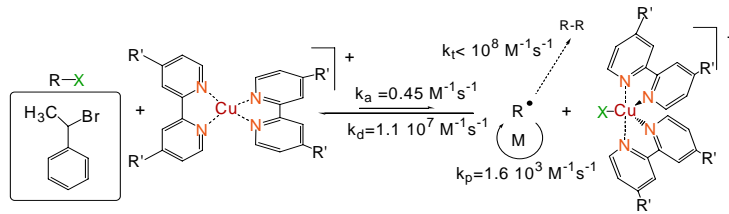
-> Acrylates & Lower Temp Additives & New Nitroxides (Acids, Dicumyl peroxides)



Solomon, D.H., et al. *U.S. Patent*, **1986**, 4,581,429.
 Georges, M.K., et al. *Macromolecules* **1993**, *26*, 2987.
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How ATRP Works: Styrene, CuBr/dNbpy, 110 °C



Frequency of molecular events at chain end; $\tau = 1/(k[C])$

- activation: $\tau = 22$ s
- propagation: $\tau = 0.12$ ms
- deactivation: $\tau = 0.018$ ms (*6 times faster than propagation !!!*)
- termination: $\tau = 0.1$ s (*i.e. 800 times slower than propagation !*)

Concentrations:

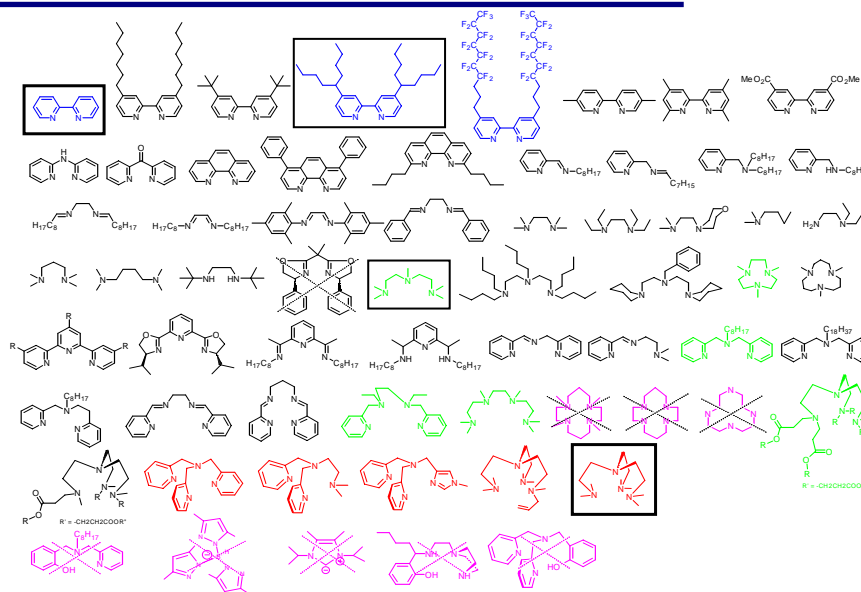
[M] = 5 M
 [R-Br] = 10^{-1} M
 [Cu^IBr/2dNbpy] = 10^{-1} M
 [Cu^{II}Br₂/2dNbpy] = 5×10^{-3} M
 [P*] $\gg 1 \times 10^{-7}$ M

→ Chain wakes up every 20 s, adds monomer only every 120 s (2 min; i.e. 3 h needed for DP=100) & dies after 100,000s (30 h)

cf> In the case of MA, CuBr/PMDETA, 90 °C, chain wakes up every 330 s (5 min), adds 14 monomer units, goes back to sleep for 5 min & dies after 100 days.

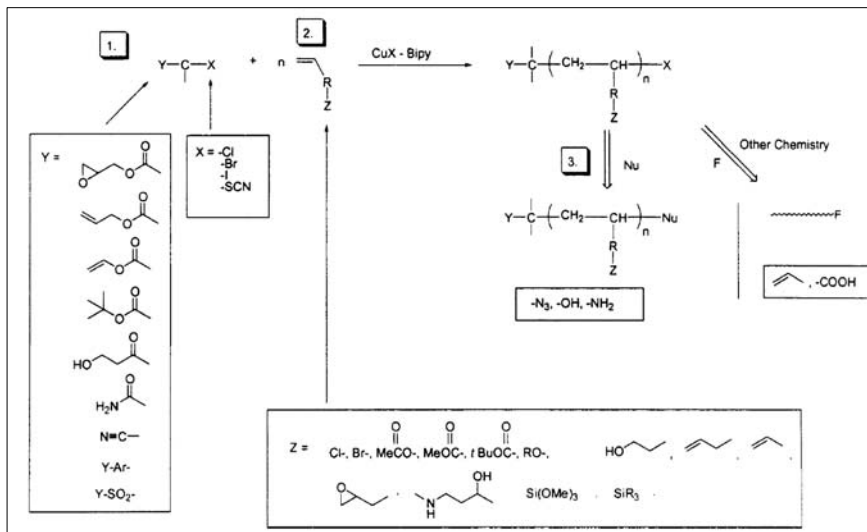
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Ligands Used in Copper-Mediated ATRP



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Nano-Structured Materials *via* ATRP



Matyjaszewski K. et al. *Chem. Rev.* 2001, 101, 2921. *Chem. Mater.* 2001, 13, 3436. *Adv. Mater.* 1998, 10, 901. *Prog. Polym. Sci.* 2001, 26, 337.

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Comparison of Various CRP Systems

➤ ATRP

- + Especially well suited for LMW functional oligomers (\$, rates)
- + May be useful for difficult block copolymers
- + Very good for hybrids and transformations
- + Easy to incorporate end/side functionalities
- Catalyst should be removed/recycled

➤ RAFT

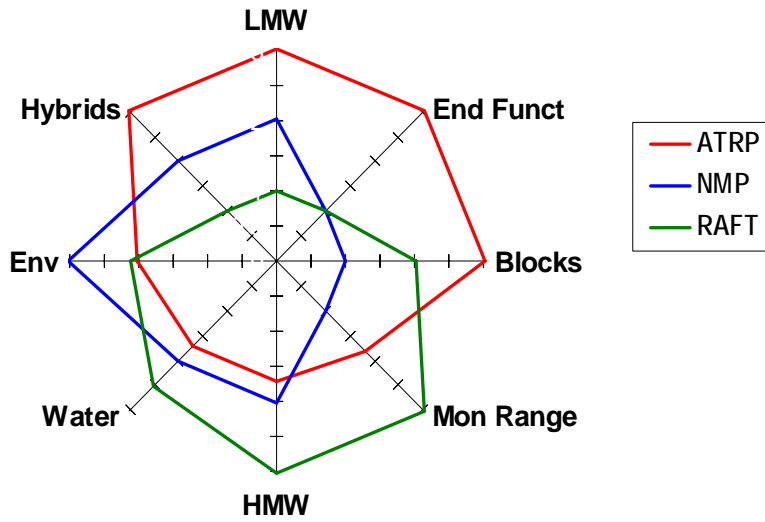
- + Easy for various homopolymers
- + May be unique for difficult monomers and HMW blocks
- Control of EG limited by % of decomposed initiator, Retardation for LMW, Stars and More complex architectures?
- New, more friendly transfer agents needed (\$\$, smell, color, removal)

➤ SFRP, NITROXIDES

- + no metal present
- + alkoxyamines may act as stabilizers
- \$, limited range of monomers for TEMPO
- very difficult for MMA even with new nitroxides

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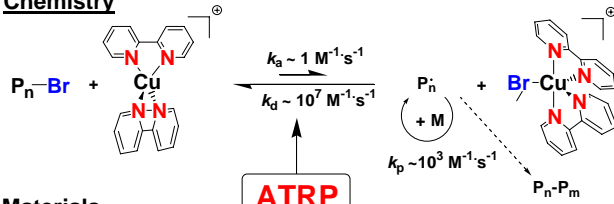
Comparative Advantages of CRPs



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Constituents of CRP/ATRP: Mechanisms, Processes, Materials

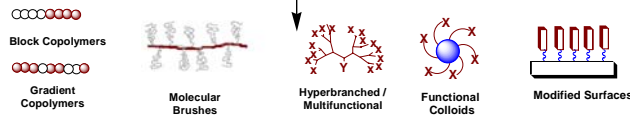
Chemistry



Mechanisms:

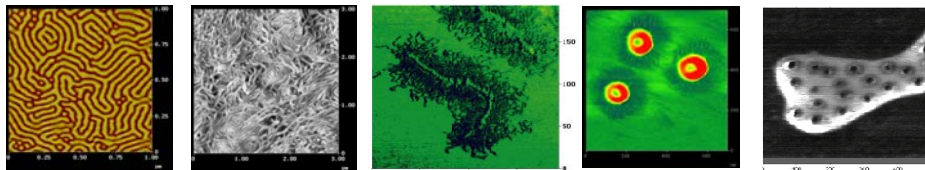
- Catalyst Structure
- Ligand Design
- Model Kinetics
- Polymerization
- Modeling

Materials



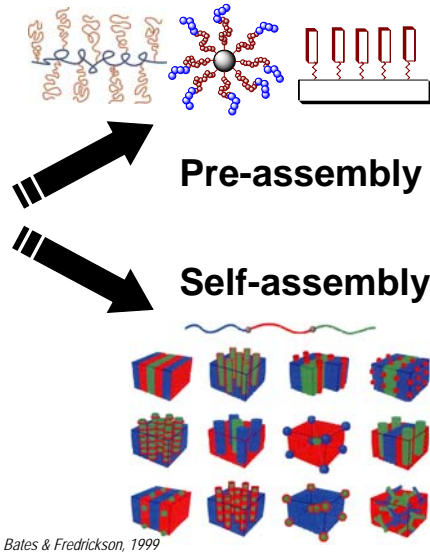
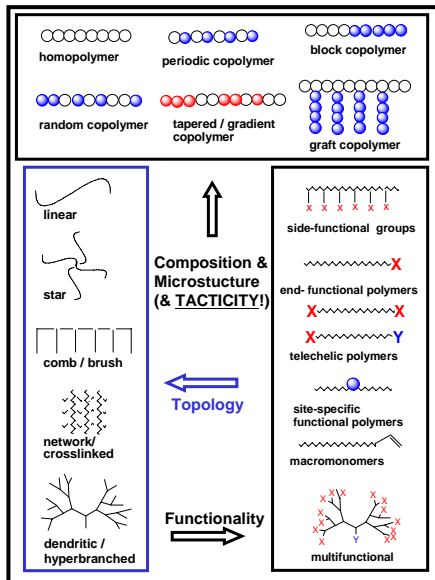
Processes:

- Catalyst Optimization
- Catalyst Recycling
- Monomer Range
- Functional Initiators
- Reaction Media
- Reaction Conditions



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CRP Controls Molecular & Nanostructures



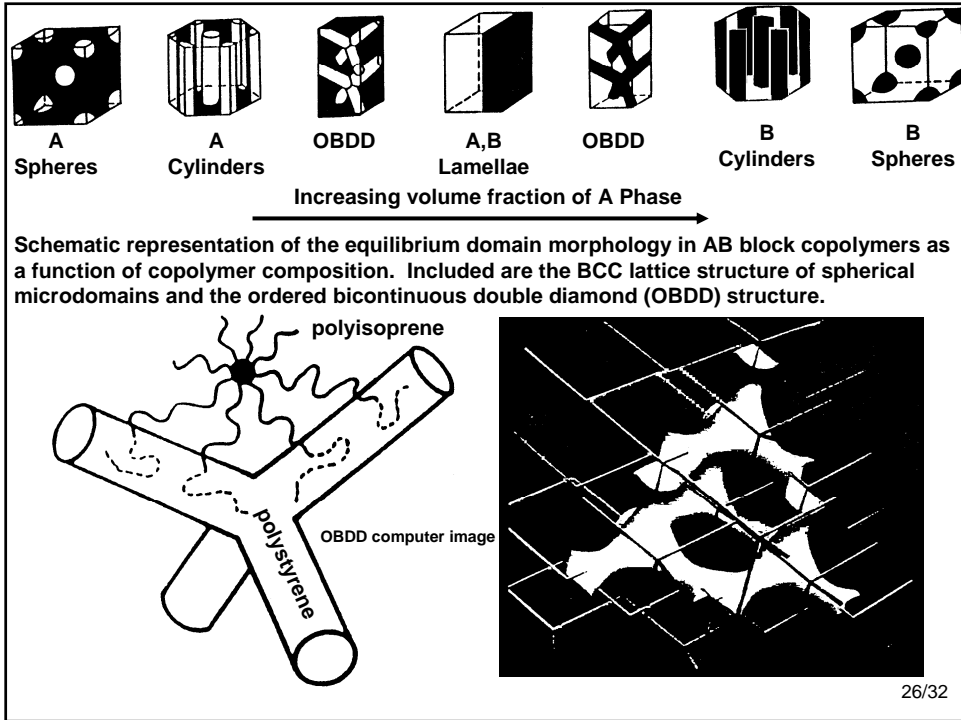
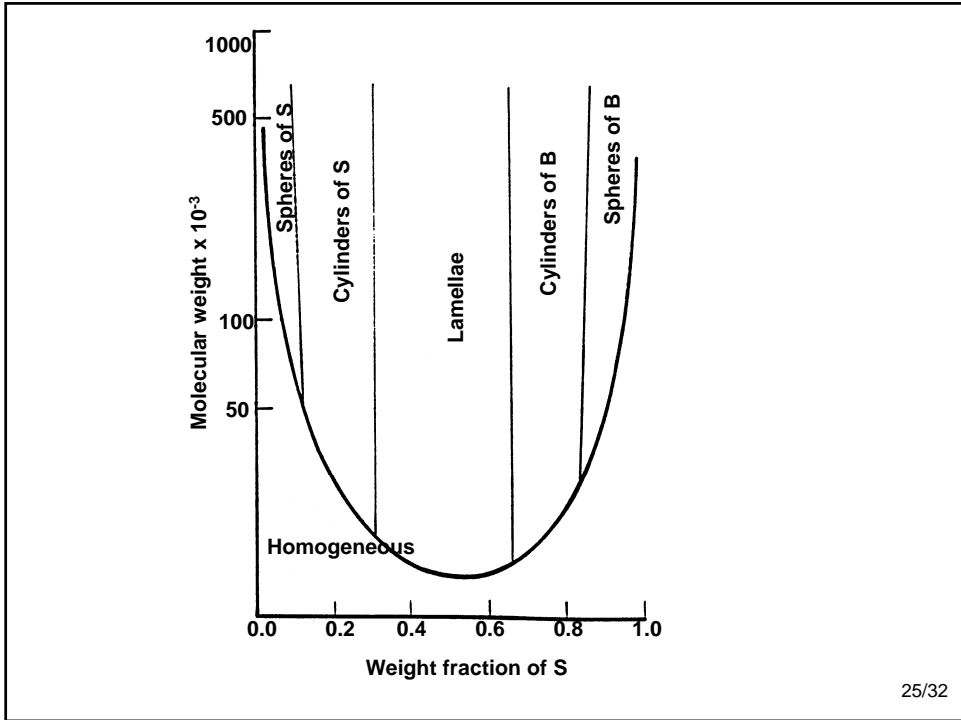
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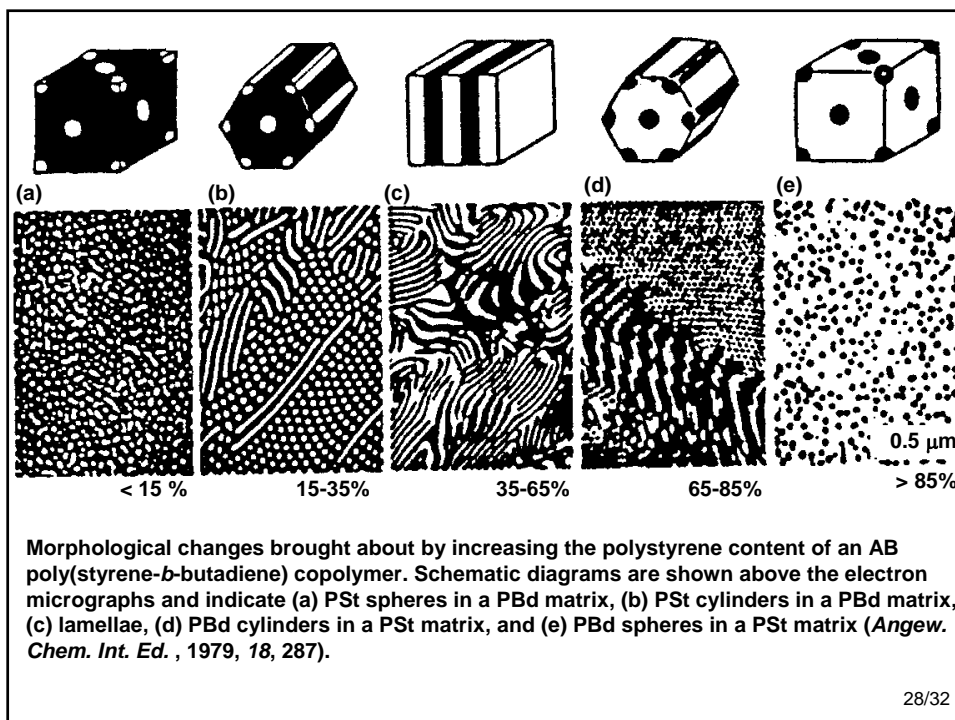
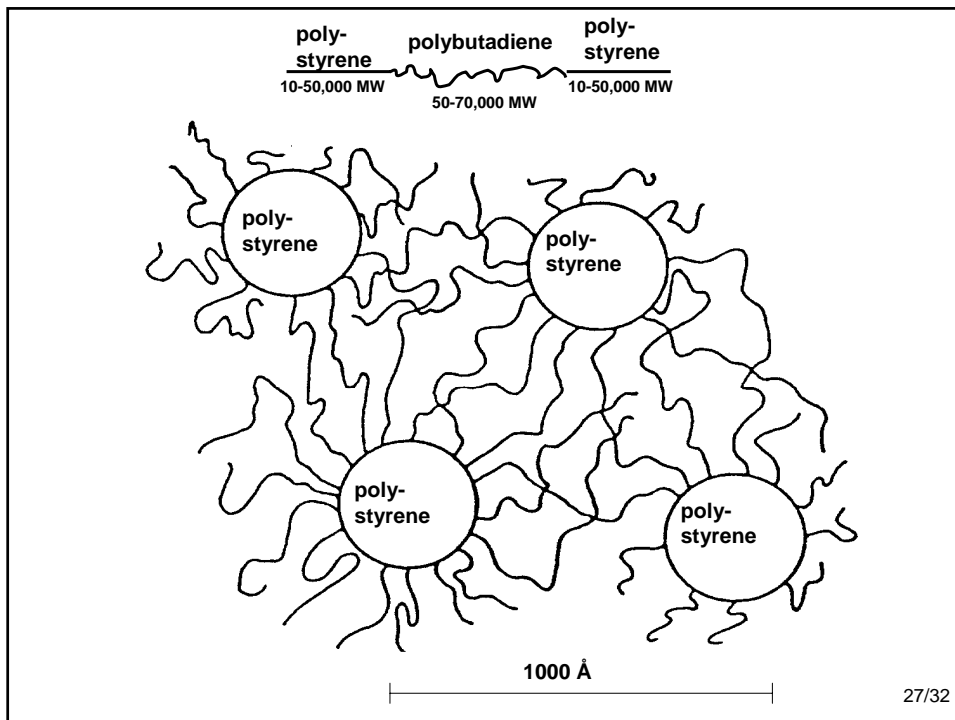
Block and Graft Copolymer Morphology

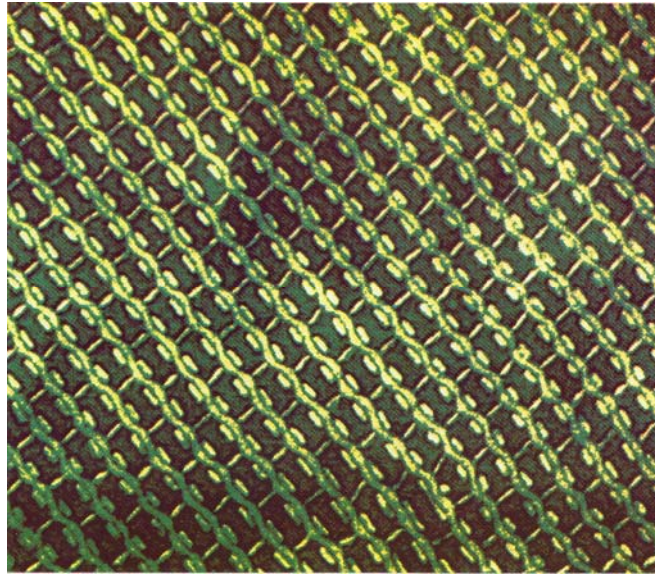
Driving Forces:

1. Minimize domain surface area/domain volume ratio
2. Limited by localization of junction between segments at domain boundary
3. Entropic limitation - maintain uniform density

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“Knitting with Block Copolymers”

ABC triblock copolymer of poly(styrene)-*b*-poly(isoprene)-*b*-poly(methyl methacrylate)
Cover of “Physics Today”, 1999

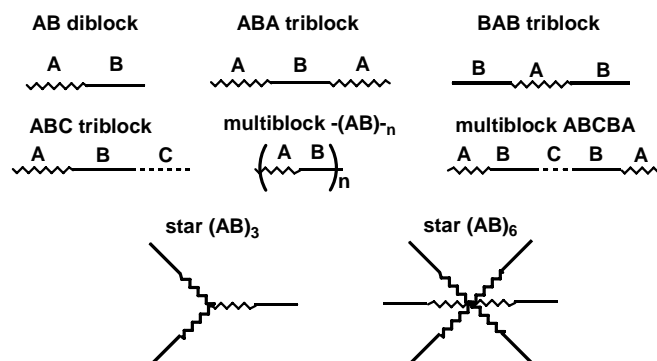
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Block Copolymers

Methods of Synthesis of Block Copolymers

1. Block Copolymers by Anionic Living Polymerization Techniques
2. Block Copolymers by Cationic Polymerization
3. Block Copolymers by Coupling Reactions between Preformed Functional Blocks
4. Block Copolymers by Coordination Polymerization
5. Block Copolymers by Conventional Free Radical Copolymerization Techniques
6. Block Copolymers by Controlled Radical Copolymerization Techniques
7. Block Copolymers by Site Transformation Techniques
8. Block Copolymers by Step-Growth Procedure

Types of Block Copolymers

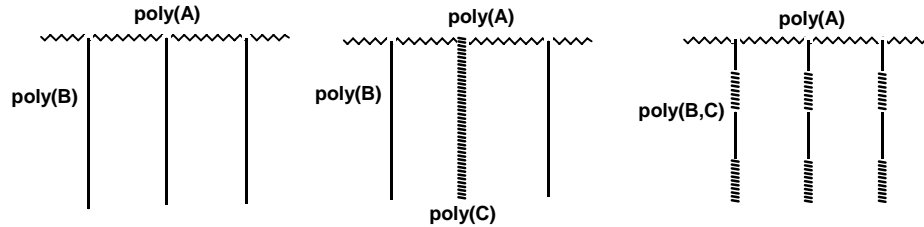


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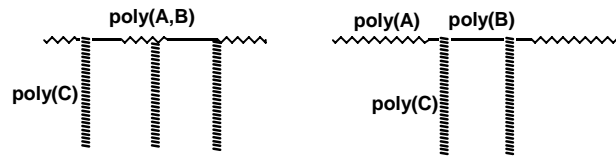
Graft Copolymers

Types of Graft Copolymers

Homopolymer in the backbone, different (co)polymer grafts



Copolymer in the backbone, homopolymer grafts



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Methods of Synthesis of Graft Copolymers

1. "Grafting from" Methods
2. "Grafting onto" Methods
3. Graft Copolymer Synthesis via Macromonomers ("Grafting through")
4. Graft Copolymers by Free Radical Grafting Techniques

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