Thomas Group

TEXAS A&M UNIVERSITY

Catalyst Transfer Polymerization Reactions Past, Present, Future

2-22-2022

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Texas A&M University

Outline

Part I. Properties of Polymers
- Dispersity
- Growth

Part II. The Discovery
- McCullough Group
- Yokozawa Group
  - Gradient Copolymers

Part III. Ring-Walking
- van der Boom Group

Part IV. Mechanistic Studies
- Rate-Determining Step
- Ring-walking Efficiency

Part V. Applications
- Gomez Group

Properties of Polymers: Dispersity

Weight-average molecular weight (M_W)
Number-average molecular weight (M_n)

$$Đ = \frac{M_W}{M_n}$$

Example: Mixture of $\frac{1}{3}$ pentane, $\frac{1}{3}$ hexane, $\frac{1}{3}$ heptane

Pentane 72 $\frac{g}{mol}$

Hexane 86 $\frac{g}{mol}$

Heptane 100 $\frac{g}{mol}$

Total Mass 258 $\frac{g}{mol}$

Weight-average molecular weight (M_W)

$$M_W = \left(\frac{72}{258}\right)72 + \left(\frac{86}{258}\right)86 + \left(\frac{100}{258}\right)100$$

$$= 20.1 + 30.0 + 38.8 = 88.9$$

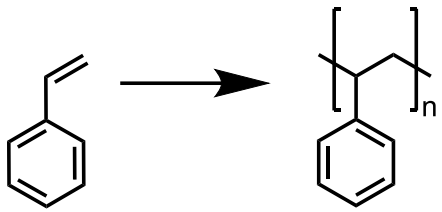
Most of the weight was in heptane (43.6 %)

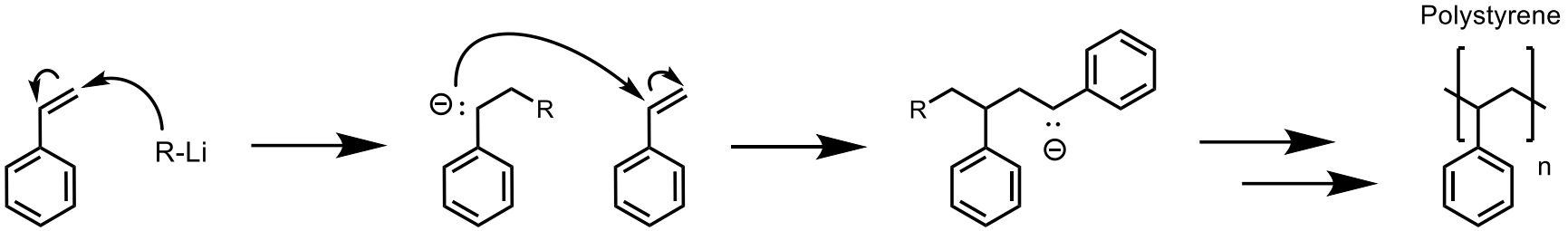
Number-average molecular weight (M_n)

$$M_n = \frac{1}{3}(72) + \frac{1}{3}(86) + \frac{1}{3}(100) = 86$$

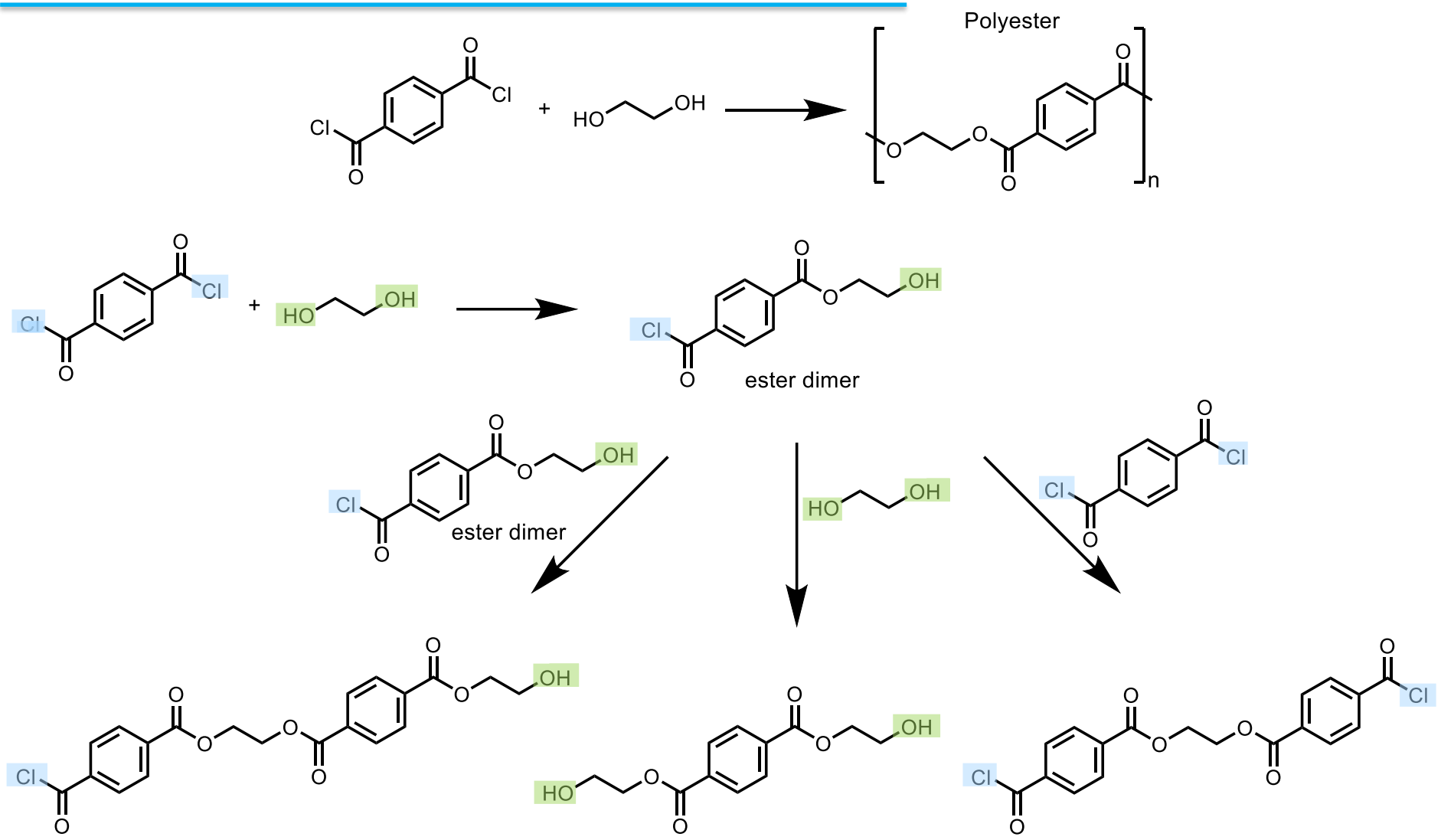
$$Đ = \frac{M_W}{M_n} = \frac{88.9}{86} = 1.03$$

Properties of Polymers: Chain-Growth

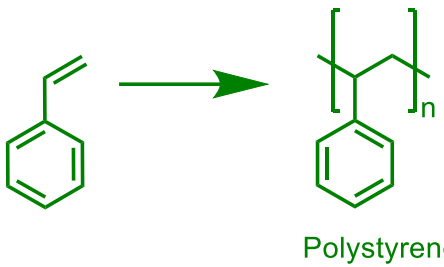


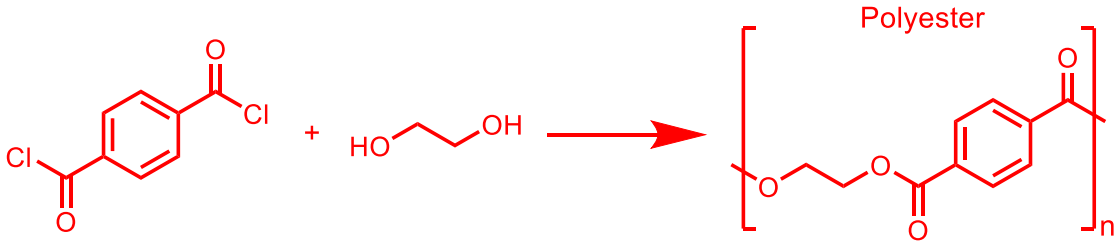


Properties of Polymers: Step-Growth

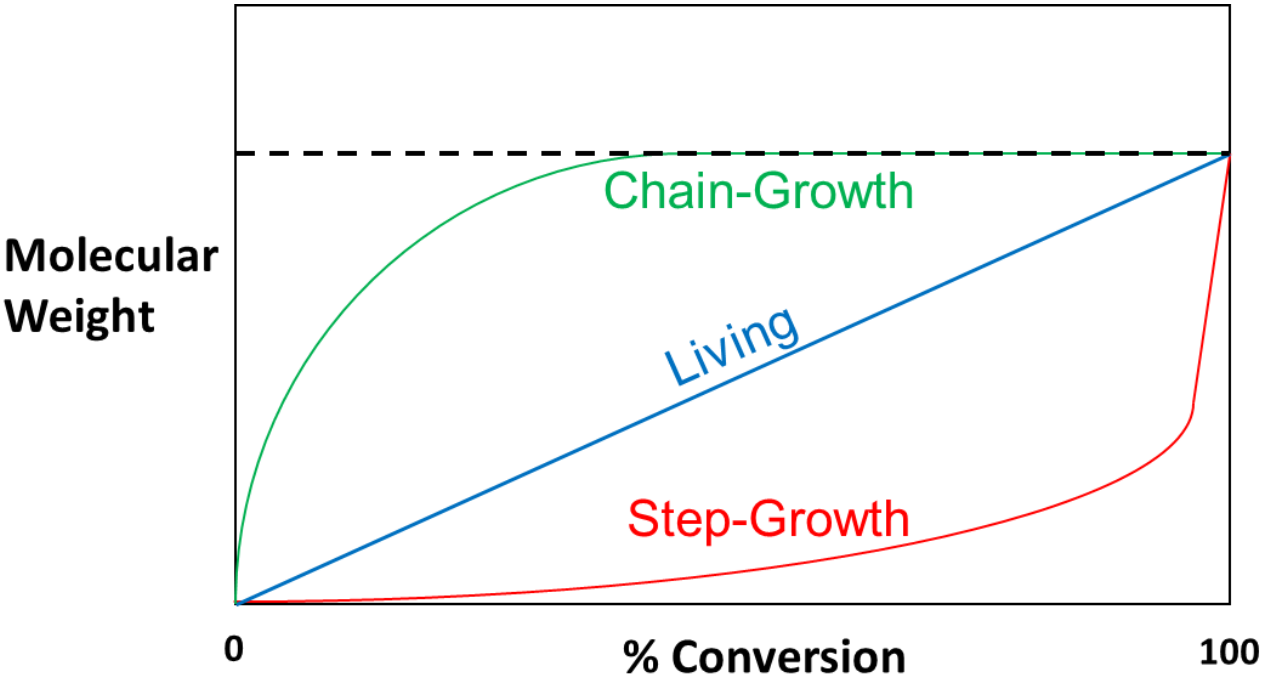


Properties of Polymers: Growth

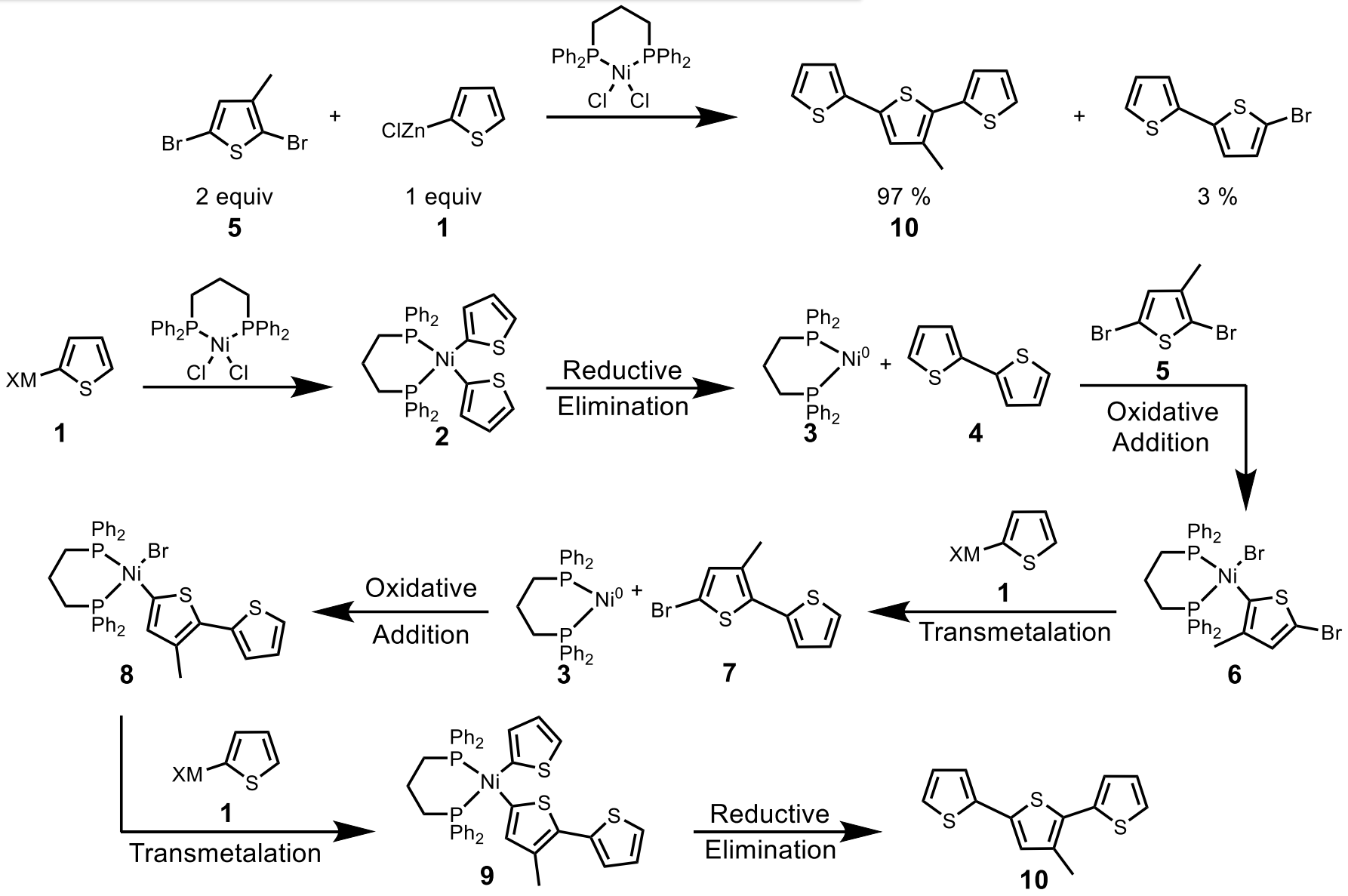




Catalyst Transfer Polymerization

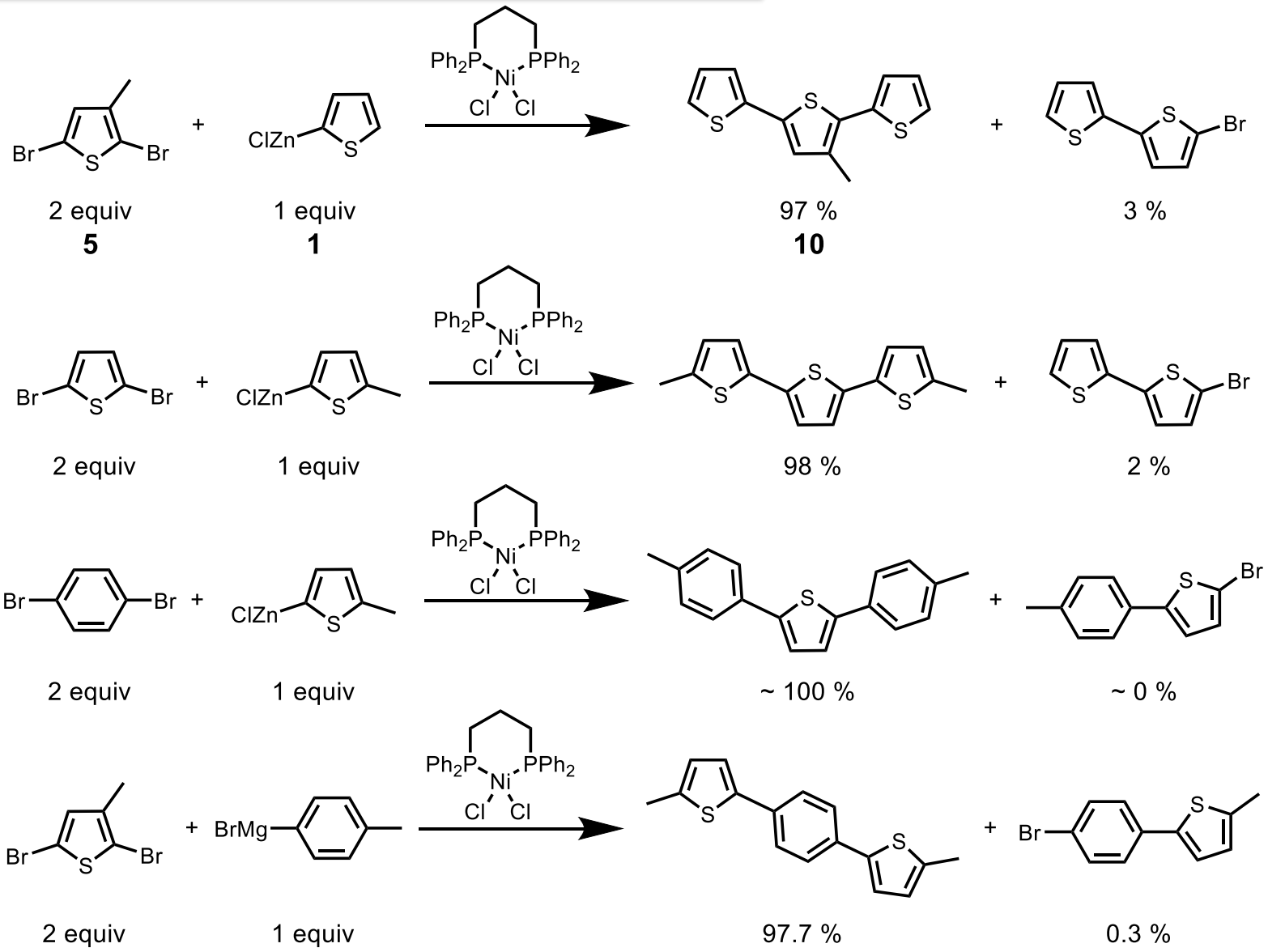


McCullough Group - dpppNiCl$_2$



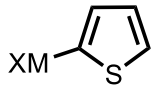
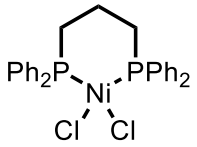
Sheina, E.E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 10, 3526–3528.

Screening Reactions

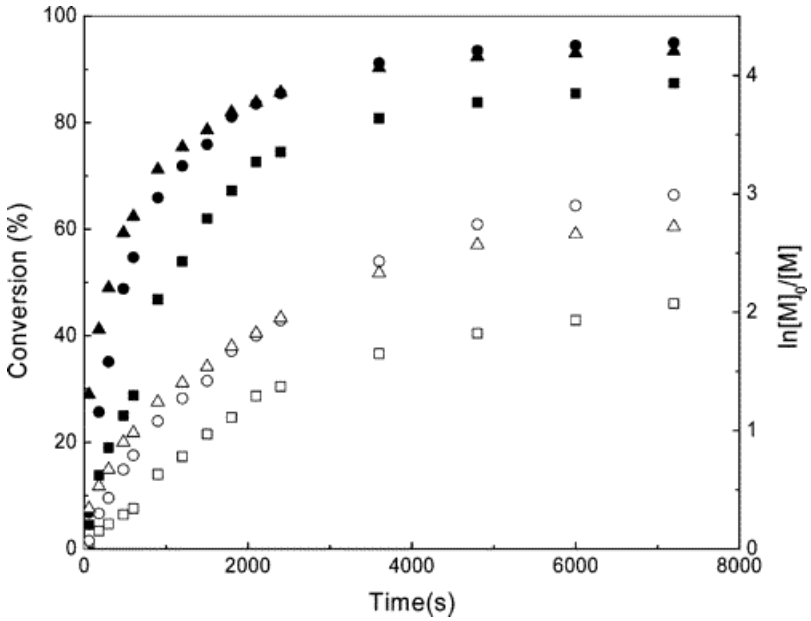


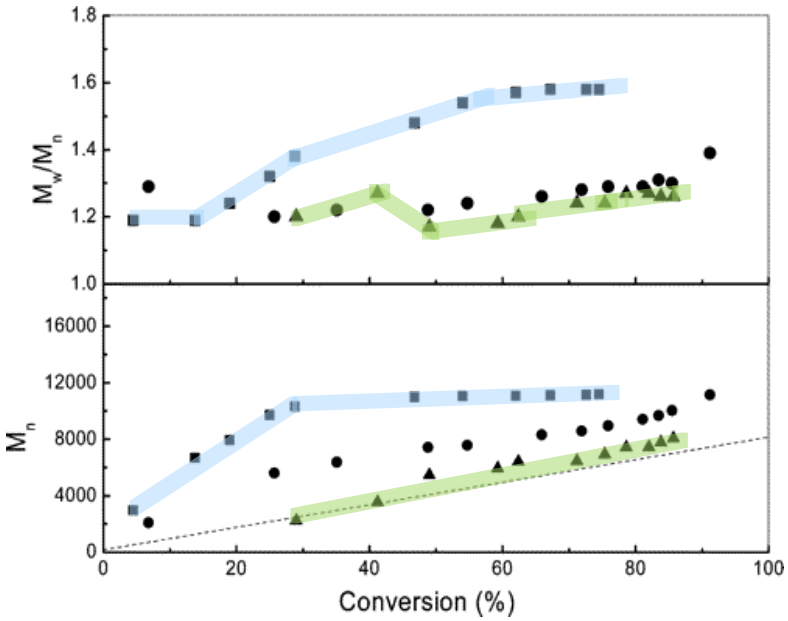
Sheina, E.E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 10, 3526–3528.

More Evidence of Chain Growth Polymerization Pt. 1

Ratio	▲	●	■
 1	49	57	136
	75 mM	75 mM	75 mM
	1	1	1
	1.5 mM	1.3 mM	0.55 mM

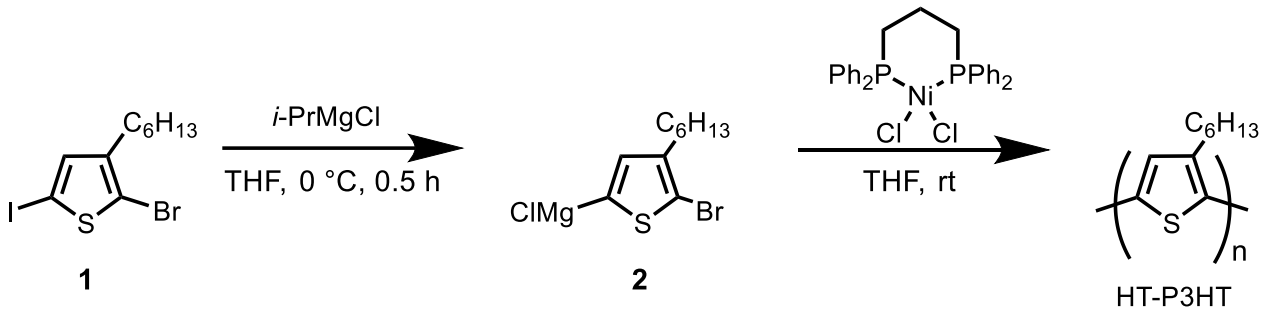
▲	Narrow dispersity
●	Highest conversion *
■	Broad dispersity High molecular weights

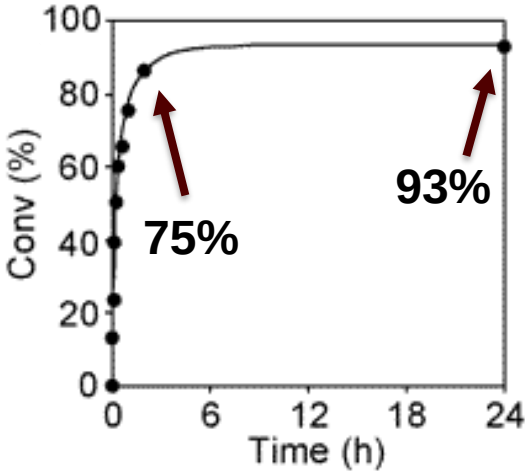


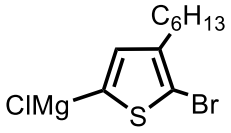


Sheina, E.E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 10, 3526–3528.

Yokozawa Group - $dpppNiCl_2$

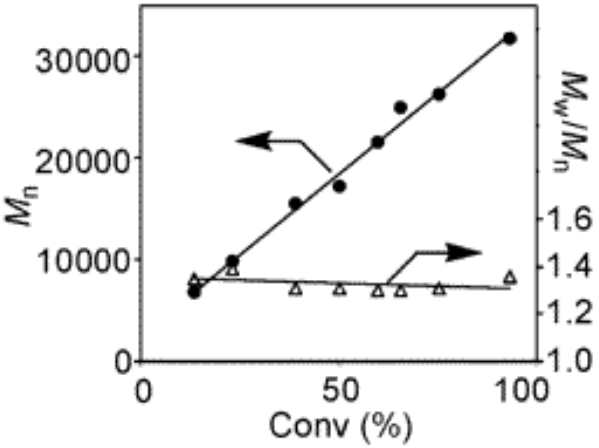




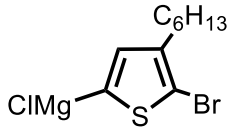


2

Molecular Weight



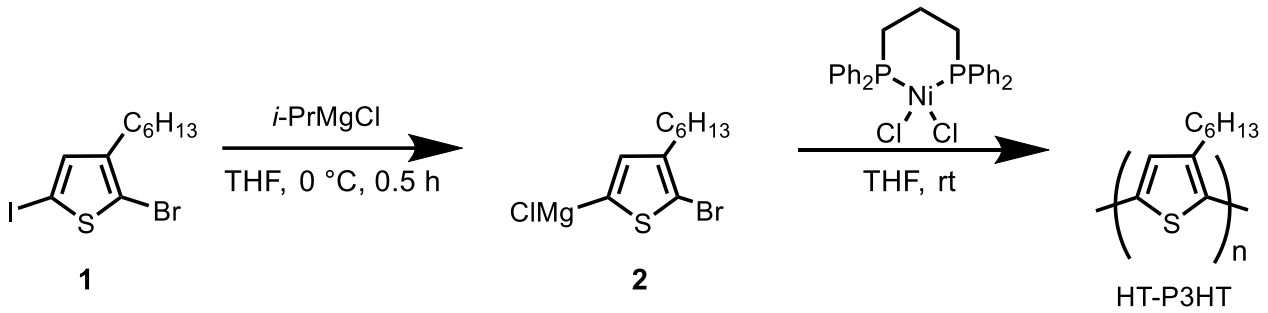
Dispersity

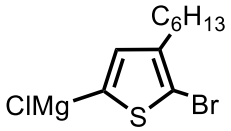
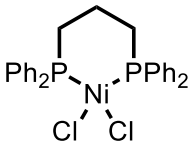


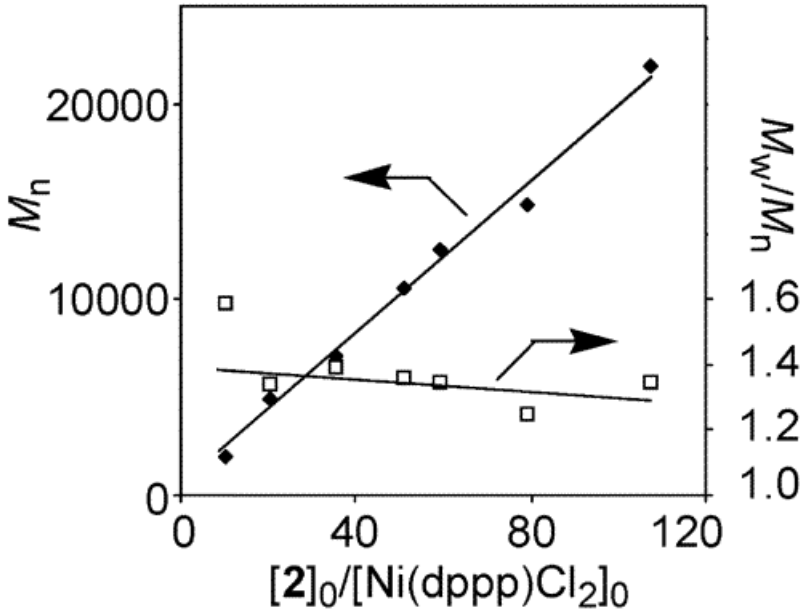
2

Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 4, 1169–1171.

More Evidence of Chain Growth Polymerization



Ratio	10	60	109
 **2**	0.12 M	0.12 M	0.12 M
	11.8 mM	2 mM	1.1 mM

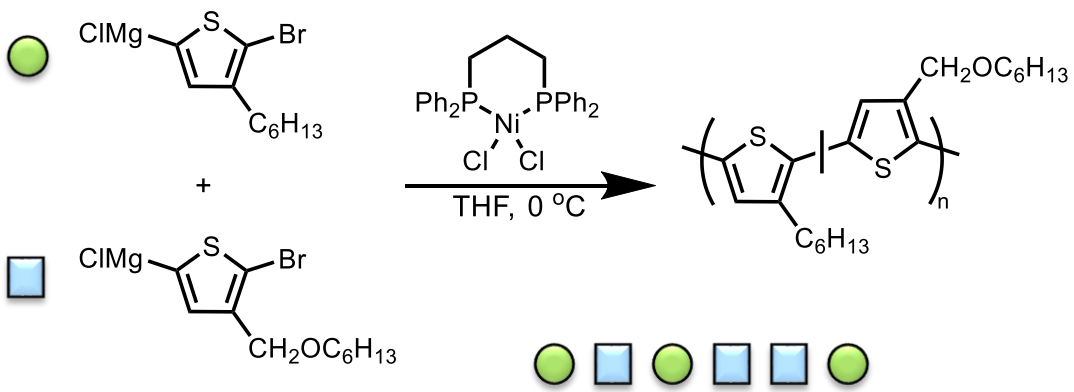


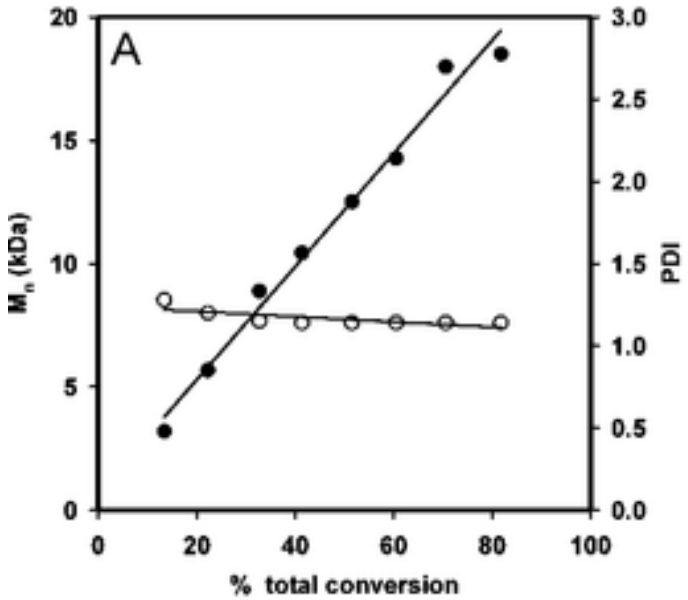
Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 4, 1169–1171.

Gradient π-Conjugated Copolymers

After Monomer Addition

GPC Trace	Conv	M_n	M_w/M_n
B	90 %	8900	1.34
A	93 %	17200	1.34

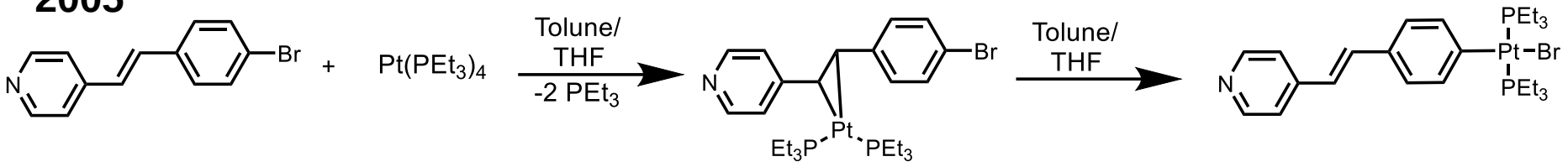




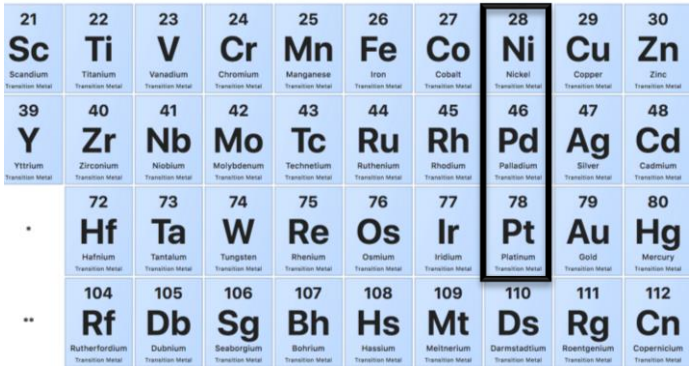
Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 4, 1169–1171.
Locke, J. R.; McNeil, A. J. *Macromolecules* **2010**, *43*, 21, 8709-8710.

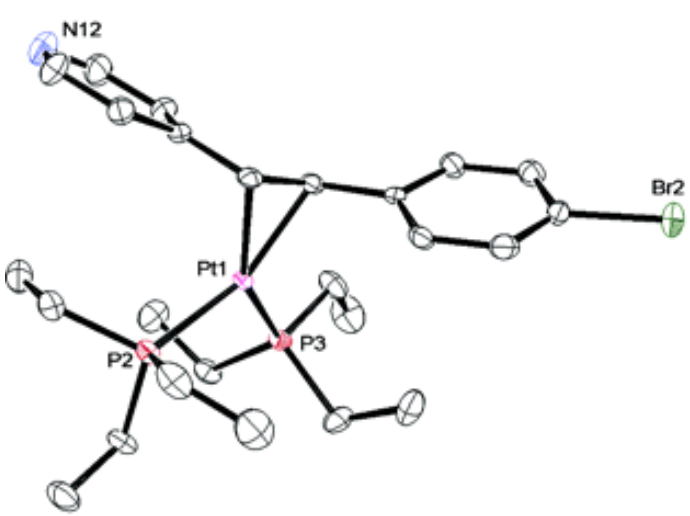
Isolation & Characterization of Pt η^2-complex

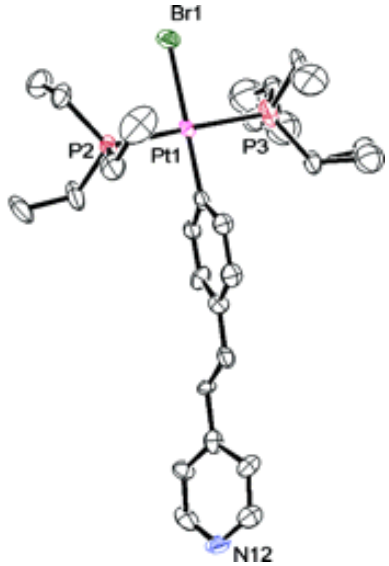
2005



1 **2** **3**







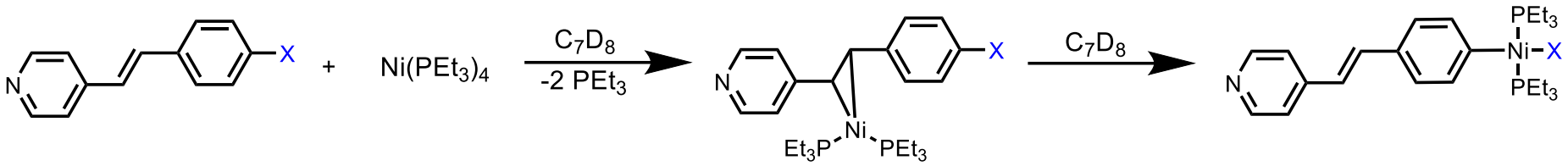
J_{PP} = 42.7 Hz

$^{31}P\{^{1}H\}$ NMR: δ 15.6 ppm, 14.7 ppm

$^{31}P\{^{1}H\}$ NMR: δ 12.45 ppm

Strawser, D.; Karton, A.; Zenkina, O. V.; Iron, M. A.; Shimon, L. J. W.; Martin, J. M. L.; van der Boom, M. E. *J. Am. Chem. Soc.* **2005**, *127*, 26, 9322−9323.

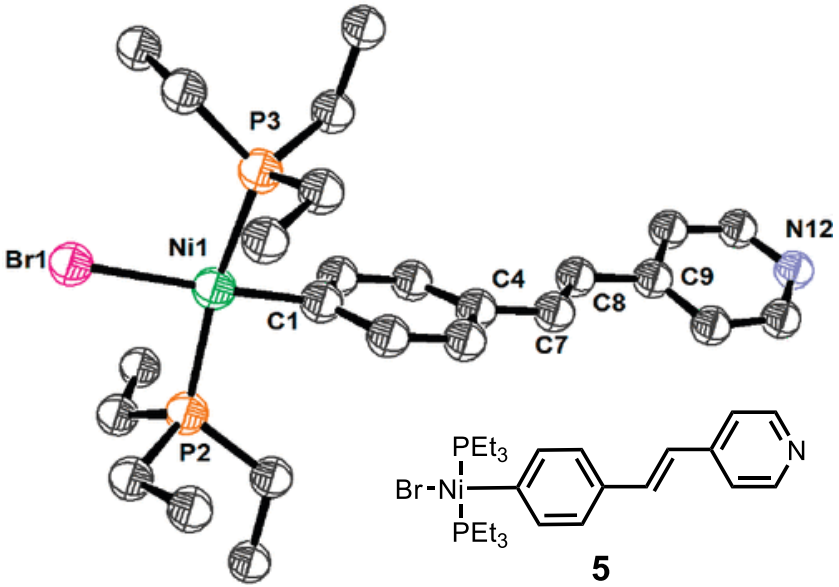
Characterization of Ni η^2-complex



1 X=Br
2 X=I

3 X=Br
4 X=I

5 X=Br
6 X=I



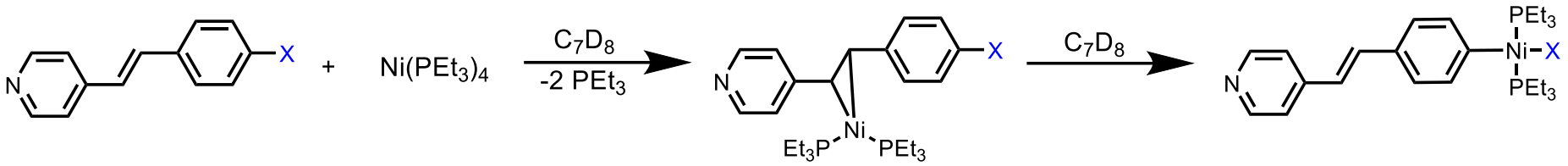
5

Complex	$^{31}P\{^{1}H\}$ δ	J_{PP}
3	16.9 ppm 18.3 ppm	39.7 Hz
5	11.24 ppm	-

Similar to 2005 Pt studies

Zenkina, O. V.; Karton, A.; Freeman, D.; Shimon, L. J. W.; Martin, J. M. L.; van der Boom, M. E. *Inorg. Chem.* **2008**, *47*, 12, 5114–5121.

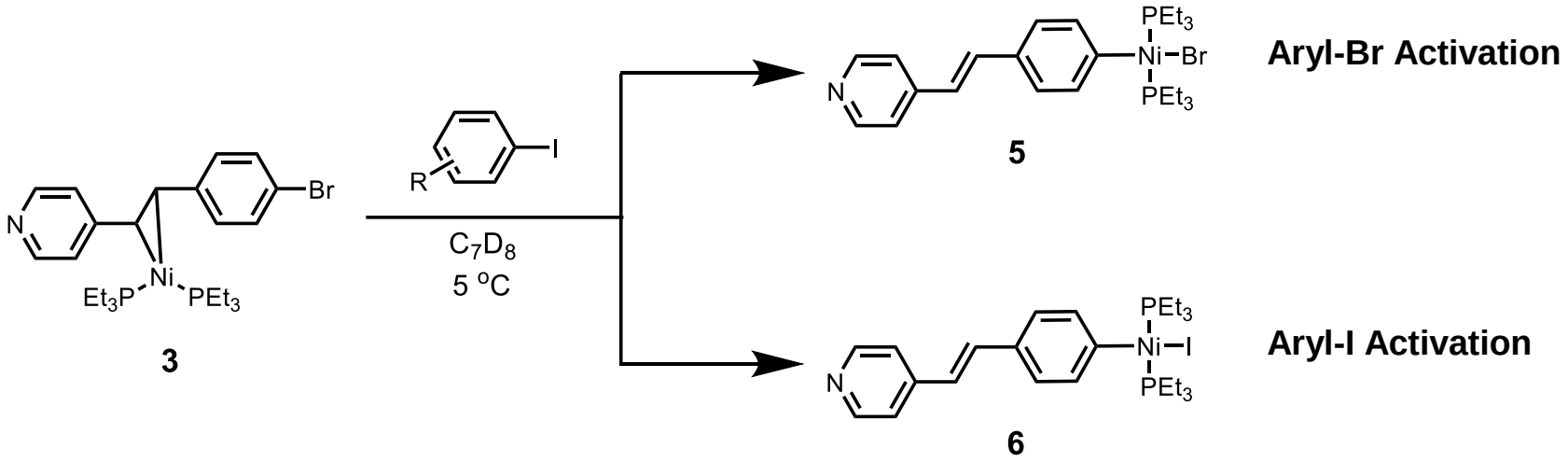
Experiment to Determining Reaction Pathway



1 X=Br
2 X=I

3 X=Br
4 X=I

5 X=Br
6 X=I

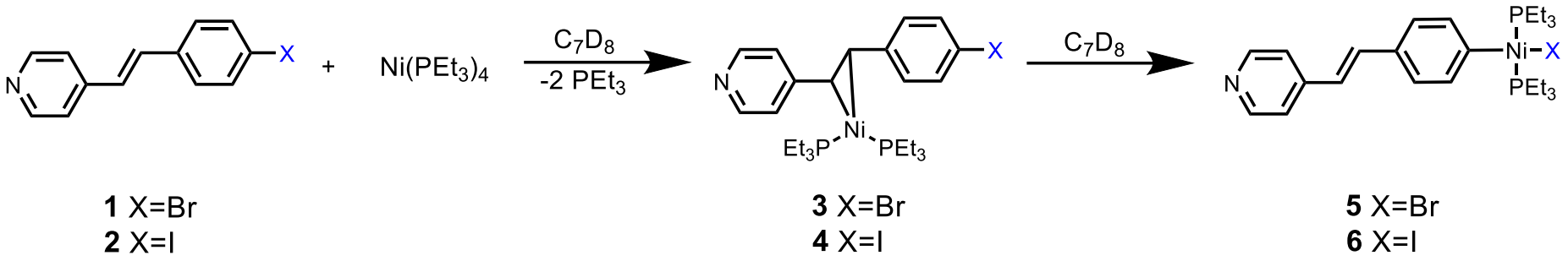


Aryl-Br Activation

Aryl-I Activation

Zenkina, O. V.; Karton, A.; Freeman, D.; Shimon, L. J. W.; Martin, J. M. L.; van der Boom, M. E. *Inorg. Chem.* **2008**, *47*, 12, 5114–5121.

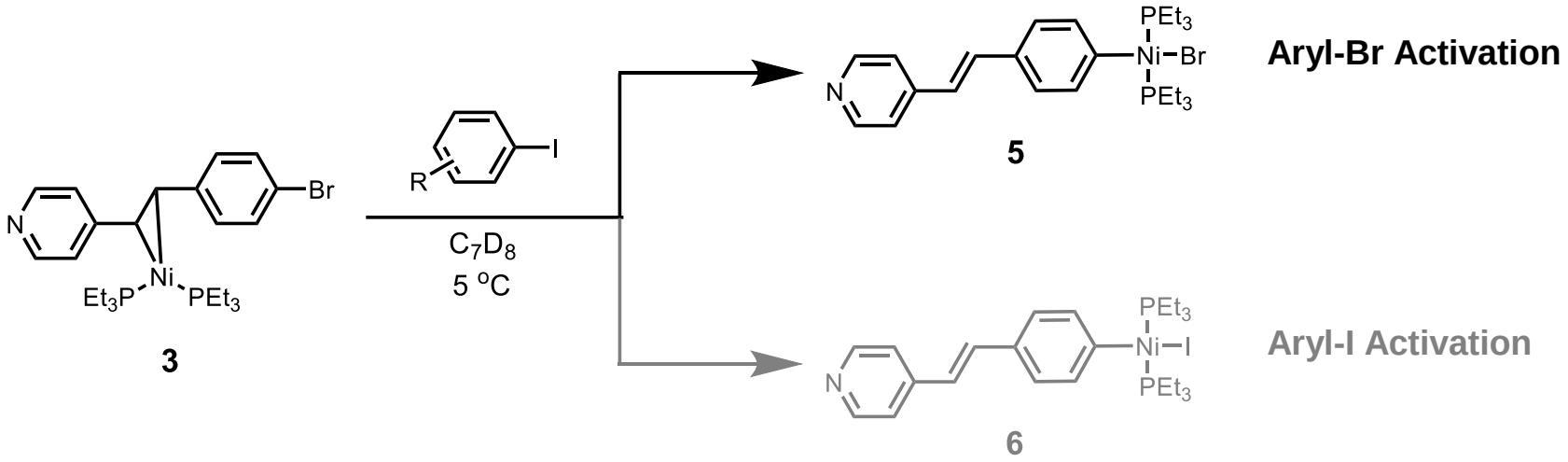
Intramolecular Process by Ni η^2-complex



1 X=Br
2 X=I

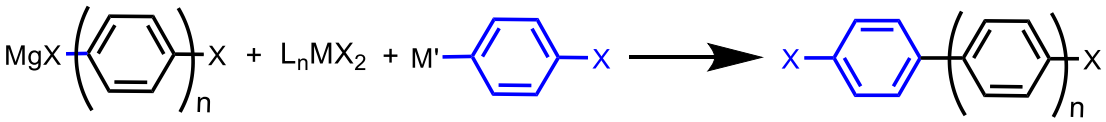
3 X=Br
4 X=I

5 X=Br
6 X=I



Zenkina, O. V.; Karton, A.; Freeman, D.; Shimon, L. J. W.; Martin, J. M. L.; van der Boom, M. E. *Inorg. Chem.* **2008**, *47*, 12, 5114–5121.

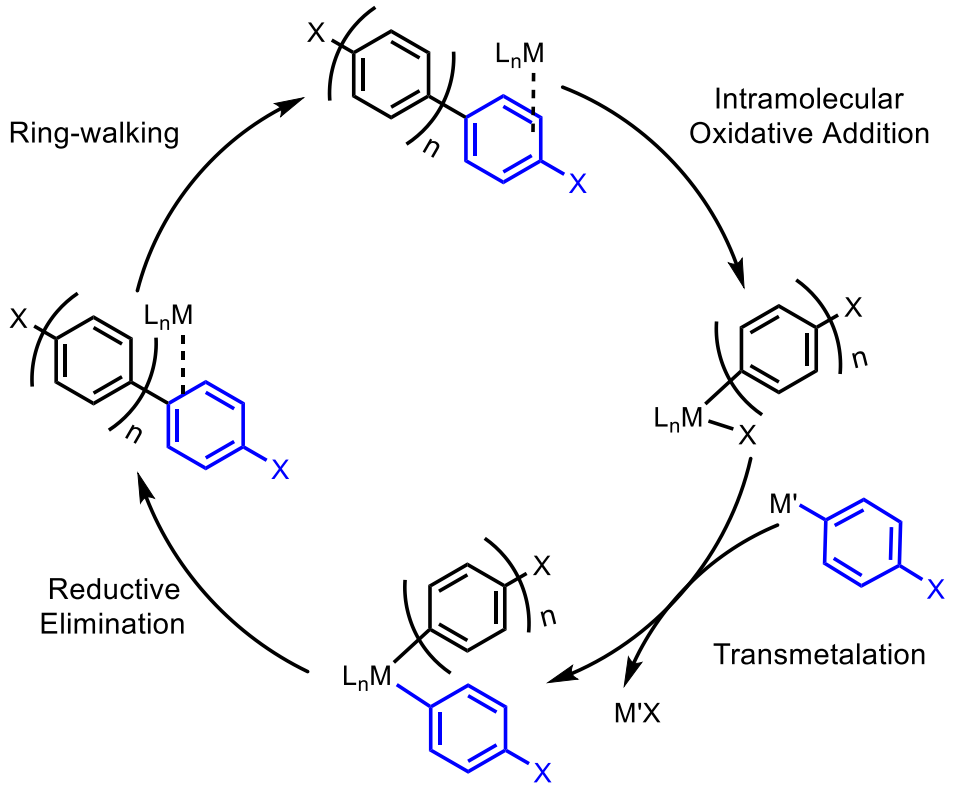
Catalyst Transfer Polymerization Mechanism



Key differences:

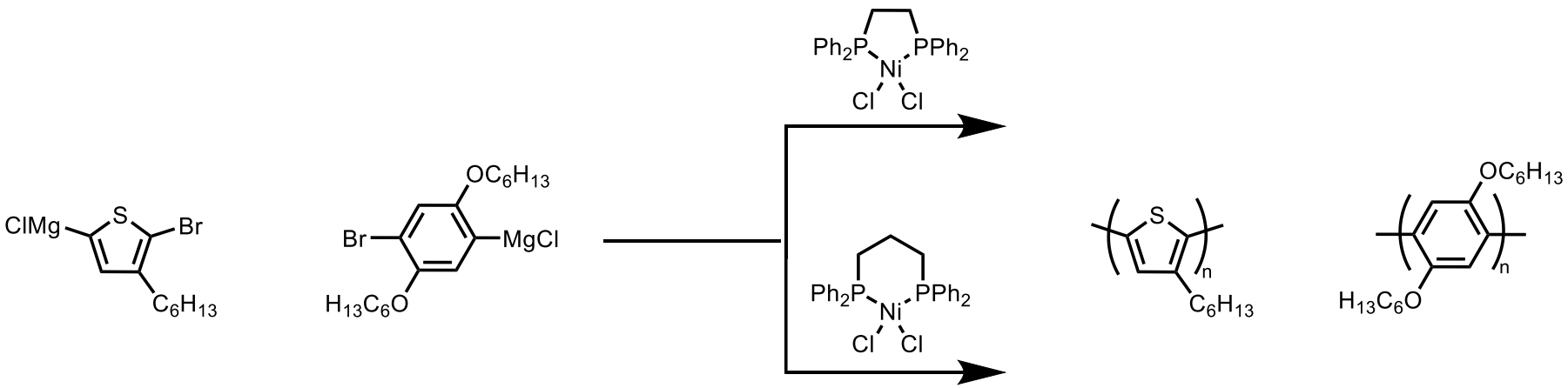
Metal-polymer π-complex

Ring-walking



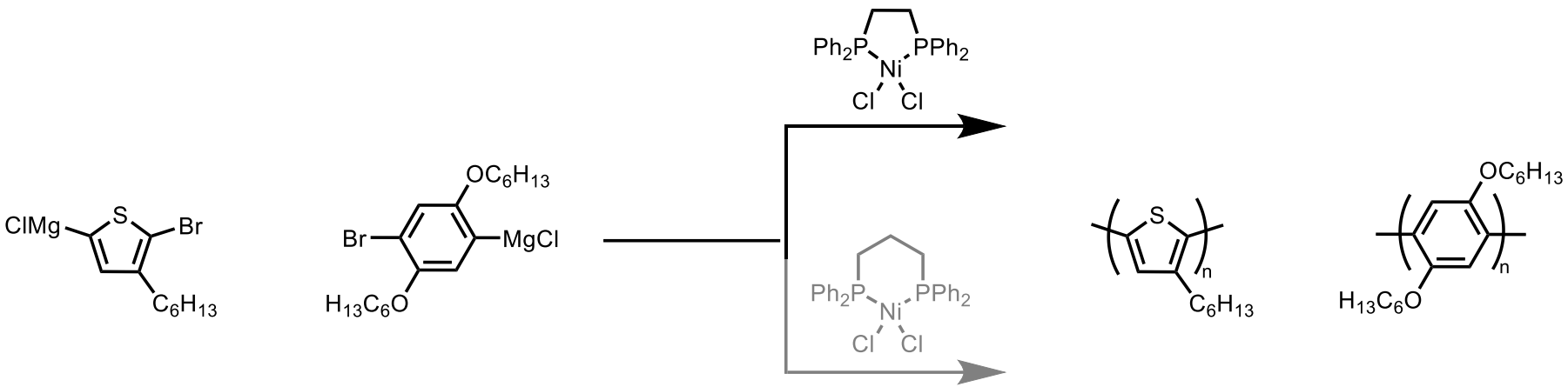
Leone, A. K.; Goldberg, P. K.; McNeil, A. J. *J. Am. Chem. Soc.* **2018**, *140*, 25, 7846–7850.

Rate Determining Step: Ligand and/or Monomer Dependent?



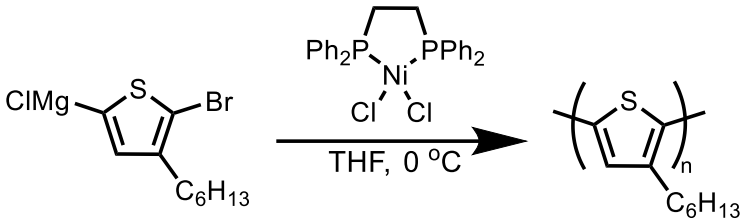
Lanni, E. L.; McNeil, A. J. *Macromolecules* **2010**, *43*, **19**, 8039-8044.
Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573-16579.

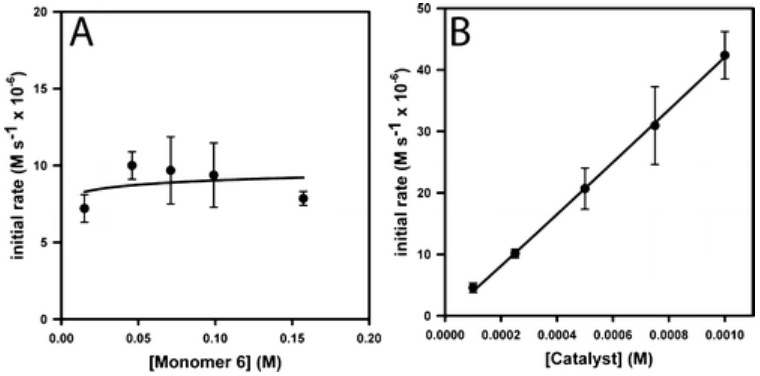
Rate Determining Step: $(dppe)NiCl_2$



Lanni, E. L.; McNeil, A. J. *Macromolecules* **2010**, *43*, **19**, 8039-8044.
Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573-16579.

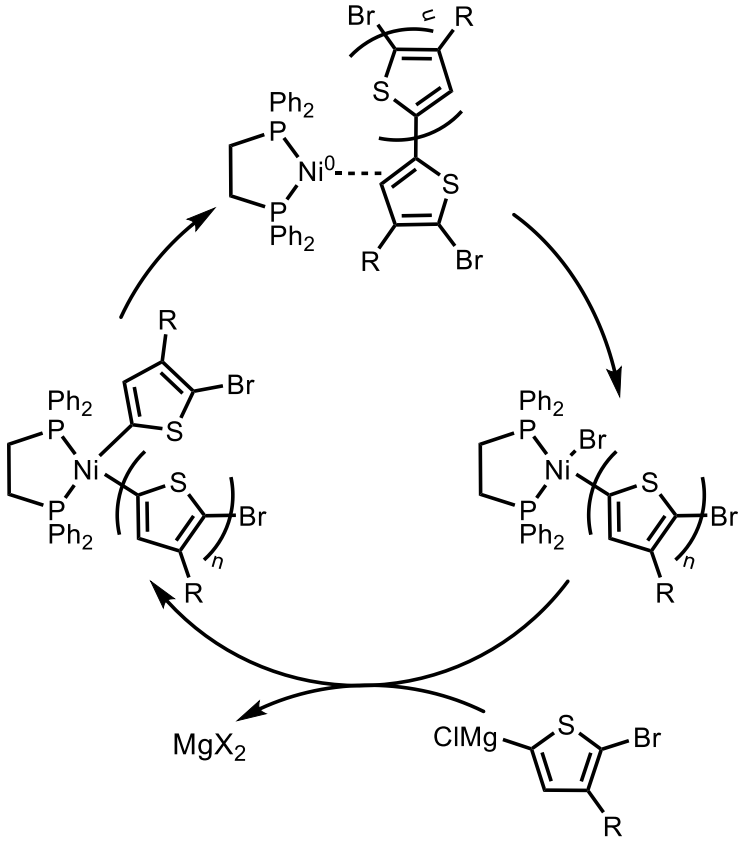
Transmetalation Not RDS with Thiophene Monomer

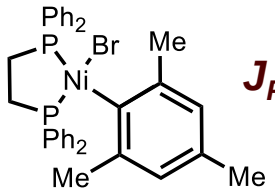




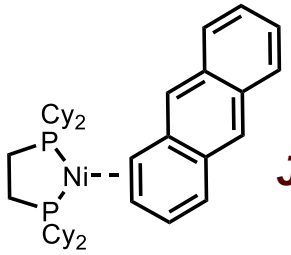
0th order

1st order





J_{PP} = 15 Hz

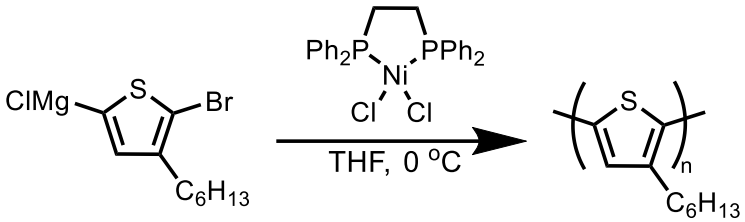


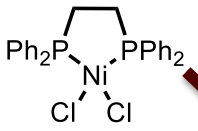
J_{PP} = 68 Hz

What about oxidative addition and reductive elimination?

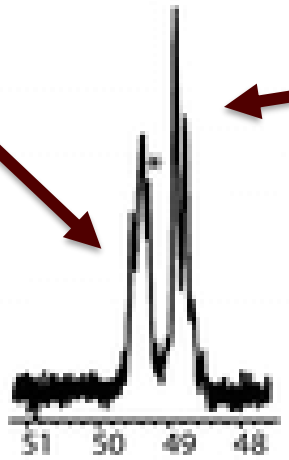
Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573-16579.

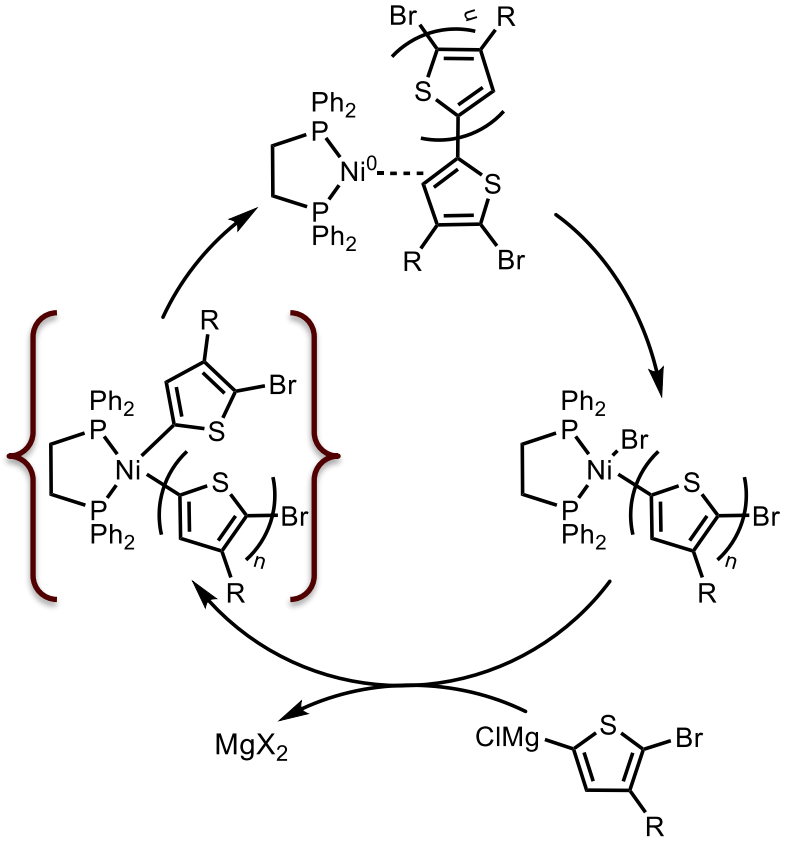
Finding RDS with Thiophene Monomer

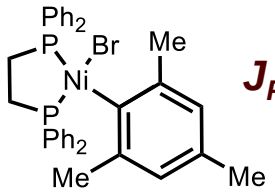




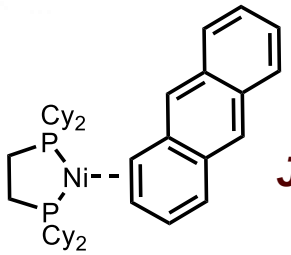
J_{PP} = 24 Hz







J_{PP} = 15 Hz

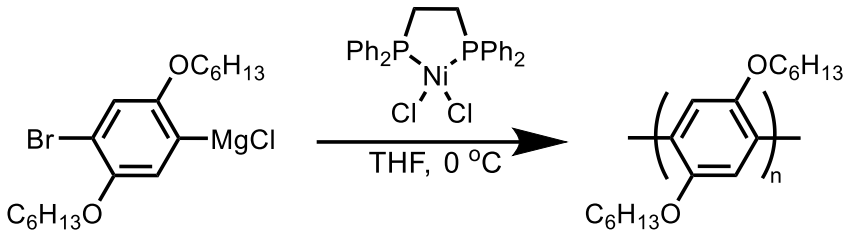


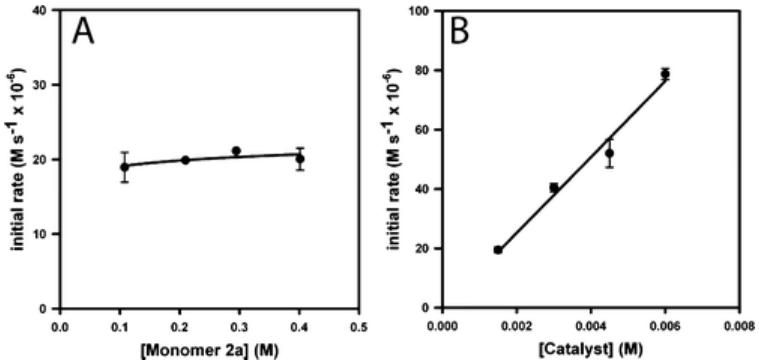
J_{PP} = 68 Hz

RDS:
Reductive Elimination

Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573-16579.

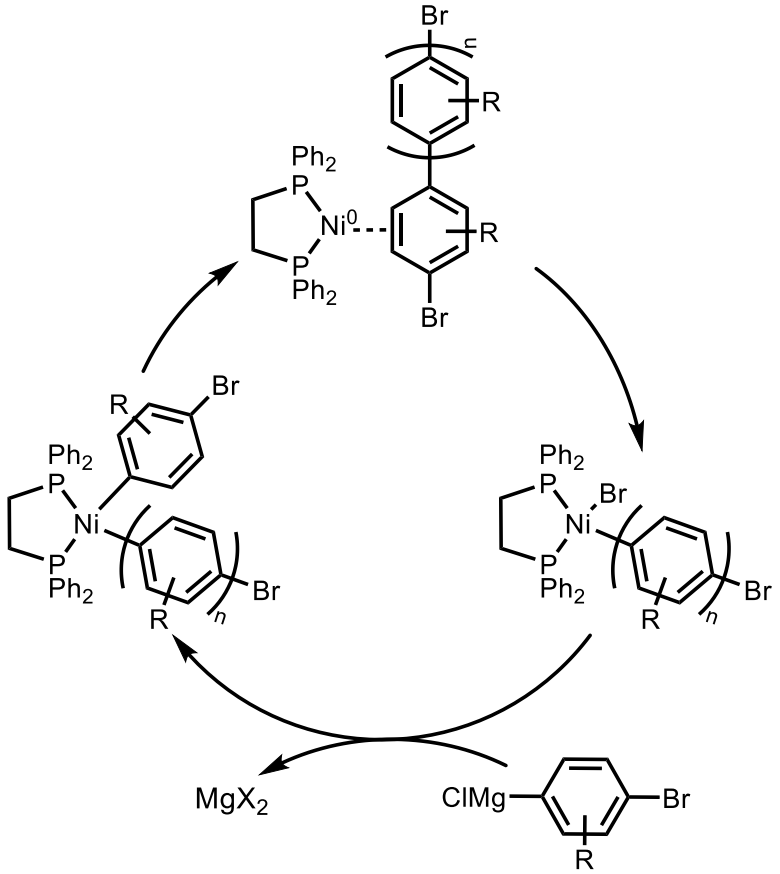
Transmetalation Not RDS with Hexyloxyphenylene Monomer

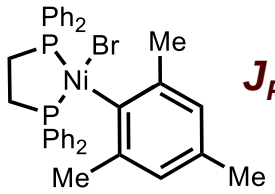




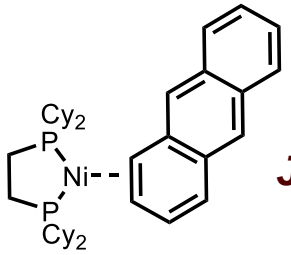
0th order

1st order





J_{PP} = 15 Hz

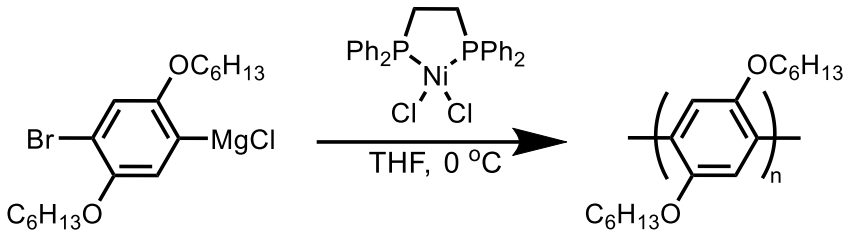


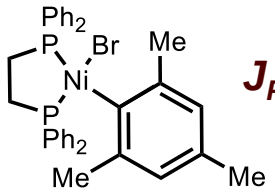
J_{PP} = 68 Hz

What about oxidative addition and reductive elimination?

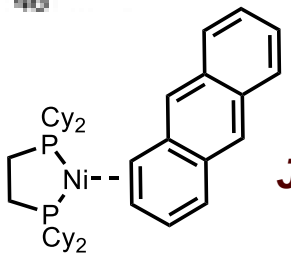
Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573-16579.

Finding RDS with Hexyloxyphenylene Monomer





J_{PP} = 15 Hz

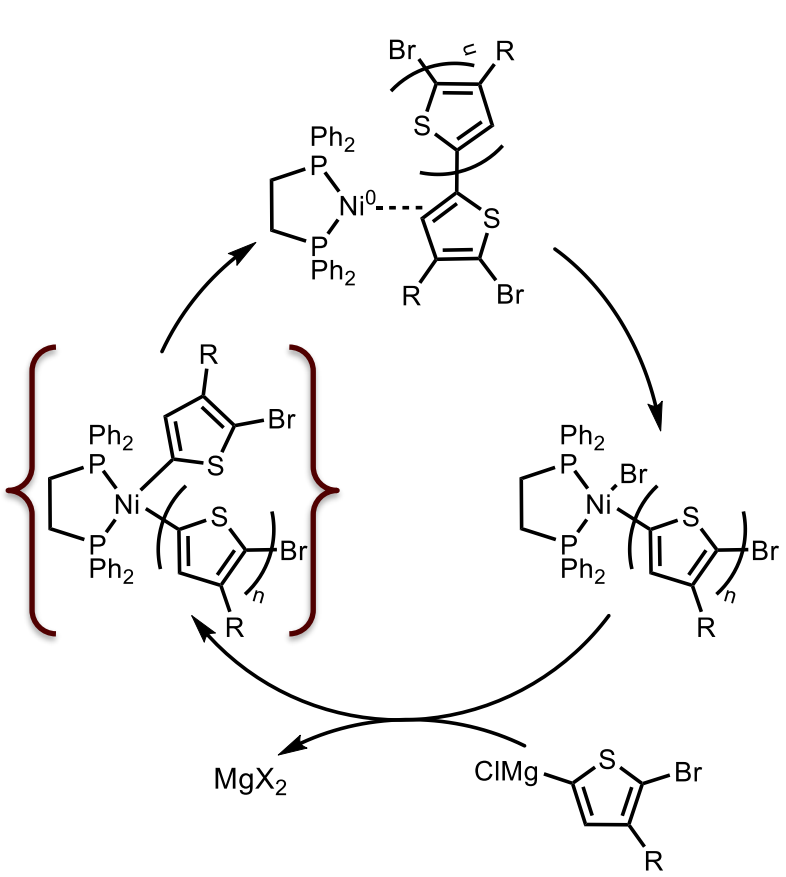


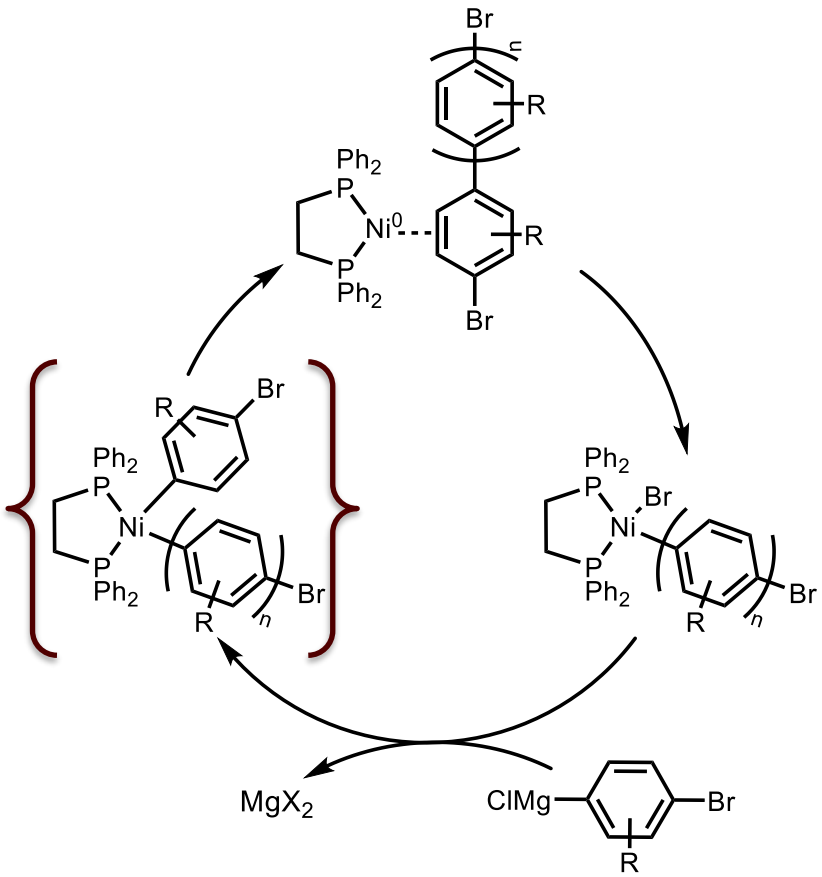
J_{PP} = 68 Hz

RDS:
Reductive Elimination

Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573-16579.

RDS: Not Monomer Dependent for (dppe)$NiCl_2$



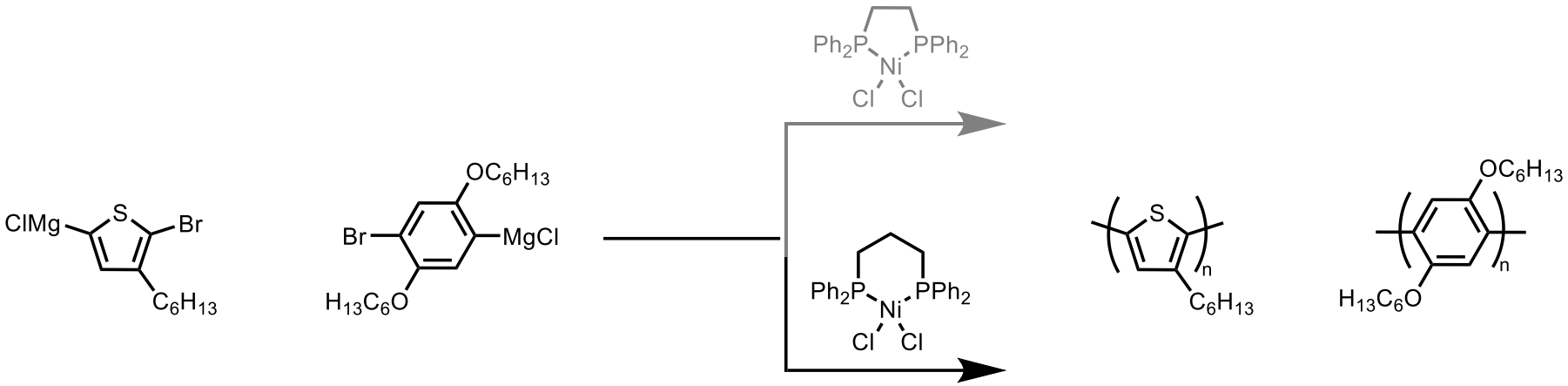


RDS for (dppe)$NiCl_2$: Reductive Elimination

Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573-16579.

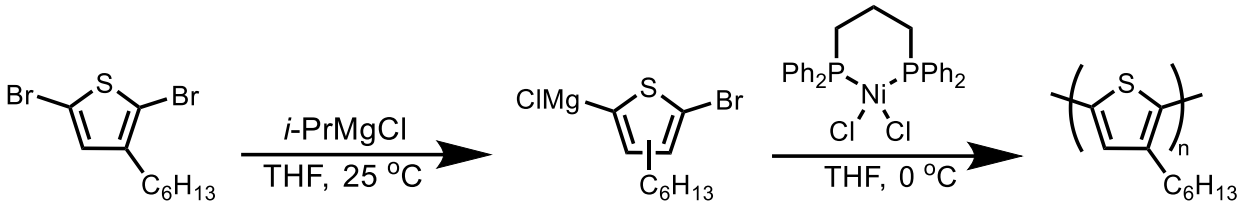
Rate Determining Step : $(dppp)NiCl_2$

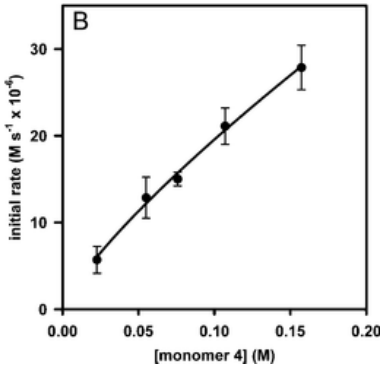
RDS for $(dppe)NiCl_2$: Reductive Elimination

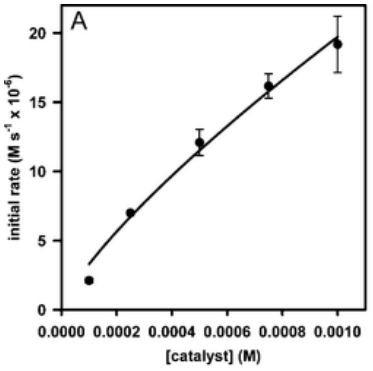


Lanni, E. L.; McNeil, A. J. *Macromolecules* **2010**, *43*, **19**, 8039-8044.
Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573-16579.

RDS: Transmetalation?

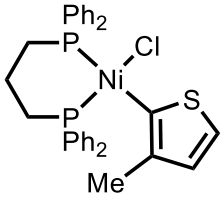




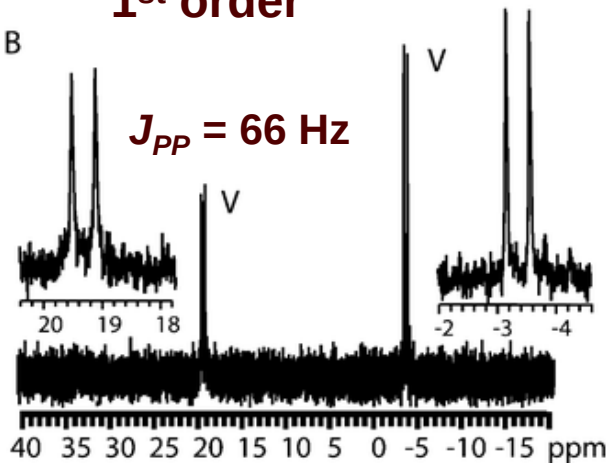


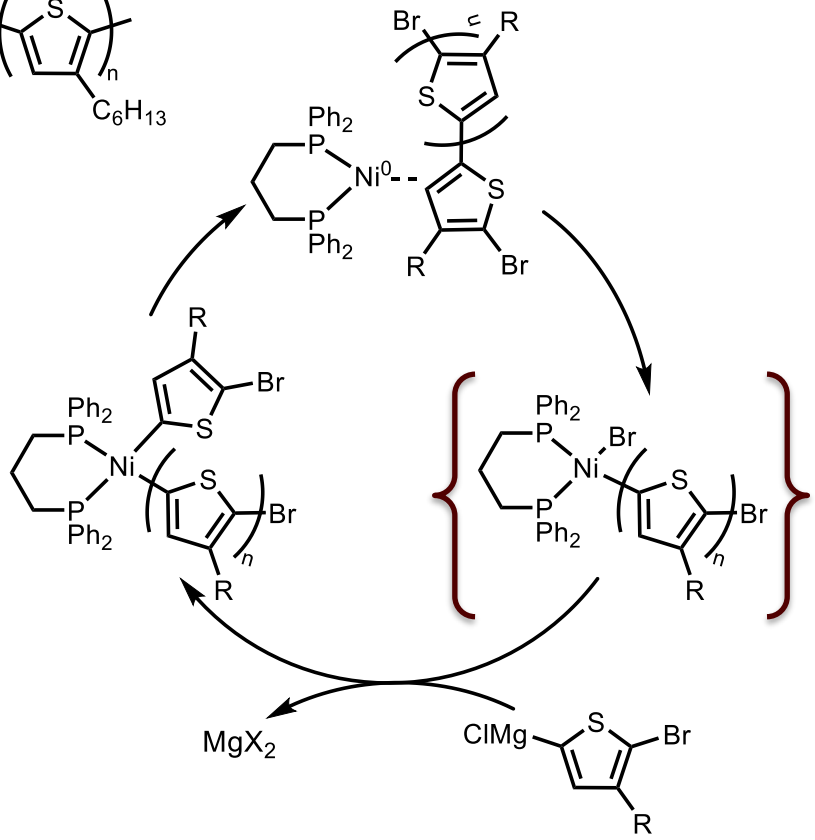
1st order

1st order



J_{PP} = 64 Hz

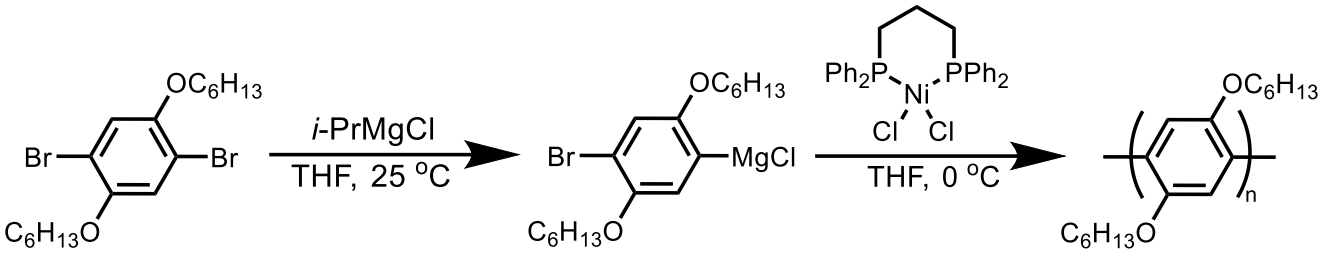


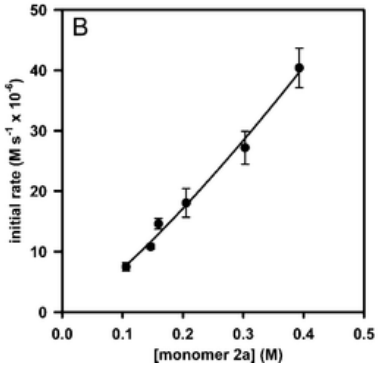


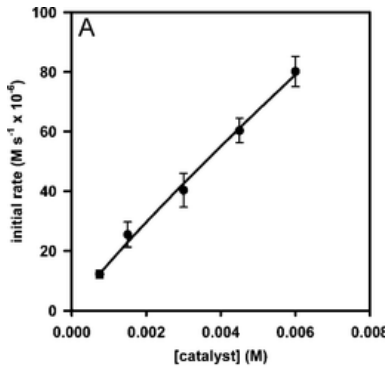
RDS: Transmetalation

Lanni, E. L.; McNeil, A. J. *Macromolecules* **2010**, *43*, **19**, 8039-8044.

RDS: Transmetalation?

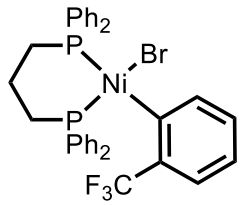




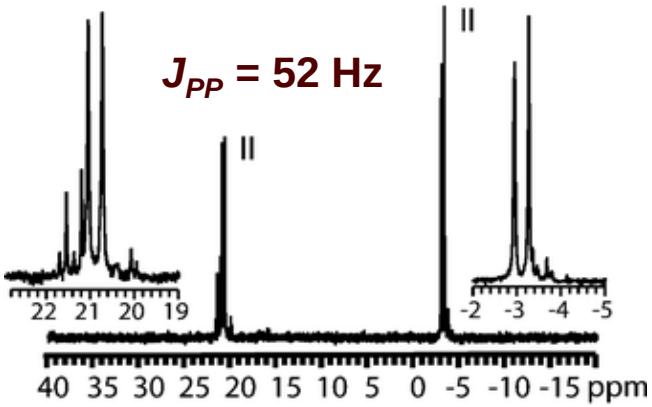


1st order

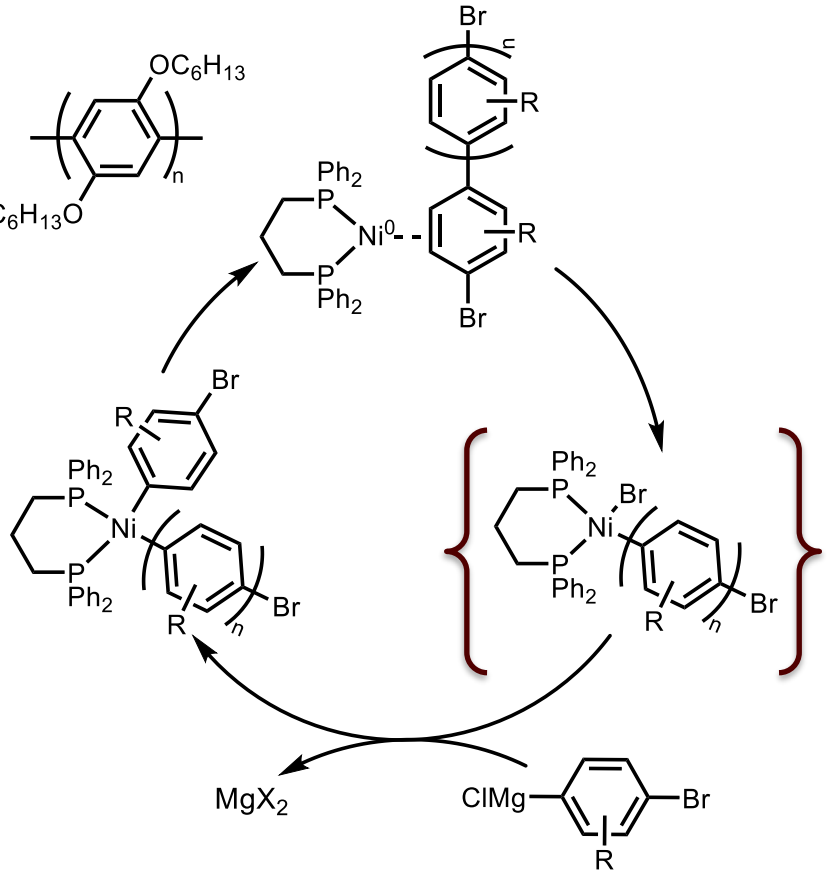
1st order



J_{PP} = 59 Hz



J_{PP} = 52 Hz

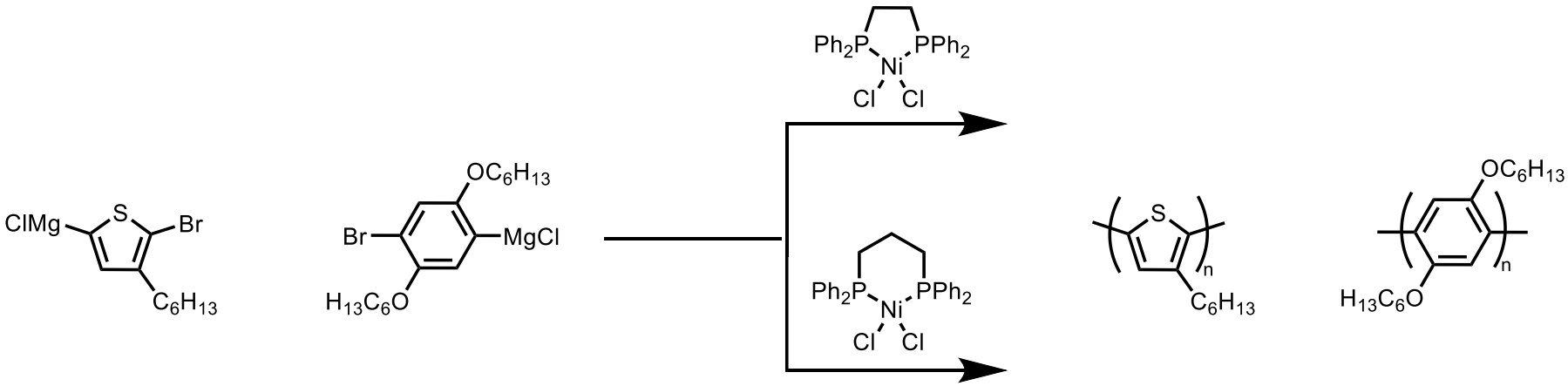


RDS: Transmetalation

Lanni, E. L.; McNeil, A. J. *Macromolecules* **2010**, *43*, **19**, 8039-8044.

Rate Determining Step: Ligand Dependent

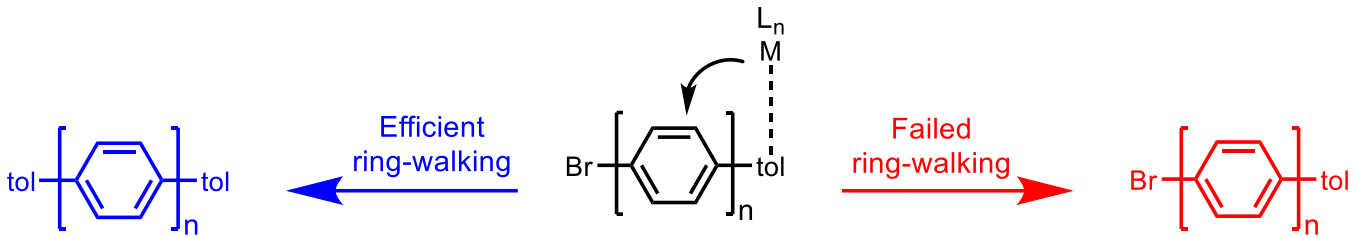
RDS for (dppe)$NiCl_2$: Reductive Elimination

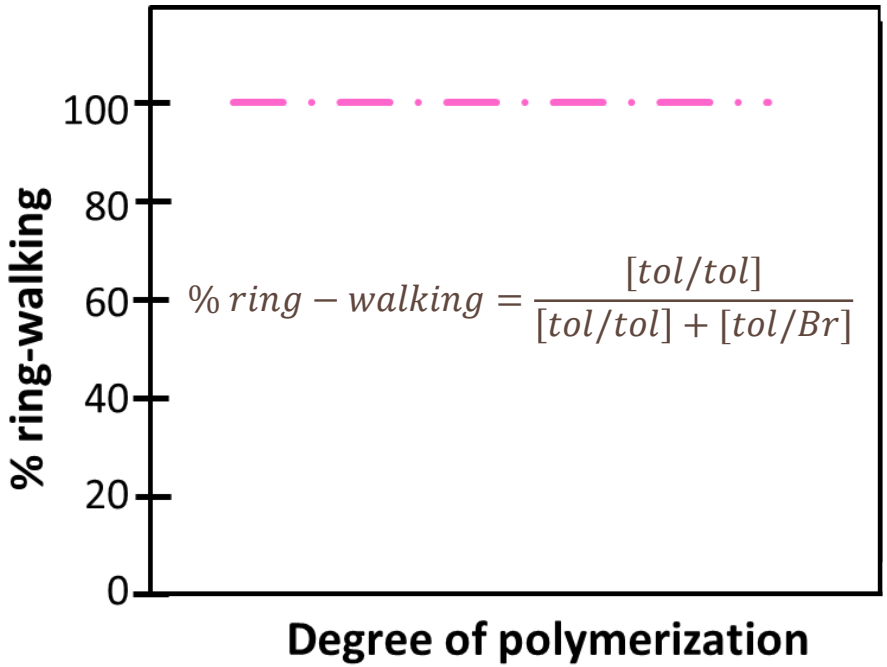


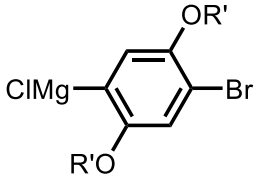
RDS for (dppp)$NiCl_2$: Transmetalation

Lanni, E. L.; McNeil, A. J. *Macromolecules* **2010**, *43*, **19**, 8039-8044.
Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573-16579.

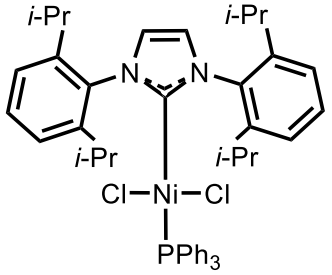
Ring-Walking Efficiency: 100 %



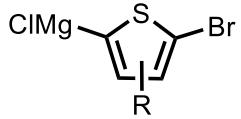




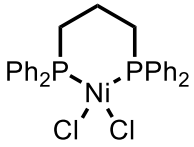
BHP



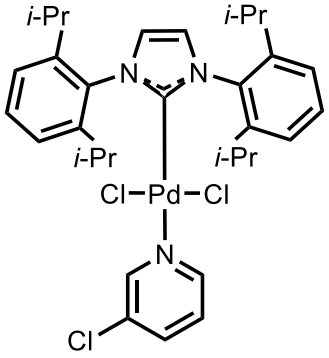
$(PPh_3)Ni(IPr)Cl_2$



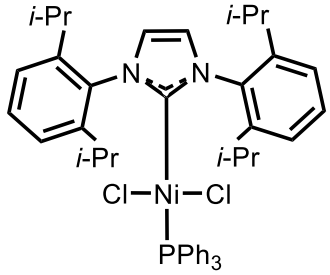
3DT



$(dppp)NiCl_2$



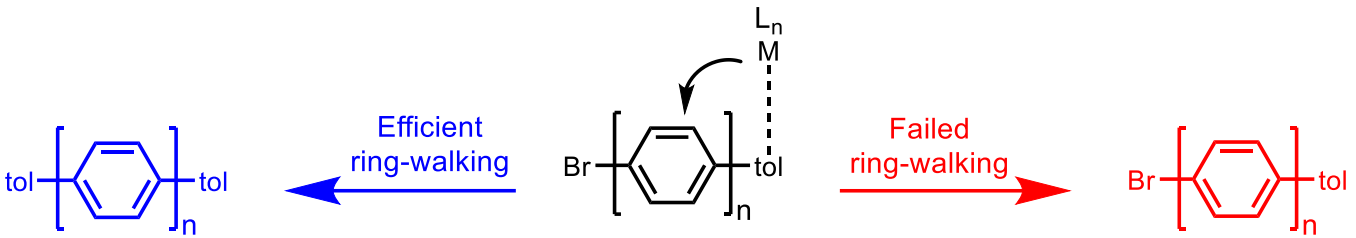
(3-Clpy)Pd(IPr)Cl_2

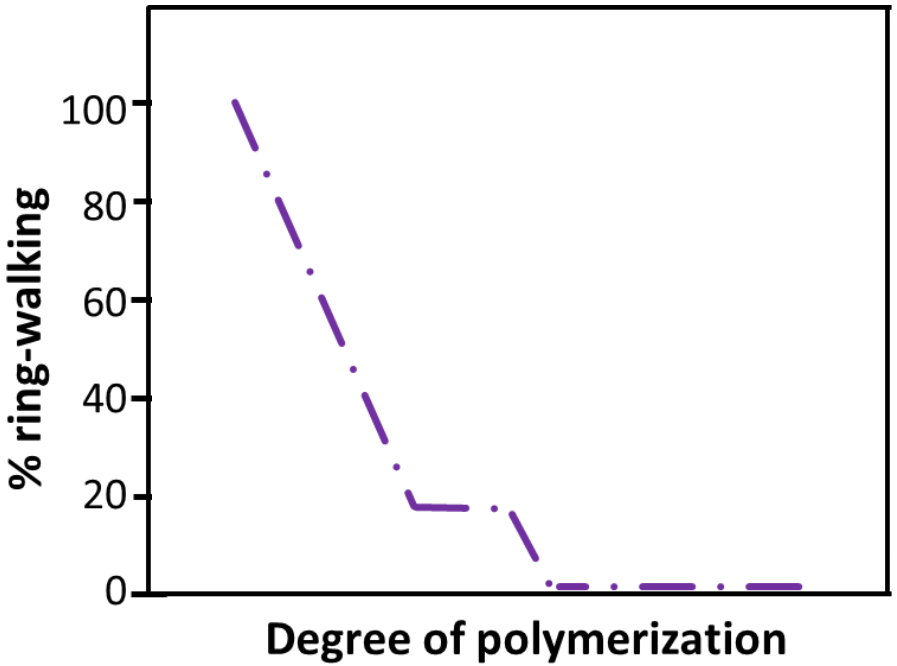


$(PPh_3)Ni(IPr)Cl_2$

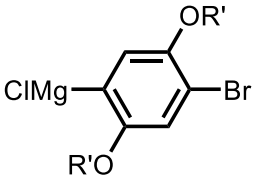
Leone, A. K.; Goldberg, P. K.; McNeil, A. J. *J. Am. Chem. Soc.* **2018**, *140*, 25, 7846–7850.

Ring-Walking Efficiency: Decreasing

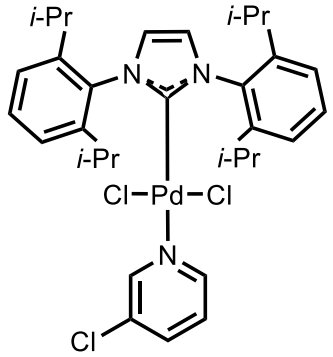




$$\%\ ring-walking = \frac{[tol/tol]}{[tol/tol] + [tol/Br]}$$



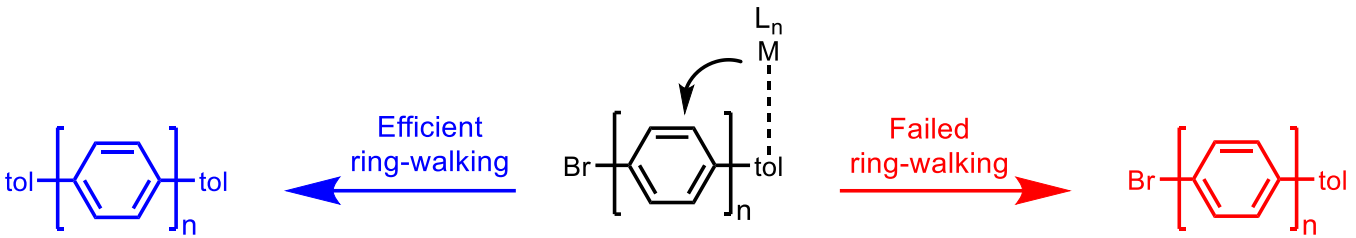
BHP

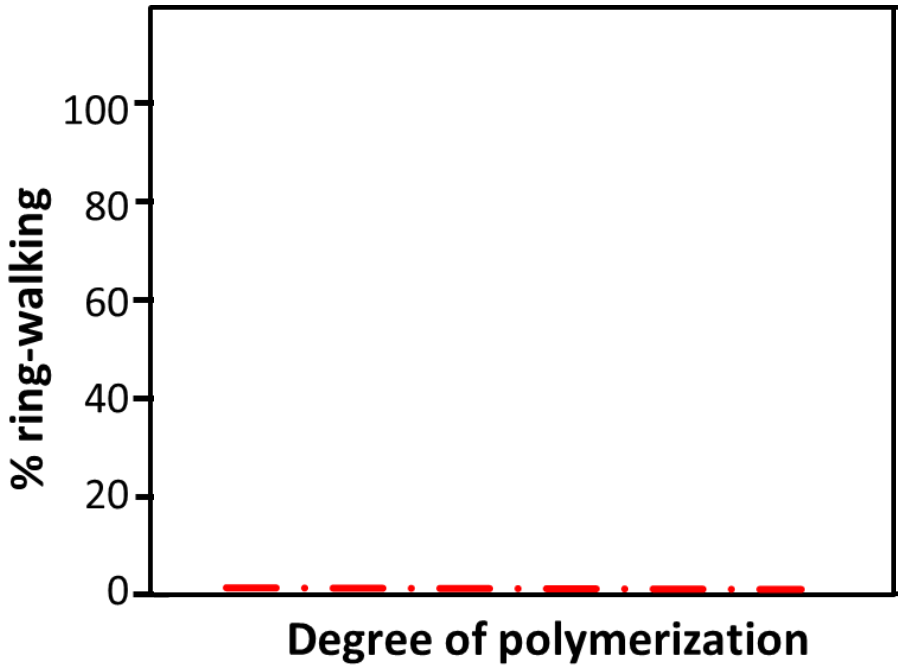


(3-Clpy)Pd(IPr)Cl_2

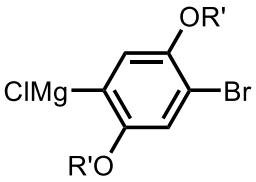
Leone, A. K.; Goldberg, P. K.; McNeil, A. J. *J. Am. Chem. Soc.* **2018**, *140*, 25, 7846–7850.

Ring-Walking Efficiency: 0 %

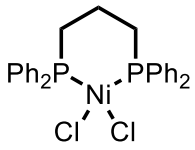




$$\%\ ring-walking = \frac{[tol/tol]}{[tol/tol] + [tol/Br]}$$



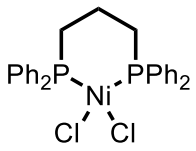
BHP



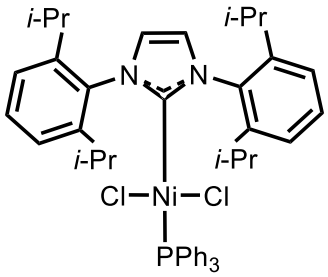
(dppp)$NiCl_2$

Leone, A. K.; Goldberg, P. K.; McNeil, A. J. *J. Am. Chem. Soc.* **2018**, *140*, 25, 7846–7850.

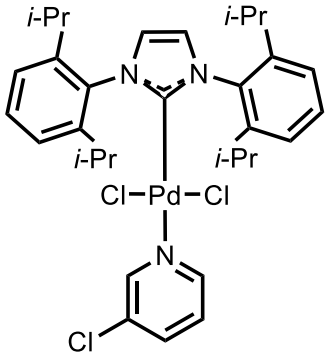
Ring-Walking Efficiency: MALDI-TOF/MS



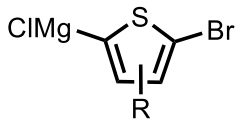
(dppp)$NiCl_2$



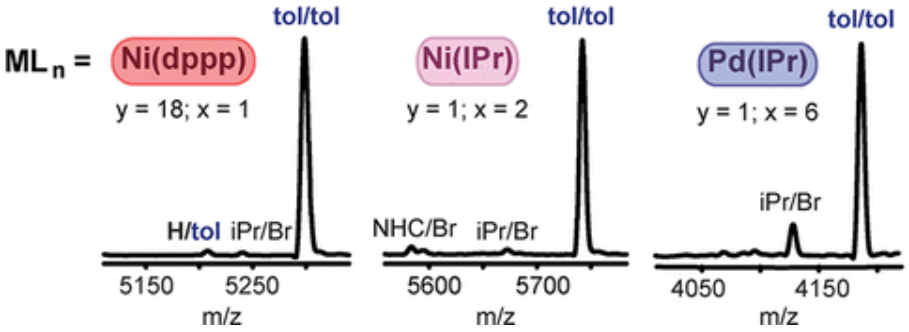
(PPh_3)Ni(IPr)Cl_2

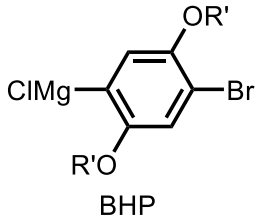


(3-Clpy)Pd(IPr)Cl_2

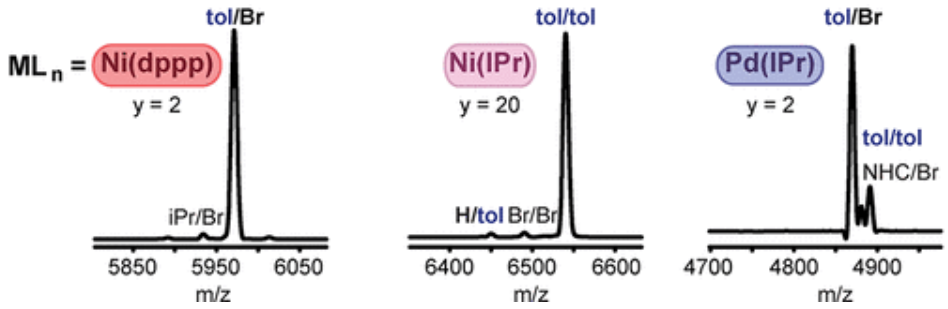


3DT



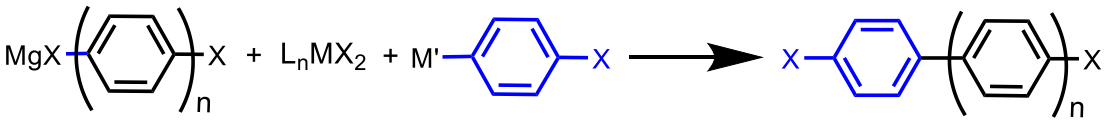


BHP



Leone, A. K.; Goldberg, P. K.; McNeil, A. J. *J. Am. Chem. Soc.* **2018**, *140*, 25, 7846–7850.

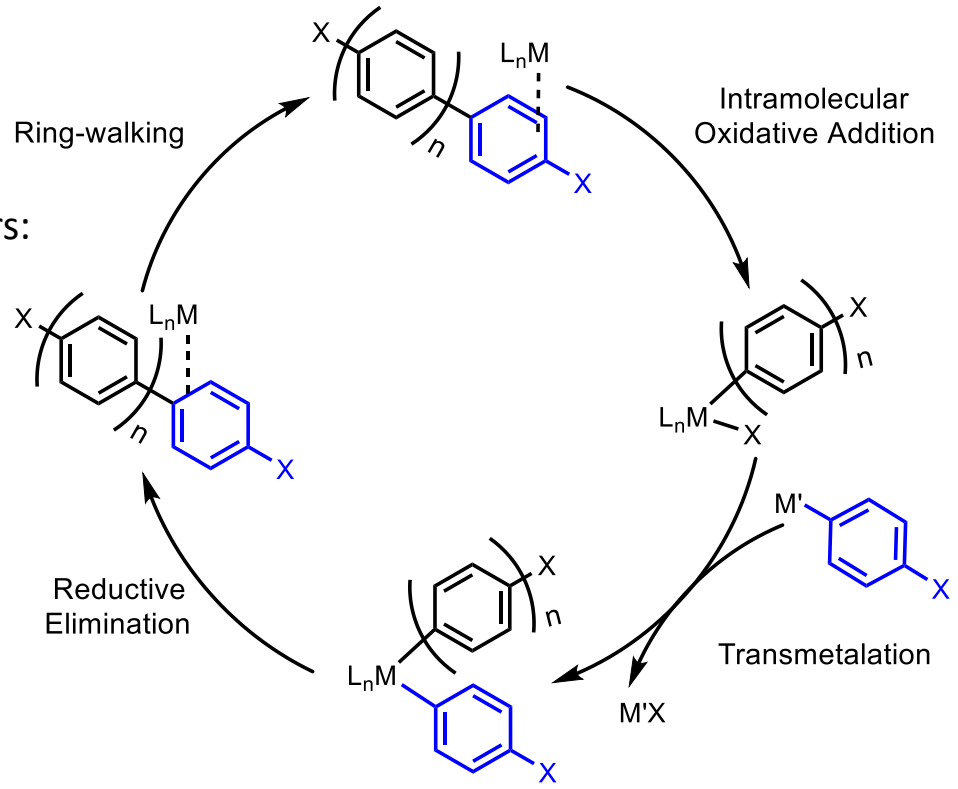
Catalyst Transfer Polymerization Reactions



Key differences:
Metal-polymer π-complex
Ring-walking

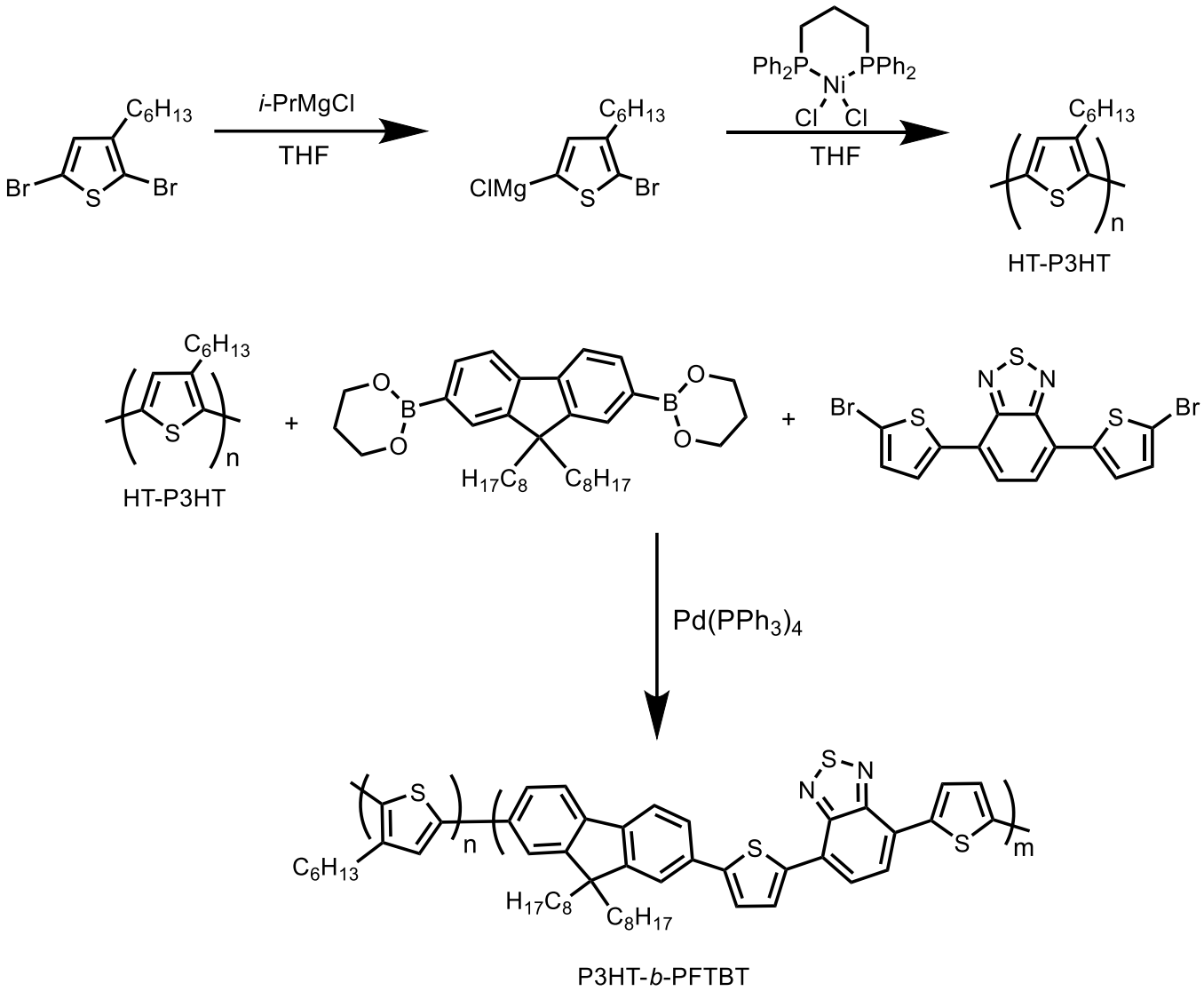
Control properties of polymers:
Length
Sequence
End groups

Living polymerizations:
Catalyst
Monomer



Leone, A. K.; Goldberg, P. K.; McNeil, A. J. *J. Am. Chem. Soc.* **2018**, *140*, 25, 7846–7850.

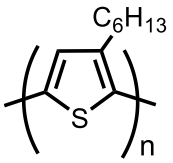
Synthesis of Block Copolymers



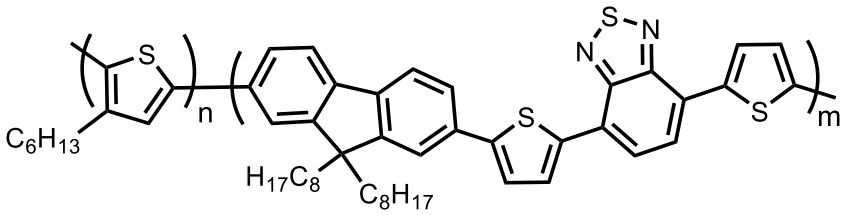
Le, T.P.; Smith, B. H.; Lee, Y.; Litofsky, J. H.; Aplan, M. P.; Kuei, B.; Zhu, C.; Wang, C.; Hexemer, A.; Gomez, E. D. *Macromolecules* **2020**, *53*, 6, 1967–1976 .

Synthesis of Block Copolymers

Polymer (ψ_{P3HT})	M_n $\left(\frac{kg}{mol}\right)$	M_w $\left(\frac{kg}{mol}\right)$	$Đ$
P3HT (1.0 P3HT)	7.9	12.3	1.54
P3HT-*b*-PFTBT (0.4 P3HT)	16.3	23.5	1.44
P3HT-*b*-PFTBT (0.22a P3HT)	12.5	17.1	1.36
P3HT-*b*-PFTBT (0.22b P3HT)	17.9	23.4	1.31



HT-P3HT



P3HT-*b*-PFTBT

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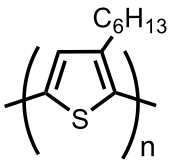
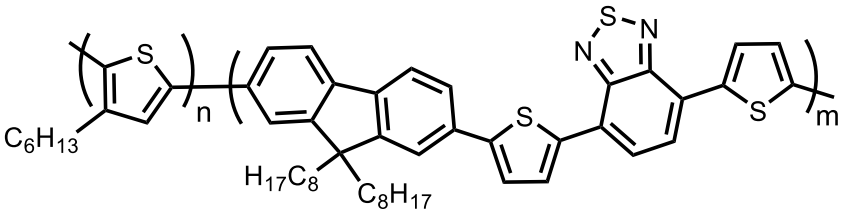
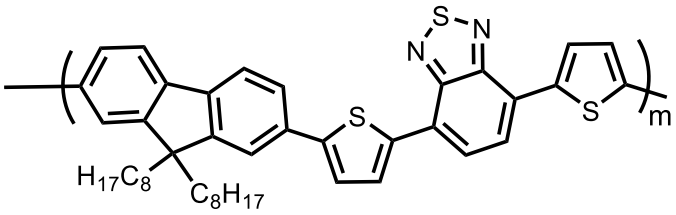
Thermal Annealing Results



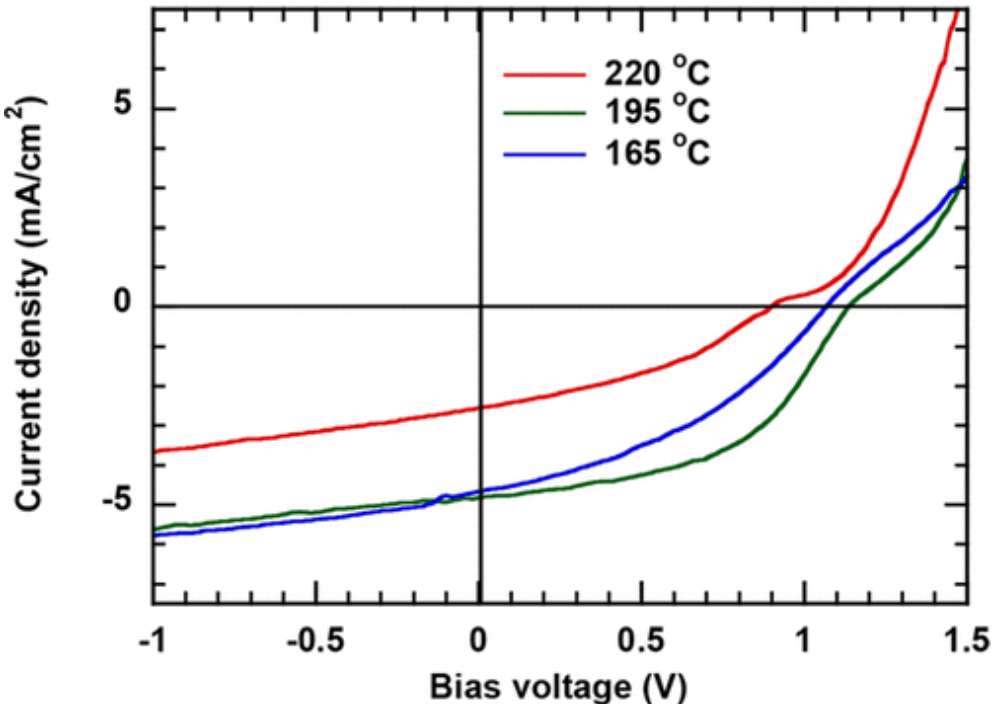
HT-P3HT



P3HT-*b*-PFTBT



PFTBT



220 ℃ : P3HT melted, PFTBT crystalline

195 ℃ : P3HT and PFTBT crystalline

165 ℃ : P3HT crystalline

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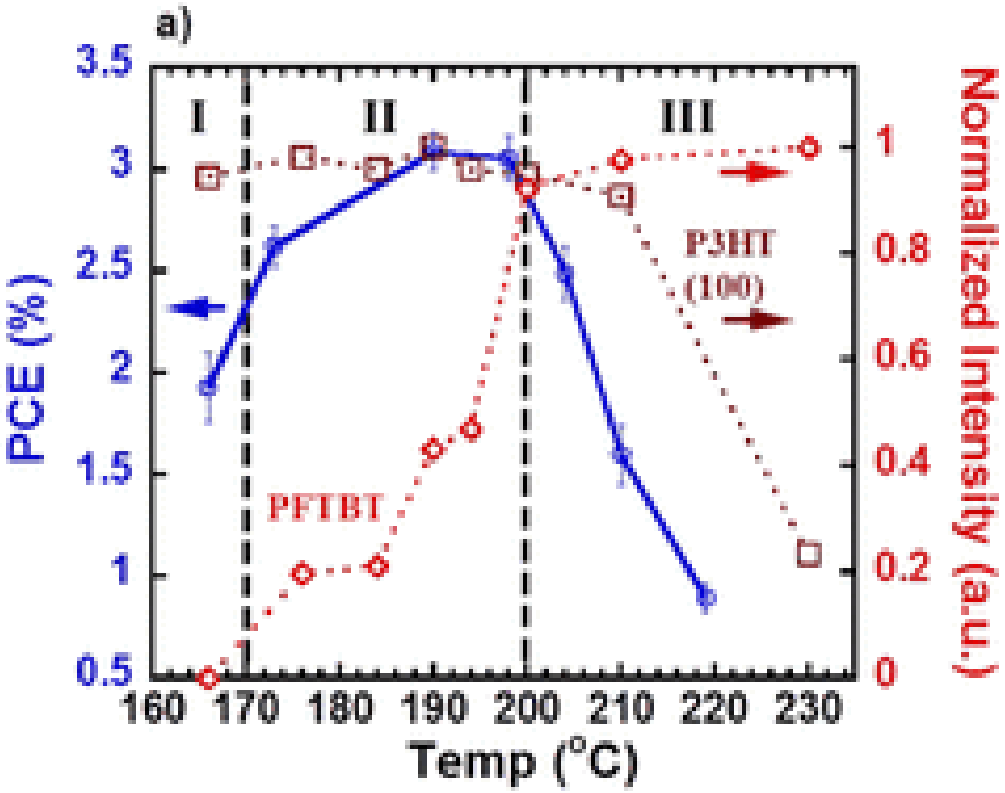
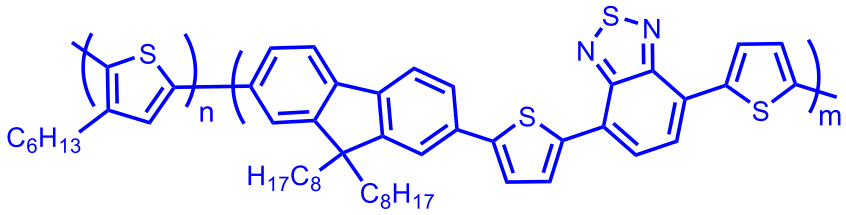
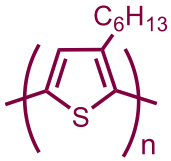
Temperature vs Solar Cell Performance: Power Conv. Eff.

Ratio between power output and power input

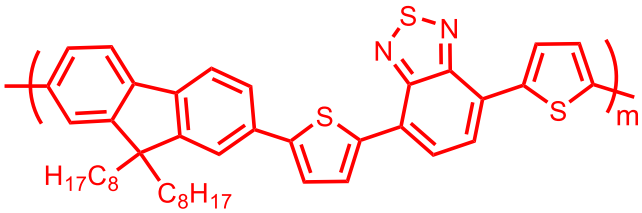




P3HT-*b*-PFTBT



P3HT



PFTBT

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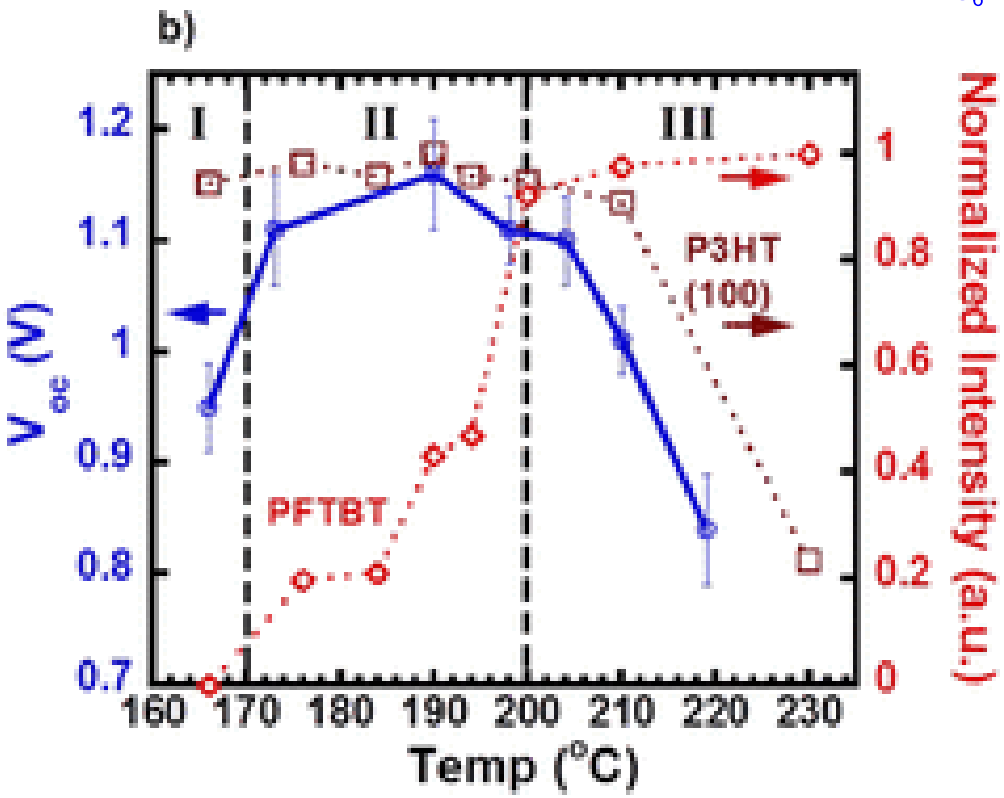
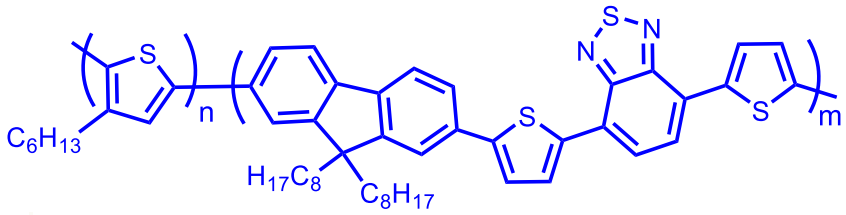
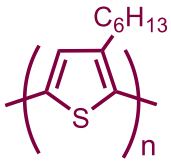
Temperature vs Solar Cell Performance: Open-Circuit Voltage

Maximum voltage at zero current

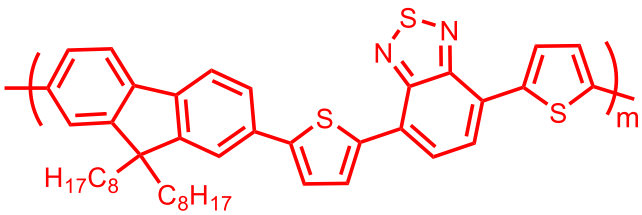




P3HT-*b*-PFTBT



P3HT



PFTBT

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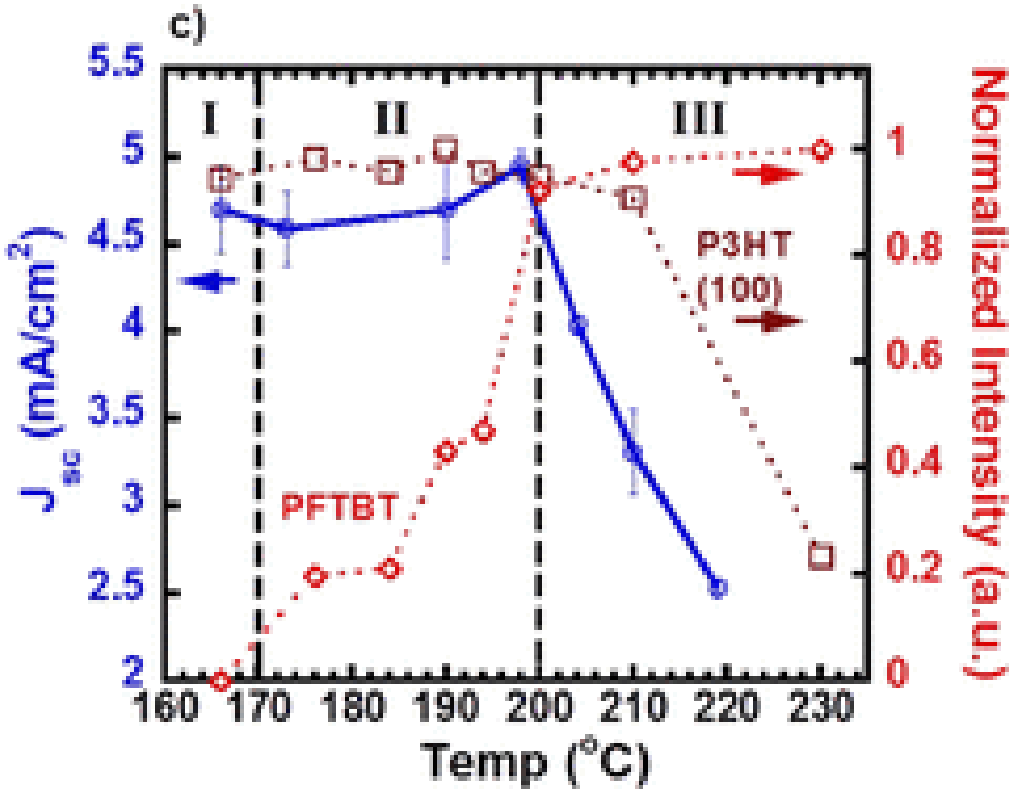
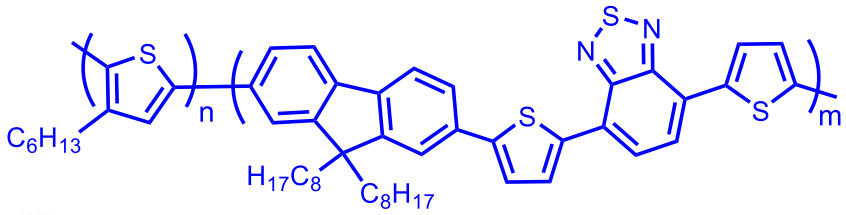
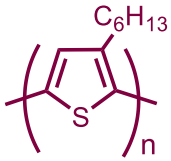
Temperature vs Solar Cell Performance: Short-Circuit Current

Current when voltage is zero

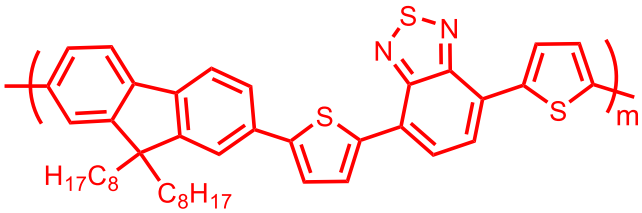




P3HT-*b*-PFTBT



P3HT



PFTBT

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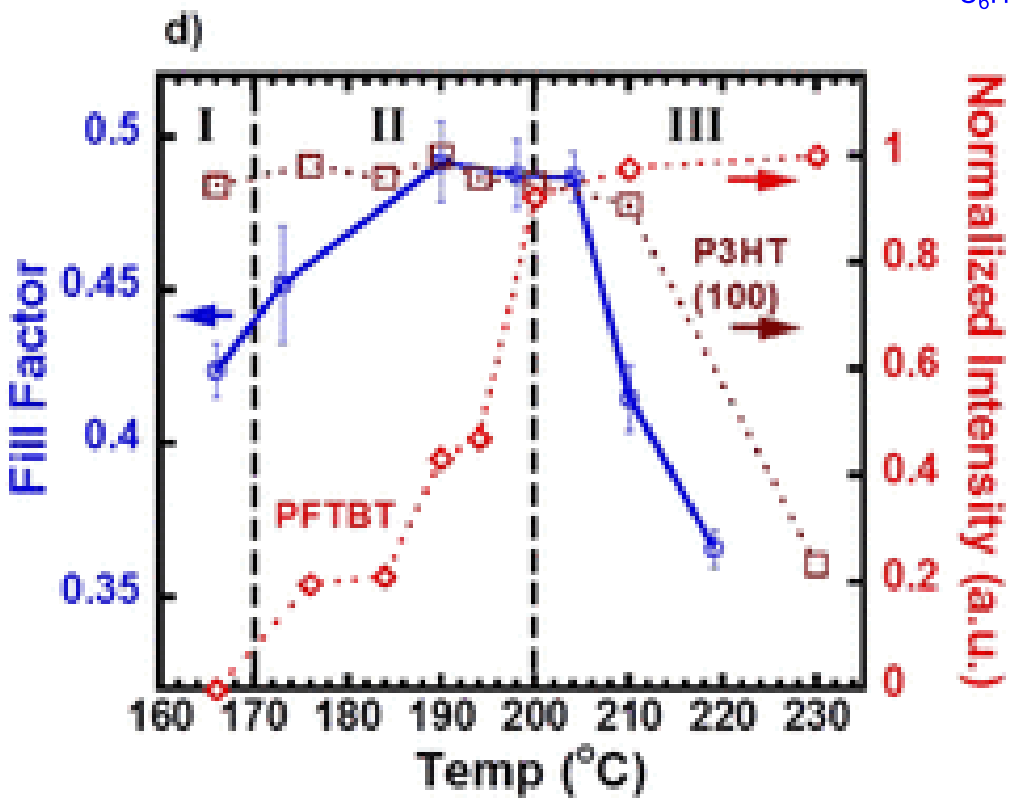
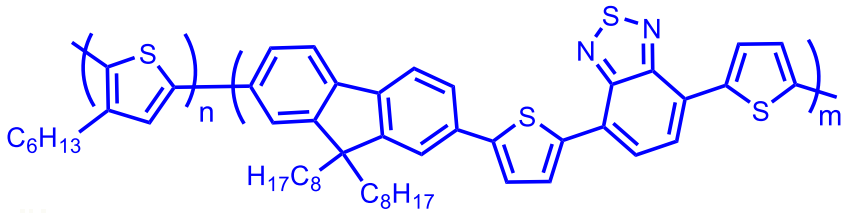
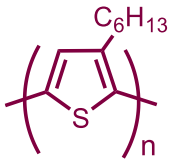
Temperature vs Solar Cell Performance: Fill Factor

Ratio of maximum power and the product of open-circuit voltage and short-circuit current

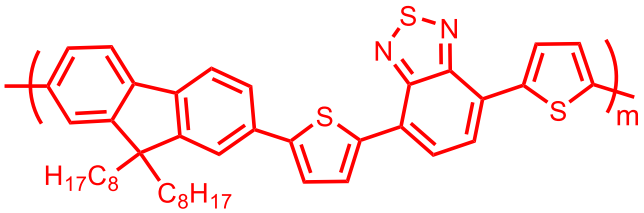




P3HT-*b*-PFTBT



P3HT



PFTBT

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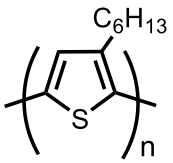
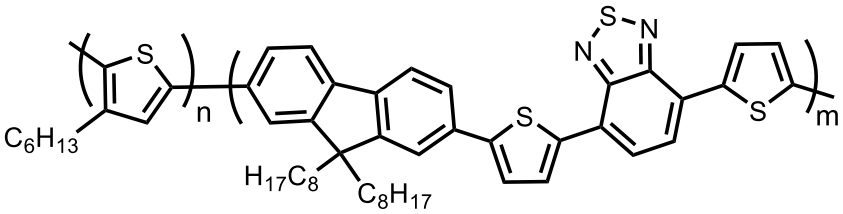
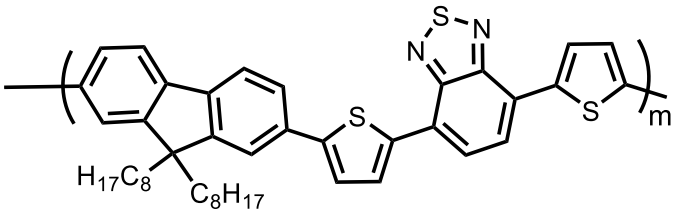
Electron Mobility from Transistors



HT-P3HT

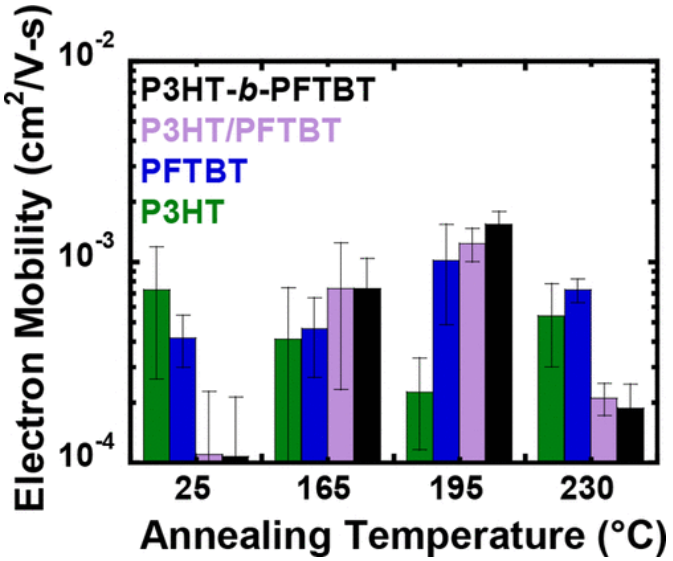


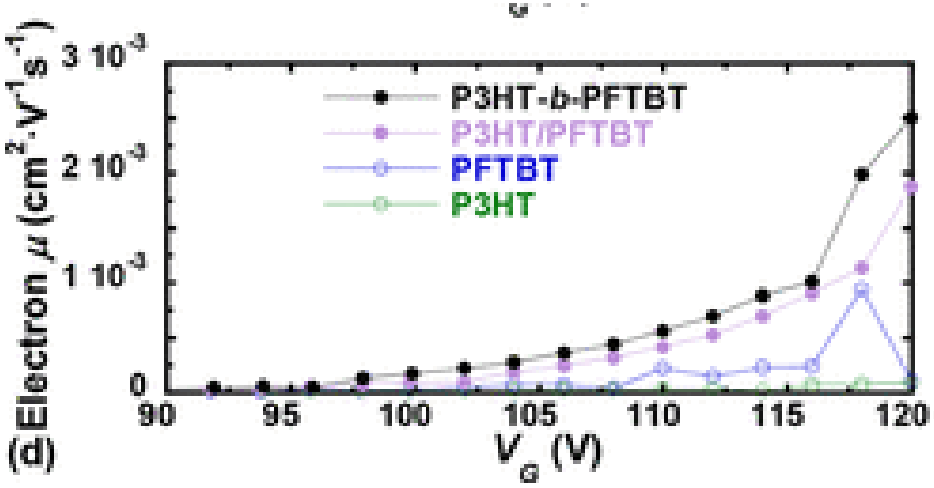
P3HT-*b*-PFTBT



PFTBT

How quickly electrons move through the material





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Thank you!

Questions?