Heteroatom Radical Controlled Polymerization

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Outline

1. Introduction and background

2. Boryl radical mediated CRP

3. Silyl radical involved RP

4. Summary

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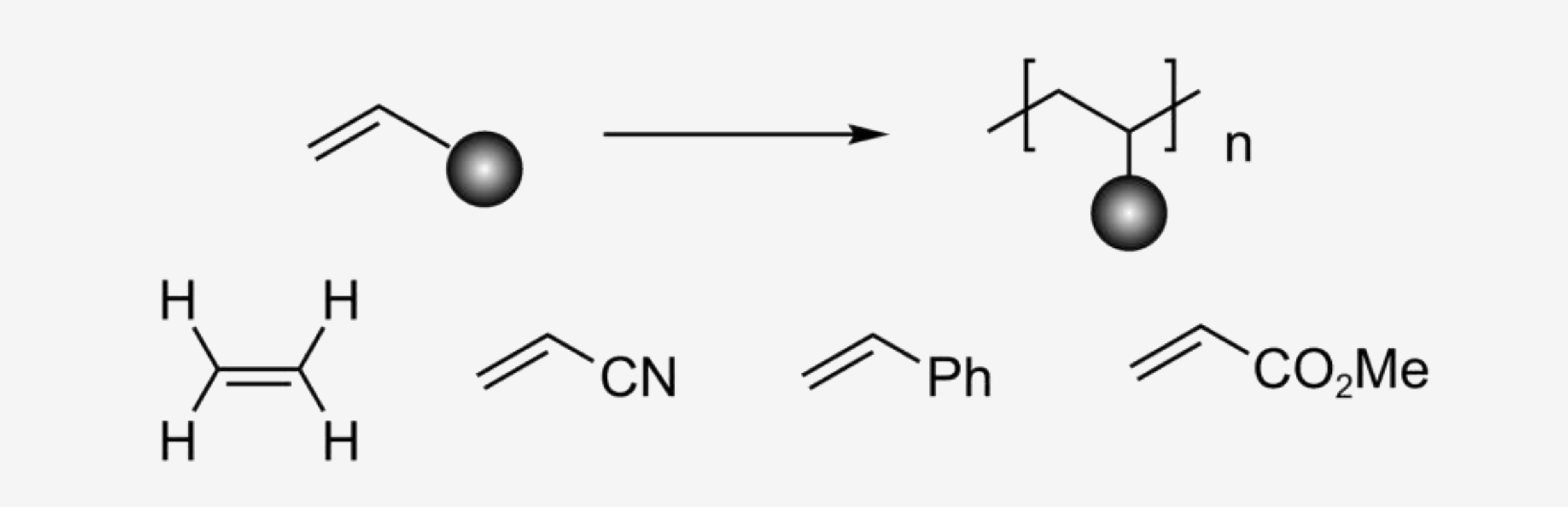
Radical Polymerization



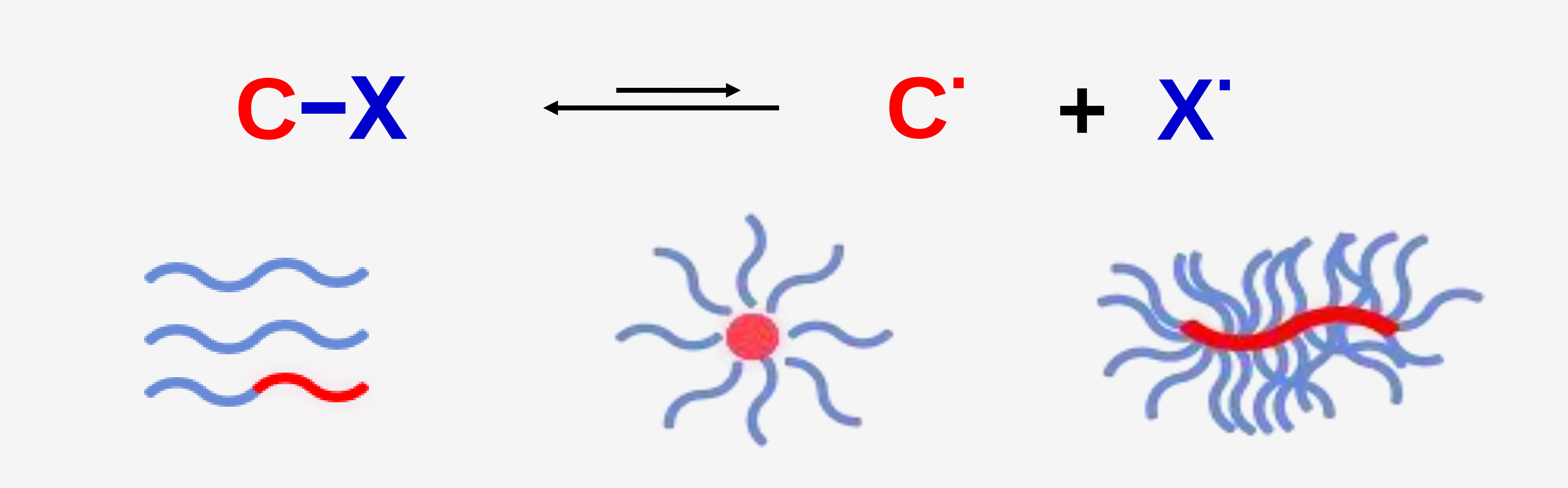
Broad monomer scope, various processes,

large-scale industrialization

Limitations: No control over molecular weight/topology, broad molecular weight distribution, etc.

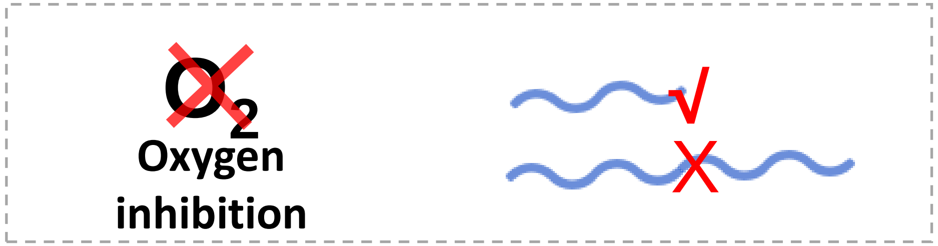
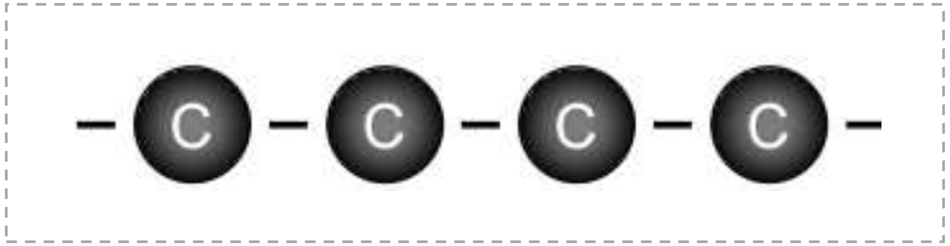
Solution?

Controlled Radical Polymerization



Reversible Deactivation Radical Polymerization

Controlled Radical Polymerization, “Living” Radical Polymerization

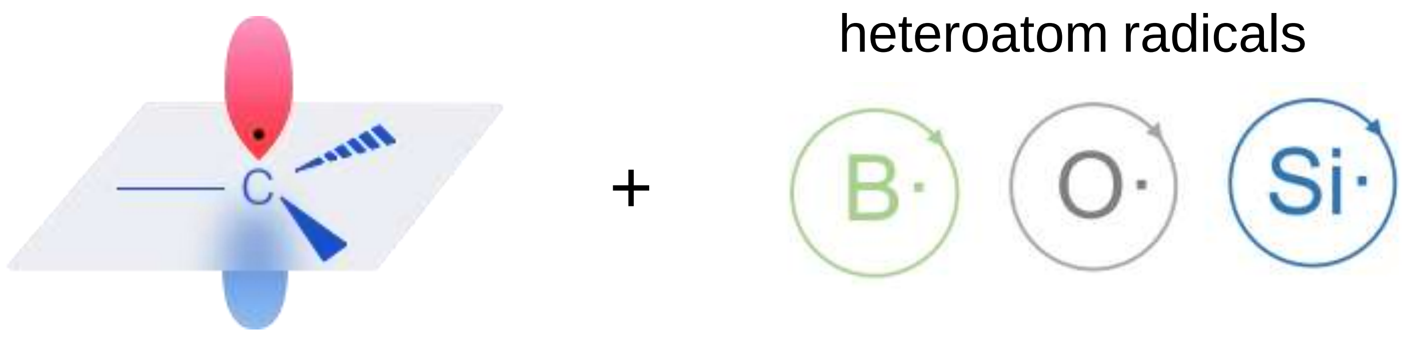
Limitation 1: termination	Limitation 2: carbon-based
	

Introducing heteroatom radicals

By introducing heteroatom radicals,

how to regulate the reactivity of carbon radicals?

how to introduce heteroatom in polymer main chain?



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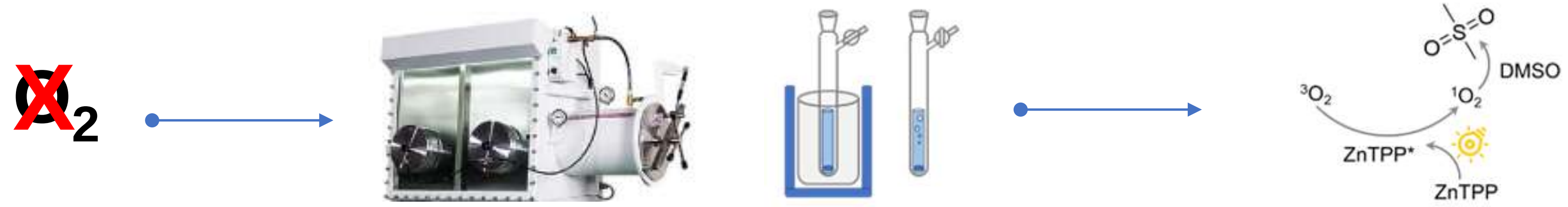
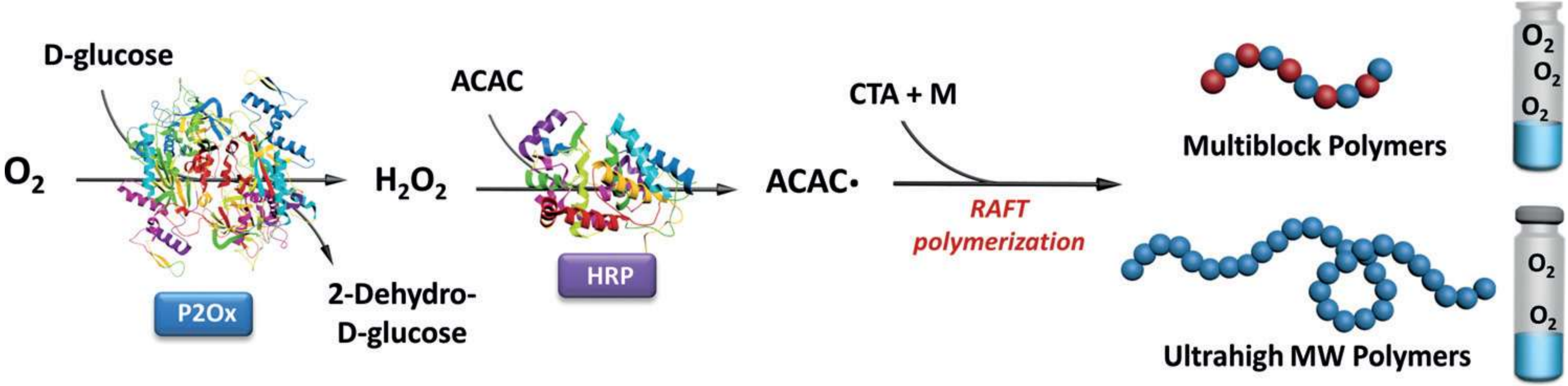
Organoboron and Oxygen Co-initiation

Oxygen is Radical Scavenger in Radical Polymerization

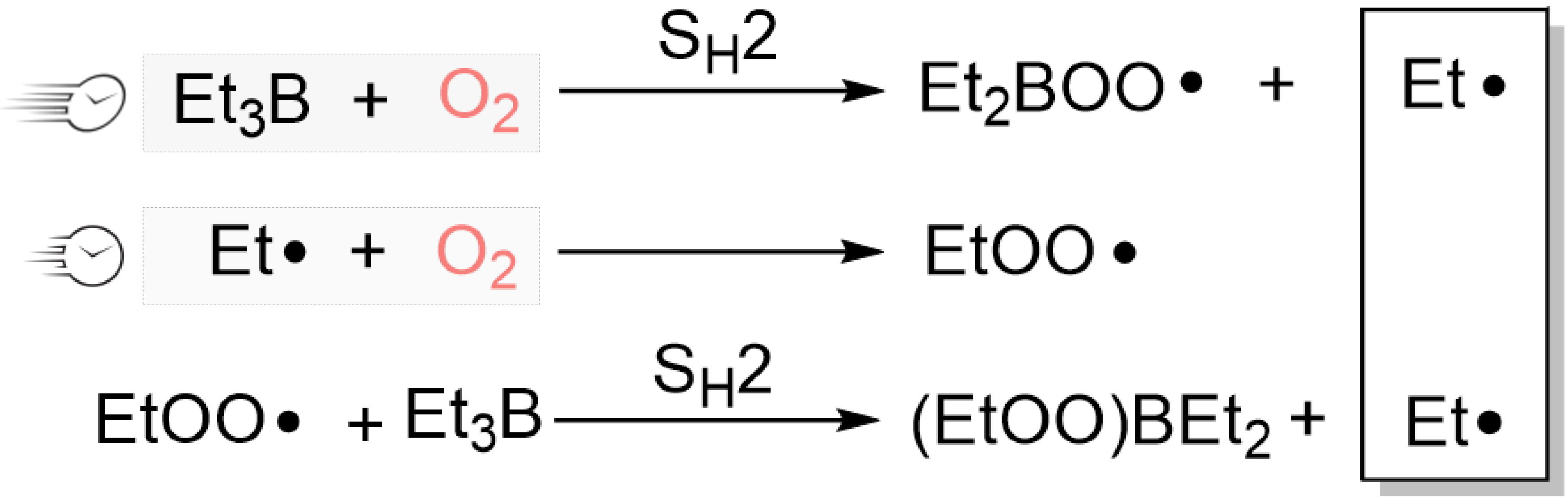




C. Boyer, *Chem. Soc. Rev.*, **2018**, 47, 4357–4387; Zesheng An, *Angew. Chem. Int. Ed.* **2017**, 56, 13852–13856.

Organoboron and Oxygen Co-initiation

Self-oxidation of alkylborane



X. Pan* et al., *Angew. Chem. Int. Ed.*, **2018**, 57, 9430. *Macromolecules*, **2020**, 53, 3700; **2021**, 54, 6000.

Organoboron and Oxygen Co-initiation

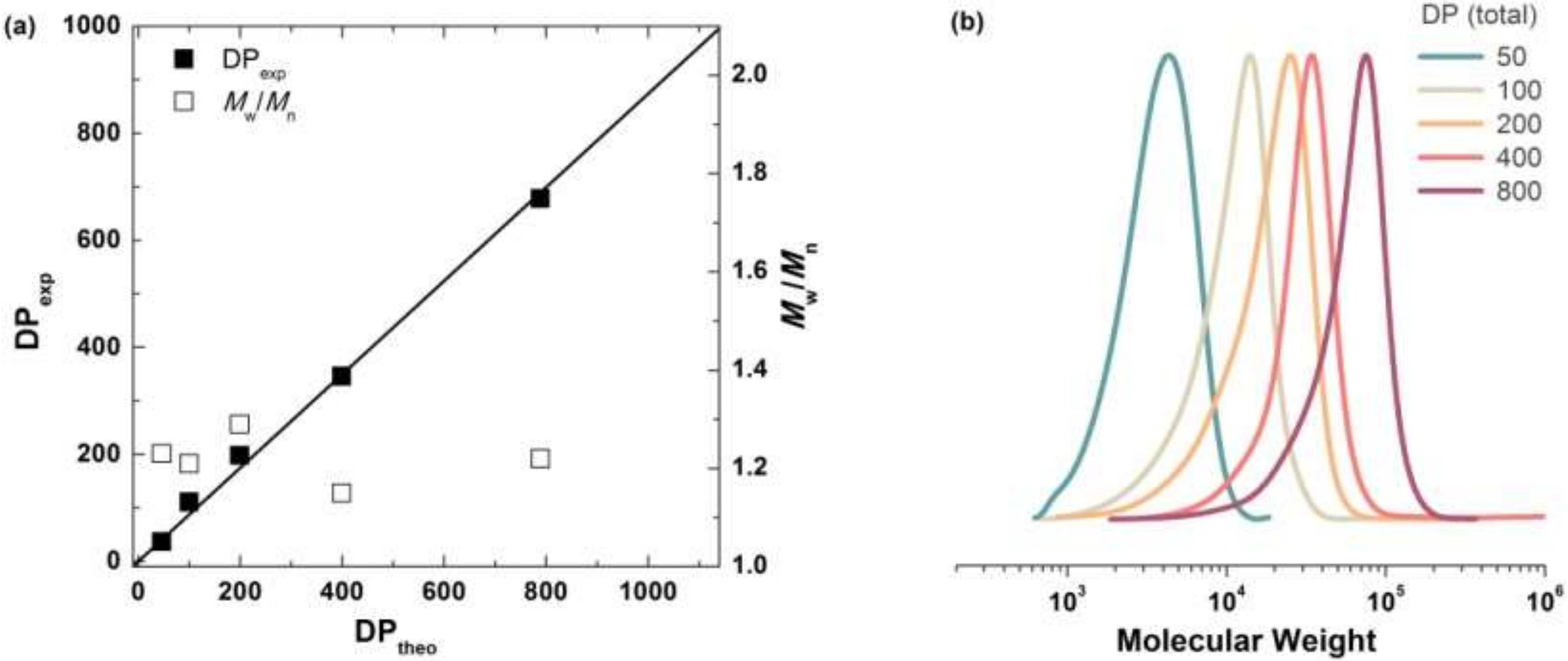
Entry	Solvent	Et_3B	Time	Conversion	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
1	DMSO	2.0	15 mins	>95%	33000	29200	1.15
2	DMSO	2.0	60 mins	-	-	-	-
3	DMF	2.0	15 mins	87%	30200	28000	1.20
4	MeCN	2.0	15 mins	71%	24700	23200	1.18
5	DMSO	0.5	15 mins	10%	3800	2000	1.12
6	DMSO	1.0	15 mins	77%	26700	19000	1.14
7	DMSO	4.0	15 mins	>98%	34000	20400	1.66

nitrogen atmosphere (entry 2)

Reaction conditions: $[MA]_0$:$[CTA\text{-}1]_0$:$[Et_3B]_0$ = 400:1:x, $[MA]_0$ = 8 M, Et_3B solution injected at once, ambient temperature and atmosphere

X. Pan* et al., *Angew. Chem. Int. Ed.*, **2018**, 57, 9430. *Macromolecules*, **2020**, 53, 3700; **2021**, 54, 6000.

Organoboron and Oxygen Co-initiation



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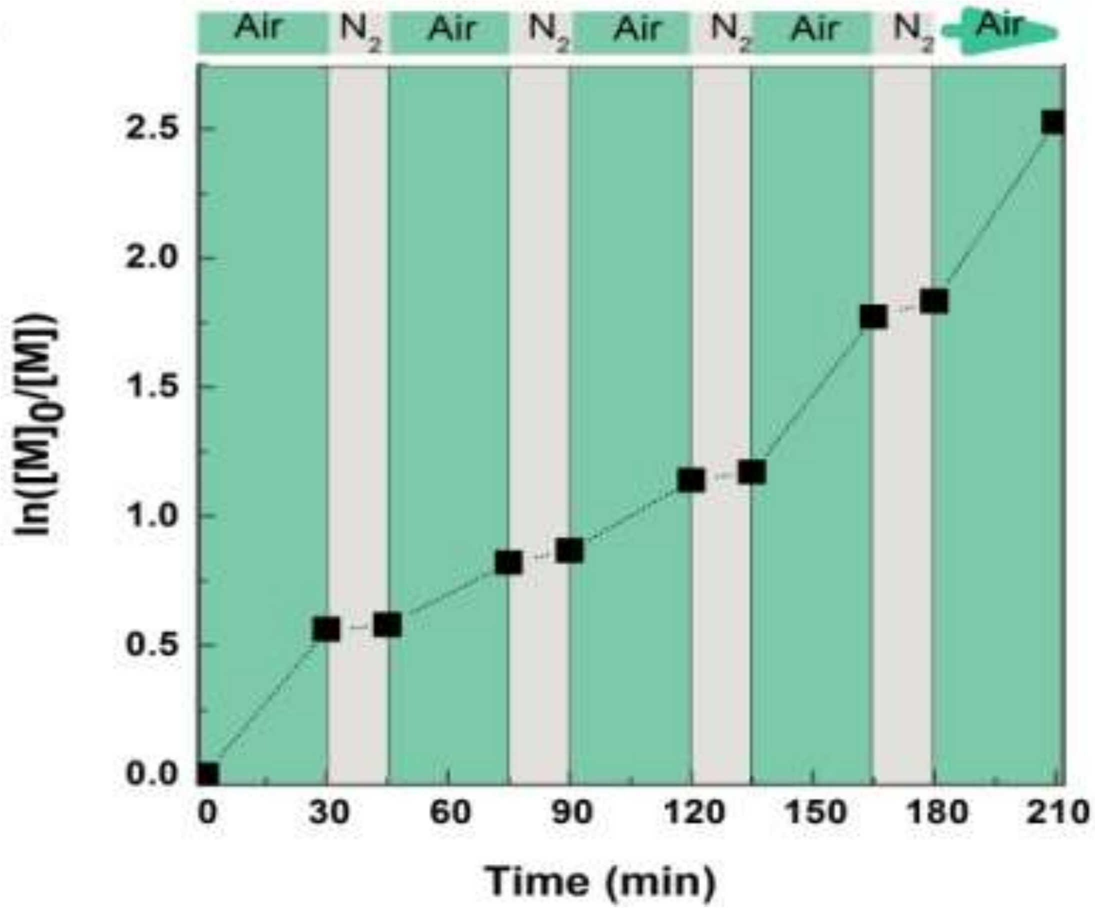
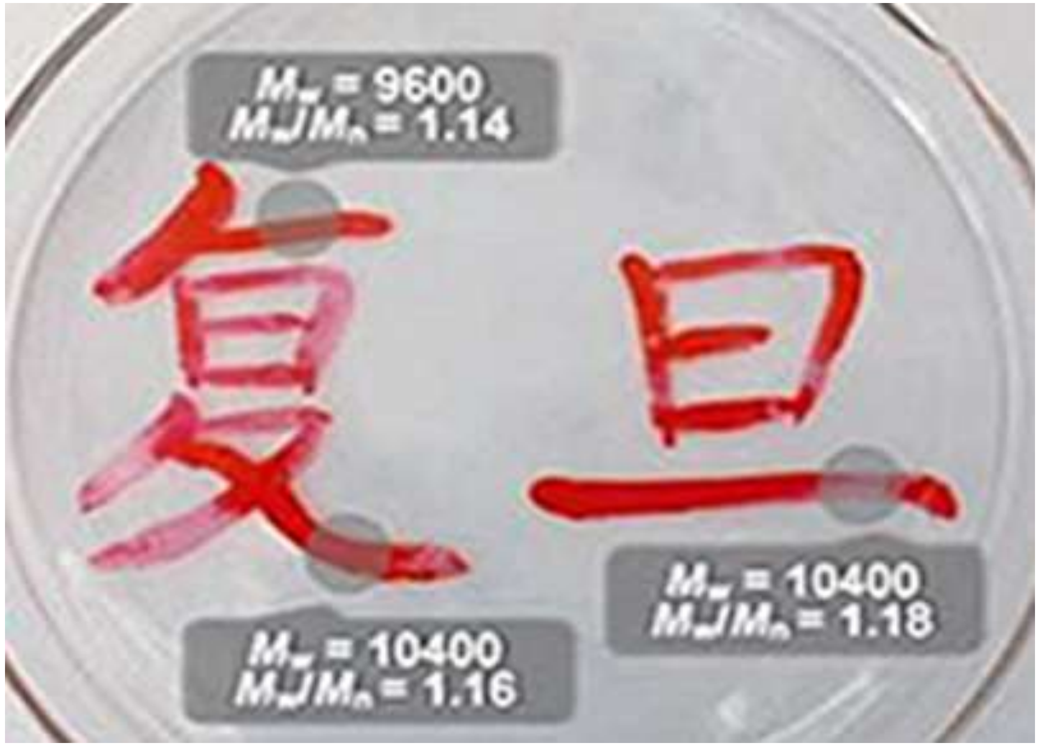
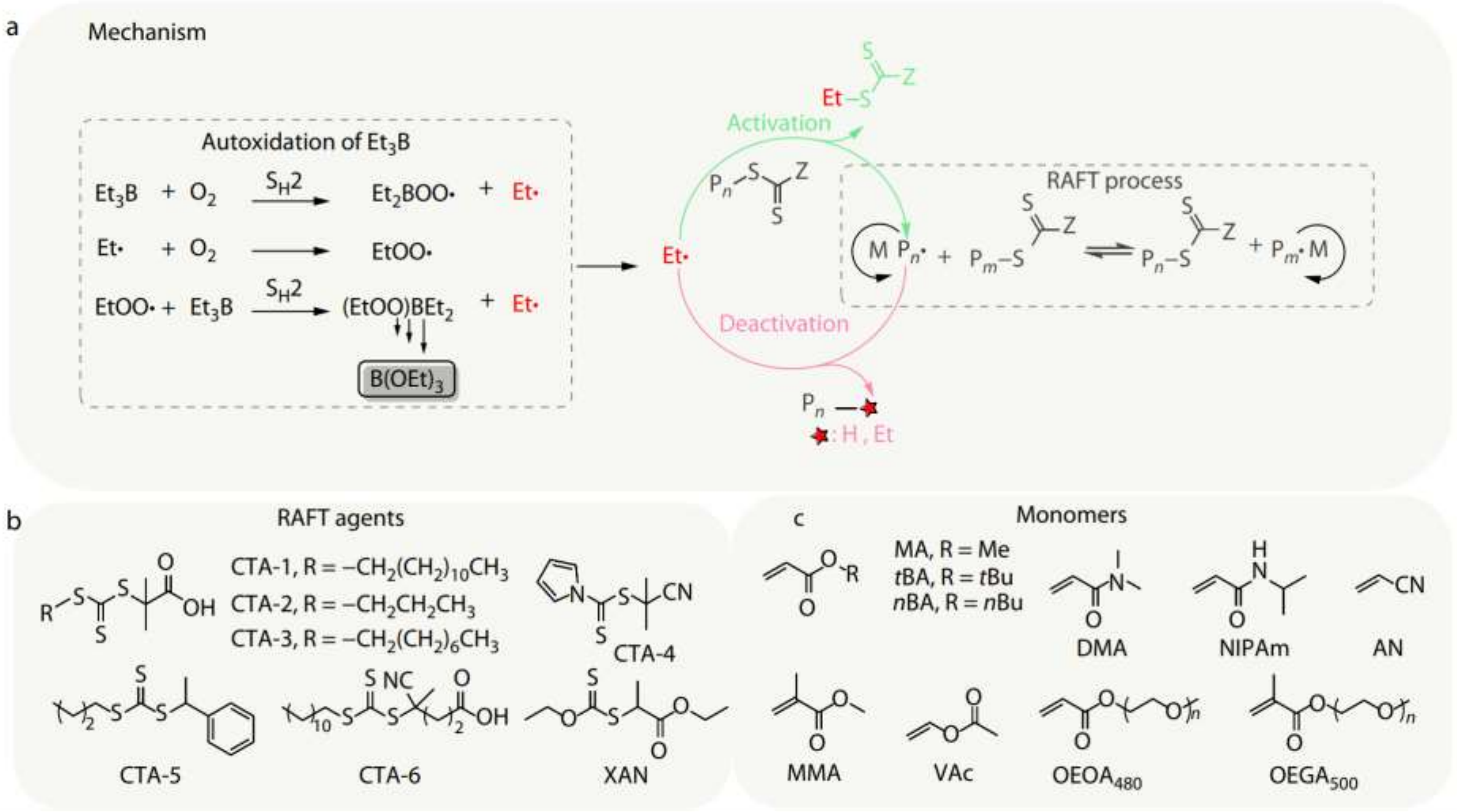




X. Pan* et al., *Angew. Chem. Int. Ed.*, **2018**, 57, 9430. *Macromolecules*, **2020**, 53, 3700; **2021**, 54, 6000.

Organoboron and Oxygen Co-initiation

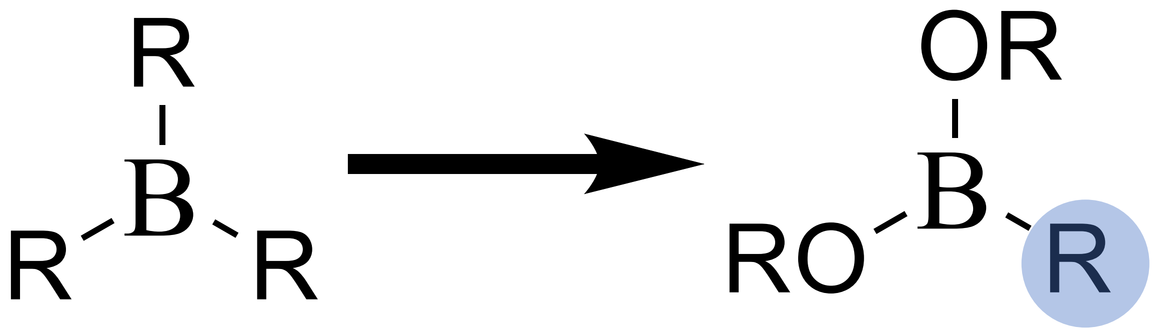
Removal of chain end and aqueous conditions



X. Pan* et al., *Chinese J. Polym. Sci.* **2020**, 38, 1178-1184.

Organoboron and Oxygen Co-initiation

Towards UHMW



>1 radical formed
limited radical structure
rapid autoxidation

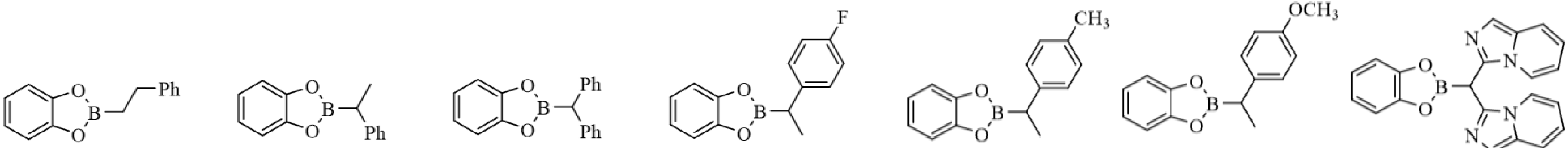
tuned autoxidation rate
only **ONE** radical formed
various radical structure
primary, secondary, benzylic..
electronic property…

X. Pan* et al., *Cell Rep. Phy. Sci.* **2020**, *1*, 100073. (Highlighted by Prof. Boyer in *Chem,* **2020**, 6, 1203)

Organoboron and Oxygen Co-initiation

Model Polymerization by Borane Radical Initiator

$$1600\ \text{MA} \xrightarrow[\text{8.0 M DMSO, rt, air, 3.5 h}]{\textbf{CTA-1}\text{, B-Cat}} \text{PMA}$$

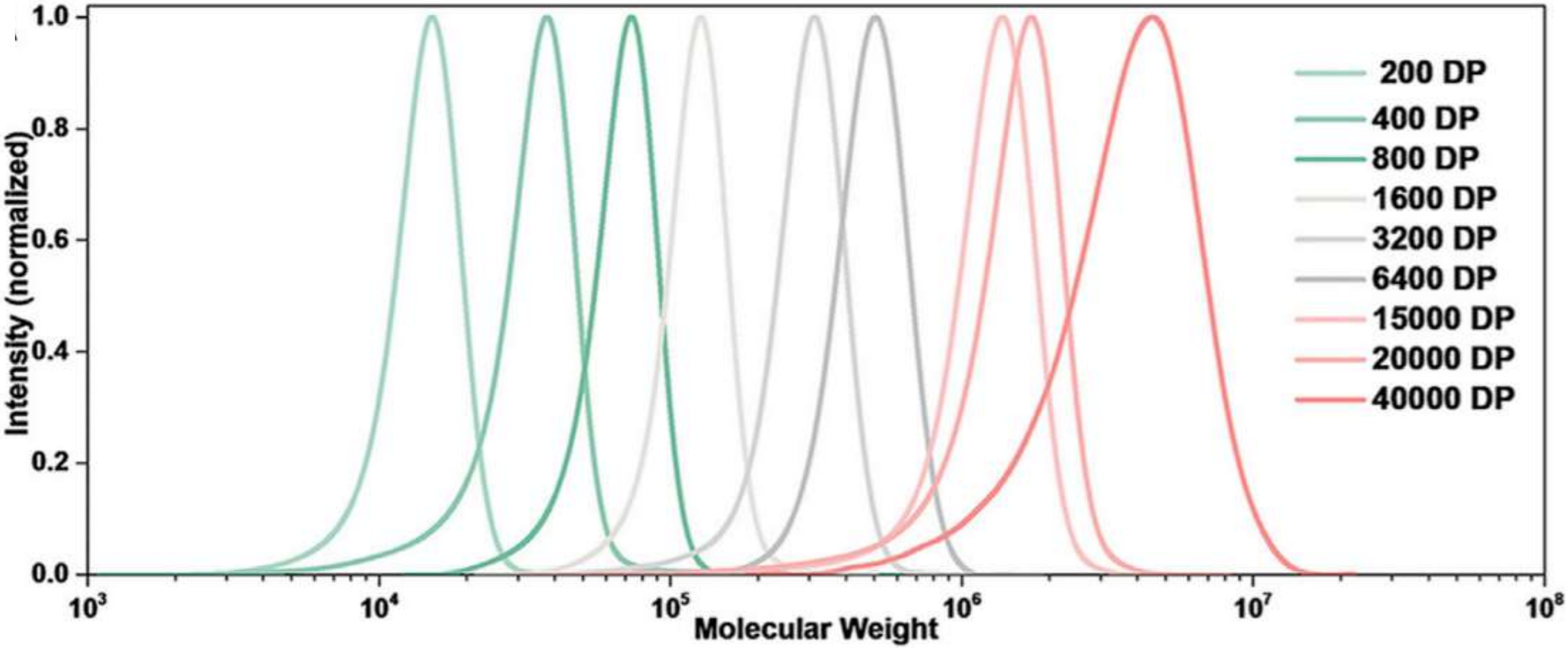


B-Cat-1	**B-Cat-2**	**B-Cat-3**	**B-Cat-4**	**B-Cat-5**	**B-Cat-6**	**B-Cat-7**
Conv. = 53%	Conv. = 89%	Conv. = 30%	Conv. = 70%	Conv. = 82%	Conv. = 70%	Conv. = 0
M_n = 53,267	M_n = 111,447	M_n = 34,002	M_n = 75,002	M_n =92,394	M_n = 73,629	
$Đ$ = 1.15	$Đ$ = 1.10	$Đ$ = 1.11	$Đ$ = 1.09	$Đ$ = 1.09	$Đ$ = 1.10	
	15000 DP					
	Conv. = 92%					
	M_n = 1072,74					
	$Đ$ = 1.09					

X. Pan* et al., *Cell Rep. Phy. Sci.* **2020**, *1*, 100073. (Highlighted by Prof. Boyer in *Chem,* **2020**, 6, 1203)

Organoboron and Oxygen Co-initiation

UHMW polymers



X. Pan* et al., *Cell Rep. Phy. Sci.* **2020**, *1*, 100073. (Highlighted by Prof. Boyer in *Chem,* **2020**, 6, 1203)

Organoboron and Oxygen Co-initiation

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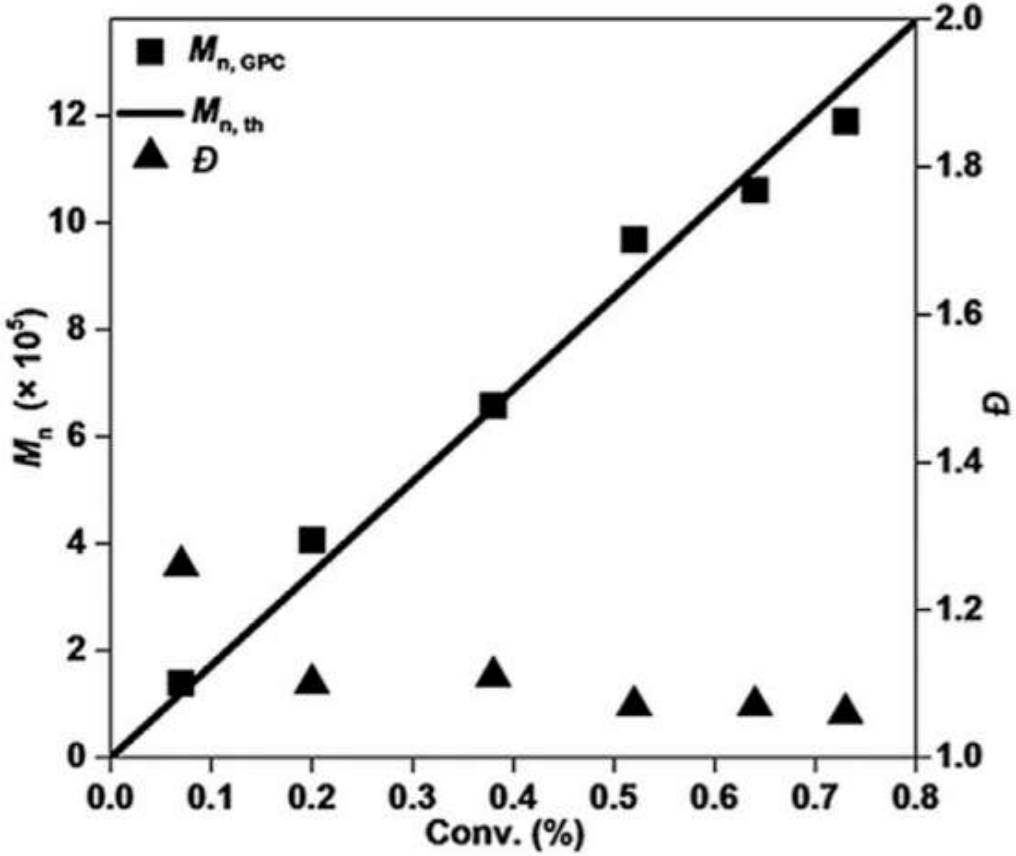
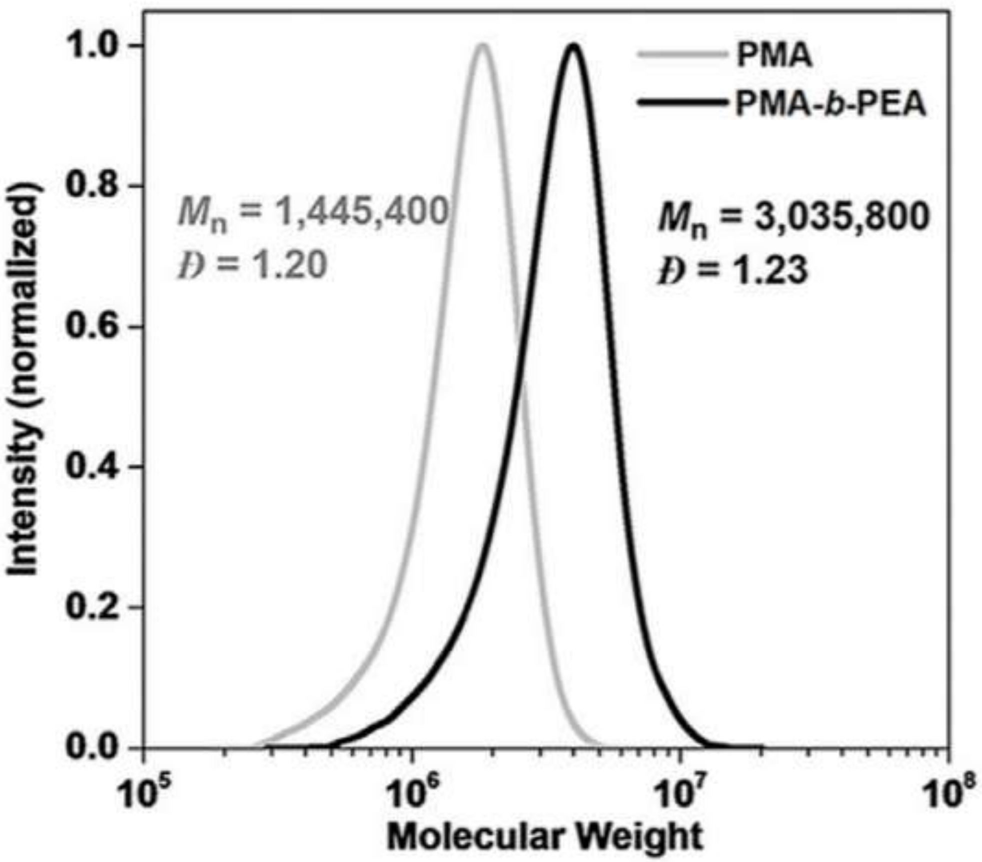
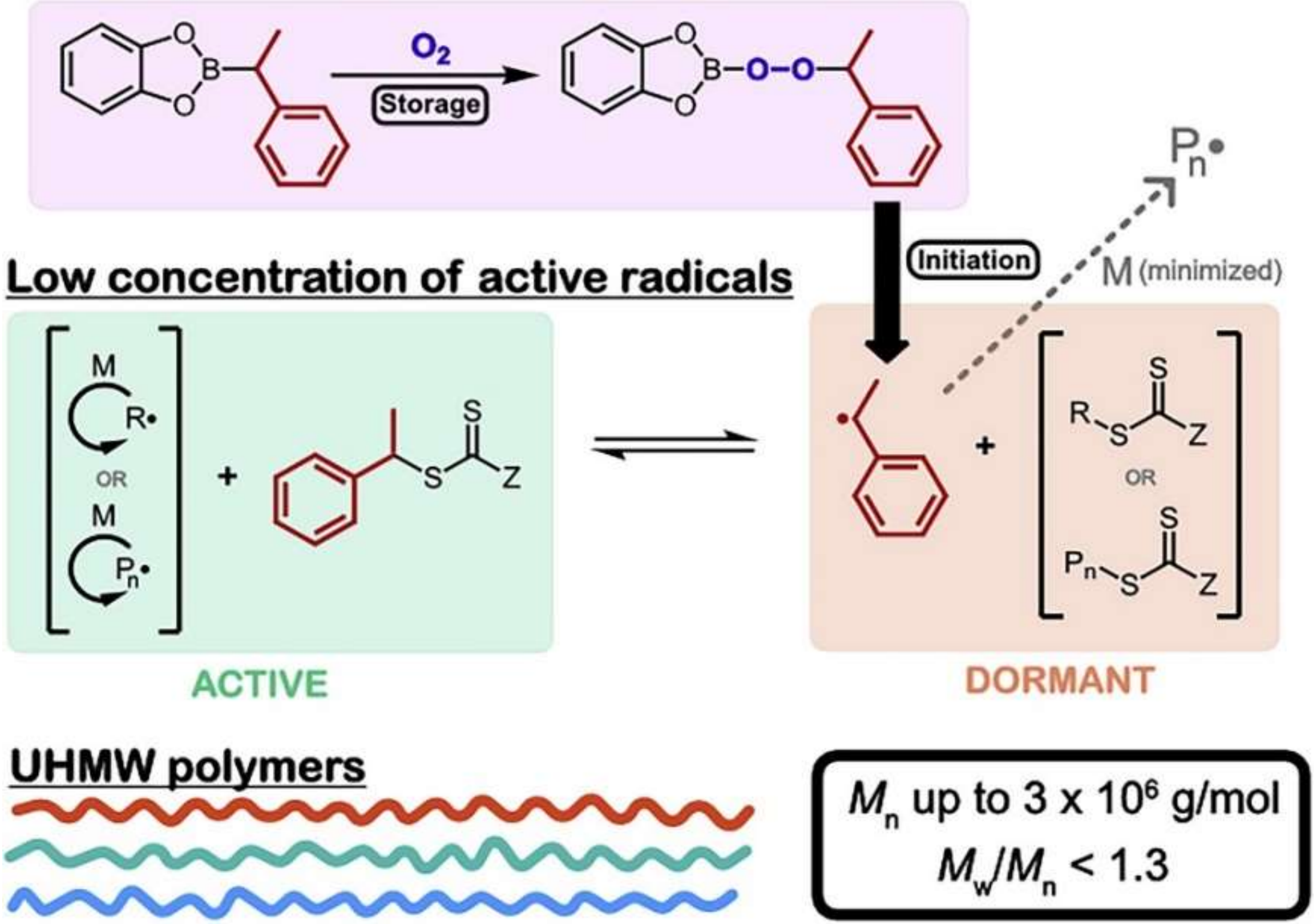




X. Pan* et al., *Cell Rep. Phy. Sci.* **2020**, *1*, 100073. (Highlighted by Prof. Boyer in *Chem,* **2020**, 6, 1203)

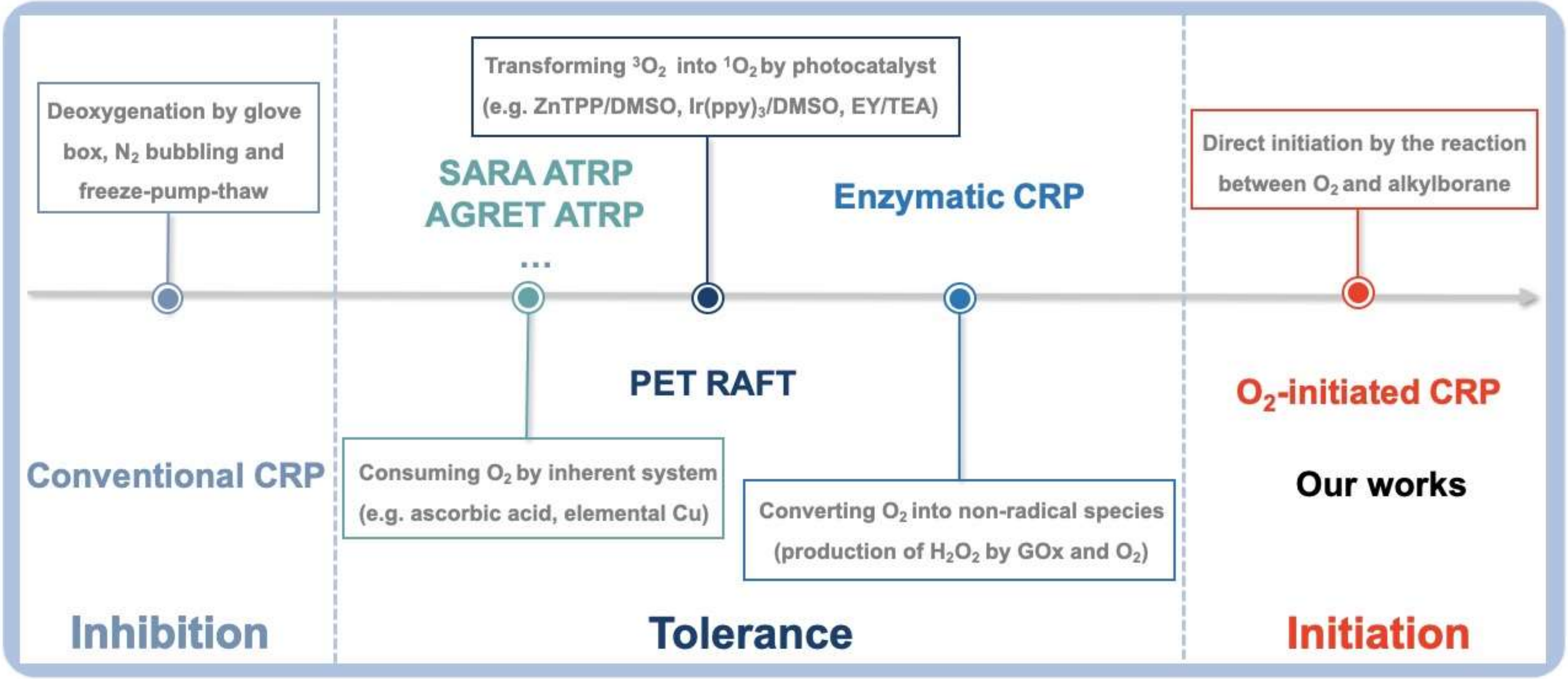
Organoboron and Oxygen Co-initiation

Proposed mechanism



C. Boyer, *Chem*, **2020**, 6, 1203.

Organoboron and Oxygen Co-initiation



Controlled radical polymerization: from oxygen inhibition and tolerance to oxygen initiation. *Chinese J. Polym. Sci.* **2021**, 39, 1084-1092. (invited, Feature Article, Special Topic: Reversible Deactivation Radical Polymerization)

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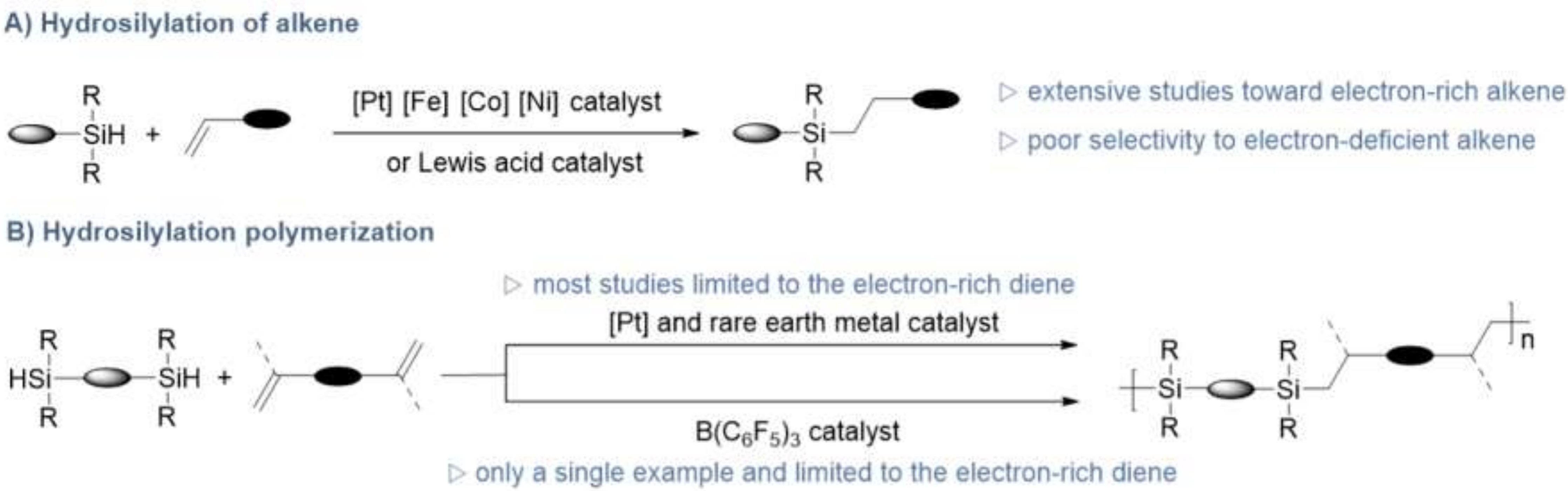
Radical Hydrosilylation Polymerization



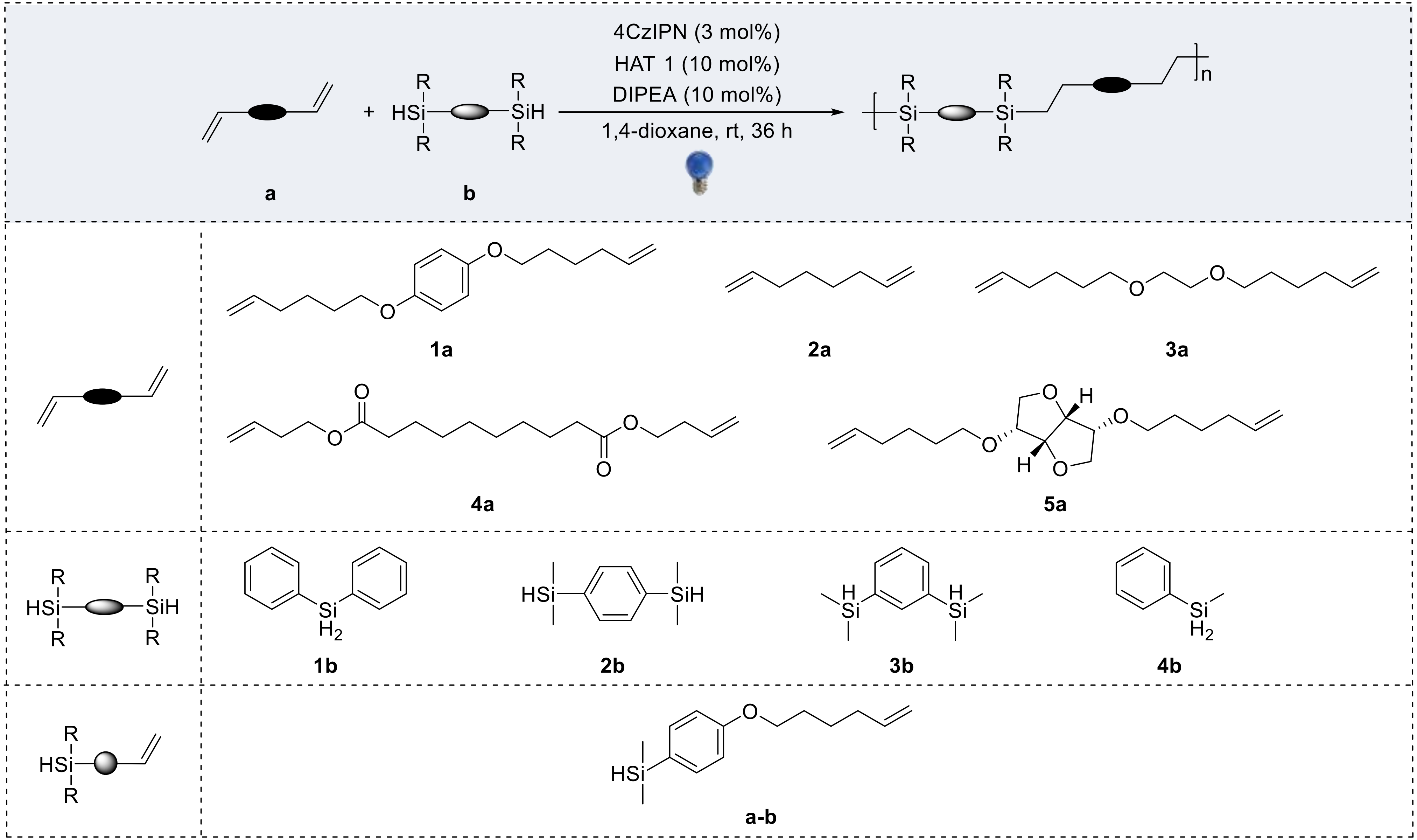
POSSIBILITY?:

Hydrosilylation polymerization via radical mechanism

Si-H → Si radical by photoredox and HAT catalysis

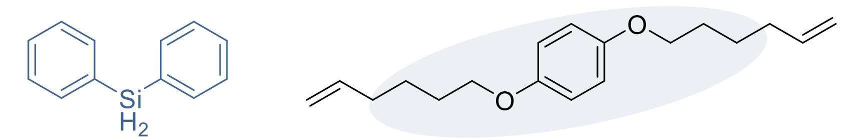
Seewon Joung, Jeung Kim, Sukbok Chang, Craig Hawker

Radical Hydrosilylation Polymerization

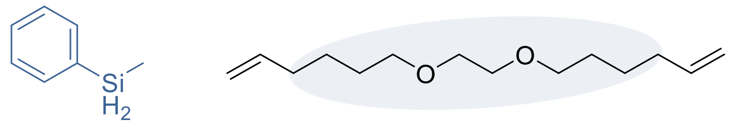


J. Am. Chem. Soc., **2021**, 143, 19167. (Highlighted by Benjamin List, *Synfacts,* **2022**, 18, 0078)

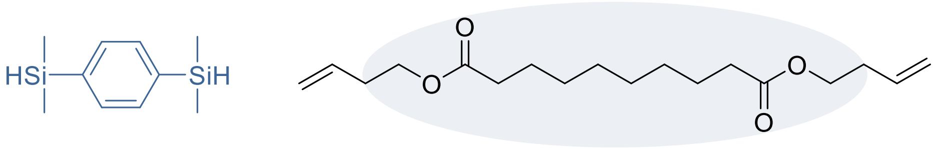
Radical Hydrosilylation Polymerization



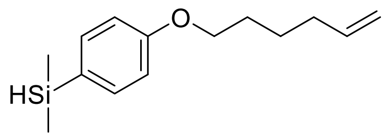
Conv. 99%, M_n = 14100, Đ = 2.08



Conv. 91%, M_n = 6600, Đ = 1.46

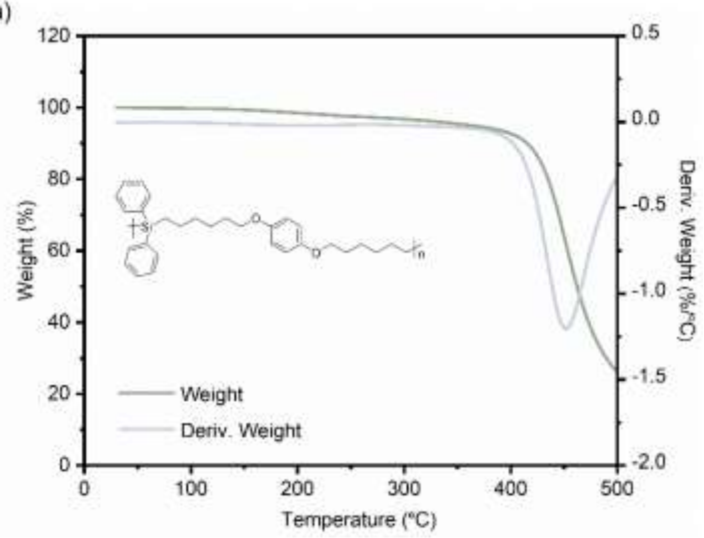


Conv. 92%, M_n = 7600 , Đ = 1.47

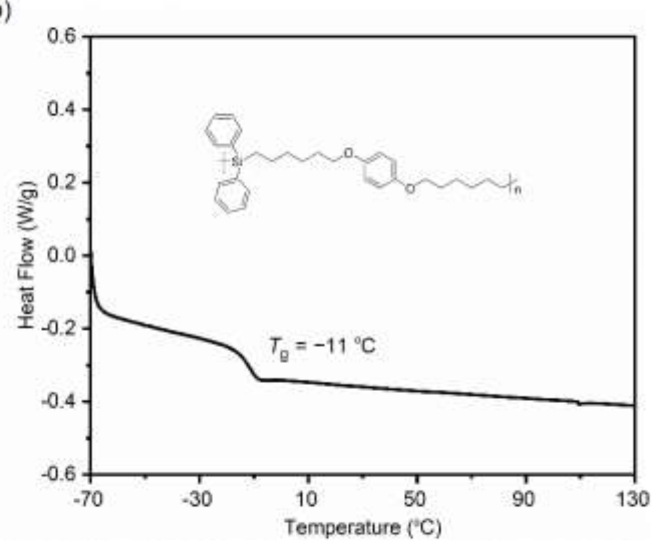


Conv. 82%, M_n = 4600 , Đ = 1.60

a)



b)



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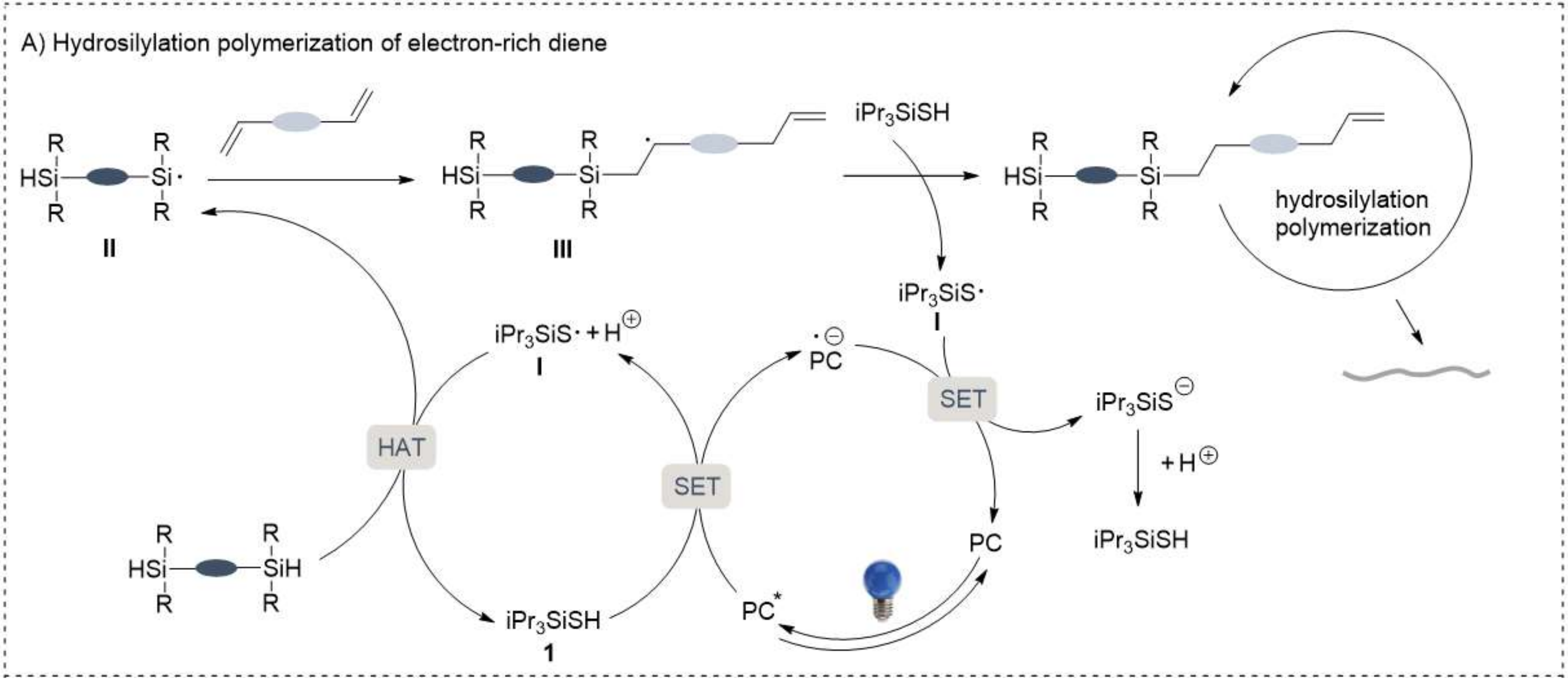
Radical Hydrosilylation Polymerization



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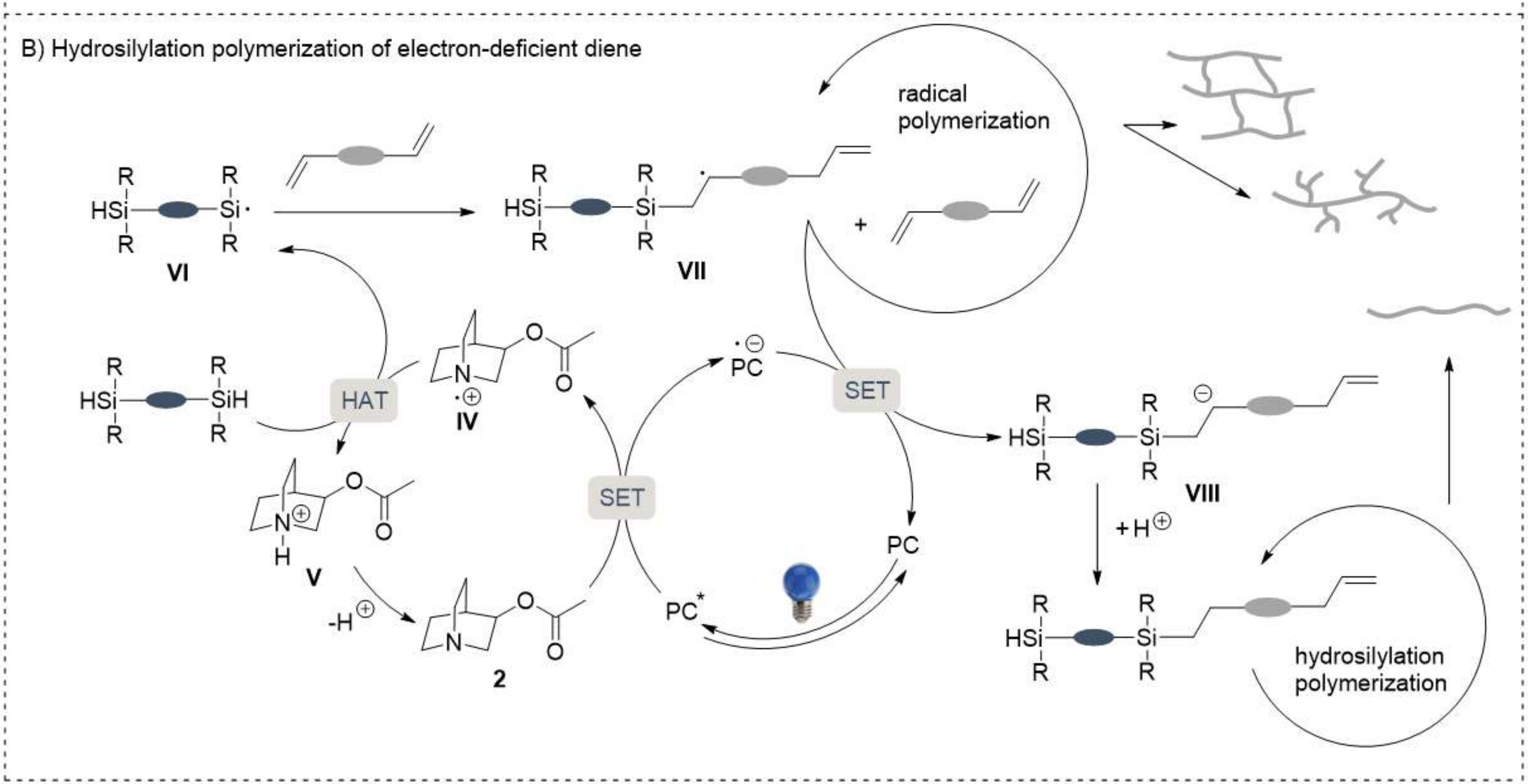
Radical Hydrosilylation Polymerization



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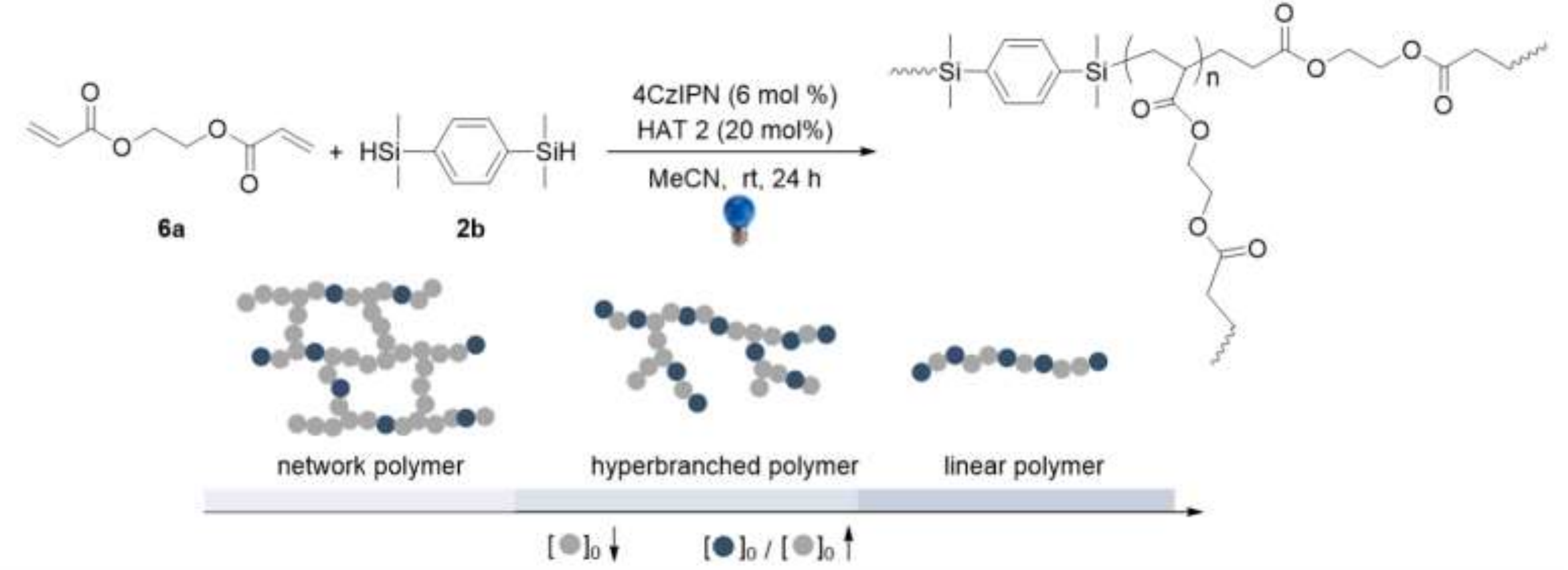
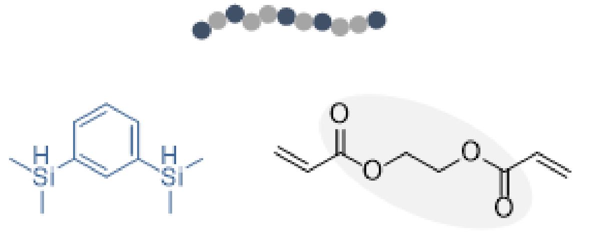
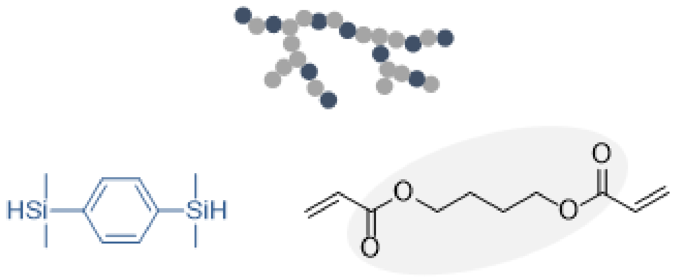
Radical Hydrosilylation Polymerization

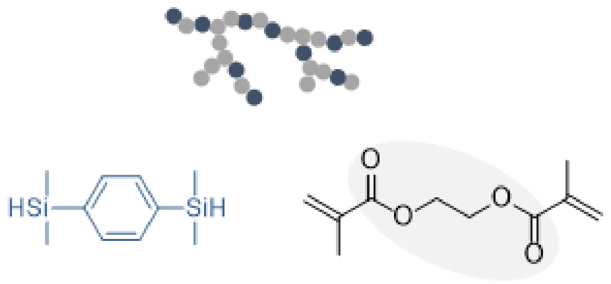




C=C conv. >99%, Si−H/C=C = 0.92
M_n = 7900, Đ = 1.22



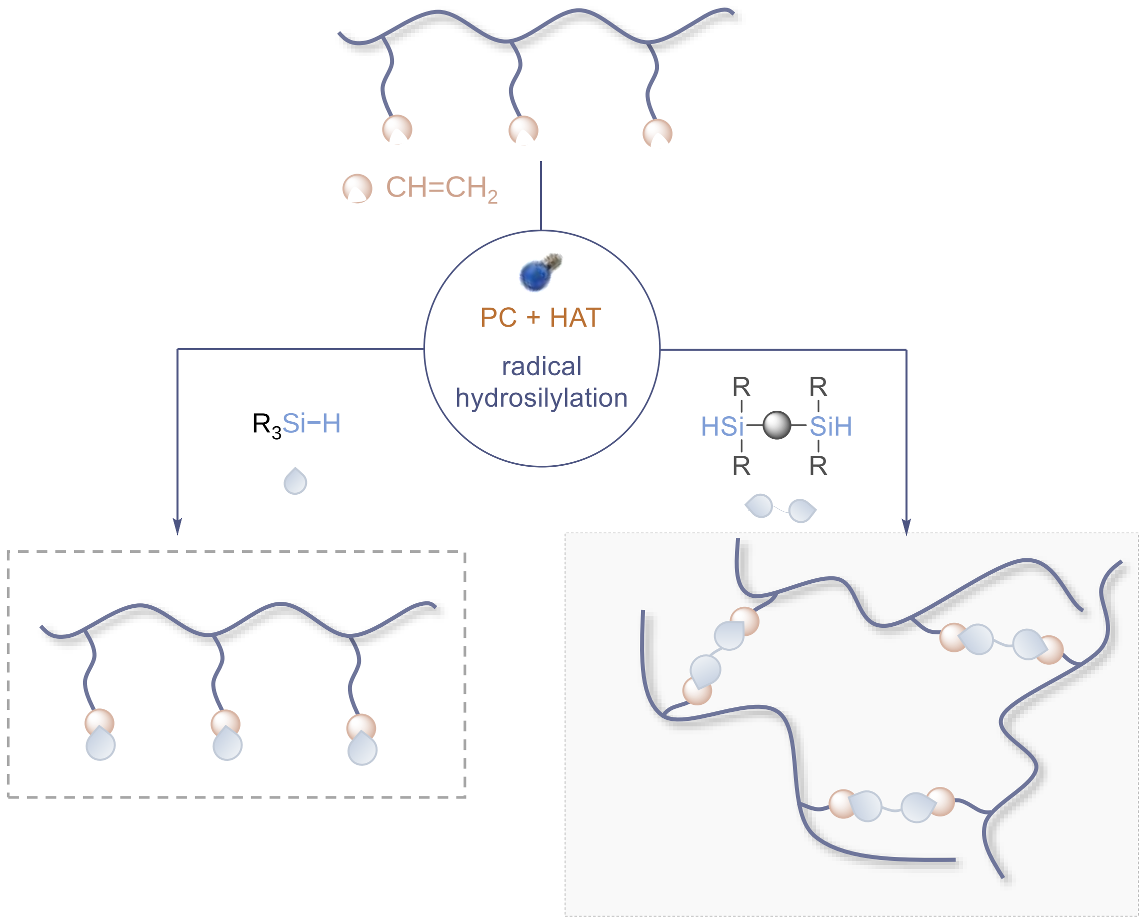
C=C conv. >99%, Si−H/C=C = 0.43
M_n = 12900, Đ = 1.40

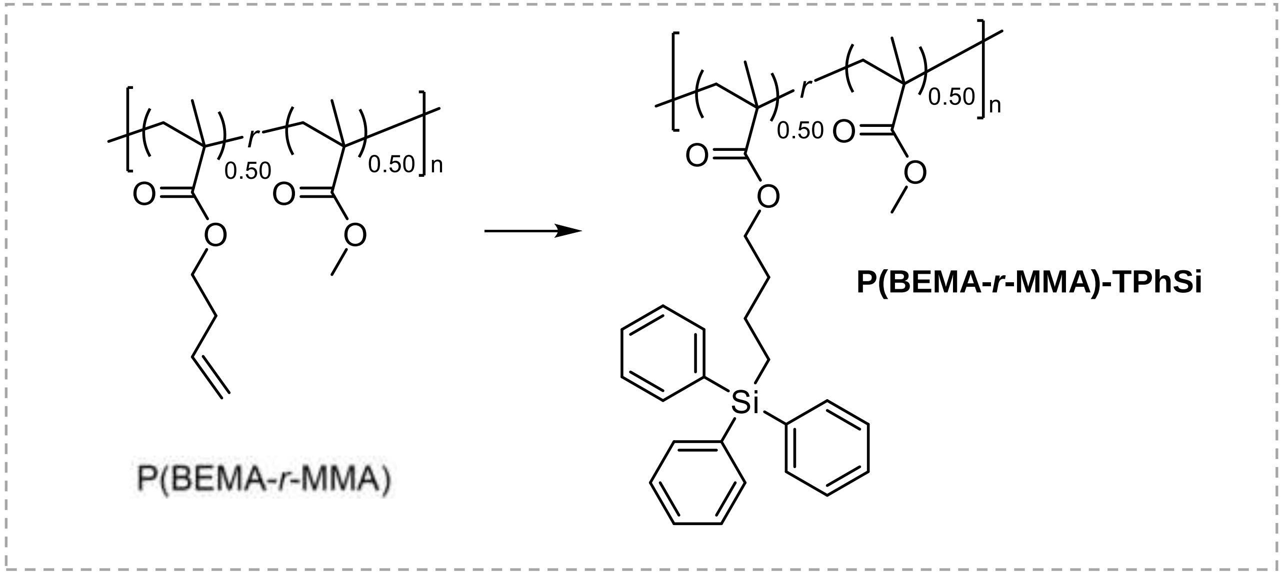


C=C conv. >99%, Si−H/C=C = 0.46
M_n = 8700, Đ = 1.55

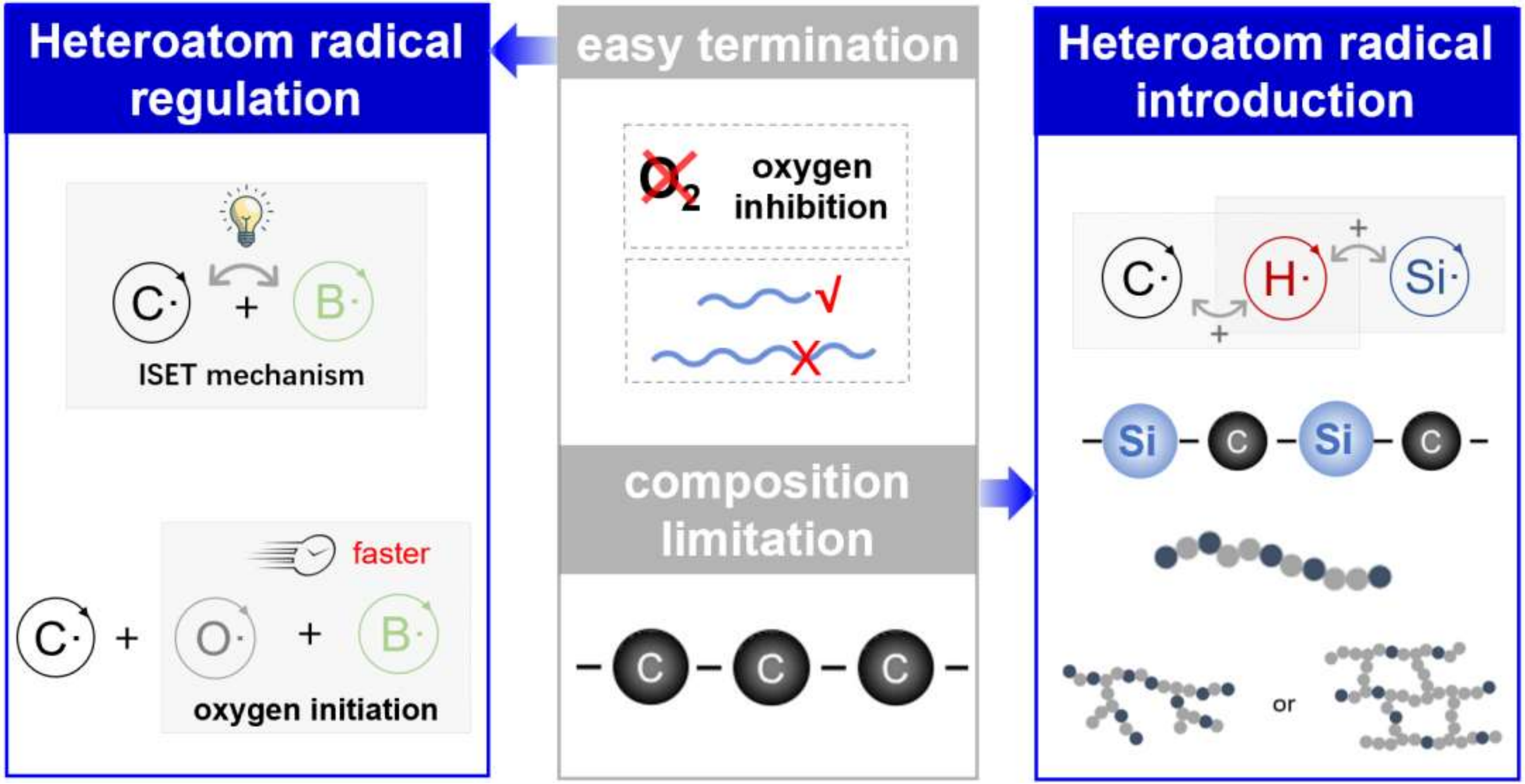
J. Am. Chem. Soc., **2021**, 143, 19167. (Highlighted by Benjamin List, *Synfacts,* **2022**, 18, 0078)

Radical Hydrosilylation Post-Modification





Summary



Heteroatom radical regulation
C·
+
B·
ISET mechanism
faster
C·
+
O·
+
B·
oxygen initiation
easy termination
O_2
oxygen inhibition
√
X
composition limitation
C
C
C
Heteroatom radical introduction
C·
H·
Si·
+
+
Si
C
Si
C
or

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