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Polymers supported Electroactive Species for Antifouling Applications

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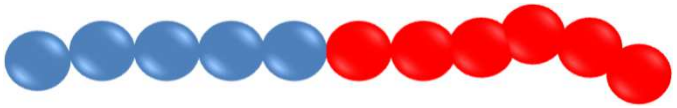
AF-ElectroCoatings project
http://af-electrocoatings.univ-tln.fr

Polymers supported Electroactive Species for Antifouling Applications

Frédéric GOHIER

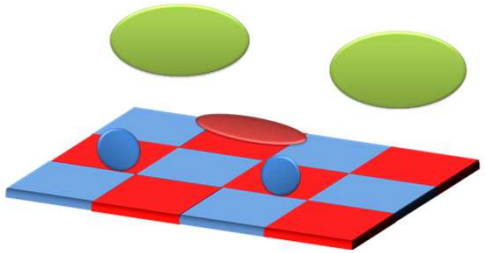
18th ICMCF TOULON, 19- 24th June 2016

Strategy for AF-ElectroCoatings :



Block copolymers

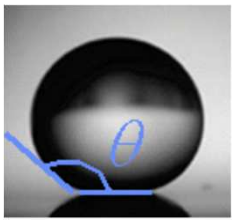
Self-assembling →

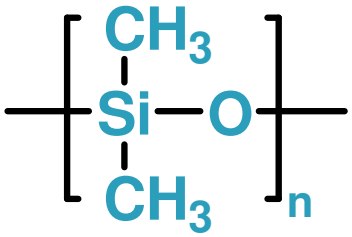


Nano-structuration → Reduced adhesion

➢ Need of two blocks chemically different which lead to different surface energies

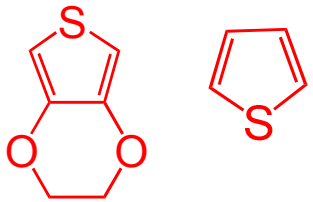
➢ Low surface energy
➢ Low adhesion force





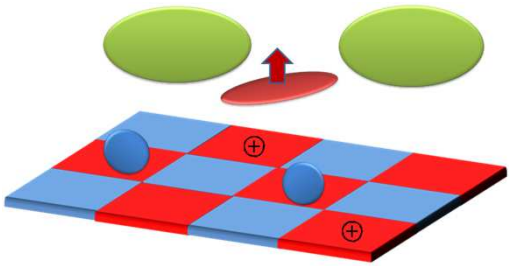
[11]Duong *et al.* Polymer 2014, 55, 39.

➢ Redox systems based on

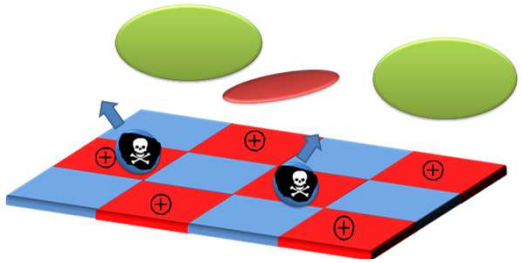


➢ **Acivation** by electrical potential application
➢ Charges transfer from surfaces to microorganisms

[10]T. Matsunaga *et coll. Biotechnol Bioeng* 1998, *59*, 374.

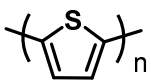


Moderate oxidation → Desorption

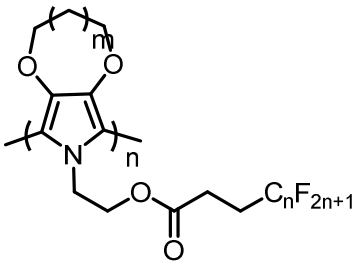


Strong oxidation → Death and cleaning

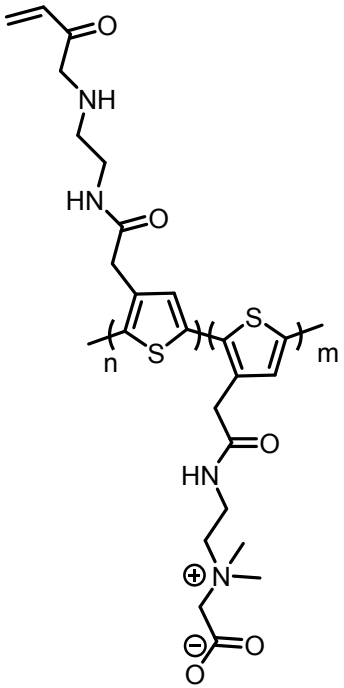
Research on Polymers for Antifouling



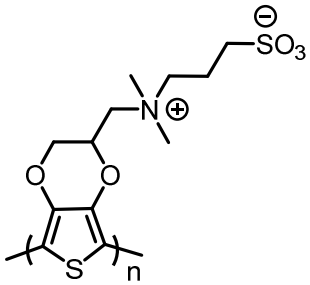
Pernites, R. B.; Santos, C. M.; Maldonado, M.; Ponnapati, R. R.; Rodrigues, D. F.; Advincula, R. C. *Chem Mater* **2012**, *24*, 870.



Darmanin, T.; Guittard, F. *J. Am. Chem.Soc.* **2009**, *131*, 7928.



Cao, B.; Tang, Q.; Li, L.; Lee, C.-J.; Wang, H.; Zhang, Y.; Castaneda, H.; Cheng, G. *Chemical Science* **2015**, *6*, 782.

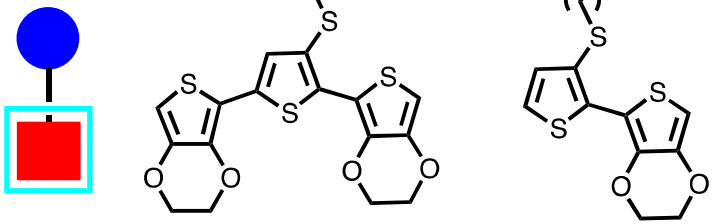


Cao, B.; Lee, C.-J.; Zeng, Z.; Cheng, F.; Xu, F.; Cong, H.; Cheng, G. *Chemical Science* **2016**, *7*, 1976.

Monomers Syntheses

Acrylic monomer

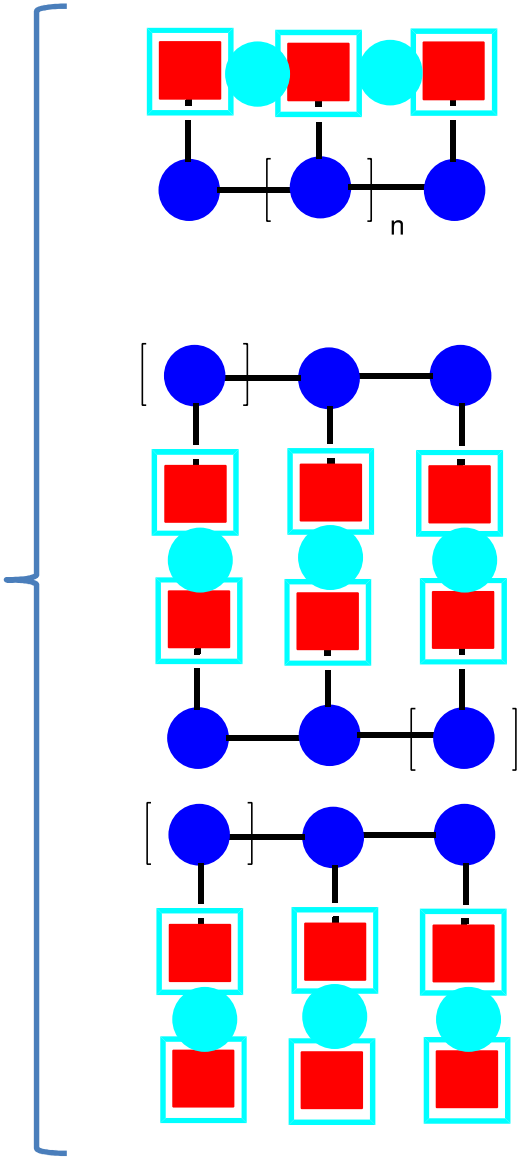
Thiophene moiety with or without EDOT



Polymerizable targets

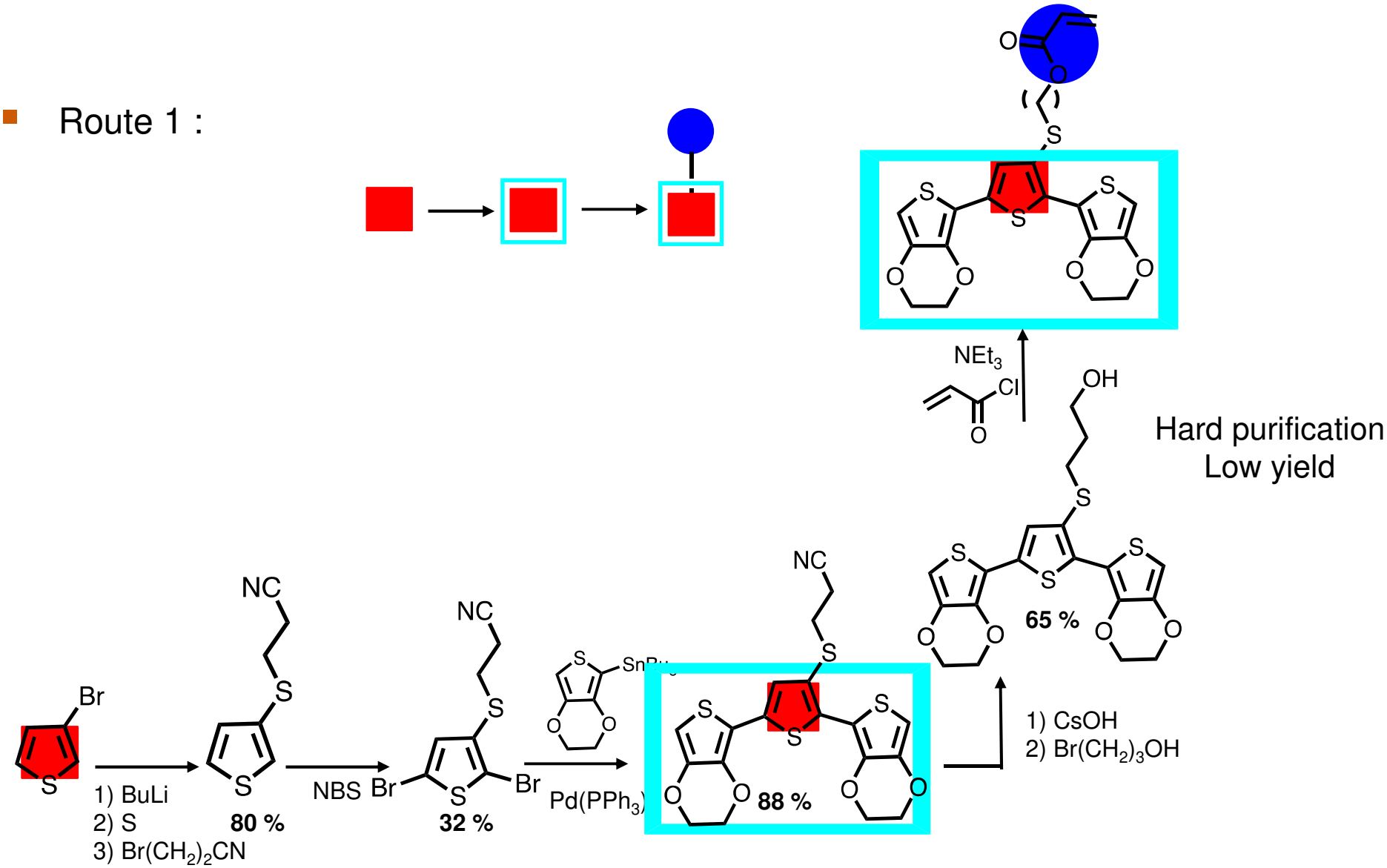
Other Target

Radical Polymerization and Polymerization by oxydation



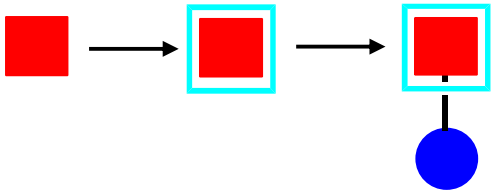
Monomers Syntheses

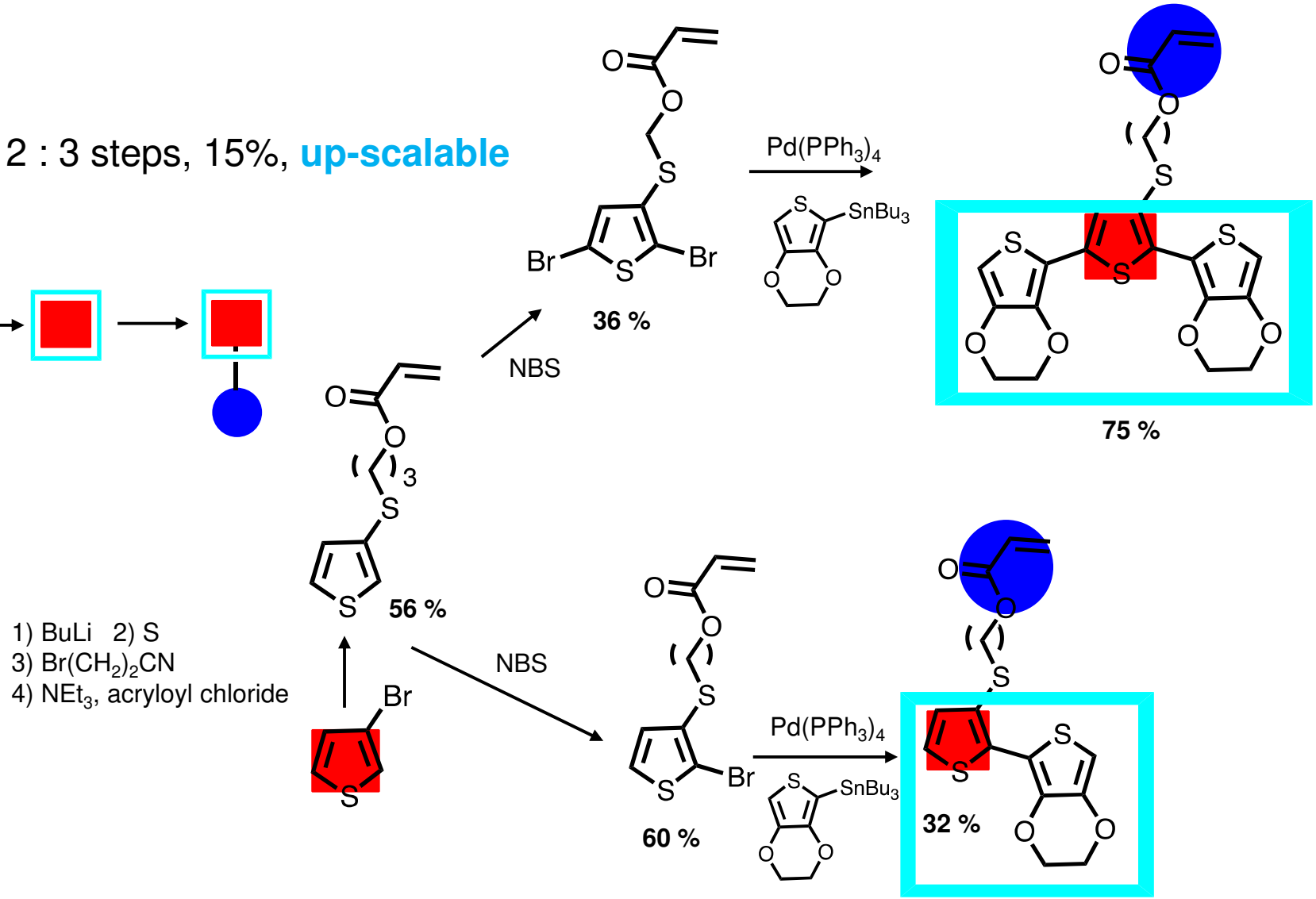
- Route 1 :



Monomers Syntheses

- Route 2 : 3 steps, 15%, **up-scalable**



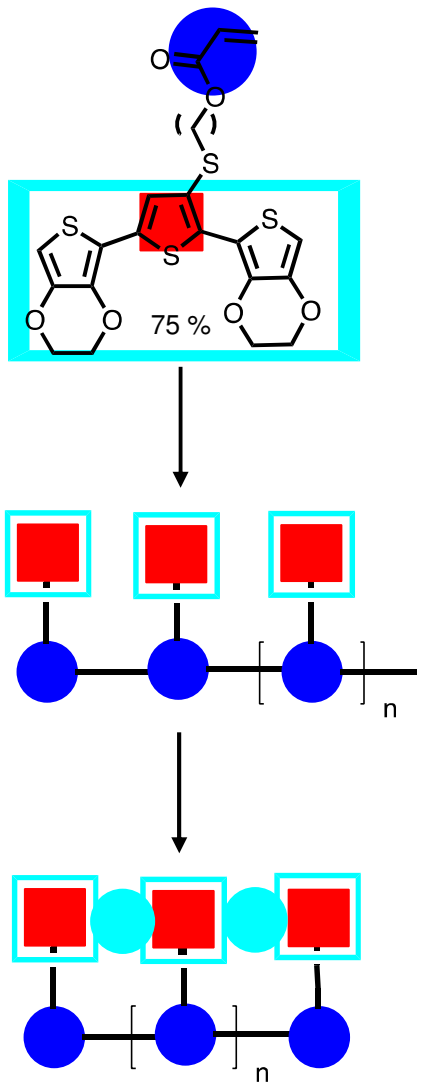


Conjugated polymer synthesis

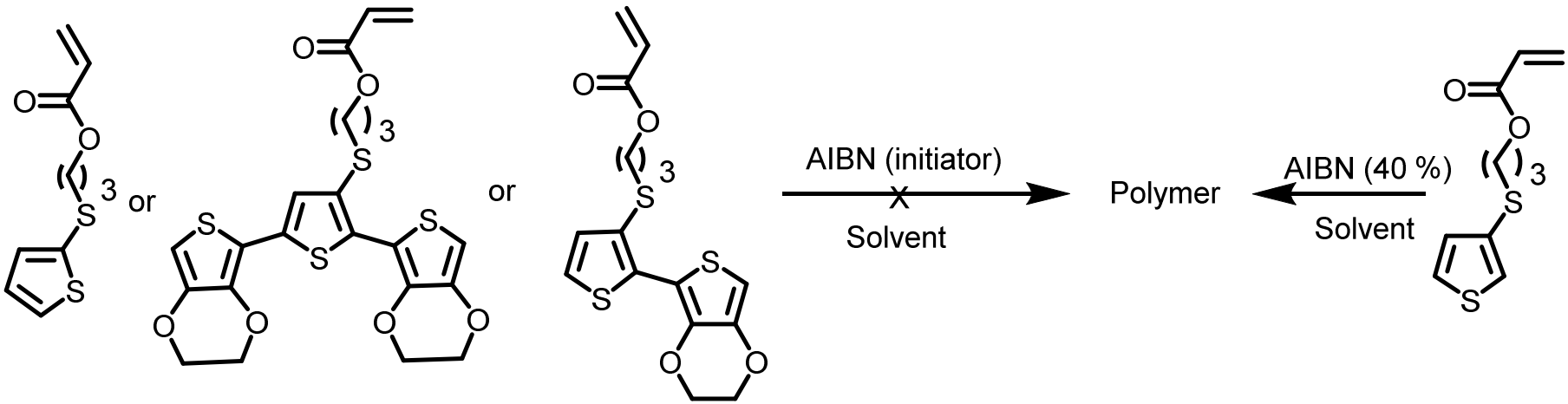
- **Two ways**

  - Polymers formation via radical polymerization of acrylate?

  - Obtention of conjugated polymer by electrochemical way?



Radical polymerization



- Starting monomers: radical transfer of H in α of S

  Very low yield

- Attempts realized by controlled radical polymerization (RAFT process) : idem

- Important amount of AIBN : Polymers of small size (low $\overline{Mn}$)

Envisaged solution: protection of α positions of thiophènes

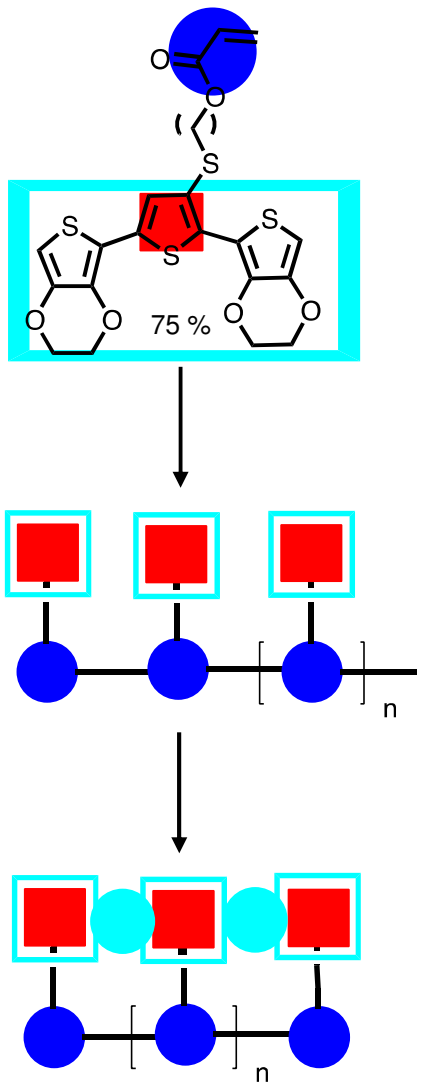
Conjugated polymer synthesis

- **Two ways**

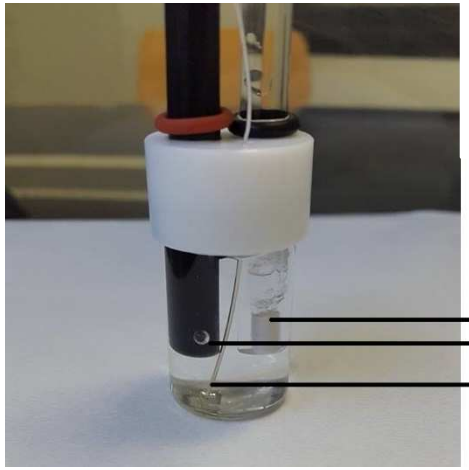
  - Polymers formation via radical polymerization of acrylate?

    Yes, but the obtained polymers possess low Mn with hight quantity of initiator

  - Obtention of conjugated polymer by electrochemical way?



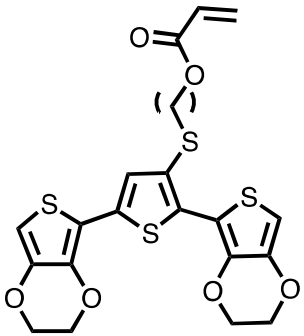
Electrochemistry

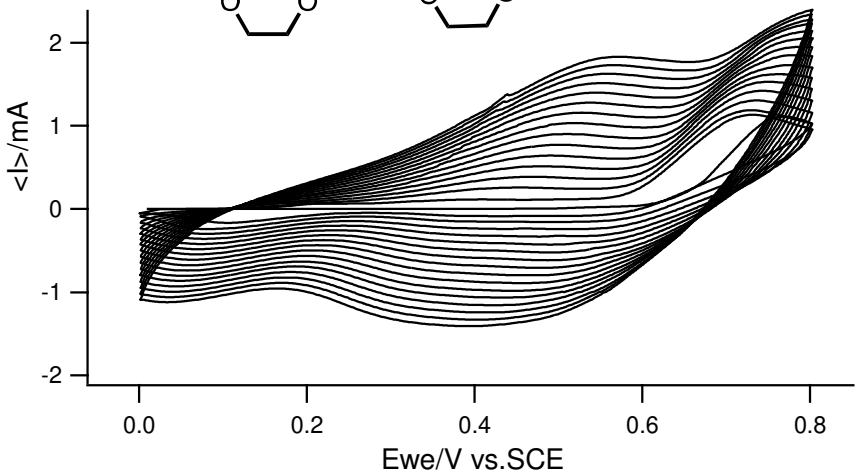


1- Saturated Calomel
2- Pt / Au / GC
3- Pt

1 Reference
2 Working Electrode
3 CE

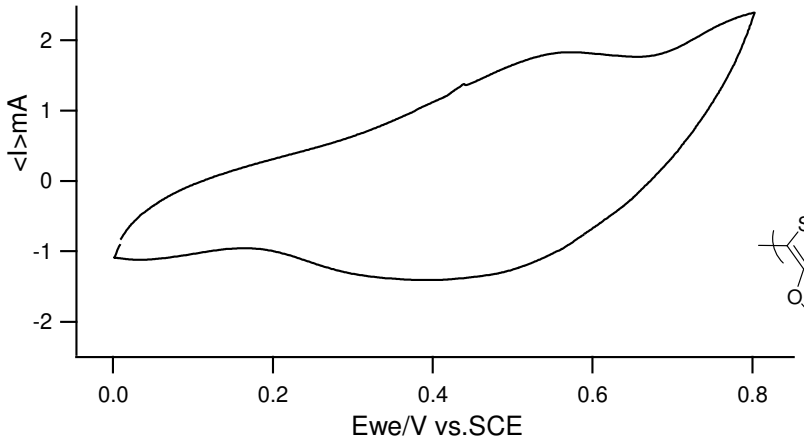
Oxidative polymerization on ITO

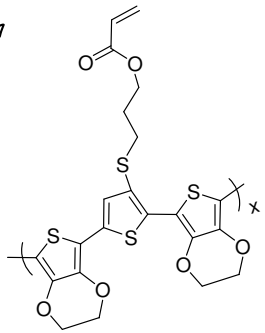




Cyclic voltamperometry in 0.1 M Bu_4NPF_6 in CH_3CN, 100 mV/s E we/V vs.SCE

Conjugated polymer response





Cyclic voltamperometry of conjugated polymer in 0.1 M Bu_4NPF_6 in CH_3CN, 100 mV/s E we/V vs.SCE

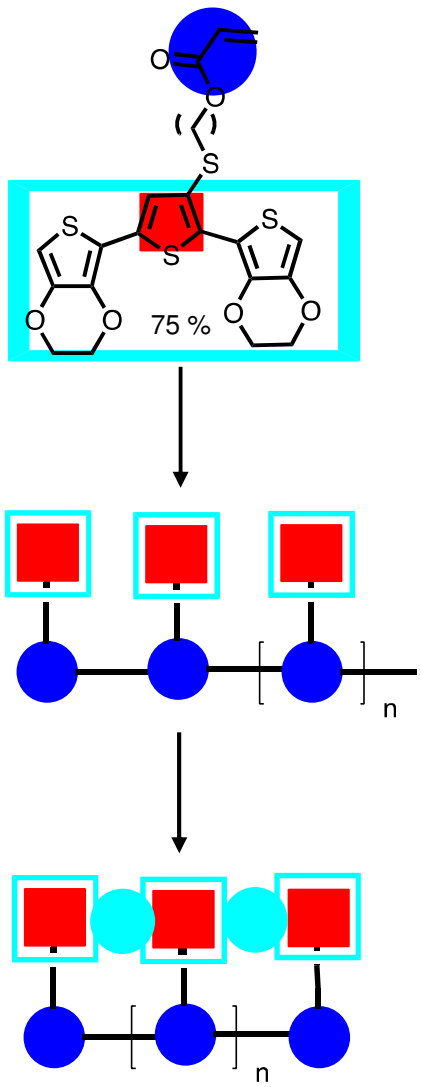
0,2 V < Electroactivity < 1V

Conjugated polymer synthesis

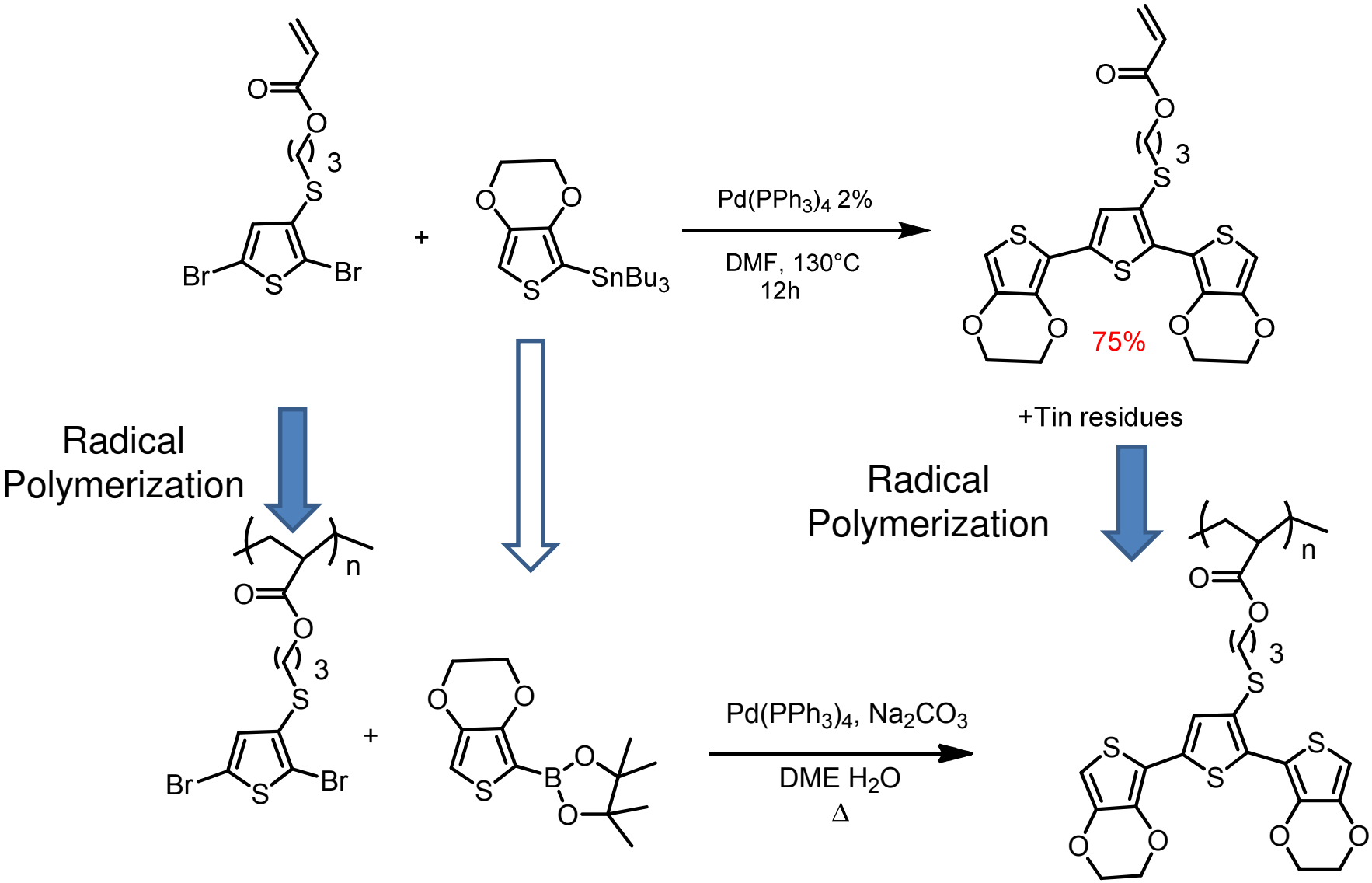
- **Two ways**

  - Polymers formation via radical polymerization of acrylate?
    Yes, but the obtained polymers possess Low Mn with hight quantity of initiator
    Solution: protection of α positions of thiophene

  - Obtention of conjugated polymer by electrochemical way? Yes, with an electroactivity domain between 0.2 and 1V.

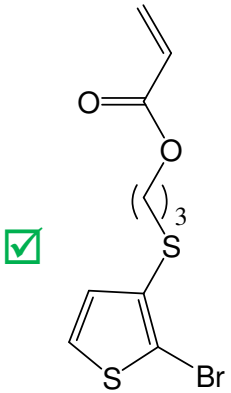


Polymerization of brominated intermediates

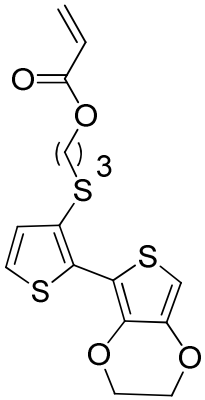


Polymerization of brominated intermediates

Abilities to polymerize by classical radical polymerization



1



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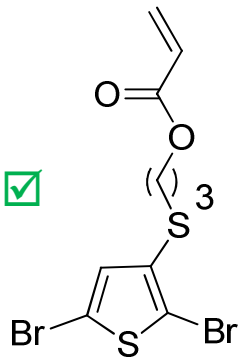

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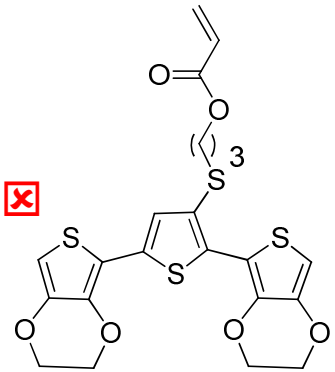

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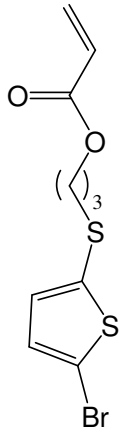

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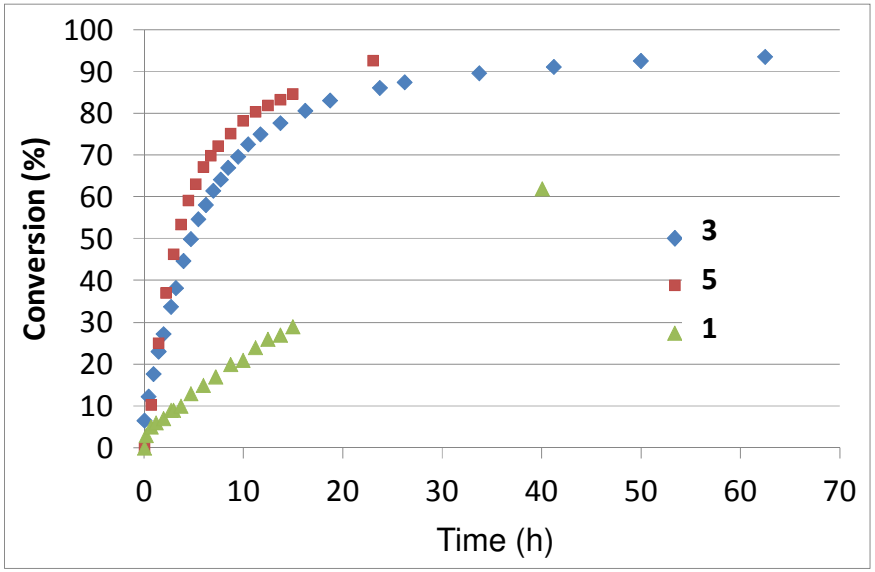


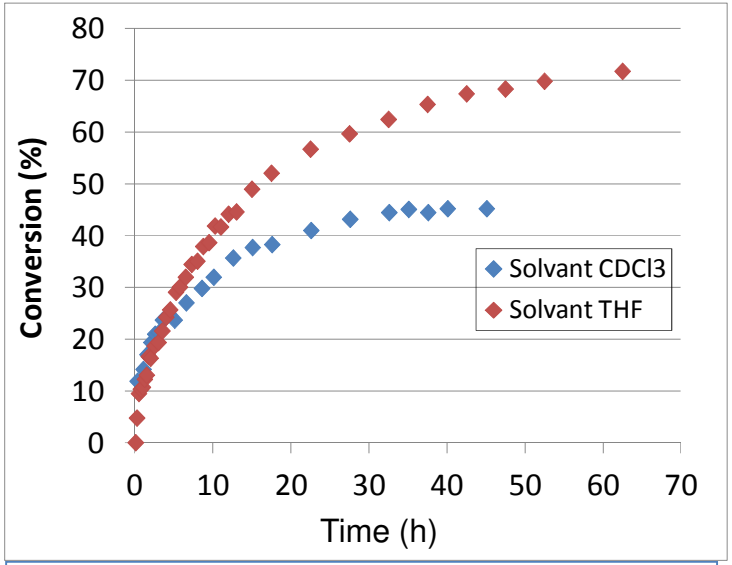
AIBN, T = 65°C

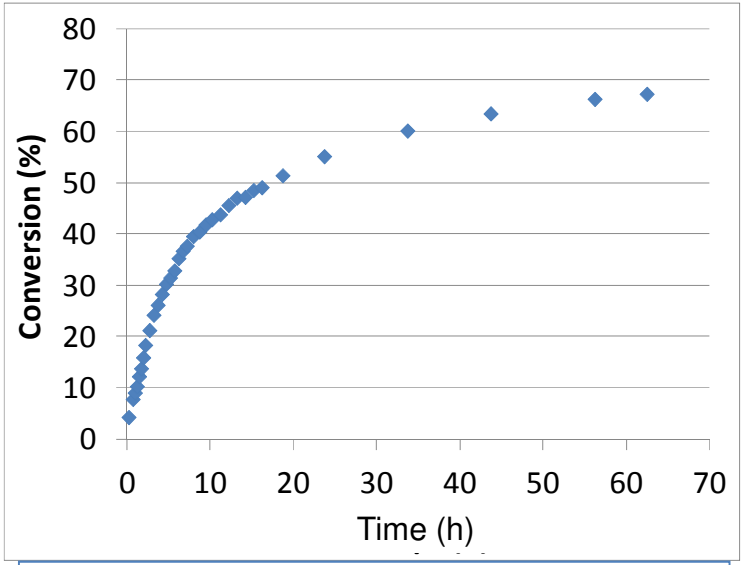
Solvent : THF-d_8

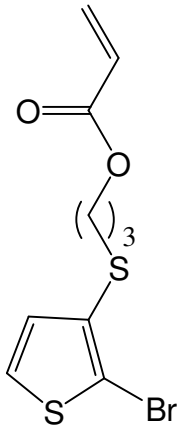
Polymerization of brominated intermediates

Abilities to polymerize by RAFT process

RAFT: Reversible Addition-Fragmentation chain transfer polymerization







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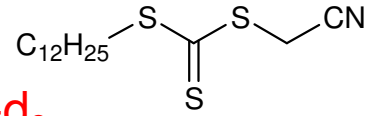
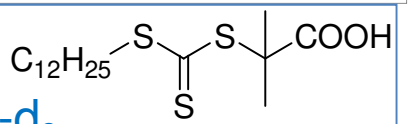
CTA : 

Solvent : THF-d_8

M_n (theo) : 5000 (g/mol)

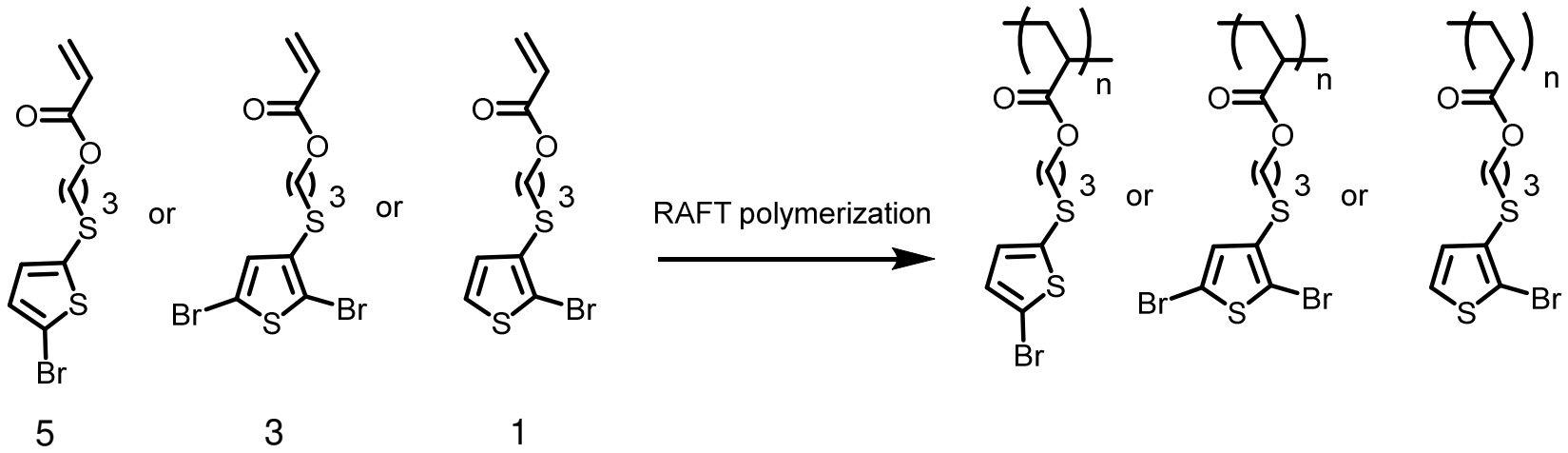
CTA : 

Solvent : THF-d_8

M_n (theo) : 5000 (g/mol)

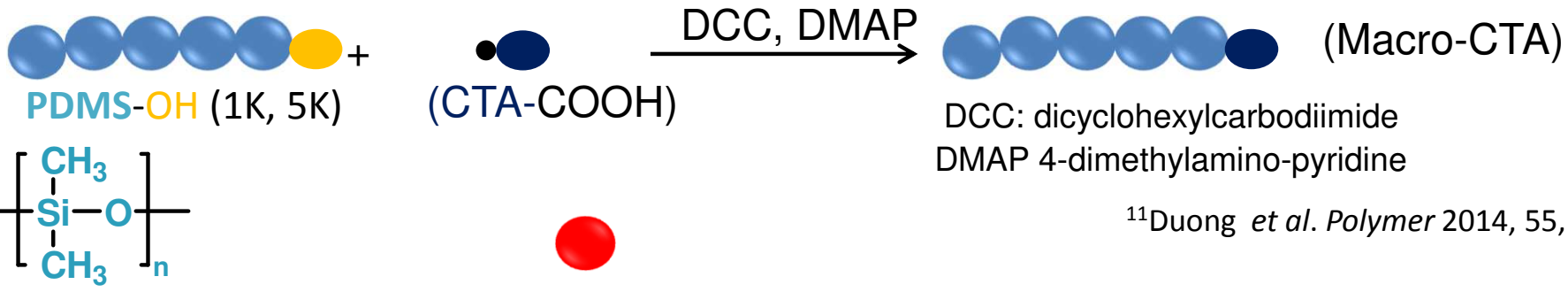
M_n (g/mol)			Ip
Calculated	RMN-^{1}H	TD-SEC	
3800	4100	4800	1,15

Polymerization of brominated intermediates

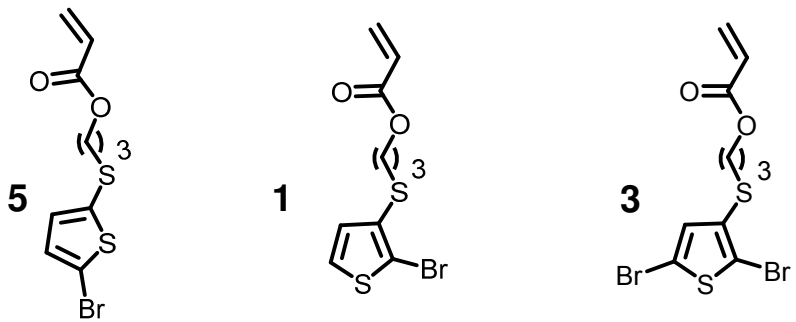


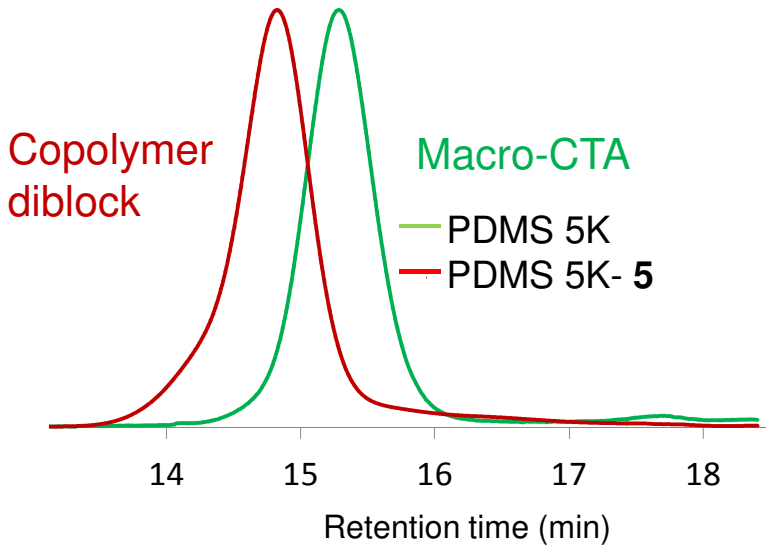
Monomer	Type	M_n (g/mol)	Ip	T_g (°C)
1	Homopolymer	5K ÷16K	< 1,4	-15 ÷ -12
3	Homopolymer	5K ÷ 28K	< 1,4	-9 ÷ -6
5	Homopolymer	5K ÷ 25K	< 1,4	-23 ÷ -18

Copolymer synthesis

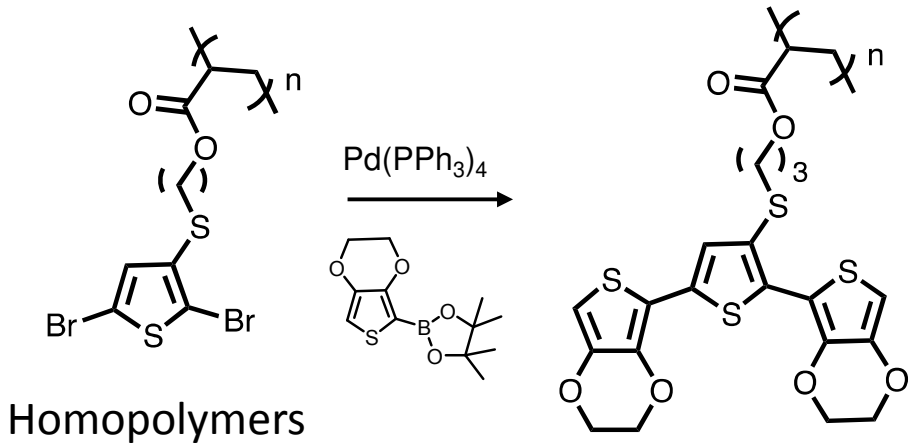


Copolymer based on	M_n (g/mol)	Ip	T_g (°C)	
			PDMS	2e bloc
1	7K-36,4K	1,2	-	-
3	16,8K	1,2	-126	-12
5	7K ÷ 21K	< 1, 3	-125	-24 ÷ -20





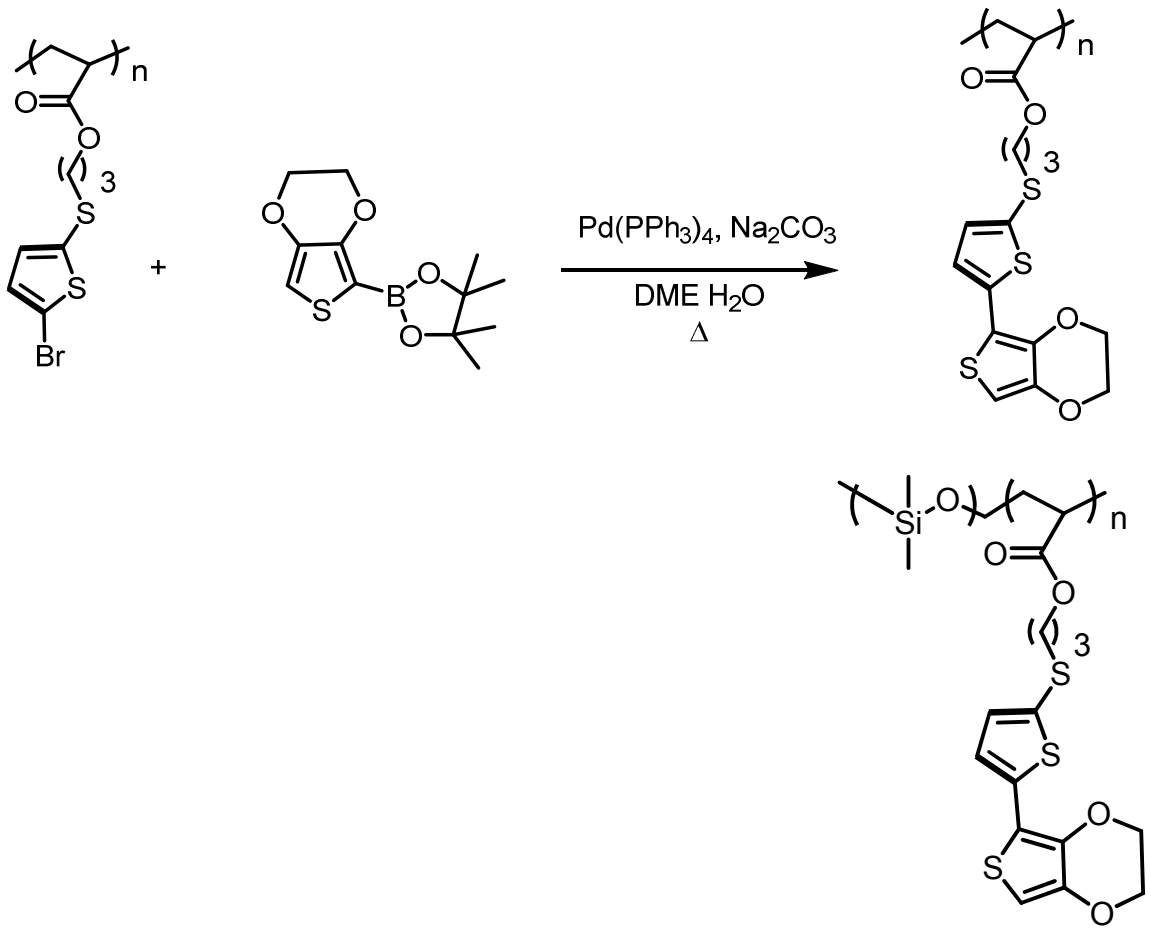
Postfunctionalization of copolymers



Homopolymers
Copolymers

→ Insoluble polymer/copolymer

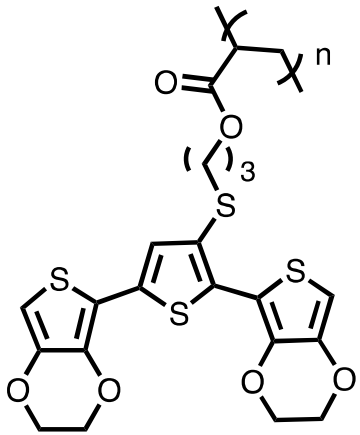
Postfunctionalization of copolymers

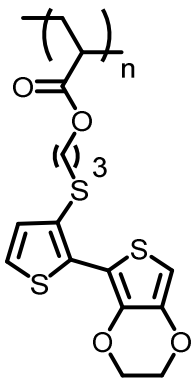


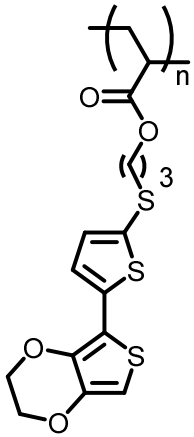
- Soluble polymers and copolymers

Conclusions

- Development of new materials with an acrylate backbone

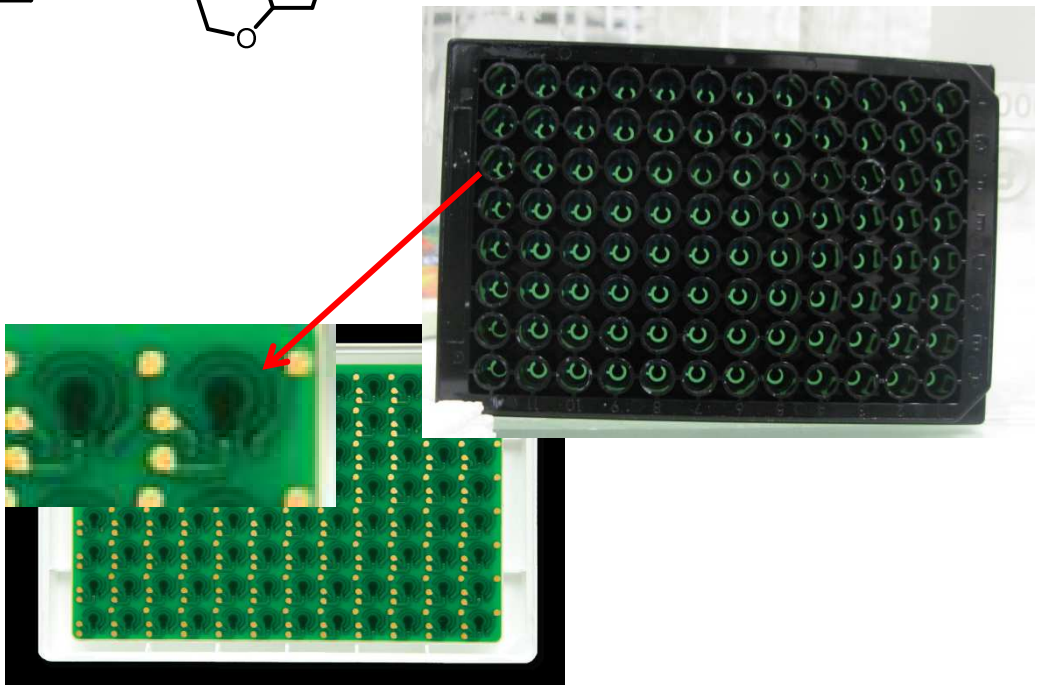






Homopolymers
Copolymers

- Electropolymerization



Perspectives:

- Antifouling tests
- Surfaces studies

➡ Presentation of Hugues Brisset

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