Living Cationic Polymerization

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Outline

- History/Timeline
- Initiation
- Reversible Termination
- Telechelic Polymers
- Applications

Joseph P. Kennedy

Univ. of Akron (OH)

Mitsuo Sawamoto

Kyoto University (Japan)

History

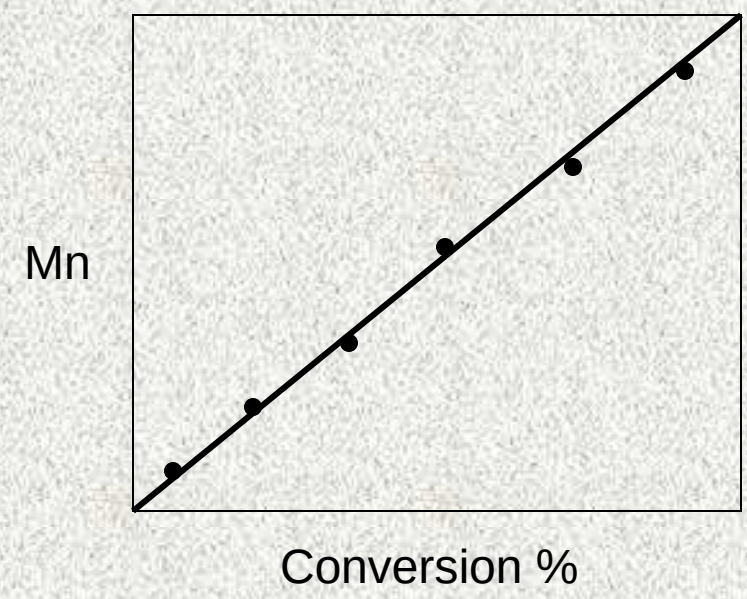
- 1956 Szwarc: Demonstrates Living Anionic Polymerization
- 1957-60 Kennedy exposed to Cationic Polymerization while at Exxon
- 1979-83 Kennedy Shows First Evidence of “Livingness” in Cationic Polymerizations
- 1984 Sawamoto Demonstrates Living Cationic Polym. Using vinyl ether and HI/I_2
- 1987 Kennedy Publishes First Example of Living Polymerization of Isobutylene

The Concept

- A Living Polymerization Requires…
  - Mn increases linearly with monomer conversion
  - Can resume polymerization by adding more monomer
  - Very narrow PDIs (~1.03 - 1.10)

Szwarc did it with anions;

What about cations??



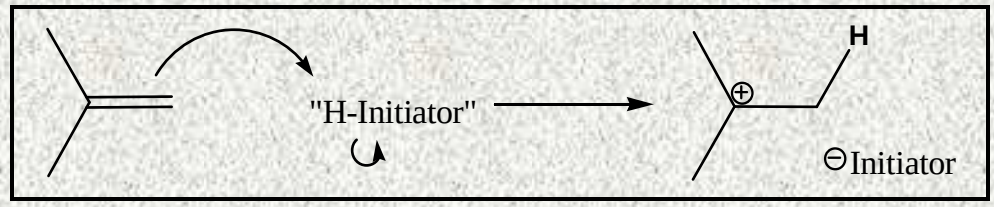
The Challenge

- Chain Transfer is the KILLER
  - Lower Mn and larger PDIs
  - How to Prevent?

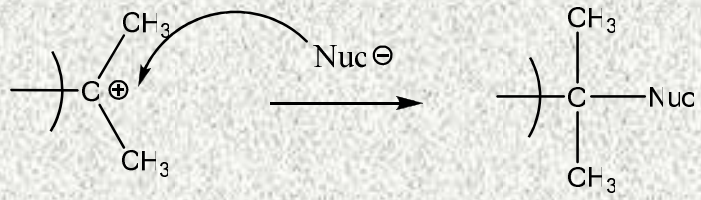
- Propagation is very *fast*
  - Exothermic → heat → more chain transfer
  - Lower Temps

How else? *Choice of initiator is key*

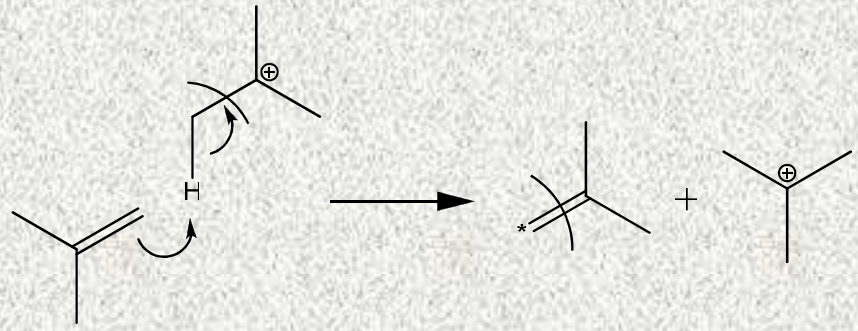
Preventing Chain Transfer



Termination:



Chain Transfer via Elimination:



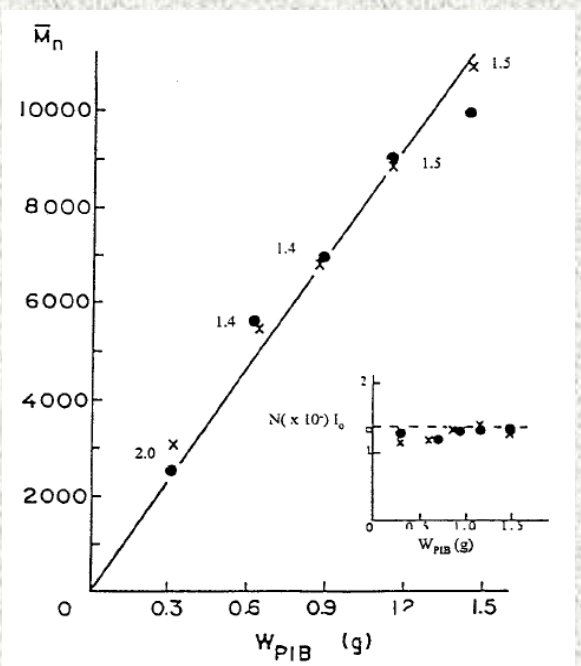
Counteranion of initiator must be:

- poor nucleophile
- Non-basic

Initiation

- Kennedy's Early Work

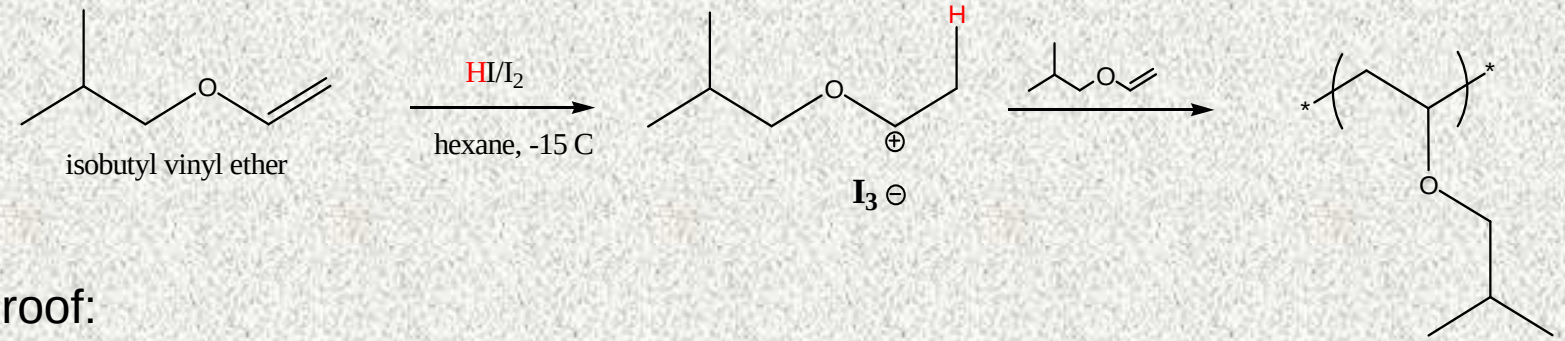
cumyl acetate



Kennedy, J.P., J. Polym. Sci., **1999**, *37,* 2285

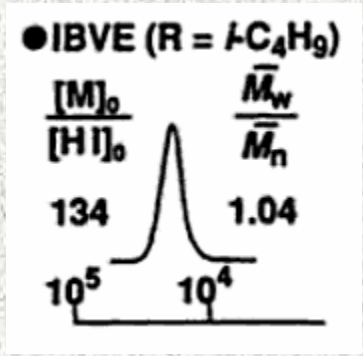
Initiation

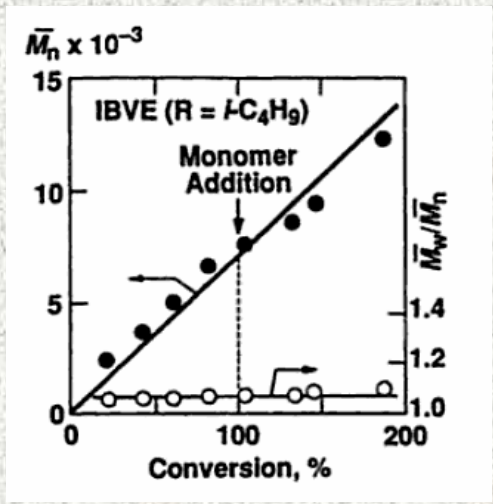
- Sawamoto's HI/I_2 System



isobutyl vinyl ether

Proof:

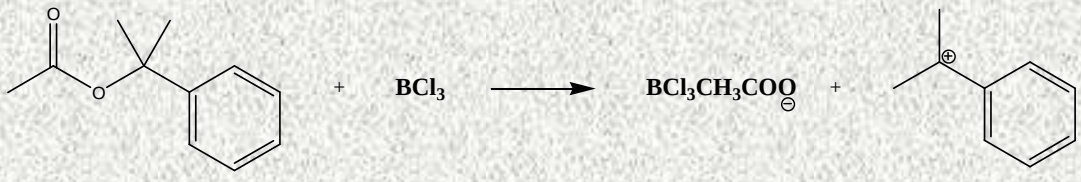


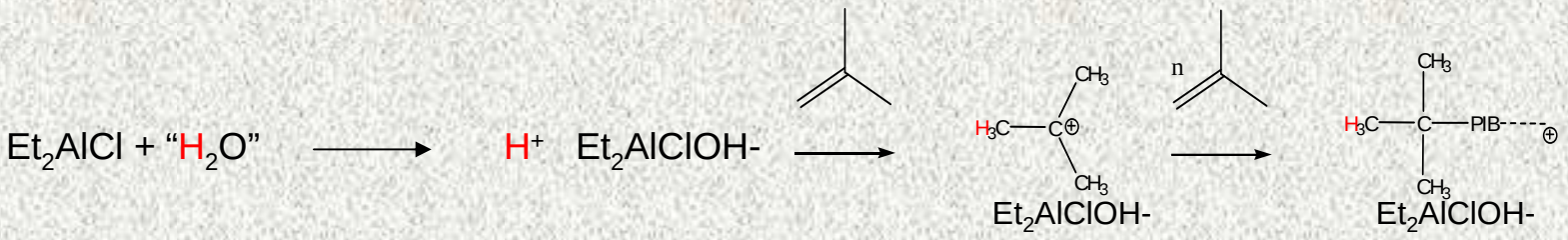


Sawamoto, et al. *Macromolecules,* **1984**, *17,* 265

Scope

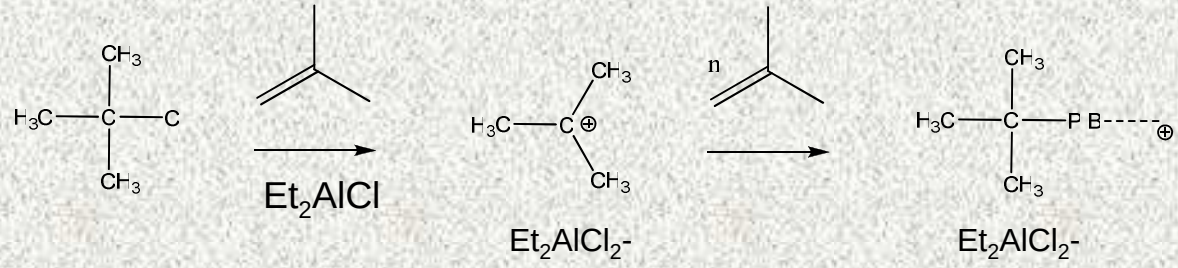
- Initiators





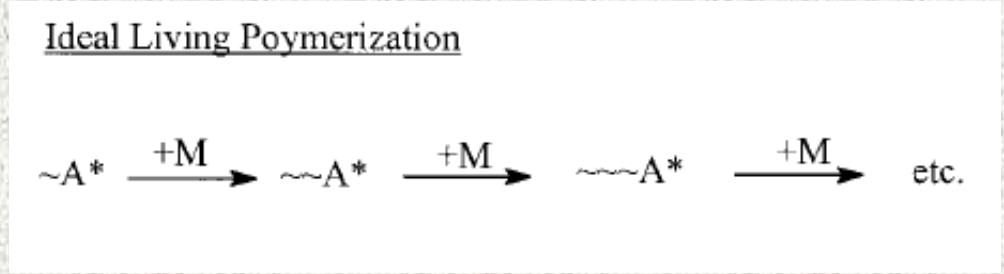
*Many other Protonic Acid/Lewis Acid Combos: $HCl/SnCl_4$, $HCl/TiCl_4$, TFA/Et_2AlCl, etc.

PIB = poly(isobutylene)



Kennedy, J.P., J. Polym. Sci., **1999**, *37,* 2285

Case of Ideal Living Polymerization



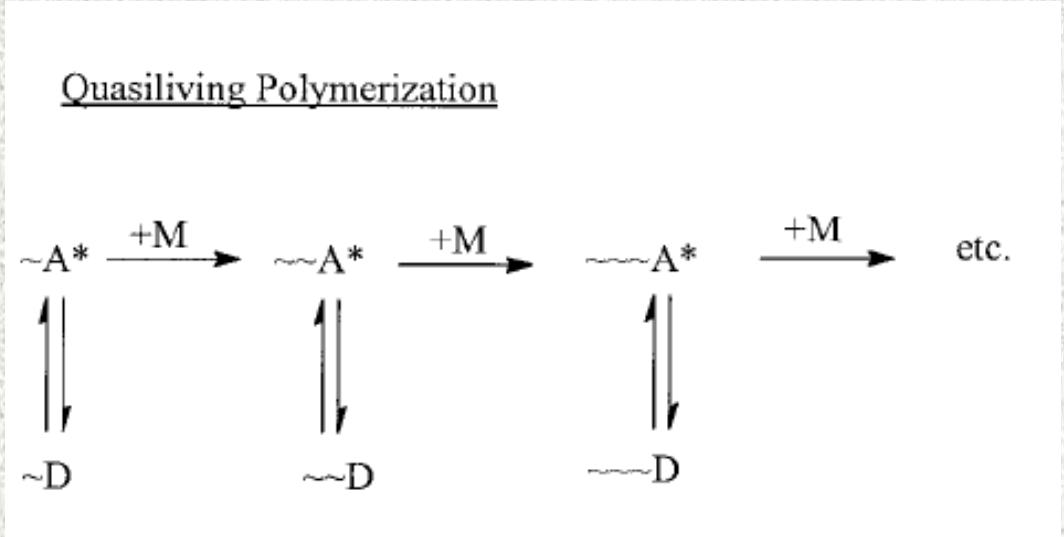
~A* = active propagating species

- All ~A* active all the time
- NO chain transfer or termination

But Carbocations are much more short-lived (rearrangement, elimination, etc.) than anions, So how is a "Living" Polymerization possible?

Kennedy, J.P., J. Polym. Sci., **1999**, *37,* 2285

Reversible Termination



~D = Dormant species

- Termination and Chain Transfer *does* occur, but are *reversible*
- These rates are much higher than that of propagation

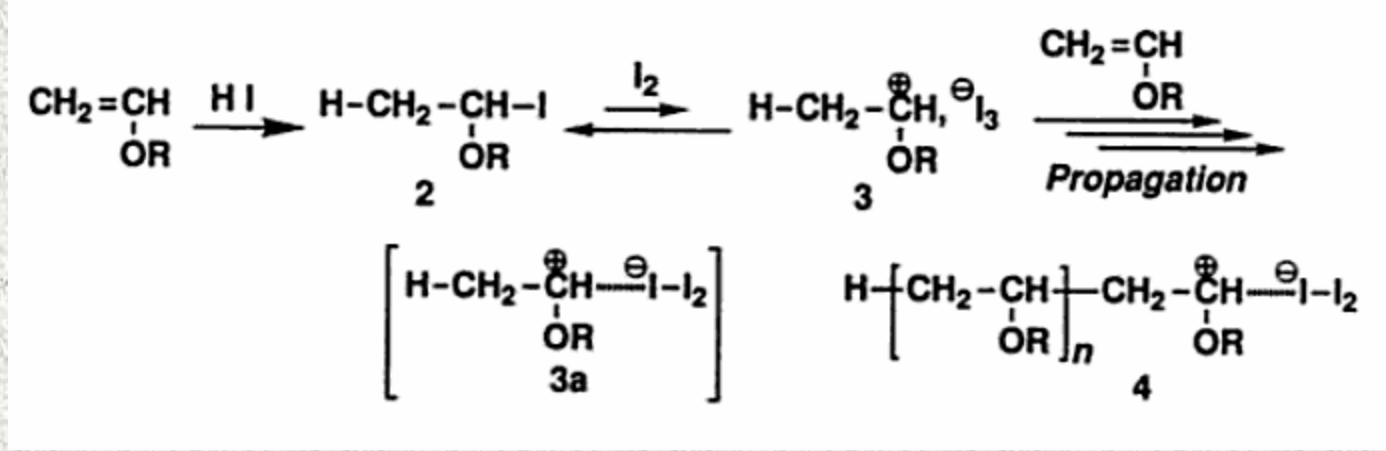
*compare to TEMPO!

"All living cationic polymerizations are, in fact, quasi-living systems"

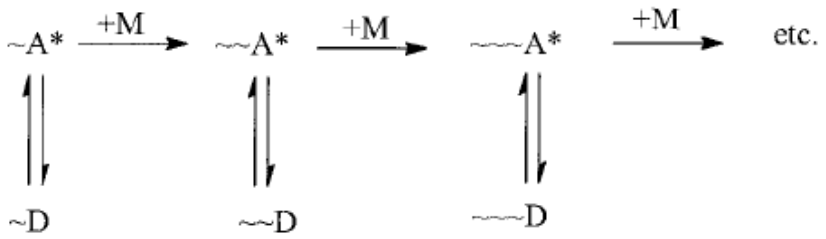
Kennedy, J.P., J. Polym. Sci., **1999**, *37,* 2285

Reversible Termination

- Sawamoto

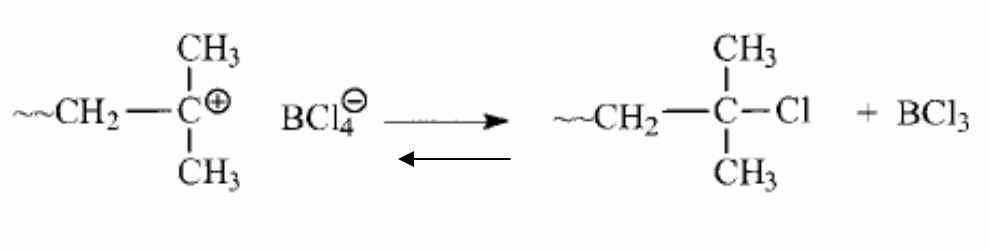


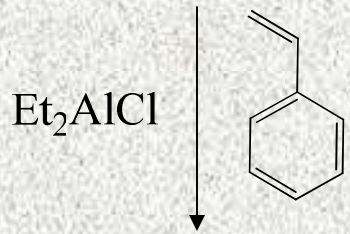
Quasiliving Polymerization



Sawamoto, Matyjaszewski, Cationic Polymerizations, 1996 p294

Reversible Termination





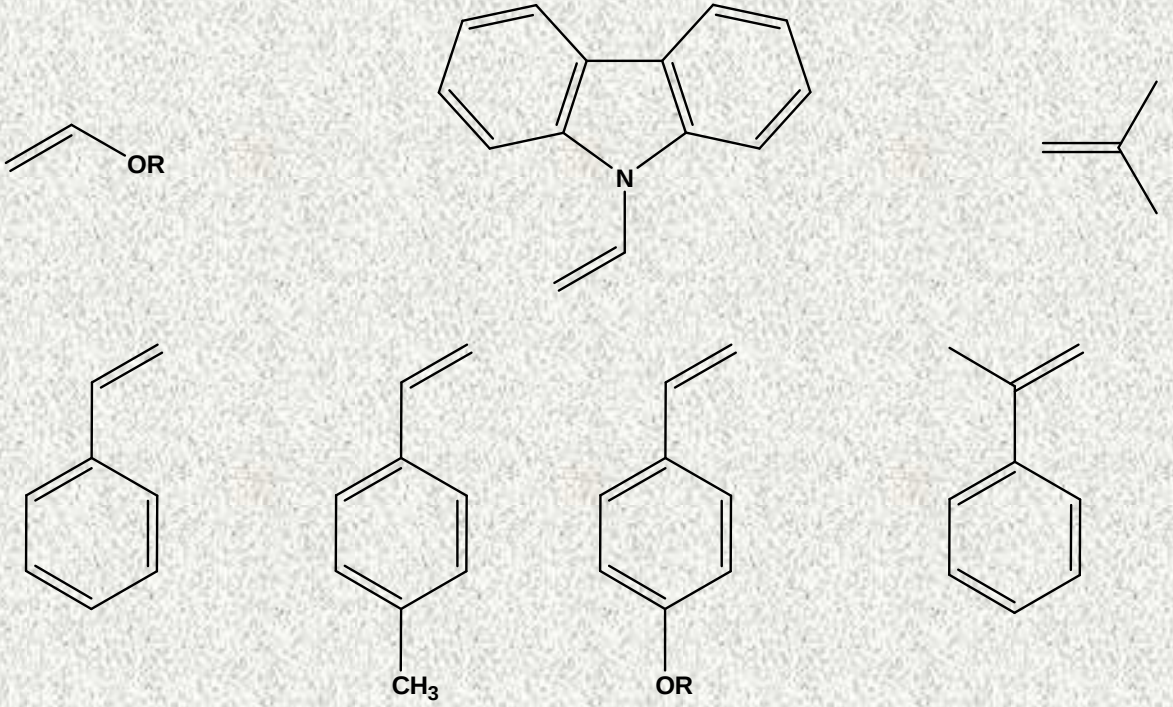
Block Copolymer

Mn increased linearly with conversion → First evidence of living polymerization

Kennedy et al, J Macromol Sci. **1982,** *A18*, *1229*

Scope

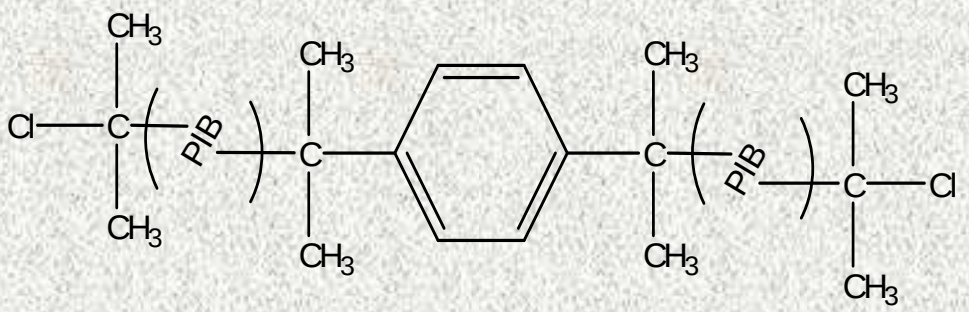
Monomers:



Telechelic Polymers

- Definition: Polymers that contain *functionalized* endgroups

ie.



Styrene

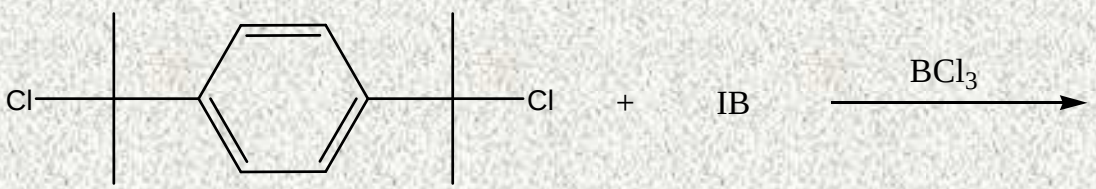
Et_2AlCl

Styrene-PIB-Styrene Triblock Polymer!

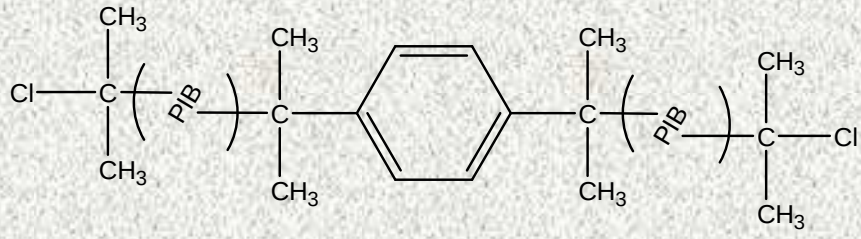
Kennedy, et al. J. Macromol. Sci. **1979**

Telechelics: Synthesis

- Made from “Inifers” (Initiator-Transfer Agents)
  - “agents that effect controlled initiation and propagation in the absence of chain transfer to a monomer”



“inifer”



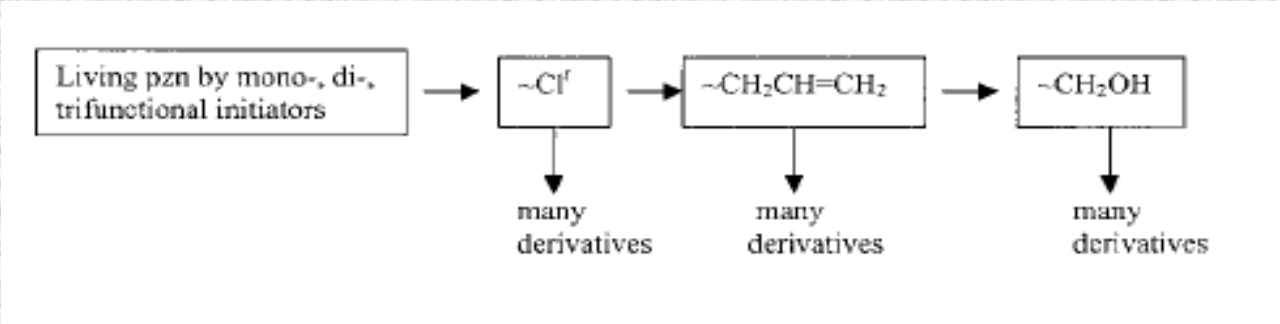
Telechelic polymer

Kennedy, et al. J. Macromol. Sci. **1979**

PIB = poly(isobutylene)

Telechelics

- Other end groups are accessible



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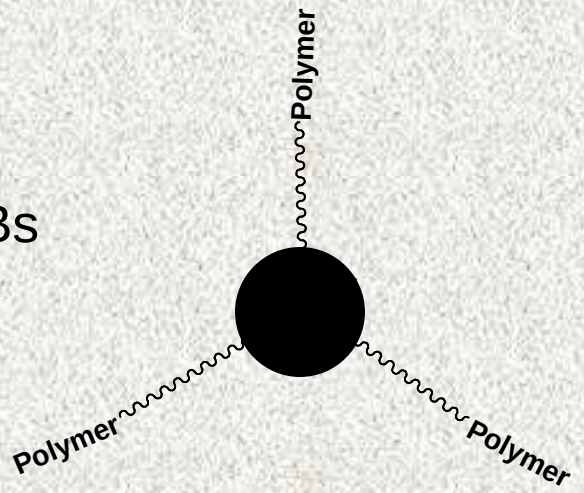
Applications

- Towards Industrial Scale
  - Thermoplastic elastomers
    - ie. PIB-Sty block copolymers
    - Easily made, cheap starting materials, superior mechanical properties
- Telechelics
  - Low MW → adhesives/sealants
    - Epion™ : silyl and allyl terminated PIBs
  - Specialty applications
    - Star-branched polymers



Questions?