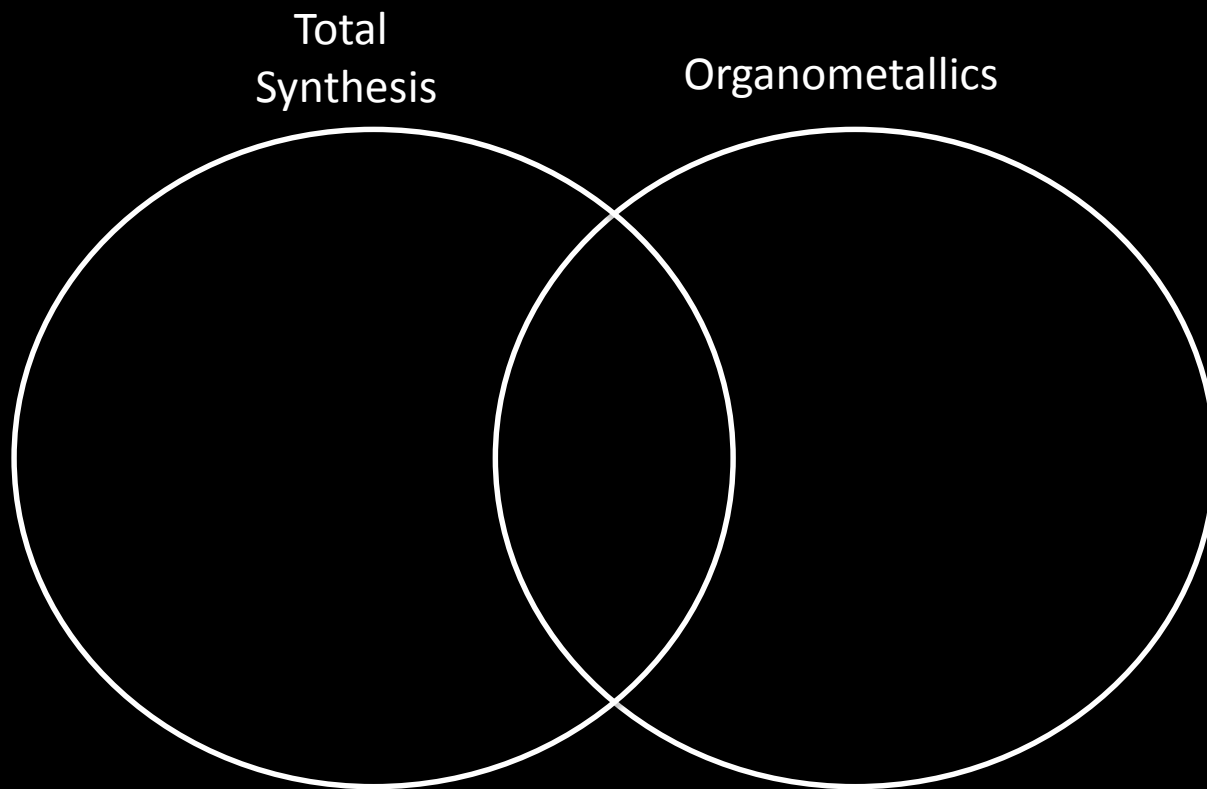


Wednesday Meeting

Controlled Polymerizations

10/15/2014
Ki-Young Yoon

Organometallics : A Friend of Total Synthesis

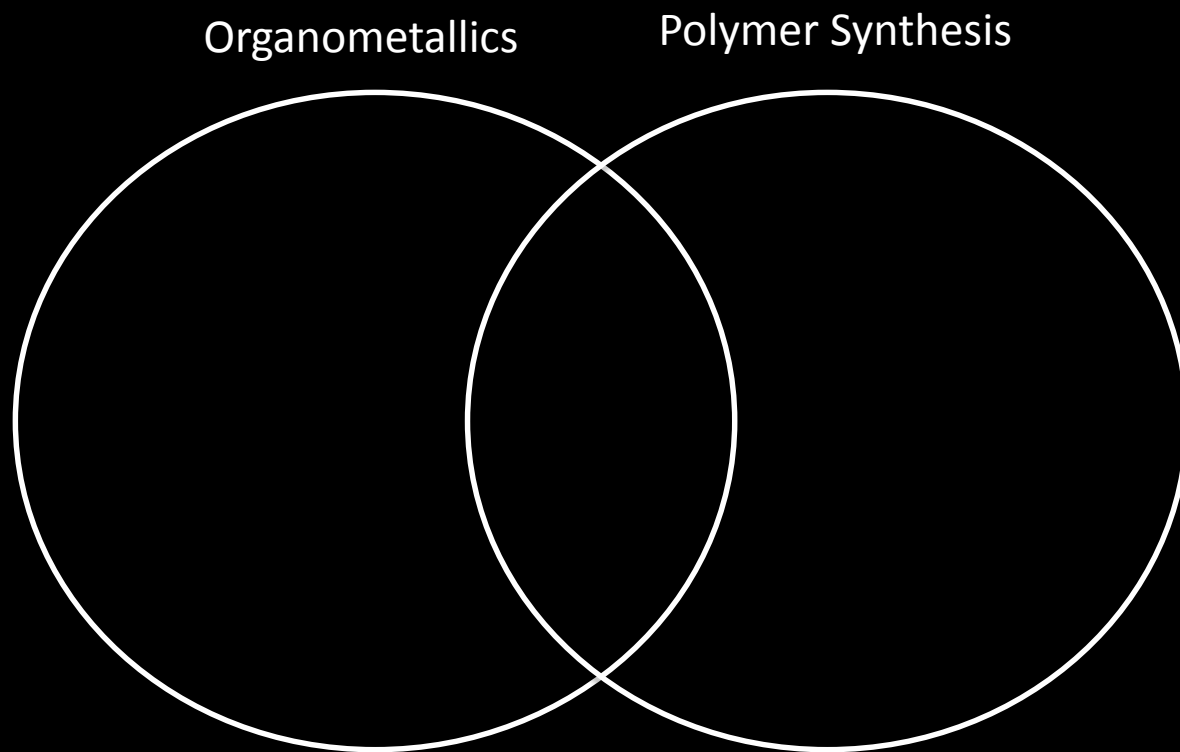


e.g. Barry Trost

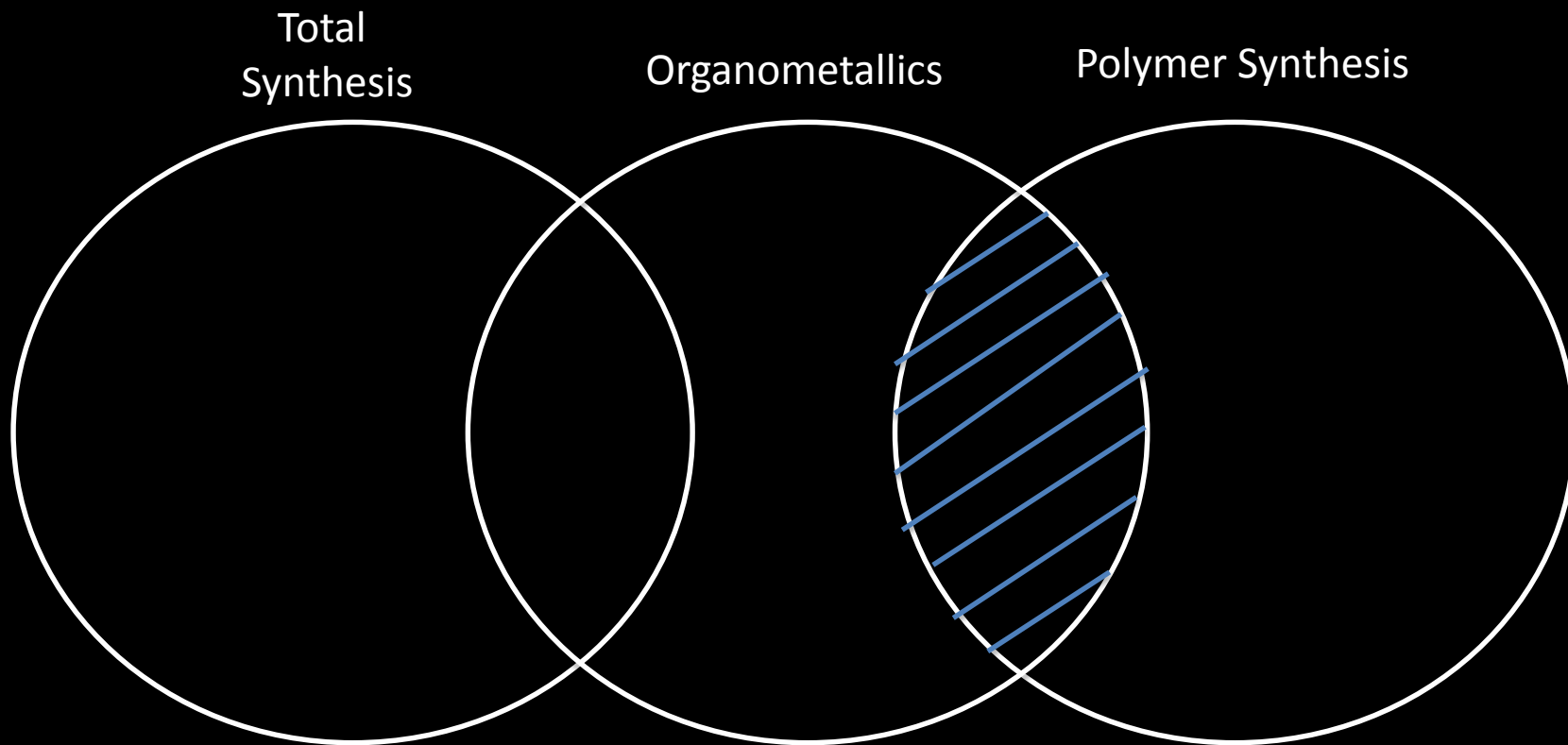


Organometallics : A Friend of Polymer Synthesis

e.g. Bob Grubbs



Organometallics : Still Blue Ocean Area



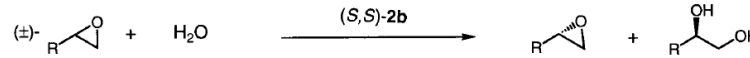
In theory, every organometallic reaction can branch out into polymerization

Organometallics : Still Blue Ocean Area

Hydrolytic kinetic resolution

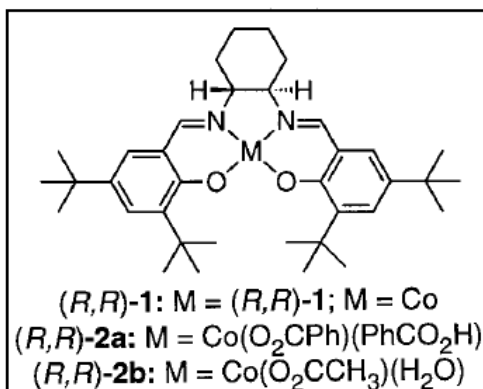
E. Jacobson *Science* **1997**, 277, 936

Table 1. Hydrolytic kinetic resolution of terminal epoxides with water catalyzed by **2b**. The values for k_{rel} were calculated using the equation $k_{rel} = \ln[(1 - c)(1 - ee)]/\ln[(1 - c)(1 + ee)]$, where ee is the enantiomeric excess of the epoxide and c is the fraction of epoxide remaining in the final reaction mixture (4).



Entry	R	Concentration		Time (hours)	Epoxide		Diol		k_{rel}
		2b (mol %)	Water (equiv)		ee (%)	Isolated yield (%)	ee (%)	Isolated yield (%)	
1	CH ₃	0.2	0.55	12	>98	44	98	50	>400
2	CH ₂ Cl	0.3	0.55	8	98	44	86	38	50
3	(CH ₂) ₃ CH ₃	0.42	0.55	5	98	46	98	48	290
4	(CH ₂) ₅ CH ₃	0.42	0.55	6	99	45	97	47	260
5	Ph	0.8	0.70	44	98	38	98*	39*	20
6	CH=CH ₂	0.64	0.50	20	84	44	94	49	30
7	CH=CH ₂	0.85	0.70	68	99	29	88	64	30

*After recrystallization.



J. Coates *J. Am. Chem. Soc.* **2008**, 130, 17658

J|A|C|S
COMMUNICATIONS

Published on Web 12/09/2008

Enantioselective Polymerization of Epoxides: A Highly Active and Selective Catalyst for the Preparation of Stereoregular Polyethers and Enantiopure Epoxides

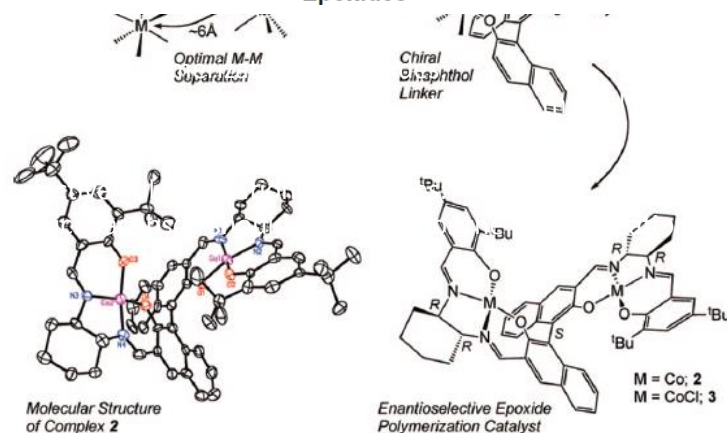


Table 1. Enantioselective Polymerization of Racemic Epoxides Catalyzed by **3**/[PPN][OAc]: Measurement of s^a

entry	epoxide subs. (R)	[epox]/[3]	time (h)	conv. (%) ^b	$ee_{(SM)}$ (%) ^c	[<i>mm</i>] (%) ^d	$ee_{(P)}$ (%) ^e	<i>s</i> -factor ^f	M_n (kg/mol) ^g	M_w/M_n ^g
1	Me	4000	0.25	34	51 (<i>R</i>)	98.6	99.1	370	26.4	1.8
2	Et	1000	0.25	22	29 (<i>R</i>)	98.8	99.2	330	61.4	2.0
3	^{<i>n</i>} Bu	667	0.33	19	24 (<i>R</i>)	98.6	99.1	260	76.8	2.1
4	Ph	1000	17.0	20	26 (<i>R</i>)	94.4	96.1	63	98.9	1.9

Contents

1. Polymerization Mechanism

- o Step-growth polymerization
- o Chain-growth polymerization
- o Step-growth vs. Chain-growth

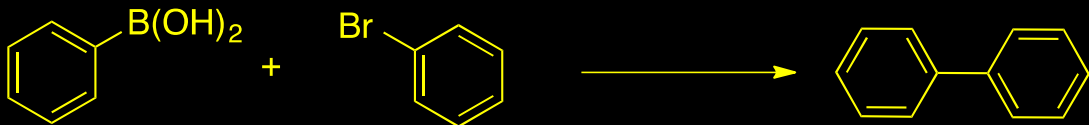
2. Efforts to turn Step-growth polymerization into Chain-growth polymerization

- o GRIM polymerization
- o Pd-catalyzed chain-growth polymerization

Polymer is a mixture

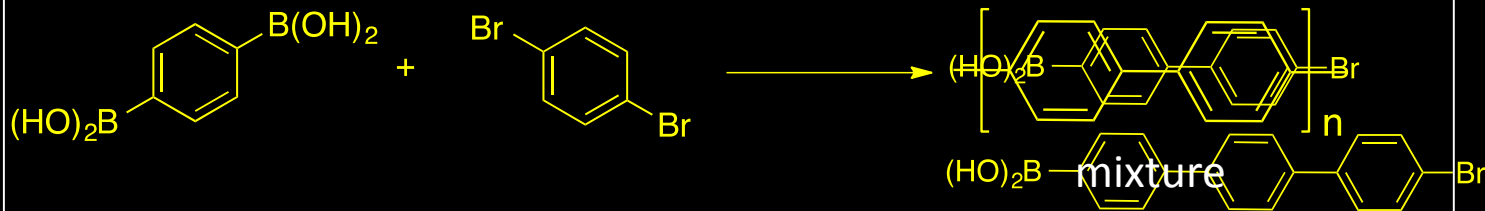
Polymer is not a pure substance. It is a mixture

Organic reaction



Single pure product

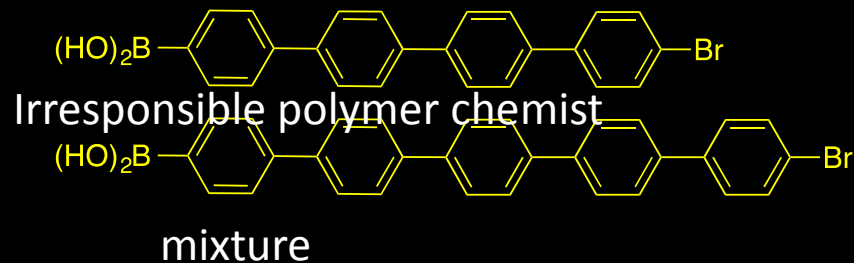
Polymerization



Molecular Weight Distribution

\Rightarrow **Average** Molecular Weight

- M_n , M_w , PDI ($=M_w/M_n$)



Polymer molecular weight

Number Average Molecular Weight, M_n

$$\overline{M}_n = \sum_i X_i M_i = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

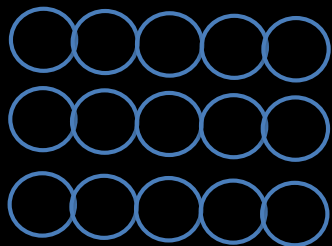
Weight Average Molecular Weight, M_w

$$\overline{M}_w = \sum_i W_i M_i = \frac{\sum_i w_i M_i}{\sum_i w_i} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

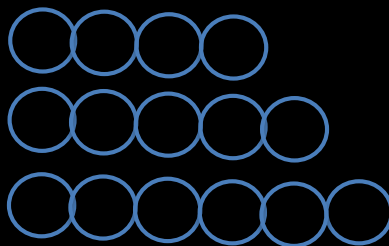
$$PDI = M_w/M_n > 1 \quad (M_w > M_n)$$

Danny's	Credit	Grade	Credit*Grade
PhysOrg	3	4.0 (A)	12
Calculus	2	3.0 (B)	6
History	1	2.0 (C)	2
Mn	(4.0+3.0+2.0)/3	=3	
Mw	(12+6+2)/6	=3.666	

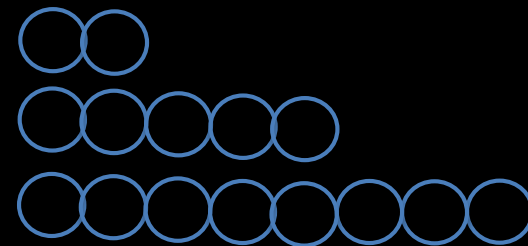
The smaller PDI means the NARROWER distribution of polymer



PDI=1

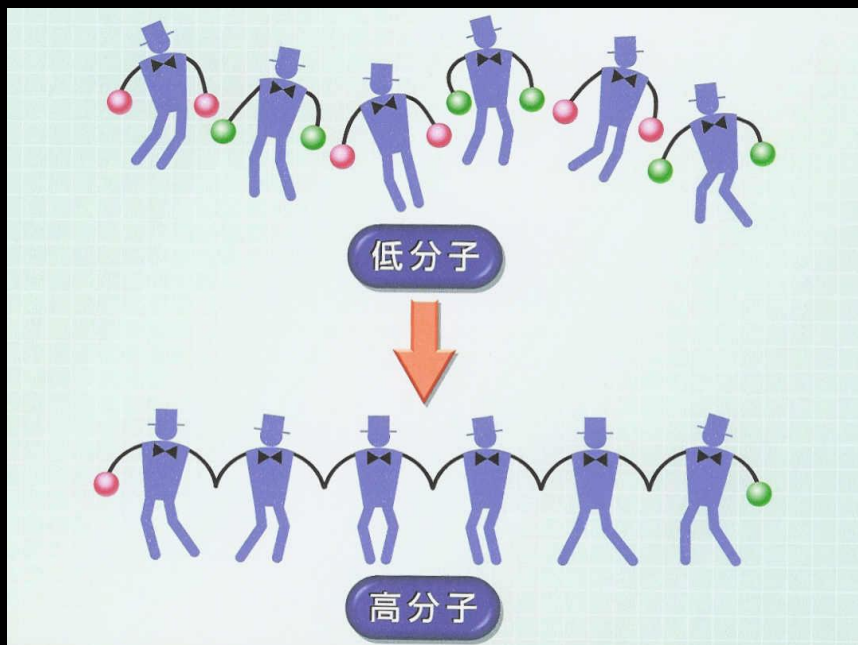


PDI is smaller (>1)

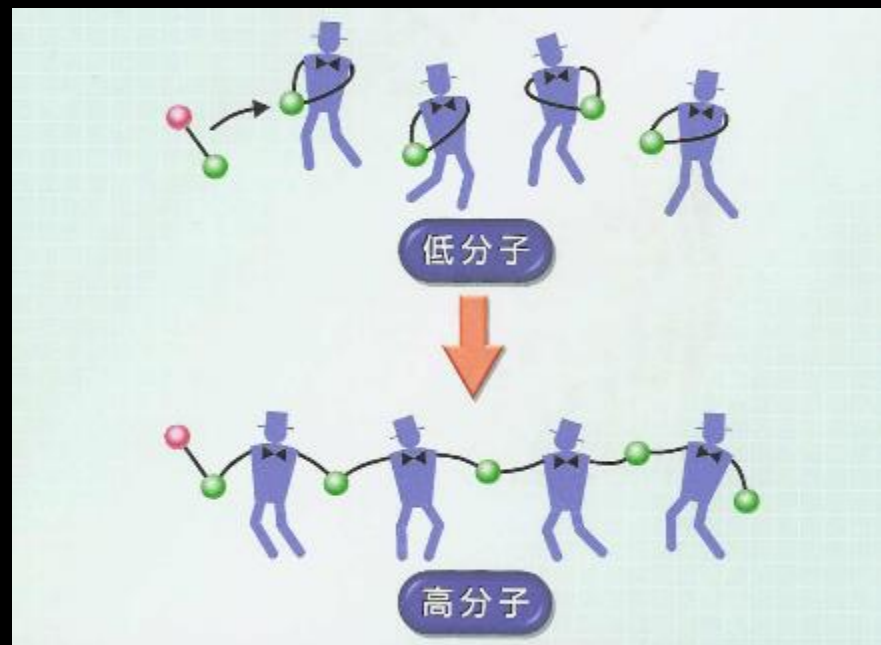
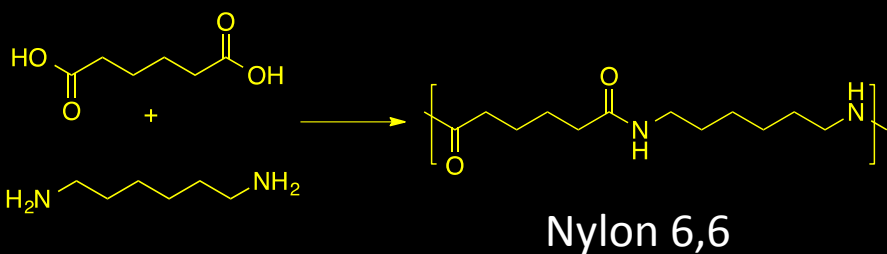


PDI is larger (>1)

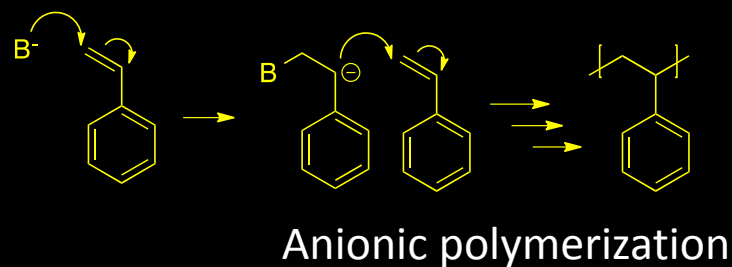
Polymer Growing Mechanism



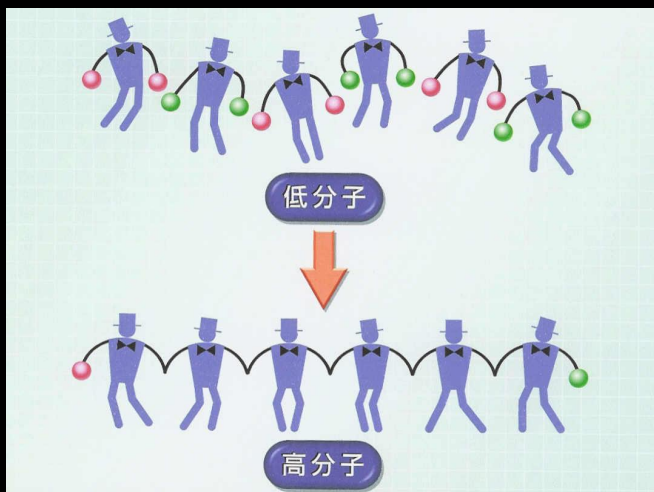
Step-growth polymerization



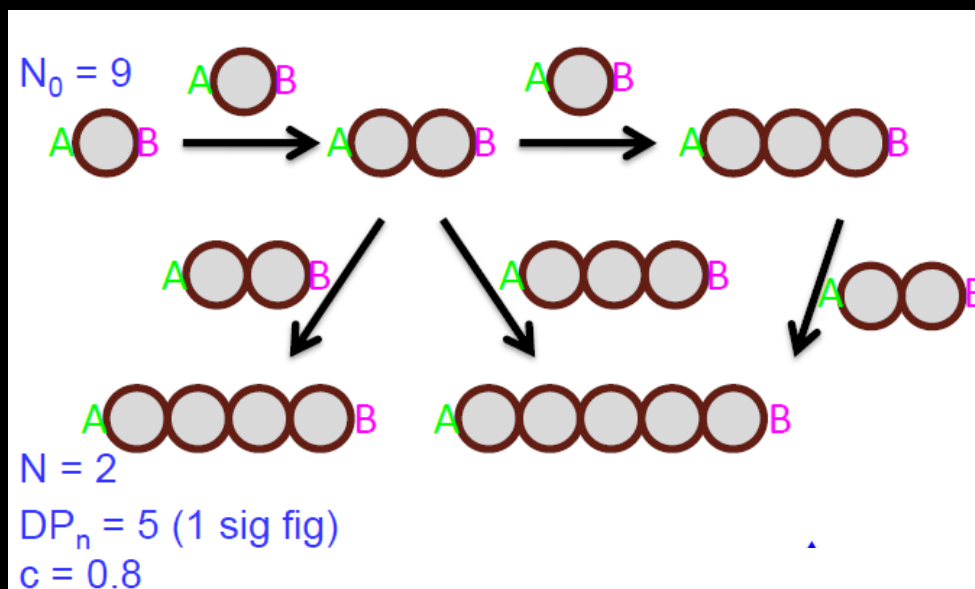
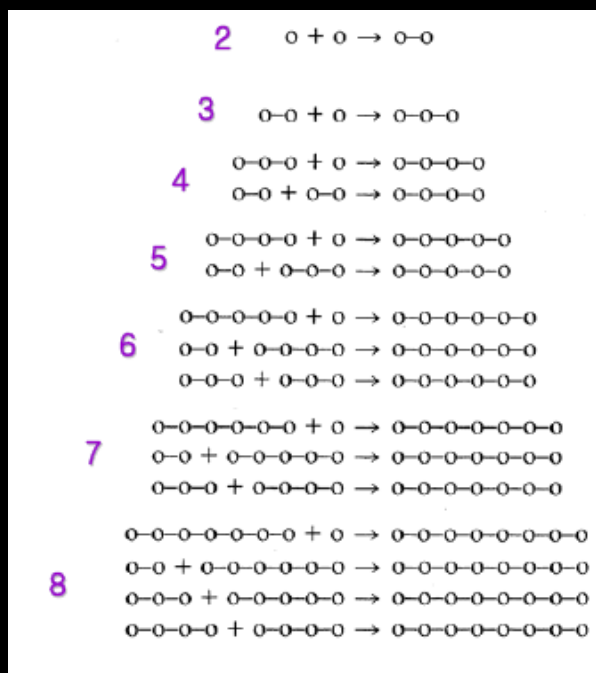
Chain-growth polymerization



Step-Growth Polymerization



- Connecting one-by-one
- More OrgChem-like polymerization (Any Coupling rxns)



More about step-growth plz



Wallace Carothers

- Father of polymerizations
- Worked at Dupont
- Inventor of Nylon
- Killed himself when 41

$$DP = \frac{1}{1-p}, PDI = 1+p$$

p = monomer conversion

DP = Degree of polymerization

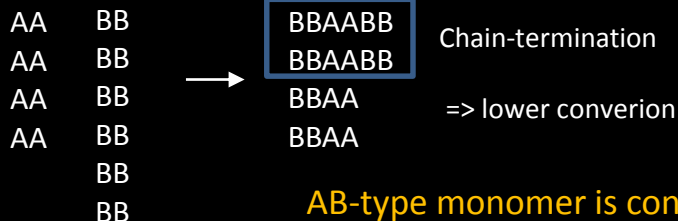
(DP=5 of polymer has 5 monomer in it)

2 major Issues of step-growth polymerization

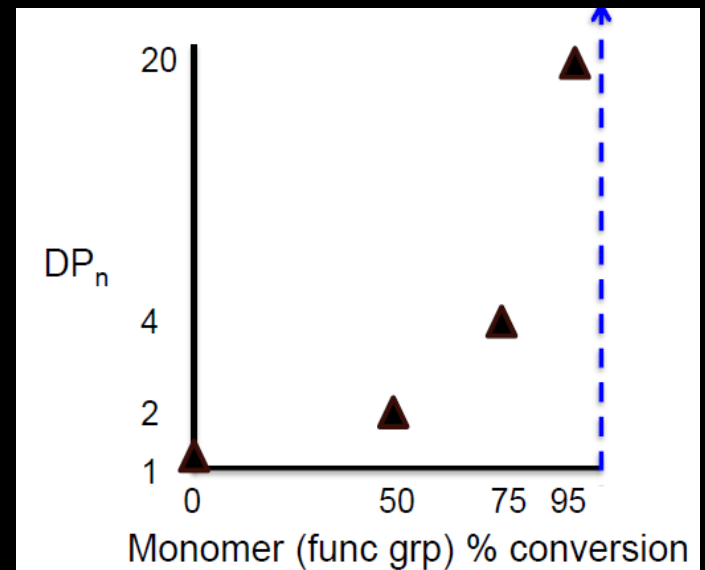
1) Higher monomer conversion

90% → DP=10 95% → DP=20 99% → DP=100

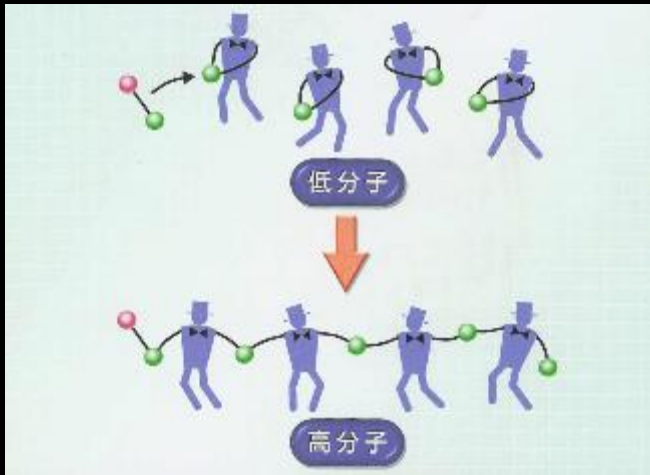
2) Stoichiometric equivalence of functional groups



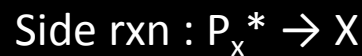
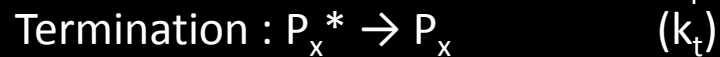
AB-type monomer is conceptually good



Chain-Growth Polymerization



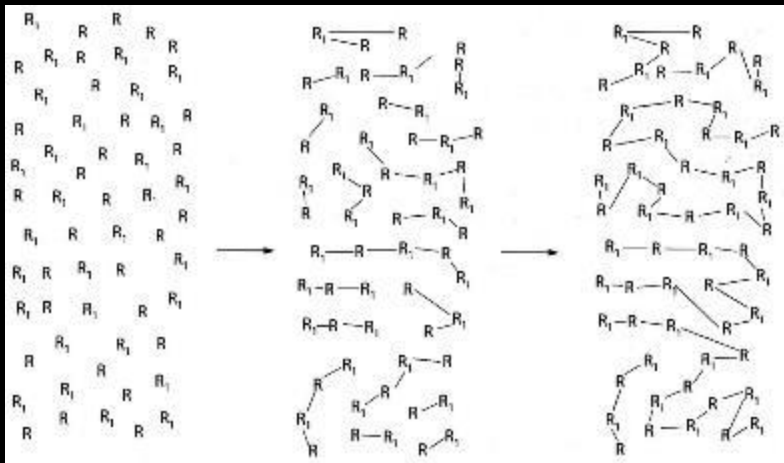
(c.f. chain reaction)



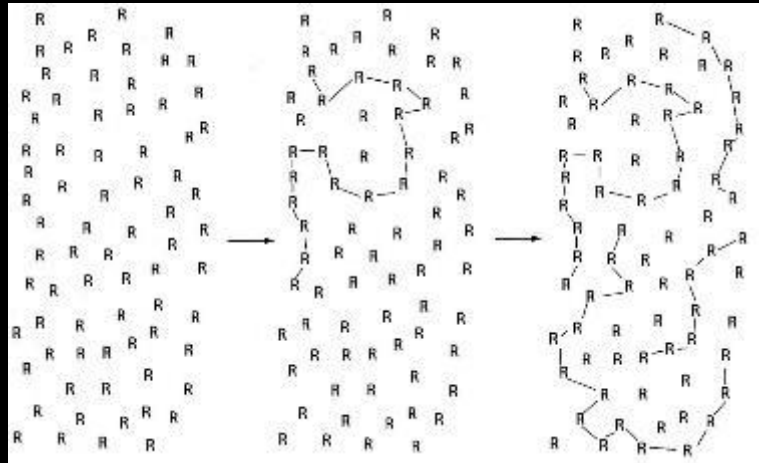
Always needs the initiator.

Initiators don't have to be catalysts

Step-growth

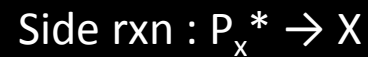
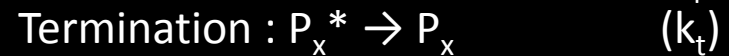
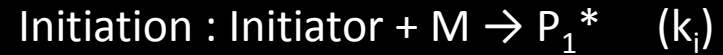
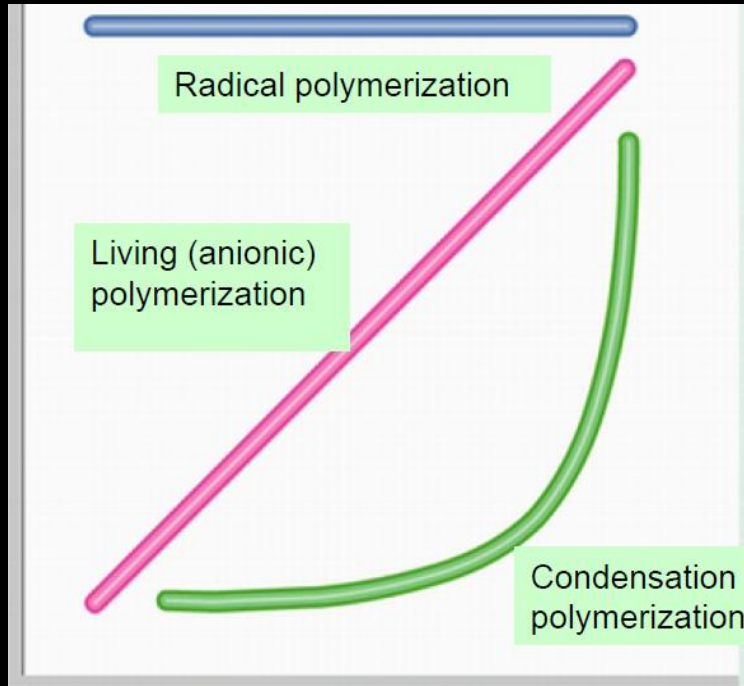


Chain-growth



More about chain-growth plz

MW vs P



Issue of the chain-growth polymerization

To manipulate k_i , k_p , k_t , k_{tr}

=> For living polymerization

What is living polymerization ??

What is living polymerization

I. Special (or Ideal) class of chain-growth polymerization where

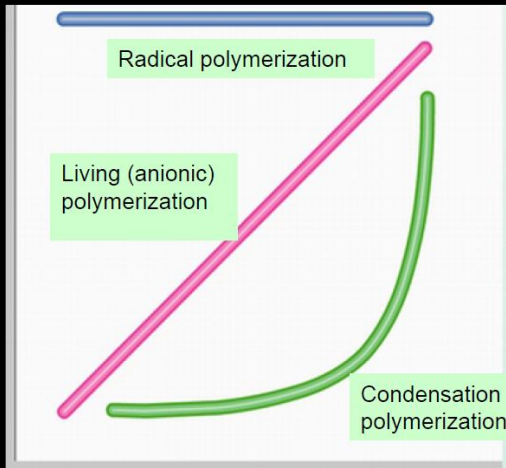
1. Narrow PDI (<1.2)
2. Molecular weight (M_n) is well-controlled by [Monomer]/[Initiator] or conversion
3. After all consumption of monomer, further addition of monomer results in continue polymerization
→ Block copolymers can be synthesized.

(AAAAAAAAABBBBBBBBBBBCCCCCCCCCCCC)

II. To achieve living polymerization

1. $k_p \gg k_t$
2. k_i/k_p high enough
3. absence of side reactions such as chain transfer reaction

What is living polymerization



$k_i/k_p >$ high enough
 $K_p/k_t >$ very high
 $K_p/k_{tr} >$ very high



We can control MW of polymers

Fast Initiation (k_i/k_p)



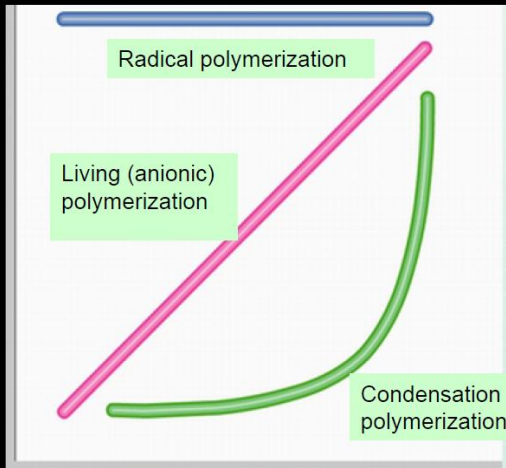
Fast propagation (k_p/k_t),
but not too fast (k_i/k_p)



Ideally no termination
Little termination ($k_p \gg k_t$)



What is ~~living~~ Controlled polymerization



$k_i/k_p > \text{high enough}$

$K_p/k_t > \text{very high}$

$K_p/k_{tr} > \text{very high}$



We can control MW of polymers

Living = no termination (too ideal)

Controlled polymerization is preferred.

Anionic polymerization is thought of as only polymerization that can be real living.
Anionic polymerization can be living polymerization in the absence of moisture

PDIs of Successful anionic polymerizations (normally <1.05)

Step-growth vs Chain-growth

“ can you make a nice polymer with MW=5000 ?”

Step-growth guy says,

$$DP = \frac{1}{1-p} , PDI = 1+p$$

“ okay, the MW of my monomer is 500,
so what I am supposed to do is just stop the polymerization at the moment when conversion is 90%.

⇒ Practically impossible.

Chain-growth guy says,

“ okay, the MW of my monomer is 500,
So what I am supposed to do is just use my initiator with the ratio of monomer/initiator=10 “

Chain-growth polymerization can control the molecular weight of the polymer

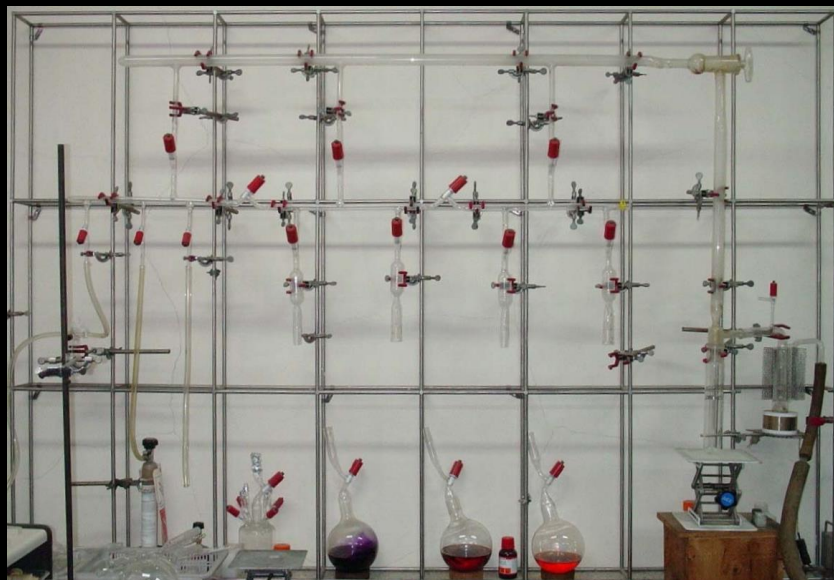
⇒ Prediction.

⇒ Reproducibility

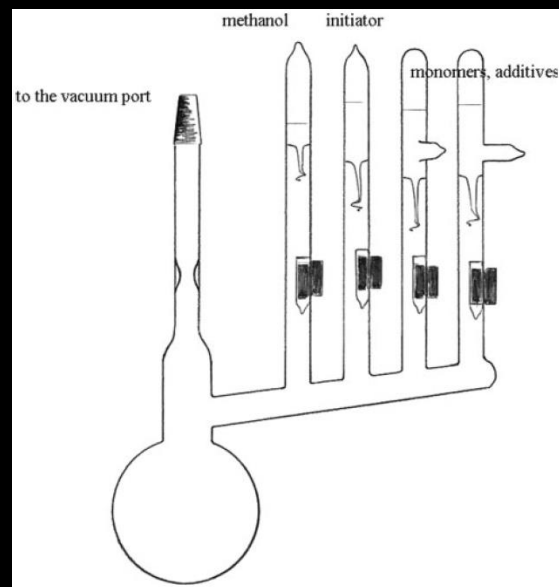
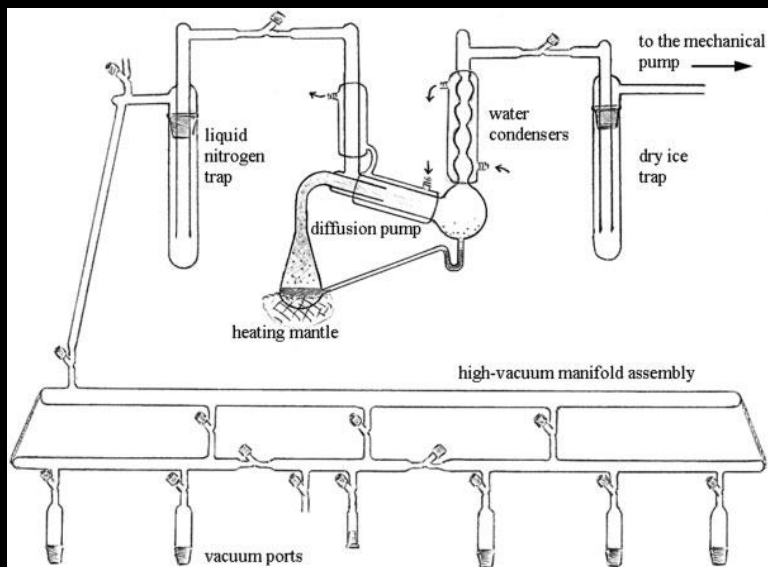
Those who use chain-growth polymerization predict they will have $M_n=5000$,
while those who use step-growth polymerization pray for that.

Predict or Pray?

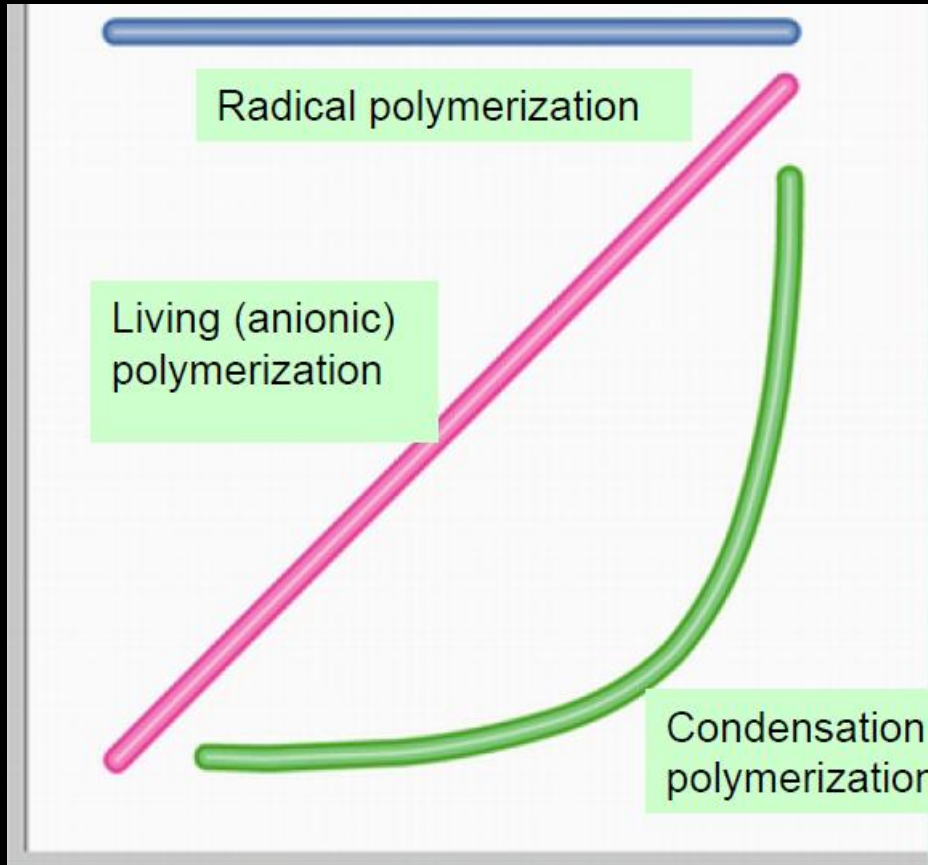
Anionic polymerization : Super Geek Chemistry



Powerful but not synthesist-friendly polymerization



Example of the controlled polymerization



RP)
Transfer (RAFT)
n (NMP)

RAFT

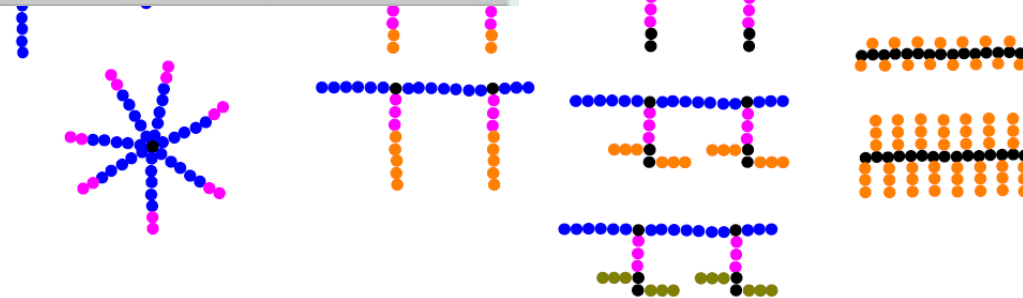
NMP

izzardo
D, Australia)

Hawker
(UCSB)

uge impact on the material field

Architecture

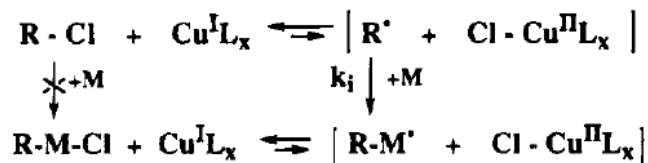


Example of the controlled polymerization

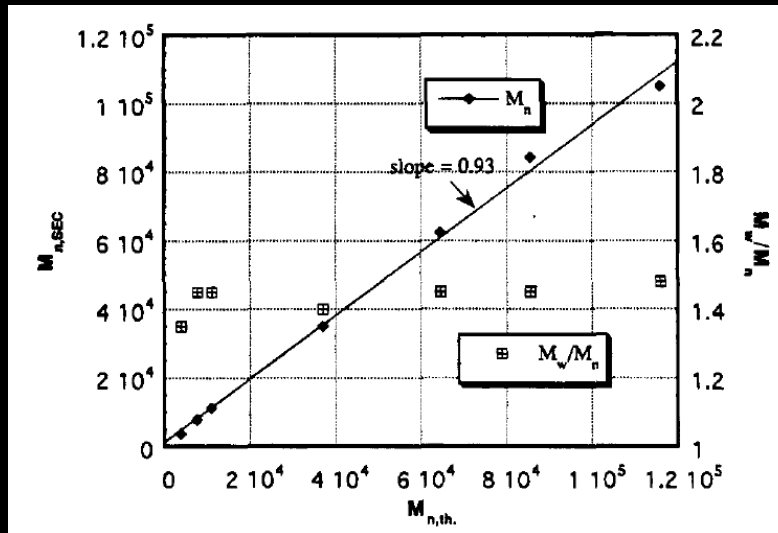
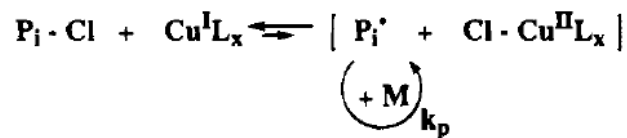
Atom-transfer radical polymerization (ATRP) – maintains low concentration of active radical

Scheme 1

Initiation:



Propagation:

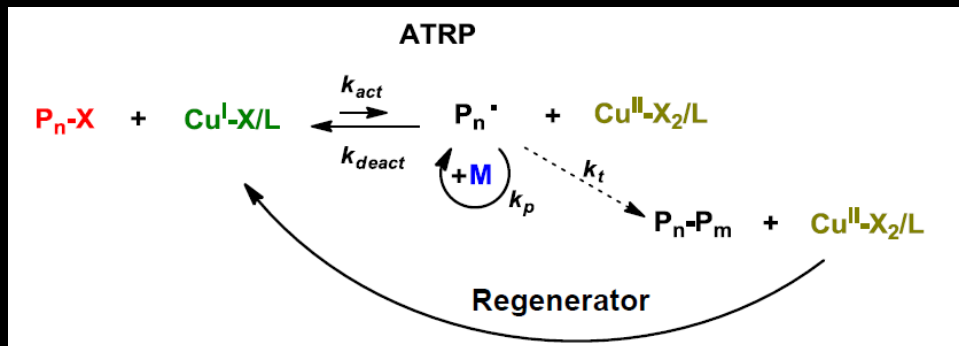


Matyjaszewski JACS 1995, 117, 5614

Nowadays, generally PDI < 1.2

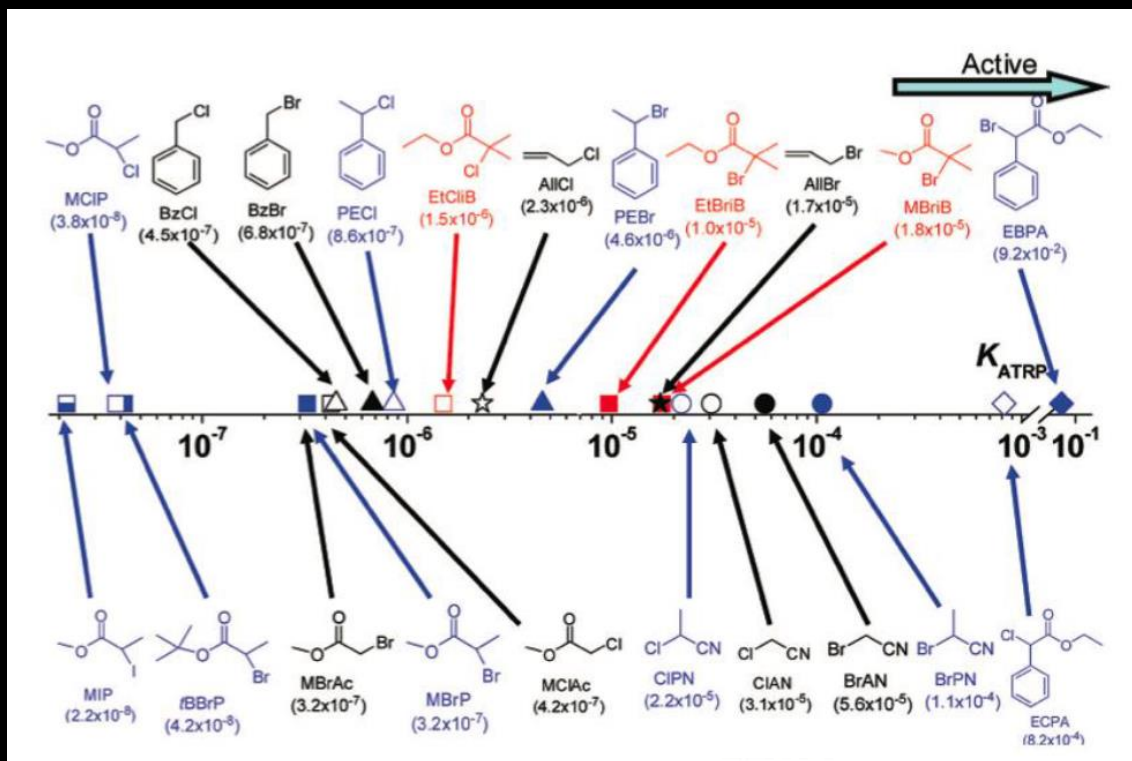
Example of the controlled polymerization

Atom-transfer radical polymerization (ATRP) – maintains low concentration of active radical



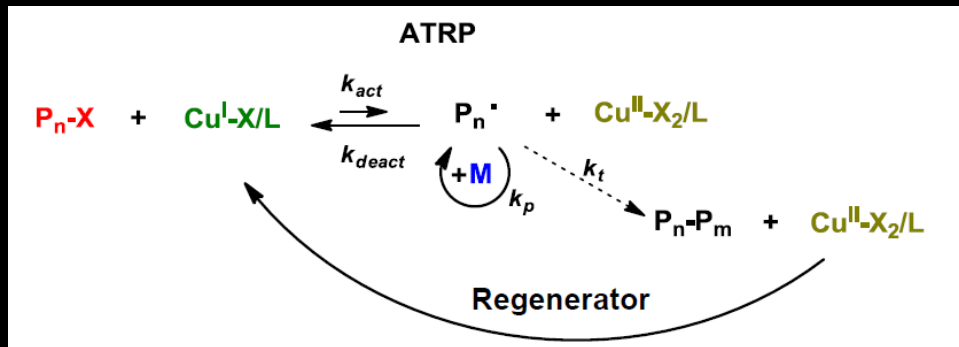
Matyjaszewski, *Chem. Rev.*, **2001**, 101, 2921

Initiator – R-X
Catalyst – Cu(I)

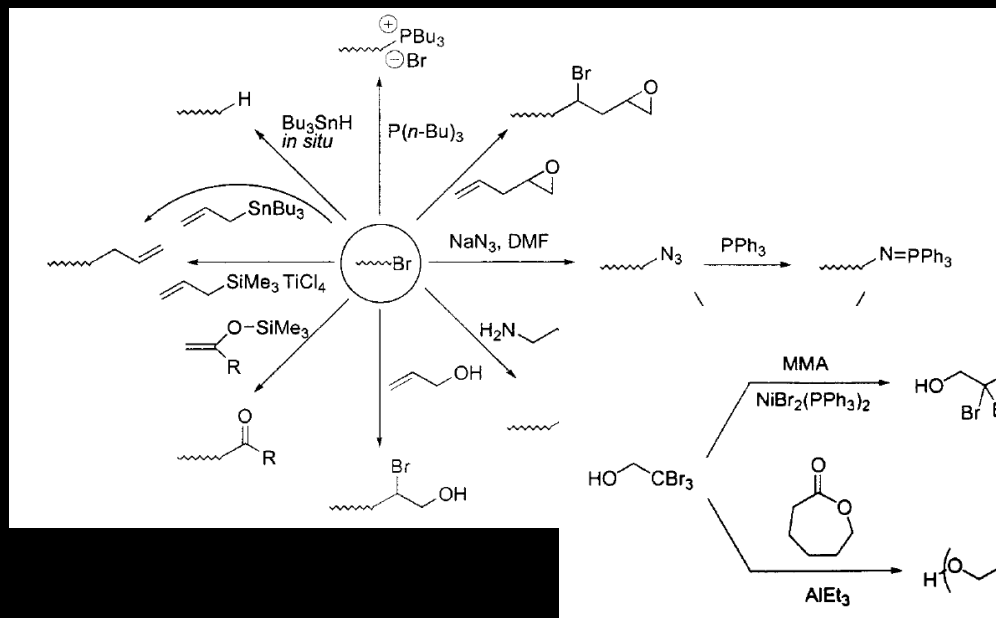


Example of the controlled polymerization

Atom-transfer radical polymerization (ATRP) – maintains low concentration of active radical

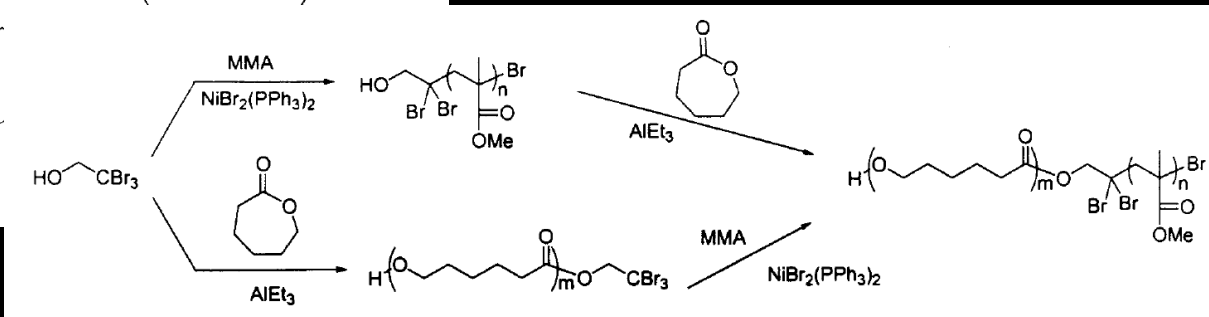


Matyjaszewski, *Chem. Rev.*, **2001**, 101, 2921



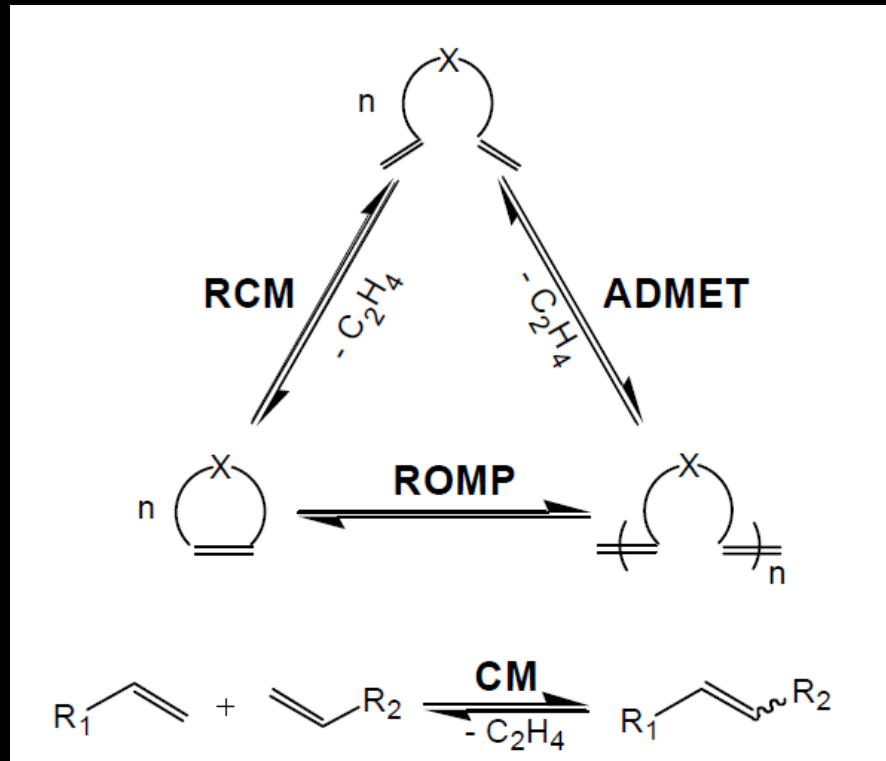
1. Relatively easy to functionalize polymer end-group.

2. Easily combined with other polymerization methods



Example of the controlled polymerization

Metathesis polymerization



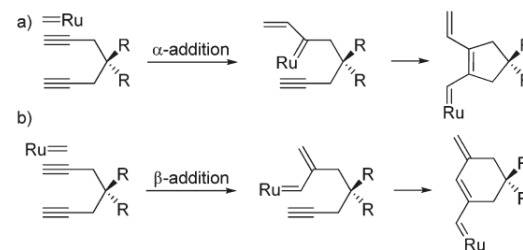
Conceptually

ROMP : chain-growth polymerization

- Catalyst is at the chain end after ring opening

ADMET : step-growth polymerization

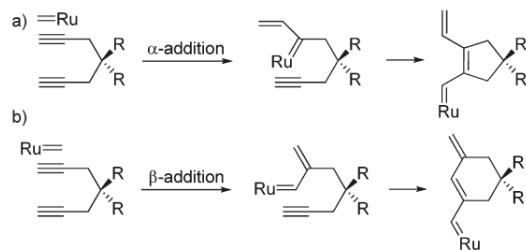
- Catalyst is gone after cross metathesis



Example of the controlled polymerization

Metathesis cyclopolymerization

Scheme 1. Cyclopolymerization of 1,6-Heptadiyne Derivatives: (a) Five-Membered-Ring Unit Produced from α -Addition of a Metal Carbene and (b) Six-Membered Ring from β -Addition



Buchmeiser, *ACIEE* **2003**, 42, 5965

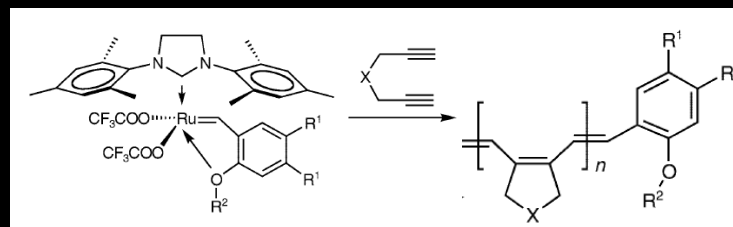


Table 1: Results of the polymerization with catalysts 1–4.^[a]

Poly(acetylene)	Cat.	Solvent	M_n (theor.)	M_n (LS)	M_w (LS)	PDI (LS)
poly(DEDPM) ₁₀₀	1	CH_2Cl_2	11 975	10 400	16 800	1.62
poly(ECMCH) ₅₀	1	CH_2Cl_2	17 485	11 100	28 700	2.59
poly(DEDPM) ₅	2	CH_2Cl_2	1 389	5 600	7 300	1.30
poly(DEDPM) ₁₀	2	CH_2Cl_2	2 571	7 000	11 000	1.57
poly(DEDPM) ₃₀	2	CH_2Cl_2	7 296	13 100	21 400	1.63
poly(DEDPM) ₅₀	2	CH_2Cl_2	12 021	16 200	26 400	1.63
poly(DEDPM) ₇₀	2	CH_2Cl_2	16 747	20 000	22 000	1.10
poly(DEDPM) ₁₀₀	2	CH_2Cl_2	23 835	27 500	42 400	1.54
poly(ECMCH) ₅₀	2	CH_2Cl_2	17 517	13 000	22 400	1.72
poly(DEDPM) ₅₀	3	H_2O	11 975	7 700	16 000	2.08
poly(ECMCH) ₅₀	3	H_2O	17 485	8 100	10 400	1.28
poly(DEDPM) ₅₀	4	H_2O	12 021	9 500	13 100	1.38
poly(DEDPM) ₁₀₀	4	H_2O	23 835	12 700	15 600	1.23

$k_i/k_p >$ high enough

$K_p/k_t >$ very high

$K_p/k_{tr} >$ very high



We can control MW of polymers

Slow initiation $\Rightarrow k_i/k_p$ isn't high

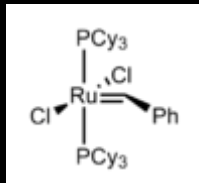
\Rightarrow broad MW distribution

\Rightarrow PDI is large (>1.3)

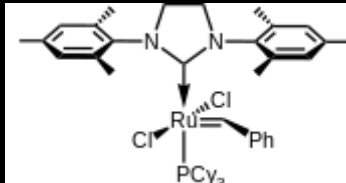
Example of the controlled polymerization

Metathesis cyclopolymerization

Grubbs 1G

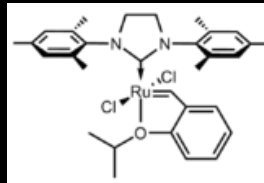


Grubbs 2G



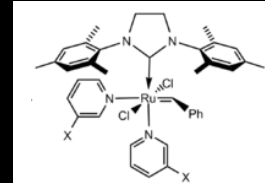
Slow initiator

Hoveyda-Grubbs 2G



Slower initiator
with good thermal stability

Grubbs 3G



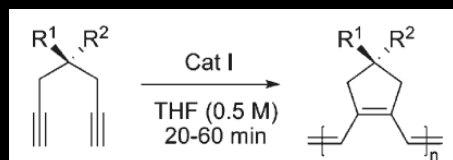
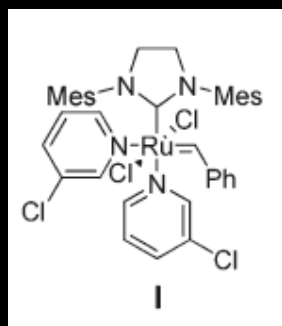
Fast initiator

Widely used
only in polymer fields

Example of the controlled polymerization

Metathesis cyclopolymerization

Tae-Lim Choi, *J. Am. Chem. Soc.* **2011**, 133, 11904



Buchmeiser, *ACIEE* **2003**, 42, 5965

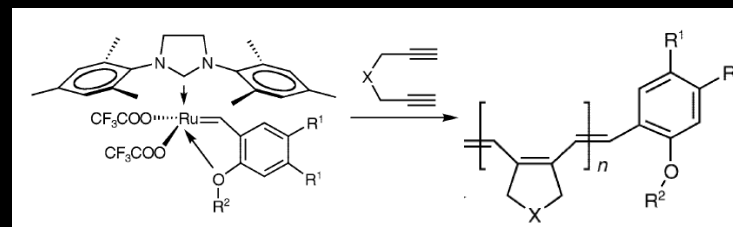


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poly(ECMCH) ₅₀	1	CH ₂ Cl ₂	17 485	11 100	28 700	2.59
poly(DEDPM) ₅	2	CH ₂ Cl ₂	1 389	5 600	7 300	1.30
poly(DEDPM) ₁₀	2	CH ₂ Cl ₂	2 571	7 000	11 000	1.57
poly(DEDPM) ₃₀	2	CH ₂ Cl ₂	7 296	13 100	21 400	1.63
poly(DEDPM) ₅₀	2	CH ₂ Cl ₂	12 021	16 200	26 400	1.63
poly(DEDPM) ₇₀	2	CH ₂ Cl ₂	16 747	20 000	22 000	1.10
poly(DEDPM) ₁₀₀	2	CH ₂ Cl ₂	23 835	27 500	42 400	1.54
poly(ECMCH) ₅₀	2	CH ₂ Cl ₂	17 517	13 000	22 400	1.72
poly(DEDPM) ₅₀	3	H ₂ O	11 975	7 700	16 000	2.08
poly(ECMCH) ₅₀	3	H ₂ O	17 485	8 100	10 400	1.28
poly(DEDPM) ₅₀	4	H ₂ O	12 021	9 500	13 100	1.38
poly(DEDPM) ₁₀₀	4	H ₂ O	23 835	12 700	15 600	1.23

entry	monomer	[M]/[I]	temp (°C)	M_n (kDa) ^a	PDI ^a	yield (%) ^b
1	1	100	RT	41.7	1.81	87
2	1	25	0	12.3	1.09	>99
3	1	50	0	25.4	1.19	81
4	1	100	0	40.6	1.16	97
5	1	150	0	54.4	1.44	94
6	2	25	0	14.6	1.06	93
7	2	50	0	27.3	1.10	93
8	2	100	0	46.7	1.28	96
9	2	150	0	57.6	1.29	>99
10	3	25	0	14.3	1.06	85
11	3	50	0	24.0	1.14	80
12	3	100	0	34.9	1.15	>99
13	3	150	0	50.7	1.28	87
14	4	25	−10	8.9	1.13	97
15	4	50	−10	19.3	1.11	79
16	4	100	−10	39.6	1.2	89
17	4	150	−5	54.9	1.43	87

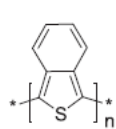
Fast initiation

Polymer with narrow MW distribution

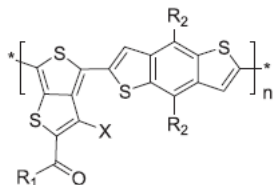
Step-growth polymerization

Advantage of the step-growth polymerization

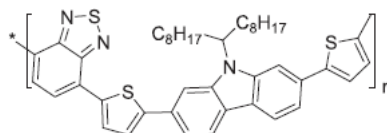
- a tool to produce **alternating copolymers** (ABABABABABABABABABABABAB)



PITN



PCDTBT



PTB1: X=H, R₁=n-dodecyloxy, R₂=n-octyloxy

PTB2: X=H, R₁=2-ethylhexyloxy, R₂=n-octyloxy

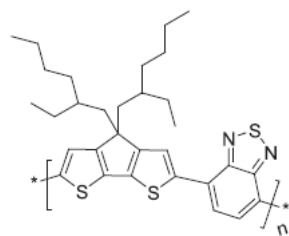
PTB3: X=H, R₁=2-ethylhexyloxy, R₂=n-octyl

PTB4: X=F, R₁=n-octyloxy, R₂=2-ethylhexyloxy

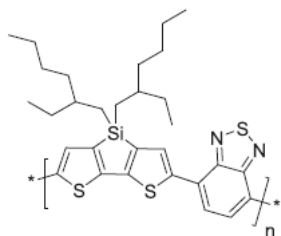
PTB5: X=H, R₁=n-octyloxy, R₂=2-ethylhexyloxy

PTB6: X=H, R₁=2-butyloctyloxy, R₂=n-octyloxy

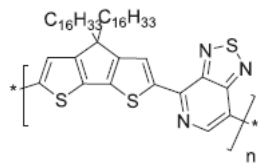
PTB7: X=F, R₁=2-ethylhexyloxy, R₂=2-ethylhexyloxy



PCPDTBT



PSBTBT



PCPDTPT

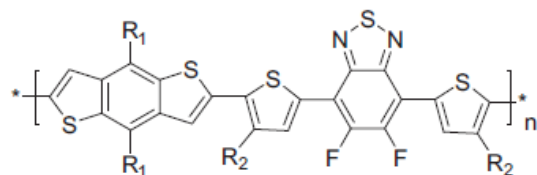
Good for structural diversity

Currently,

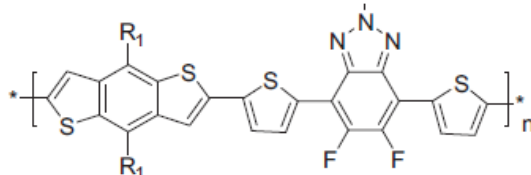
Most of the conducting polymers in organic electronics

Are produced in the step-growth manner.

Stille
Kumada
Suzuki



PBnDT-DTffBT: R_1 =3-butylnonyl,
 R_2 =2-ethylhexyl



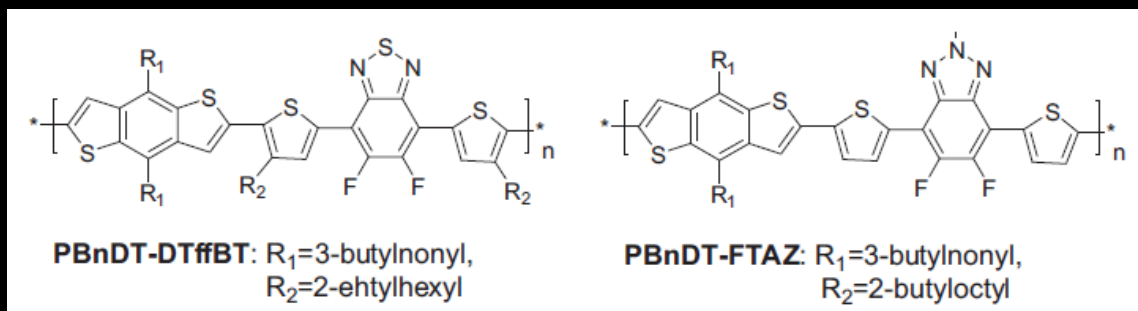
PBnDT-FTAZ: R_1 =3-butylnonyl,
 R_2 =2-butyloctyl

Step-growth polymerization for organic electronics?

Low bandgap conducting polymers = DA repeating unit

(D – electron-rich aromatic ring

A – electron-poor aromatic ring)



Alternating copolymers are made in Step-growth manners.

Reproducibility is one of the high priorities in Organic electronics.

Unpredictable polymerization is currently being used for organic electronics.

Possible to Change Step-growth polymerization into chain-growth polymerization ?

Catalyst transfer ??

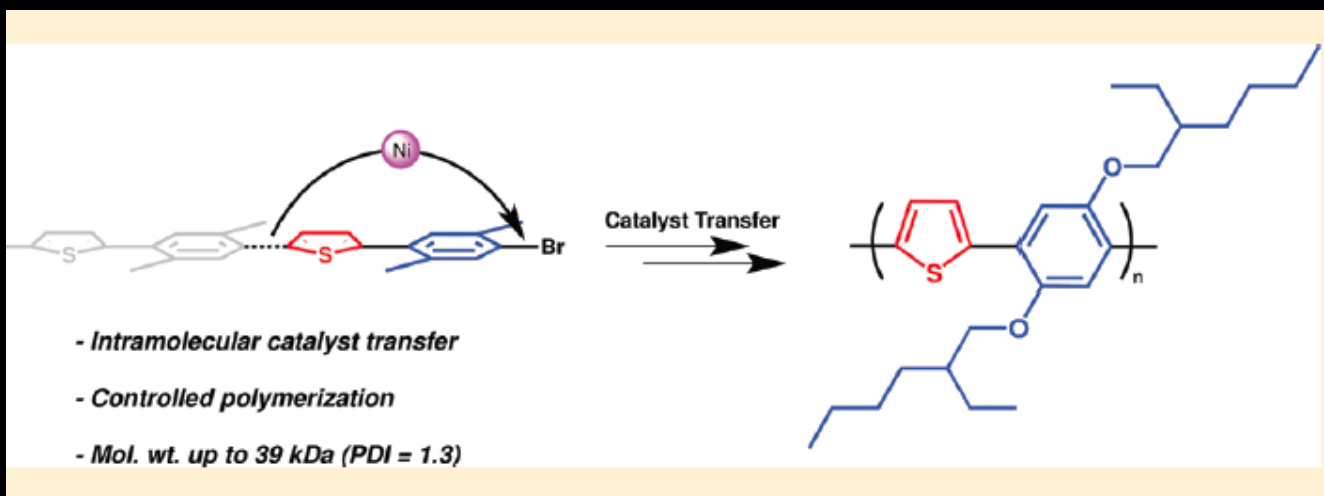
(Intrinsically) Step-growth

Stille
Kumada
Suzuki

Intrinsically chain-growth

ROMP
Typical Radical polymerization
Anionic polymerization

What if ?



Apple vs Samsung



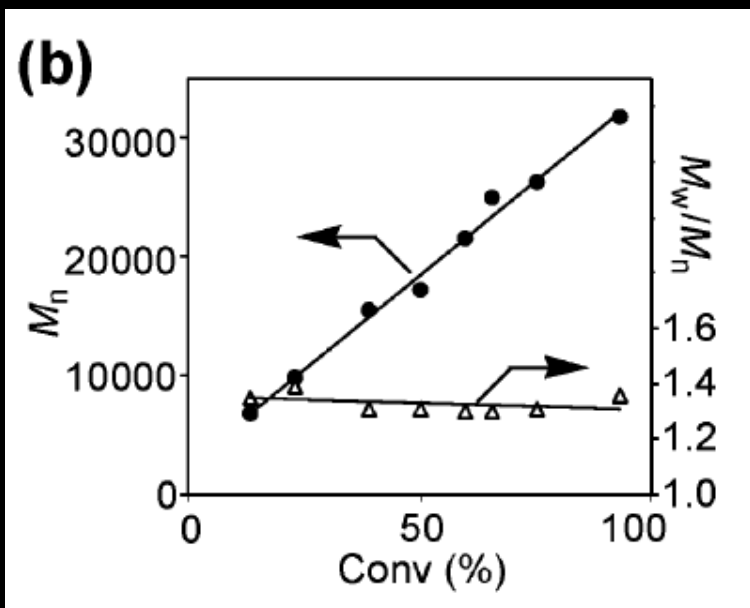
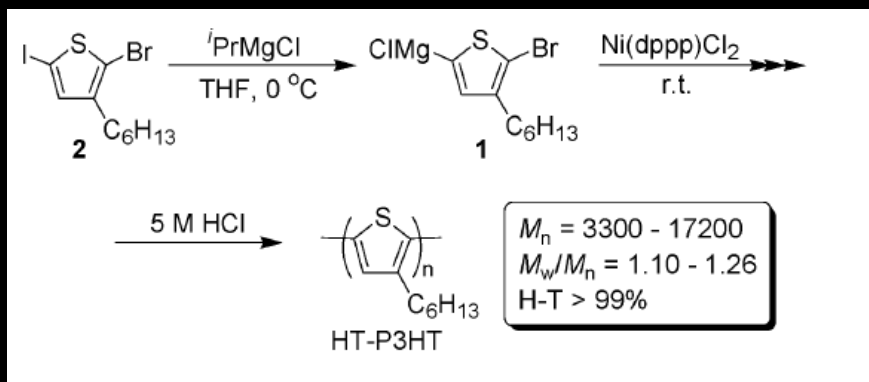
King of Innovation



King of Renovation

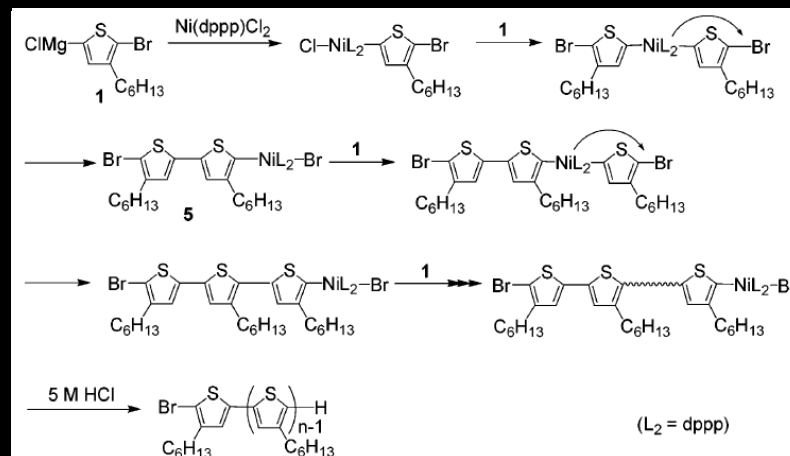
GRIM method

Grignard metathesis polymerization



Chain-growth polymerization kinetics

McCullough *J. Chem. Soc., Chem. Commun.* 1992, 70
 McCullough *Adv. Mater.* 1999, 3, 250
 Yokozawa *Macromolecules*, 2004, 37, 1169
 Yokozawa *JACS*, 2005, 127, 17542



Catalyst Transfer

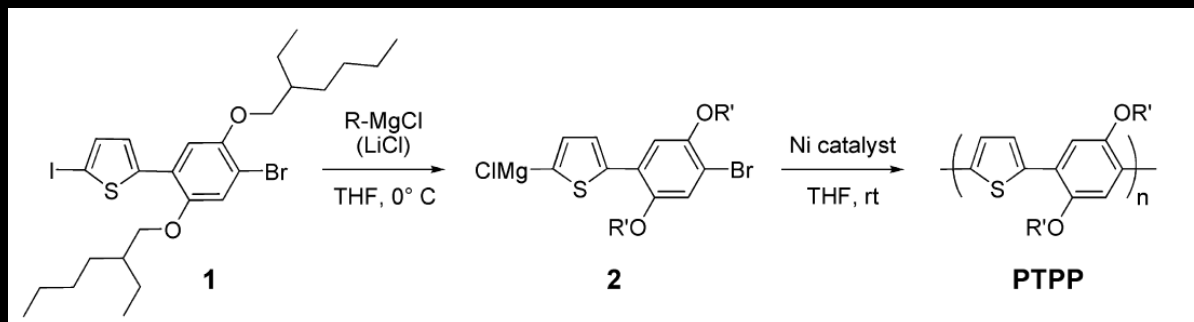
Reductive elimination
 followed by intramolecular oxidative addition

Electron density of arene may work as a directing group

GRIM method

Grignard metathesis polymerization

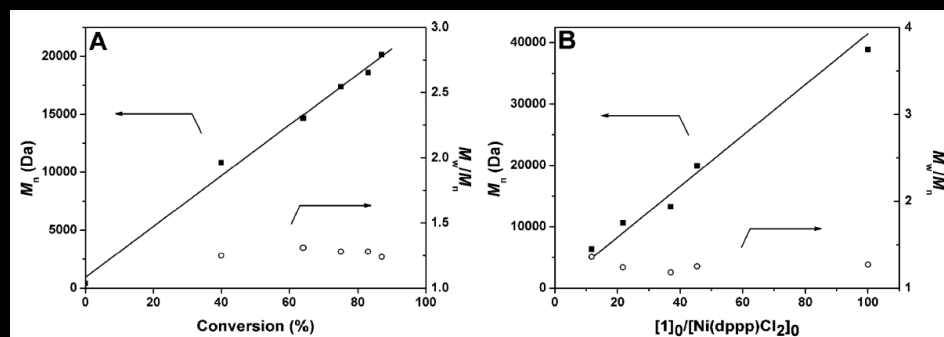
Bielawski *Macromolecules*, 2012 ,45, 2321



AB-Alternating copolymer

Table 1. Polycondensation of **2** with Various Ni Catalysts^a

entry	catalyst	equiv of LiCl	Grignard reagent	M_n^b	M_w/M_n^b
1	Ni(dppe)Cl ₂	0	ⁱ PrMgCl	12 000	2.03
2	Ni(dppp)Cl ₂	0	ⁱ PrMgCl	3 700	1.32
3	Ni(dppe)Cl ₂	1.0	ⁱ PrMgCl	12 000	1.74
4 ^c	Ni(dppp)Cl ₂	1.0	ⁱ PrMgCl	14 500	1.33
5	Ni(dppe)Cl ₂	1.0	^t BuMgCl	15 200	2.03
6	Ni(dppp)Cl ₂	1.0	^t BuMgCl	10 500	1.53

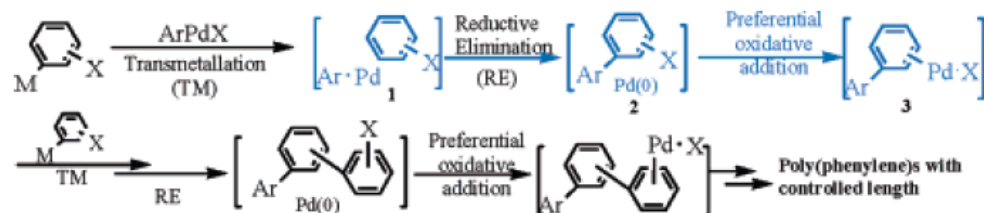


Pd Catalyst Transfer

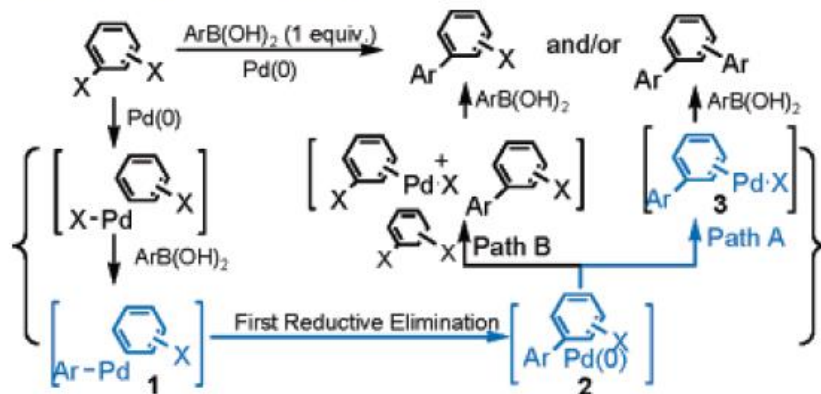
In 2005,

Qiao-Sheng Hu, *JACS*, 2005 ,127, 10006

Scheme 1. Hypothetic Controlled Pd(0)-Catalyzed Cross-Coupling Polymerization of AB-Type Monomers



Scheme 2. Pd(0)-Catalyzed Cross-Couplings of Dihalobenzenes with 1 equiv of Arylboronic Acids



Pd Catalyst Transfer

In 2005,

Qiao-Sheng Hu, *JACS*, 2005 ,127, 10006

Table 2. Room-Temperature Pd(0)-Catalyzed Cross-Couplings of 1,2-Dihalobenzenes with Arylboronic Acids^a

$\text{C}_6\text{H}_3\text{X}_2 + (\text{HO})_2\text{B-Ar} \xrightarrow[\text{K}_3\text{PO}_4, \text{ THF, r.t., 20 h}]{2.5\% \text{ Pd}_2(\text{dba})_3/10\% \text{ } t\text{-Bu}_3\text{P}} \text{C}_6\text{H}_3\text{X-Ar} + \text{C}_6\text{H}_3\text{Ar}_2$				
Entry	Dihalide	Ar-B(OH) ₂	Mono : Di ^b	Yield(%) ^c
1			<1 : >99	96
2			2 : 98	98
3			<1 : >99	96.5
4			4 : 96	90
5			<1 : >99	94
6			<1 : >99	92
7			<1 : >99	78
8			<1 : >99	82
9			>99 : <1	99 ^d
10			21 : 79	72

Table 3. Room-Temperature Pd(0)-Catalyzed Cross-Couplings of Dihaloarenes with Arylboronic Acids^a

$\text{X-Ar-X} + (\text{HO})_2\text{B-Ar}' \xrightarrow[\text{K}_3\text{PO}_4, \text{ THF, r.t., 20 h}]{2.5\% \text{ Pd}_2(\text{dba})_3/10\% \text{ } t\text{-Bu}_3\text{P}} \text{Ar'-Ar-X} + \text{Ar'-Ar-Ar}'$				
Entry	Dihalide	Ar-B(OH) ₂	Mono : Di ^b	Yield(%) ^c
1			0.3 : 99.7 (1 : 332)	96
2			1.5 : 98.5	91
3			1 : 99	86
4			3 : 97	43
5			6 : 94	23
6			9 : 91	80

Pd Catalyst Transfer

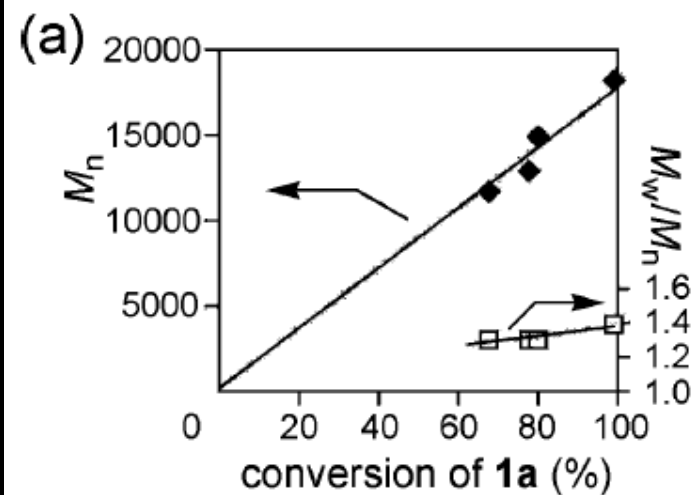
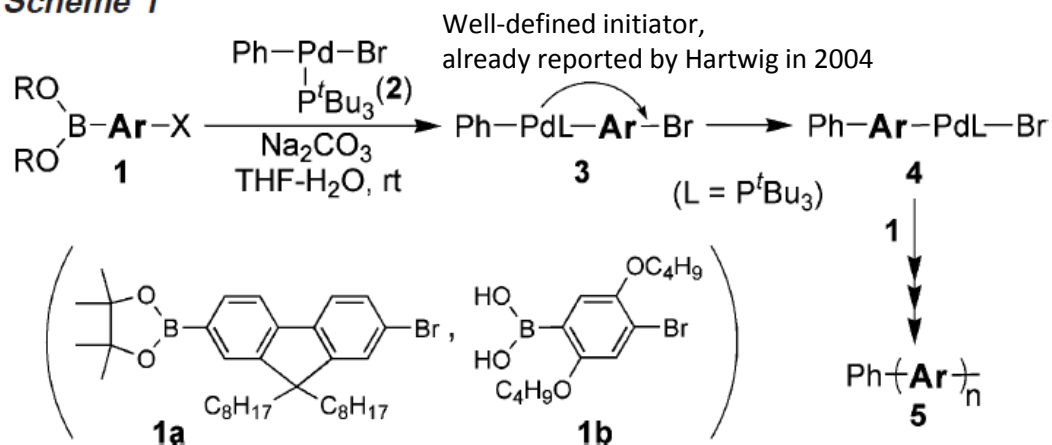
In 2007,

“Now my turn. Thank you for your nice study, Dr. Hu”

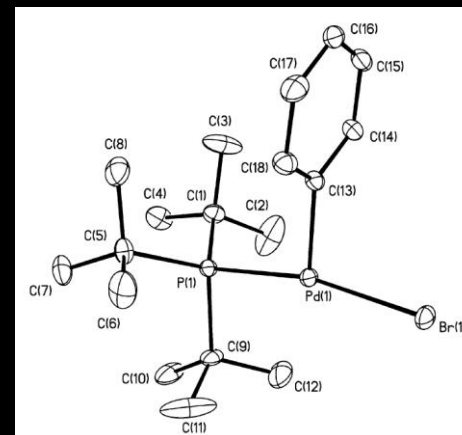
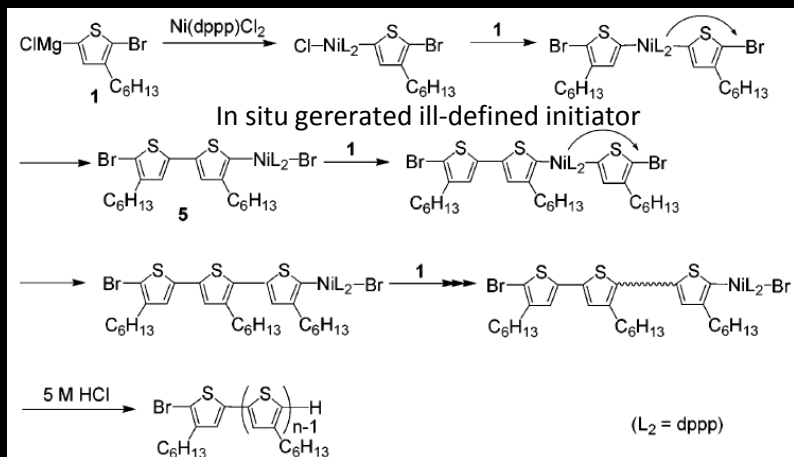
- Yokozawa

Yokozawa, *JACS*, 2007 ,129, 7236

Scheme 1



Chain-growth kinetics



Pd Catalyst Transfer

In 2013,

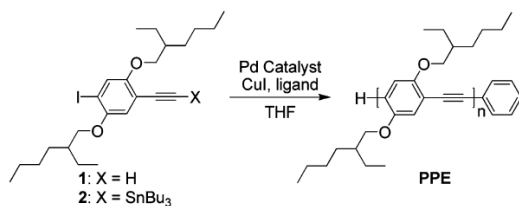
“Now my turn. Thank you for your idea, Dr. Yokozawa”

- Bielawski

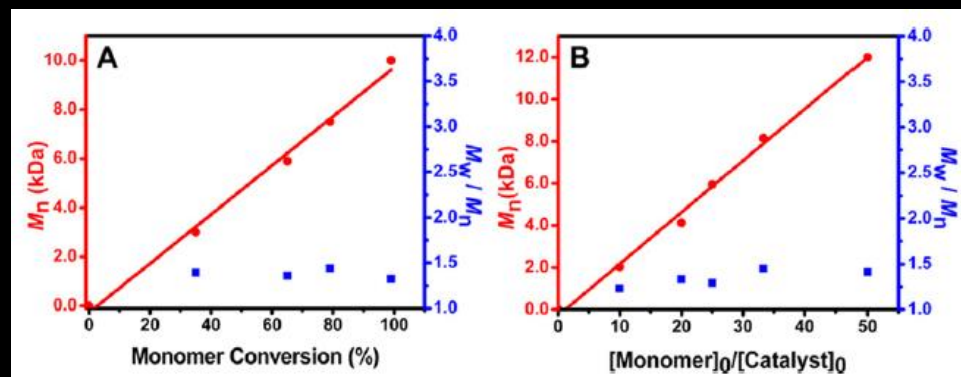
Bielawski, *JACS*, 2013 ,135, 4984

Why not Stille??

Scheme 1. Chain-Growth Synthesis of PPE^a



^aPd Catalyst = PhPd(*t*-Bu₃P)Br; ligand: see Table 1.



Chain-growth kinetics

Table 1. Syntheses of PPEs under Various Conditions^a

entry ^b	CuI (mol %)	ligand (mol %)	M_n^c (kDa)	\bar{D}^c (M_w/M_n)	yield (%) ^d
1	20	PPh ₃ (20)	10.8	1.28	58
2	20	PCy ₃ (20)	5.0	1.31	26
3	20	P(2-furyl) ₃ (20)	17.2	1.69	99
4	20	P(<i>t</i> -Bu) ₃	6.8	1.60	64
5	0	PPh ₃ (20)	7.6	1.54	63
6	20	none	5.6	1.47	30
7	20	PPh ₃ (20)	14.4	1.47	94
8	10	PPh ₃ (10)	11.0	1.34	88
9	10	PPh ₃ (15)	10.0	1.38	72
10	2	PPh ₃ (2)	3.6	1.43	37

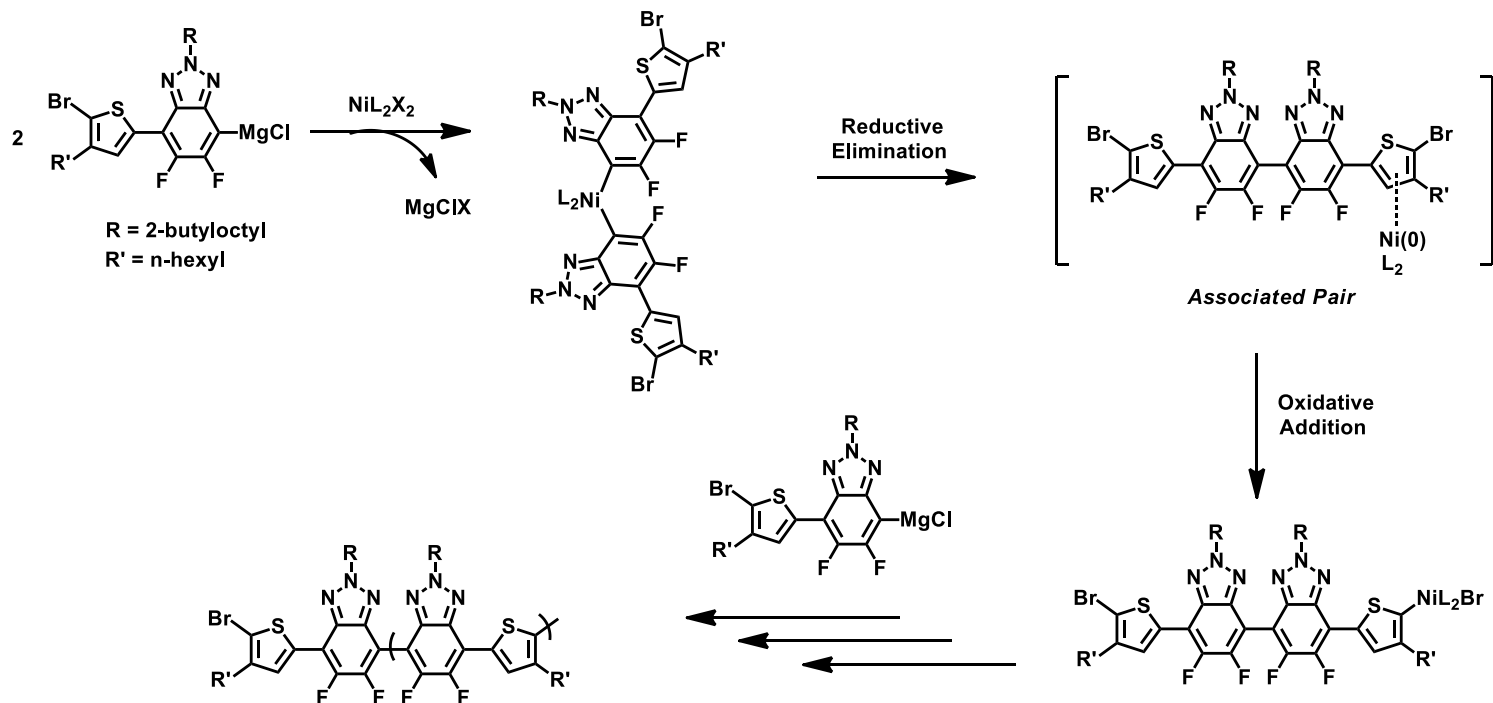
Initiation step is transmetallation step, which is RDS of C-C coupling.

k_i/k_p should be not high

DA-alternating copolymer

Coming soon,

Chain-growth polymerization kinetics



Electron-poor arene ring also have directing ability?

Conclusion

Now, Polymer Chemists are kind of responsible.

Keep your eyes on polymerizations

Scheme 2. Proposed Mechanistic Pathways Leading to the Formation of H/Br end-Capped PTPP

