π-Conjugated Polymers

OUTLINE

Lect. 1:

Conjugated polymers: The use of a Band Model, Geometry, Excited States.

Lect. 2:

Conjugated Polymers: Bandgap Engineering.

Lect. 3:

Synthetic Methods toward Conjugated Polymers.

Outline Part 3

- **Introduction**
- **Material specifications**
- **Direct synthetic routes**
- **Precursor routes**

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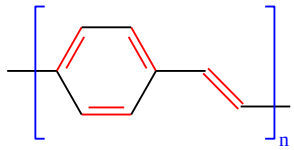
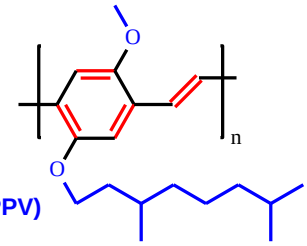
HyMaD HYBRID MATERIALS DESIGN

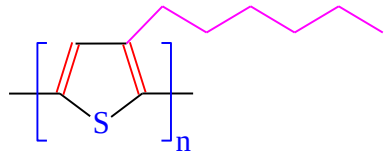
Applications as Semi-Conductor



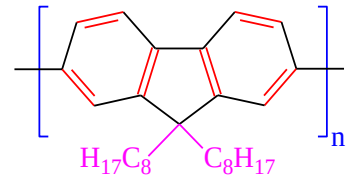
Poly(Phenylene Vinylene) (PPV)



OC_1C_{10}-PPV



RR-Poly(3-HexylThiophene) (P3HT)



Poly(DiOctyl-Fluorene) (PDOF)

Plastic Electronics

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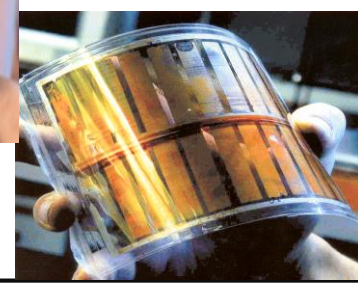
HyMaD HYBRID MATERIALS DESIGN

Plastic Electronics



Printed

Electronics

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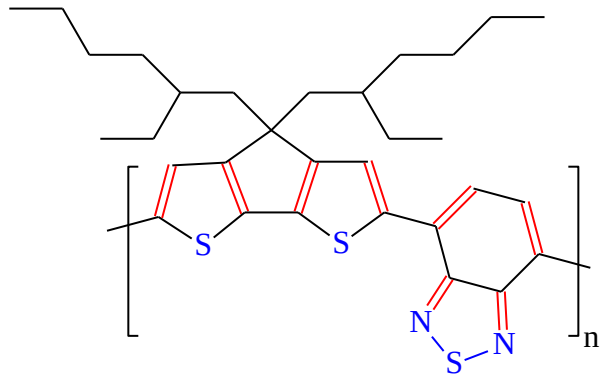
HyMaD HYBRID MATERIALS DESIGN

Outline Part 3

- **Introduction**
- **Material specifications**
- **Direct synthetic routes**
- **Precursor routes**

Synthesis of Conjugated Polymers



Poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-CycloPenta[2,1-b;3,4-b']-DiThiophene)-*alt*-4,7-(2,1,3-BenzoThiadiazole)]

PCPDTBT

Material Specifications

Elektronic Specifications

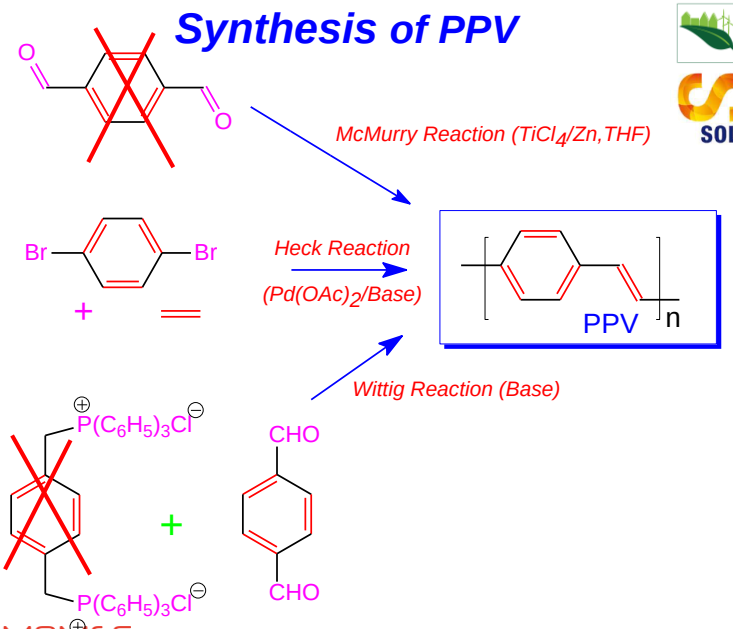
- **Low Defect Level in Conjugated System**
- **High Mobility of Charge Carriers**
- **Appropriate Electrochemical properties (E_{ox} and E_{red})**
- **High Thermal Stability of the Conjugated System**
- **(some cases) Supramolecular Order**

Material Specifications

Polymer Specifications

- **Simple Monomer Synthesis (Scalability!)**
  - **Po R. et al., Macromolecules (2015) 48 (3), pp 453–461**
- **Straightforward polymerization chemistry**
- **Processible from common solvents**
- **Sufficient High Molecular Weight (M_w > 30 000)**
- **Reasonable polydispersity (1 < PD < 3)**
- **High Thermal Stability**

Synthesis of PPV



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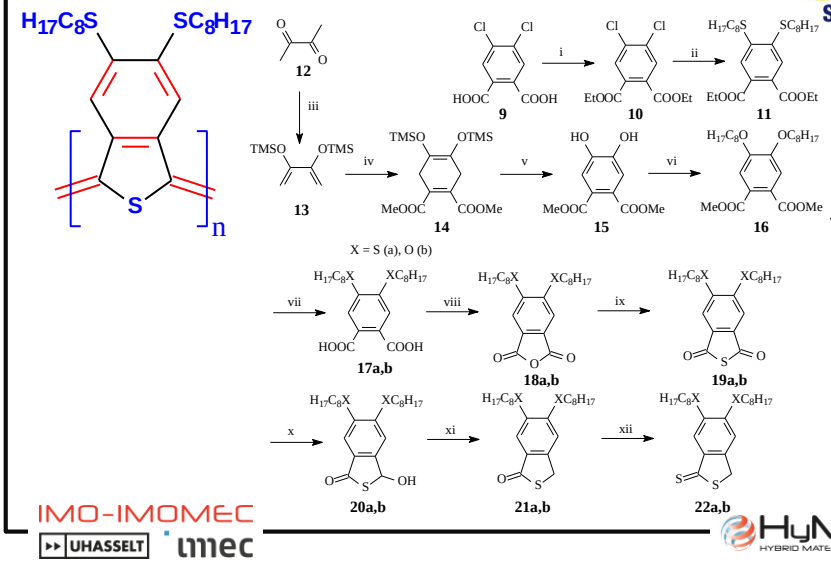
HyMaD HYBRID MATERIALS DESIGN

Low Band Gap Conjugated Polymers



IMO-IMOMEC UHASSELT imec

HyMaD HYBRID MATERIALS DESIGN

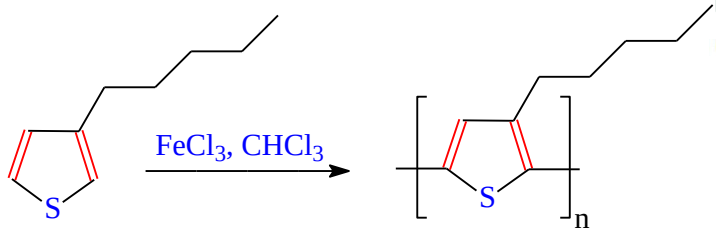
Outline Part 3

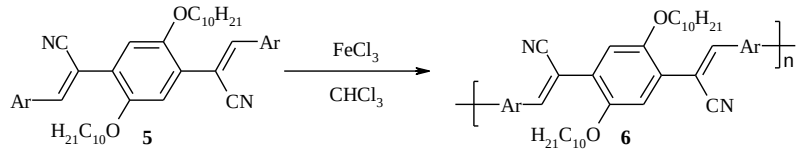
- Introduction
- Material specifications
- Direct synthetic routes
- Precursor routes

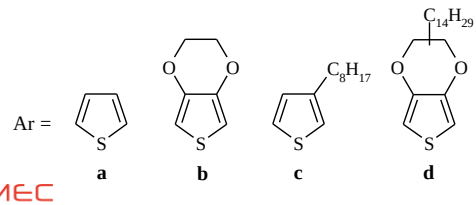
Outline Part 3

- Direct synthetic routes
  - Oxidative polymerization
  - McCullough method (based on Kumada coupling)
  - Rieke Method (based on Negishi coupling)
  - Suziki coupling
  - Stille and Sonogashira coupling
  - Yamamoto Coupling
- Precursor routes

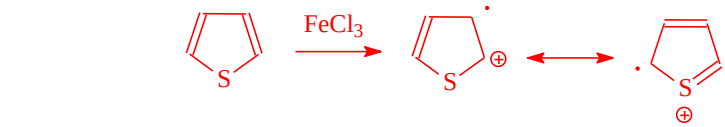
Oxidative Polymerization

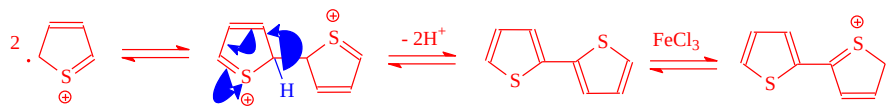


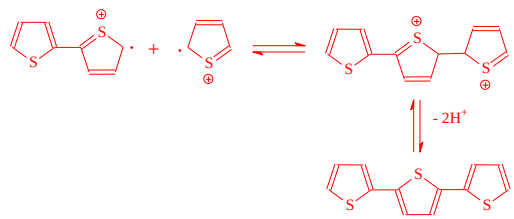




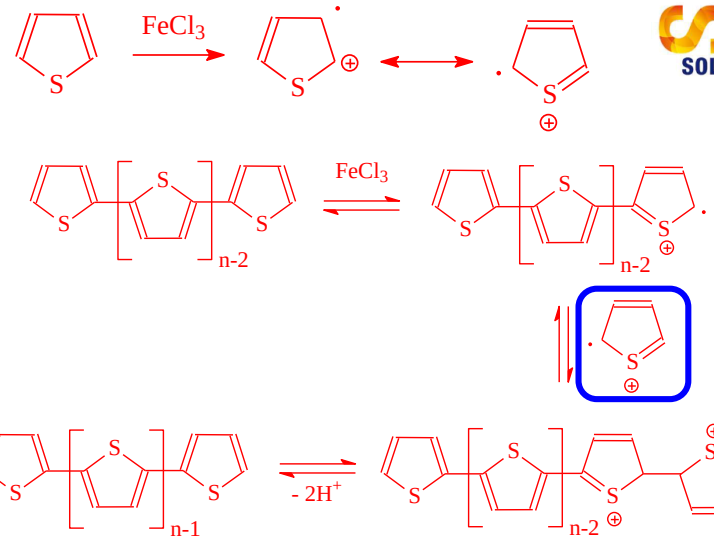
Oxidative Polymerization





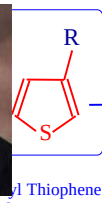


Oxidative Polymerization

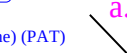


Regio-Regular Conjugated Polymers

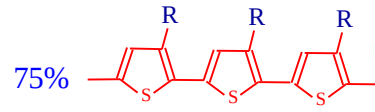
Nobel prize 2010 Chemistry

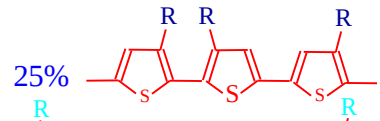


l Thiophene) (PAT)

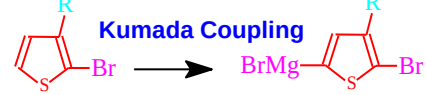


a.





Kumada Coupling



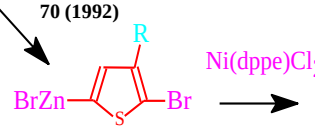
b.

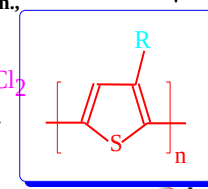
Negishi Coupling

Chen T-A., Rieke R. D.; J. Am. Chem. Soc., 114, 10087 (1992)

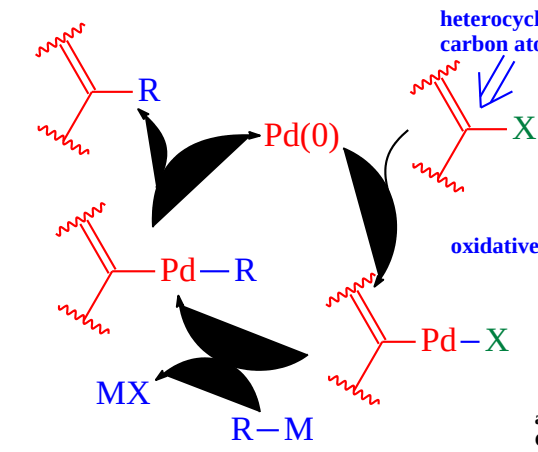
> 98% Regioregular

McCullough R. D., Lowe R.D.; J. Chem. Soc. Chem. Commun., 70 (1992)





Mechanism of cross-coupling



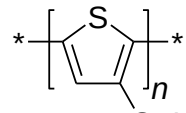
a. Osaka and R. D. McCullough, Acc. Chem. Res., 41, 1202-1214 (2008)

b. E. L. Lanni and A. J. McNeil, J. Am. Chem. Soc. 131, 16573-16579 (2009)

Regioregular P3ATs

Rieke coupling

'P3HT' = P36T



P3*m*T C_mH_{2m+1}

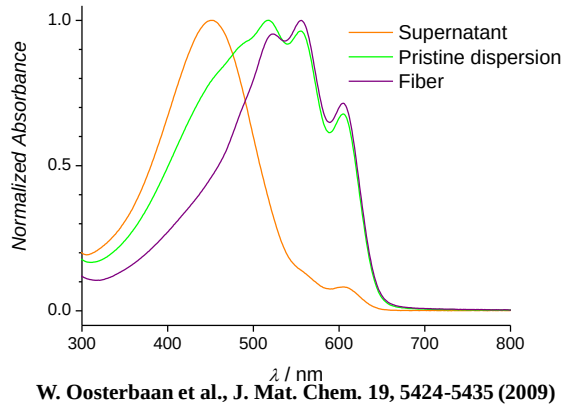
		GPC (MW *vs* PS)			^{1}H-NMR	UV-Vis	DSC
m	Yield %	M_n /10^3	M_w /10^3	*PD*	*RR*	λ_{max} / nm ($CHCl_3$)	T_m / °C (peak)
3		-	-	-	96.1		290
4	75	19.5	44.7	2.29	96.5		281
5	79	16.7	32.3	1.93	94.5	451	249
6	80	23.7	42.6	1.80	94.5	450	234
7	67	24.4	39.9	1.64	97	451	198
8	73	28.0	46.5	1.66	97	451	210
9	50	25.9	37.8	1.46	98	449	187

W. Oosterbaan et al., J. Mat. Chem. 19, 5424-5435 (2009)

Fiber formation & isolation

Example: 0.5 wt % P35T in p-Xylene:

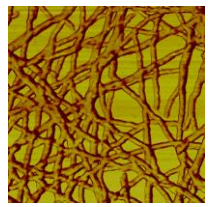
1. Dissolve at 80 ° C → clear orange solution
2. Slowly cool to room temperature → colour changes to dark red
3. Isolation by centrifugation



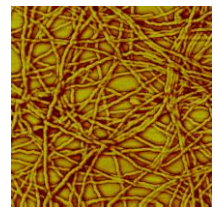
W. Oosterbaan et al., J. Mat. Chem. 19, 5424-5435 (2009)

AFM (tapping mode, 1 x 1 μm)

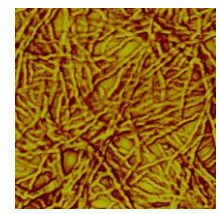
P33T



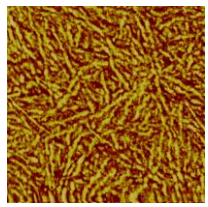
P34T



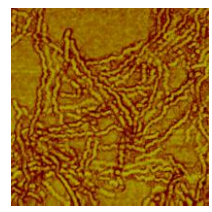
P35T



P37T



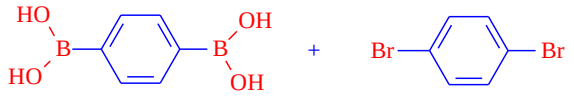
P39T



Fiber sizes:
Height: 5—10 nm
Width: 20 nm
Length: 0.5—4 μm

W. Oosterbaan et al., J. Mat. Chem. 19, 5424-5435 (2009)

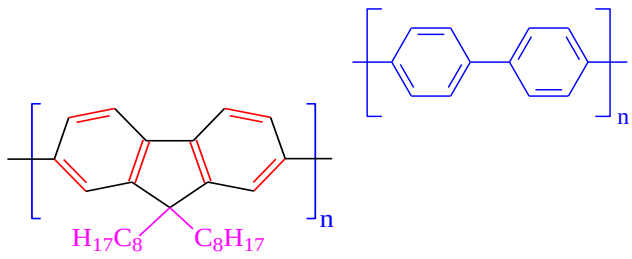
Poly(p-Phenylene) Derivatives



Suzuki Coupling

K_2CO_3

$Pd(PPh_3)_4$



Poly(dioctyl-fluorene) (PDOF)

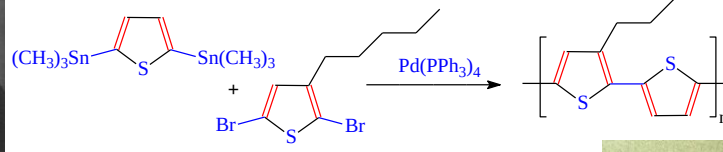
Nobel prize 2010 Chemistry

M. Seki, Synthesis 18, 2975-2992 (2006)

Other cross-couplings

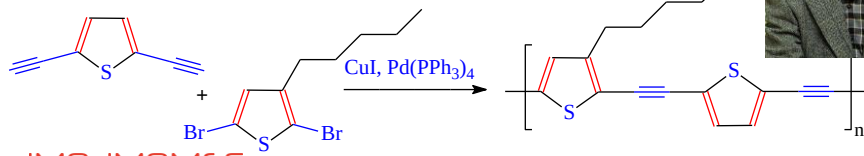
Stille cross-coupling

Cordovilla C. et al., ACS Catal., (2015) 5 (5), 3040–3053



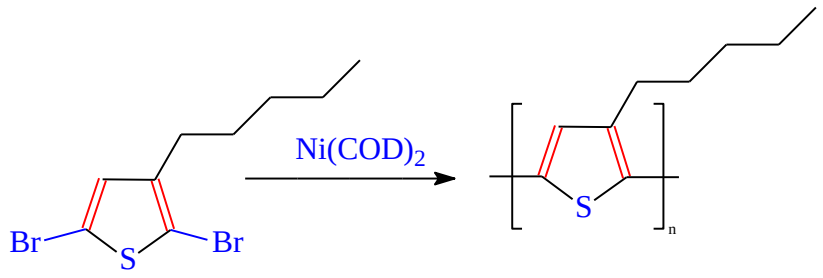
Sonogashira cross-coupling

M. Seki, Synthesis 18, 2975-2992 (2006)



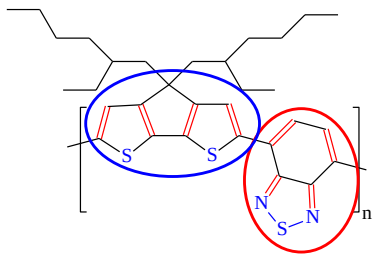
Other cross-couplings

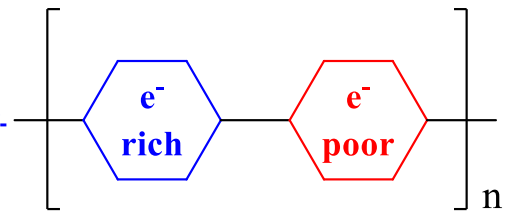
Yamamoto cross-coupling



N. Blouin and M. Leclerc, Acc. Chem. Res. 41 (9), 1110-1119 (2008)

Low Bandgap Polymers?





Poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-CycloPenta[2,1-b;3,4-b']-DiThiophene)-*alt*-4,7-(2,1,3-BenzoThiadiazole)]

PCPDTBT

Bundgaard, E., Krebs, F. C., *Sol. Energy Mater. Sol. Cells* 2007, *91*, 954

Low Bandgap Polymers?

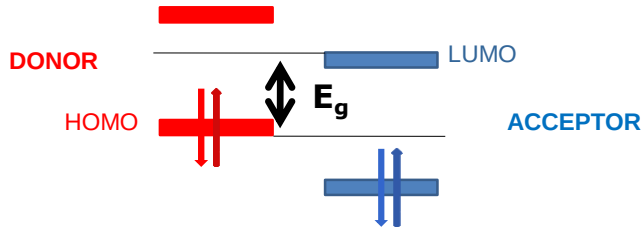
Design strategy for low bandgap: DONOR-ACCEPTOR COPOLYMERS

Increase the double bond character of the single bonds

– D – A – D – A – D – A – ⟷ – D^+ = A^- – D^+ = A^- – D^+ = A^- –

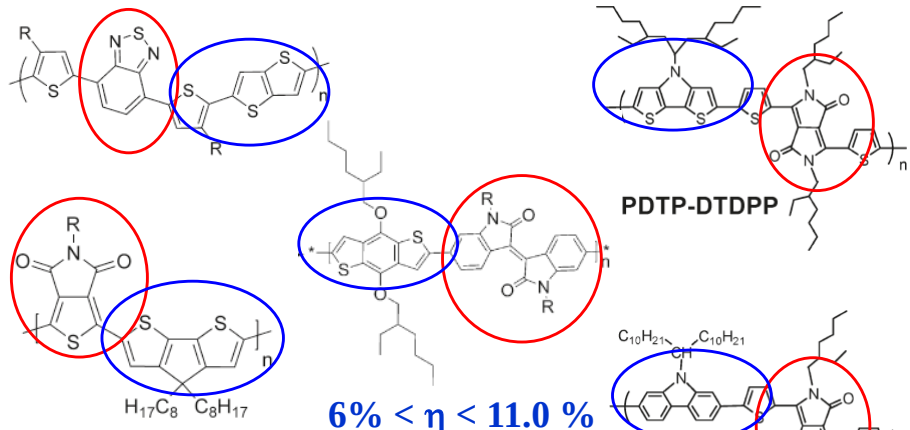
Reduction of the bond length alternation

Lowering of the bandgap E_g



Havinga, E. E.; Tenhoeve, W.; Wynberg, H. "A new class of small band-gap organic polymer conductors": Polymer Bulletin (1992) 29 (1-2) p 119-126

Low Bandgap Polymers?



$6\% \leq \eta \leq 11.0\ \%$

J. Roncali , Acc Chem Res (2009) 42 (11), 1719-1730

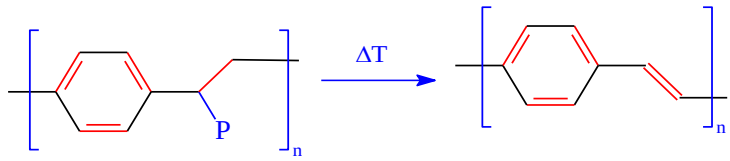
Outline Part 3

- Direct synthetic routes
  - Oxidative polymerization
  - McCullough method → *PolyThiophene Derivatives*
  - Rieke Method
  - Suziki coupling
  - Stille and Sonogashira coupling → *LBG Derivatives*
  - Yamamoto Coupling
- Precursor routes

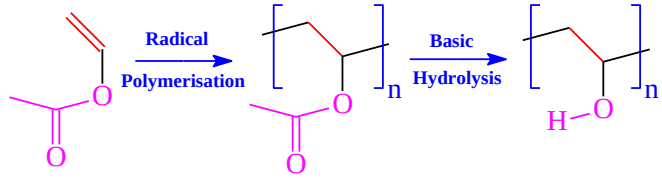
Outline Part 3

- Introduction
- Material specifications
- Direct synthetic routes
- Precursor routes

Precursor Routes toward Conjugated Polymers



Poly(Phenylene Vinylene) (PPV)



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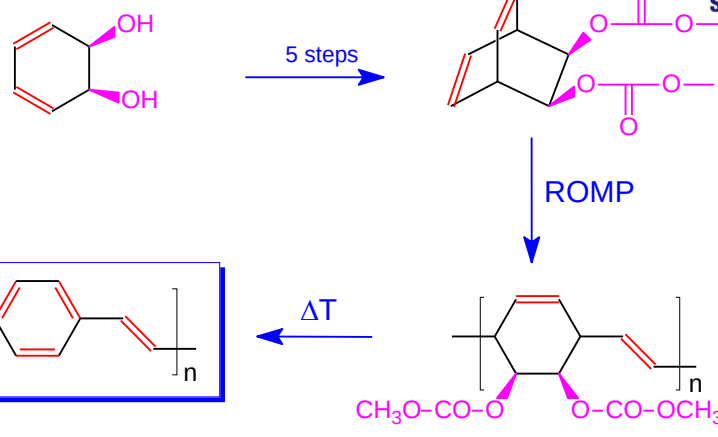
Precursor Polymers

Grubbs PPV Precursor route

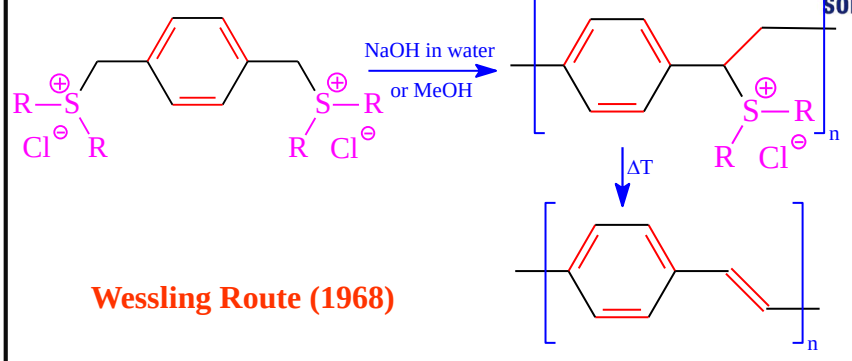


V. P. Conticello et al, J. Am. Chem. Soc., 114, 9708-9710 (1992)

IMO-IMOMEC UHASSELT imec

HyMaD HYBRID MATERIALS DESIGN

Polymerisation Reactions of Para-Quinodimethane Systems

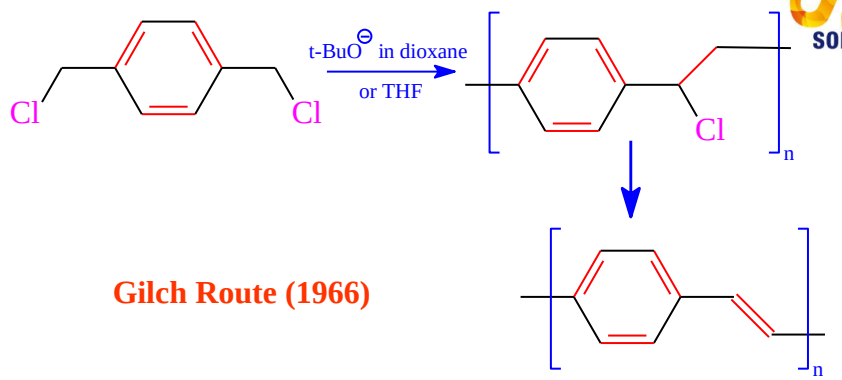


Wessling Route (1968)

Poly(Phenylene Vinylene) (PPV)

R. A. Wessling, J. Polym. Sc.; Polym. Symp., 72, 55 (1985)

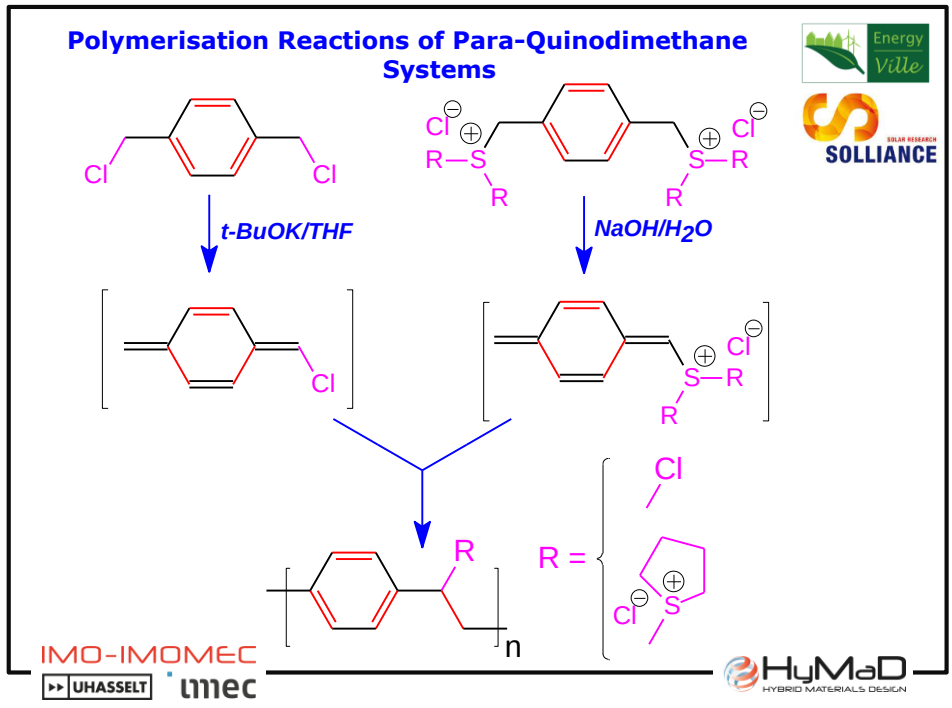
Polymerisation Reactions of Para-Quinodimethane Systems

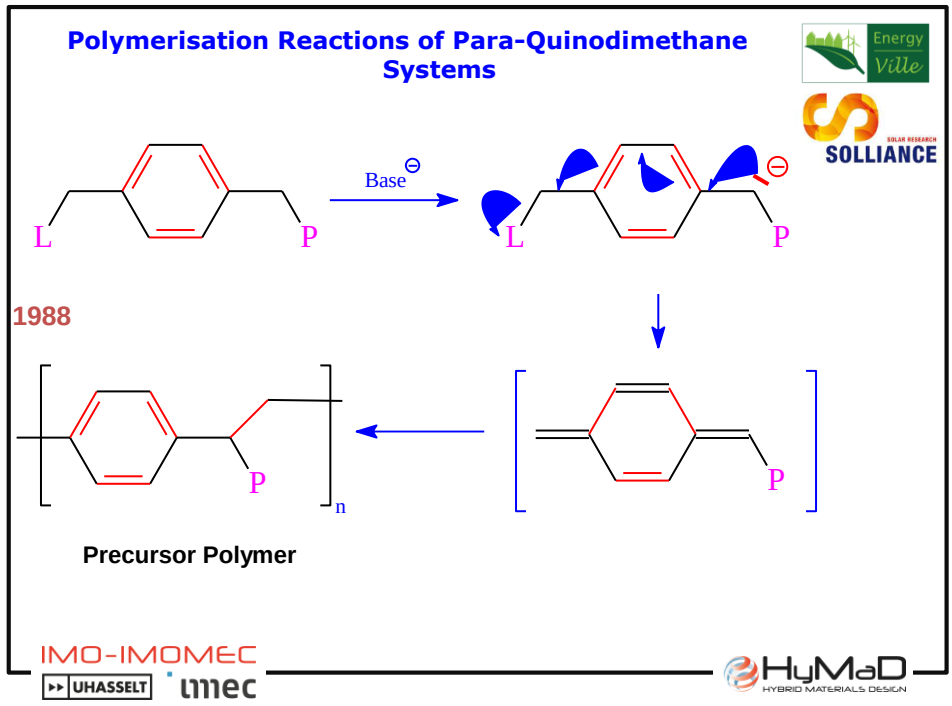


Gilch Route (1966)

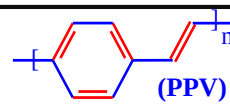
Poly(Phenylene Vinylene) (PPV)

H. G. Gilch, W. L. Wheelwright; J. Polym.Sc.; part A, 4, 1337 (1966)


Polymerisation Reactions of Para-Quinodimethane Systems
Cl
Cl
t-BuOK/THF
NaOH/H2O
R
n
R =
Cl
S
IMO-IMOMEC
UHASSELT
imec
HyMaD
HYBRID MATERIALS DESIGN
Energy Ville
SOLLIANCE

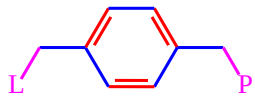

Polymerisation Reactions of Para-Quinodimethane Systems
Base
L
P
1988
n
Precursor Polymer
IMO-IMOMEC
UHASSELT
imec
HyMaD
HYBRID MATERIALS DESIGN
Energy Ville
SOLLIANCE

Synthesis

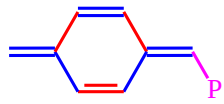


(PPV)

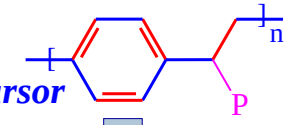
Precursor Routes - General Scheme



STEP 1

p-QM 

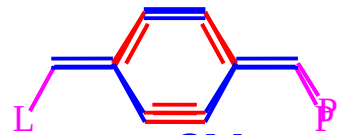
STEP 2



Precursor

STEP 3

Conjugated Polymer



p-QM **L = leaving group**

P = polariser

Gilch (1966): L = P = Cl

Wessling (1968): L = P = $SR_2^+X^-$

Sulfinyl (1992): L = Cl ; P = S(O)R

Xanthate (1995): L = P = SC(S)OR

Dithiocarbamate (2003): L = P = $SC(S)NR_2$

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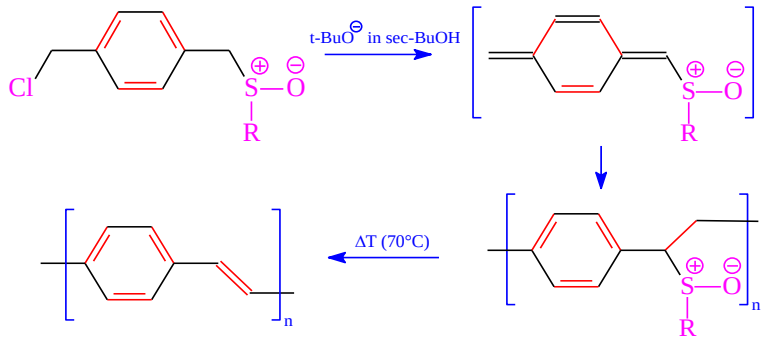
Polymerisation Reactions of Para-Quinodimethane Systems



Poly(Phenylene Vinylene) (PPV)

M_w = 200.000; Yield = 80%

Sulphinyl Route (1992)

F. Louwet, D. Vanderzande, J. Gelan, J. Mullens; Macromolecules; 1995, 28, 1330

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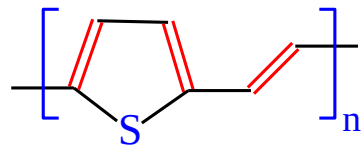
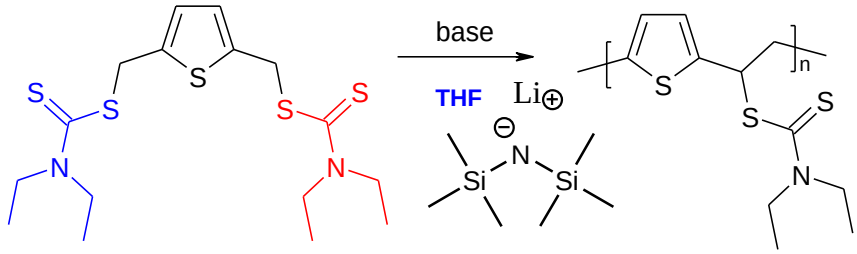
Dithiocarbamate Precursor Route



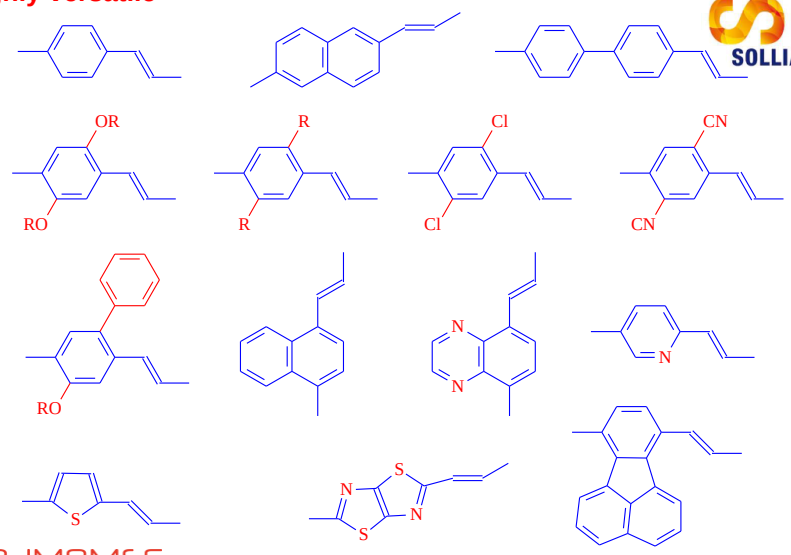
Poly(2,5-Thienylene Vinylene) (PTV)



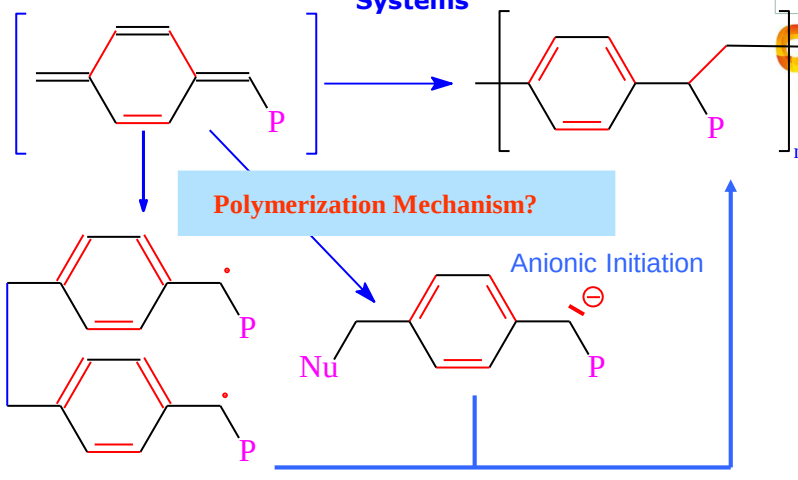
H. Diliën et al., Macromolecules 43, 10231-10240 (2010)

Polymerisation Reactions of Para-Quinodimethane Systems

Highly versatile



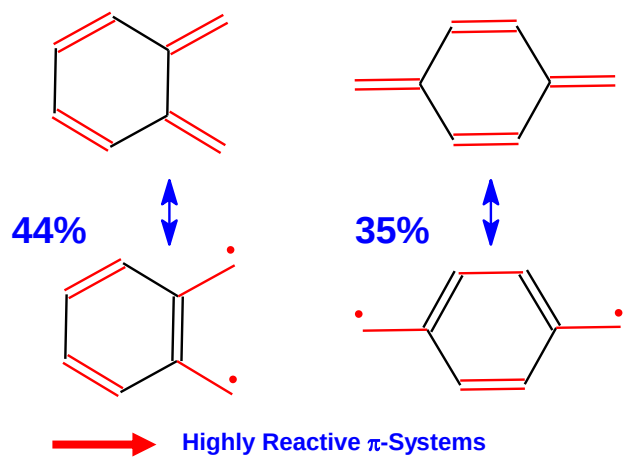
Polymerisation Reactions of Para-Quinodimethane Systems



L. Hontis et al., Macromolecules 36, 3035-3044 (2003)

I. Cosemans et al. , Macromolecules 44, 7610-7616 (2011)

Ortho and Para-Quinodimethane Systems



Highly Reactive π-Systems

P. C. Hiberty, P. Karafiloglou; Theoretica Chimica Acta; 1982, 171-177.

Conclusions

- Several very reliable synthetic methods exist toward the synthesis of conjugated polymers
- Typically they are versatile, give rise to acceptable Mn
- Give rise to low defects levels in the chemical structure
- In some cases efforts to avoid residues of catalysts is an issue
- Purification of the resulting polymer is of great importance <=> materials should be used in electronics

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Lecture Schedule 31th of May 2024

10:15 - 11:00	Lecture 1
11:00 - 11:10	short break
11:10 - 11:55	Lecture 2
11:55 - 12:05	short break
12:05 - 12:50	Lecture 3
12:50 - 13:50	Lunch
13:50 - 14:35	Lecture 4
14:35 - 14:45	short break
14:45 - 15:30	Lecture 5
15:30 - 15:40	short break
15:40 - 16:25	Lecture 6

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