

Group Transfer Polymerization (GTP)

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History of Group Transfer Polymerization



Owen W. Webster

- Group transfer polymerization (GTP) was discovered over 40 years ago under DuPont's exploratory research project.
- Because of the *living* nature, it allows one to make block and other specialized polymer chain architecture.
- DuPont used the process to make dispersing agents for pigmented inks and automobile finishes.



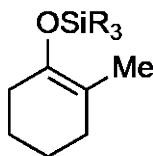


Outline

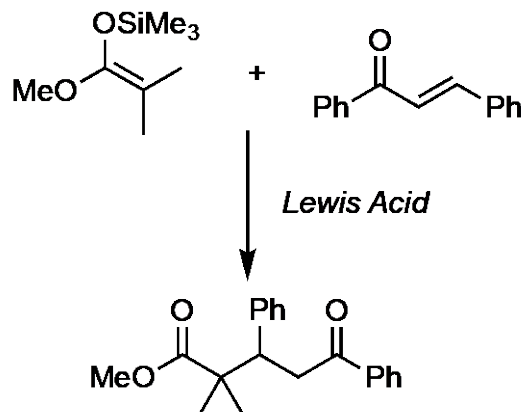


- **Living Polymerization**
- **Nucleophilic anion mediated GTP**
- **Acid mediated GTP**
- **Summary**

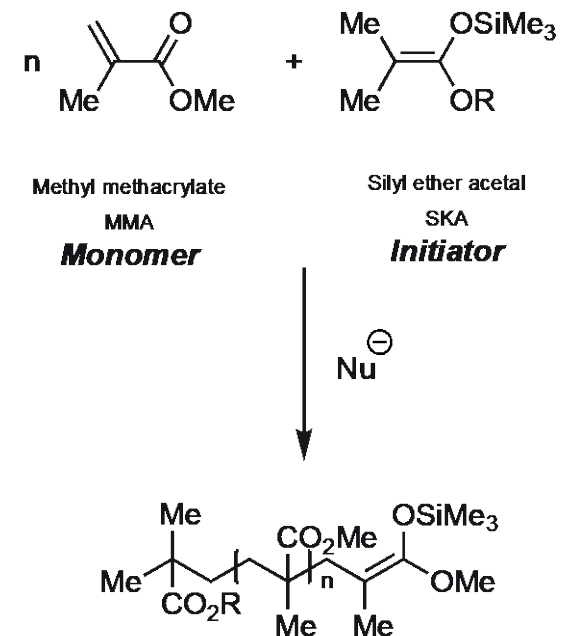
Organic root



Silyl enol ethers
Stork, House, Ojima and Nagai **1960s**



Silyl ketene acetal as Micheal donor
Mukaiyama 1970s



Silyl ketene acetal as initiator
Group Transfer Polymerization 1980s

- *The genesis of many polymerization methods can be traced directly to methods developed by synthetic organic chemists*
- *Ring-Opening Metathesis Polymerization (ROMP): Grubbs catalyst and Tebbe reagent*



Outline



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Living Polymerization

- Basic polymer chemistry concepts

$$M_n = \frac{\sum_{i=1}^N N_i M_i}{\sum_{i=1}^N N_i}$$

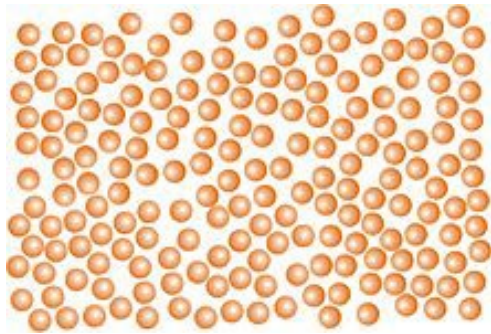
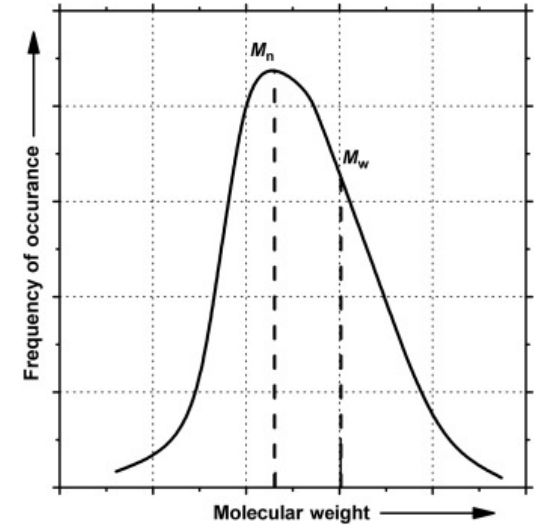
Number-average Molecular Weight

$$M_w = \frac{\sum_{i=1}^N w_i M_i}{\sum_{i=1}^N w_i} = \frac{\sum_{i=1}^N N_i^2 M_i}{\sum_{i=1}^N N_i M_i}$$

Weight-average Molecular Weight

$$\bar{D} = \frac{M_w}{M_n}$$

Dispersity: Molecular weight distribution, always larger than 1



\bar{D} close to 1
Uniform



\bar{D} much larger than 1

Living Polymerization

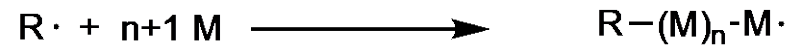
Chain Polymerization

Radical polymerization

Initiation



Propagation



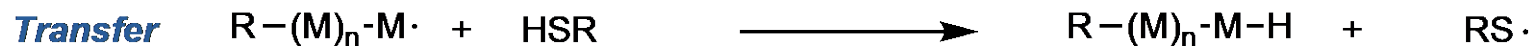
Termination



or



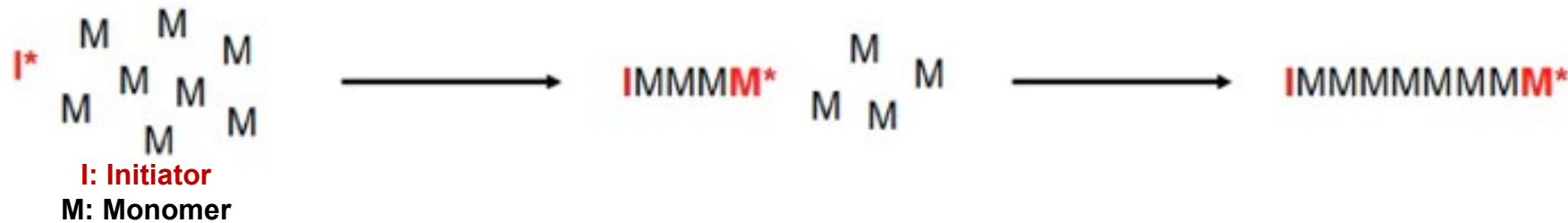
Transfer



Growth of a polymer chain proceeds exclusively by reactions between monomers and active sites on the polymer chain with regeneration of the active sites at the end of each growth step.

Living Polymerization

Living Polymerization



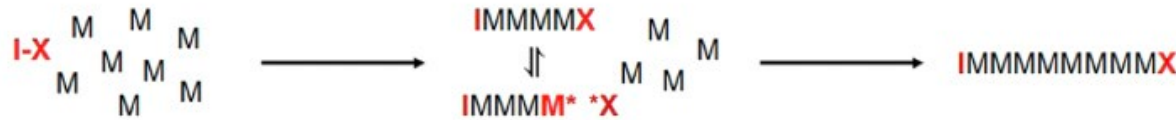
- No termination and irreversible transfer
- Rate of initiation (k_i) is greater than the rate of propagation (k_p)
- Irreversible addition of monomer to active site
- Extreme narrow molecular weight distribution (dispersity, \bar{D} , approaches 1)

$$\text{theor. } M_n = \frac{[M]_0}{[I]_0}$$

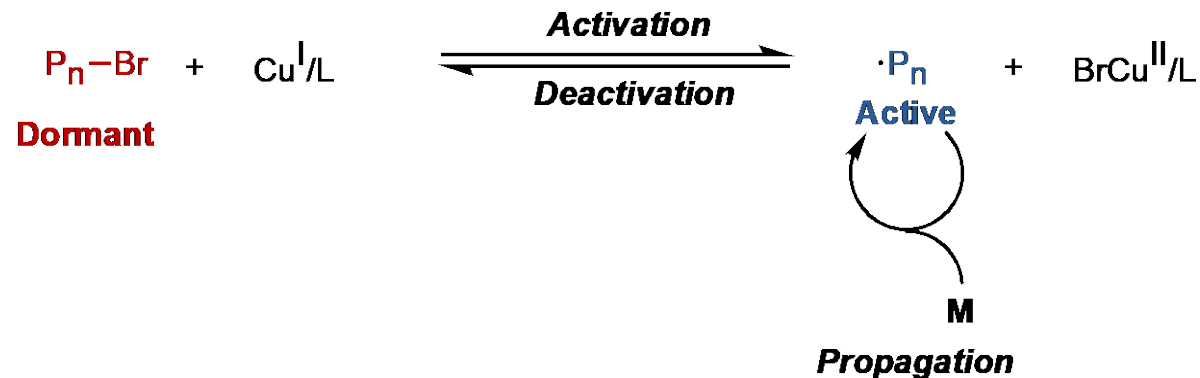
Living Polymerization

▪ Reversible Deactivation Polymerization

- Reversible termination of active chain ends



Atom Transfer Radical Polymerization (ATRP)



- Decreasing the concentration of active-site

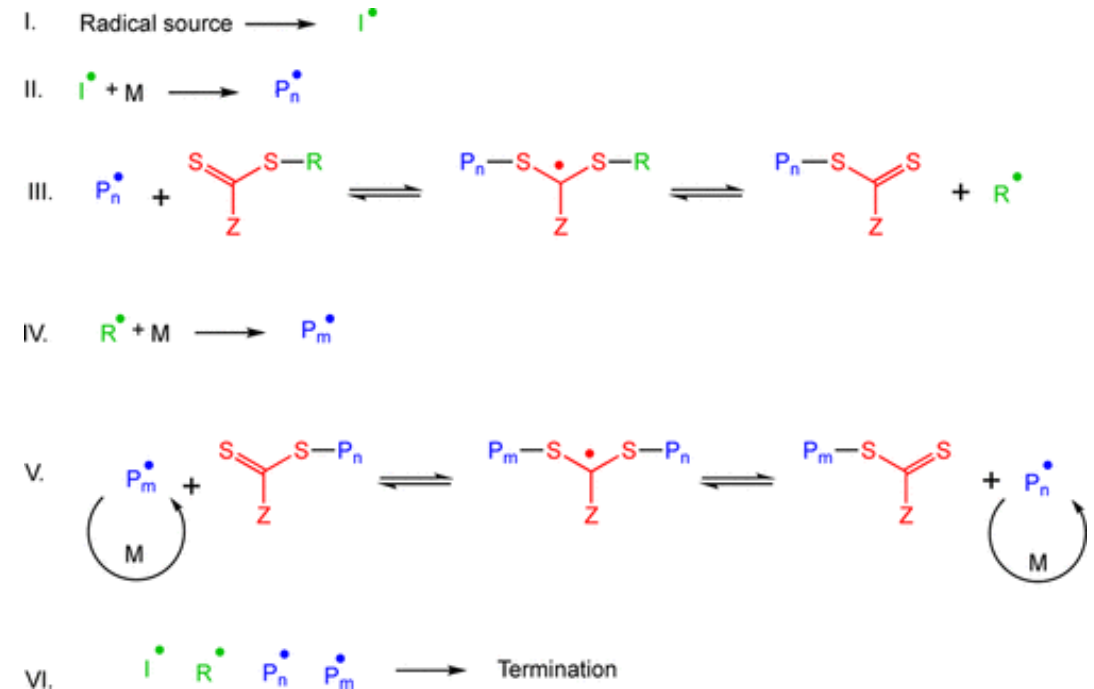
- Living-like method: retain the important characteristics of living polymerizations, chiefly low \bar{D} and efficient chain-end functionalization

- Irreversible termination or transfer reactions are inevitable because of radical nature

Living Polymerization

Reversible Deactivation Polymerization

Rapid degenerate exchange between dormant and active chain ends



Reversible addition–fragmentation chain transfer (RAFT)

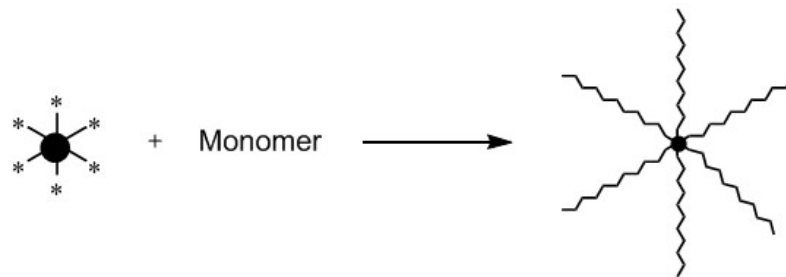
Living Polymerization

- Control Molecular Weight and Dispersity

$$\text{theor. } M_n = \frac{[M]_0}{[I]_0} \approx \text{exp. } M_n$$

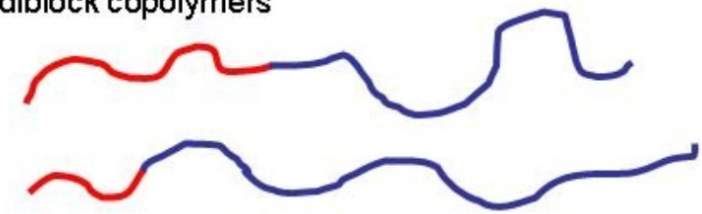
$$\mathcal{D} \rightarrow 1$$

- Synthesis of specialized polymer chain architecture



Star polymer

diblock copolymers



Block copolymer



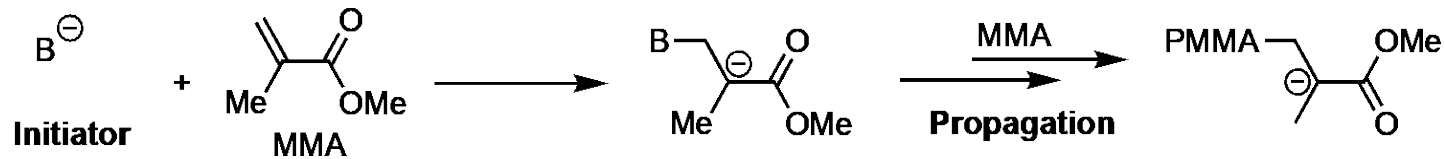
Outline



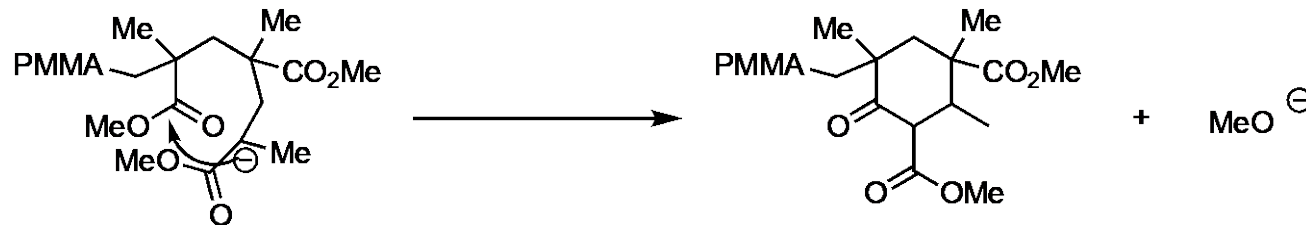
- Living Polymerization
- **Nucleophilic anion mediated GTP**
- Acid mediated GTP
- Summary

Nucleophilic Anion

▪ Anionic Polymerization of Methyl Methacrylate (MMA)



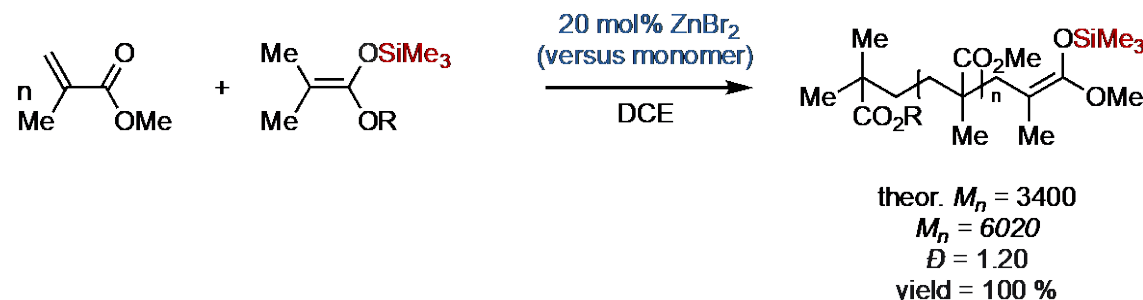
Termination: Backbiting



- *Anion is a relative stable species*
- *Living polymerization cryogenically*
- *High cost of cryogenic reaction*
- *Hard to commercialize*
- *Termination Mechanism: Backbiting*

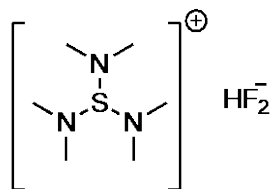
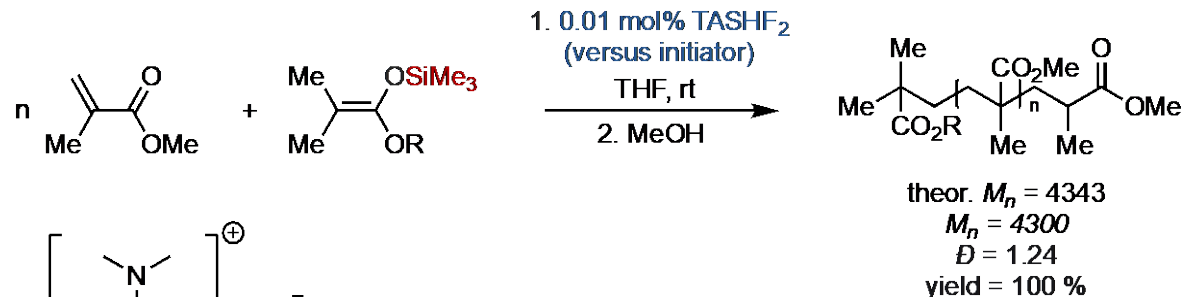
Nucleophilic Anion

First Attempt: Lewis Acid as Catalyst



Macromolecules, Vol. 17, No. 7, 1984

Serendipitous breakthrough:



tris(dimethylamino)sulfonium hexafluorophosphate
 TASHF_2

- Inspired by Mukaiyama-Michael addition
- Using ZnBr_2 suggested by Barry M. Trost
- Poor molecular weight control
- Large amount of catalyst

- Small amount of catalyst: without costly purification
- Living polymerization: good molecular weight control

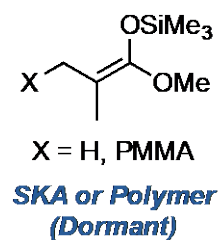
Nucleophilic Anion

■ Association Mechanism

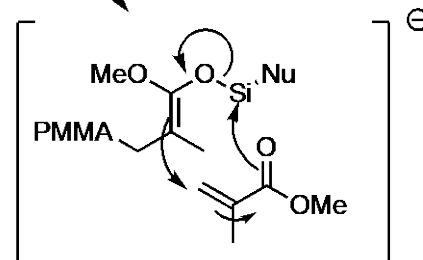
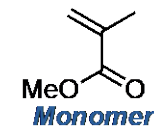
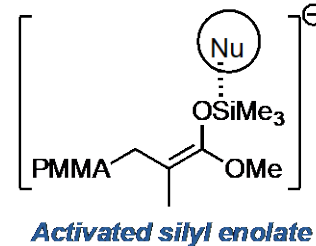
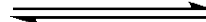
- Initially proposed by researchers in DuPont
- The source of group transfer polymerization suggested by Trost



Barry M. Trost



+

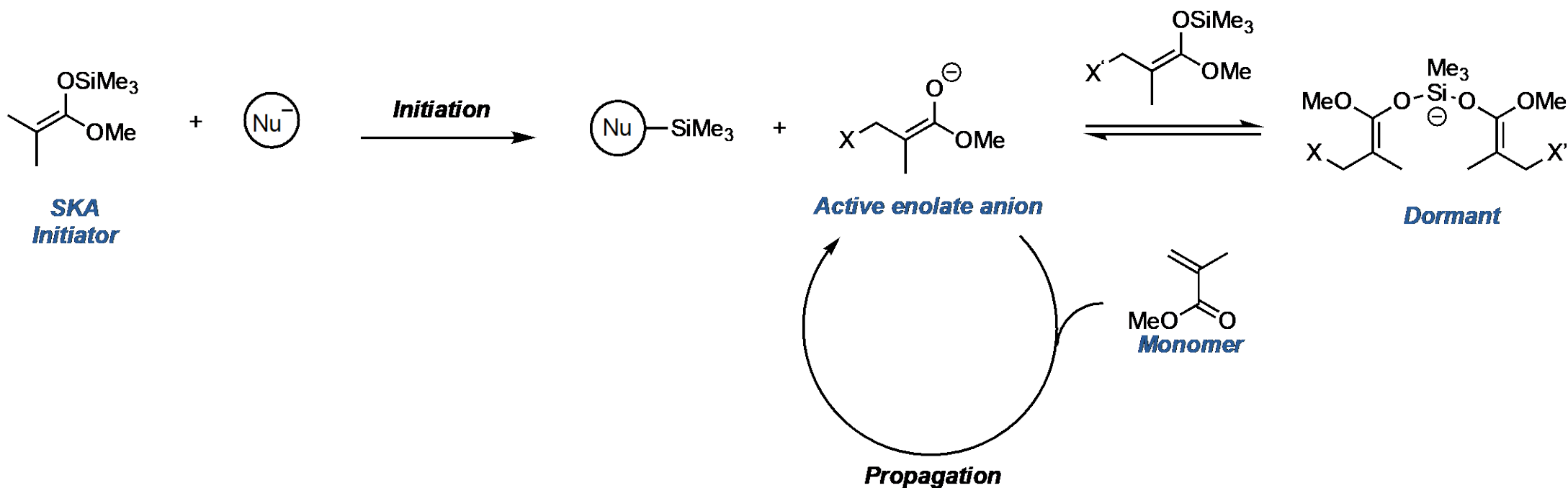


*Intramolecular transfer of the silyl group
Concerted mechanism*

Propagation

Nucleophilic Anion

- Dissociation Mechanism



Nucleophilic Anion

- Two reasons why people support association initially

- Reaction under room temperature

The ability to carry out the living polymerization of methyl methacrylate at ambient temperature and above, which certainly stands in sharp contrast to conditions required for living anionic polymerization of alkyl methacrylates, e.g. -78 °C,

- Absence of exchange of silyl groups

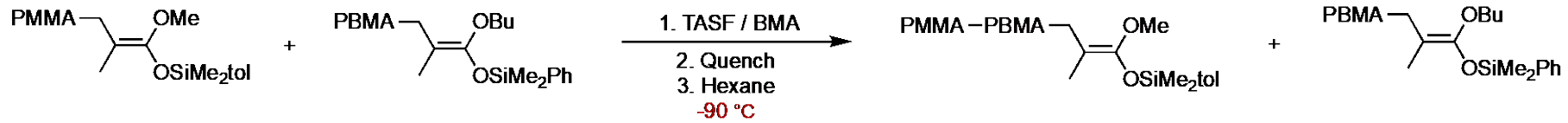
No exchange reported between silyl groups on growing polymer chains as would be required by the dissociative anionic mechanisms.

Nucleophilic Anion

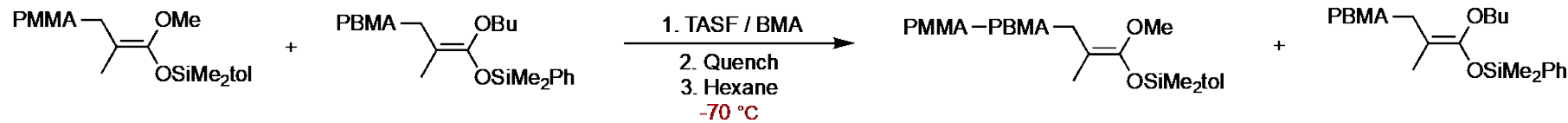
- Experimental evidences supporting dissociation mechanism

- Silyl group exchange experiment

DuPont

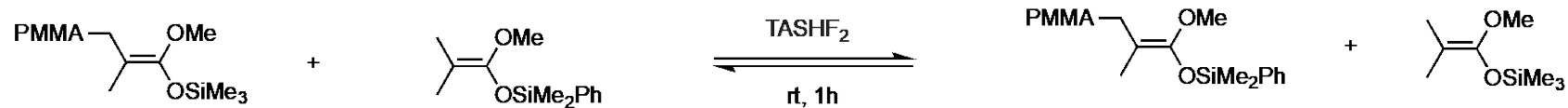


No silyl exchange



complete scrambling

Quirk's double-labeling experiment

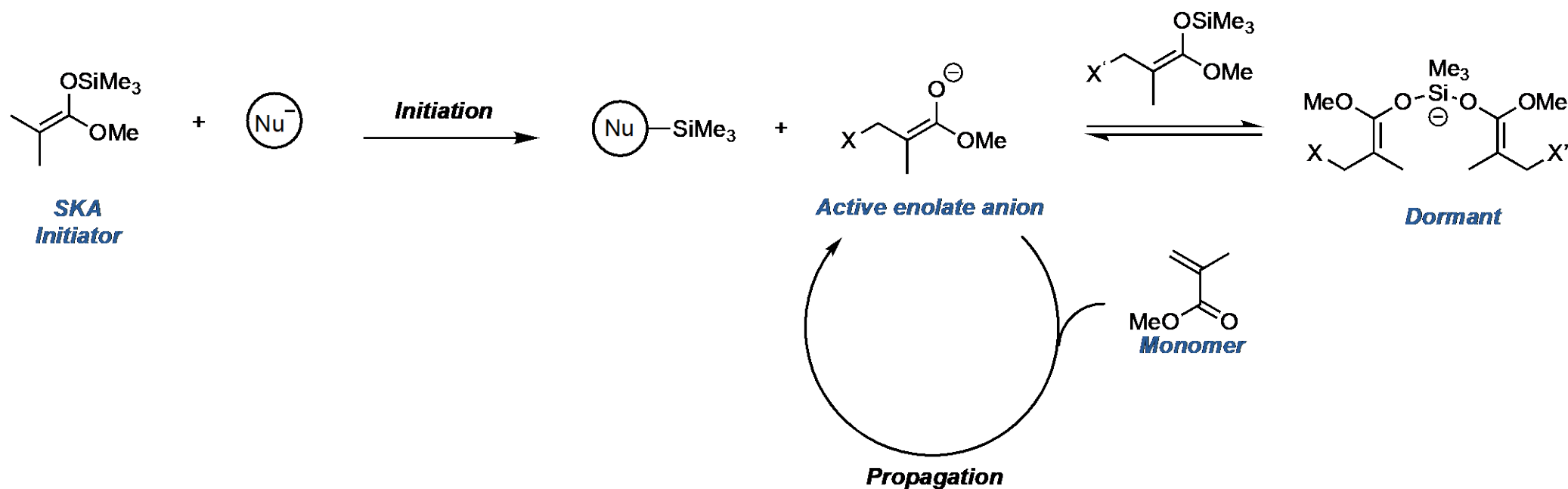


SKA

80% exchange

Nucleophilic Anion

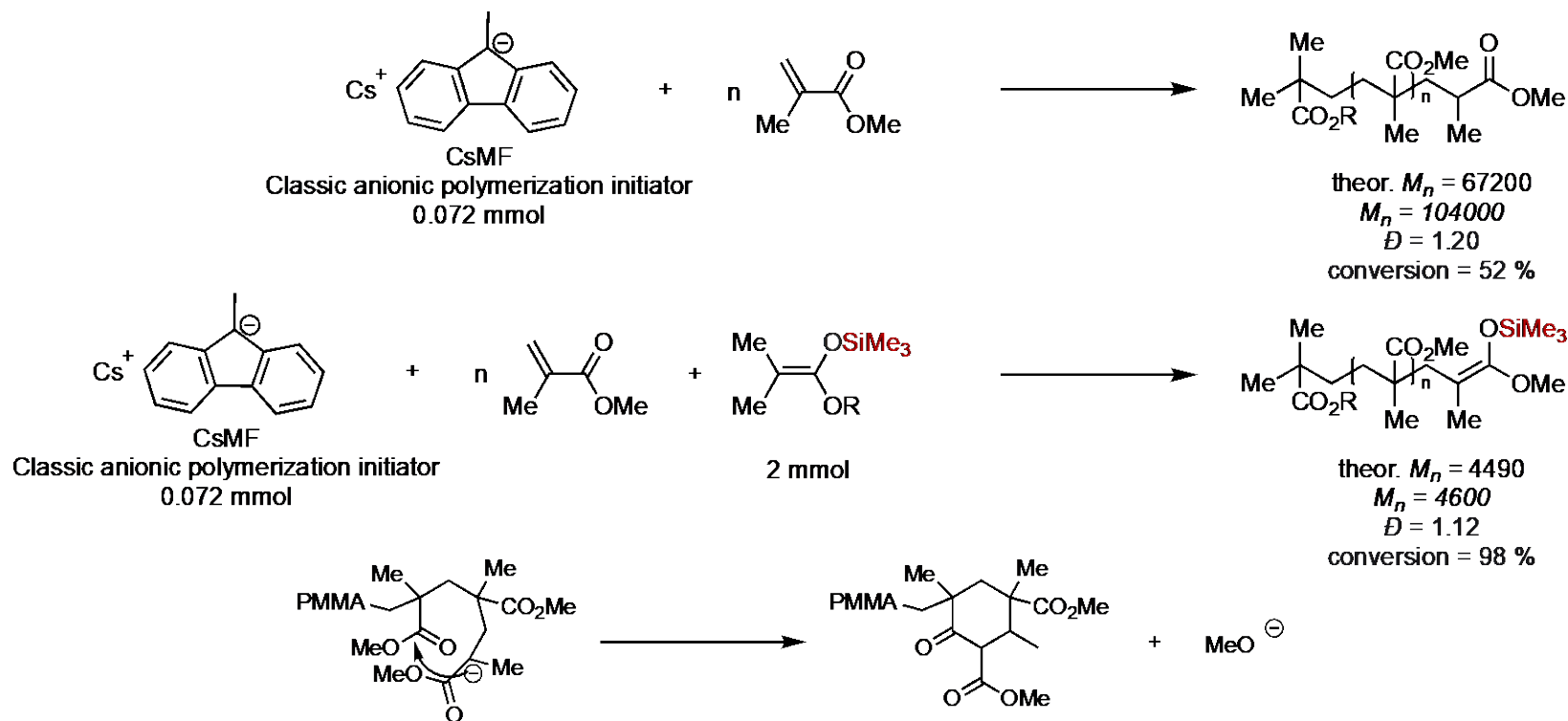
- Dissociation Mechanism



Nucleophilic Anion

Experimental evidences supporting dissociation mechanism

- SKA render RT anionic polymerization living: Quirk

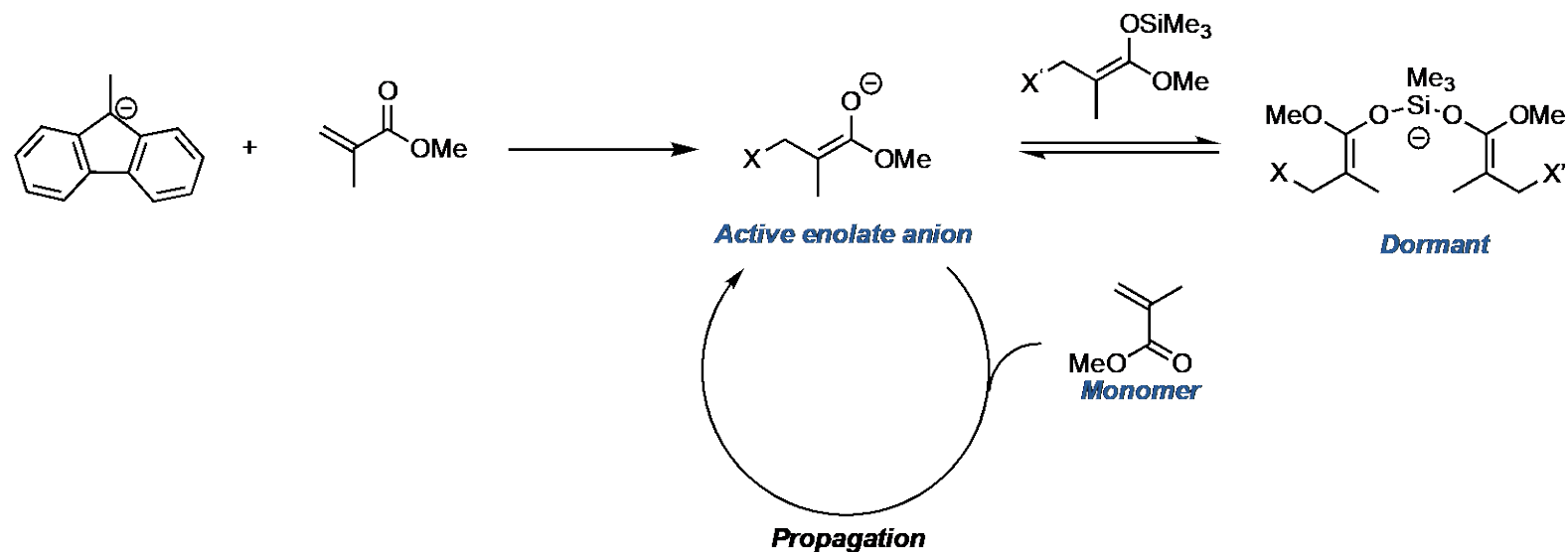


- Molecular weight could not be controlled in traditional anionic polymerization
- Better molecular weight control and conversion by addition of SKA
- How to explain the result?

Nucleophilic Anion

- Experimental evidences supporting dissociation mechanism
 - SKA render RT anionic polymerization living

Dissociation Mechanism

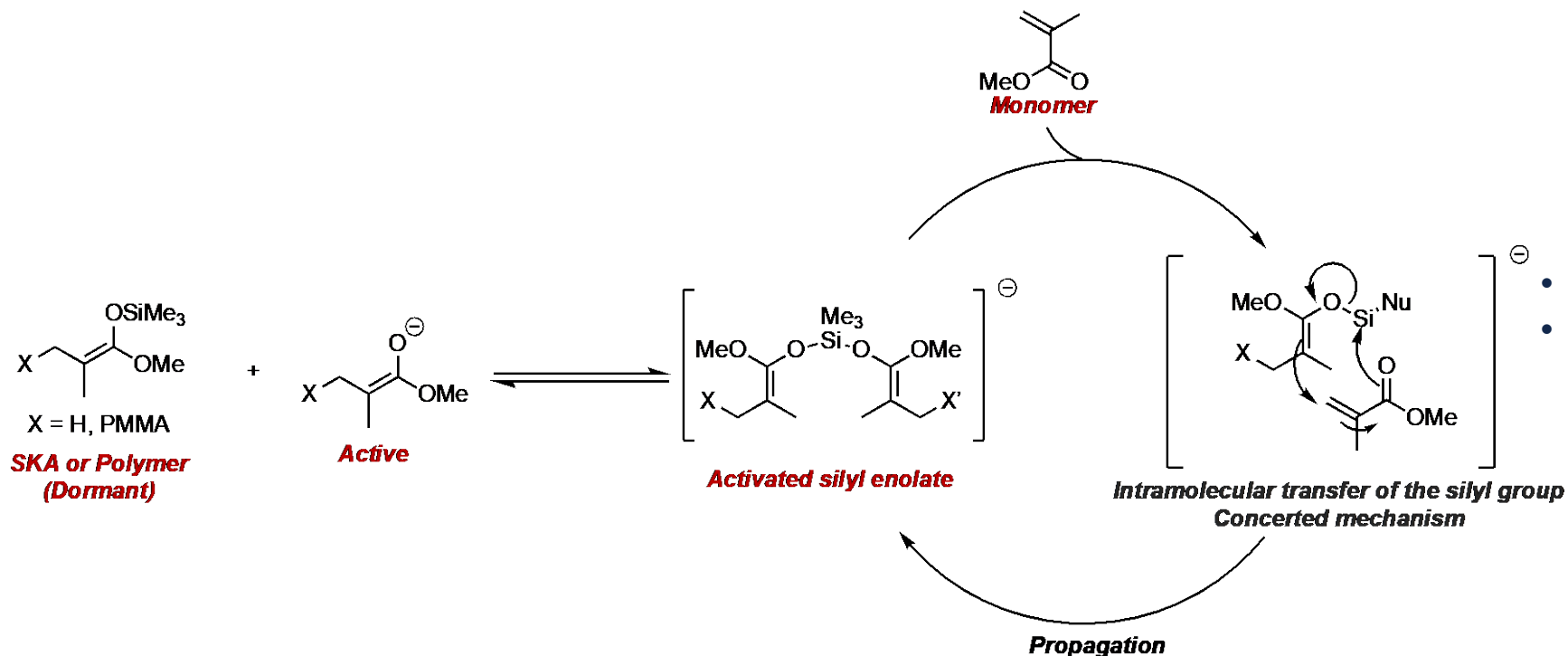


- *Perfect explanation*
- *Anion can be stabilized by SKA chain end*

Nucleophilic Anion

- Experimental evidences supporting dissociation mechanism
 - SKA render RT anionic polymerization living

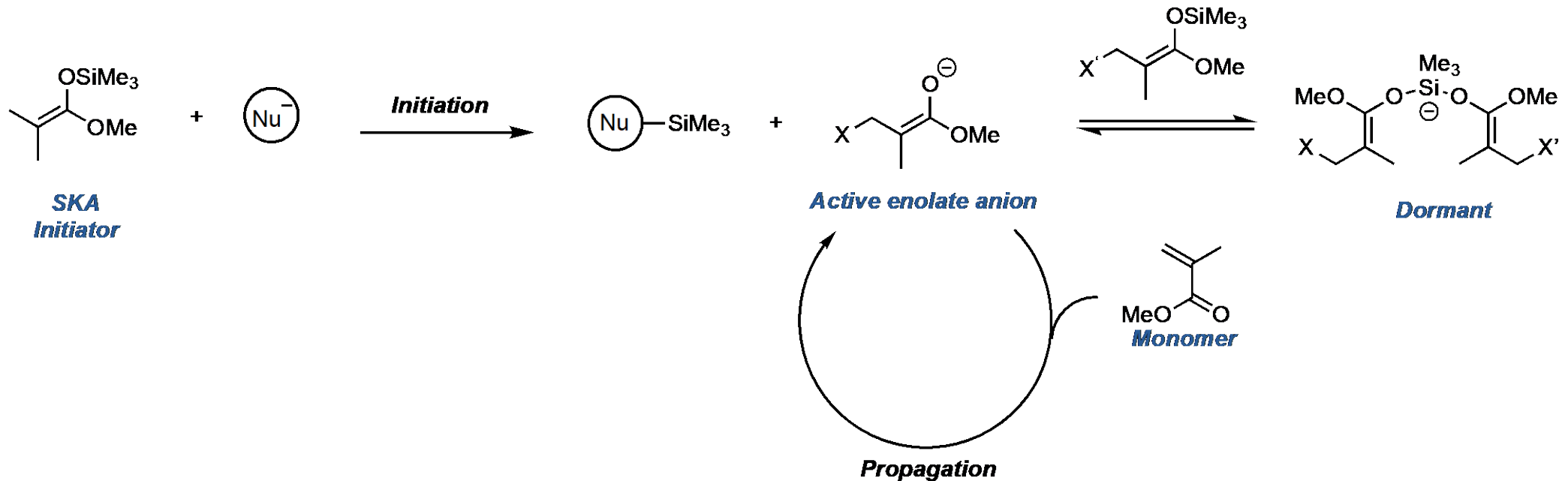
Association Mechanism



- Two active site in the reaction
- Living polymerization requires two different active species have same propagation rate

Nucleophilic Anion

- Experimental evidences supporting dissociation mechanism



More evidence:

- Unusual negative reaction order (-0.27) kinetic dependence on SKA (initiator)
- The need for low catalyst concentration
- The need for large unreactive counterions for GTP

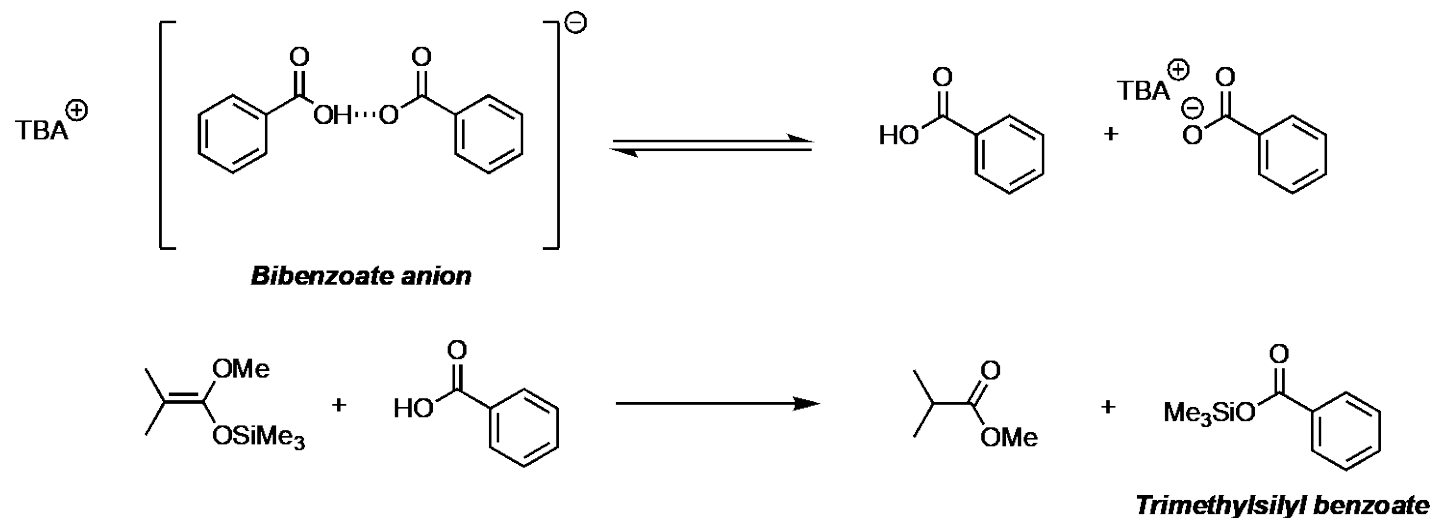
Nucleophilic Anion

Technology Transfer

- Process scale up studies

A room temperature process was better than -80 °C but still would require refrigeration to cool the reactor. Therefore, a process operating at 80 °C would be ideal, which would allow river-water-cooled reflux condensers to cool the reactor and the process would not be cost effective (THF as solvent).

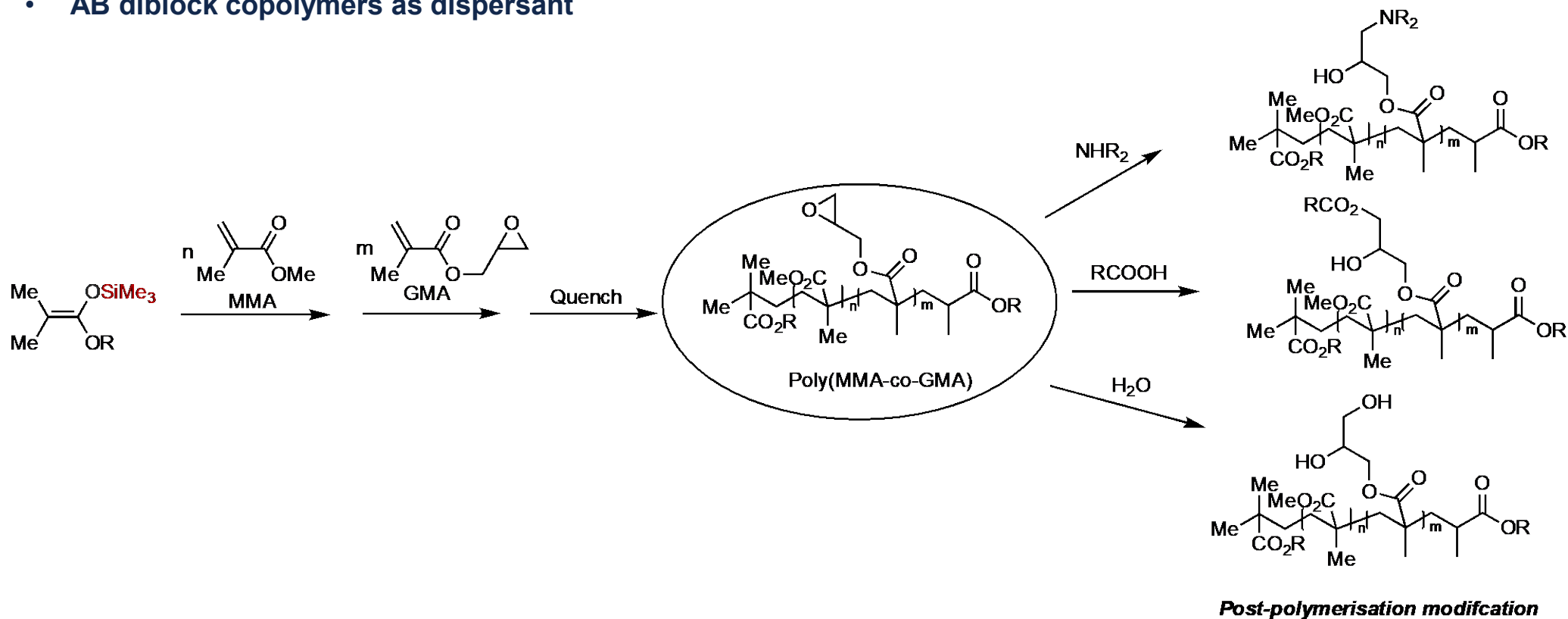
- Carboxylic acid salt as catalyst



- Less reactive than bifluoride
- Better molecular weight control at 80 °C
- Not work at lower temperature

Nucleophilic Anion

- Commercialization of GTP in DuPont
 - AB diblock copolymers as dispersant



Nucleophilic Anion

Commercialization success of GTP in DuPont

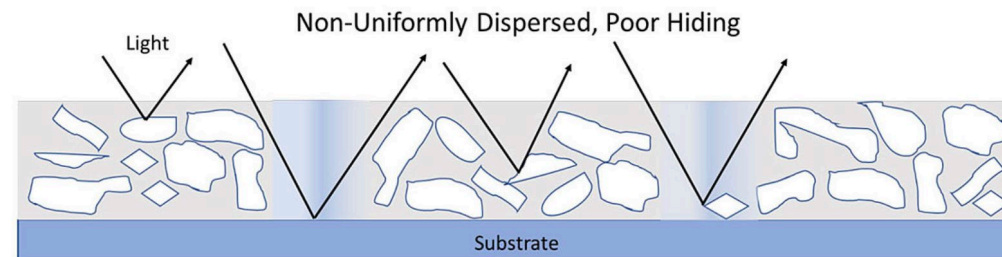
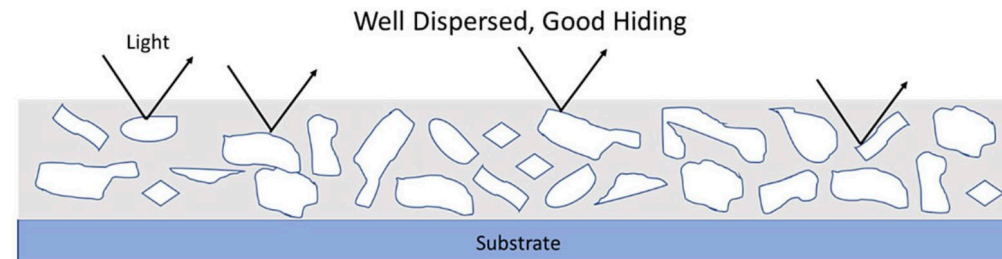
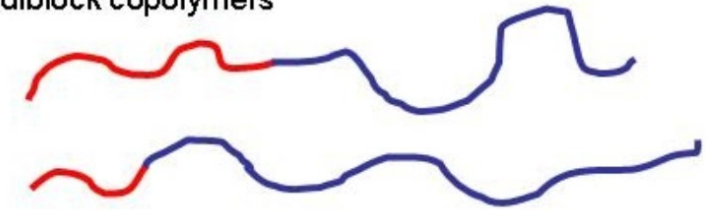
AB block polymers as dispersant

- Dispersants for water-based printing ink for jet printers
- In aqueous systems the hydrophobic region (PMMA) attaches to the pigment and the hydrophilic region (PMGA after modification) extends into the water phase

What is the function of dispersant?

- Help the liquid wet out the pigment and help remove air trapped on the surface or within agglomerates.
- Help in the dispersion process by allowing the agglomerates and aggregates to break up easier.
- Help stabilize the dispersion and coating to prevent flocculation, settling, flooding or floating

diblock copolymers



<https://www.pcimag.com>



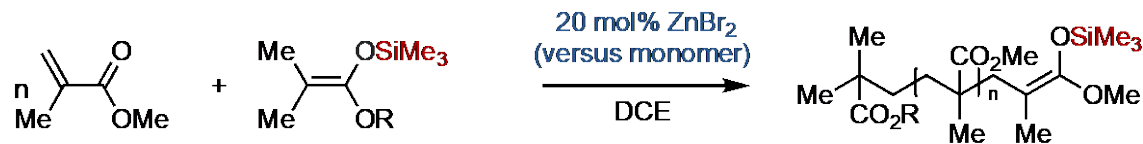
Outline



- Living Polymerization
- Nucleophilic anion mediated GTP
- **Acid mediated GTP**
- Summary

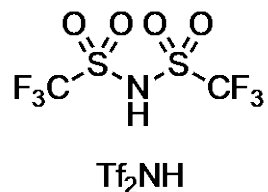
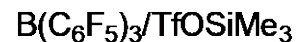
Acid mediated GTP

Acid-Catalyzed GTP

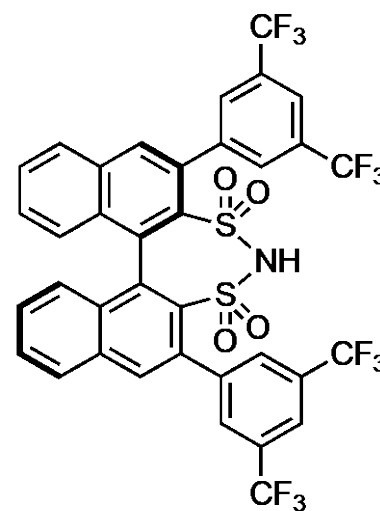
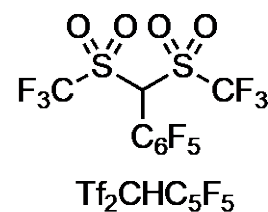


theor. $M_n = 3400$
 $M_n = 6020$
 $\bar{D} = 1.20$
 yield = 100 %

Catalysts / Precatalyst

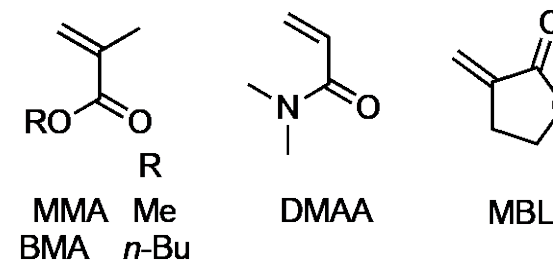


TTPB



List's sulfonimide

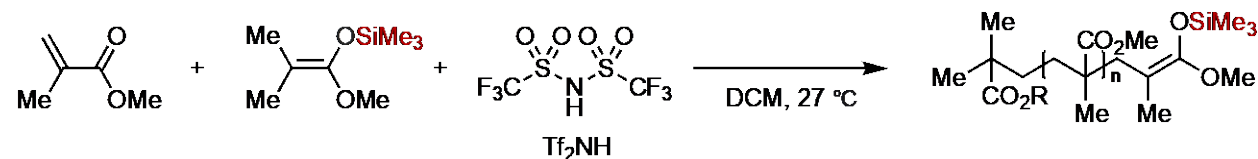
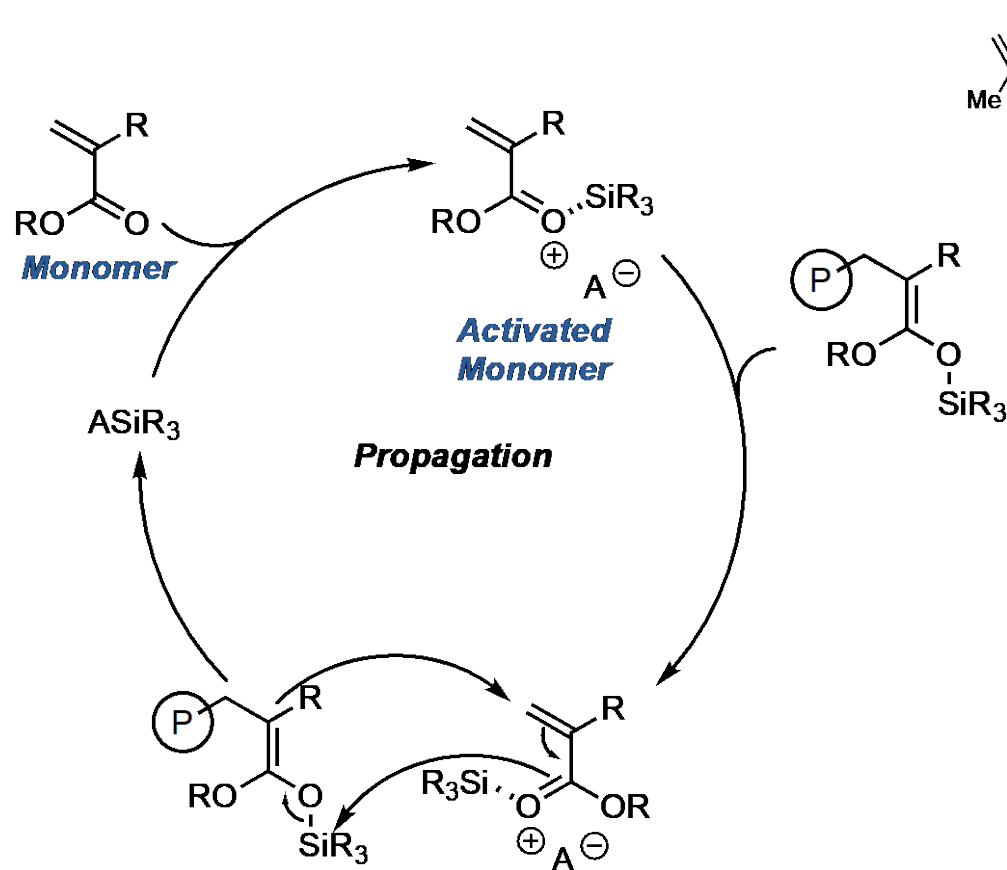
Monomer



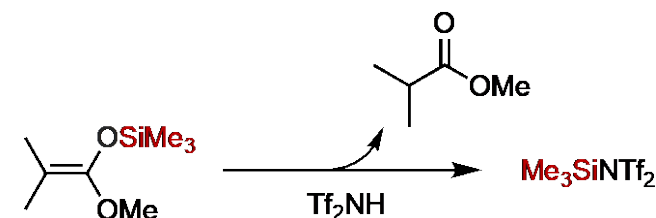
- Inspired by Mukaiyama Michael addition
- Strong organic Lewis acid or Brønsted acid
- Donating solvents inhibiting polymerization, e.g. THF, DMF
- Avoid termination resulted from back-biting: without anion

Acid mediated GTP

Proposed Mechanism



- Generally, different catalyst systems have similar propagation mechanism: silylium cation or other activated silyl species activates monomer. Then, silyl ketene acetal chain-end reacts with activated monomer.
- However, different catalyst systems have distinct initiation mechanism: how to generate silylium?
Initiation



Acid mediated GTP

▪ Acid-Catalyzed GTP

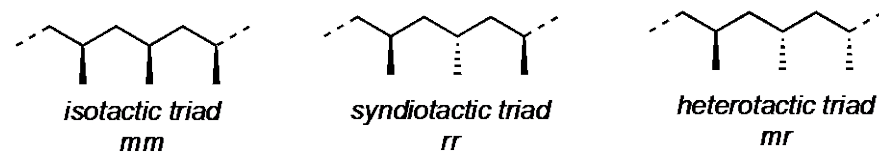
- Example: strong organic Brønsted acid

Tacticity

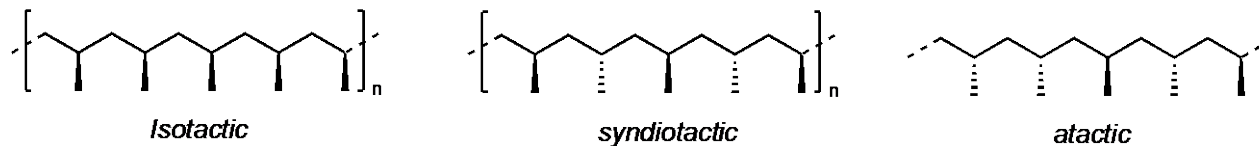
Diad



Triad



Polymer



- Tacticity is the relative stereochemistry of adjacent chiral centers within a macromolecule.
- Tacticity always affect physical characteristics, e.g. crystallinity
- Application:
 - Polymer of high strength is required: Isotactic or Syndiotactic
 - Rubber: Atactic

Acid mediated GTP

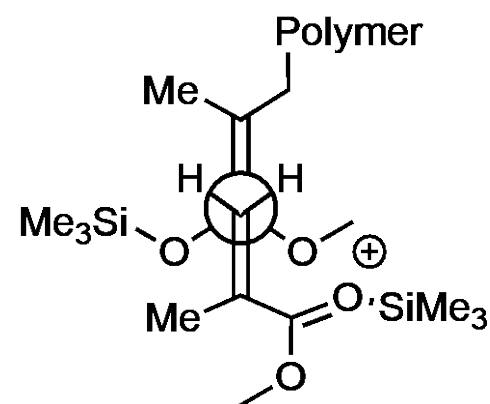
Acid-Catalyzed GTP

- Example: strong organic Brønsted acid

Mechanism and stereoregularity

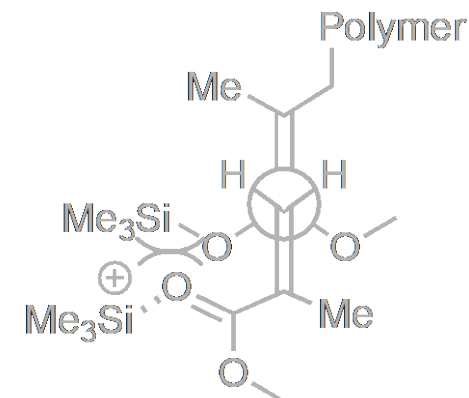
| time (h) | temp (°C) | $M_{n,SEC}^b$ | M_w/M_n^b | conv ^c (%) | tacticity ^d (%) | | |
|----------|-----------|---------------|-------------|-----------------------|----------------------------|-----------|-----------|
| | | | | | <i>mm</i> | <i>mr</i> | <i>rr</i> |
| 9 | 27 | 13800 | 1.05 | 92.4 | 1 | 27 | 72 |
| 72 | −40 | 13300 | 1.03 | 97.3 | 0 | 13 | 87 |
| 168 | −55 | 14000 | 1.04 | > 99 | 0 | 10 | 90 |

Speculation of the Syndiotactic Control



Favored TS

- Adapted from Mukaiyama Micheal addition



Disfavored TS



Outline



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Summary

- ***Living nature of group transfer polymerization***

GTP allows one to make block and other specialized polymer chain architecture, and make polymers with highly controlled molecular weight and dispersity.

- ***Debated mechanism of group transfer polymerization mediated by nucleophilic anion***

Association mechanism was the earliest proposed mechanism of GTP catalyzed by nucleophilic anion, which was also the source of name, group transfer polymerization. However, after more mechanistic study had been done, dissociation mechanism was concerned as the real mechanism.

- ***Group transfer polymerization mediated by acid***

With the development of strong organic Lewis acid and Brønsted acid. Acid-catalyzed GTP have become a popular area of academic research again.

Review

- Fuchise, K.; Chen, Y.; Satoh, T.; Kakuchi, T., Recent progress in organocatalytic group transfer polymerization. *Polymer Chemistry* **2013**, 4 (16), 4278-4291.
- Chen, E. Y. X., Coordination Polymerization of Polar Vinyl Monomers by Single-Site Metal Catalysts. *Chemical Reviews* **2009**, 109 (11), 5157-5214.
- Webster, O. W., The discovery and commercialization of group transfer polymerization. *Journal of Polymer Science Part A: Polymer Chemistry* **2000**, 38 (16), 2855-2860.

Chapter

- Webster, O. W., Group Transfer Polymerization: A Critical Review of Its Mechanism and Comparison with Other Methods for Controlled Polymerization of Acrylic Monomers. In *New Synthetic Methods*, Springer Berlin Heidelberg: Berlin, Heidelberg, 2004; pp 1-34.

Questions?