Ni or Pd Catalyst for Synthesis of Conjugated Polymers

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Wednesday Literature Talk
4/22/2015

Content

- **Organometallic Polycondensation for Conjugated Polymers(Yamamoto polymerization)**
- **Kumada–Tamao Coupling Polymerization with Ni(II) Catalyst**
- **Suzuki–Miyaura Coupling Polymerization with Pd Catalyst**

Conjugated Polymers

•**Conjugated polymers are organic macromolecules which consist at least of one backbone chain of alternating double- and single-bonds such as polyphenylvinylene (PPV) and polythiophenes (PT). .**

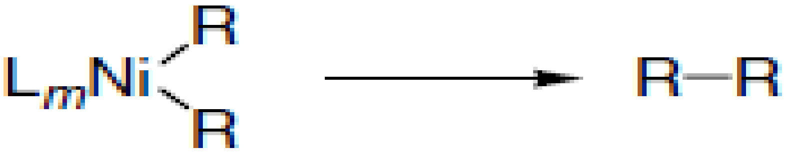
- **Applications**: p-Conjugated polymers containing aromatic rings in the backbone have potential applications as organic electronic materials and devices such as field effect transistors (FETs), organic light-emitting diodes (OLEDs), and photovoltaic cells. .

- **Synthetic methods**: condensation polymerization methods, such as electrochemical polymerization and metalmediated polycondensation reactions. .

C-C bond formation on Ni and Pd

Basic Organometallic reaction of Ni

- Diorganonickel(II) complexes NiR_2L_m undergo reductive coupling (or reductive elimination) reactions to give R–R.



(L = neutral ligand such as 2,2′-bipyridyl (bpy) and tertiary phosphine):

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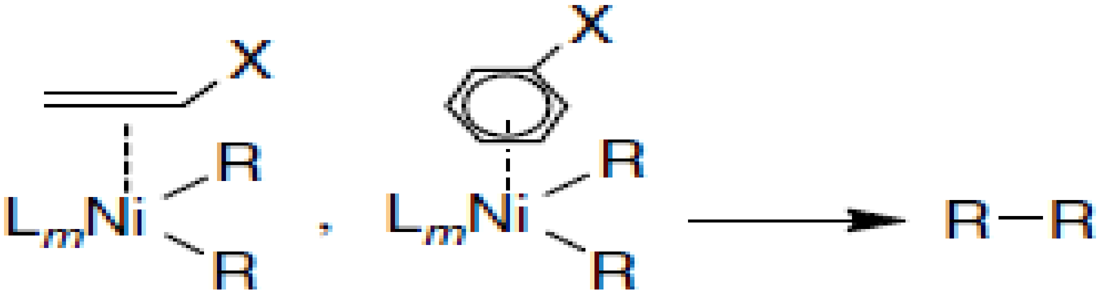
Organometallic Polycondensation for Conjugated Polymers

- The Ni–R bond in NiR2Lm is considered to be polarized as $Ni^{\delta+}$-$R^{\delta-}$, whereas the reductive elimination produces an electrically neutral R–R molecule. Then, the reductive elimination is assumed to involve electron migration from the R group to Ni, and this electron migration is considered to be enhanced by coordination of an electron-withdrawing olefin (e.g., CH_2CHCN and CH_2CHBr) and an aromatic compound (e.g., C_6H_5CN, C_6H_5Br)



(Ni-R bond is activated)

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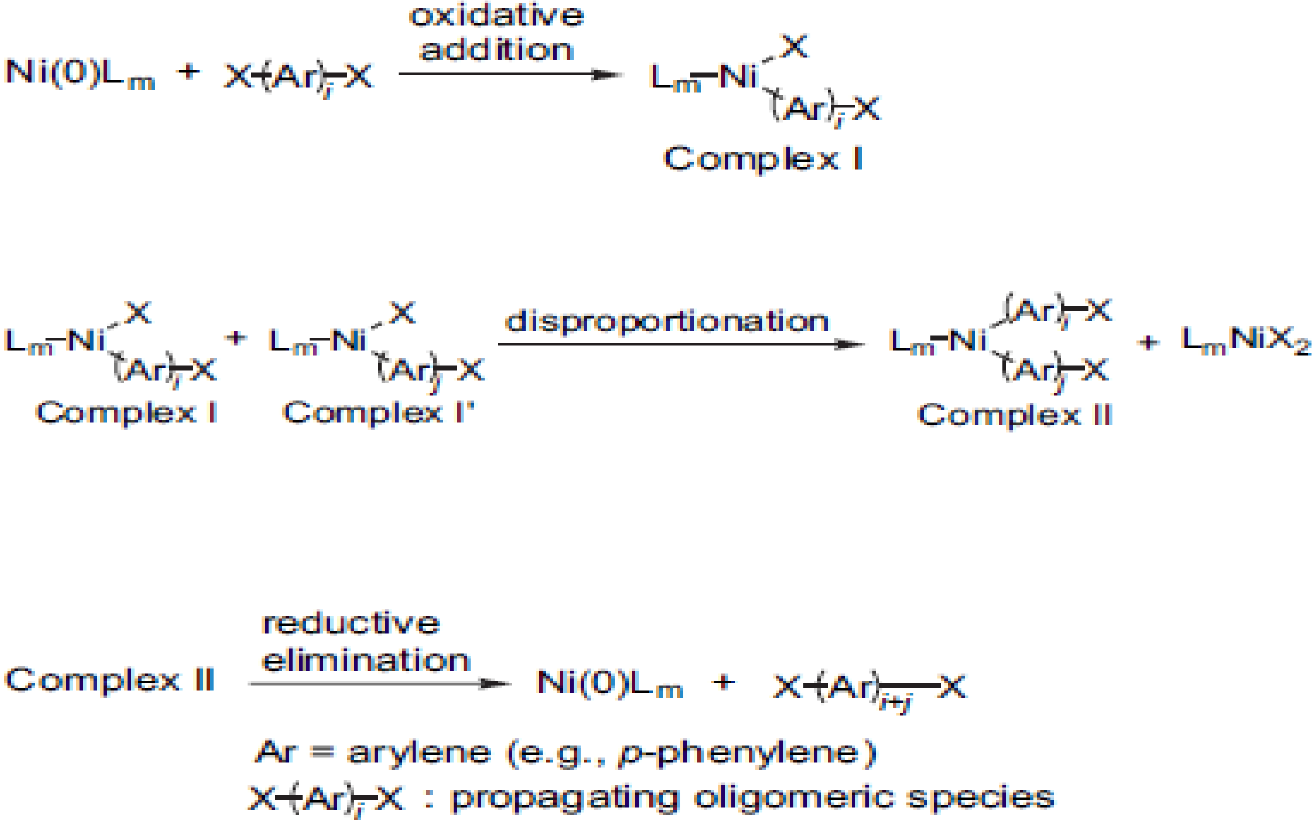
Mechanistic aspects for Ni(0)-promoted polycondensation

The C-C coupling reaction by Ni catalyst contains three fundamental reaction steps:



Ar = arylene (e.g., *p*-phenylene)
$X\text{-}(Ar)_i\text{-}X$: propagating oligomeric species

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- The reductive elimination is a key step in Ni-catalyzed organic syntheses: .

$$n\mathrm{X{-}Ar{-}X} + n\mathrm{Mg} \rightarrow n[\mathrm{X{-}Ar{-}MgX}] \xrightarrow{\text{Ni-complex}} {-}(\mathrm{Ar})_n{-} \qquad [3]$$

$$n\mathrm{X{-}Ar{-}X} + n\mathrm{Ni(0)L}_m \rightarrow {-}(\mathrm{Ar})_n{-} + n\mathrm{NiX_2L}_m \qquad [4]$$

- In some case, Ni(0)Lm formed in situ by chemical such as Zn, NaH and hidrazine hydrate or electrochemical reduction of Ni(II) compound are also usable in polycondensation, following a catalytic reaction: .

$$n\mathrm{X{-}Ar{-}X} + n\mathrm{Zn}\ (\text{or } 2e^-) \xrightarrow{\text{Ni-complex}} {-}(\mathrm{Ar})_n{-} + n\mathrm{ZnX_2}\ (\text{or } 2\mathrm{X}^-)$$

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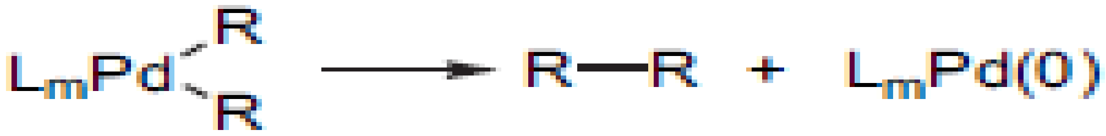
- Pd complexes are also known as useful catalysts for various polymerization reaction. Reductive of R-R from diorganopalladium(II) complexes.



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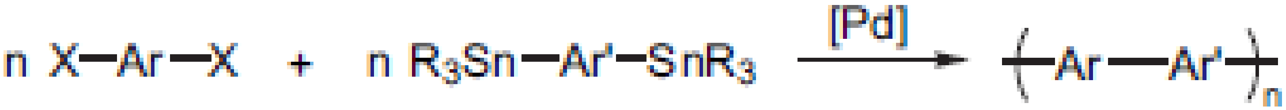
Pd- catalyzed synthesis of conjugated polymers

- **Several Pd-catalyzed C-C coupling reactions have been applied to synthesis of conjugated polymers**

Suzuki polymerization

Sonagashira polymerization

Stille polymerization



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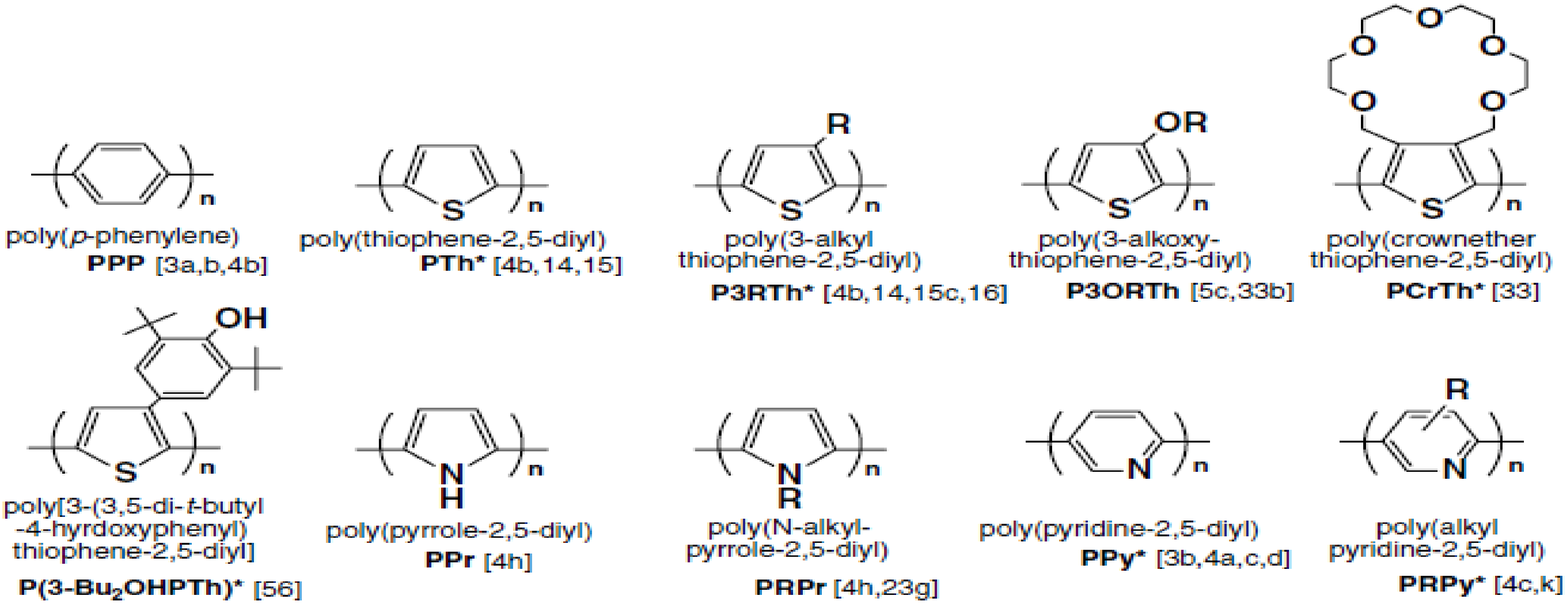
Some Examples From Yamamoto Group



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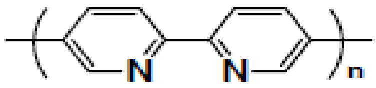
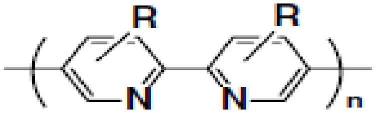
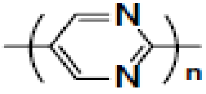


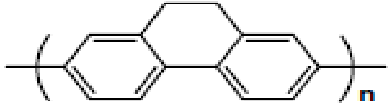
poly(2,2'-bipyridine-5,5'-diyl)
PBpy* [4c,e]



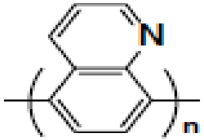
poly(dialkyl-2,2'-bipyridine-5,5'-diyl)
PRBpy* [4c,k]



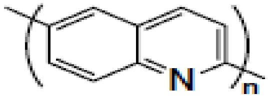
poly(pyrimidine-2,5-diyl)
PPyrim* [4j,19h]



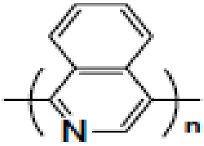
poly(9,10-dihydro-phenanthrene-2,7-diyl)
PH_2Ph* [6a]



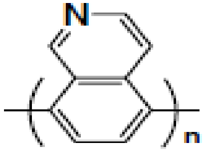
poly(quinoline-5,8-diyl)
P(5,8-Q)* [4i]



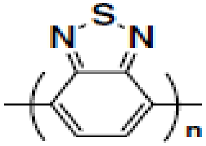
poly(quinoline-2,6-diyl)
P(2,6-Q)* [6b,26a]



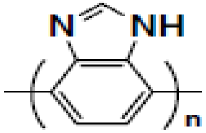
poly(isoquinoline-1,4-diyl)
P(1,4-iQ)* [4i]



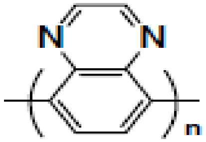
poly(isoquinoline-5,8-diyl)
P(5,8-iQ)* [6b]



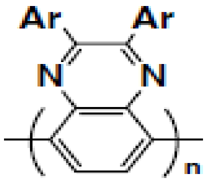
poly(benzo-[*d*][2,1,3]thiadiazole-4,7-diyl)
P(4,7-Btd)*[4m]



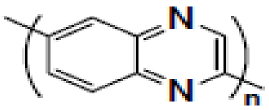
poly(benz-imidazole-4,7-diyl)
P(4,7-Bim)* [4m,19f]



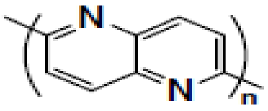
poly(quinoxaline-5,8-diyl)
P(5,8-Qx)* [51a]



poly(2,3-diarylquinoxaline-5,8-diyl)
P(5,8-diArQx)* [51a]

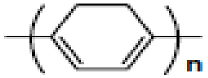


poly(quinoxaline-2,6-diyl)
P(2,6-Qx)* [26a,51a]

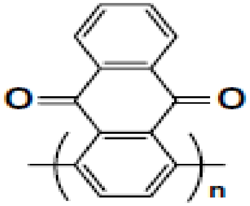


poly(1,5-naphthyridine-2,6-diyl)
P(2,6-Nap)*[6c]

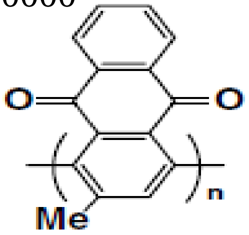
Mw~ 260000



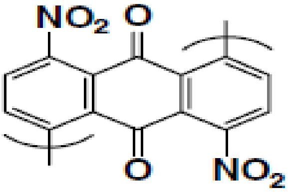
poly(1,3-cyclohexadiene-1,4-diyl)
PCyh* [22c]



poly(anthraquinone-1,4-diyl)
P(1,4-AQ)* [22b,32a]



poly(2-methyl-anthraquinone-1,4-diyl)
P(2-Me-1,4-AQ)* [22b,32a]



poly(4,8-dinitro anthraquinone-1,5-diyl)
$P(4,8-NO_2-1,5-AQ)$*[20i,32b]

Mw~ 190000

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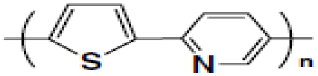
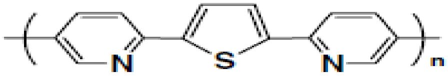
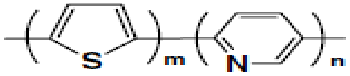


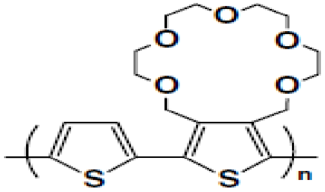
Copoly 1*[12e,23a,b]
and its analogues



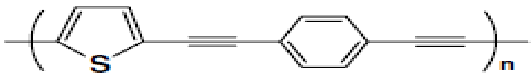
Copoly 2* [12e,23a,b]
and its analogues



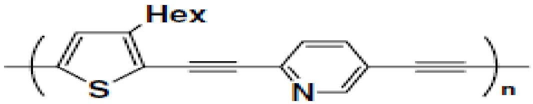
Copoly 3* [12e,23d]
and its analogues



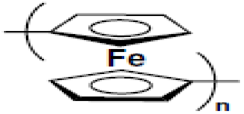
Copoly 4* [33]
and its analogues



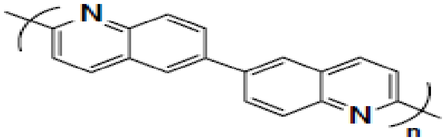
PAE 1* [9a,b]
and its analogues



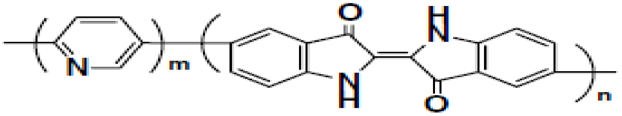
PAE 2* [9c,d]
and its analogues



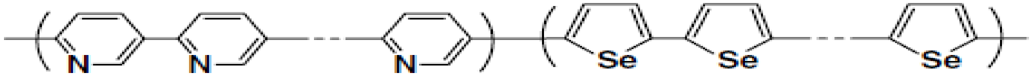
poly(ferrocene-1,1'-diyl)
PFc [35a,39m]



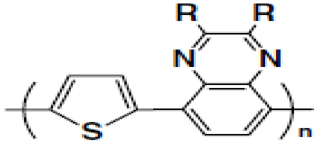
poly(6,6'-biquinoline-2,2'-diyl)
P(2,2'-bQ)* [6c]



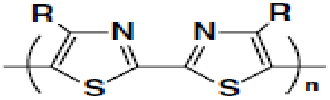
PPy-I* [4l]



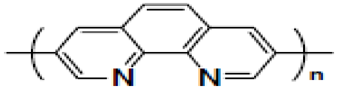
block type copolymer* [12e]



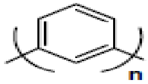
Copoly 5* [12e,m]
and its analogues



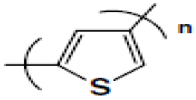
poly(4,4'-dialkyl-2,2'
-bithiazole-5,5'-diyl)
P4RBTz* [21a,38h]



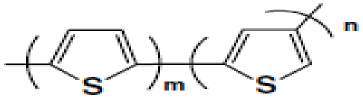
poly(1,10-phenanthroline-3,8-diyl)
PPhen* [27,28a]



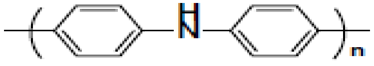
poly(*m*-phenylene)
PMP* [3c,h,i]



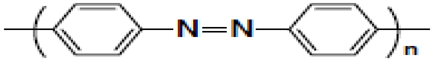
poly(thiophene
-2,4-diyl)
P(2,4-Th)* [15c]



Copoly 6* [3h,15c]



poly(diphenylamine-4,4'-diyl)
PDPA [19a,b,i] and its analogues



poly(azobenzene-4,4'-diyl)
PAzb* [19a]

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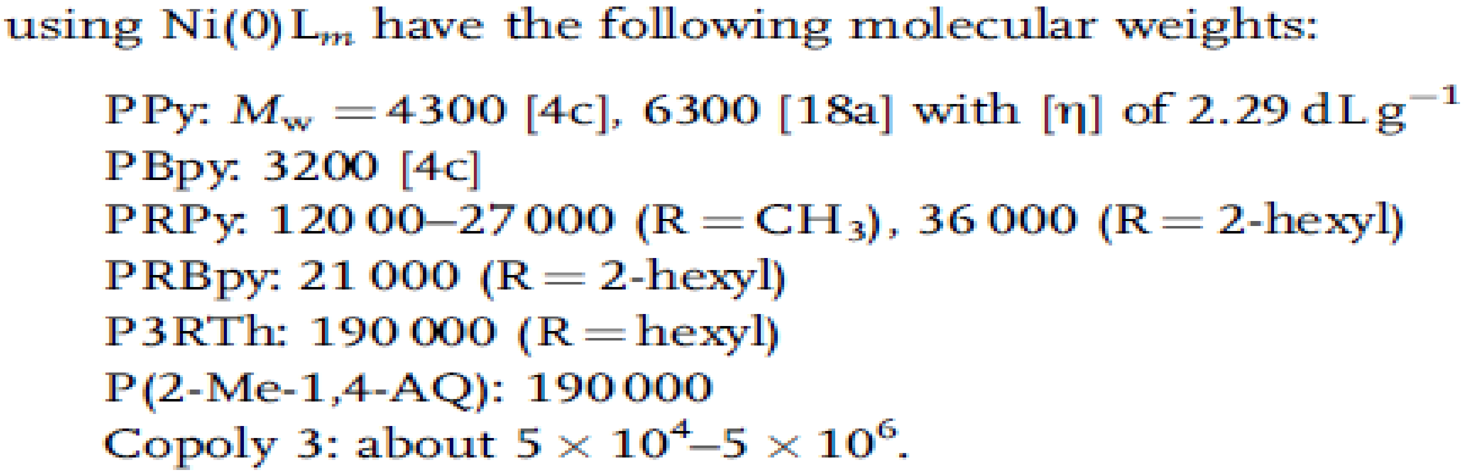
Molecular weight of polymer from Ni(0)-catalyzed polymerization



using Ni(0)L_m have the following molecular weights:

PPy: $M_w = 4300$ [4c], 6300 [18a] with [η] of 2.29 dL g^{-1}
PBpy: 3200 [4c]
PRPy: 12000–27000 ($R = CH_3$), 36000 (R = 2-hexyl)
PRBpy: 21000 (R = 2-hexyl)
P3RTh: 190000 (R = hexyl)
P(2-Me-1,4-AQ): 190000
Copoly 3: about 5×10^4–5×10^6.

In summary: the molecular weight of polymer by the organometallic polymerization seems to depend on the solubility and crystallinity of the polymers. There seems to be a trend that crystalline polymers have a lower molecular weight. Less crystalline and/or soluble propagating species (especially those with an alkyl chain) give a higher molecular weight polymer. .

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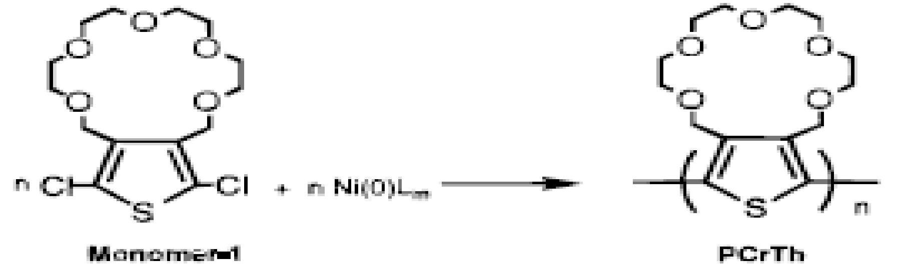
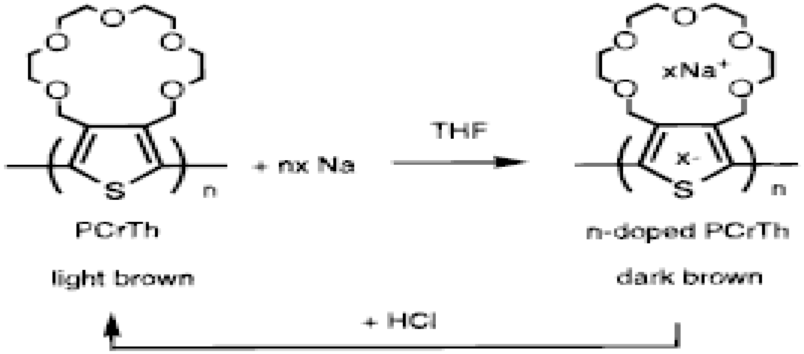
Poly(thiophene-2,5-diyl)s with a Crown Ethereal Subunit



Ni(0)L_m: a mixture of bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)$_2$)
and 2,2'-bipyridiyl (bpy).

Mw 460 000

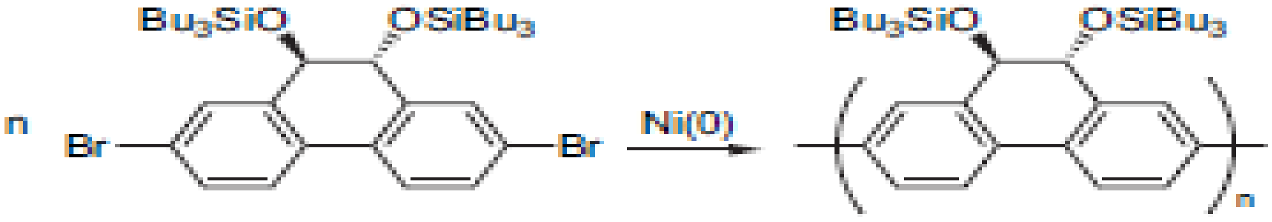


Stability in air

T. Yamamoto, et al. *Macromolecules* **1997,** *30,* 7158-7165

Chiral polymer

- Poly(9,10-disubstituted-9,10-dihydrophenanthrene-2,7-diyl)s such as $PH_2Ph(9,10\text{-}OSiBu_3)$ were light emitting and showed strong circular dichroism



(*R*,*R*)-H_2Ph (9,10-$OSiBu_3$)Br_2

(*R*,*R*)-PH_2Ph (9,10-$OSiBu_3$)

R = R' = butyl : PH_2Ph (9,10-$OSiBu_3$) ; *Mn* = 9800 ; M_w = 19600.
R = methyl ; R' = octadecyl : PH_2Ph (9,10 - $OSiMe_2Ocd$) ; M_n = 69000 ; M_w = 207000.

Yamamoto, T., Asao, T., and Fukumoto, H. *Polymer*, **2004**, *45*, 8085;
Iijima, T.; Yamamoto, T. *Chem. Lett*., **2005**, 1672;

There are two basic types of polymerization, chain-growth polymerization and step-growth polymerization

Chain-growth Polymerization

This type of polymerization is a three step process, namely, initiation, propagation and termination.

Step-growth Polymerization

This polymerization method typically produces polymers of **lower** molecular weight than chain reactions and requires higher temperatures to occur. Unlike addition polymerization, step-wise reactions involve two different types of di-functional monomers or end group that react with one another, forming a chain.

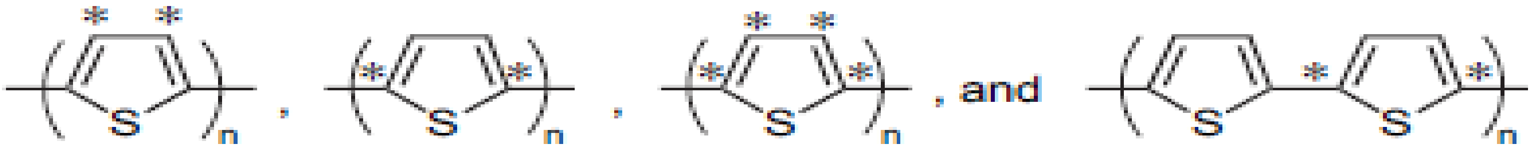
- step-growth polymerization, have a latent potential to involve a chain growth polymerization mechanism. the catalyst activates the polymer end group, followed by reaction with the monomer and the transfer of the catalyst to the elongated polymer end group.

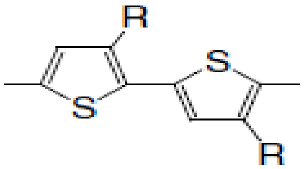
Catalyst-Transfer Condensation Polymerization

Kumada–Tamao Coupling Polymerization with Ni Catalyst

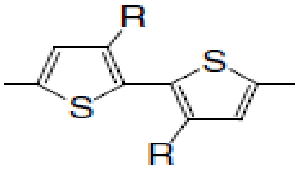
Polythiophene (PTh)

- PTh was designed as the first well characterized and stable π-conjugated polymer.

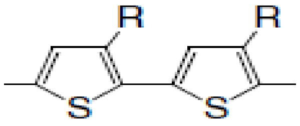




s-*trans* (head-to-tail)



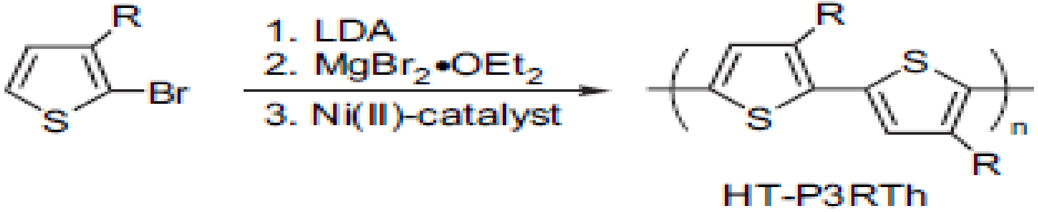
s-*trans* (head-to-head)



s-*cis* (head-to-tail)

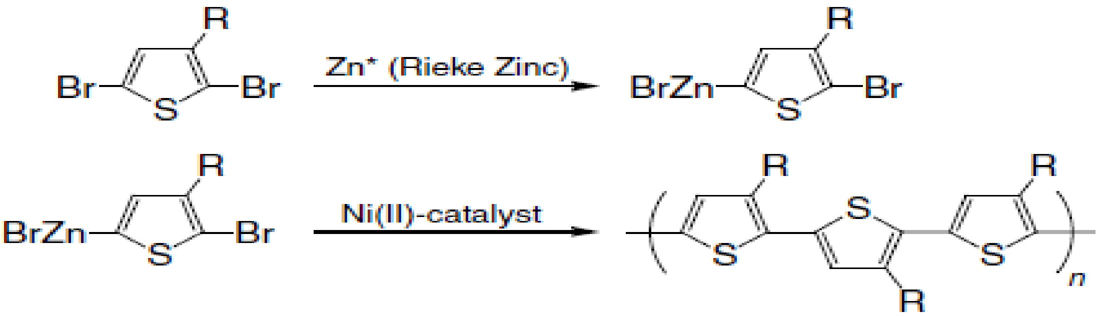
Polythiophene (PTh)

•McCullough et al. introduced Grignard reagent selectively to the 5-position of RTh ring and polymerized it with Ni catalyst, producing the high molecular weight polymer with Broad PDI (~2).



J. Org. Chem. 1993,58, 904-912 McCullough RD, et al. J. Am Chem Soc **1993**,*115*, 4910.

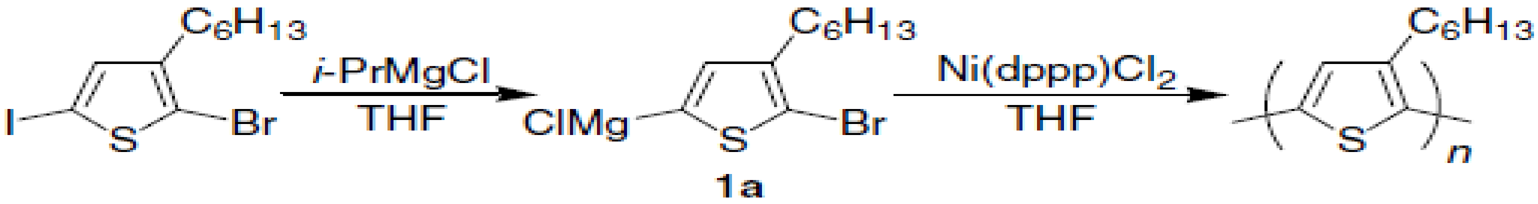
•On the other hand, Rieke et al reported that regio-controlled organozinc reagent obtained regioregular P3RTh, in which th amount of head-tail product was as high as 98.5%.



Chen, T.,Wu, X., and Rieke, R.D. J. Am. Chem. Soc., **1995**, *117*, 233;

Polythiophene (PTh)

- Yokozawa and coworkers found that use the exact amount of isopropyl magnesium chloride generated the Grignard monomer **1a** from the bromoiodothiophene, which polymerized with Ni catalyst at room temperature in controllable fashion.



Mn:28,700
PDI: 1.1

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

- After a detailed study of the polymerization of **1a**, four important points were clarified:

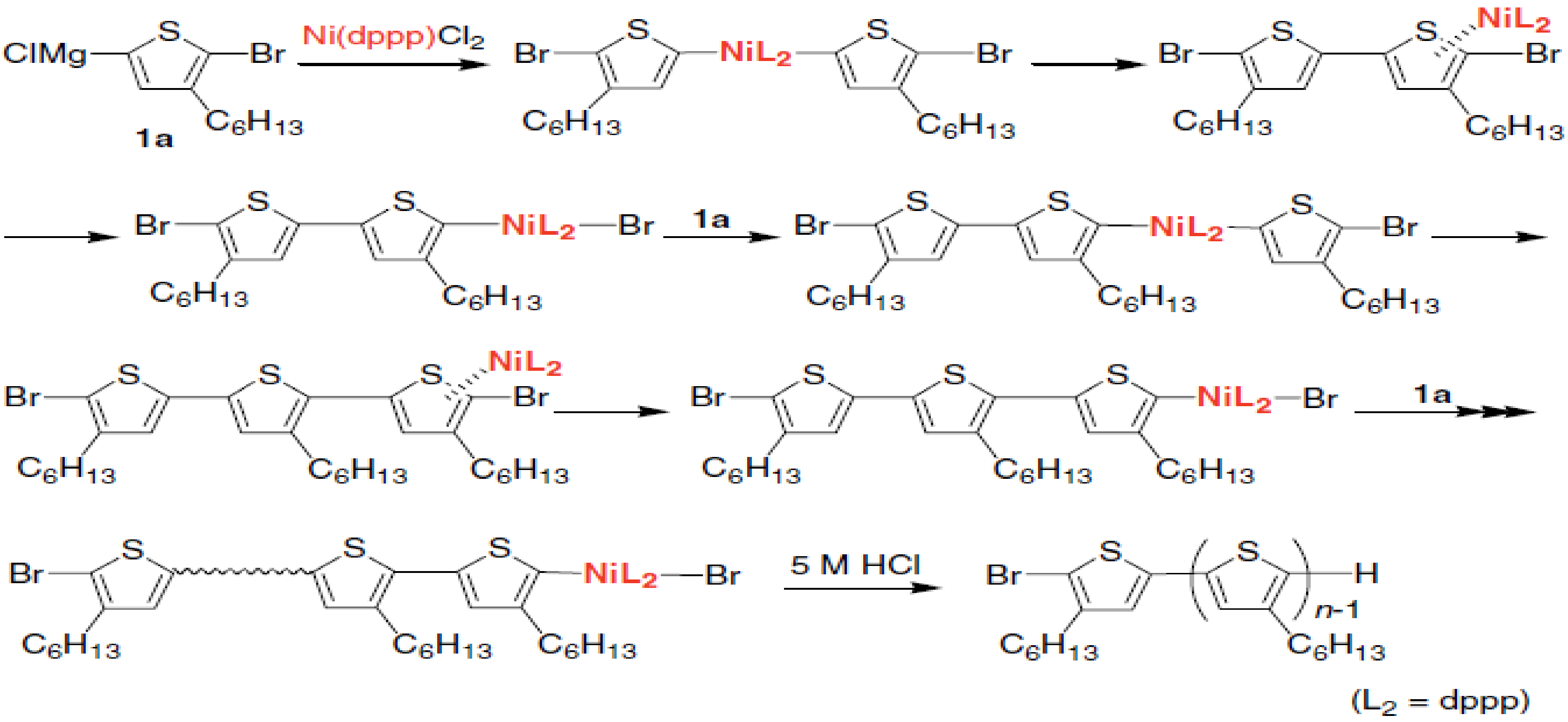
(i) the polymer end groups are uniform among molecules; one end group is Br and the other is H;

(ii) the propagating end group is a polymer–Ni–Br complex;

(iii) one Ni molecule forms one polymer chain;

(iv) the chain initiator is a dimer of **1a** formed in situ

Catalyst-transfer condensation polymerization mechanism



Preparation of Conductive Polymer Brushes

- Kiriy and coworkers used $(PPh_3)_2Ni(Ph)Br$ as an initiator and synthesized Ph-terminated poly(3-hexylthiophene) brushes via surface-initiated chain growth polymerization.

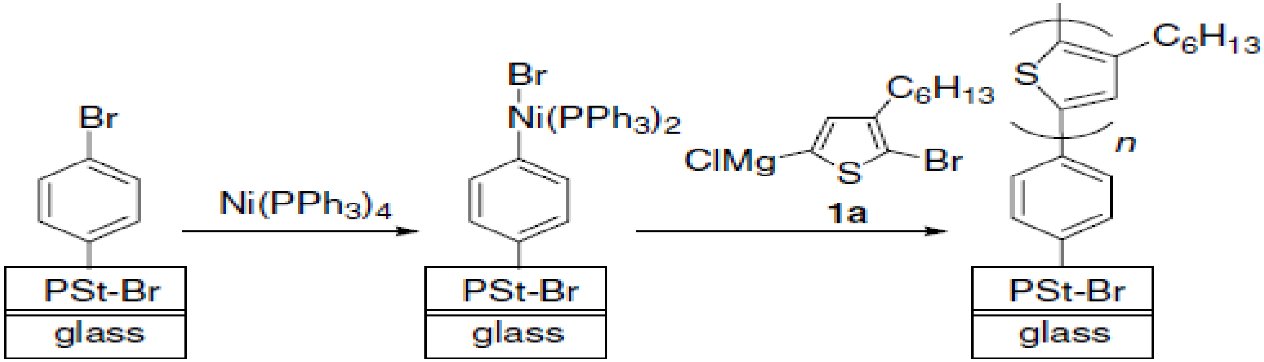
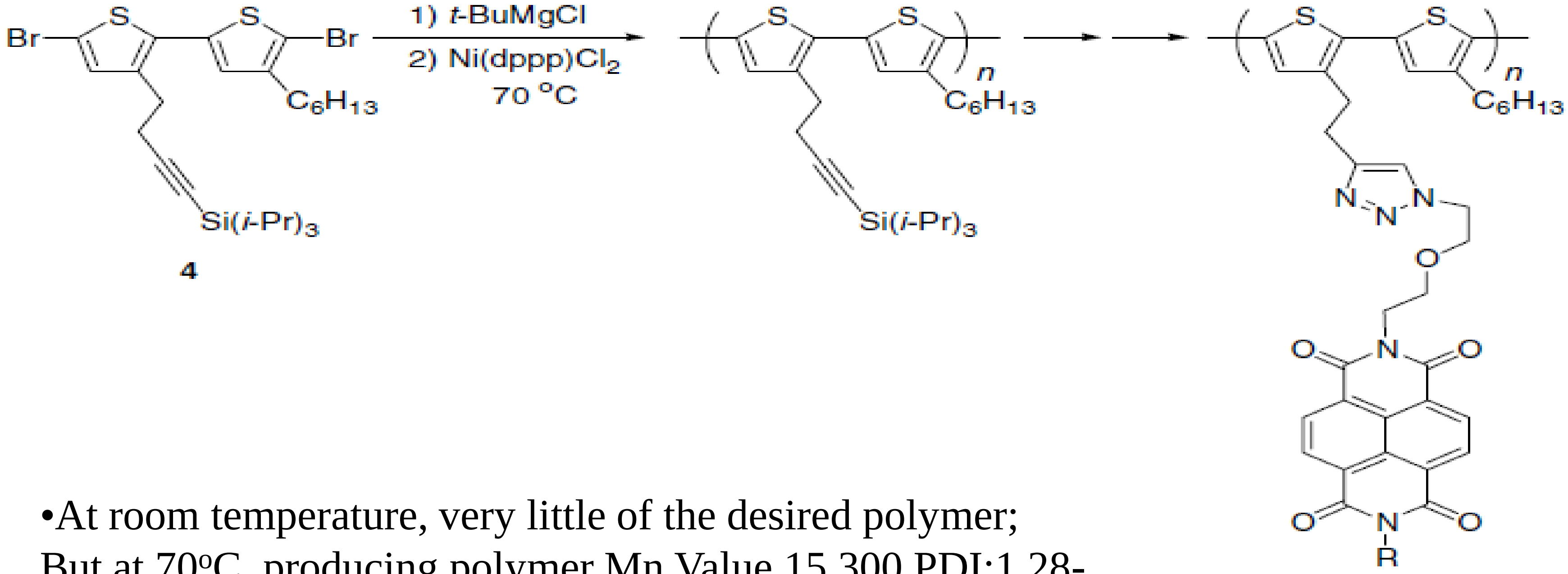


photo-cross-linked
poly(4-bromostyrene)
films

Kiriy, A. et al. J. Am. Chem. Soc. **2007**, *129*, 6626–6632;
Macromolecules, **2008**,*41*, 7383–7389.

Block Polythiophenes

- **the polymerization of thiophene dimer with Ni(dppp)Cl_2**

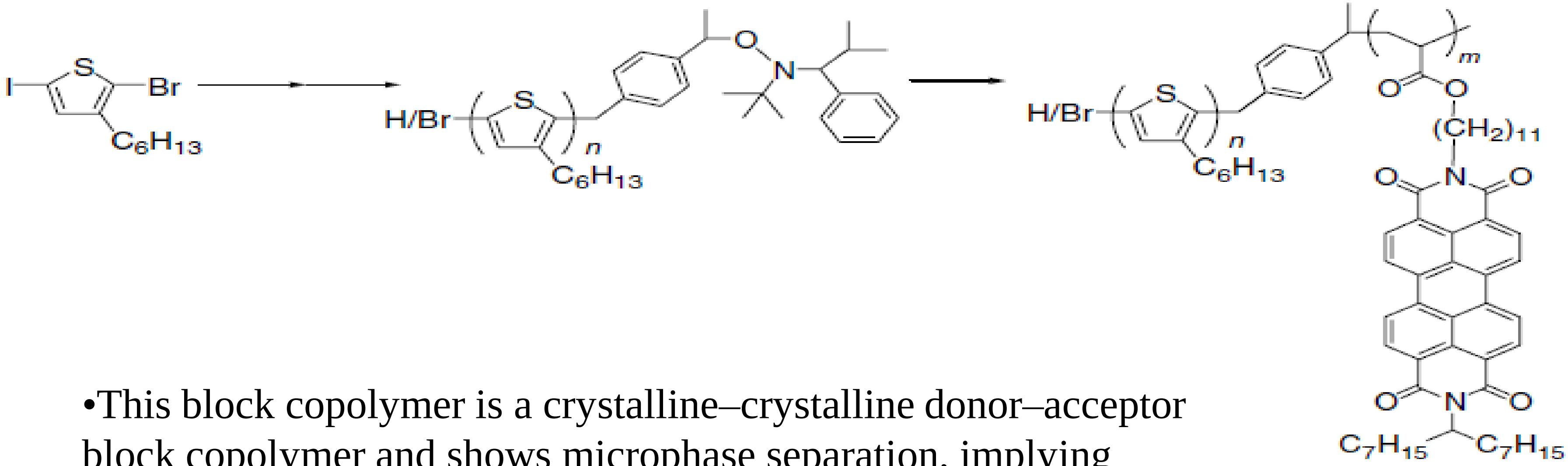


- At room temperature, very little of the desired polymer;

But at 70^{o}C, producing polymer Mn Value 15,300 PDI:1.28-1.35. functionalized by azide bearing a naphthalimide moiety under .click chemistry. conditions

Venkataraman, D. et al. *Macromolecules*, **2008**, *41*, 8312–8315.

Crystalline-crystalline donor-acceptor block copolymer

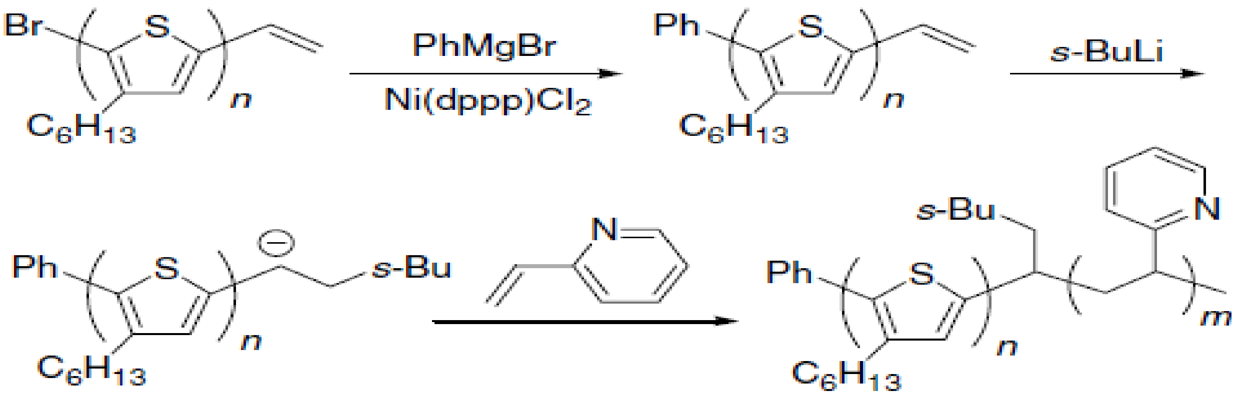


- This block copolymer is a crystalline–crystalline donor–acceptor block copolymer and shows microphase separation, implying efficient photovoltaic applications.

Sommer, M., Lang, A.S., and Thelakkat, M. Angew. Chem. Int. Ed., **2008**, *47*, 7901–7904.

block copolymers of polythiophene and poly(vinylpyridine)

- Su and coworkers synthesized block copolymers of polythiophene and poly(vinylpyridine) by means of living anionic polymerization of 4-vinylpyridine

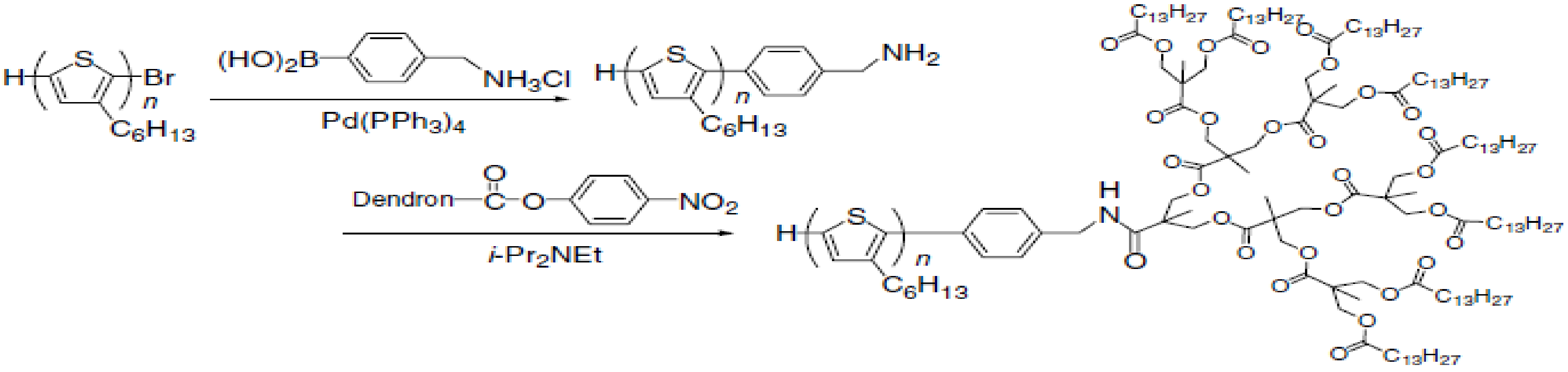


These block copolymers were able to undergo microphase separation and self-assembly into nanostructures of sphere, cylinder, and nanofiber structure with increasing polythiophene segment ratios.

. J. Am. Chem. Soc., **2007**, *129*, 11036–11038.

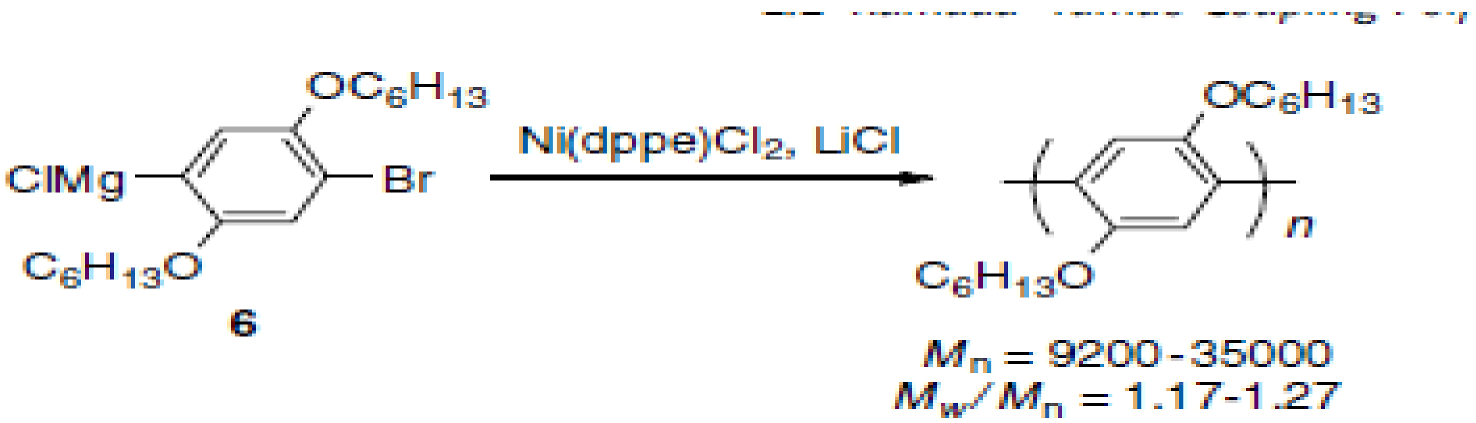
Dendron-modified polythiophene

•Frechet and coworkers reported the synthesis of a dendron-modified polythiophene, in which one terminus of poly(3-hexylthiophene) is linked to the focal point of a polyester-type dendron



Watanabe, N., Mauldin, C., and Frechet, J.M.J. *Macromolecules*,, **2007**, *40*, 6793–6795.

Polyphenylenes



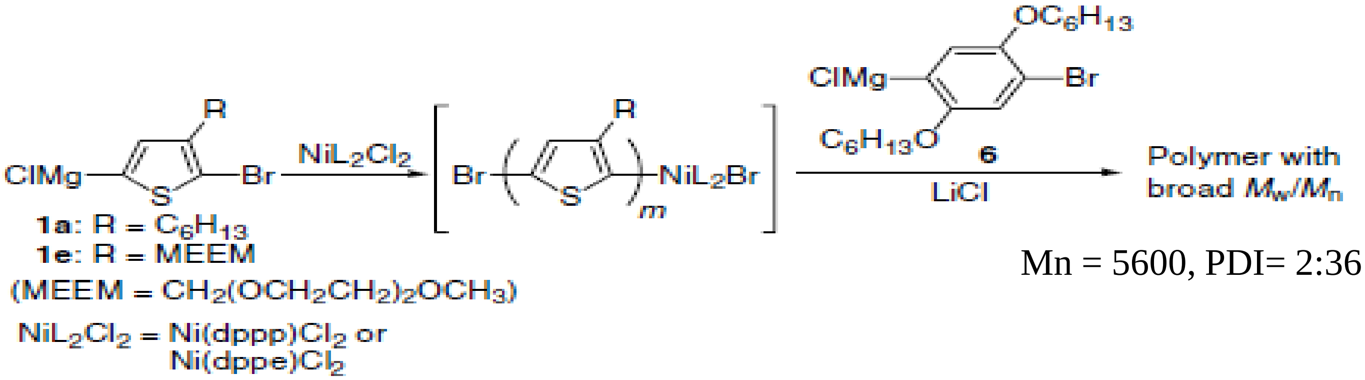
- Polymerization of monomer with Ni(II) produced low molecular weight polymer having broad PDI;
- However, adding LiCl resulted in polymer with low PDI, and that the molecular weight was controlled by feed ratio of monomer to catalyst

Yokozawa, T. et al. J. Am. Chem. Soc., **2006**, *128*, 16012–16013

Block copolymers of polythiophene and poly(p-phenylene)

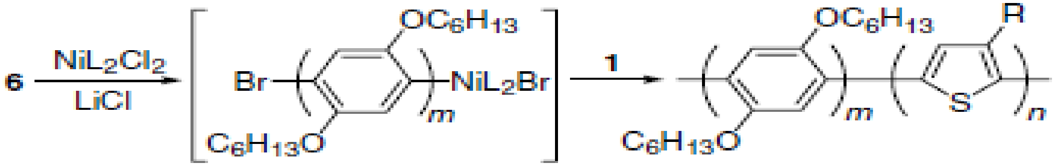
- First example of catalyst transfer polymerization for the synthesis of block copolymers consisting of a different type of conjugated polymers.

Pathway 1.



Mn = 5600, PDI= 2:36

Pathway 2.



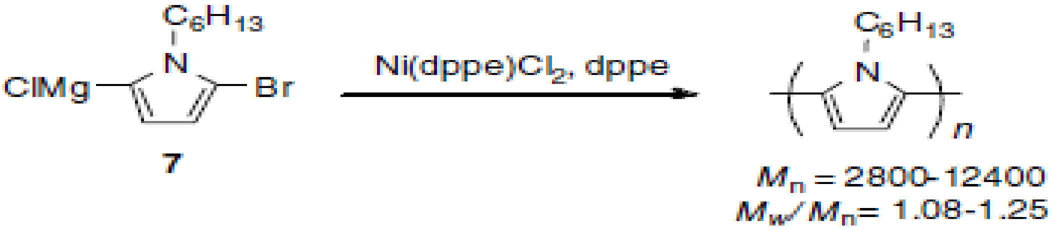
Mn = 10900, PDI= 1.11

Mn = 16200, PDI = 1.27

Why? Question 2

Yokozawa, T. *Chem. Lett.*, **2008**, *37*,1022–1023.

Polypyrroles



- polymerization of 7 with Ni(dppe)Cl2 , a polymer with PDI of 1.26 as obtained, accompanied by low-molecular-weight oligomers.
- In the presence of additional dppe, equimolar to the catalyst, at 0 °C gave the polypyrrole with a narrow PDI =1.11 without formation of by-products

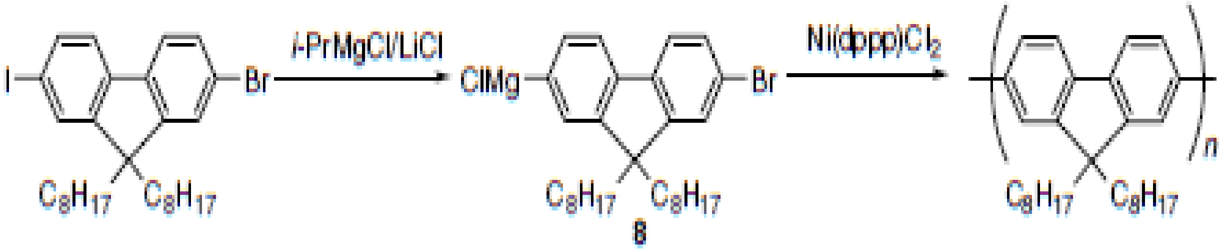
Yokozawa, T.et al. Macromolecules, **2008**, *41*, 7271–7273.

Block copolymer of poly(p-phenylene) and polypyrrole

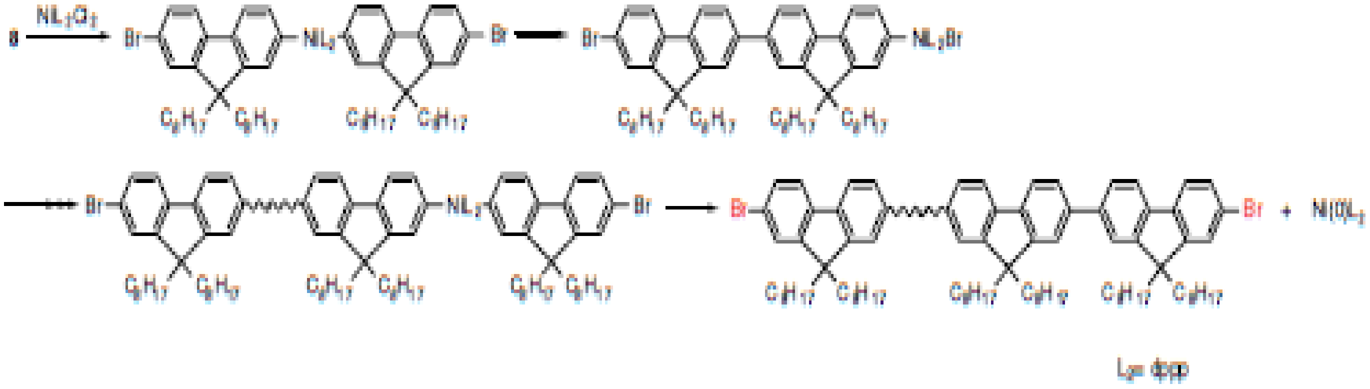
- Yokozawa and coworkers also synthesized a block copolymer of poly(p-phenylene) and polypyrrole by their method. The p-phenylene monomer was polymerized first with Ni(dppe)Cl2 in the presence of LiCl, followed by addition of pyrrole monomer and dppe to yield the desired block copolymer with a PDI around 1.16.

Yokozawa, T.et al. Macromolecules, **2008**, *41*, 7271–7273.

Polyfluorenes



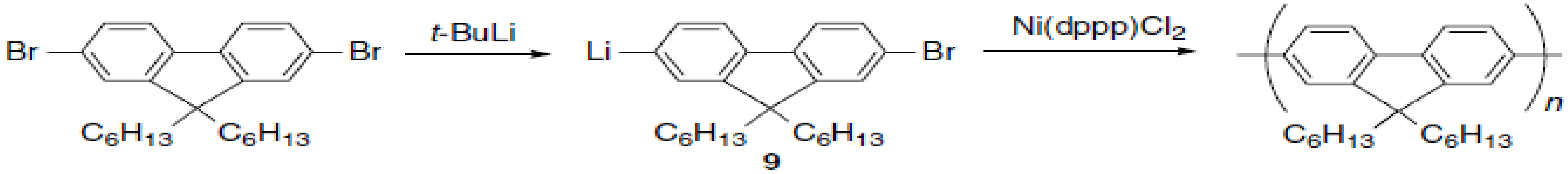
Mn: 18800–86 000; PDI : 1.49-1.77



The polymerization proceeded very fast at 0°C and was almost over in 10 min.

Geng, Y.H., et al. *Macromolecules*, **2008**, *41*, 8944–8947

The polymerization of lithiated fluorene monomer



Mn up to 32660
PDI:~2

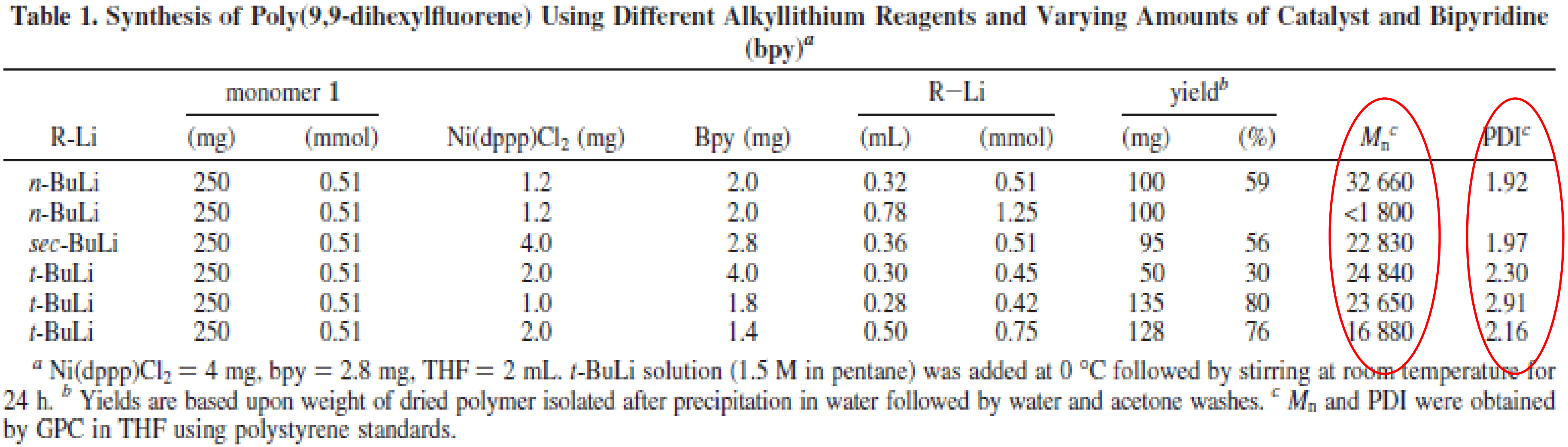


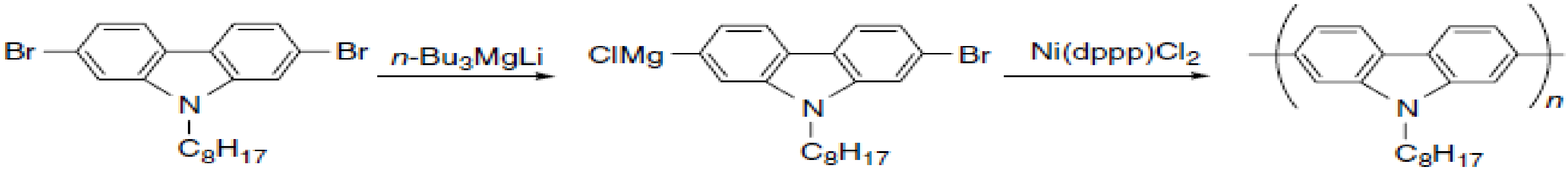
Table 1. Synthesis of Poly(9,9-dihexylfluorene) Using Different Alkyllithium Reagents and Varying Amounts of Catalyst and Bipyridine (bpy)[a]

	monomer 1				R−Li		yield[b]			
R-Li	(mg)	(mmol)	Ni(dppp)Cl_2 (mg)	Bpy (mg)	(mL)	(mmol)	(mg)	(%)	M_n[c]	PDI[c]
n-BuLi	250	0.51	1.2	2.0	0.32	0.51	100	59	32 660	1.92
n-BuLi	250	0.51	1.2	2.0	0.78	1.25	100		<1 800	
sec-BuLi	250	0.51	4.0	2.8	0.36	0.51	95	56	22 830	1.97
t-BuLi	250	0.51	2.0	4.0	0.30	0.45	50	30	24 840	2.30
t-BuLi	250	0.51	1.0	1.8	0.28	0.42	135	80	23 650	2.91
t-BuLi	250	0.51	2.0	1.4	0.50	0.75	128	76	16 880	2.16

[a] Ni(dppp)Cl_2 = 4 mg, bpy = 2.8 mg, THF = 2 mL. *t*-BuLi solution (1.5 M in pentane) was added at 0 °C followed by stirring at room temperature for 24 h. [b] Yields are based upon weight of dried polymer isolated after precipitation in water followed by water and acetone washes. [c] M_n and PDI were obtained by GPC in THF using polystyrene standards.

Carter et al. *Macromolecules*, **2008**, 41, 8977–8979

The synthesis of polycarbazole



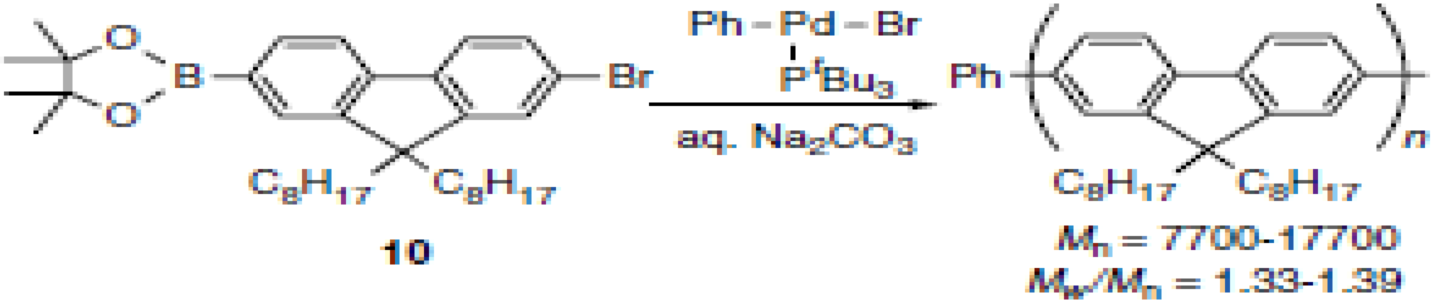
Mn = 2600
PDI = 1.23

- The magnesium halogen exchange of 2,7-dibromo-N-octylcarbazole with i-PrMgCl LiCl was significantly slower compared to both fluorene and pyrrole monomers. In contrast, lithium tributylmagnesate (n-Bu3MgLi) was effective for the magnesium halogen exchange. The polymerization of this Grignard type monomer was carried out with Ni(dppp)Cl2 to afford a polycarbazole with Mn=2600 and PDI=1.23 .

McCullough, R.D.et al. *Macromolecules* **2009**, *42*, 30-32

Suzuki–Miyaura Coupling Polymerization with Pd Catalyst

Suzuki polymerization of AB type monomer



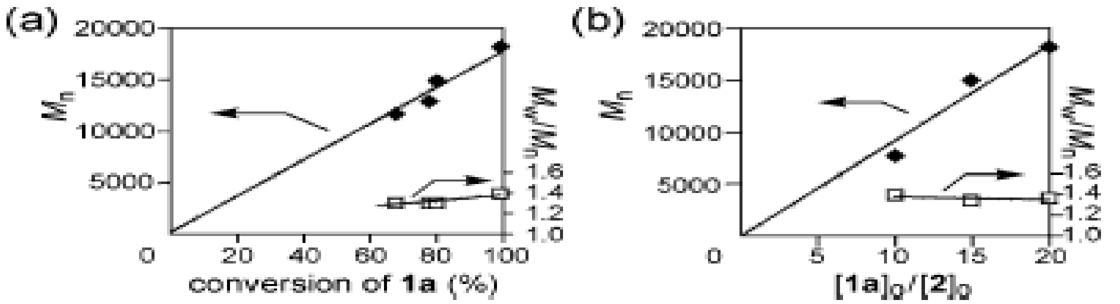
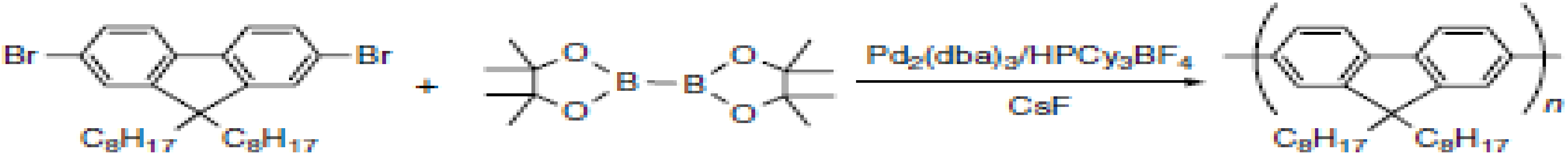


Figure 2. M_n and M_w/M_n values of poly(9,9-dioctylfluorene) as a function of (a) monomer conversion, obtained with **1a** and 5 mol % of **2** and (b) the feed ratio of **1a** to **2** ([**1a**]$_0$ = 25 mmol/L; [**2**]$_0$ = 2.5 mmol/L (10 mol %), 1.67 mmol/L (6.7 mol %), 1.25 mmol/L (5 mol %)). All the polymerizations were carried out in a mixture of THF and 2 mol/L aqueous solution of Na_2CO_3 at room temperature. M_n and M_w/M_n values were determined by GPC relative to polystyrene standards.

Yokoyama, A., Suzuki, H., Kubota, Y.,Ohuchi, K., Higashimura, H., Yokozawa, T. *J. Am. Chem. Soc.*, **2007,** *129*, 7236–7237.

One pot suzuki polymerization



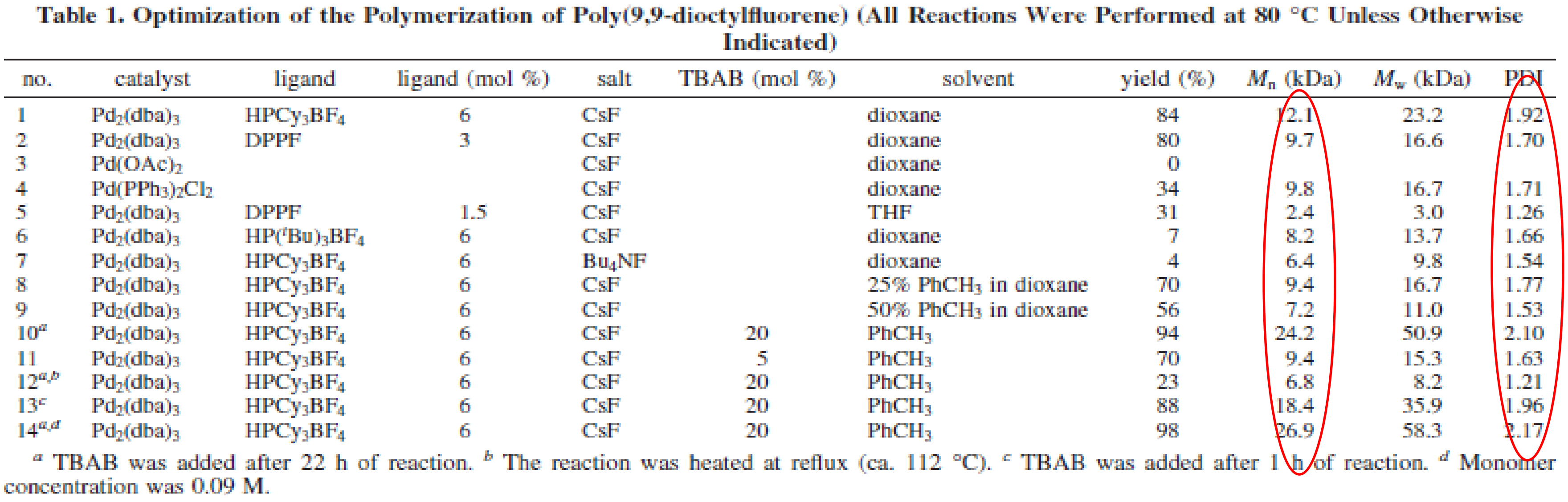


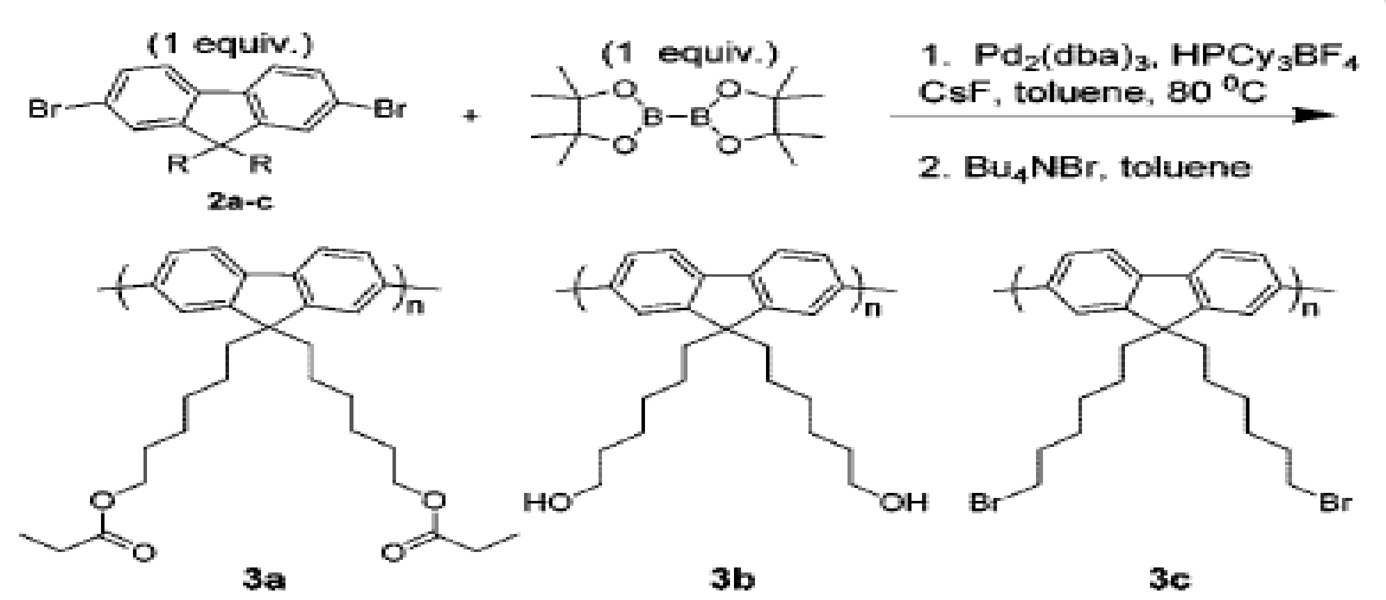
Table 1. Optimization of the Polymerization of Poly(9,9-dioctylfluorene) (All Reactions Were Performed at 80 °C Unless Otherwise Indicated)

no.	catalyst	ligand	ligand (mol %)	salt	TBAB (mol %)	solvent	yield (%)	M_n (kDa)	M_w (kDa)	PDI
1	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF		dioxane	84	12.1	23.2	1.92
2	$Pd_2(dba)_3$	DPPF	3	CsF		dioxane	80	9.7	16.6	1.70
3	$Pd(OAc)_2$			CsF		dioxane	0			
4	$Pd(PPh_3)_2Cl_2$			CsF		dioxane	34	9.8	16.7	1.71
5	$Pd_2(dba)_3$	DPPF	1.5	CsF		THF	31	2.4	3.0	1.26
6	$Pd_2(dba)_3$	$HP(^tBu)_3BF_4$	6	CsF		dioxane	7	8.2	13.7	1.66
7	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	Bu_4NF		dioxane	4	6.4	9.8	1.54
8	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF		25% $PhCH_3$ in dioxane	70	9.4	16.7	1.77
9	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF		50% $PhCH_3$ in dioxane	56	7.2	11.0	1.53
10[a]	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF	20	$PhCH_3$	94	24.2	50.9	2.10
11	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF	5	$PhCH_3$	70	9.4	15.3	1.63
12[a,b]	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF	20	$PhCH_3$	23	6.8	8.2	1.21
13[c]	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF	20	$PhCH_3$	88	18.4	35.9	1.96
14[a,d]	$Pd_2(dba)_3$	$HPCy_3BF_4$	6	CsF	20	$PhCH_3$	98	26.9	58.3	2.17

[a] TBAB was added after 22 h of reaction. [b] The reaction was heated at reflux (ca. 112 °C). [c] TBAB was added after 1 h of reaction. [d] Monomer concentration was 0.09 M.

Reynolds, J.R.et al. Macromolecules, **2009**, 42, 1445–1447.

One pot suzuki polymerization



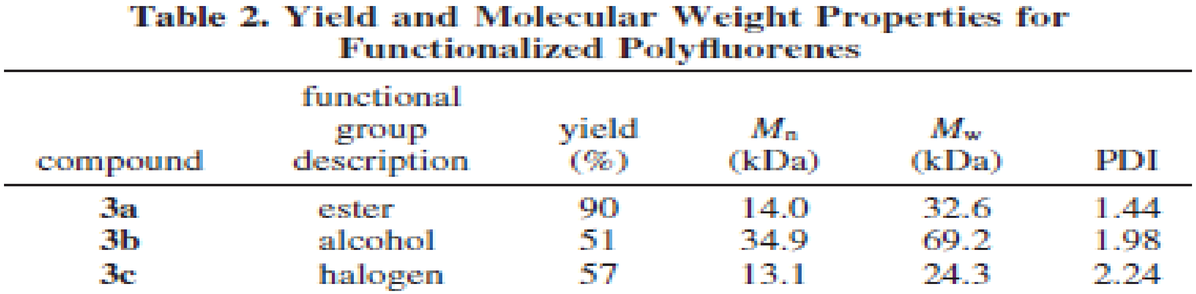
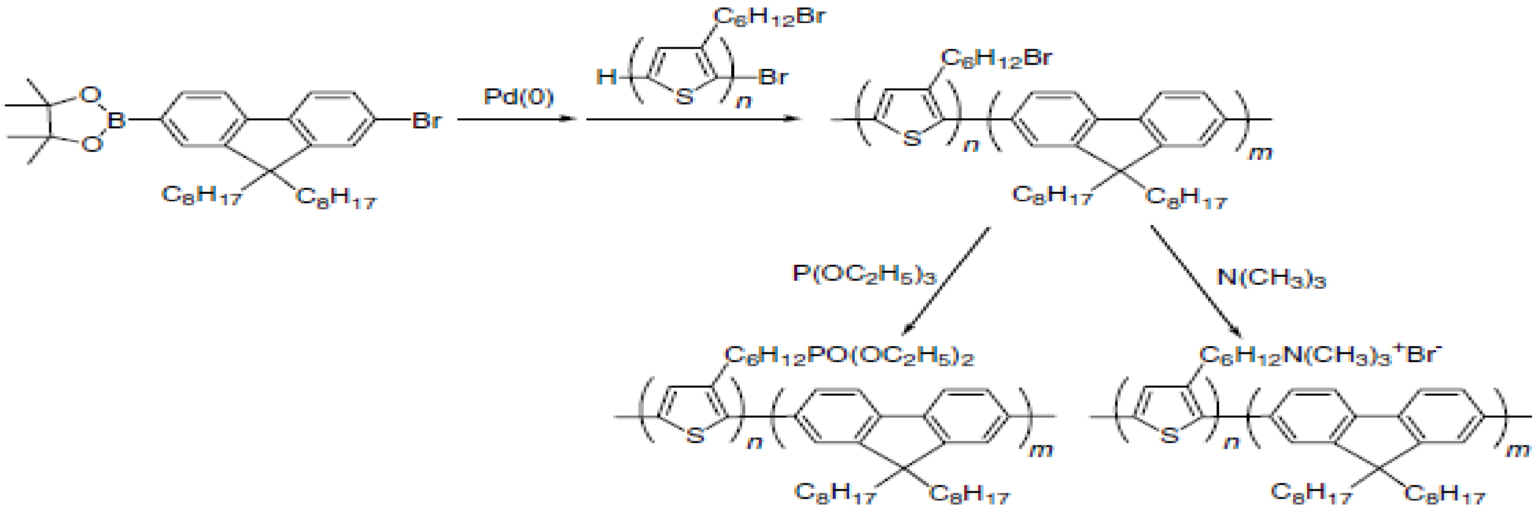


Table 2. Yield and Molecular Weight Properties for Functionalized Polyfluorenes

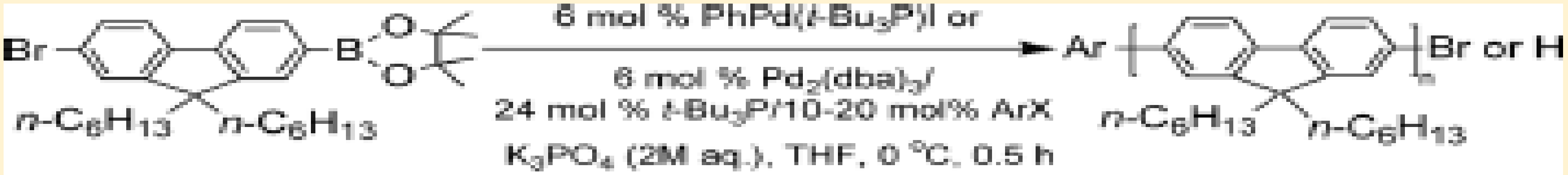
compound	functional group description	yield (%)	M_n (kDa)	M_w (kDa)	PDI
3a	ester	90	14.0	32.6	1.44
3b	alcohol	51	34.9	69.2	1.98
3c	halogen	57	13.1	24.3	2.24

Reynolds, J.R.et al. Macromolecules, **2009**, 42, 1445–1447.

Diblock Copolymer of Polythiophene and Polyfluorene by Suzuki Polymerization



Tu, G.L., Li, H.B., Forster, M., Heiderhoff, R., Balk, L.J., Sigel, R., and Scherf, U. *Small*, **2007**, *3*, 1001–1006.



PhPd(t-Bu$_3$P)I as the initiator: M_n = 14 800 (PDI = 1.33)

Pd$_2$(dba)$_3$/t-Bu$_3$P/p-BrC$_6$H$_4$I as the initiator: M_n = 15 300 (PDI = 1.15)

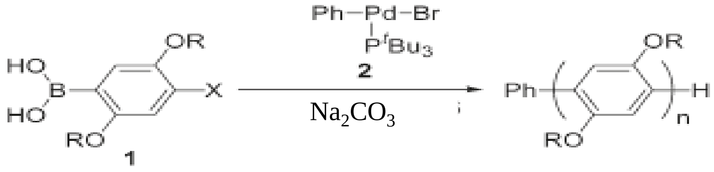
Pd$_2$(dba)$_3$/t-Bu$_3$P/p-HOCH$_2$C$_6$H$_4$Br as the initiator: M_n = 16 600 (PDI = 1.18)

entry	additive	yield (%)[b]	M_n (PDI)[c]
1	none	86	12 300 (1.29)
2	t-Bu$_3$P (1.0 equiv)	83	12 000 (1.19)
3	dba (1.5 equiv)	80	10 900 (1.24)
4	t-Bu$_3$P(1.0 equiv) + dba (1.5 equiv)	83	13 500 (1.19)

[a] Polymerization conditions: monomer (1 equiv), initiator (6 mol %), K$_3$PO$_4$ (10 equiv), THF, 0 °C, 30 min. [b] Isolated yield. [c] GPC analysis (polystyrene as standard, THF, 40 °C).

Kunlun Hong et al .Macromolecules **2015**, *48*, 967–978

Polyphenylene



1a: R = C_4H_9, X = Br
1b: R = C_6H_{13}, X = I

Mn up to 22200
PDI ~2

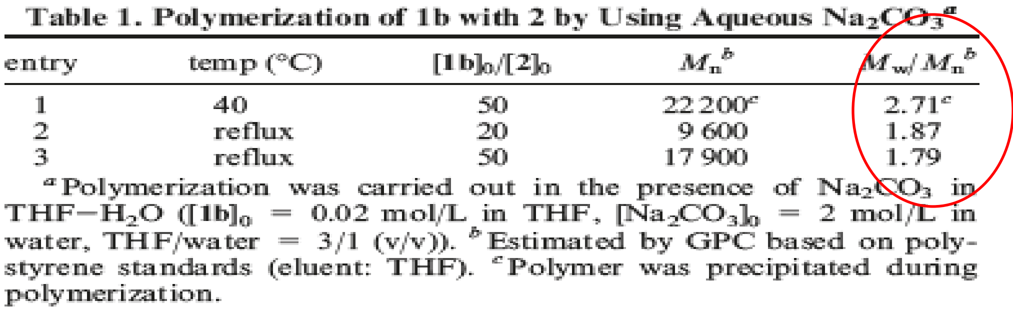
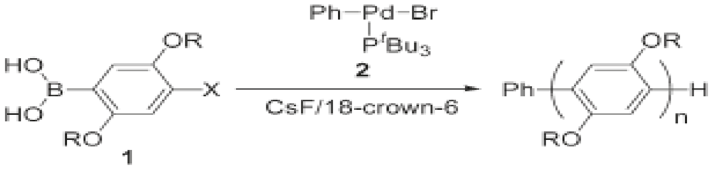


Table 1. Polymerization of 1b with 2 by Using Aqueous Na_2CO_3[a]

entry	temp (°C)	[**1b**]$_0$/[**2**]$_0$	M_n[b]	M_w/M_n[b]
1	40	50	22 200[c]	2.71[c]
2	reflux	20	9 600	1.87
3	reflux	50	17 900	1.79

[a] Polymerization was carried out in the presence of Na_2CO_3 in THF−H_2O ([**1b**]$_0$ = 0.02 mol/L in THF, [Na_2CO_3]$_0$ = 2 mol/L in water, THF/water = 3/1 (v/v)). [b] Estimated by GPC based on polystyrene standards (eluent: THF). [c] Polymer was precipitated during polymerization.



1a: R = C_4H_9, X = Br
1b: R = C_6H_{13}, X = I

Mn up to 21200
PDI ~1.5

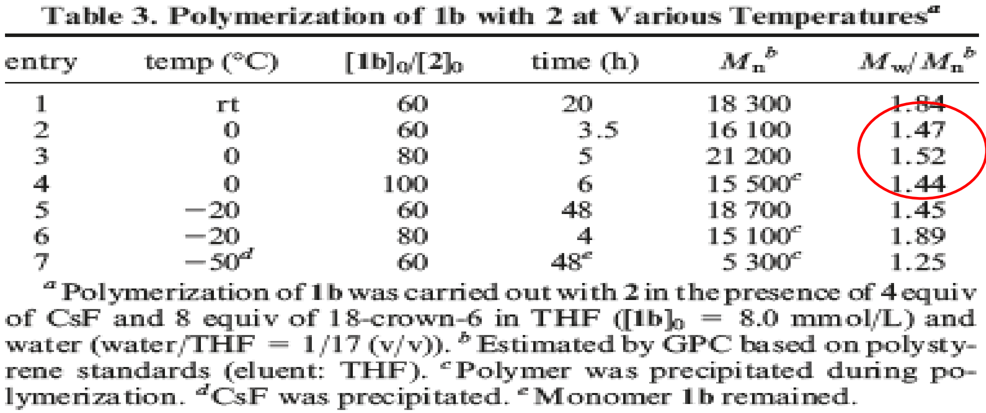


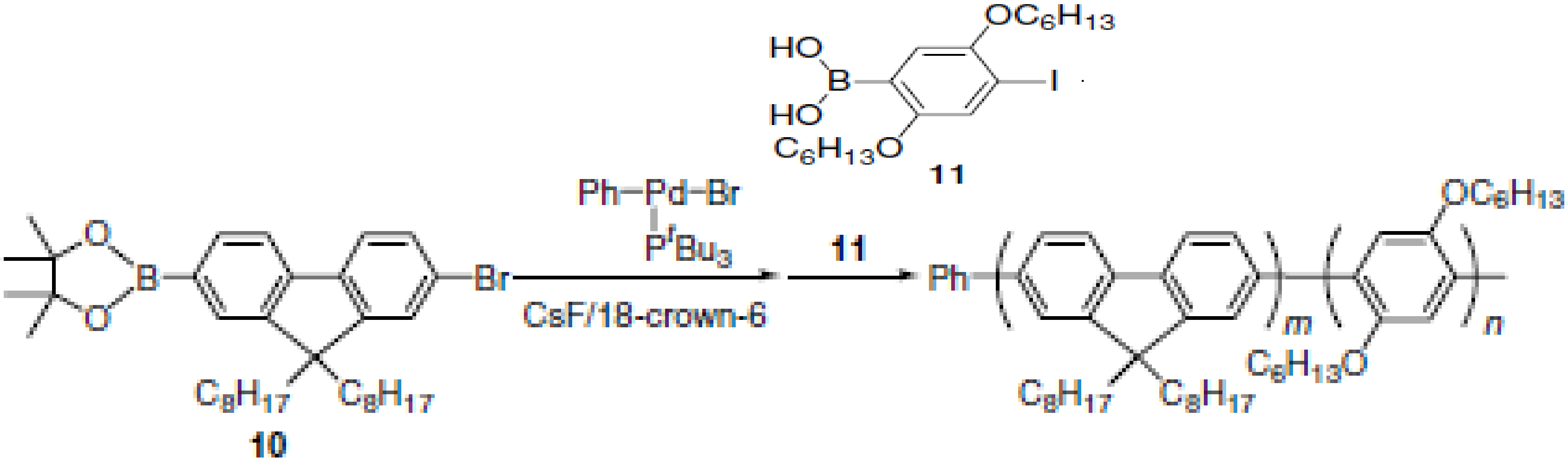
Table 3. Polymerization of 1b with 2 at Various Temperatures[a]

entry	temp (°C)	[**1b**]$_0$/[**2**]$_0$	time (h)	M_n[b]	M_w/M_n[b]
1	rt	60	20	18 300	1.84
2	0	60	3.5	16 100	1.47
3	0	80	5	21 200	1.52
4	0	100	6	15 500[c]	1.44
5	−20	60	48	18 700	1.45
6	−20	80	4	15 100[c]	1.89
7	−50[d]	60	48[e]	5 300[c]	1.25

[a] Polymerization of **1b** was carried out with **2** in the presence of 4 equiv of CsF and 8 equiv of 18-crown-6 in THF ([**1b**]$_0$ = 8.0 mmol/L) and water (water/THF = 1/17 (v/v)). [b] Estimated by GPC based on polystyrene standards (eluent: THF). [c] Polymer was precipitated during polymerization. [d] CsF was precipitated. [e] Monomer **1b** remained.

Yokozawa, T. .Macromolecules **2010**, *43*, 7095–7100

Copolymer of Polyfluorene and Polyphenylene



polymerization of 10 under these condition and then the successive polymerization of 11 were carried out to yield a block copolymer of polyfluorene and polyphenylene

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