特种聚合方法A

Advances in Polymer Chemistry

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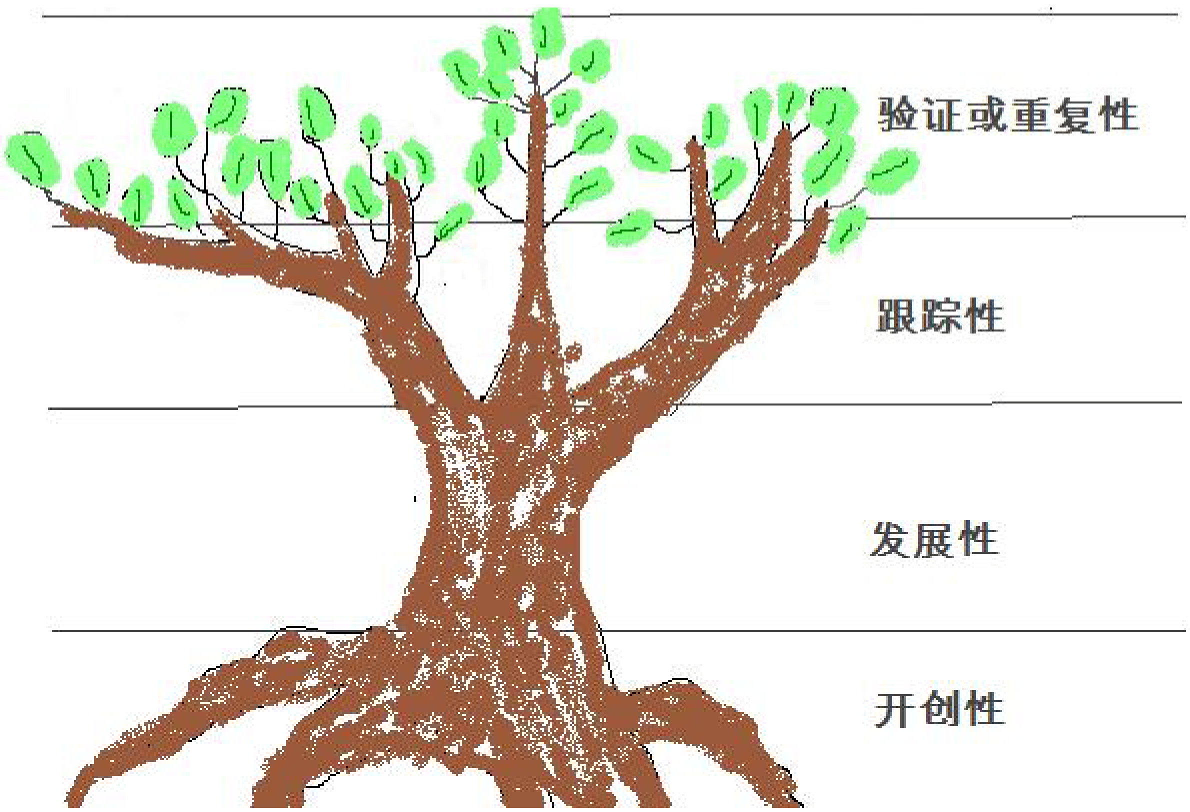
Scope & Aims

- ◆ Advanced knowledge in polymerization techniques
- ◆ Up-to-date progresses in polymer materials
- ◆ Fundamental concepts in promising polymer research areas

研究课题的分类



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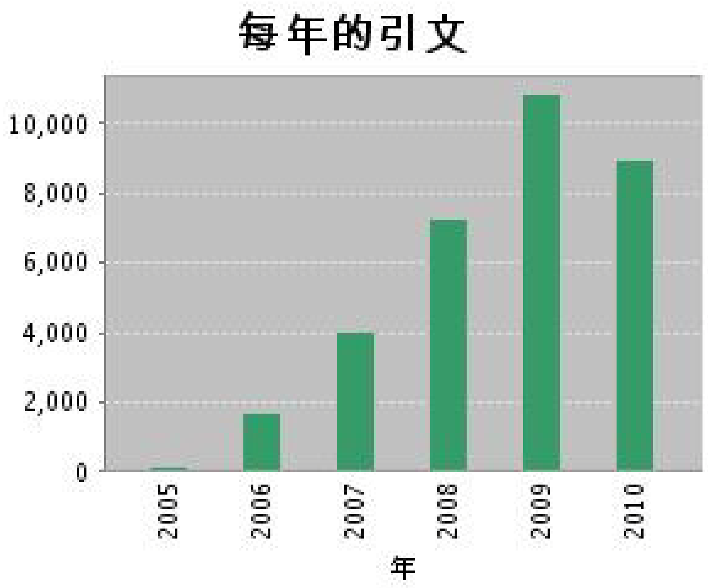
Polymer Science in China



Section 1 Advances in Polymerization (6 h)

(a) Background (1 h)

(b) Review of conventional polymerization (2 h)

(c) Novel polymerization techniques (3 h)

- Advances in living polymerization
- Living (Controlled) radical polymerization
- ROMP

Section 2 Polymer Brushes (6 h)

a) Polymer brushes from interfaces

b) Molecular brushes

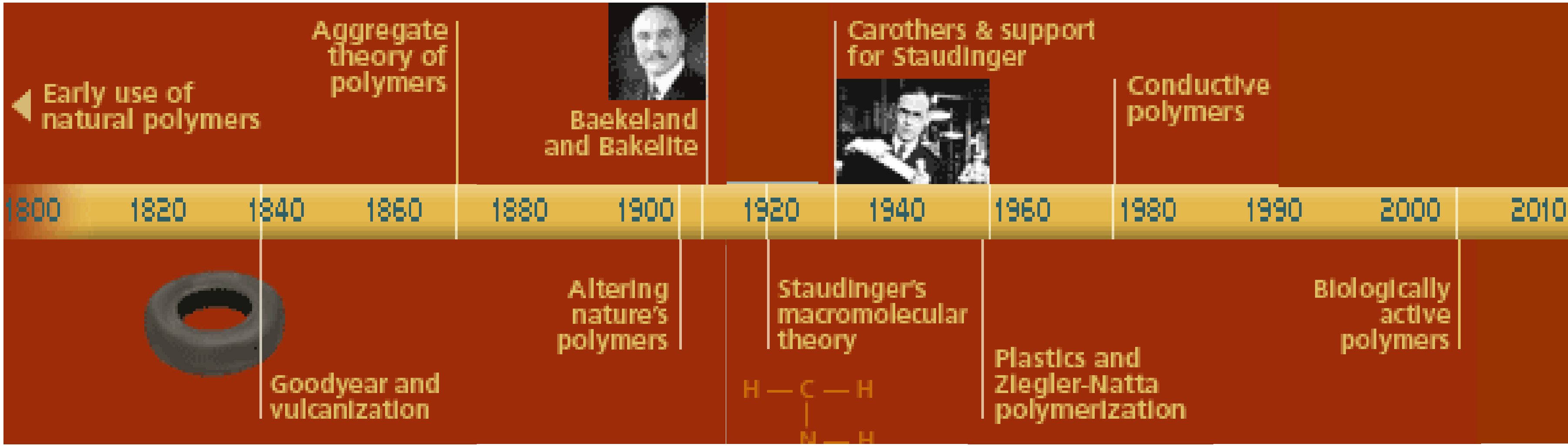
Section 3 Dendritic Polymers (9 h)

Section 4 Supramolecular Polymers (3 h)

Section 5 Polymer-Based Nano-Materials (3 h)

Section 6 Stimuli-Responsive Polymers (3 h)

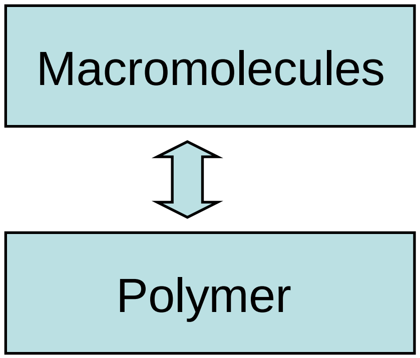
Background

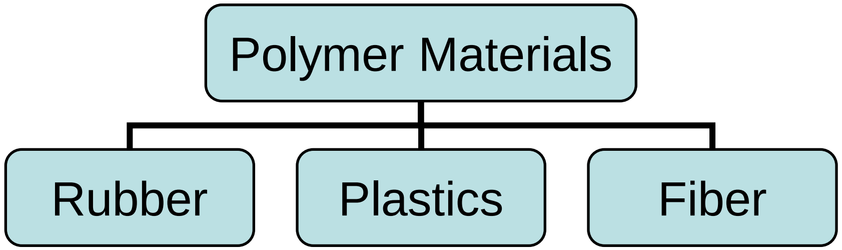


Nobel prize

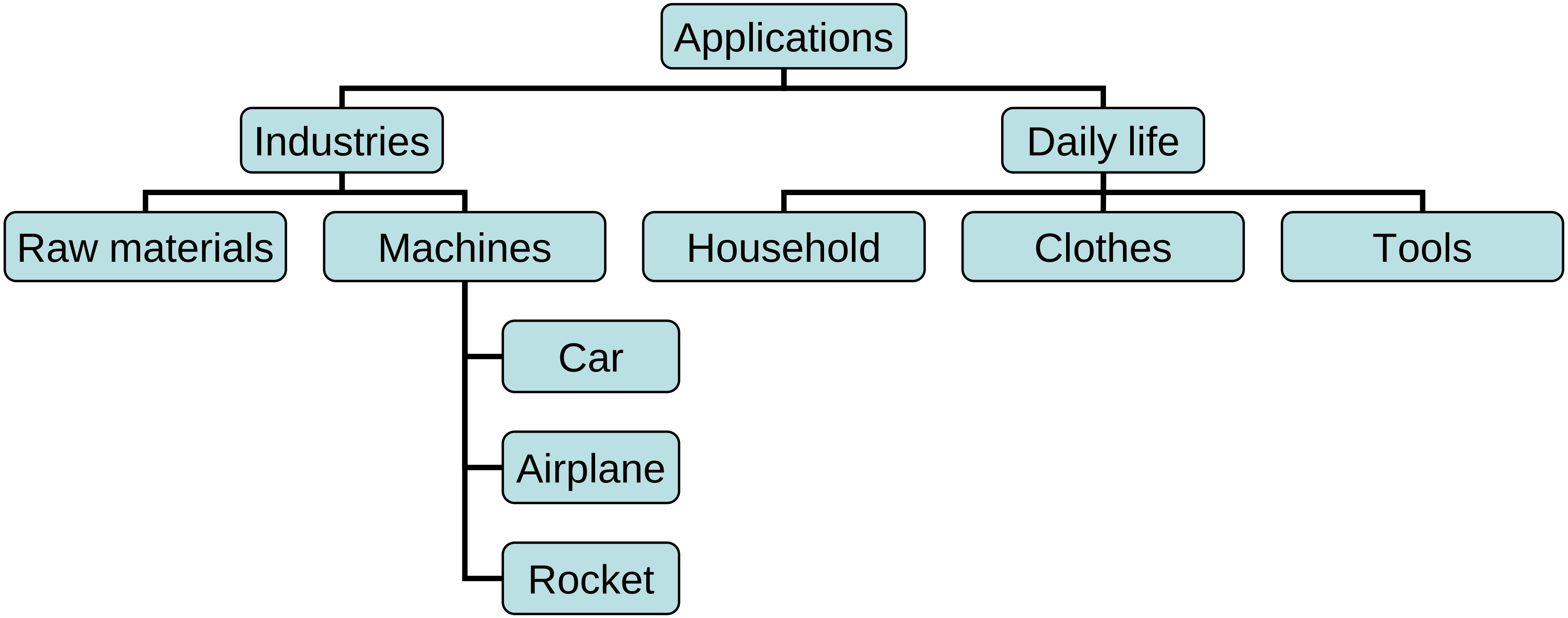
- Concept of polymer
  H. Staugínger (Ger)
  1953
- Vinyl polymers
  K. Ziegler (Ger)
  G. Natta (It)
  1963
- Polymer physics
  P. J. Flory (USA)
  1974
- Carboncation
  G. A. Olah (USA)
  1994
- Conductive polymers
  A. J. Heeger (USA)
  A. G. MacDiarmid (USA)
  H. Shirakawa (Jp)
  2000
- Y. Chauvin (Fr)
  R. H. Grubbs (USA)
  R. R. Schrock (USA)
  2005

The winner of Nobel Prize and Academician of Chinese Academy of Sciences in Polymer Science





General: PS, PE, PP, PVC
Engineering: PPO, PA, PC, PSu



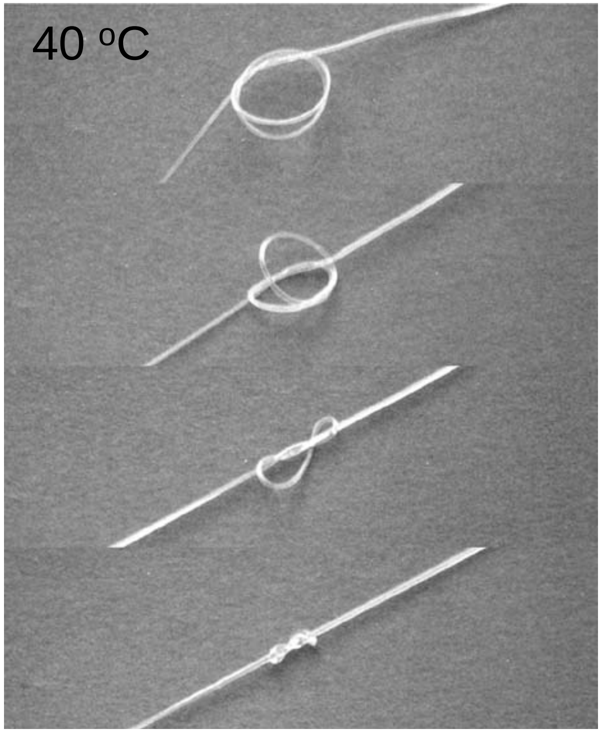

Display cabinet:
Multi-layered Carbon Fibre
Much lighter and stronger than magnesium alloy. Used for aircraft and sports cars.

Chassis made of carbon fibre and aluminum alloy

- **Polymer science**
  - **Polymer chemistry**
    - **Polymer synthesis**
    - Polymer Materials
  - Polymer physics
  - Polymer engineering

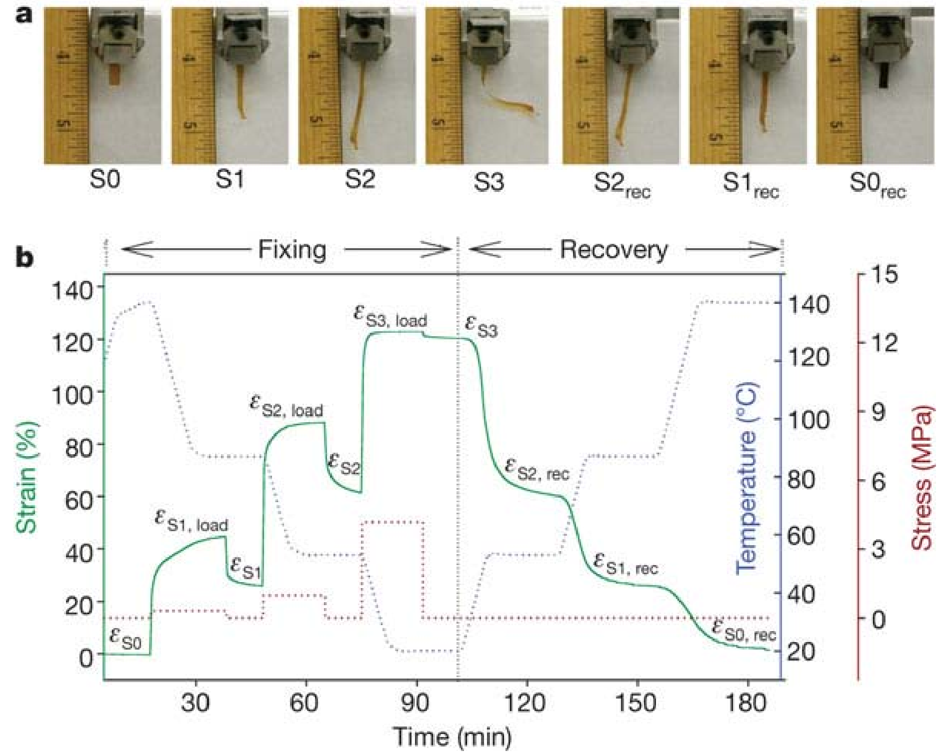
Dead materials → Live materials?

Advance-I Shape memory polymers (SMPs)



Thermoplastic PU stretching about 200%. After forming a loose knot, both ends of the suture were fixed. From top to bottom, how the knot tightened in 20 s.

A. Lendlein, *et al.* **Biodegradable, Elastic Shape-Memory Polymers for Potential Biomedical Applications**. *Science* **2002**, *296*, 1673
A. Lendlein, et al. **Multifunctional Shape-Memory Polymers**. *Adv. Mater.* **2010**, *22*, 3388

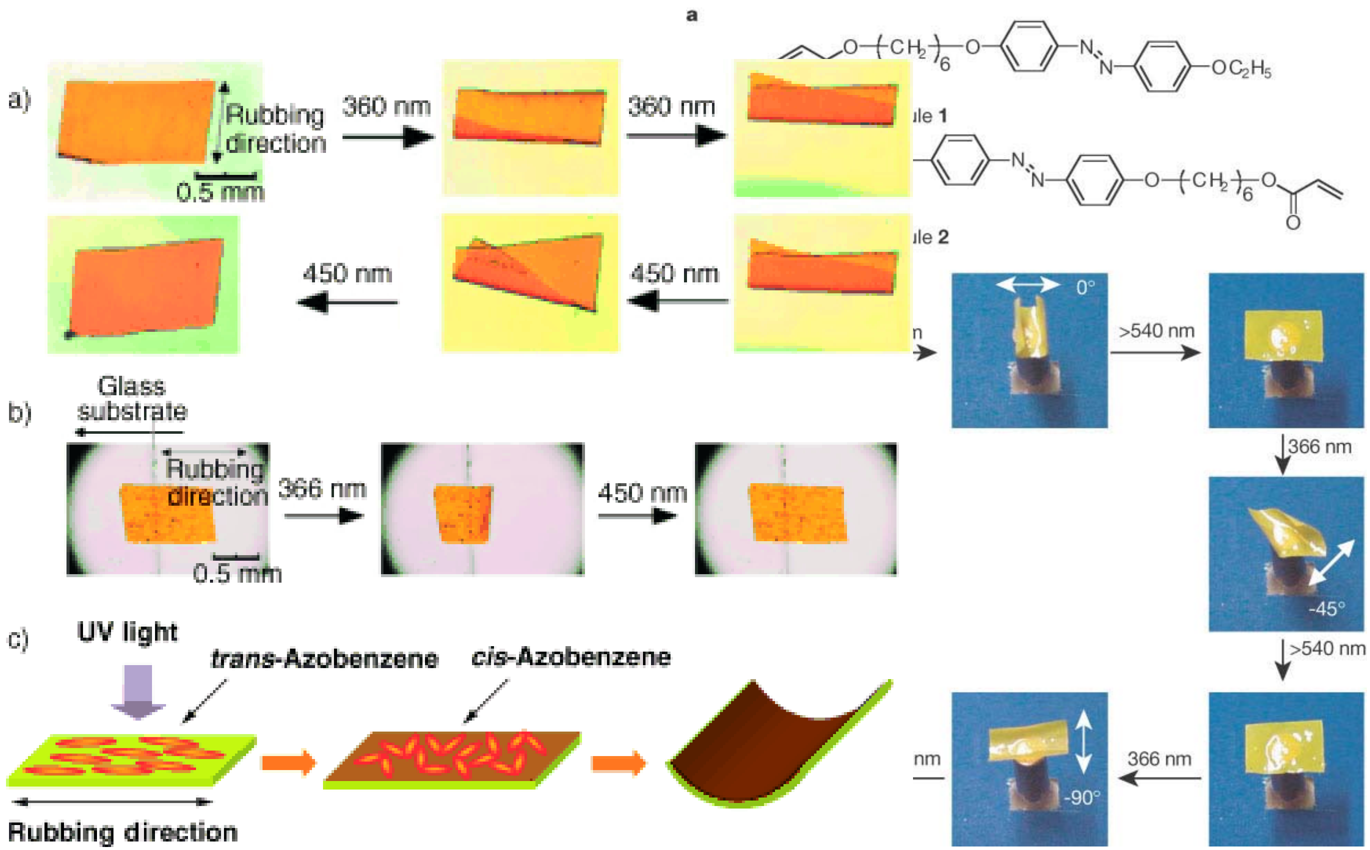


Quadruple-shape memory properties of PFSA (Nafion).

T. Xie, **Tunable polymer multi-shape memory effect**. *Nature* **2010**, *464*, 267

Movie

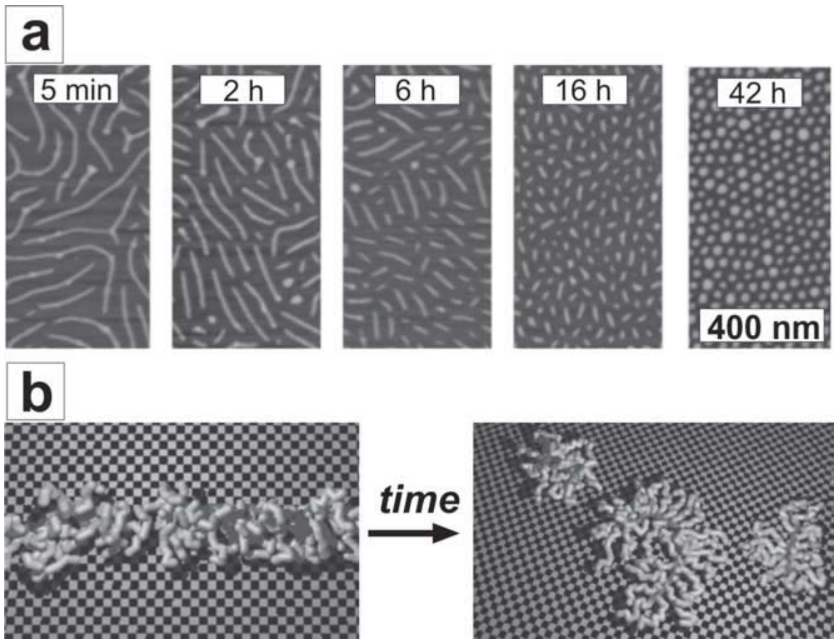
Advance-II Artificial polymer muscle

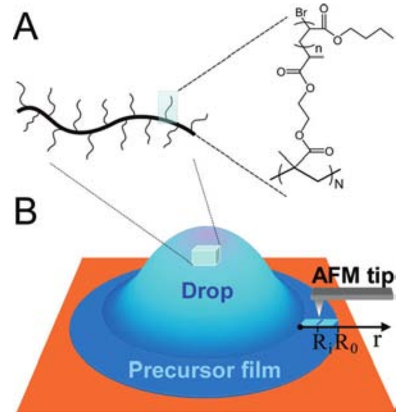


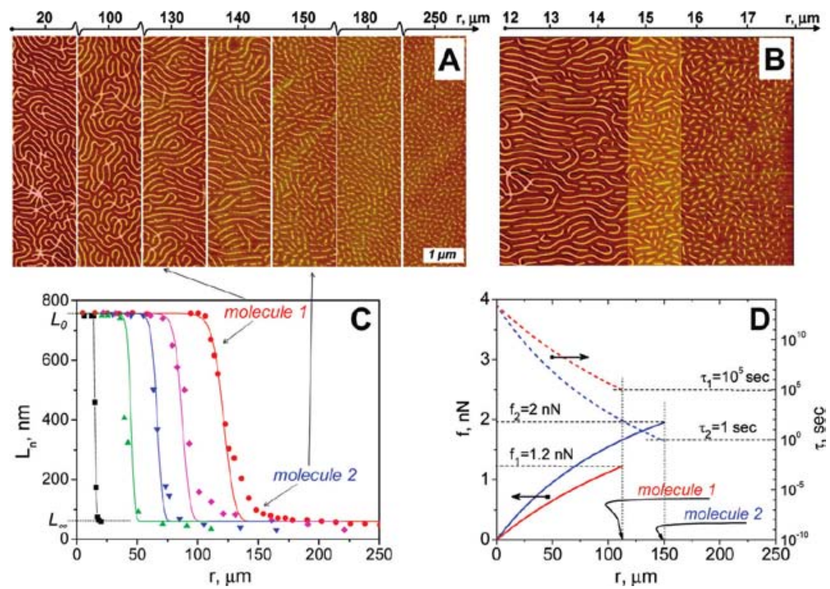
Movie

Y. Yu, M. Nakano, T. Ikeda, **Photomechanics: Directed bending of a polymer film by light**. *Nature* **2003**, *425*, 145
T. Ikeda, J. Mamiya, Y. Yu**, Photomechanics of Liquid-Crystalline Elastomers and Other Polymers.** *Angew. Chem. Int. Ed.* **2007,** *46*, 506

Advance-III Scission of polymers

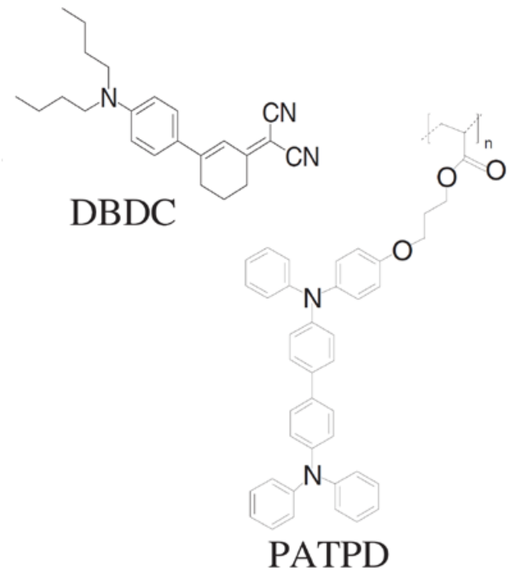


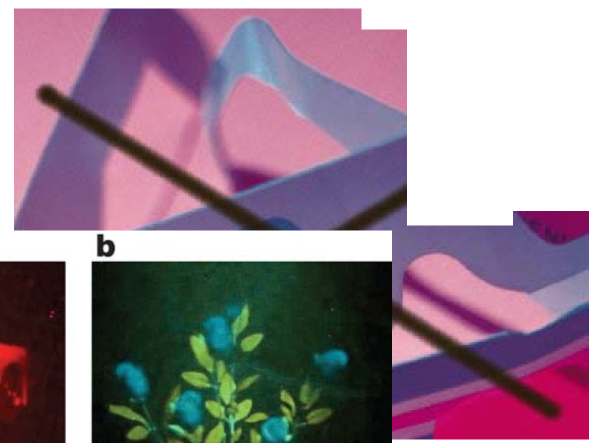


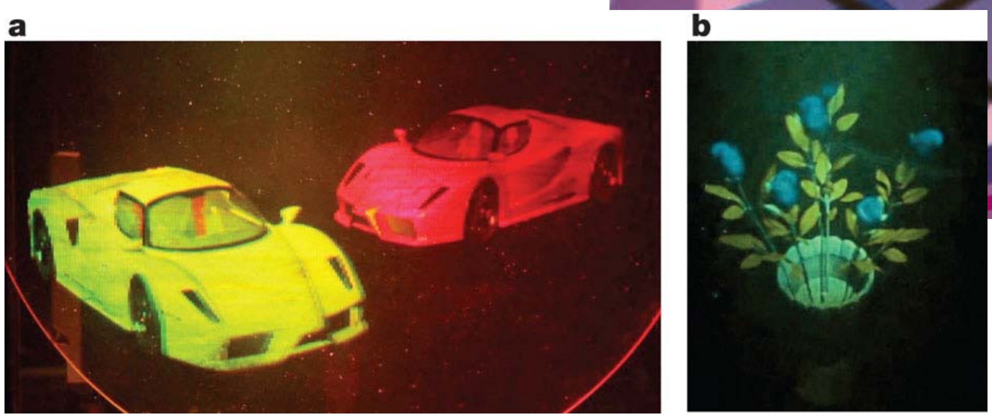


S. S. Sheiko, et al. **Adsorption-induced scission of carbon–carbon bonds**. *Nature* **2006**, *440*, 191; **“Fatal Adsorption” of brushlike macromolecules: high sensitivity of C-C bond cleavage rates to substrate surface energy**. *JACS* **2008**, *130*, 4228; **Spontaneous and specific activation of chemical bonds in macromolecular fluids**. *JACS*, **2010,** DOI:10.1021/ja105897b

Advance-IV Photorefractive polymers for holography





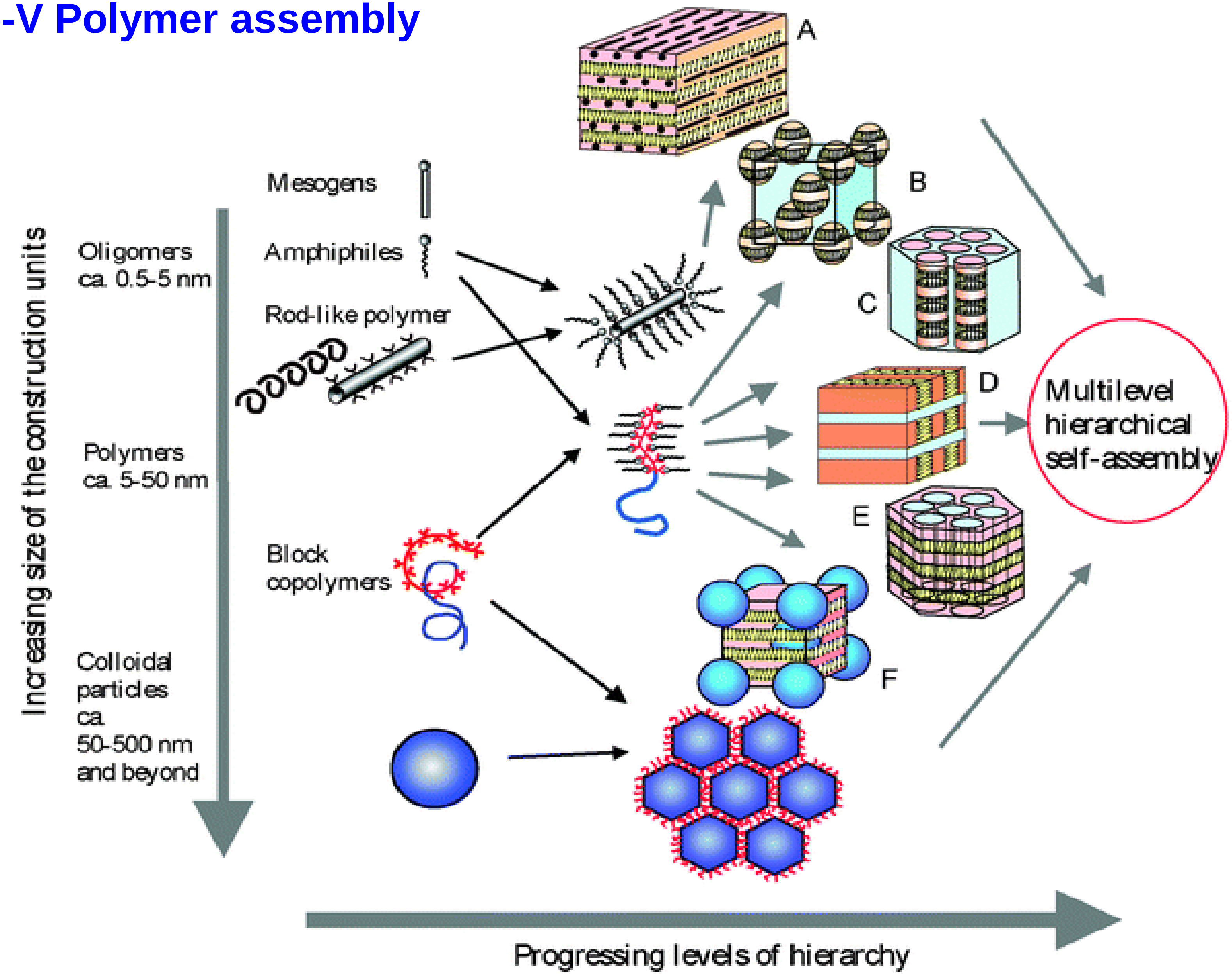


Movie

a, Hologram of two model cars recorded on a 12-inch-diameter photorefractive device in HPO geometry.
b, Hologram of a vase and flowers.

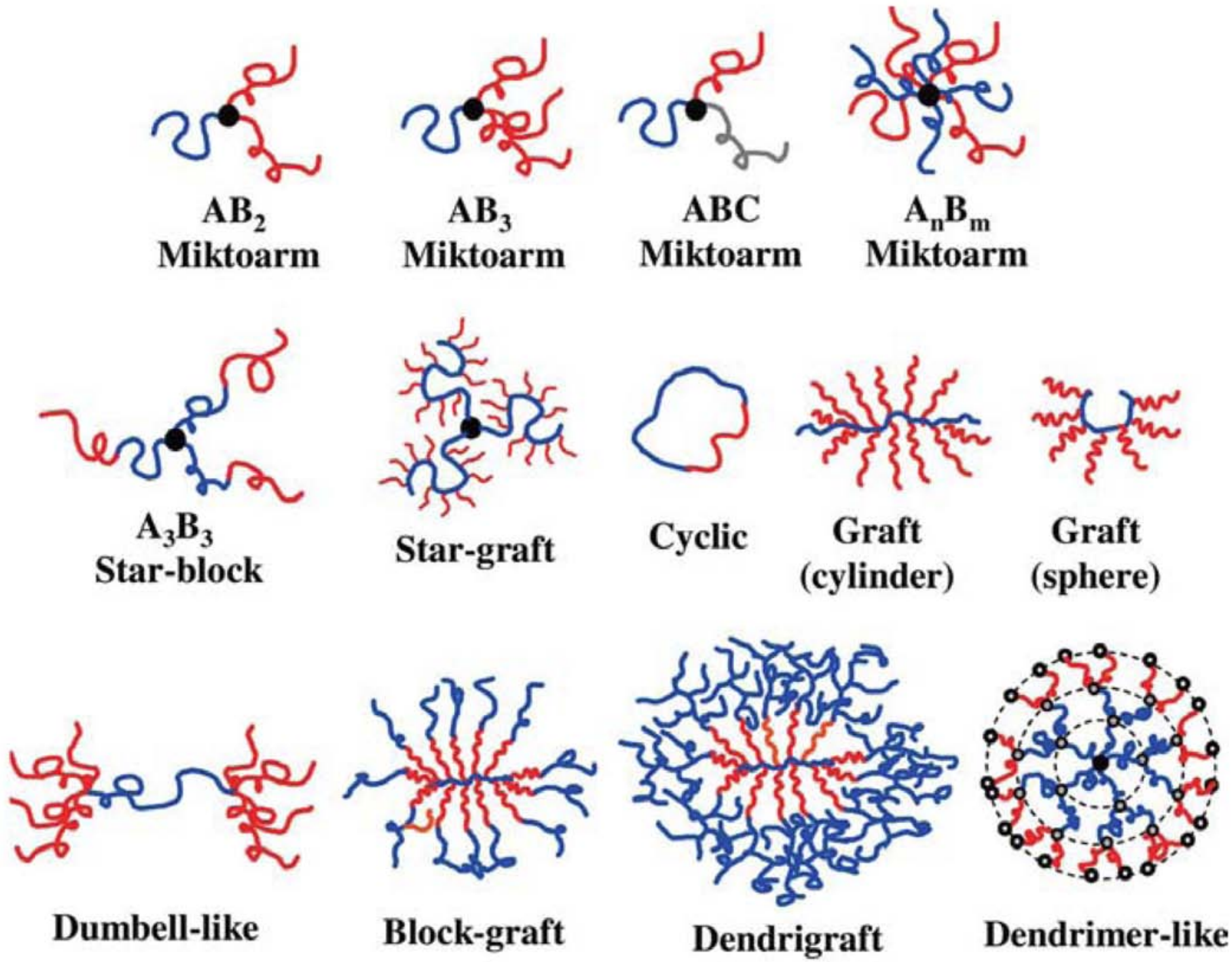
Nature **2010**, *468*, 80–83

Advance-V Polymer assembly



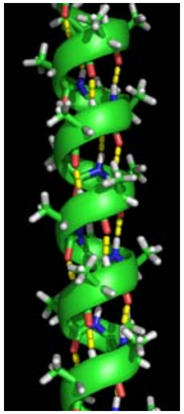
Block copolymers with a branched architecture

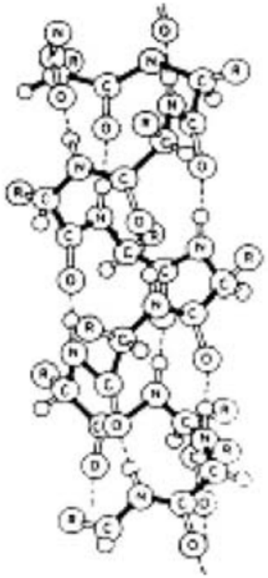
Classification:



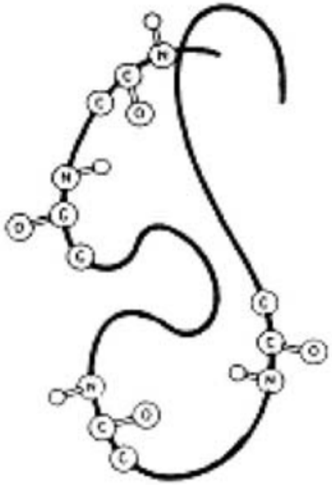
Advance-VI Polymer-polypeptide block copolymers

Secondary structures of peptides

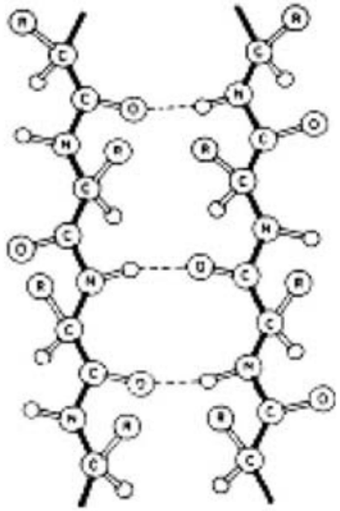




Alpha helix



random coil



beta sheet

Development of polymerization technique:

(1) chain polymerization (FRP); polycondensation

(2) 1950’s, Ziegler-Natta coordination polymerization, main advantages: tacticity control (i-PP with high melt point); high mol. weight; extremely low concentration of catalysts

(3) 1980’s, GTP and molecular design; ionic (cationic and anionic) living polymerization;

(4) 1990’s, Self-assembly of novel materials for life and information; controlled radical polymerization; biodegradable polymers; environmentally-friendly polymerization; Metalocene

(5) 1990’s-2000’s, ROMP

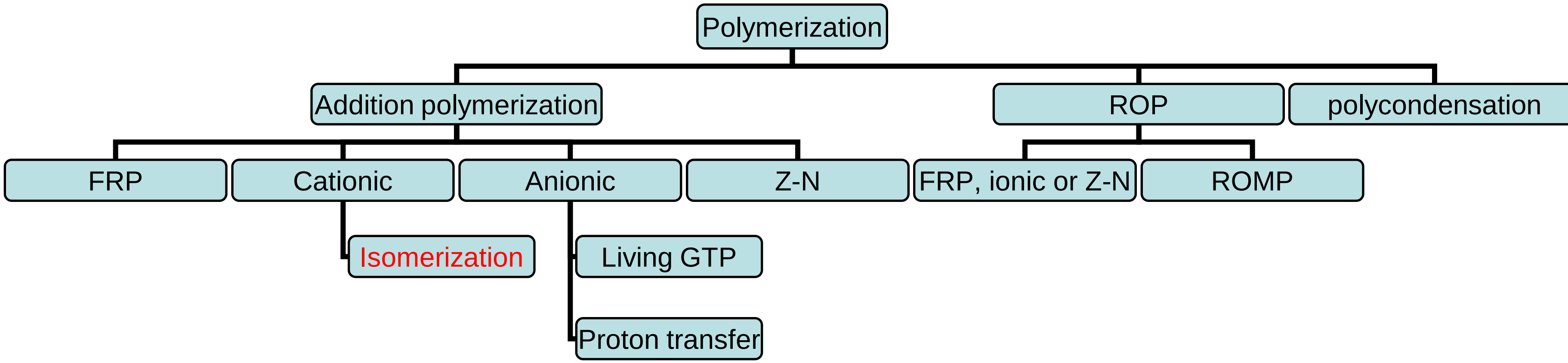
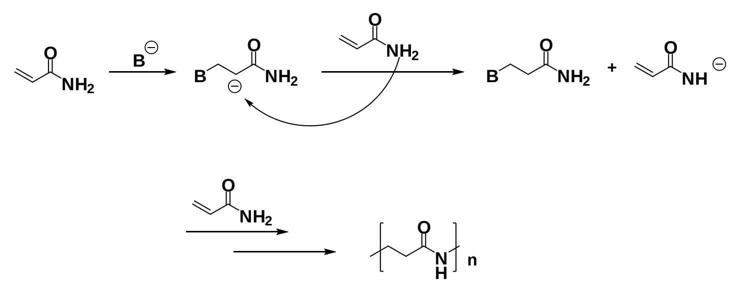


TABLE 3-1 Types of Chain Polymerization Undergone by Various Unsaturated Monomers

	Type of Initiation		
Monomers	Radical	Cationic	Anionic[a]
Ethylene	+	−	+
1-Alkyl alkenes (α-olefins)	−	−	+
1,1-Dialkyl alkenes	−	+	−
1,3-Dienes	+	+	+
Styrene, α-methyl styrene	+	+	+
Halogenated alkenes	+	−	−
Vinyl esters (CH_2=CHOCOR)	+	−	−
Acrylates, methacrylates	+	−	+
Acrylonitrile, methacrylonitrile	+	−	+
Acrylamide, methacrylamide	+	−	+
Vinyl ethers	−	+	−
N-Vinyl carbazole	+	+	−
N-Vinyl pyrrolidone	+	+	−
Aldehydes, ketones	−	+	+

Step-wise anionic polymerization



Polymerization

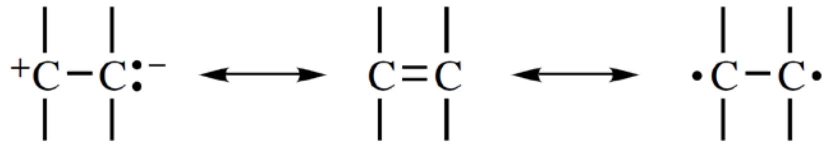
Mechanism

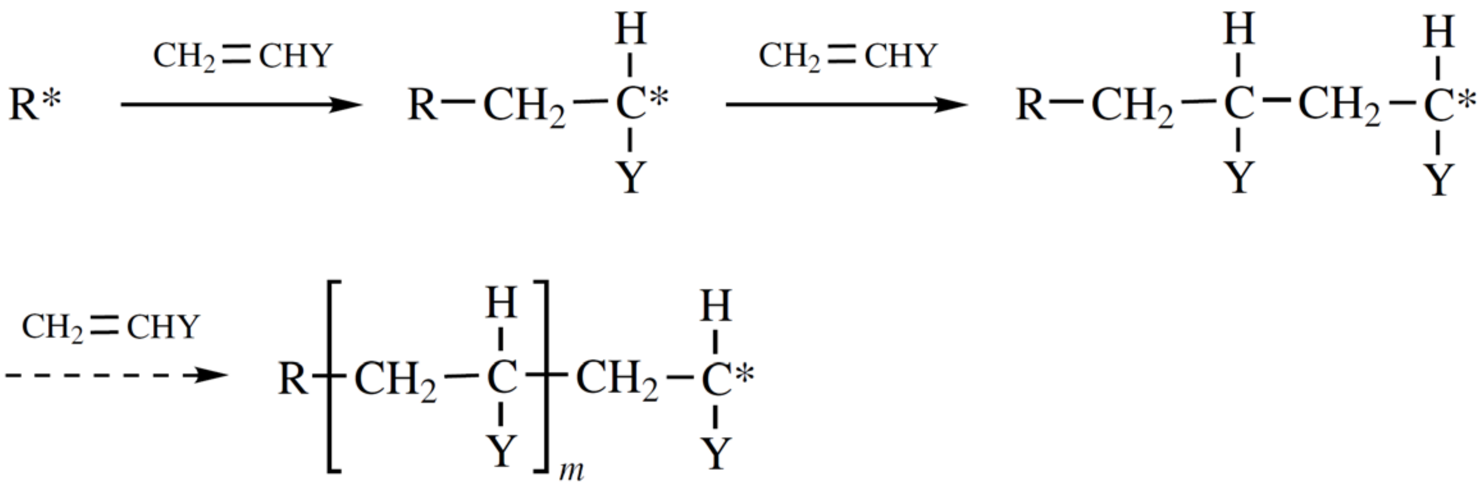
- Stepwise Polymerization
- Chain Polymerization

  Active Center

  - Free radical polymerization
  - Cationic polymerization
  - Anionic polymerization

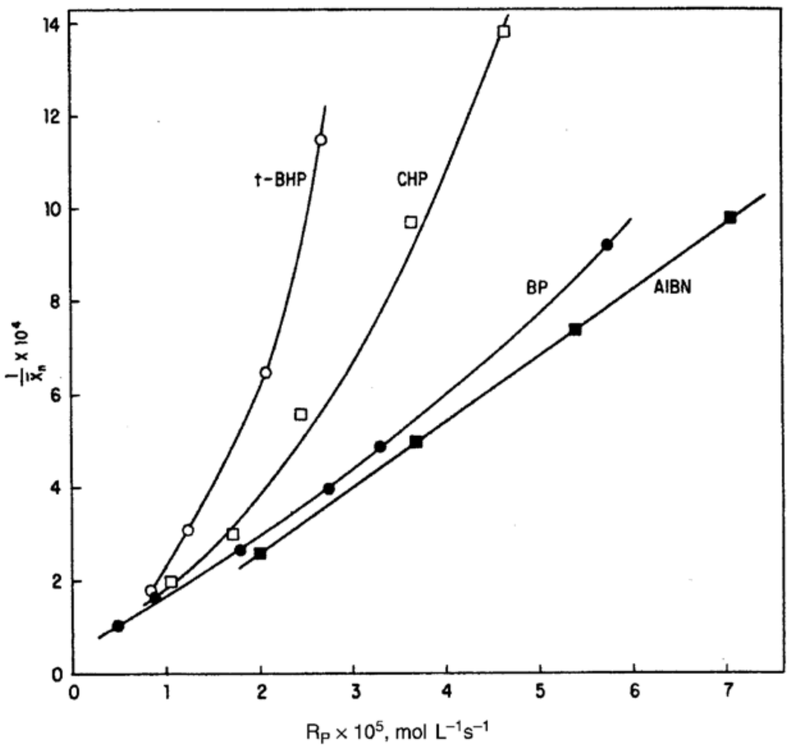
Free radical polymerization



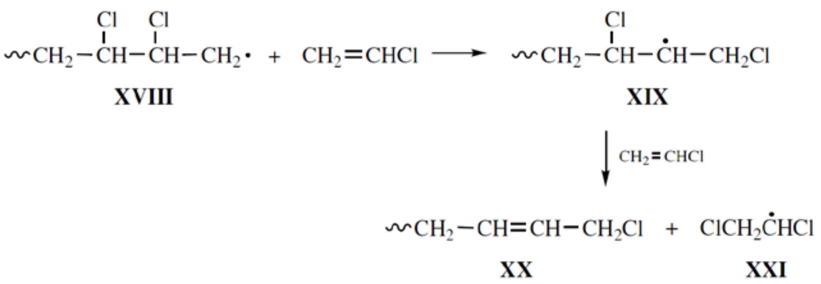


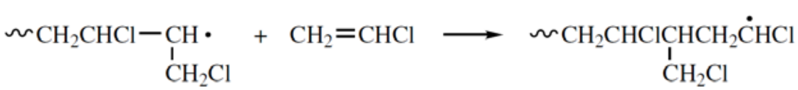
Free radical polymerization

- Chain transferring to initiator, monomer, solvent, polymer, chain-transfer-agent



Dependence of DP of styrene on the polymerization rate. The effect of chain transfer to initiator is shown for t-butyl hydroperoxide (o), cumyl hydroperoxide (□). Benzoyl peroxide (•), and azobisisobutyronitrile (♦) at 60 ºC.

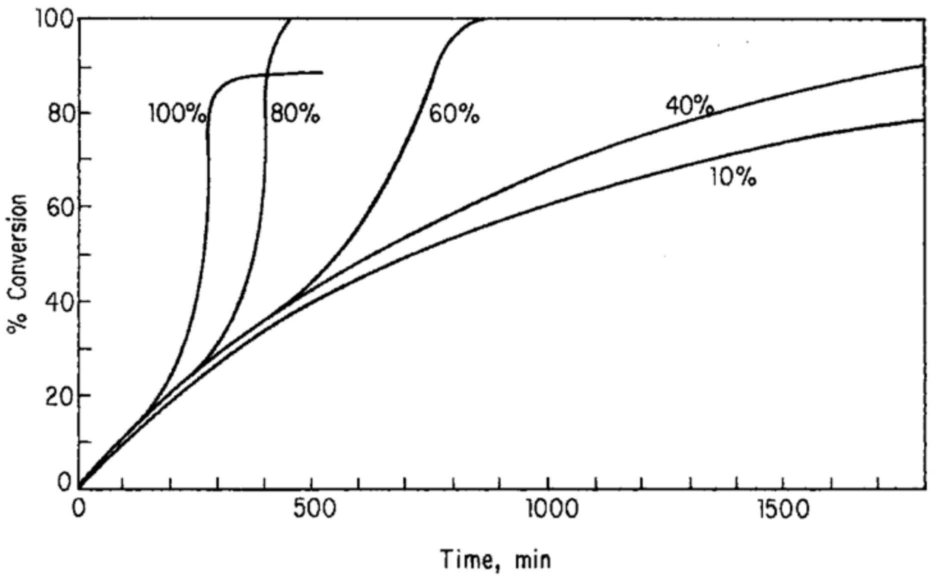




Long branches in PVC, up to about one branch per 2000 monomer units, arise from hydrogen abstraction at the CHCl group in the polymer chain

Free radical polymerization

Trommsdorf-Norrish effect (auto-acceleration)

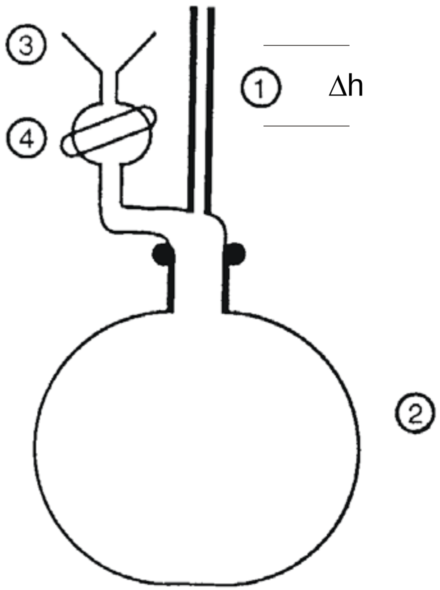


Autoacceleration in benzoyl peroxide–initiated polymerization of methyl methacrylate in benzene at 50 ^{o}C. The different plots represent various concentrations of monomer in solvent.

Emulsion, disperse, suspension polymerization!

Free radical polymerization

Dilatometry (polymerization rate constant)



Monomer ⟹ **Polymer**

Cationic polymerization

Initiation:

$$HA + RR'C{=}CH_2 \longrightarrow RR'\overset{+}{C}(CH_3)(A)^-$$

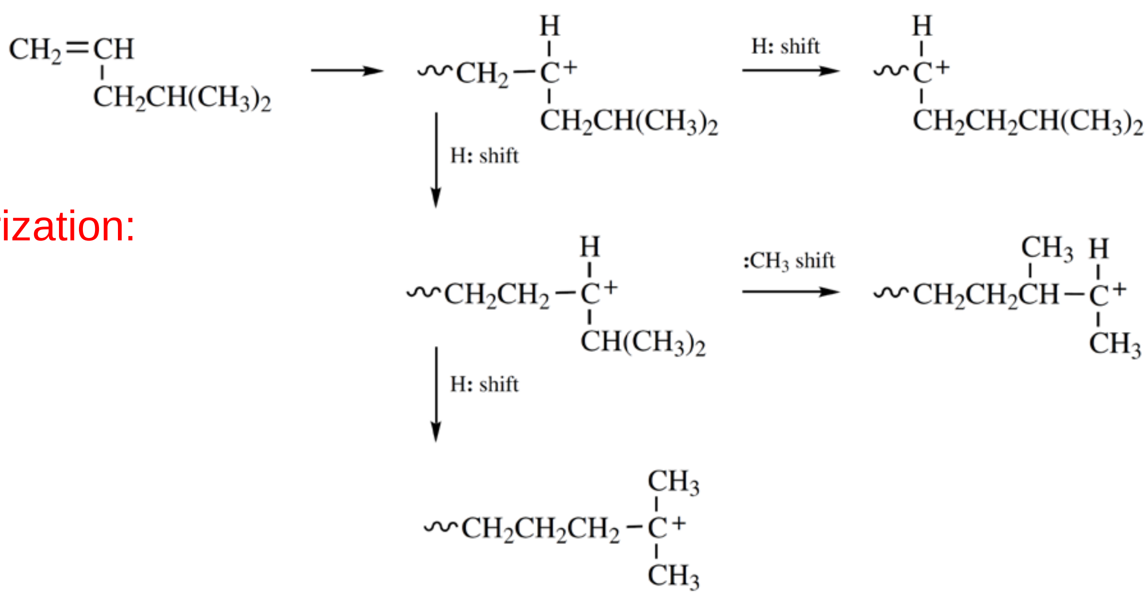
$$BF_3 + H_2O \rightleftharpoons BF_3\cdot OH_2$$

$$BF_3\cdot OH_2 + (CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_3C^+(BF_3OH)^-$$

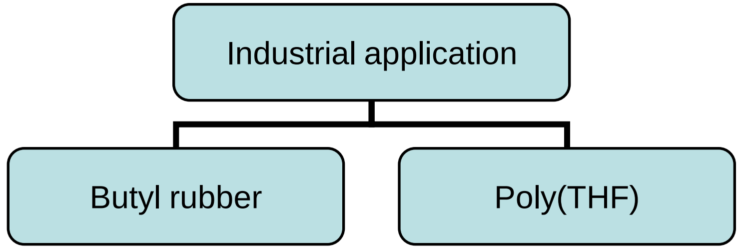
Solvent effect:

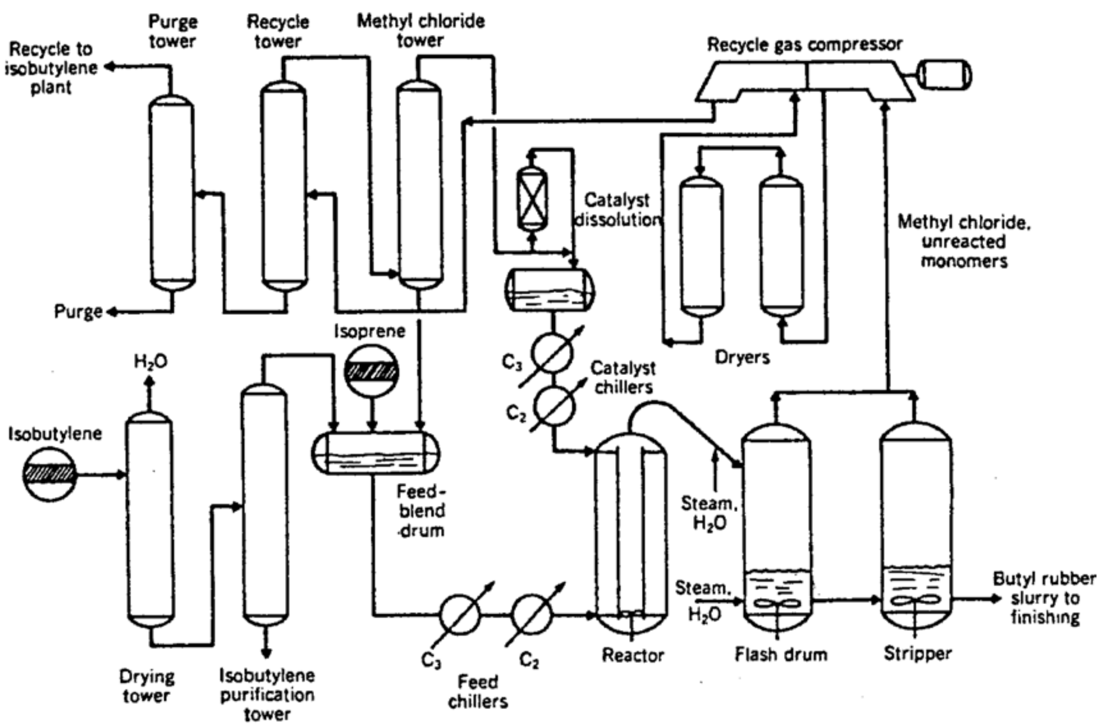
I	II	III	IV
$\sim BA$	$\sim B^+A^-$	$\sim B^+\|\|A^-$	$\sim B^+ + A^-$

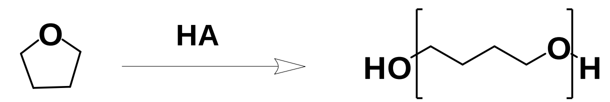
Isomerization:



Cationic polymerization







Mw 650, 1000, 2000

Polyurethane elastomers with high performance

-100~-90 ^{o}C; $AlCl_3$ (isobutylene+0.5-2.5% isoprene)

Anionic polymerization

General:

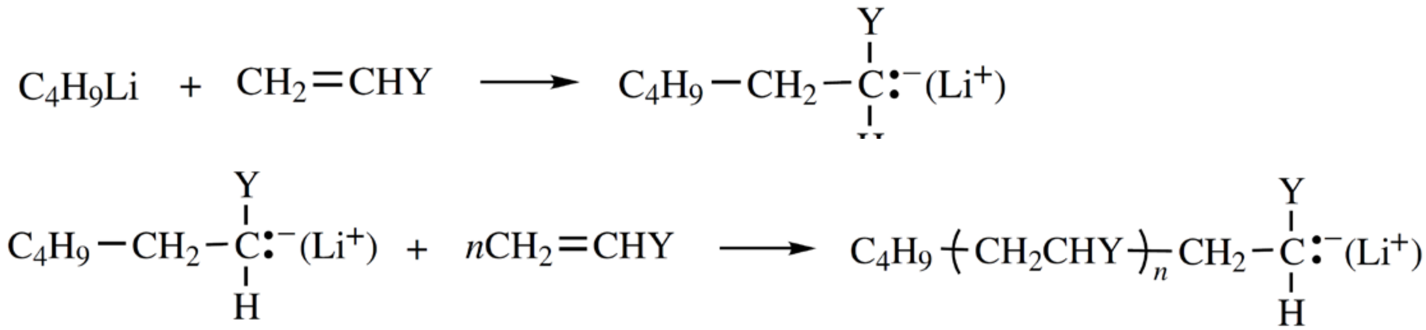
$$A^{\oplus} B^{\ominus} + M \longrightarrow B M^{\ominus} A^{\oplus} \text{- - - - - -} \xrightarrow{M} -M_n-$$

$B^{\ominus}$: Anionic active center, nucleophile

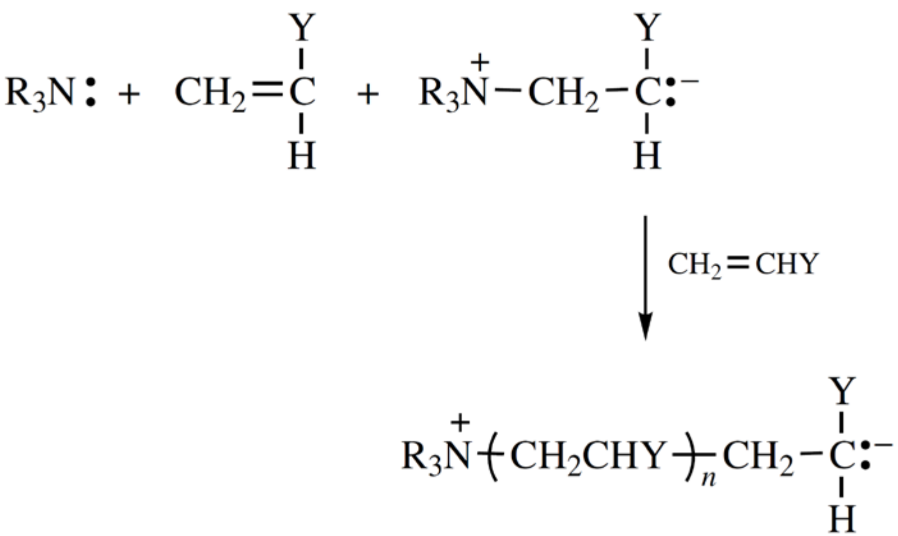
$A^{\oplus}$: anti ion, metallic ion

Anionic polymerization

Strong base:

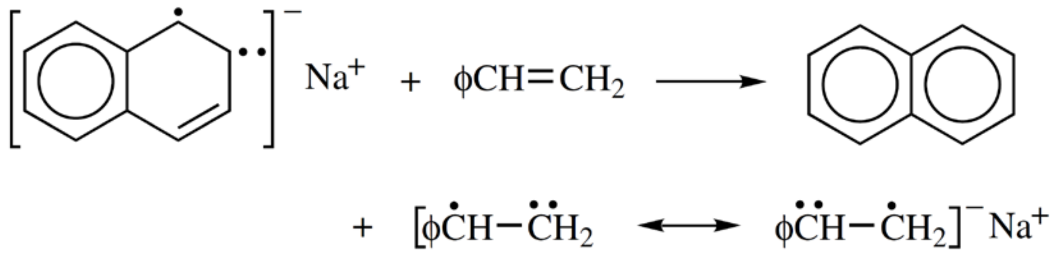


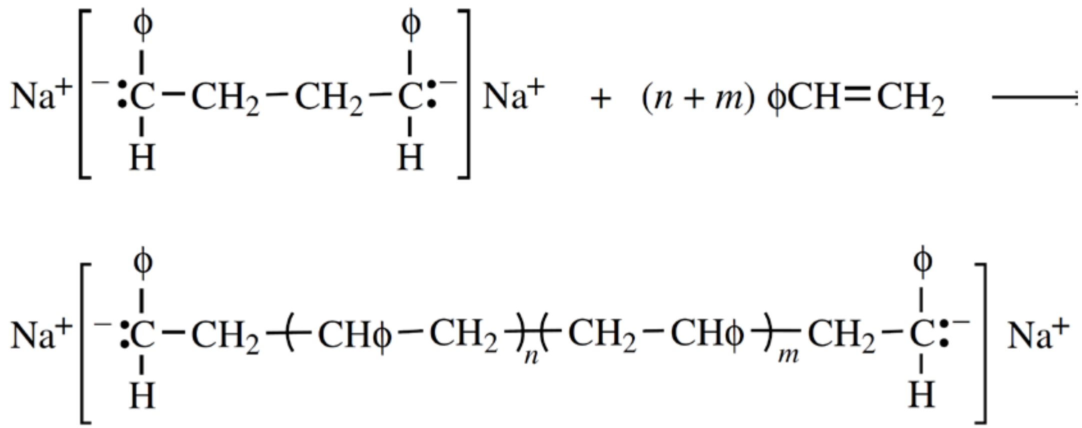
Weak base:



Anionic polymerization

Electron transfer:

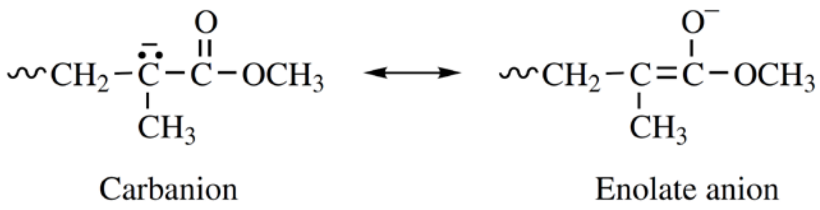




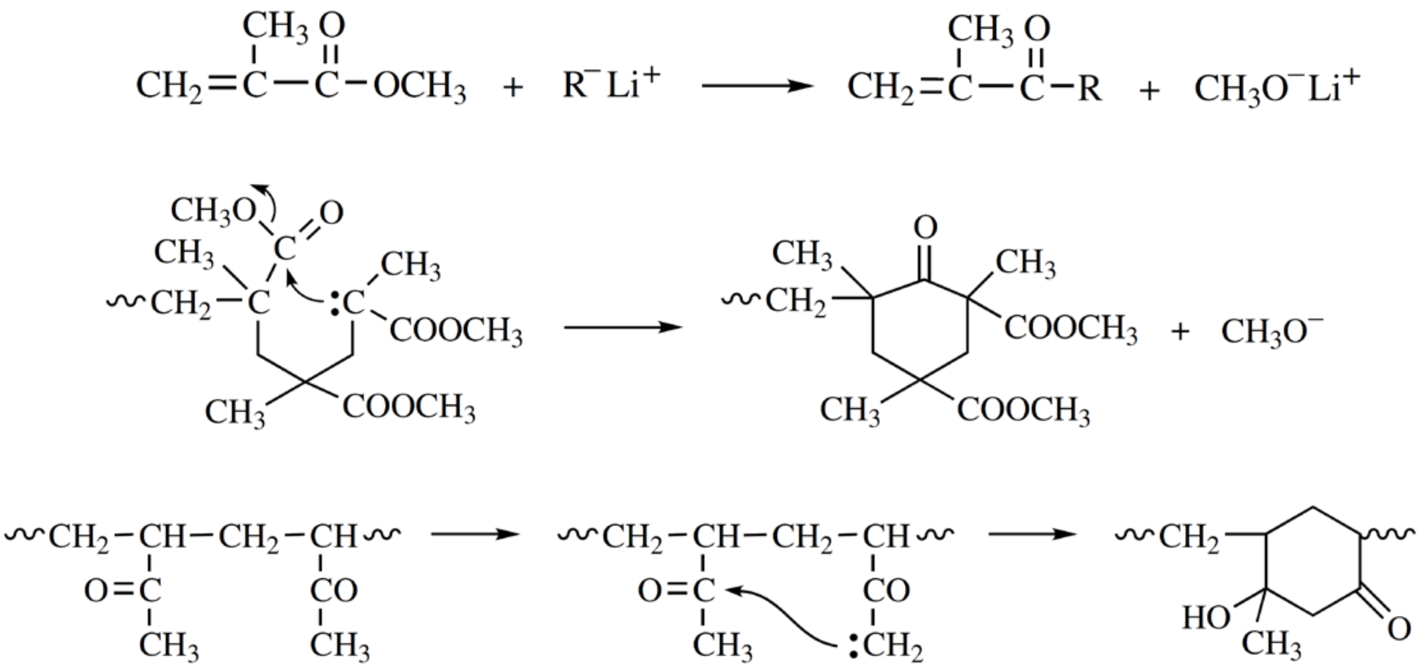
Solvent effects, temperature effect → **Stereoselectivity**

isotactic syndiotactic

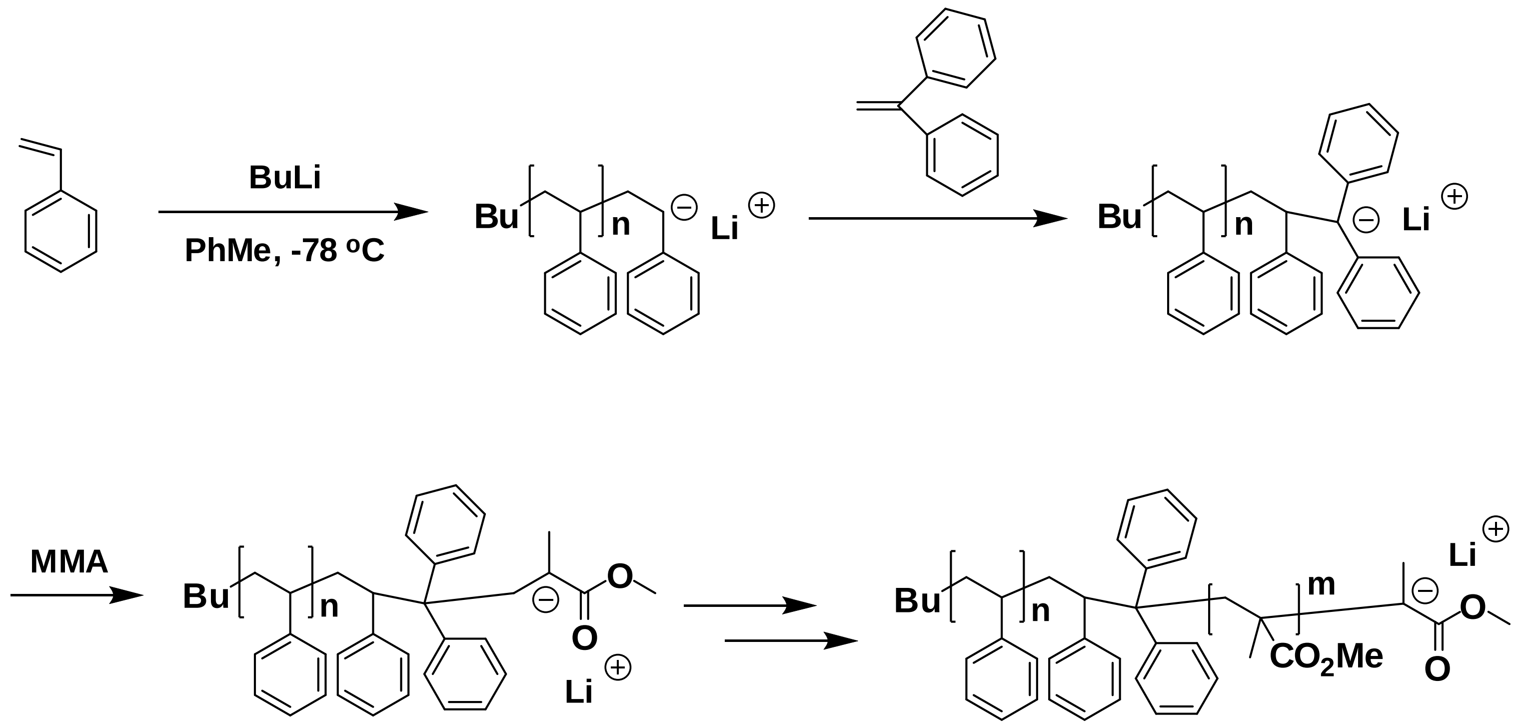
Anionic polymerization



Termination of polar monomer



Anionic polymerization for block copolymers: polystyrene-b-PMMA



Q1: Synthesis of Isotactic and Syndiotactic Poly (methyl methacrylate) from DME(1,2-dimethoxyethane) at –50 ° C or toluene at –78 ° C?

Q2: Whether it’s possible to synthesis the block copolymer via PMMA block first and PS block second? Why?

Anionic polymerization

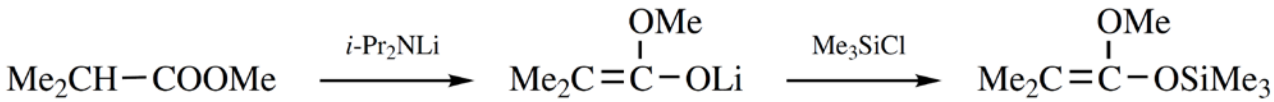
SBS synthesis

1) S → PS $\xrightarrow{+S+B}$ SBS

2) S+B → SB $\xrightarrow{+S}$ SBS

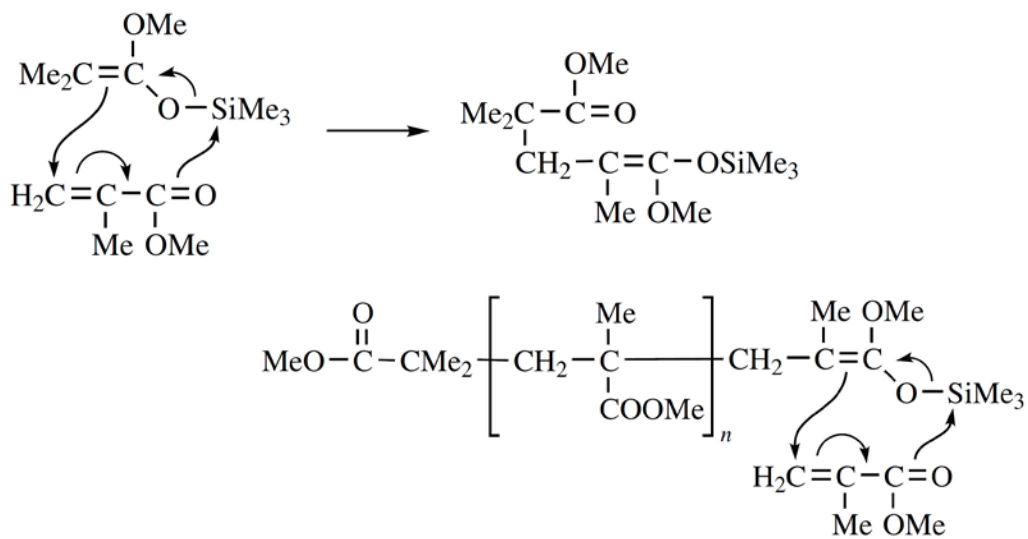
Group transfer polymerization (GTP)

Initiator:

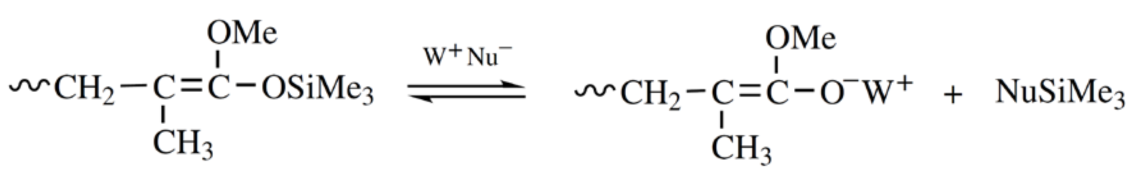


Either nucleophilic or Lewis acid catalyst needed

Electrophilic GTP:



Nucleophilic GTP:



Polycondensation

K. Pang, R. Kotek, A. Tonelli, **Review of conventional and novel polymerization processes for polyesters**. *Prog. Polym. Sci.* **2006**, *31*, 1009–1037

Coordination polymerization

E. Y.-X. Chen, **Coordination Polymerization of Polar Vinyl Monomers by Single-Site Metal Catalysts.** *Chem. Rev.* **2009,** *109,* 5157