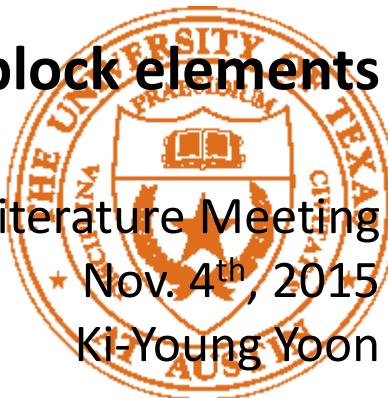


Polymers containing p-block elements

Guangbin Dong Group Literature Meeting

Nov. 4th, 2015

Ki-Young Yoon



Polymer Era

Relative Importance of the four classes of materials (Metal, Polymer, Composites, Ceramics)

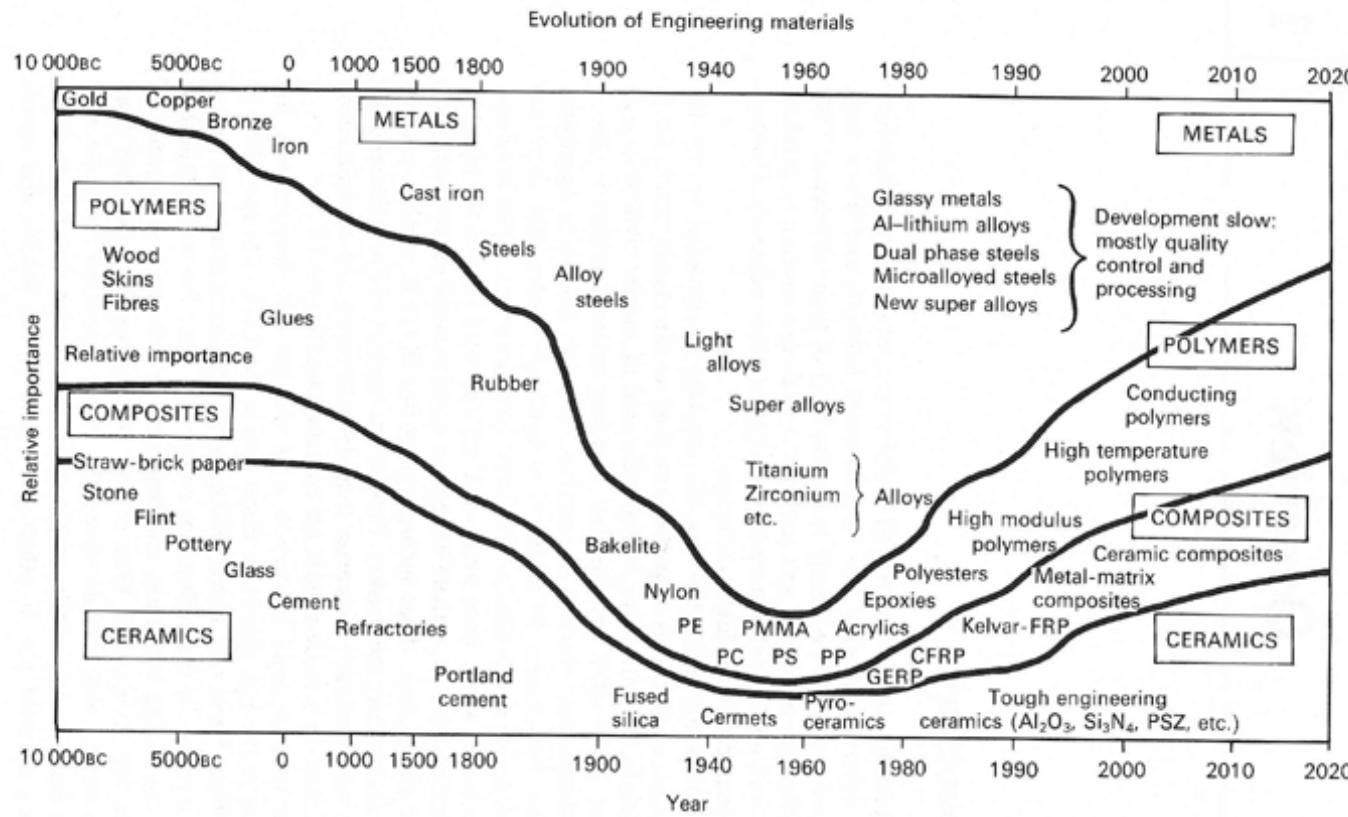
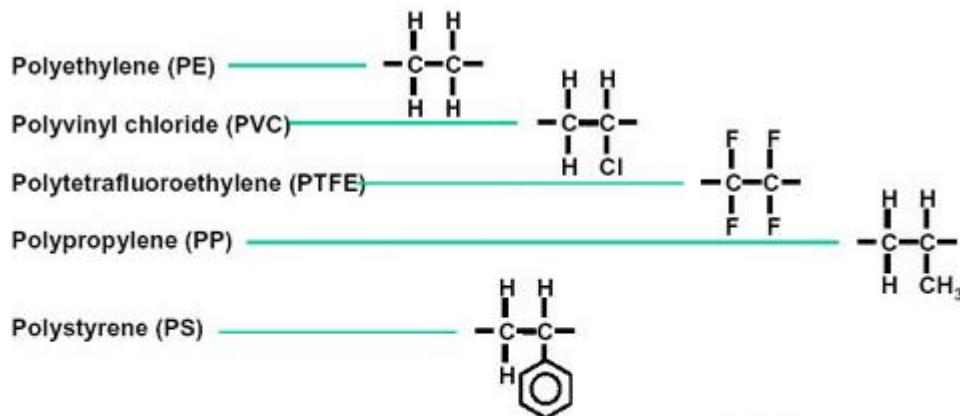


Figure 1.1 Schematic diagram showing the relative importance of the four classes of materials (ceramics, composites, polymers and metals) in mechanical and civil engineering as a function of time. The time scale is nonlinear. (Source: Ashby, 1987.)

Sudden ubiquity of polymeric materials since 20th century

Organic (C,N,O) polymers



Carbon-based polymer backbone
(C, N, O)

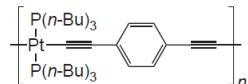
Polyester, Polyamide

Limited to incorporate various functions into polymeric materials

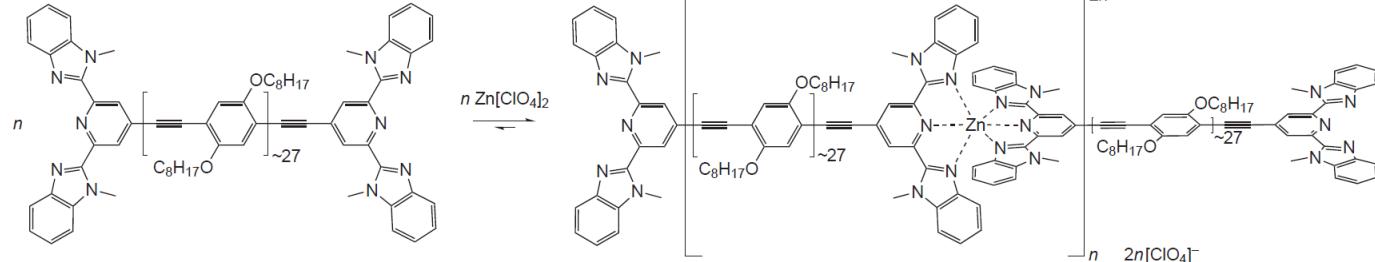
Metallopolymers

Polymer backbone containing metals (esp. transition metal)

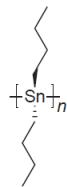
a Static binding



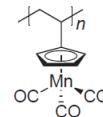
b Dynamic binding



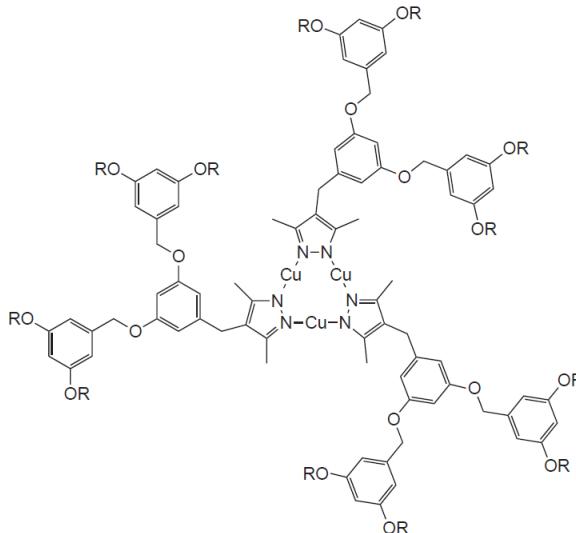
c Main chain



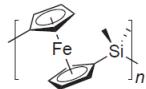
d Side chain



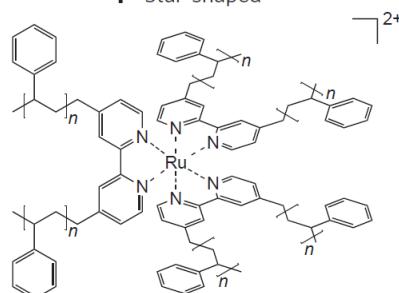
g Dendritic



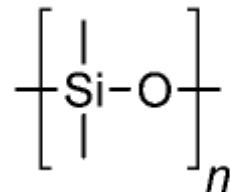
e Linear



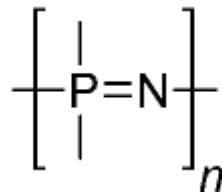
f Star-shaped



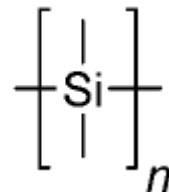
P-block Polymers



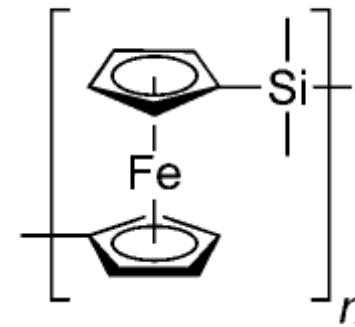
polysiloxane



polyphosphazene



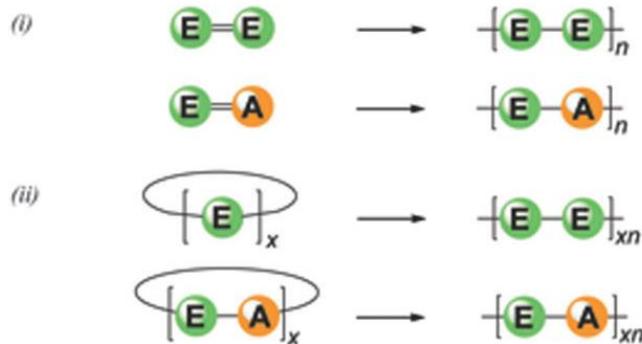
polysilane



poly(ferrocenylsilane)

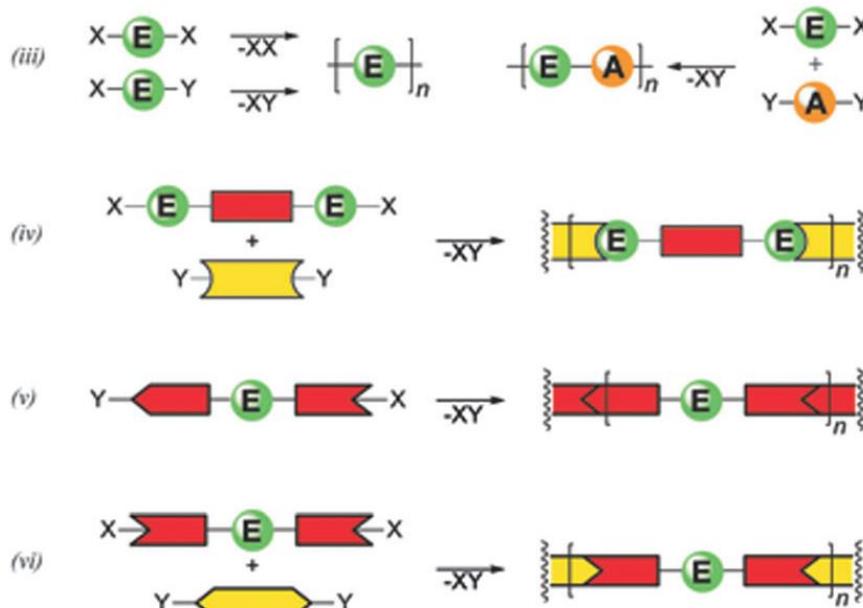
General Challenges

Chain Growth Methods



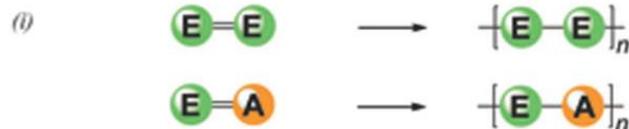
Conventional synthetic protocols to organic polymers
are difficult to use for inorganic polymer synthesis

Step Growth (Condensation) Methods



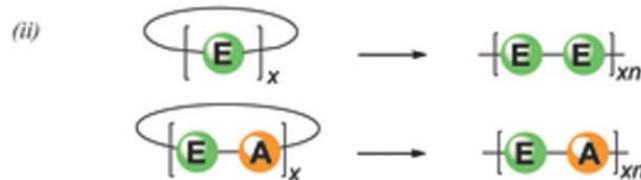
General Challenges

Chain Growth Methods



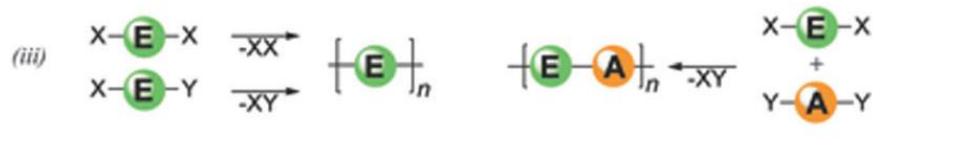
Key issue

Reactive but **stable** multiple bonds involving inorganic elements

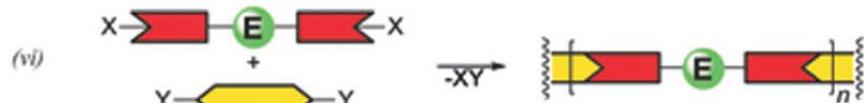
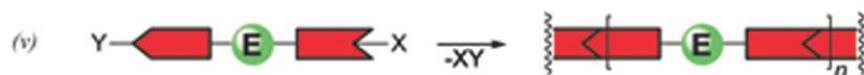
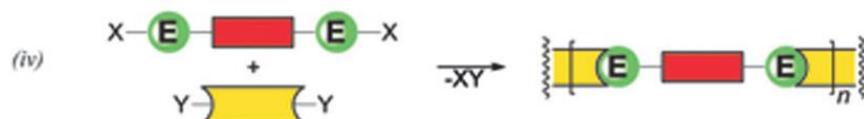


Suitably **strained** inorganic ring compounds

Step Growth (Condensation) Methods

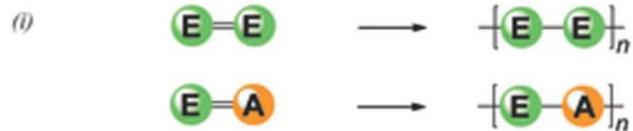


Highly **pure** monomer/stoichiometric imbalance



General Challenges

Chain Growth Methods



Key issue

Reactive but stable multiple bonds involving inorganic elements

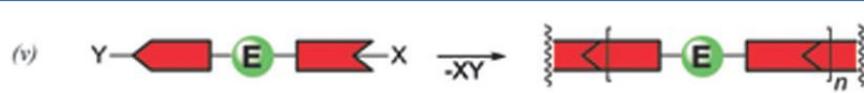
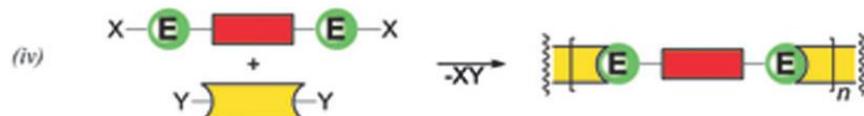


Suitably strained inorganic ring compounds

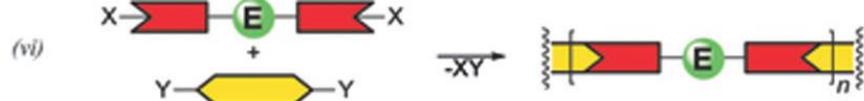
Step Growth (Condensation) Methods



Highly pure monomer/stoichiometric imbalance

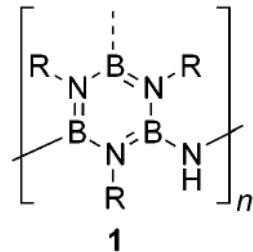


Organic spacer
-> conventional organic reaction

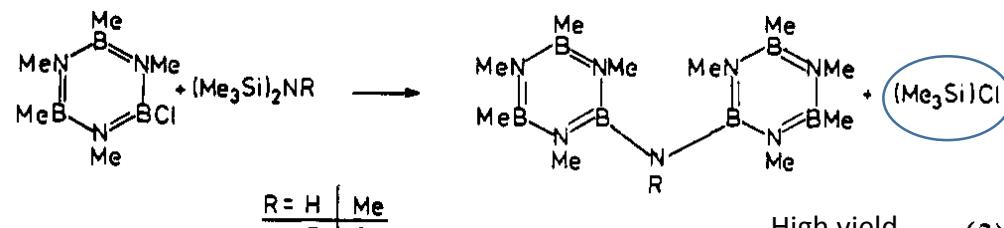
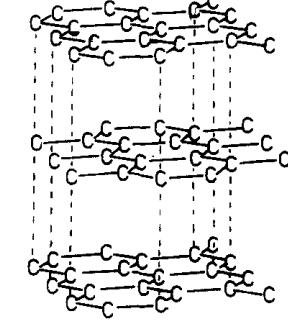
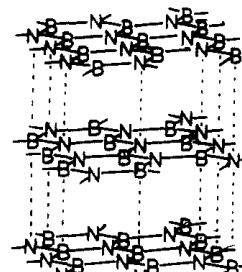


Group 13 : Boron

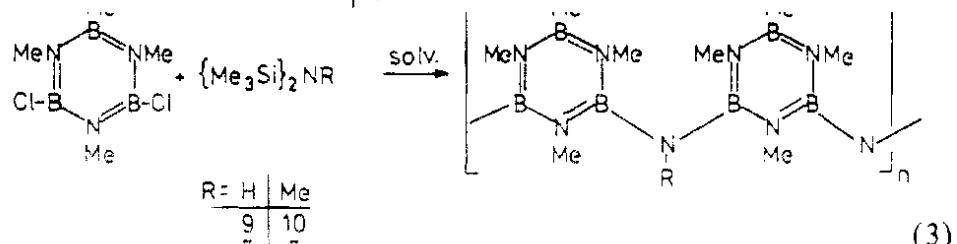
Poly(borazylene)s



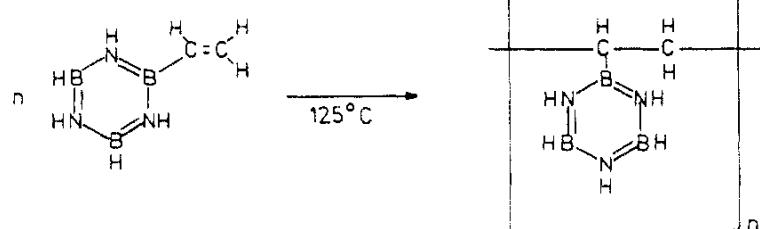
Precursors to Boron-Nitride ceramic ($[BN]_n$)



Stable and volatile Me_3SiCl



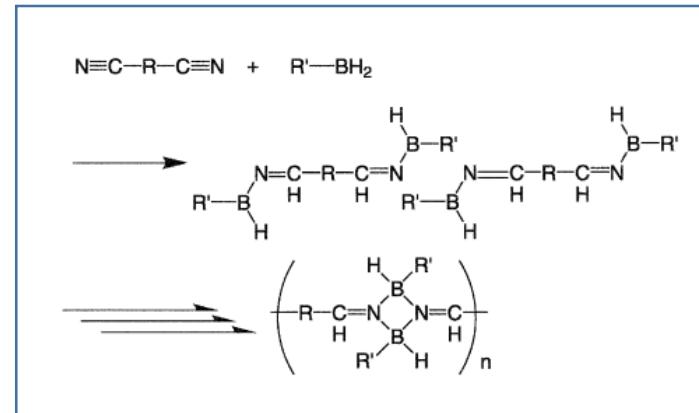
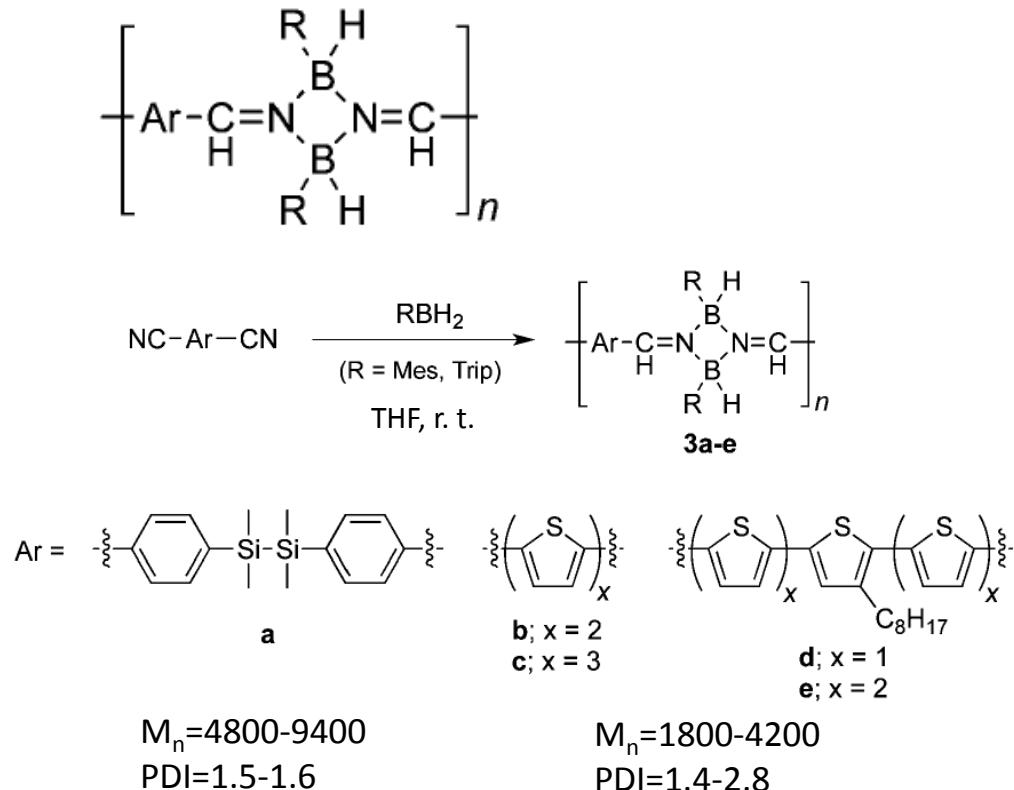
Oligomer or highly cross-linked polymer
(poor solubility, hard to characterize)



Increase solubility

Group 13 : Boron

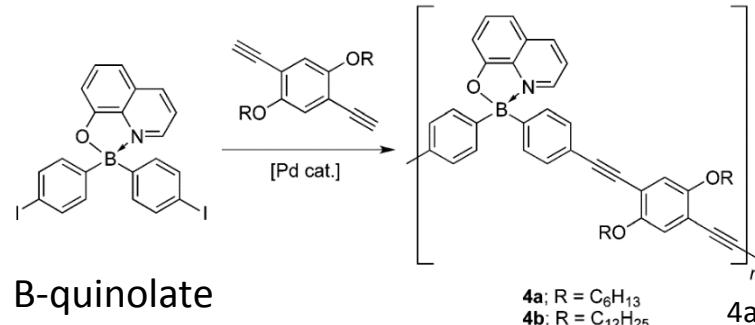
Poly(cycloborazane)s



Yellow fluorescence in both solution and solid state

Group 13 : Boron

Polymer containing organoboron heterocycles (B-quinolate)



Green-blue fluorescence material
Low quantum yield

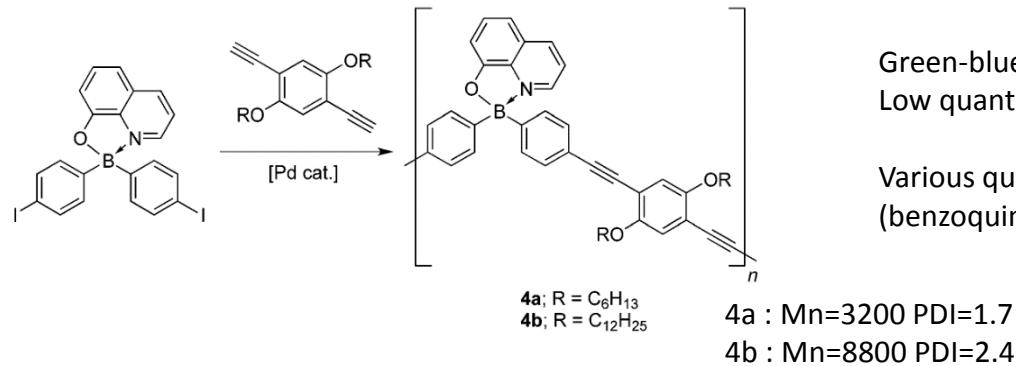
Various quinolates
(benzoquinolates, aminoquinolates, quinolone thiolates, etc.)

4a : Mn=3200 PDI=1.7
4b : Mn=8800 PDI=2.4

Macromolecules **2007**, *40*, 6

Group 13 : Boron

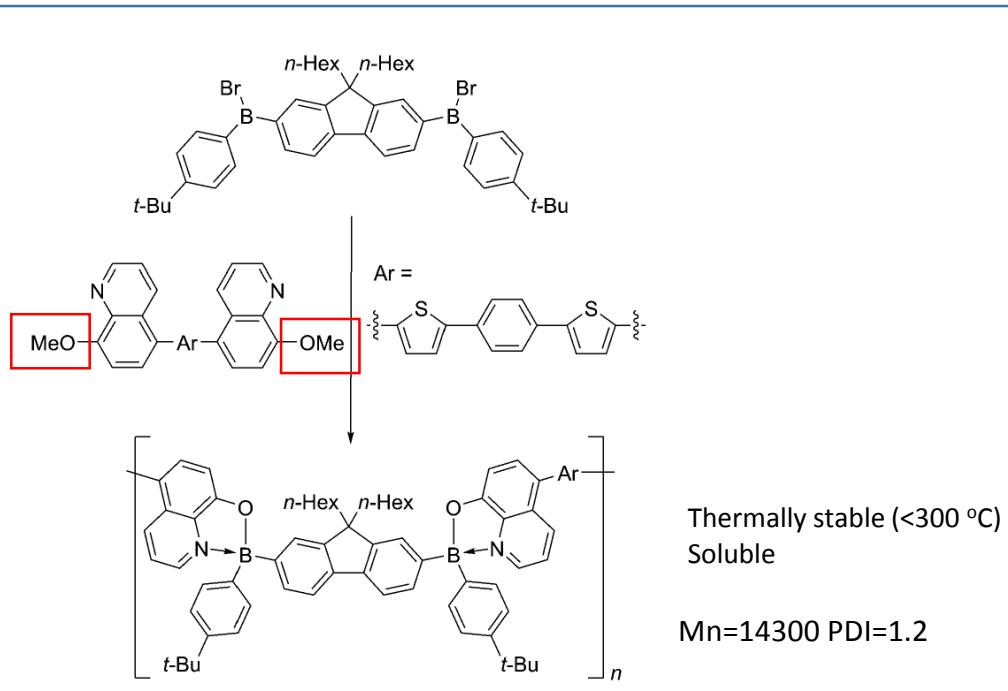
Polymer containing organoboron heterocycles (B-quinolate)



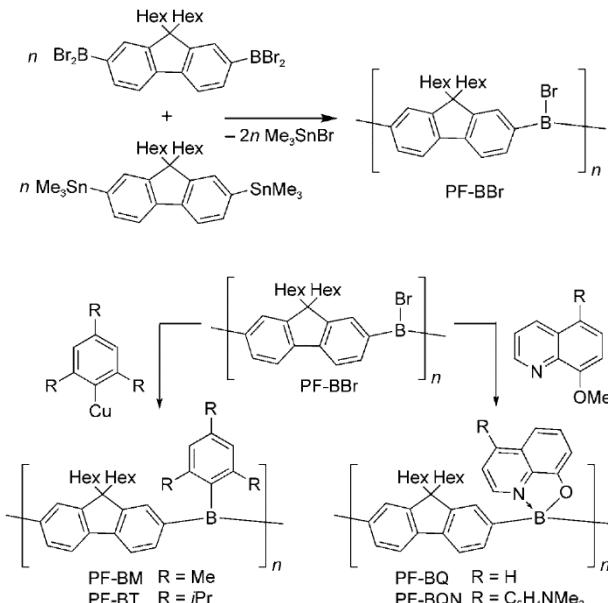
Green-blue fluorescence material
 Low quantum yield

Various quinolates
 (benzoquinolates, aminoquinolates, quinolone thiolates, etc.)

Macromolecules 2007, 40, 6



Macromolecules 2009, 42, 3448

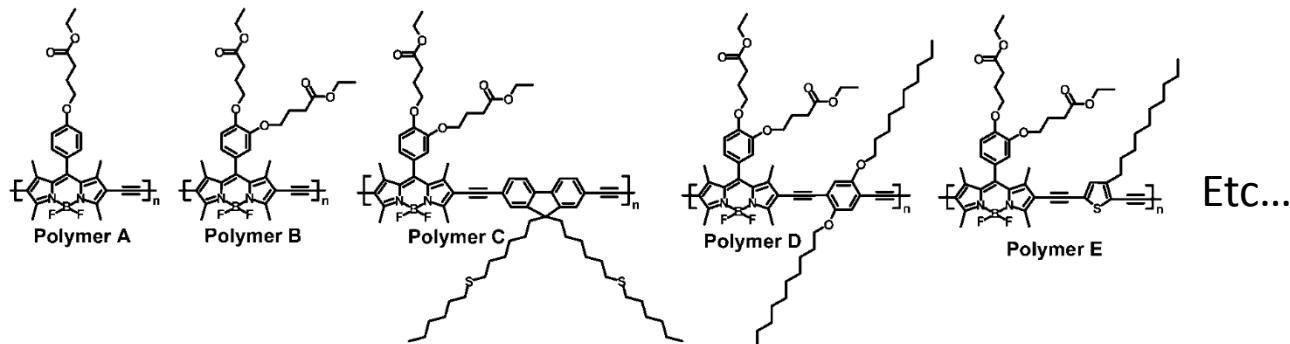
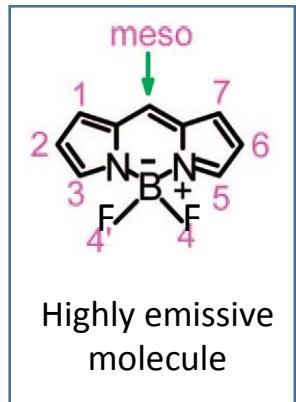


Post-functionalization

Angew. Chem., Int. Ed., 2009, **48**, 2313

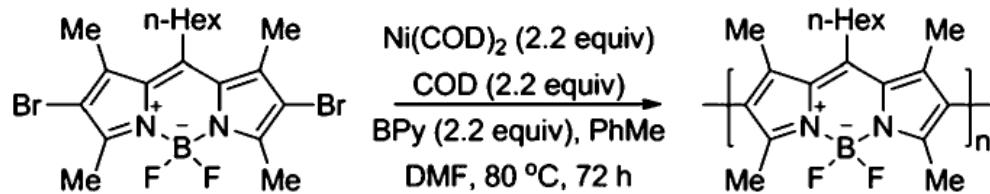
Group 13 : Boron

Polymer containing organoboron heterocycles (BODIPY)



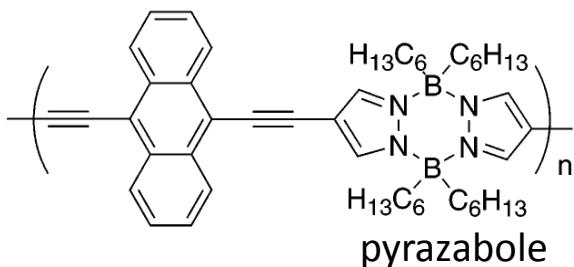
Various AB-alternating copolymer (-ABABABABABAB-)
by Sonogashira, Suzuki, Stille coupling polymerization

D. P. Gates, *Chem. Soc. Rev.* **2015**, ASAP.



BODIPY homopolymer
Mn=2630, PDI=1.59

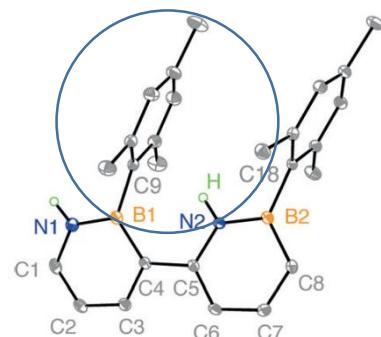
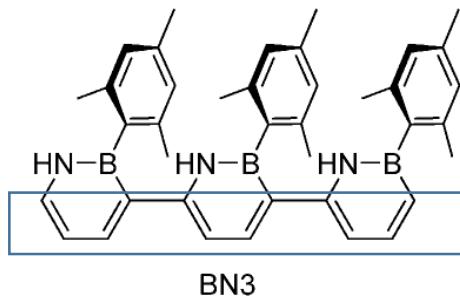
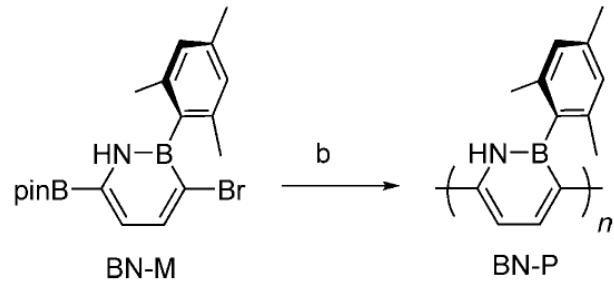
RSC Adv., 2013, **3**, 10221



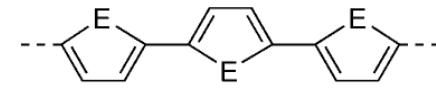
Various AB-alternating copolymer (-ABABABABABAB-)
by Sonogashira, Suzuki, Stille coupling polymerization

Group 13 : Boron

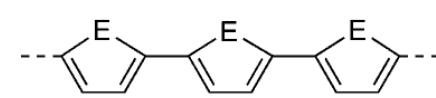
Polymer containing organoboron heterocycles (Azaborine)



NH-pi interaction



anti



syn

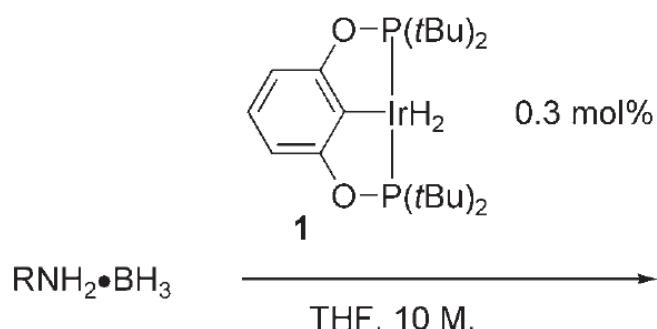
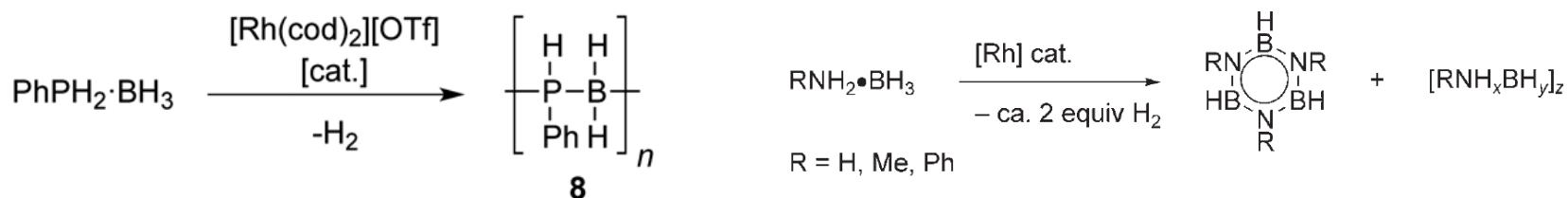


trans-cisoid PA

Group 13 : Boron

Dehydrocoupling polymerization (Amine-Borane)

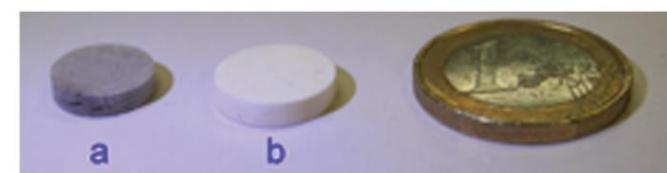
Aminoboranes : potential hydrogen storage materials



R = H, Me, nBu 0 °C to 20 °C, 20 min

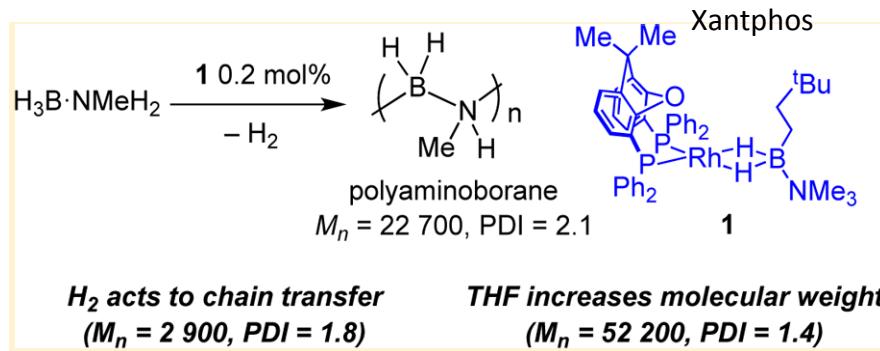
2 a-g
Mn=55200, PDI=2.9

Polyethylene/polypropylene
Analogue
Boron-Nitride ceramic precursor

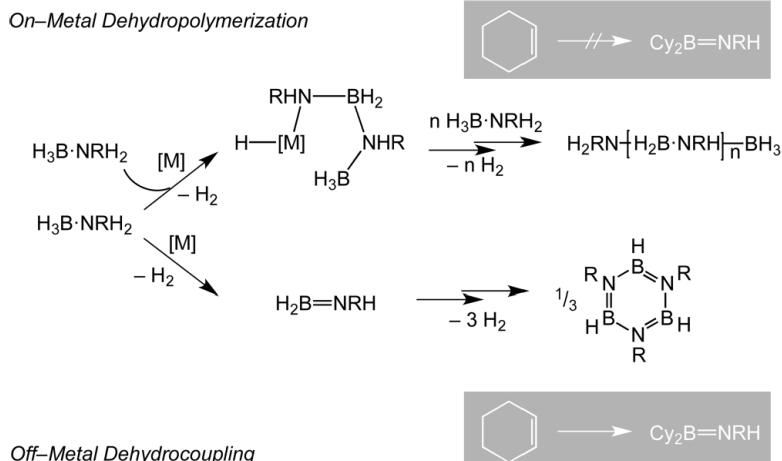


After pyrolysis at 900 °C

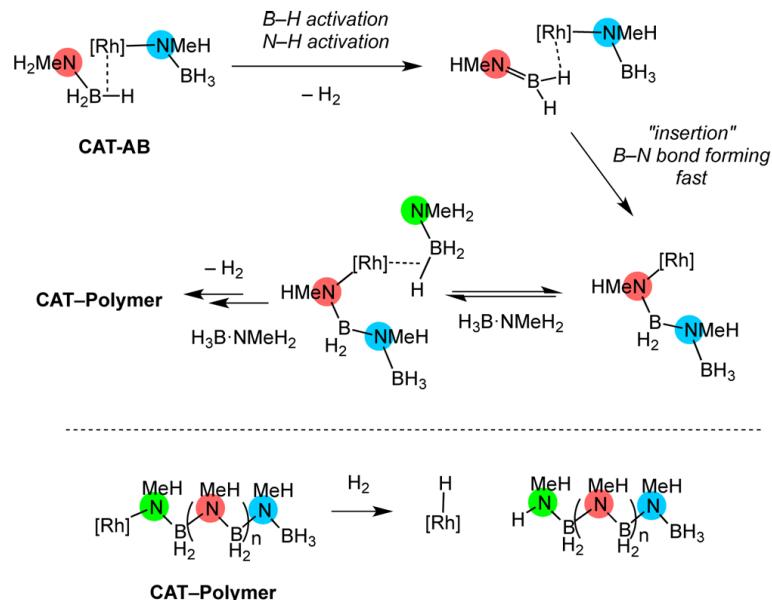
Group 13 : Boron



Scheme 2. Suggested Pathways for Dehydropolymerization, Dehydrogenation, and Hydroboration^a



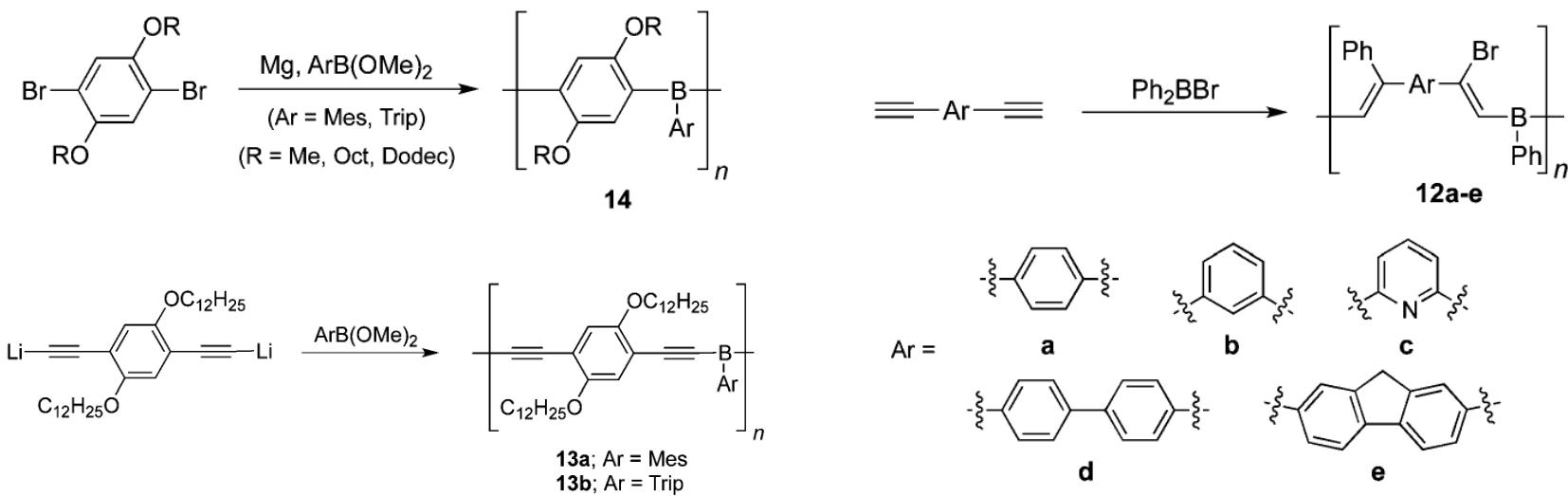
Scheme 19. Postulated Pathway, Based upon the Suggested Intermediates, for the B–N Coupling Event in H₃B·NMeH₂ Dehydropolymerization^a



$$^a[\text{Rh}] = [\text{Rh}(\text{Xantphos})(\text{H})]^+$$

Group 13 : Boron

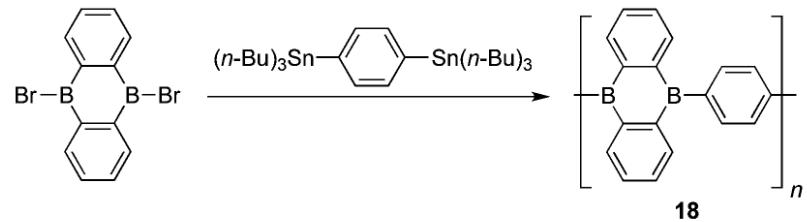
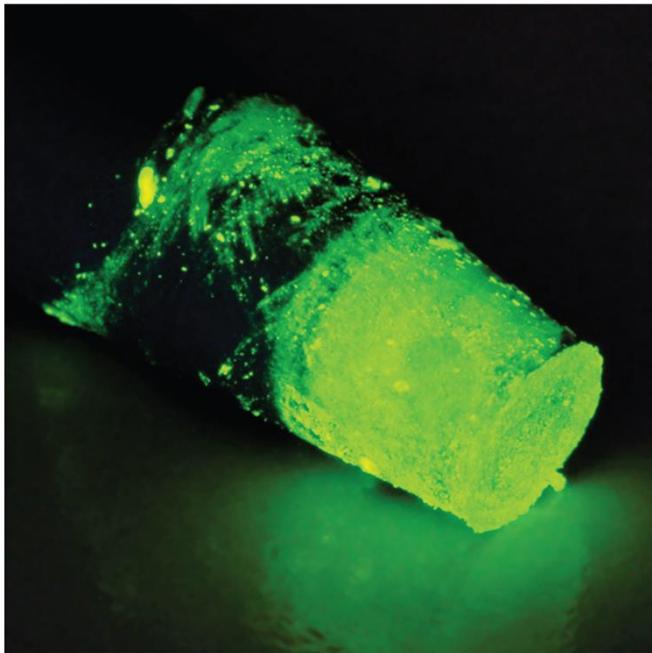
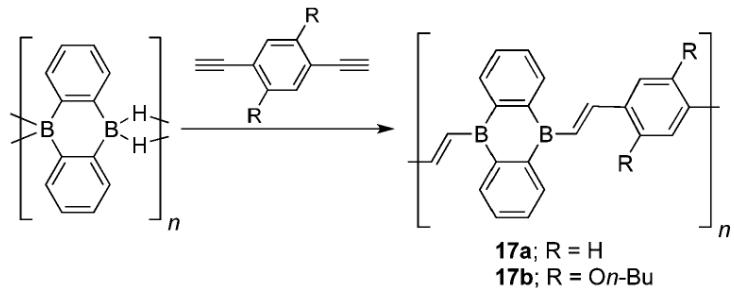
Poly(arylene/vinylene/ethynylene boranes)



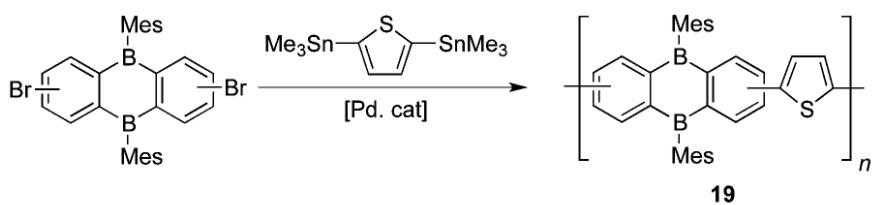
Low MW
bulky substituents needed for air/moisture stability

Group 13 : Boron

Poly(diboraanthracene)s



Air-sensitive

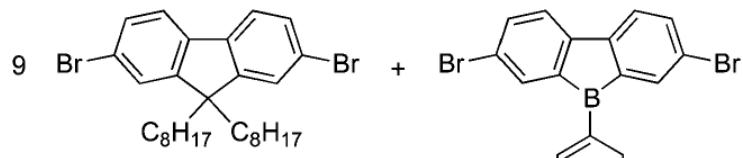


Air-stable

Group 13 : Boron

Borole-containing polymers

Promising ion sensor



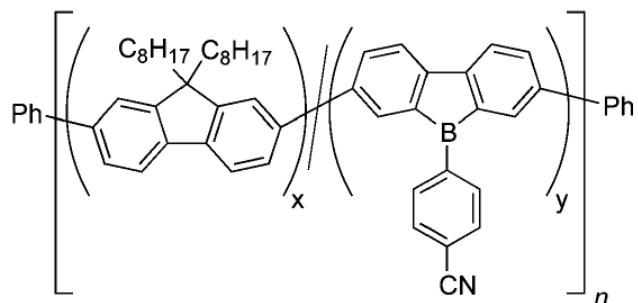
1) $\text{Ni}(\text{cod})_2$
2) PhBr

F^- , CN^-

Luminescence quenching

Br^- , Cl^- ,

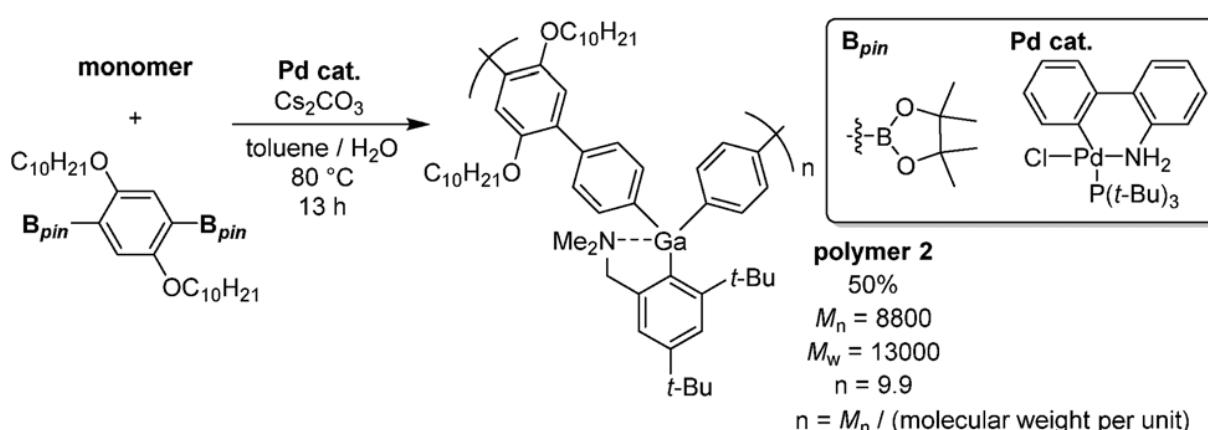
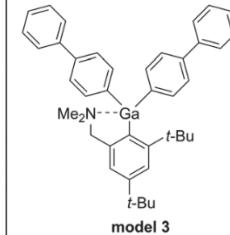
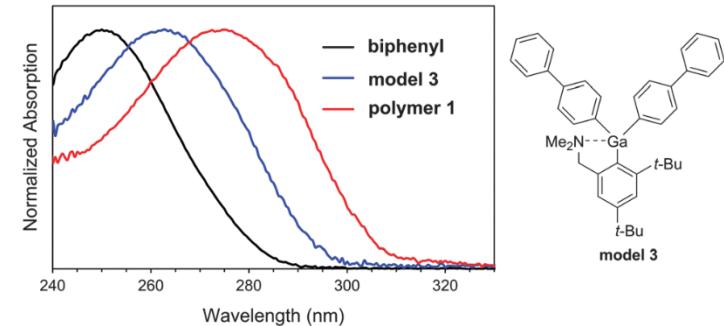
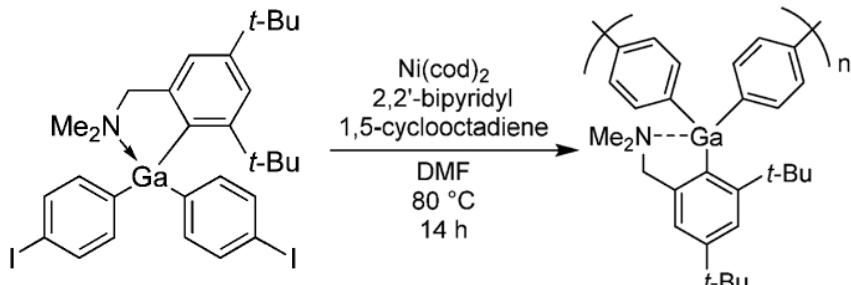
No effect



$\text{Mn}=22900$, $\text{PDI}=1.78$

Group 13 : Gallium

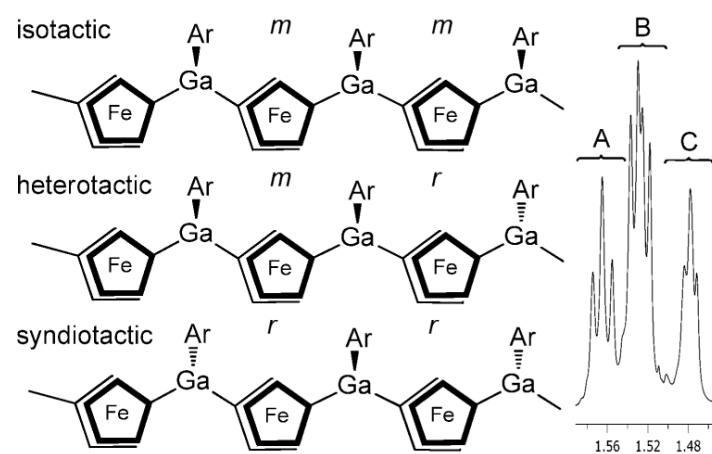
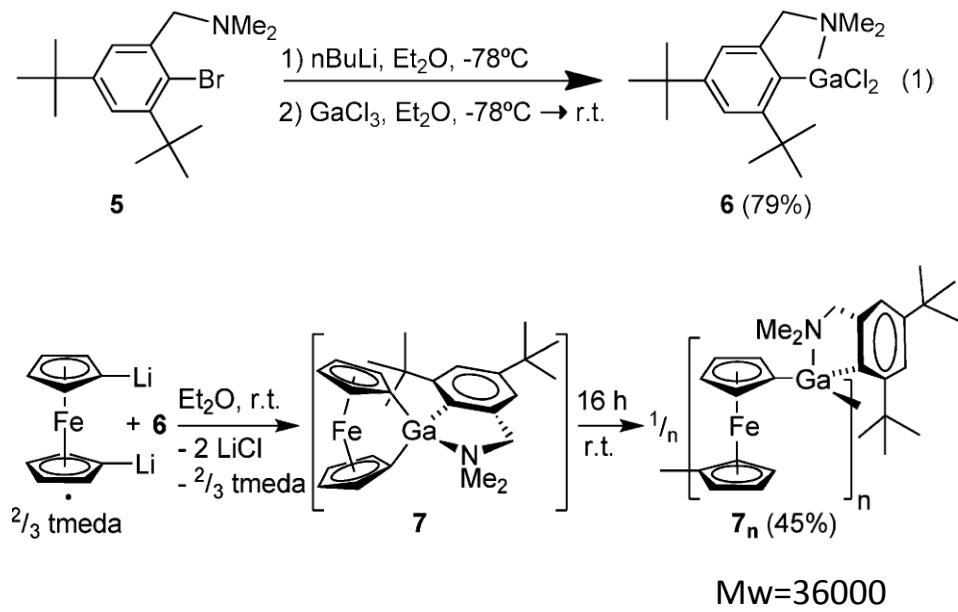
Heavier group 13 elements : inherent moisture/air instability



Weak, but still conjugation exists

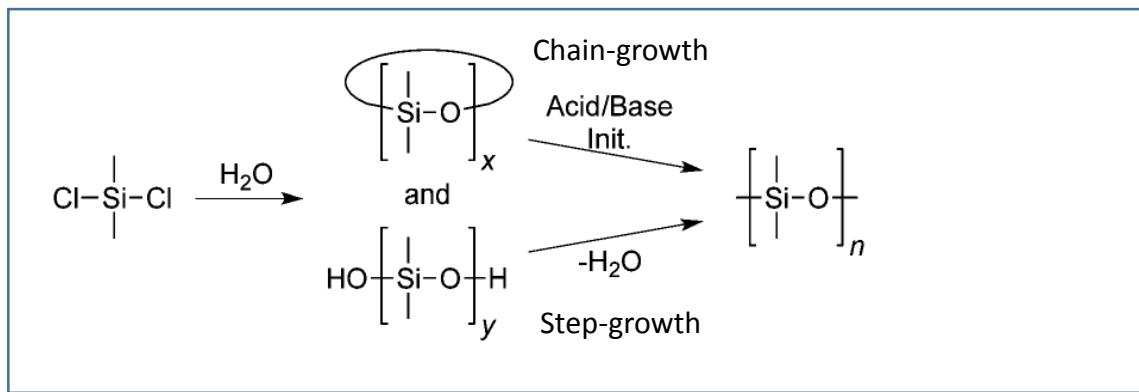
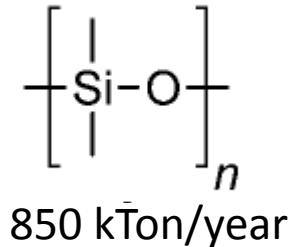
Group 13 : Gallium

Ring opening polymerization of Gallaferrocenophane

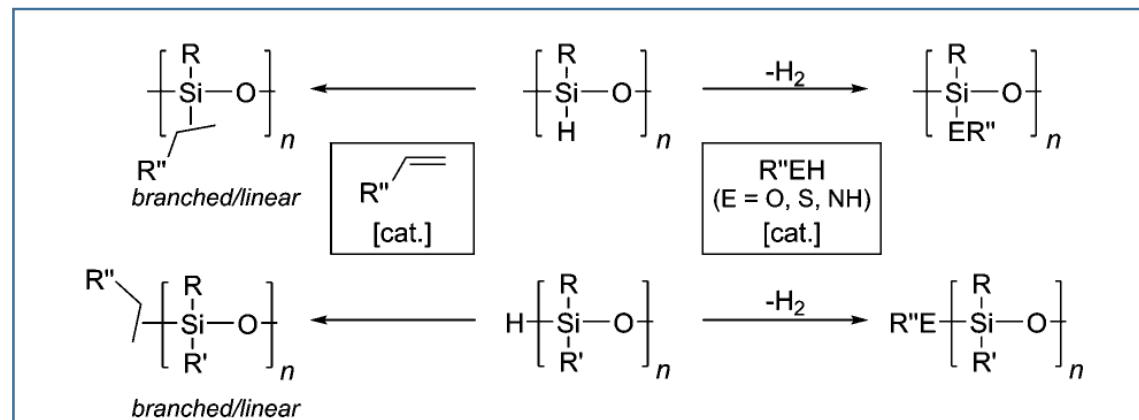


Group 14 : Silicon

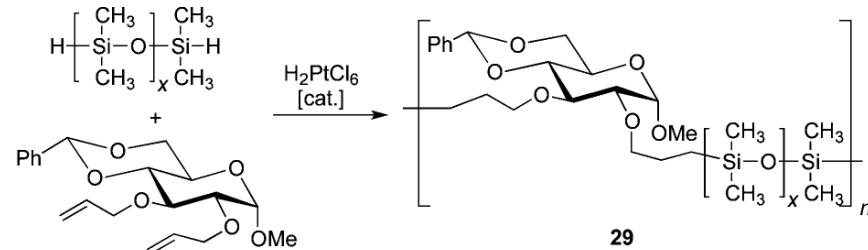
Polysiloxanes



Post-functionalizing by
Hydrosilylation



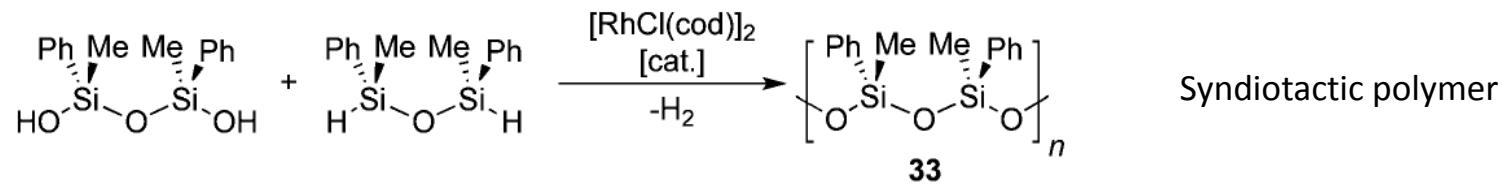
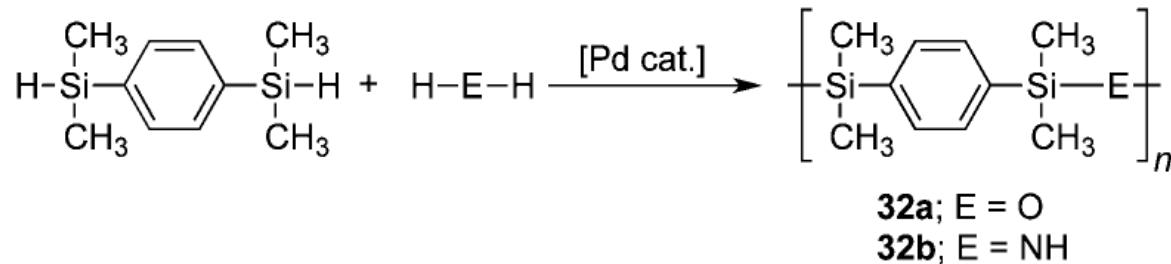
example



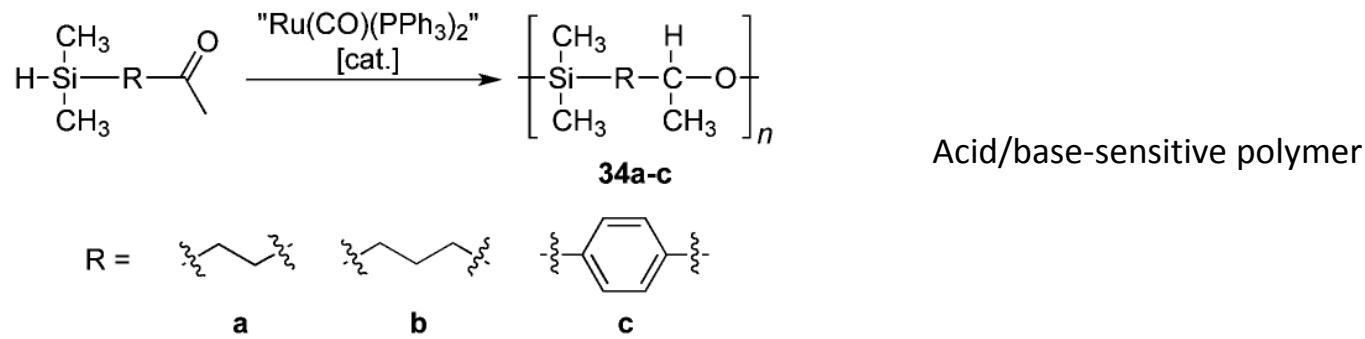
Group 14 : Silicon

Polysiloxanes by metal-catalyzed reaction

dehydrocoupling

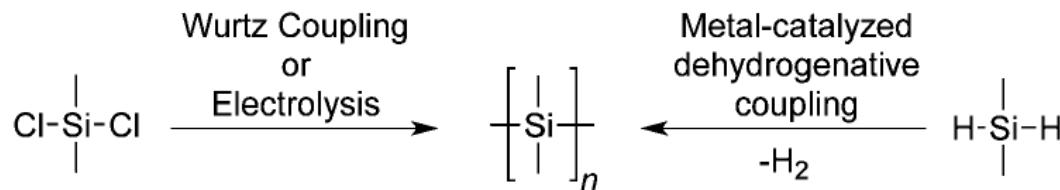


hydrosilylation



Group 14 : Silicon

Polysilanes



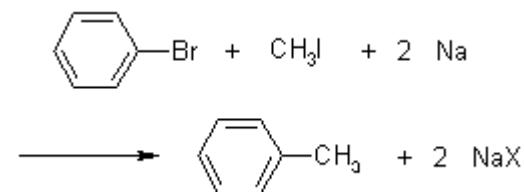
Scheme 25 General synthetic methodologies to polysilanes.

Wurtz Coupling : incompatible with functional substituents
polymodal MW distribution

Electrolysis : Low/medium MW

M-cat : Low/medium MW

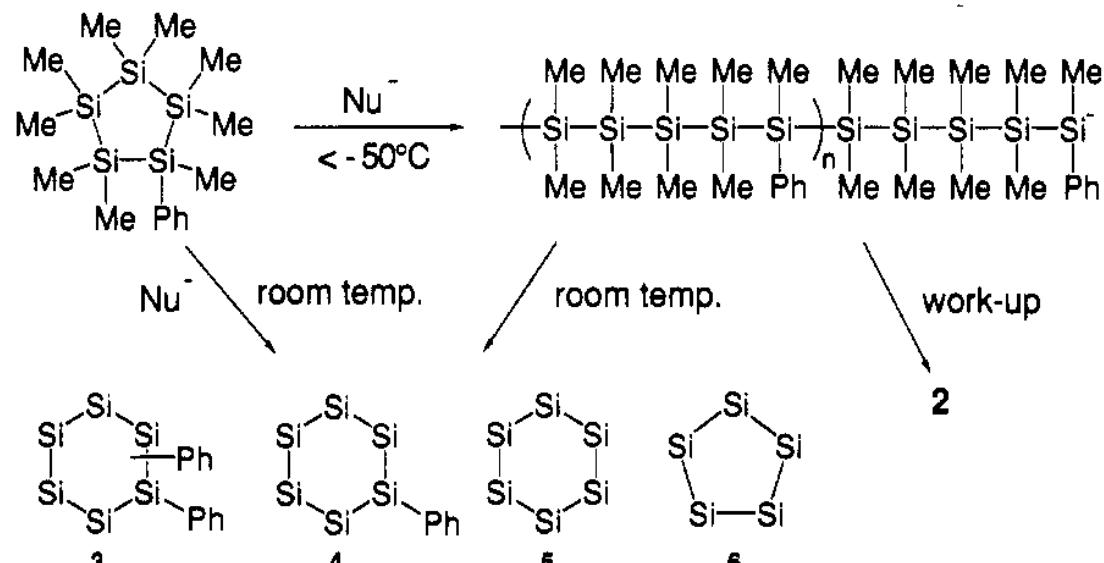
Wurtz coupling



Group 14 : Silicon

Polysilanes (Ring opening polymerization)

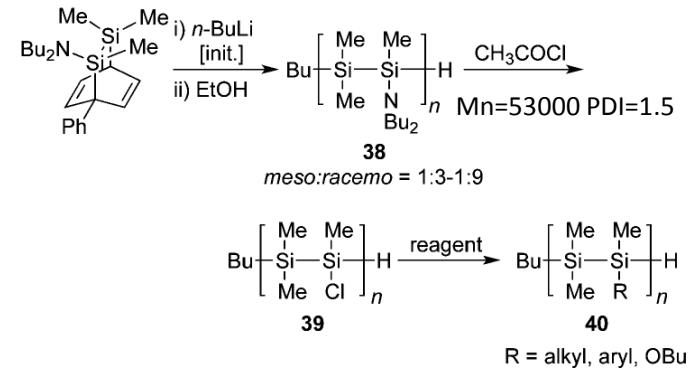
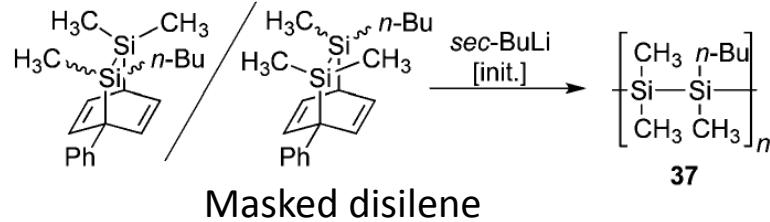
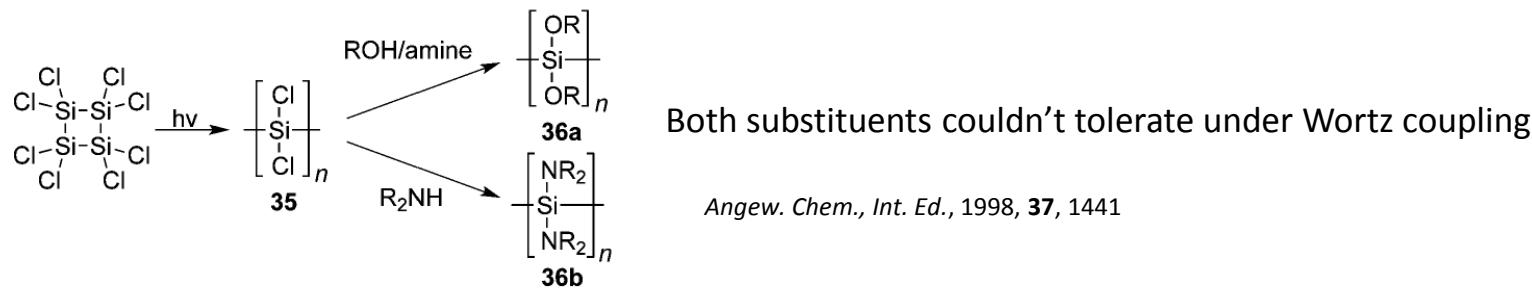
Making suitable cyclic monomers is challenging



run	initiator (mol %)	solvent	additive ^a	temp, °C	time, h	yield, ^b %	M_n^c	M_w/M_n^c
1	Bu ₄ NF (2)	THF	none	-20	1.5	17	3100	1.67
2	Bu ₄ NF (2)	THF	none	-78	24	82	8000 (6900) ^d	1.76
3	Bu ₄ NF (2)	DME	none	-50	3	74	7000	1.76
4	Me ₃ SiK (2)	THF	HMPA	-20	1	3	3900	1.62
5	Me ₃ SiK (2)	THF	HMPA	-50	2	68	17000	1.26
6	Me ₃ SiK (2)	DME	HMPA	-50	5	35	2000	1.26
7	Me ₂ PhSiK (2)	THF	none	-78	27	0		
8	Me ₂ PhSiK (2)	THF	HMPA	-78	17	81	58000	1.78
9	Me ₂ PhSiK (20)	THF	HMPA	-78	6	79	25000	1.69
10 ^e	Me ₂ PhSiK (10)	THF	18-crown-6	-78	1	83	7400 (4700) ^d	1.28
11 ^f	Me ₂ PhSiK (5)	THF	18-crown-6	-78	2 + 5	80	26000 (10900) ^d	1.48

Group 14 : Silicon

Polysilanes (Ring opening polymerization)

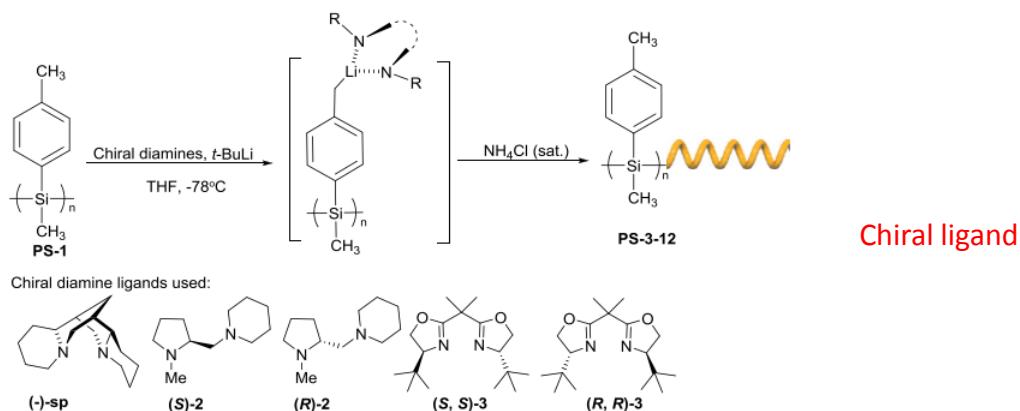
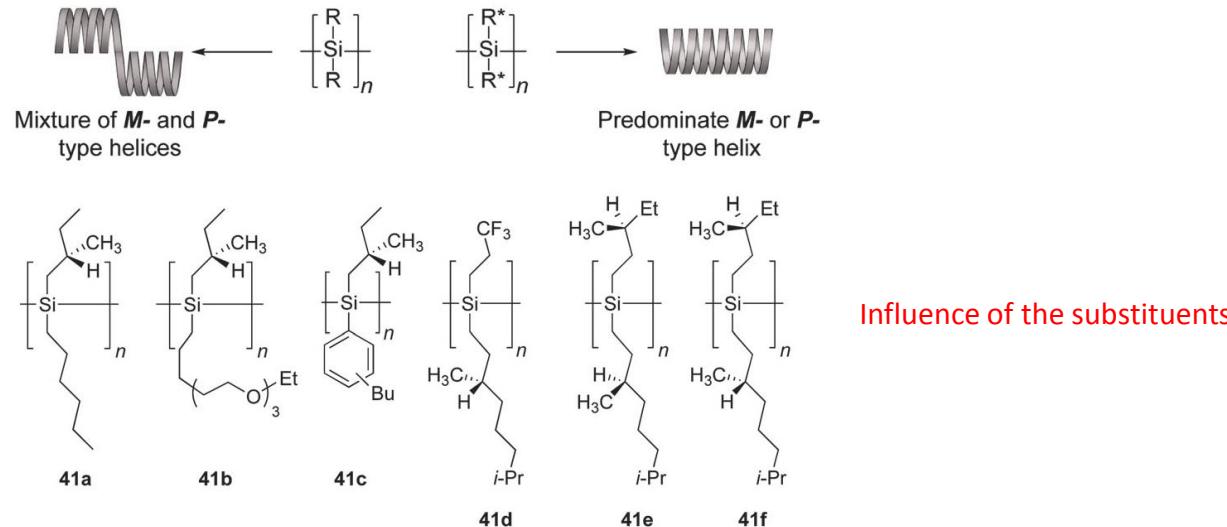


J. Am. Chem. Soc., 1989, **111**, 7641

All about substituent variation

Group 14 : Silicon

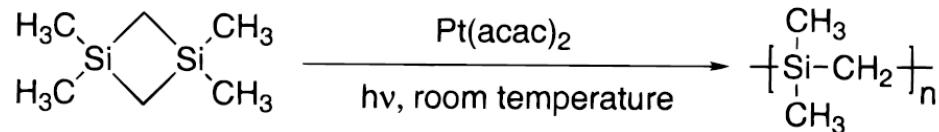
Secondary structure



Group 14 : Silicon

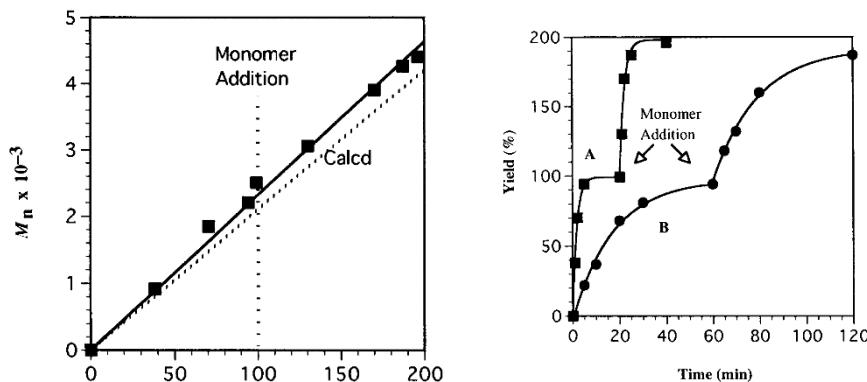
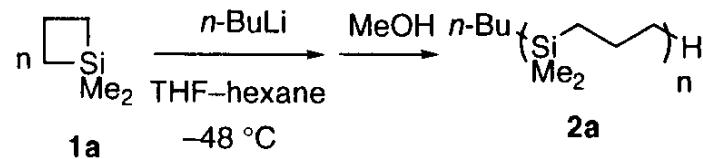
Polycarbosilanes (Ring opening polymerization)

Scheme 1



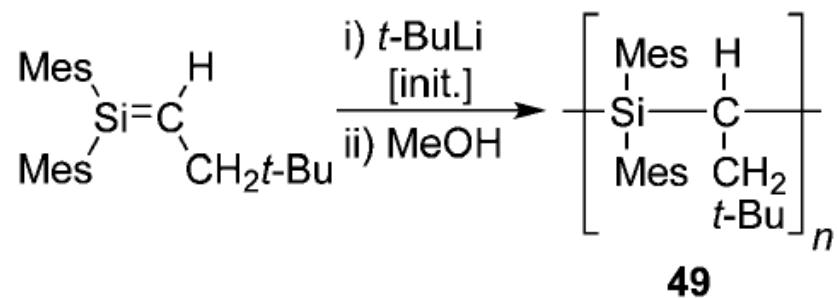
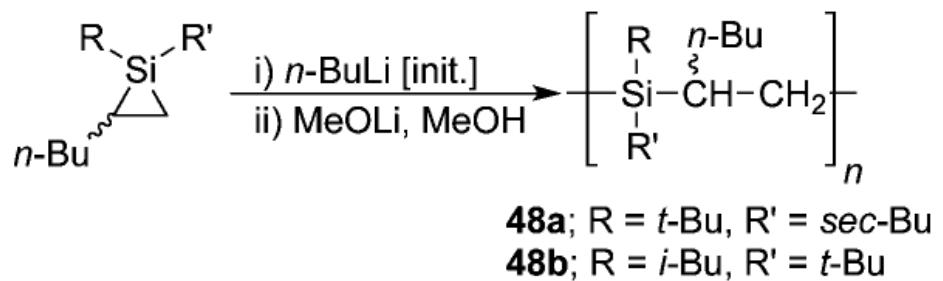
Macromolecules, 1999, **32**, 6003

Controlled/living polymerization

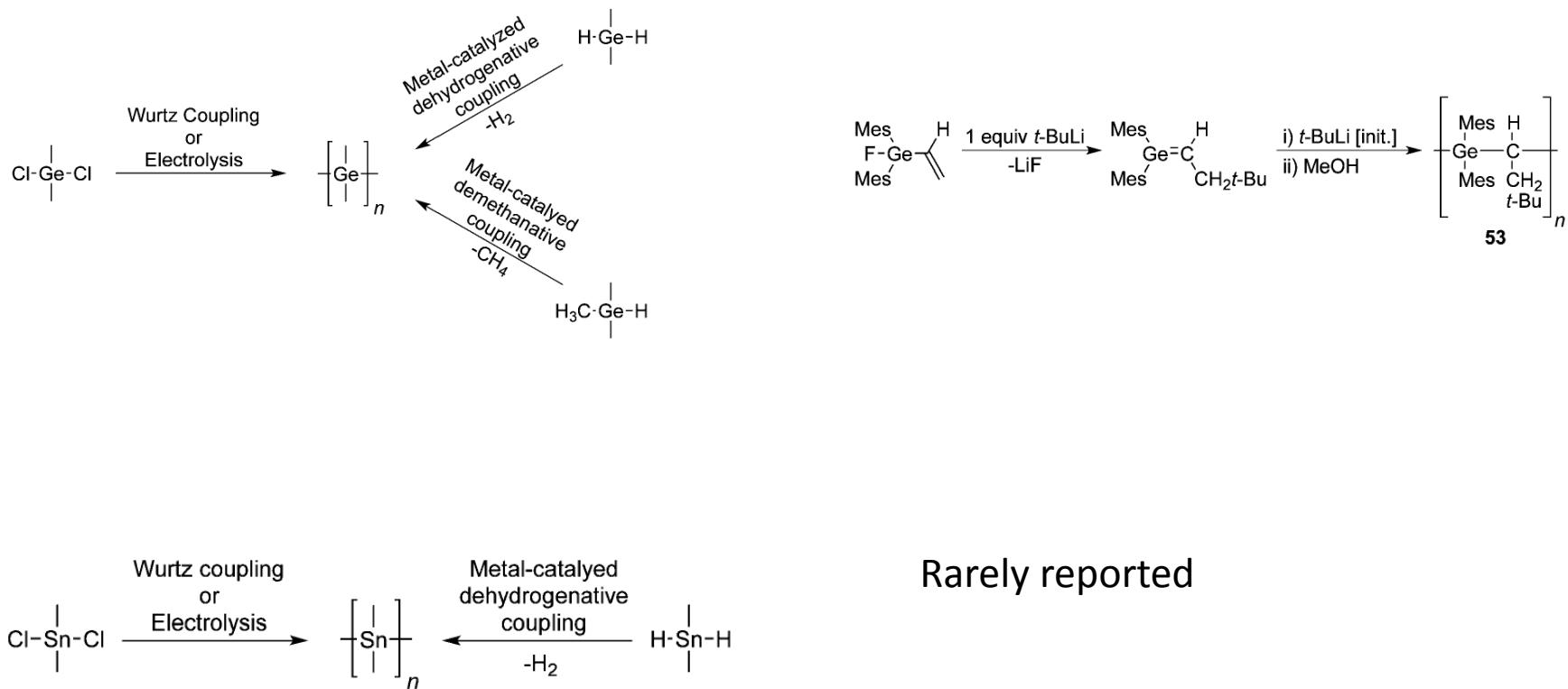


J. Polym. Sci., Part A: Polym. Chem., 1997, **35**, 3207

Group 14 : Silicon

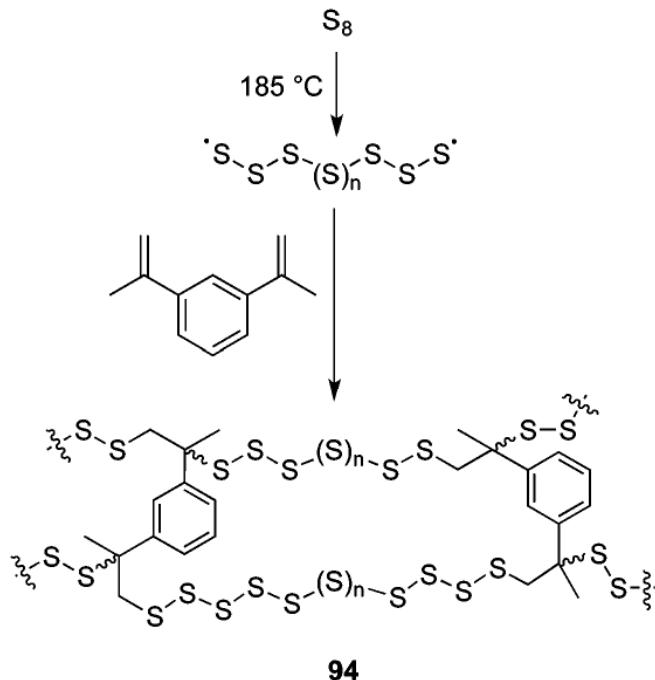
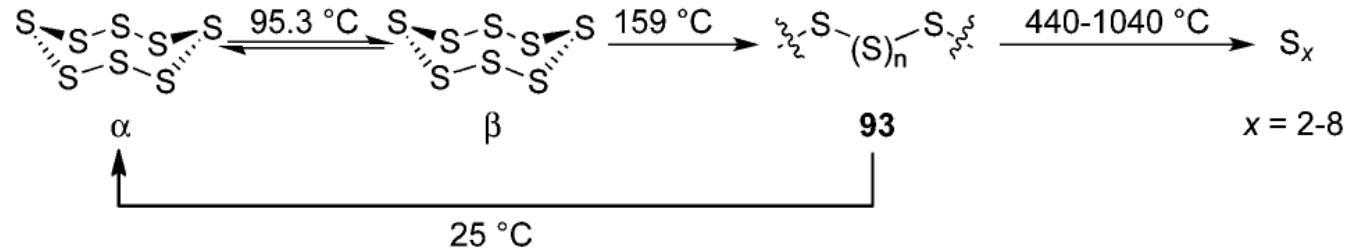


Group 14 : Germanium and Tin

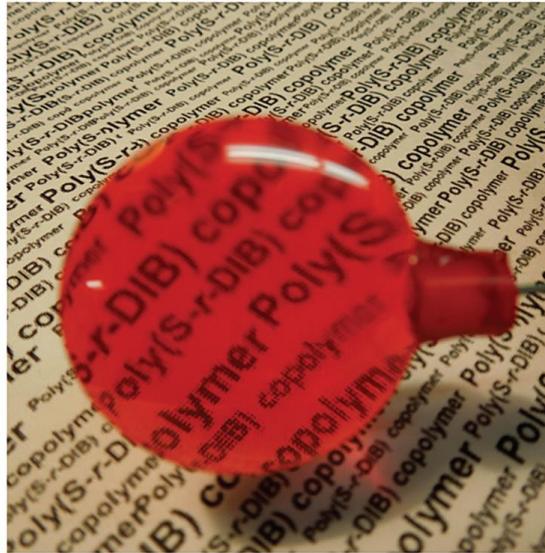


Group 16 : Sulfur

Polysulfur

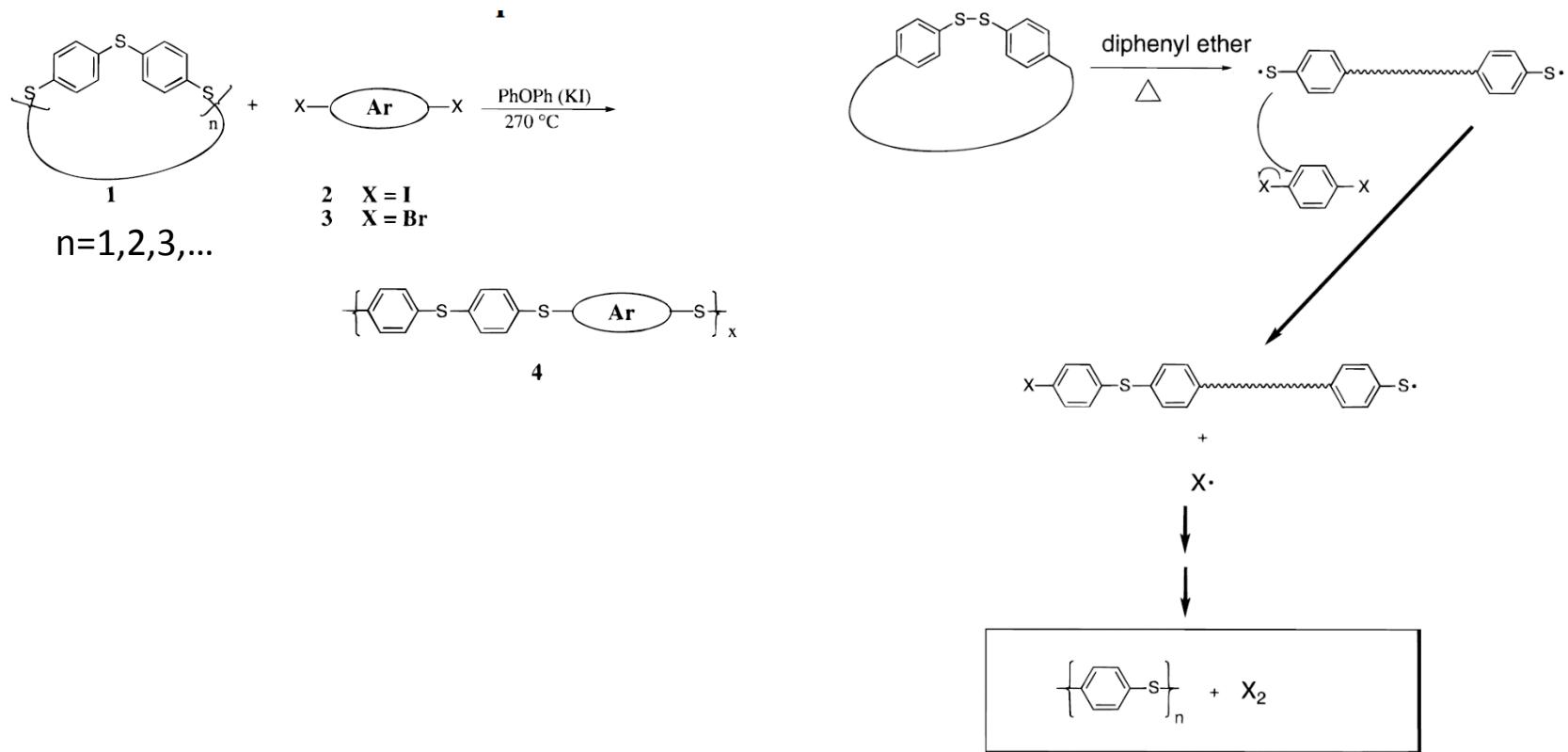


Inverse-vulcanization



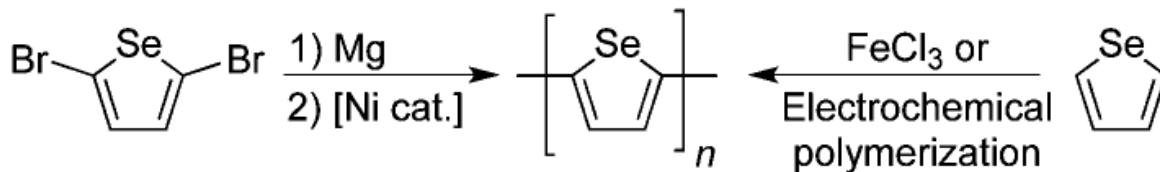
Group 16 : Sulfur

Poly(arylene sulfide)

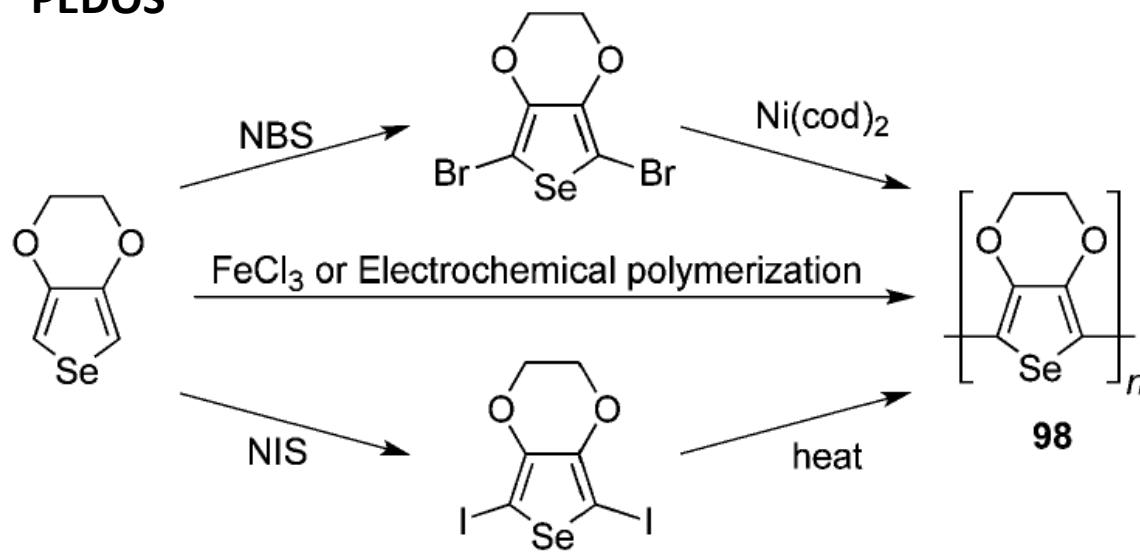


Group 16 : Sulfur/Selenium

Poly(selenophene)s

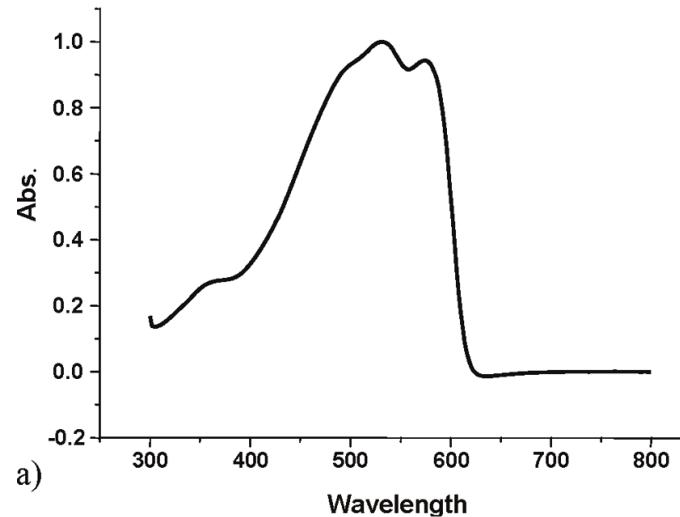
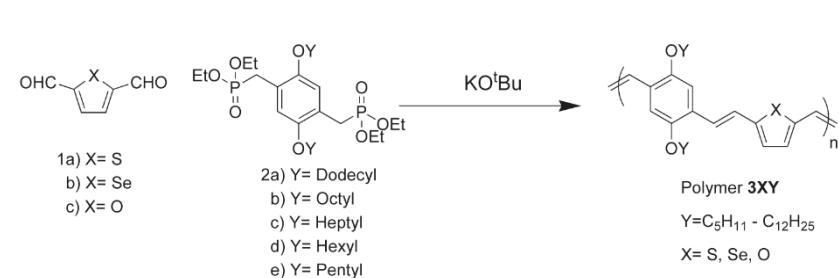
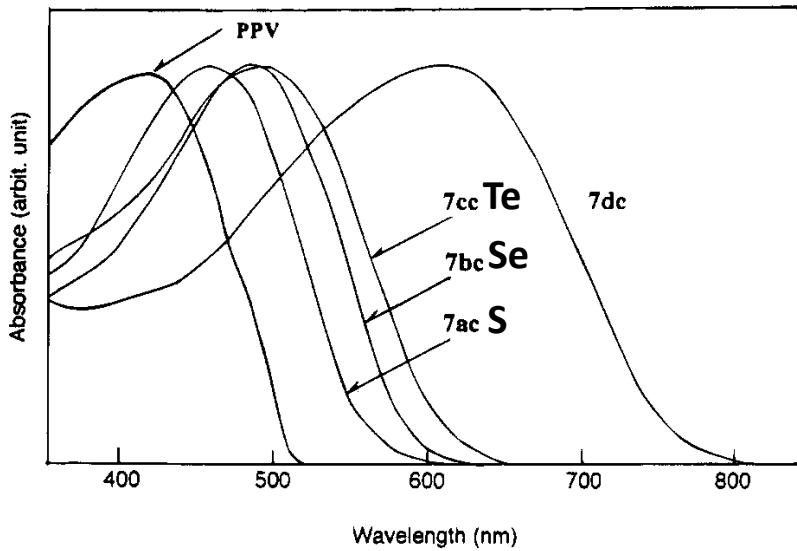
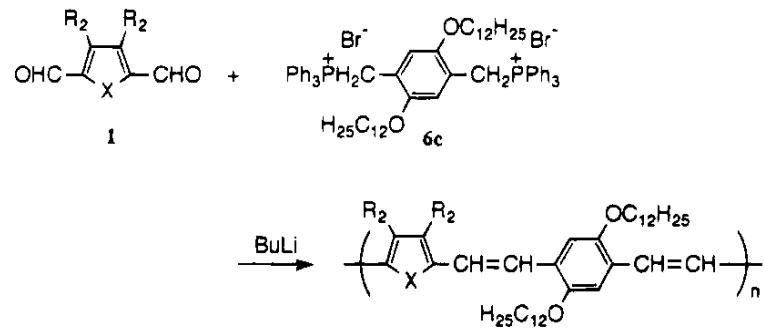


PEDOS



Group 16 : Sulfur/Selenium

Poly(selenophenylene vinylene)s



Thank you



Dong Group 2014.11