

Lecture 1:
General Introduction to Polymers

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- Synthetic *vs*. retrosynthetic analyses
- Polymers and polymerizations
- Covalent *vs*. supramolecular polymers
- Controlled properties *via* controlled macromolecular architectures
- Consideration of "cradle-to-grave"

Sophisticated Plastics

The Uniqueness and Importance of Polymers

Sophisticated Plastics

Mechanical Function

Barrier Function

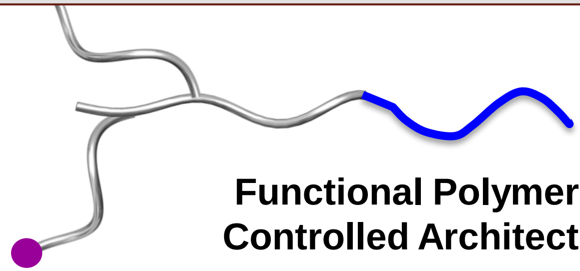
Signaling Function

For development of macroscopic to nanoscopic devices—motivated by applications but driven by fundamentals:

- Develop synthetic strategies
- Incorporate functions (pollutant clean-up, diagnostics, therapeutics, anti-fouling, *etc*.)
- Conduct rigorous characterization and test performance

Monomers & Reagents

Polymerizations & Transformations →

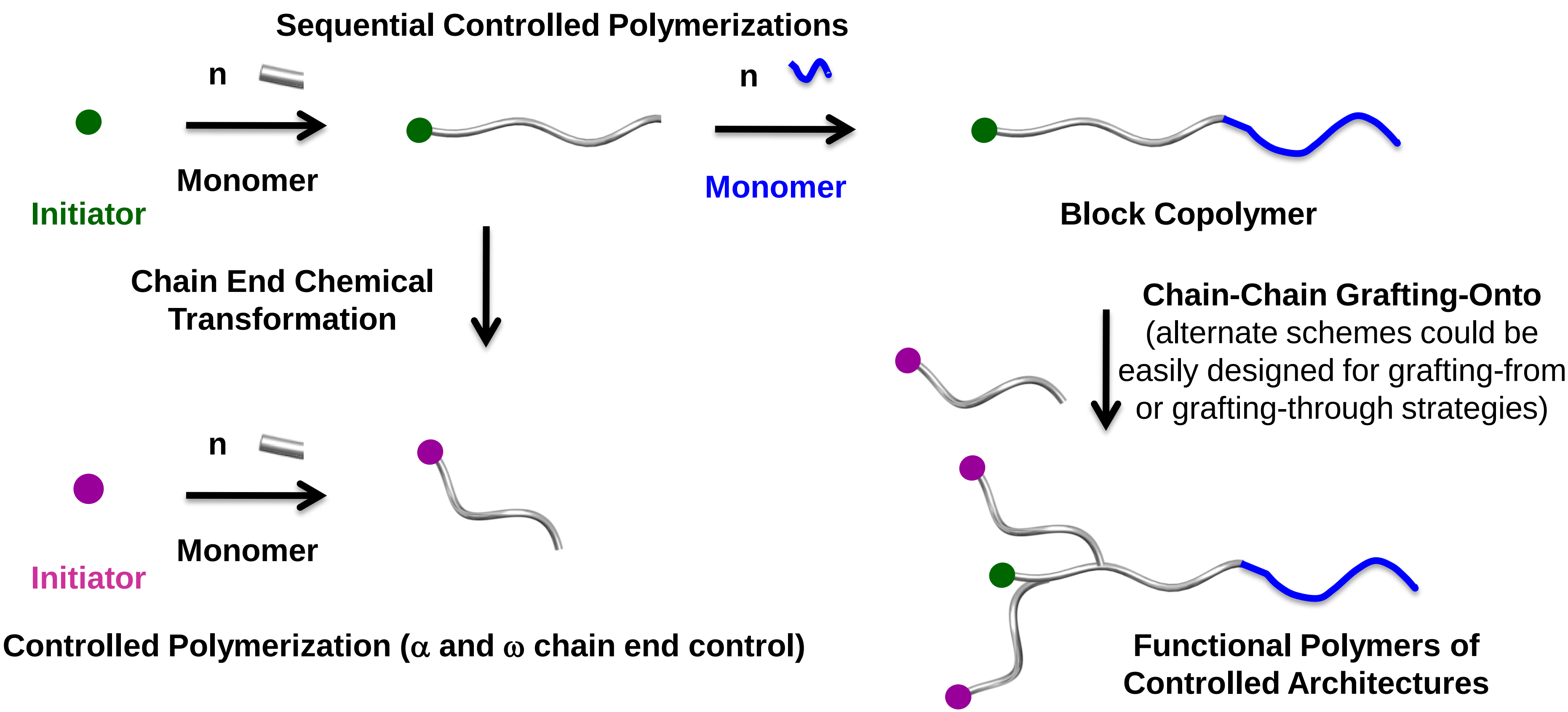


Functional Polymers of Controlled Architectures

Synthetic Analysis of Increasingly Complex Macromolecular Structures

Synthetic Approach:

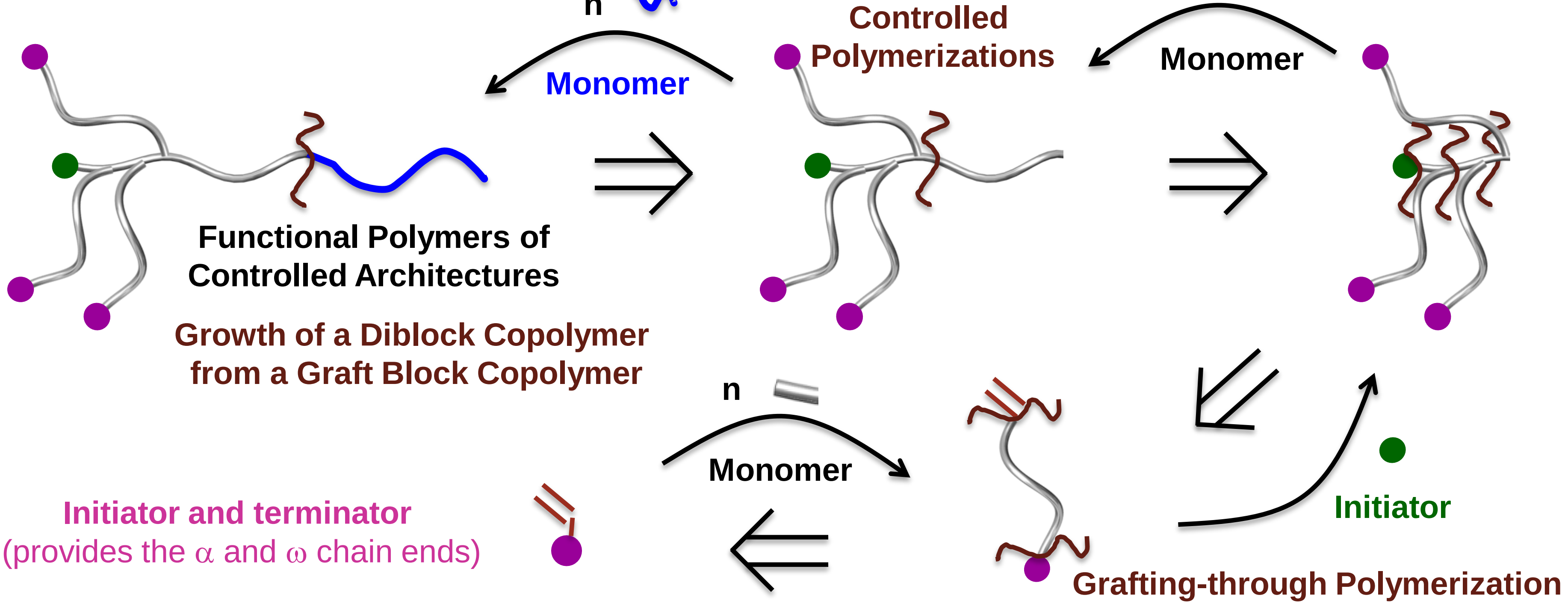
- Develop chemistries to make polymers
- Characterize their properties (provides important structure-property information)
- Determine practical applications



Retrosynthetic Analysis of Increasingly Complex Macromolecular Structures

Retrosynthetic Approach:

- Identify desired physical, chemical and mechanical properties
- Design macromolecules that are expected to possess those properties (knowledge of structure-property relationships is critical)
- Design retrosynthetic strategies by which to produce those macromolecules



Direct Synthetic *vs*. Retrosynthetic Approaches to the Preparation of Increasingly Complex Macromolecular Structures

Direct Synthetic Approach:

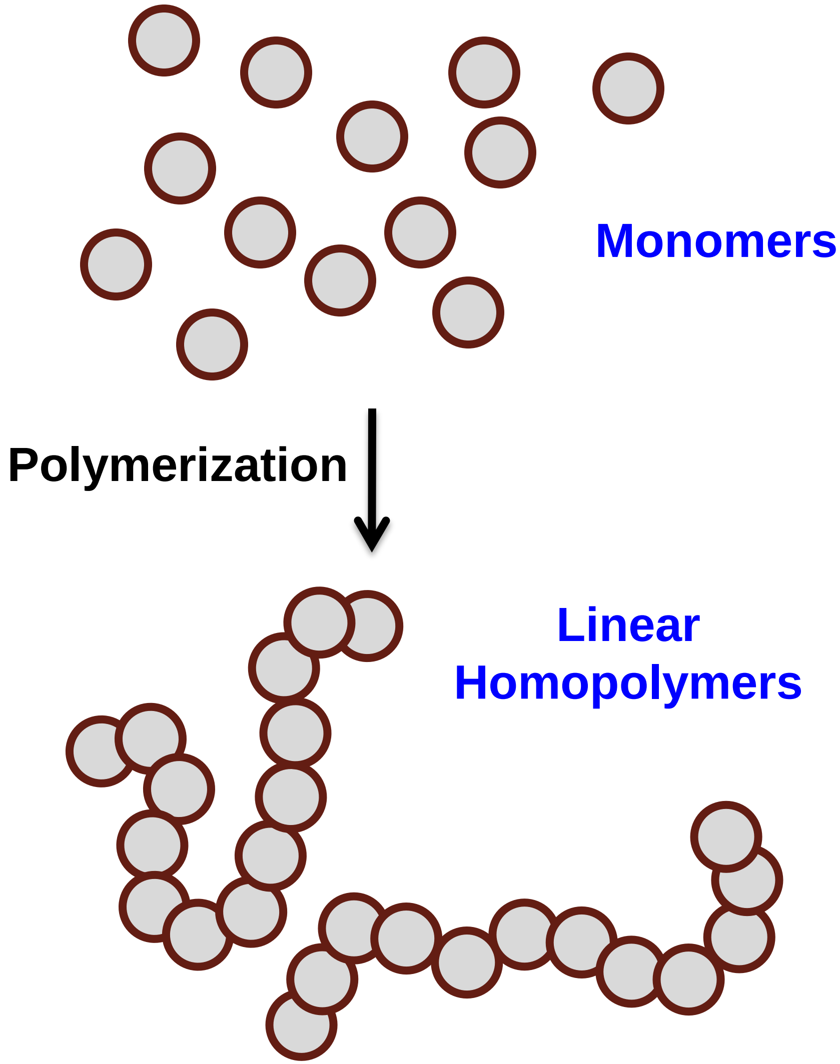
- Develop chemistries to make polymers
- Characterize their properties **(provides important structure-property information)**
- Determine practical applications

Retrosynthetic Approach:

- Identify desired physical, chemical and mechanical properties
- Design macromolecules that are expected to possess those properties **(knowledge of structure-property relationships is critical)**
- Design retro-synthetic strategies by which to produce those macromolecules

Both strategies are important to polymer / materials chemistry

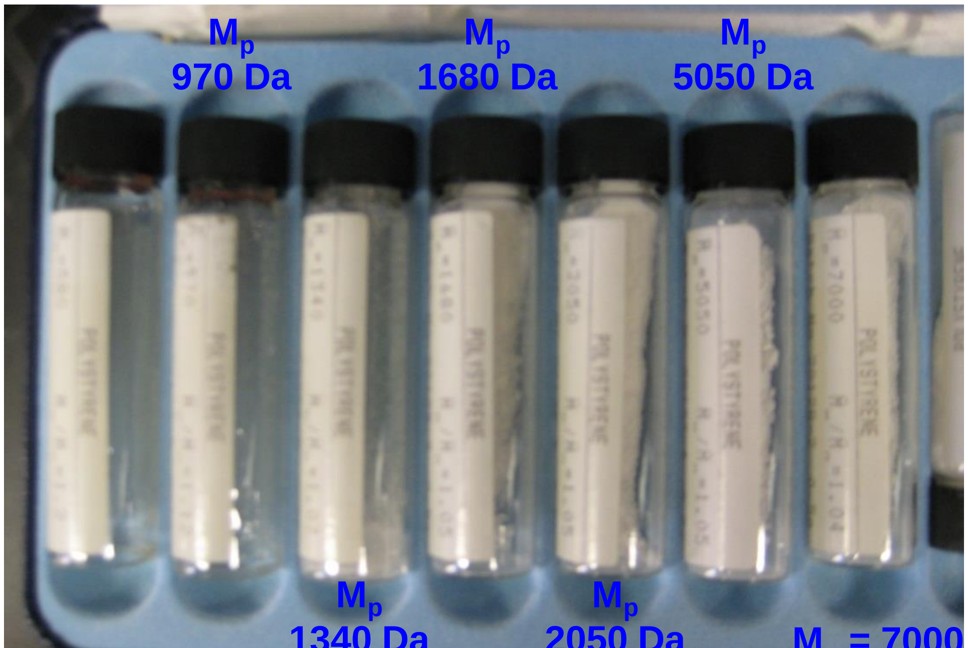
Polymers and Polymerizations



- "Polymers" = "Many mers" (many repeat units)
- Monomers are often small molecules (otherwise "macromonomer")
- Polymerization links together many copies of monomers
- For covalent polymers, polymerization involves a transition from weak intermolecular interactions to strong intramolecular bonding

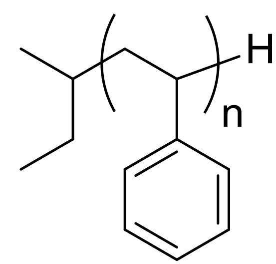
Polymers and Polymerizations

M_p = 580 Da = peak molecular weight
DP_n ~ 6 = number-average degree of polymerization
(by size exclusion chromatography, *e.g.*)
Viscous oil

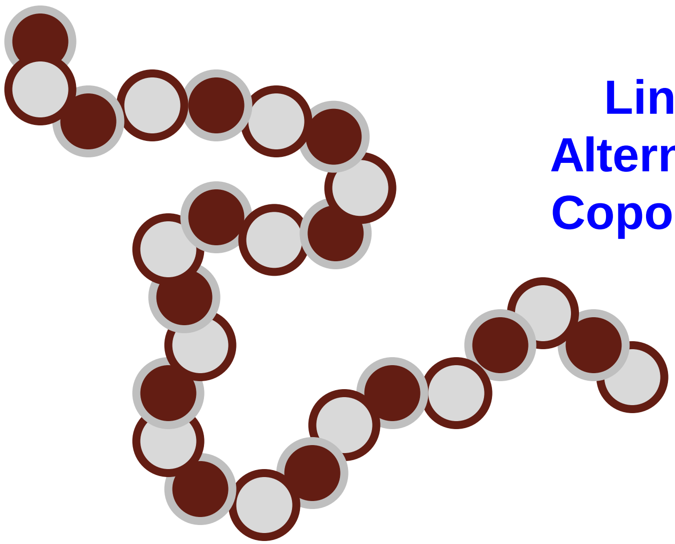


M_p = 7000 Da
DP_n ~ 70
Glassy material/powder

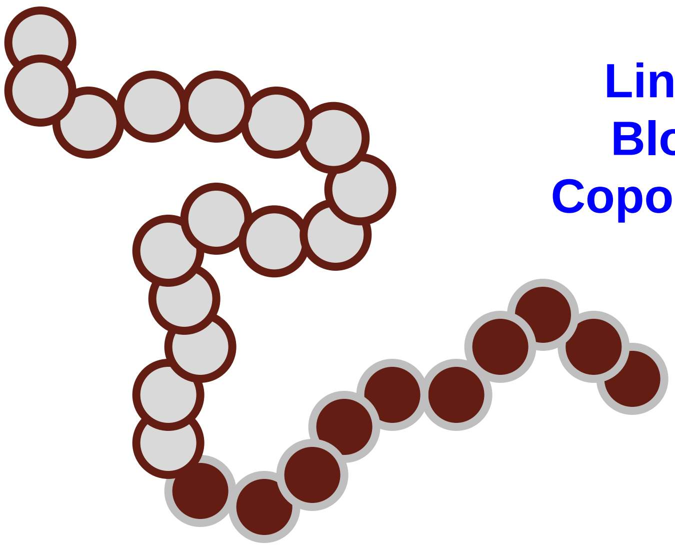
- Growth of polymer chains results in changes in physical properties
- Demo: Beads in flasks
- Example: Increasing oligomeric to polymeric styrene chain lengths (increasing n)



Polymers and Polymerizations



Linear Alternating Copolymer



Linear Block Copolymer

- Copolymers can also be formed
  - Statistical (random) copolymers
  - Alternating copolymers
  - Block copolymers
  - Gradient copolymers
- The properties can be quite different for each type
  - Monomer compositions
  - Intramolecular characteristics
  - Intermolecular interactions

Covalent *vs.* Supramolecular—Staudinger

Figure 1. Hermann Staudinger in 1964 in his Freiburg study—a year before his death.

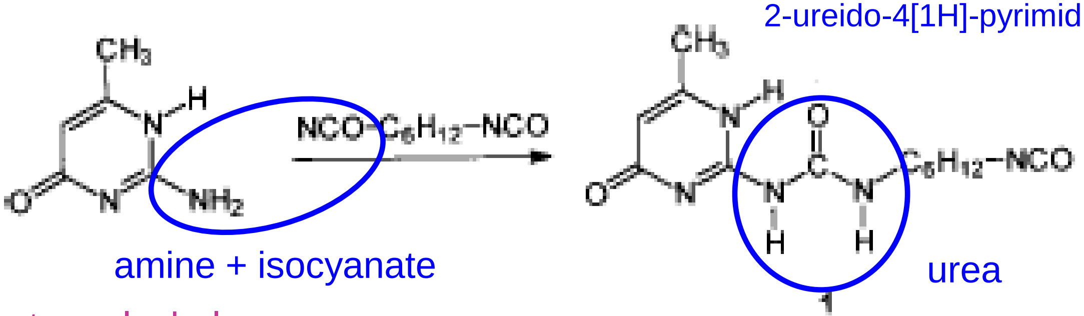
Hermann Staudinger (1881-1965)

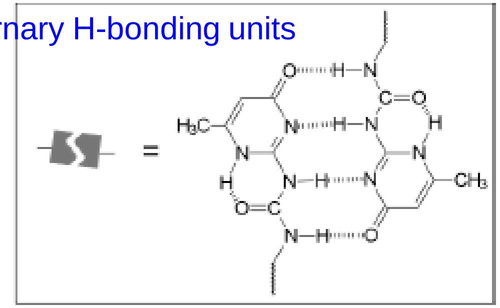
1953, Nobel Prize in Chemistry,
“for his discoveries in the field of macromolecular chemistry”; confirmation of their existence as covalent chain molecules *vs.* colloidal systems or aggregates of smaller molecules

H. Ringsdorf, “Hermann Staudinger and the Future of Polymer Research Jubilees—Beloved occasions for cultural piety”, *Angew. Chem.* **2004**, *43*, 1064-1076.

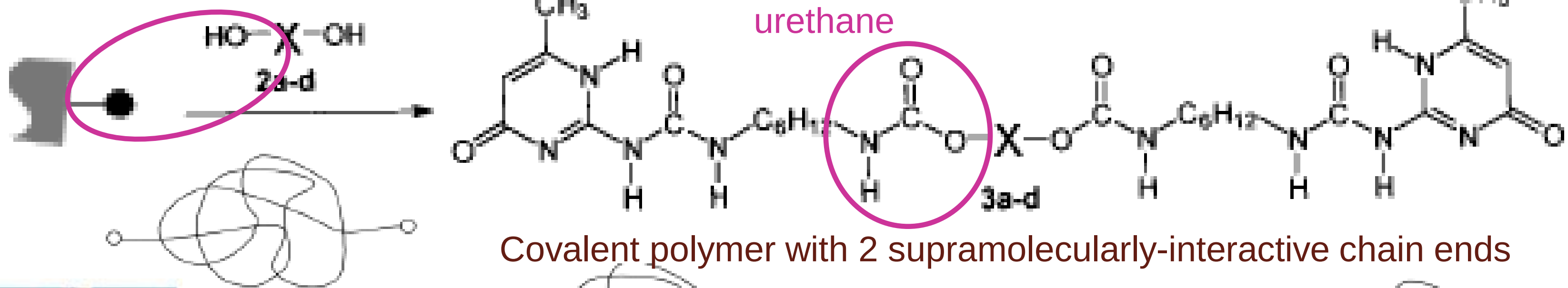
Covalent and Supramolecular—Meijer

2-ureido-4[1H]-pyrimidinone, quaternary H-bonding units





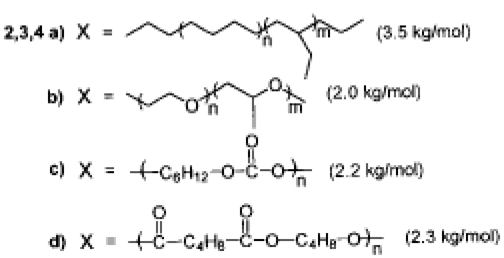
isocyanate + alcohol



Covalent polymer with 2 supramolecularly-interactive chain ends

Even chain ends are important—illustrate full structures, always!

JPSA **2010**, *48*, xiii , 15 Sept.



B. J. B. Folmer, R. P. Sijbesma, R. M. Versteegen, J. A. J. van der Rijt, E. W. Meijer *Adv. Mater.* **2000**, *12*, 874-878.

Covalent and Supramolecular Interactions

<u>Covalent Polymers</u>:
- **Robust materials**
- **Linkages can be cleaved selectively (degradable polymers)**
- Molecular weight
- Molecular weight distribution
- Architecture (topology)
- Composition

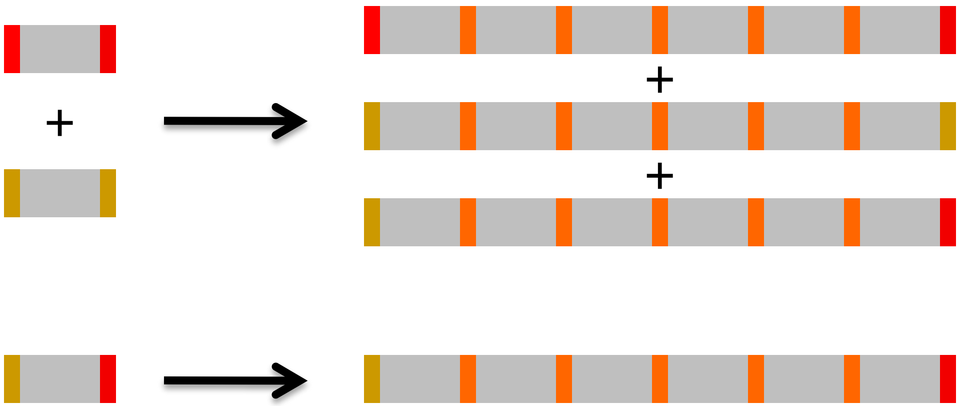
Each parameter is important to the properties

<u>Supramolecular Polymers:</u>
- **Dynamic systems**
- **Reversible assembly/disassembly**
- Molecular weight
- Molecular weight distribution
- Architecture (topology)
- Composition

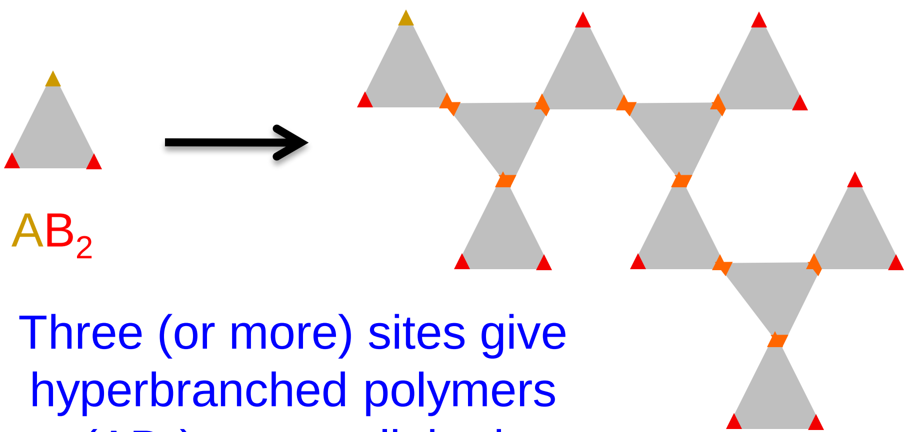
Each parameter is important to the properties

- In covalent polymers, intermolecular interactions are also important
- In supramolecular polymers, covalent connections within building blocks are also important
- Combinations provide excellent directions for tuning of materials properties, and each must be considered when designing polymer structures

Polymers and Polymerizations—Architecture



Two sites (AA + BB or AB) give linear polymer chains

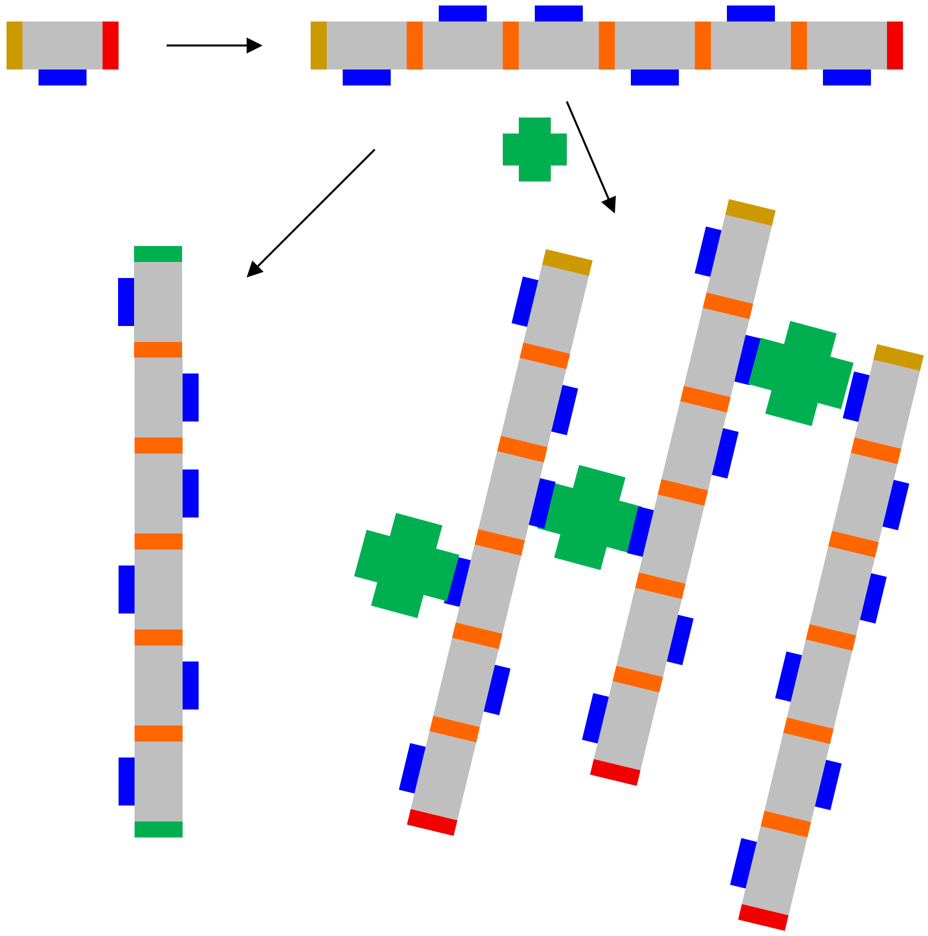


Three (or more) sites give hyperbranched polymers (AB_2) or crosslinked networks ($A_3 + B_{x\geq 2}$)

AB_{n+1}

- The number of complementary reactive sites and geometry of monomer determine macromolecular structure
- Macromolecular architecture affects greatly the physical and mechanical properties

Polymers and Polymerizations



- Remaining reactive sites allow for post-polymerization modifications at chain ends or along the backbone
- Orthogonal chemistries can be used (*e.g.*, E. W. Meijer's supramolecular polymer system (*vide supra*)—orthogonal chemistries to modify the chain ends and promote H-bonding supramolecular polymerizations of macromonomers)
- Chemical functionalization
- Crosslinking
- Unique architectures (*e.g.*, linear-dendritic hybrids)

Consideration of Cradle-to-Grave

- Consider mechanisms for deconstruction of polymers after they have served their function
  - Recycling
  - Bioresorption

- Polystyrene
  - Stable C-C backbone; linear polymer structure allows for dissolution (of intact polymer chains) in solvents
  - Solubility has led to alternatives to degradation, *e.g*. Hearon, K.; *et al*. "A High-performance Recycling Solution for Polystyrene Achieved by the Synthesis of Renewable Poly(thioether) Networks Derived from D-Limonene", *Adv. Mater.*, in press, DOI: 10.1002/adma.201304370.

- Poly(ethylene terephthalate)
  - Reactive ester backbone linkages; can be broken by hydrolysis, alcoholysis, *etc*.
  - Degradation viable, *e.g.* Fukushima, K.; *et al.* "Organocatalytic Depolymerization of Poly(ethylene terephthalate)", *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1273-1281.

- Supramolecular polymers
  - Weak intermolecular interactions can be broken temporarily and reversibly for reprocessing/recycling, e.g., Folmer, B. J. B.; et al. "Supramolecular Polymer Materials: Chain extension of telechelic polymers using a reactive hydrogen-bonding synthon", *Adv. Mater*. **2000**, *12*, 874-878.