Literature Report

Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

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Supervisor: Prof. Zhang-Jie Shi

Fudan University
2021-04-09

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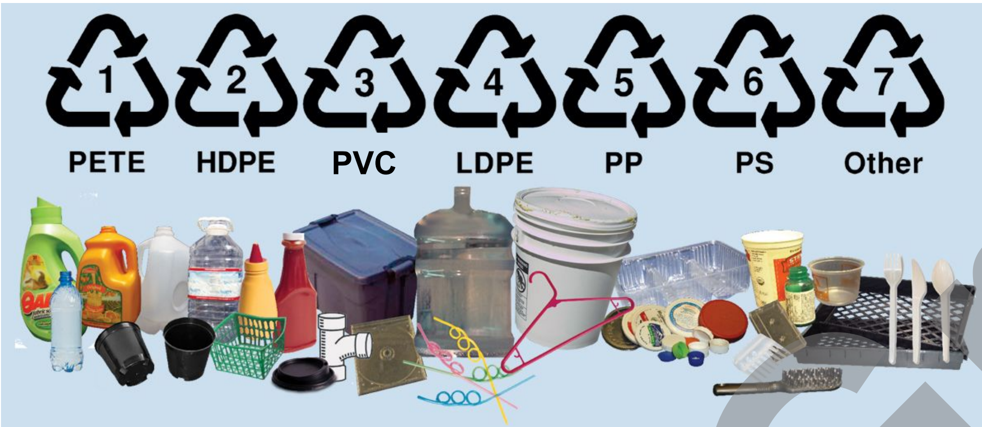
Background

Different Types of Polymers



- PETE: Polyethylene terephthalate
- HDPE: High-density polyethylene
- PVC : Polyvinyl chloride
- LDPE : Low-density polyethylene
- PP : Polypropylene
- PS : Polystyrene
- Other Plastics

Ziegler-Natta catalysts have provided a worldwide profitable industry with production of more than 160 billion pounds and creation of numerous positions. Polyethylene and polypropylene is reported to be the top two widely used synthetic plastic in the world.

Brookhart, M., et al. *Chem. Rev*. **2000**, *100*, 1169.

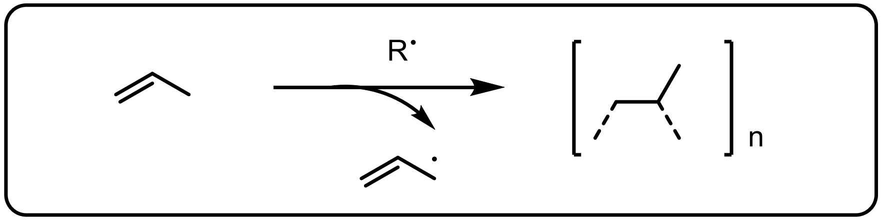
Polyethylene

Polypropylene

Contents

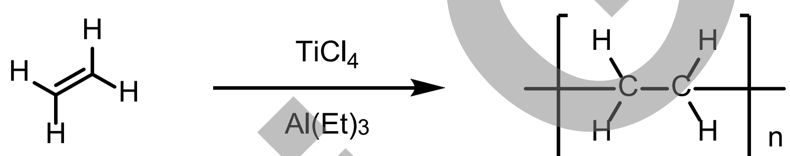
Ziegler-Natta Catalyst

Traditional Polymerization Method



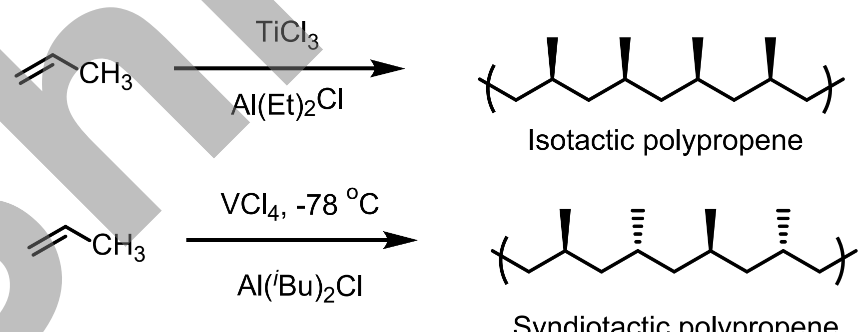
- Undesired allylic radicals lead to branched polymers
- Radical polymerization had no control over stereochemistry.

Ziegler-Natta Catalyst



Linear
Molecular weight = 10,000 – 20,000

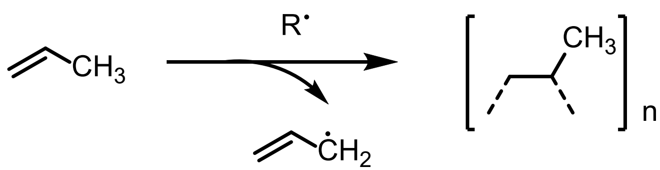
Ziegler, K., et al. *Angew. Chem. Int. Ed*. **1955**, *67*, 426.



Natta, G., et al. *J. Polym. Sci*. **1955**, *16*, 143.

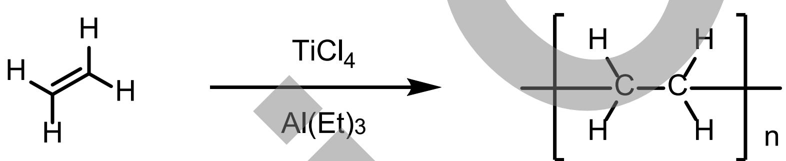
Ziegler-Natta Catalyst

Compared with Traditional Polymerization Method



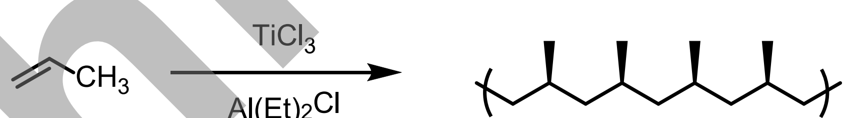
- Undesired allylic radicals lead to branched polymers
- Radical polymerization had no control over stereochemistry.

- The catalyst can give linear α-olefin polymers with high and controllable molecular weights.
- It makes the fabrication of polymers with specific tacticity possible.

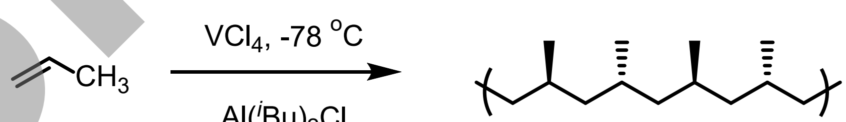


Linear
Molecular weight = 10,000 – 20,000

Ziegler, K., et al. *Angew. Chem. Int. Ed*. **1955**, *67*, 426.



Isotactic polypropene



Syndiotactic polypropene

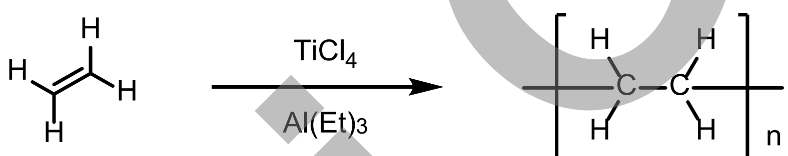
Natta, G., et al. *J. Polym. Sci*. **1955**, *16*, 143.

Ziegler-Natta Catalyst

Karl Ziegler
Nobel prize in 1963

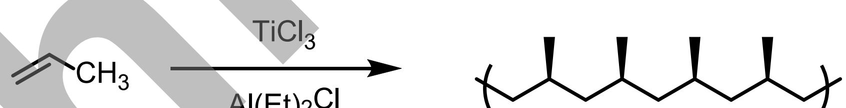
Giulio Natta
Nobel prize in 1963

"excellent work on organometallic compounds has unexpectedly led to new polymerization reactions and thus paved the way for new and highly useful industrial processes."

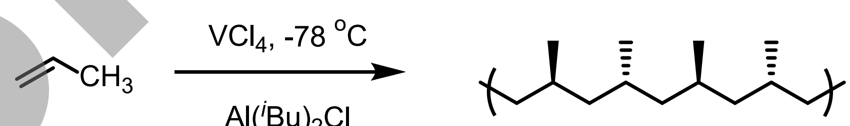


Linear
Molecular weight = 10,000 – 20,000

Ziegler, K., et al. *Angew. Chem. Int. Ed*. **1955**, *67*, 426.



Isotactic polypropene



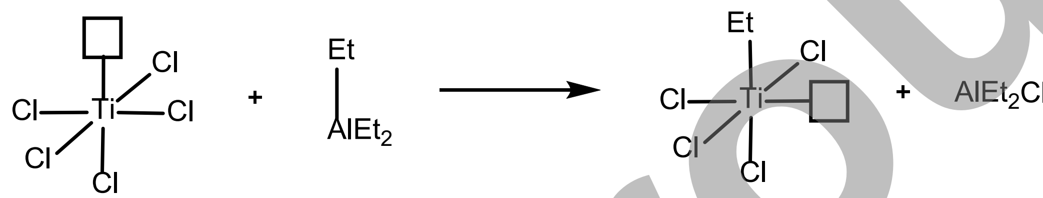
Syndiotactic polypropene

Natta, G., et al. *J. Polym. Sci*. **1955**, *16*, 143.

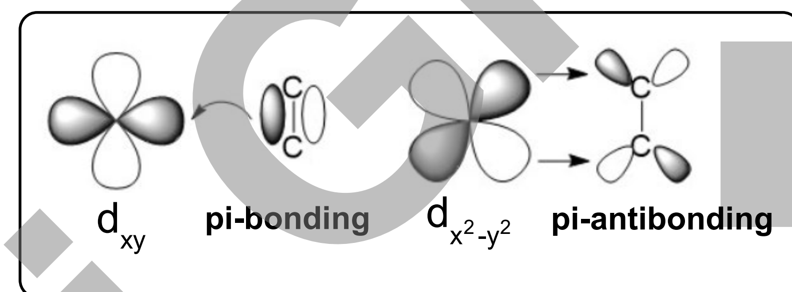
Ziegler-Natta Catalyst

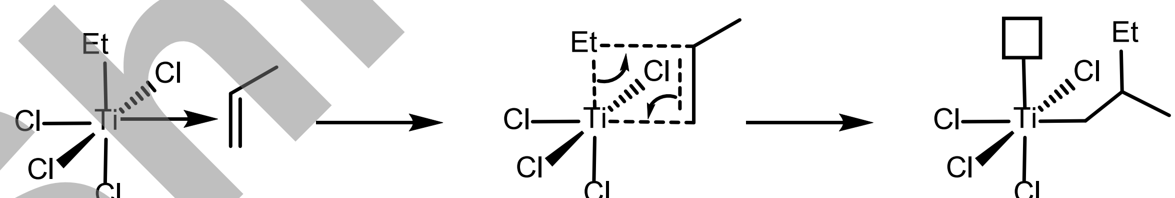
Mechanistic Study

Activation of Ziegler-Natta catalyst



Initiation step



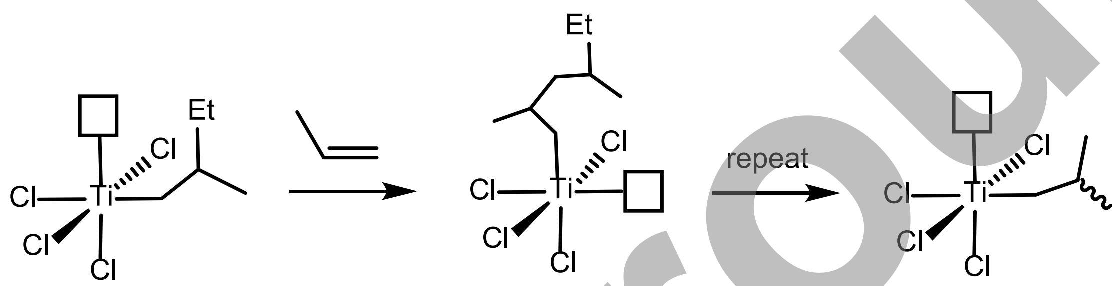


Grubbs, R. H., et al. *J. Am. Chem. Soc.* **1982**, *104*, 4479.

Ziegler-Natta Catalyst

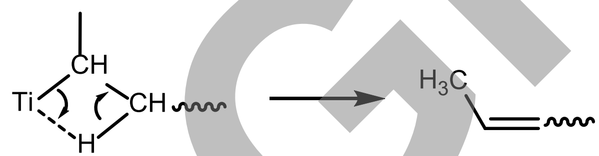
Mechanistic Study

Propagation step

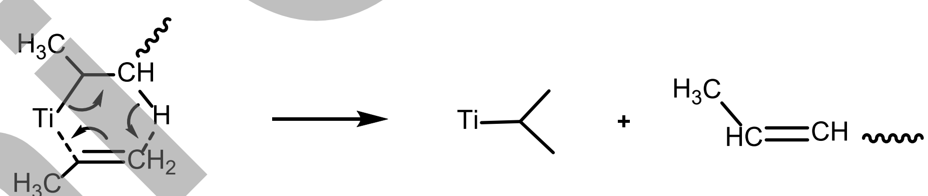


Termination step

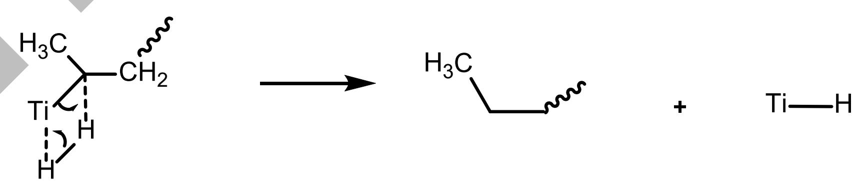
Path I



Path II



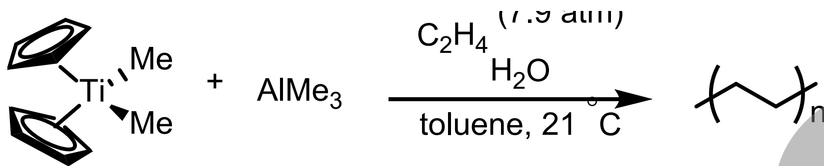
Path III



Grubbs, R. H., et al. *J. Am. Chem. Soc.* **1982**, *104*, 4479.

Ziegler-Natta Catalyst

The Second-Generation Catalysts

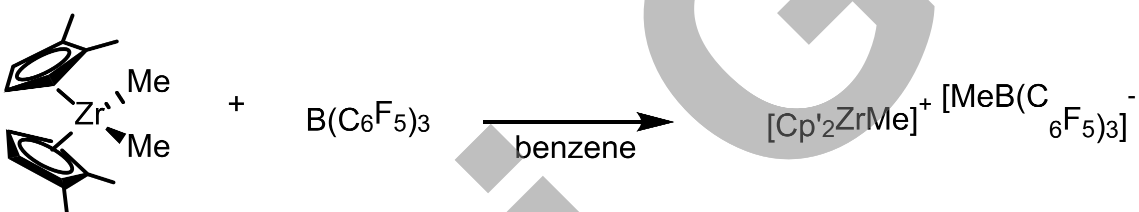


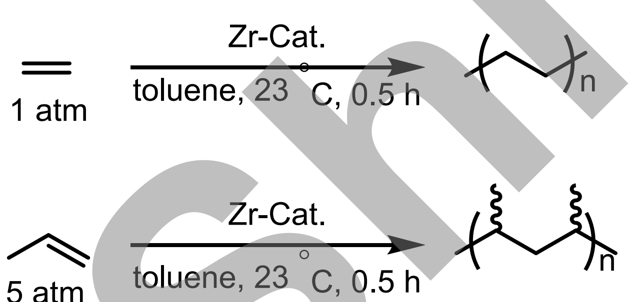
- The best activity: Al/H_2O ratios of 2:1 to 5:1
- For Al/H_2O ratios of 1:3 activity drops dramatically

Formation of methyl aluminoxanes (MAO)

Kaminsky, W., et al. *Angew. Chem. Int. Ed*. **1976**, *15*, 630.

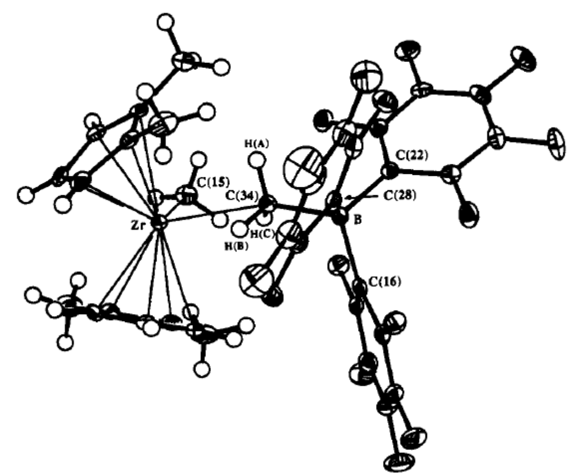
The Third-Generation Catalysts





- 4.5 x 10^6 g PE (mol of Zr)$_{-1}$ h$_{-1}$
- Similar to activity observed with MAO/Zirconocene catalysts

- 2.1 x 10^4 g PE (mol of Zr)$_{-1}$ h$_{-1}$
- Atactic Polypropylene

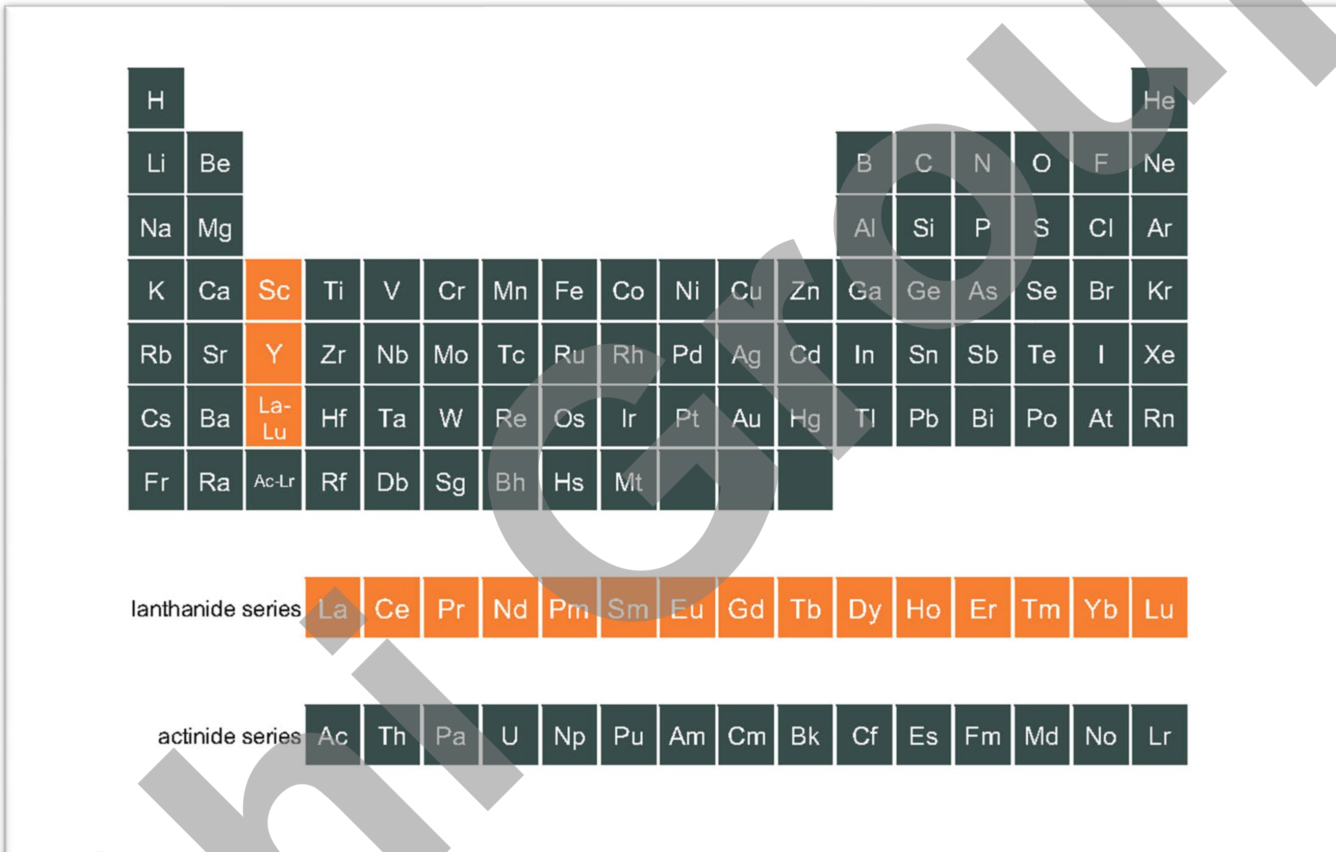


Marks, T. J., et al. *J. Am. Chem. Soc.* **1991**, *113*, 3623.

Contents

Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

Unique Properties of Rare-earth Elements

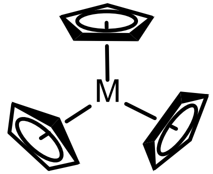


- **The most stable oxidation state of rare-earth metals is 3+.**
- **The oxidative addition and reductive elimination processes are generally difficult.**
- **Structures are mainly governed by the sterics rather than the electron numbers.**
- **Rare-earth metal ions generally show strong Lewis acidity and oxophilicity.**
- **Unique candidates for the formation of excellent single-site catalysts.**

Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

Cp-ligated Rare-earth Complexes

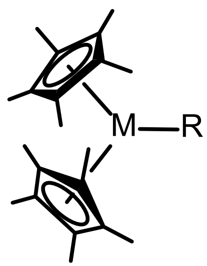
1950s



M = Sc, Y, La, Ce, Pr, Nd, Sm and Gd

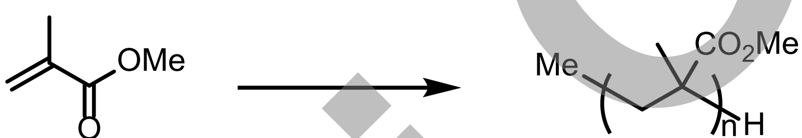
Birmingham, J. M., et al. *J. Am. Chem. Soc.* **1954**, *76*, 6210.
Ziller, J. W., et al. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 12678.
Visseaux, M., et al. *J. Organomet. Chem.* **2013**, *743*, 139.

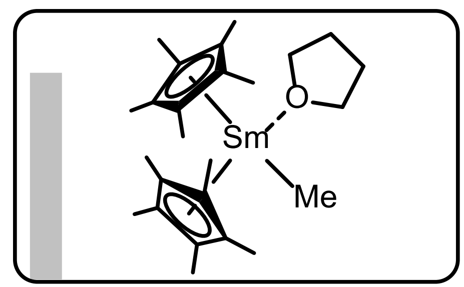
1980s



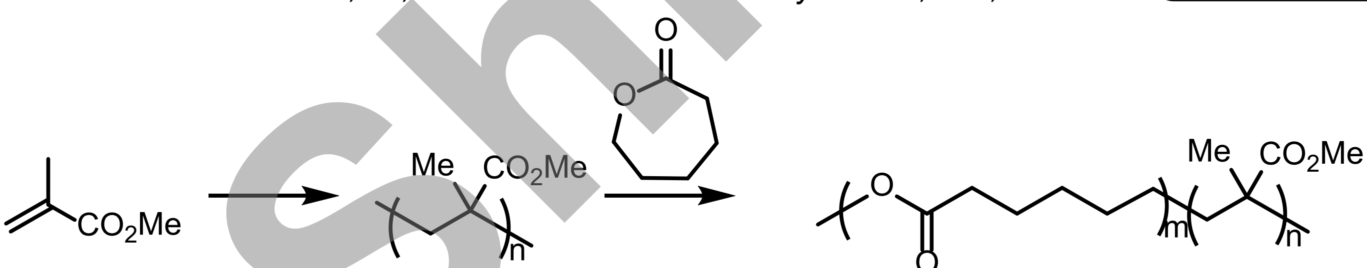
M = Lu, Ln, Yb, Er, Y, Tb,
R = *t*-C_4H_9, μ-CH_3, μ-H, CH_2SiMe_3'

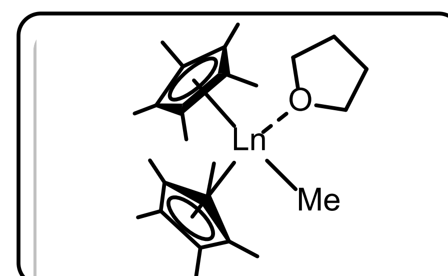
Evans, W. J., et al. *Adv. Organomet. Chem.* **1985**, *24*, 131.





Nodono, M., et al. *Macromol. Chem. Phys.* **2000**, *201*, 2282.

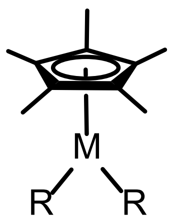




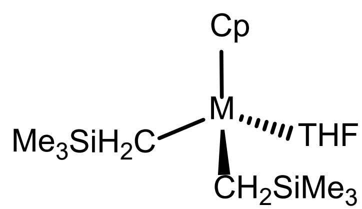
Yasuda, H. *J. Organomet. Chem.* **2002**, *647*, 128.
Chen, E. Y.-X. *Chem. Rev.* **2009**, *109*, 5157.

Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

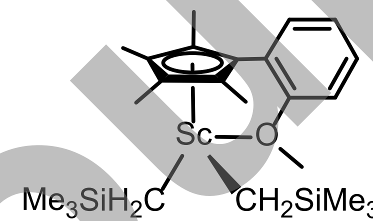
Cp-ligated Rare-earth Complexes



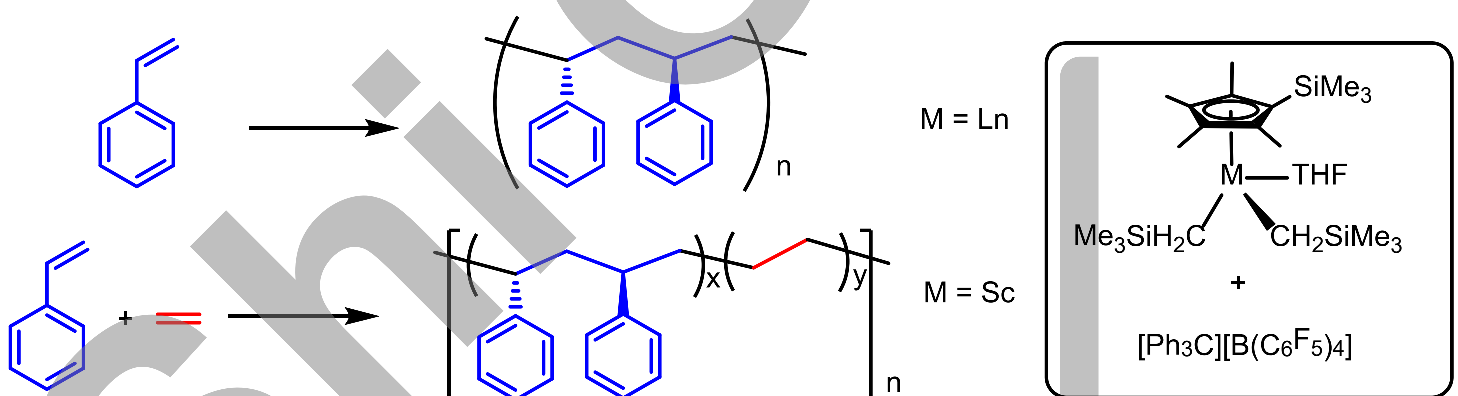
2000s



1a: Cp = C_5H_5; M = Sc
1b: Cp = C_5H_4Me; M = Sc
1c: Cp = C_5HMe_4; M = Sc
1d: Cp = C_5Me_5; M = Sc
1e-m: Cp = $C_5Me_4SiMe_3$; M = Sc, Y, Gd, Dy, Ho, Er, Tm, Lu



Hou, Z., et al. *J. Am. Chem. Soc.* **2009**, *131*, 13870.
Hou, Z., et al. *Macromolecules* **2011**, *44*, 6335.
Hou, Z., et al. *Chem. - Asian J.* **2013**, *8*, 2471.
Hou, Z., et al. *Macromolecules* **2016**, *49*, 2458.
Hou, Z., et al. *Macromolecules* **2017**, *50*, 8398.
Hou, Z., et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7173.

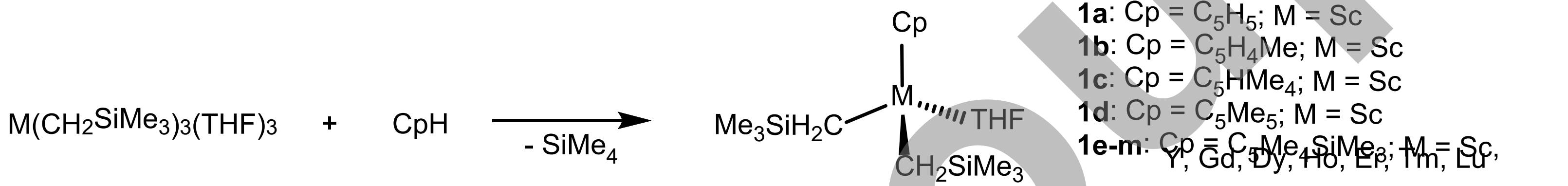


Hou, Z., et al. *J. Am. Chem. Soc.* **2004**, *126*, 13910.
Hou, Z., et al. *Acc. Chem. Res.* **2015**, *8*, 2209.

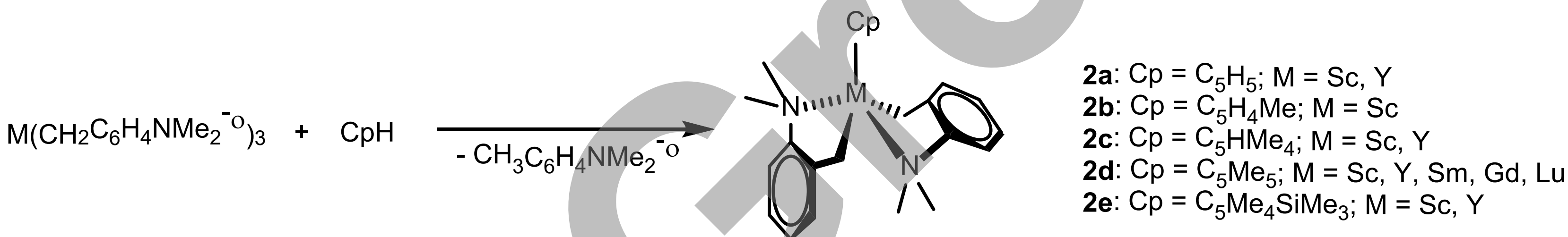
Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

Synthesis of Half-sandwich Rare-earth Complexes

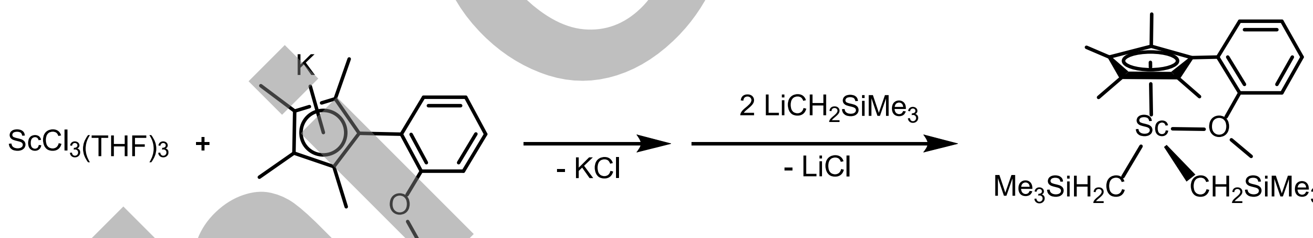
I



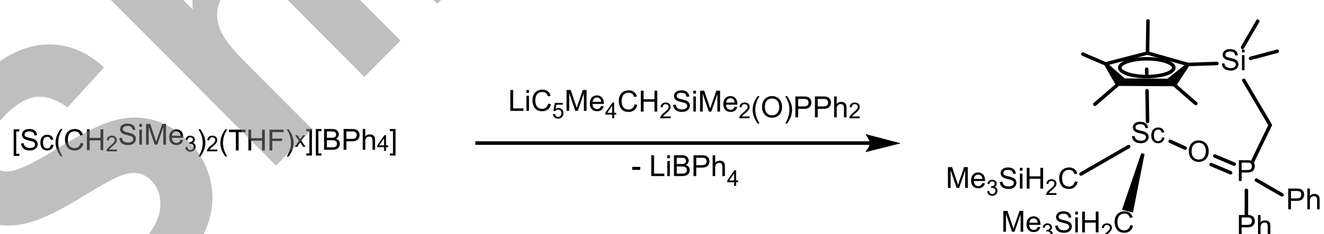
II



III

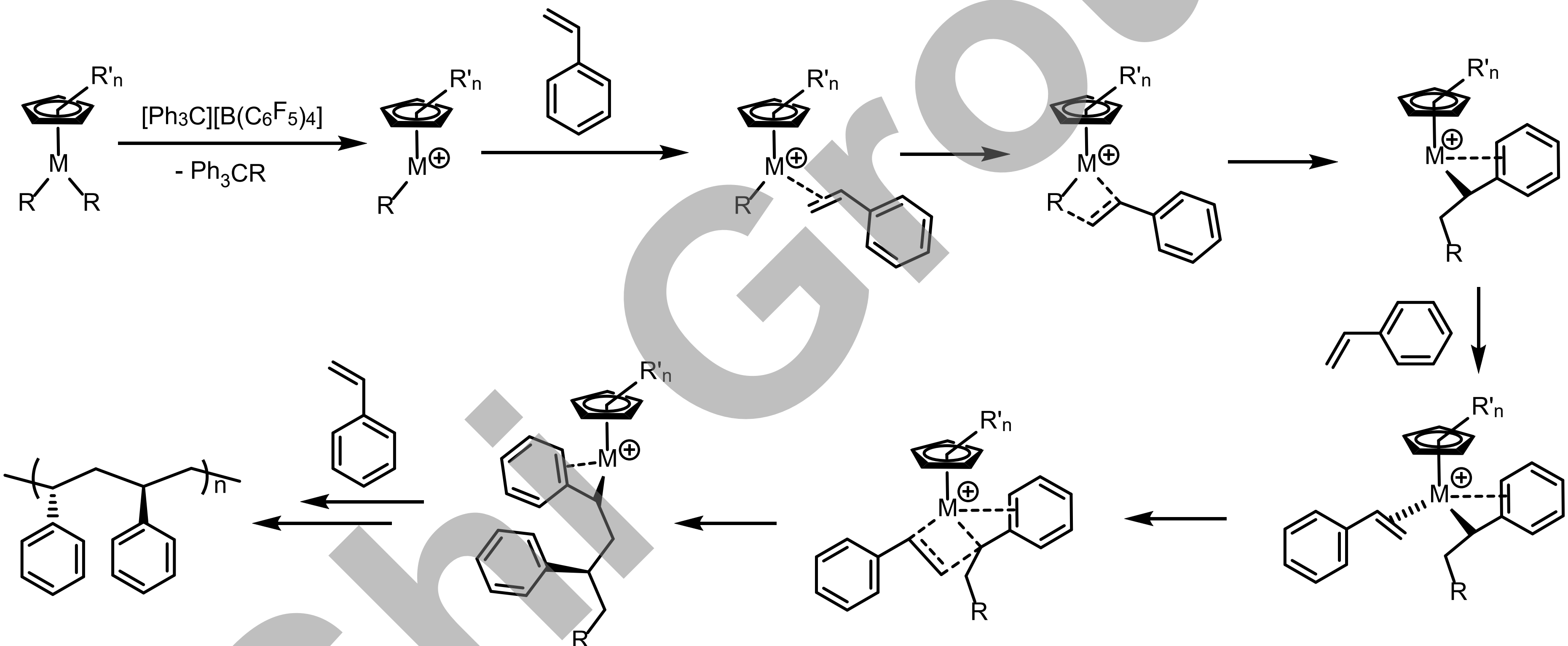


IV



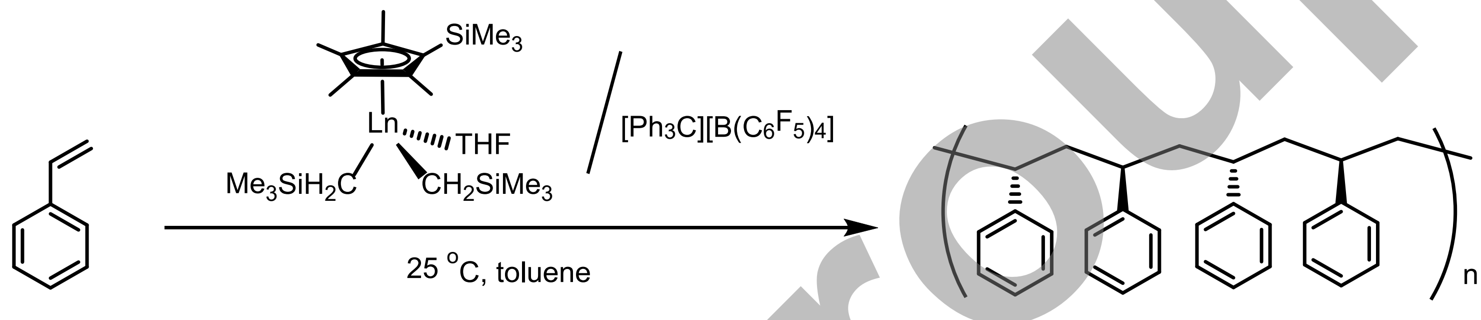
Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

General Process for Polymerization of Styrene



Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

Syndiospecific Polymerization of Styrene

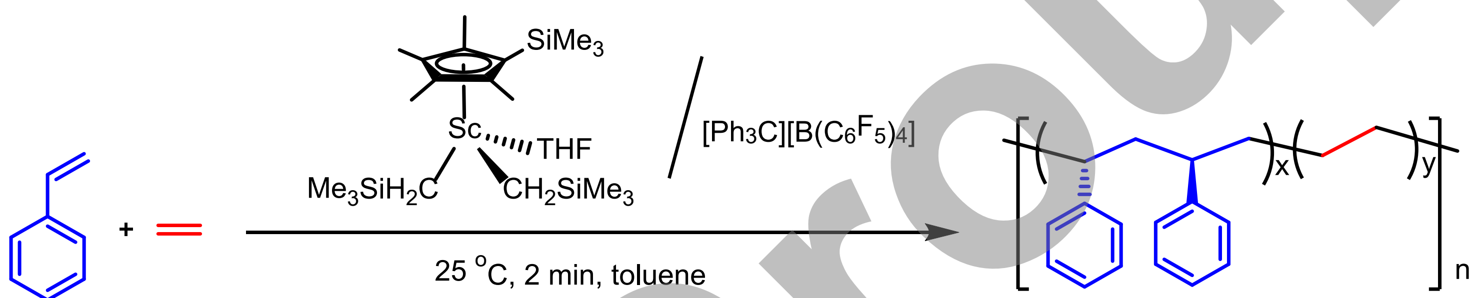


run	Ln	[M]/[Ln]	t (min)	yield[b] (%)	activity[c]	sPS[d] (%)	M_n[e] ($\times10^{-4}$)	M_w/M_n[e]	T_m[f] (°C)	efficiency[g] (%)
1	Sc	500	1	100	≥3125	100	8.85	1.38	271	58
2	Sc	700	1	100	≥4376	100	11.96	1.29	271	61
3	Sc	1000	1	100	≥6034	100	13.55	1.45	272	77
4	Sc	1500	1	100	≥9362	100	18.96	1.55	271	82
5	Sc	2000	1	100	≥12 498	100	26.94	1.36	272	77
6	Sc	2500	1	87	13 618	100	37.86	1.37	273	60
7	Y	100	30	60	13	100	1.07	1.39	269	
8	Gd	100	30	69	15	100	0.92	1.35	269	
9	Lu	100	30	25	6	100	0.49	1.38	268	

Hou, Z., et al. *J. Am. Chem. Soc.* **2004**, *126*, 13910.

Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

Syndiospecific Copolymerization of Styrene with Ethylene

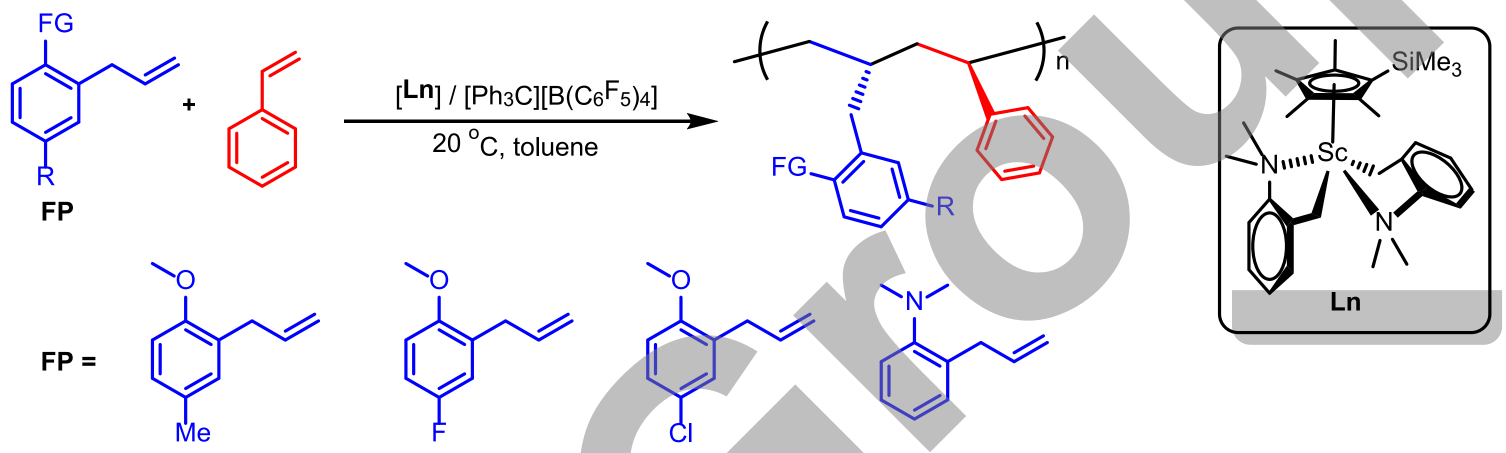


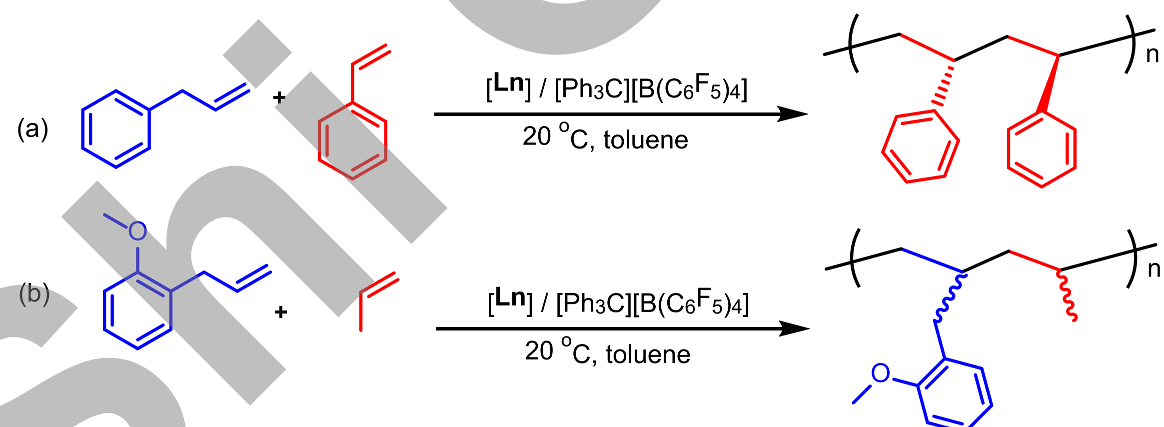
run	styrene (mmol)	ethylene (atm)	yield (g)	activity[b]	PS cont[c] (mol %)	M_n[d] ($\times10^{-4}$)	M_w/M_n[d]	T_m[e] (°C)
1	0	1	0.55	786	0	17.23	1.72	127
2	21	0	0.45	643	100	6.04	1.41	268
3	10	1	0.40	600	13	7.92	1.14	n.o.[f]
4	21	1	0.79	1123	56	11.13	1.19	214
5	31	1	0.92	1314	65	16.26	1.17	233
6	41	1	1.62	2314	87	15.09	1.26	245

Hou, Z., et al. *J. Am. Chem. Soc.* **2004**, *126*, 13910.

Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

Copolymerization of Functionalized Propylenes and Styrene



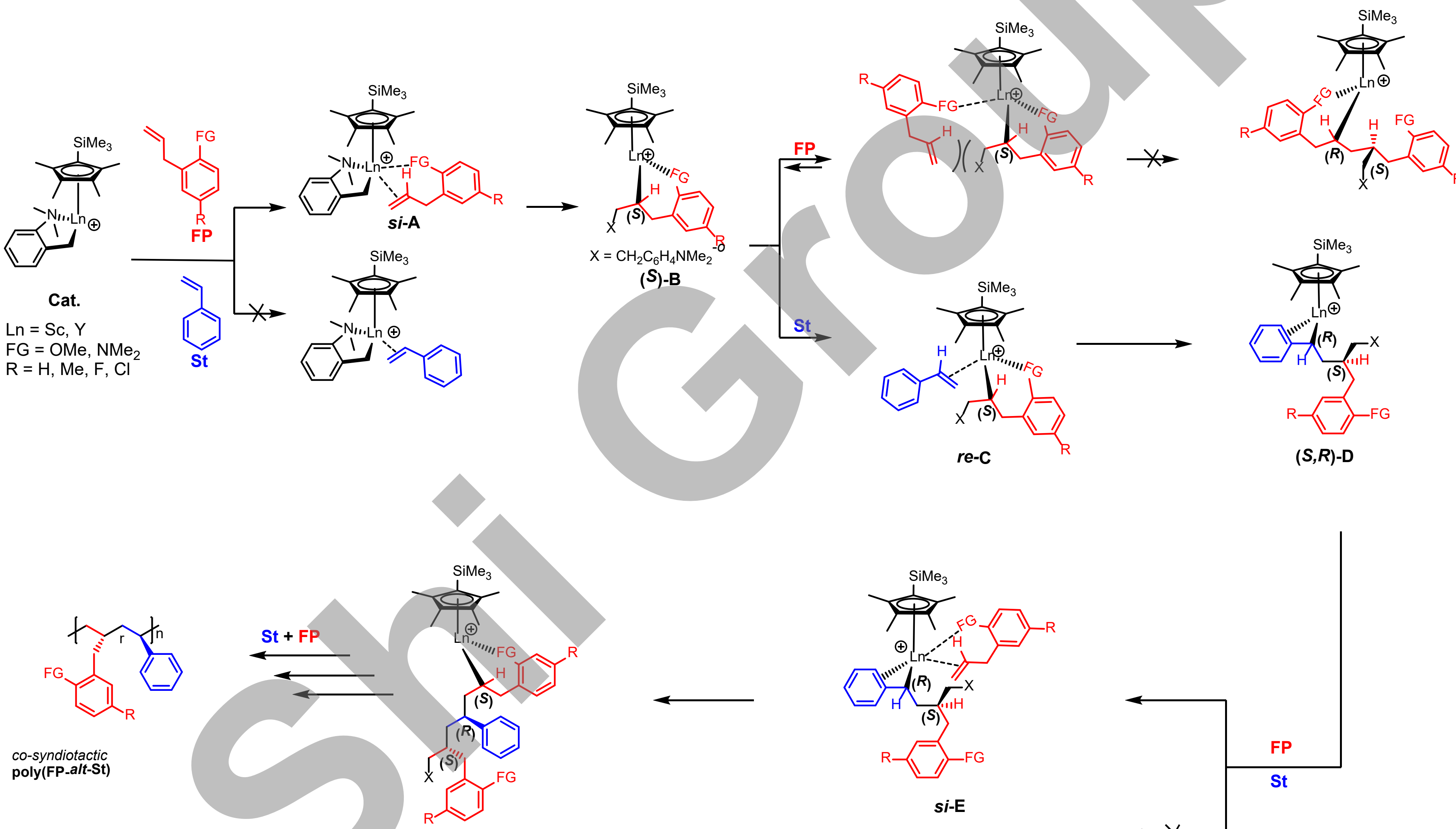


atactic copolymer
AP : P = 48 : 52

Hou, Z., et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7173.

Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

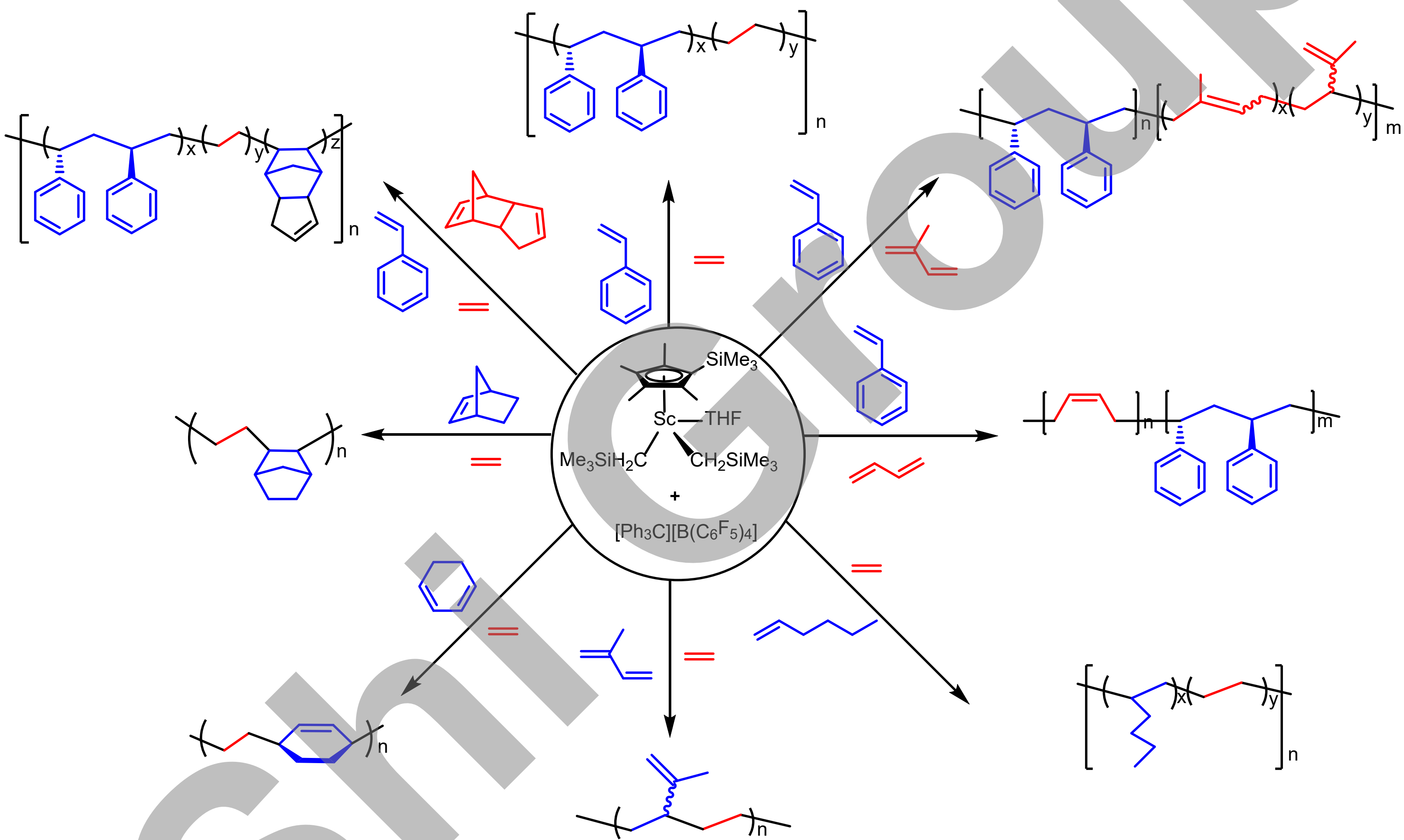
Possible Mechanism of The Co-syndiospecific Alternating Copolymerization



Hou, Z., et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7173.

Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

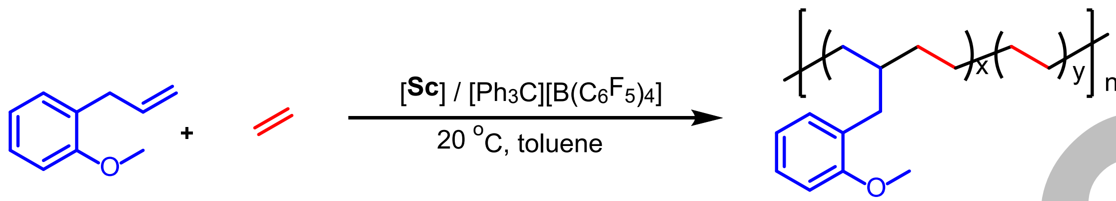
Selected Examples of Copolymerization

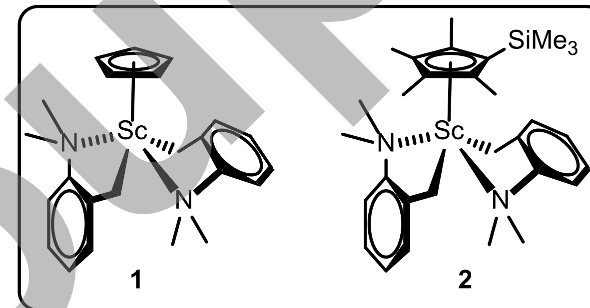


Visseaux, M., et al. *Macromolecules* **2005**, *38*, 3162.
Cui, D., et al. *Chem. - Eur. J.* **2010**, *16*, 14007.
Hou, Z., et al. *Acc. Chem. Res.* **2015**, *8*, 2209.
Anwander, R., et al. *Angew. Chem. Int. Ed.* **2008**, *47*, 775.
Hou, Z., et al. *J. Am. Chem. Soc.* **2019**, *141*, 12624.
Hou, Z., et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 7173.

Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

Synthesis of Self-Healing Polymers



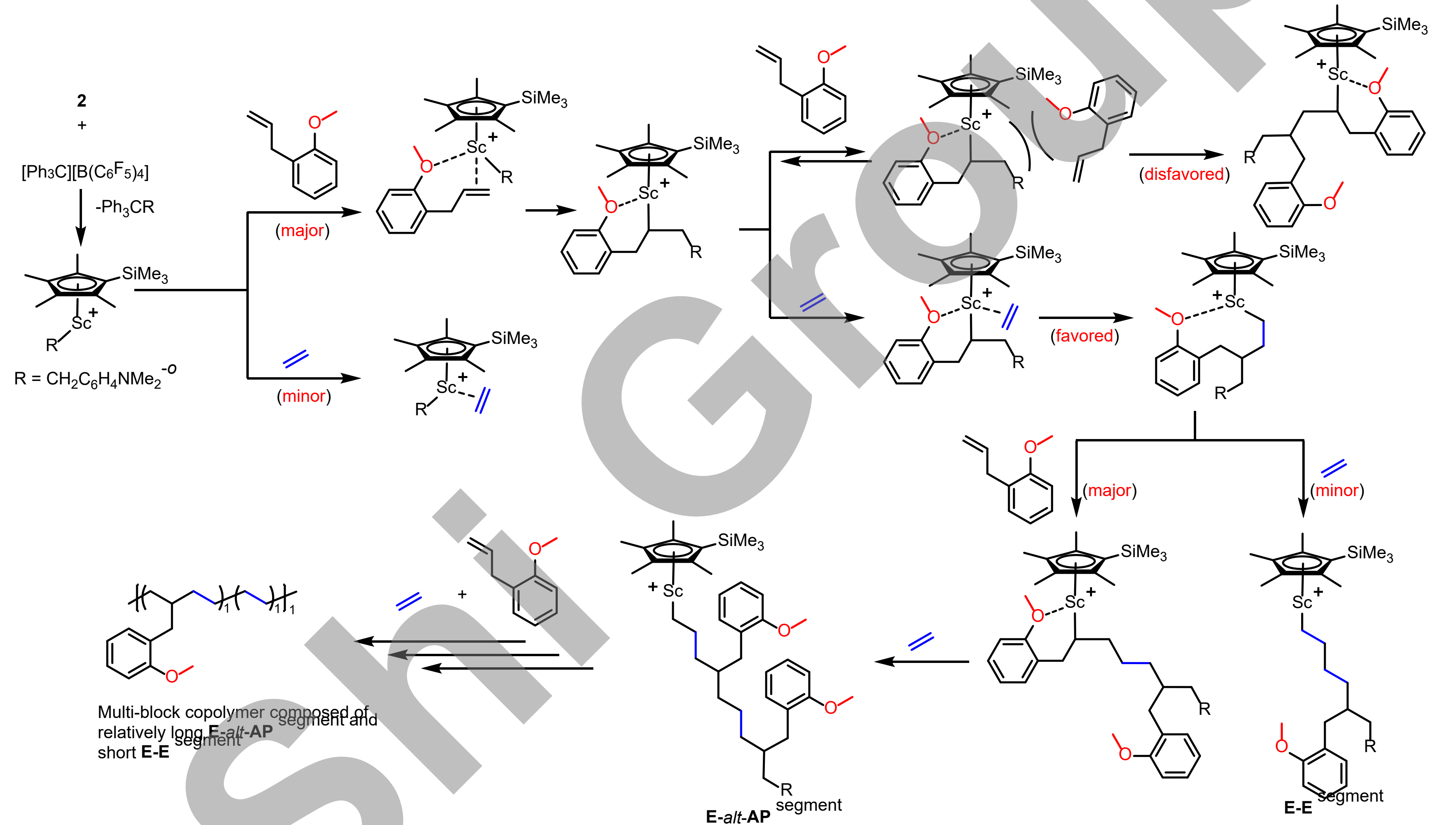


run	[Sc]	[AP]/[Sc]	Time (min)	yield (g)	AP conv (%)	activity (g mol-Sc^{-1} h^{-1} atm^{-1})	M_n (x 10^3 g mol^{-1})	M_w/M_n	AP/E	T_g (℃)	T_m (℃)
1	**1**	200/1	10	0.20	67	-	5	1.65	100/0	60	150
2	**2**	200/1	15	0.70	91	1.4 x 10^5	41 (**P1**)	1.68	39/61	-6	124
3	**2**	500/1	5	0.91	95	1.1 x 10^6	90 (**P2**)	1.58	39/61	-4	123
4	**2**	1000/1	15	1.61	85	6.4 x 10^5	173 (**P3**)	1.94	41/59	4	127
5	**2**	1000/1	6 h	3.05	84	5.1 x 10^4	344 (**P4**)	1.70	45/55	5	125
6	**2**	1000/1	24 h	8.35	92	3.5 x 10^4	552 (**P5**)	1.98	46/54	6	125

Hou, Z., et al. *J. Am. Chem. Soc.* **2019**, *141*, 3249.

Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

Possible Mechanism of Copolymerization of Ethylene and Anisylpropylene



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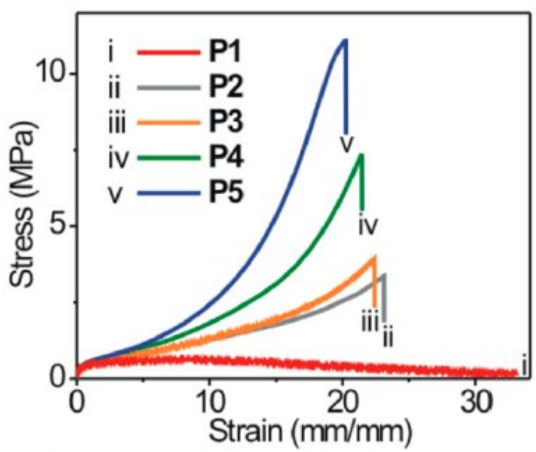
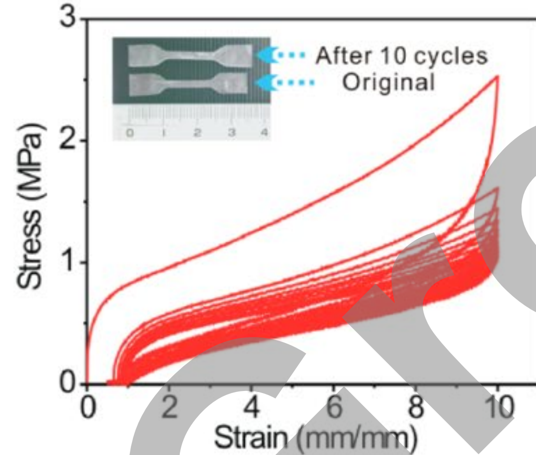
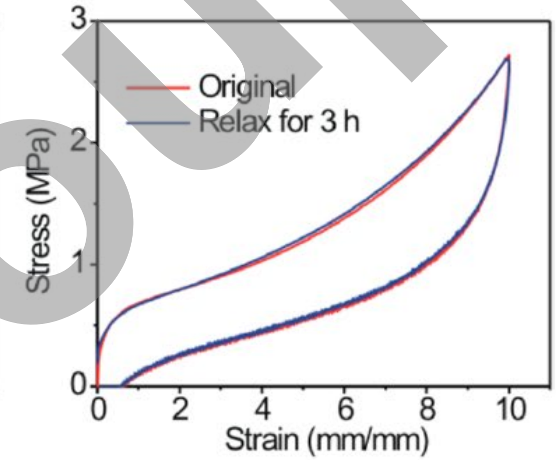
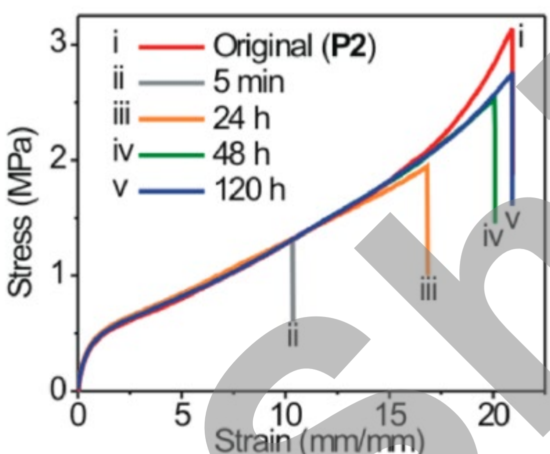
Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization

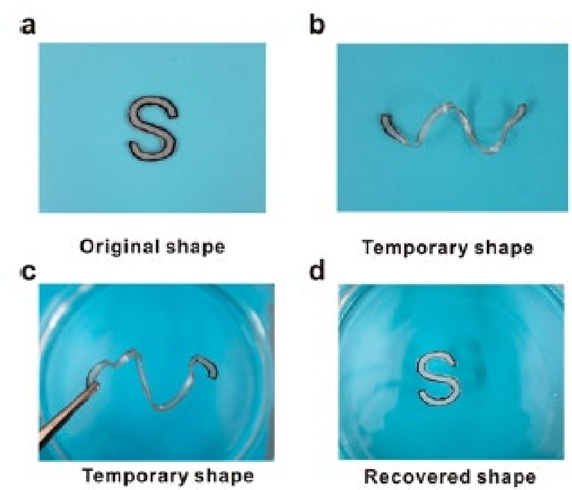
Mechanical Properties of The Copolymers











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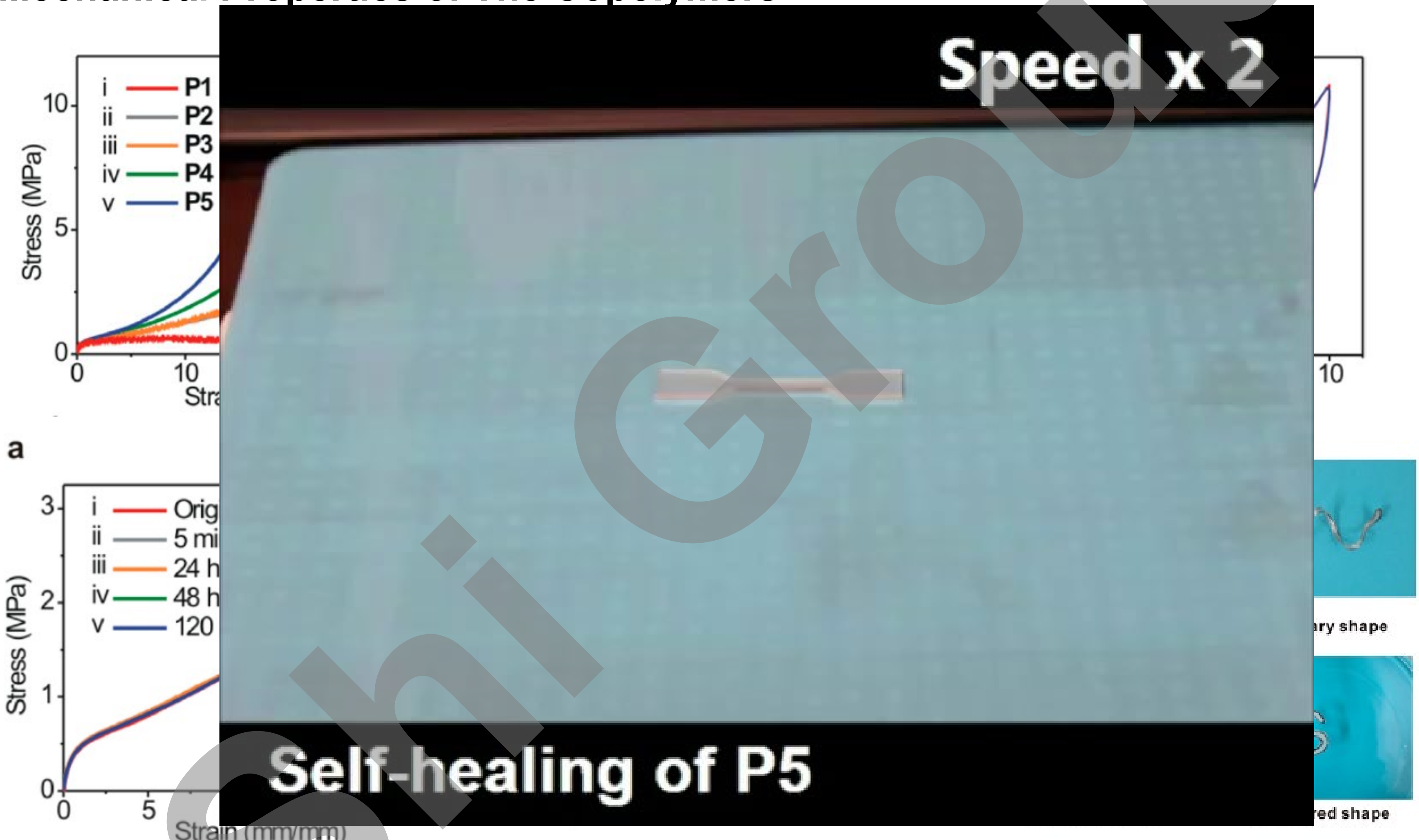

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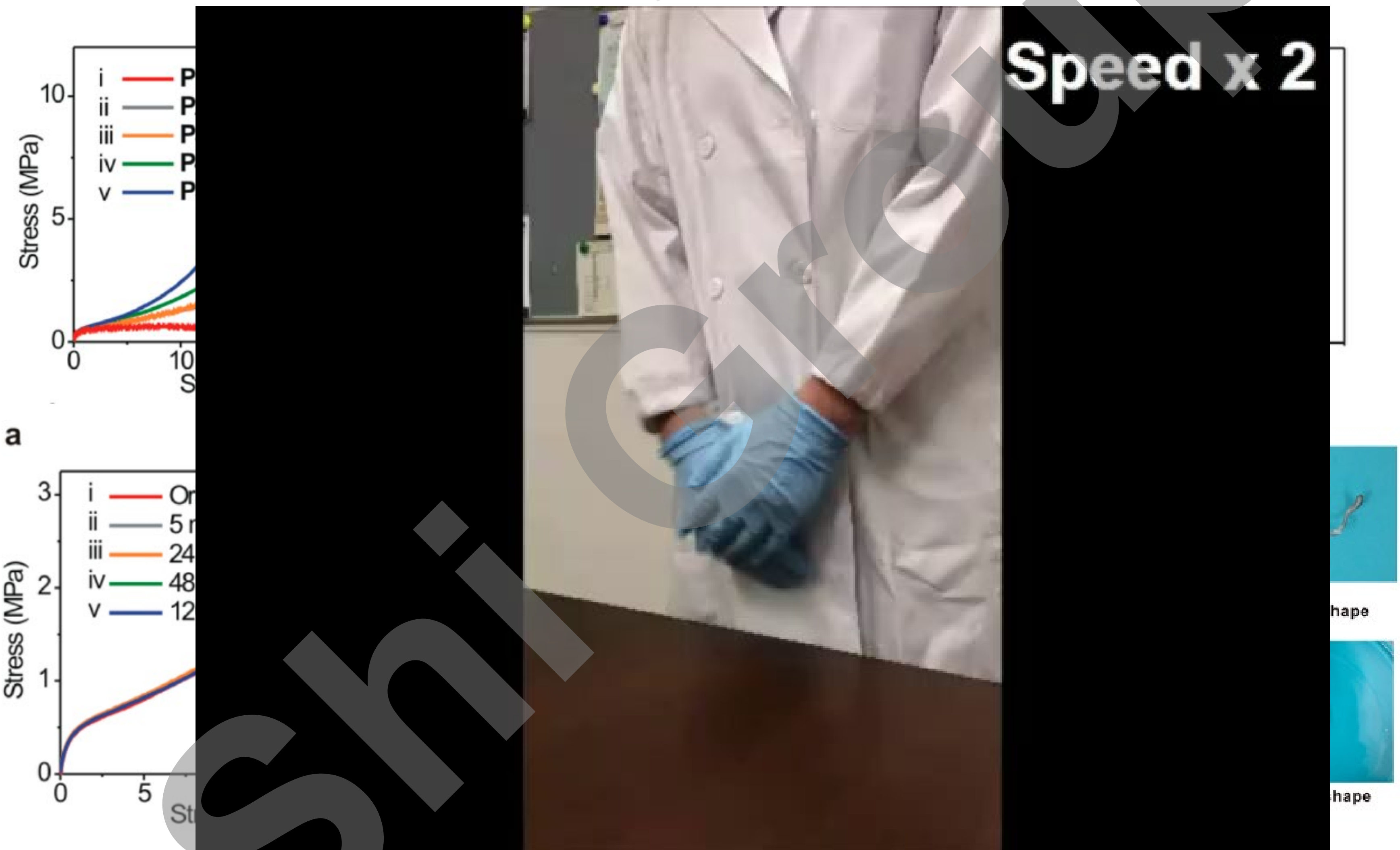

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- Synthesis of Half-sandwich Rare-earth Complexes
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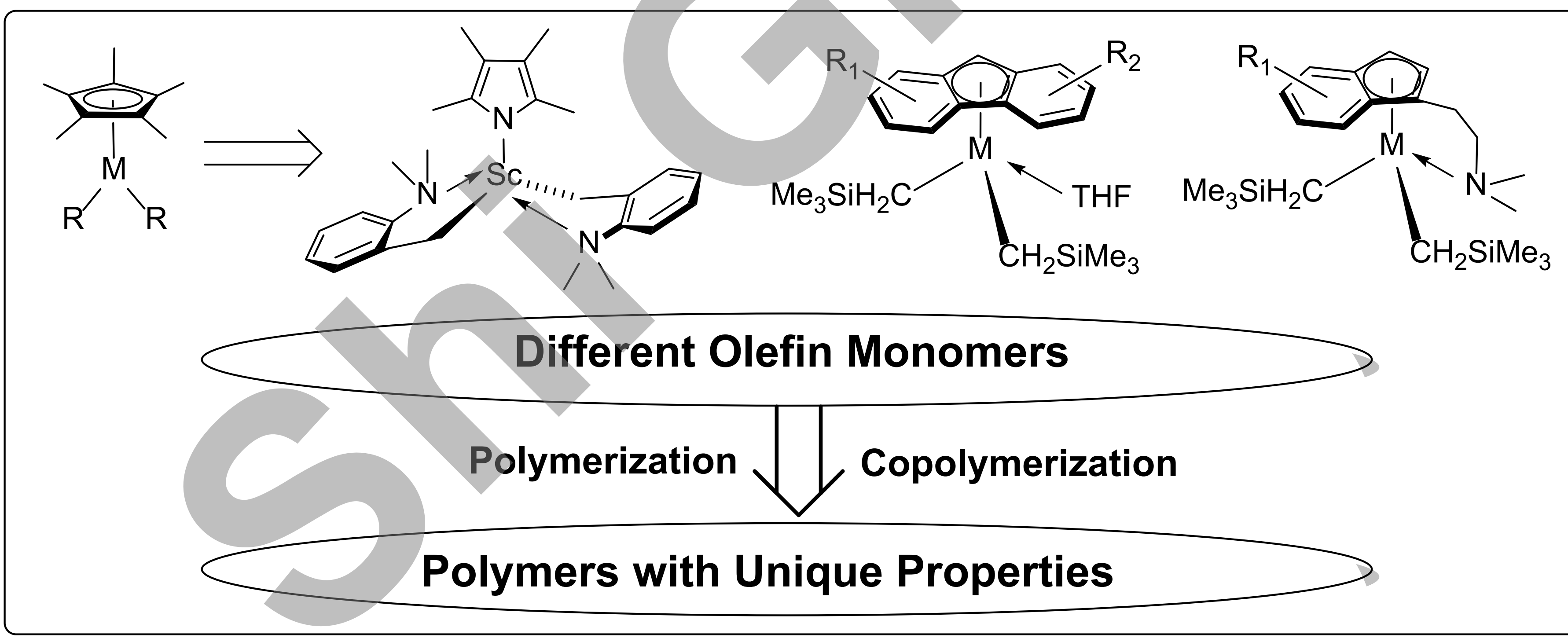
IV. Summary

Summary

- ***The high stability, strong Lewis acidity, and unsaturated C–C bond affinity of the 3+ metal ions make rare-earth metals unique candidates for the formation of excellent single-site catalysts.***
- ***Half-Sandwich Rare-Earth Catalysts** possess a more electropositive, less sterically crowded metal center and can show much higher and unique catalytic activity for the polymerization and copolymerization of a wide range of olefins.*



Thanks!