Self-healing copolymers as electrolytes for stretchable Li-ion microbatteries

Sébastien Maria

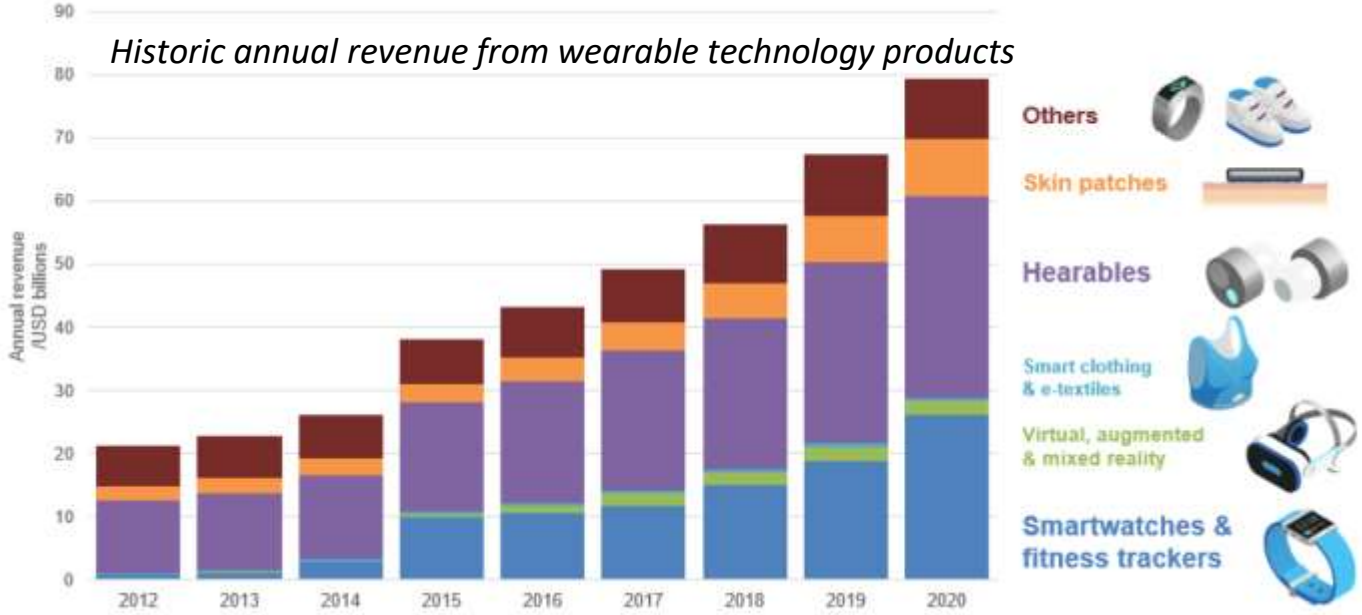
Clément Chambrial, Marion Rollet, Marc Ramuz, Thierry Djenizian, Didier Gigmes

19th February 2024


Paris
Marseille

Context: wearables technology

Historic annual revenue from wearable technology products



400 % annual revenue increased over the past ten years

Wearable insuline pomp

Heating clothes

PPE

SmartWatches

J. Hayward, Wearables Technology in 2021, A summary of Key Market Data and Trends, 2021

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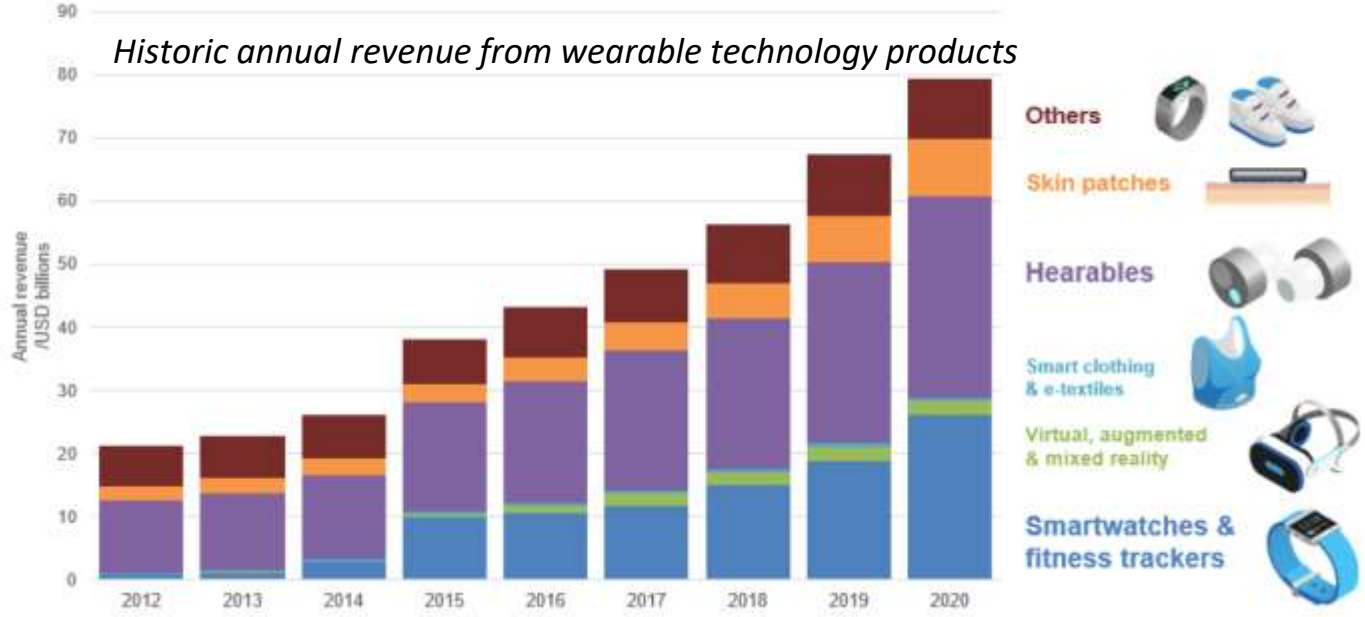

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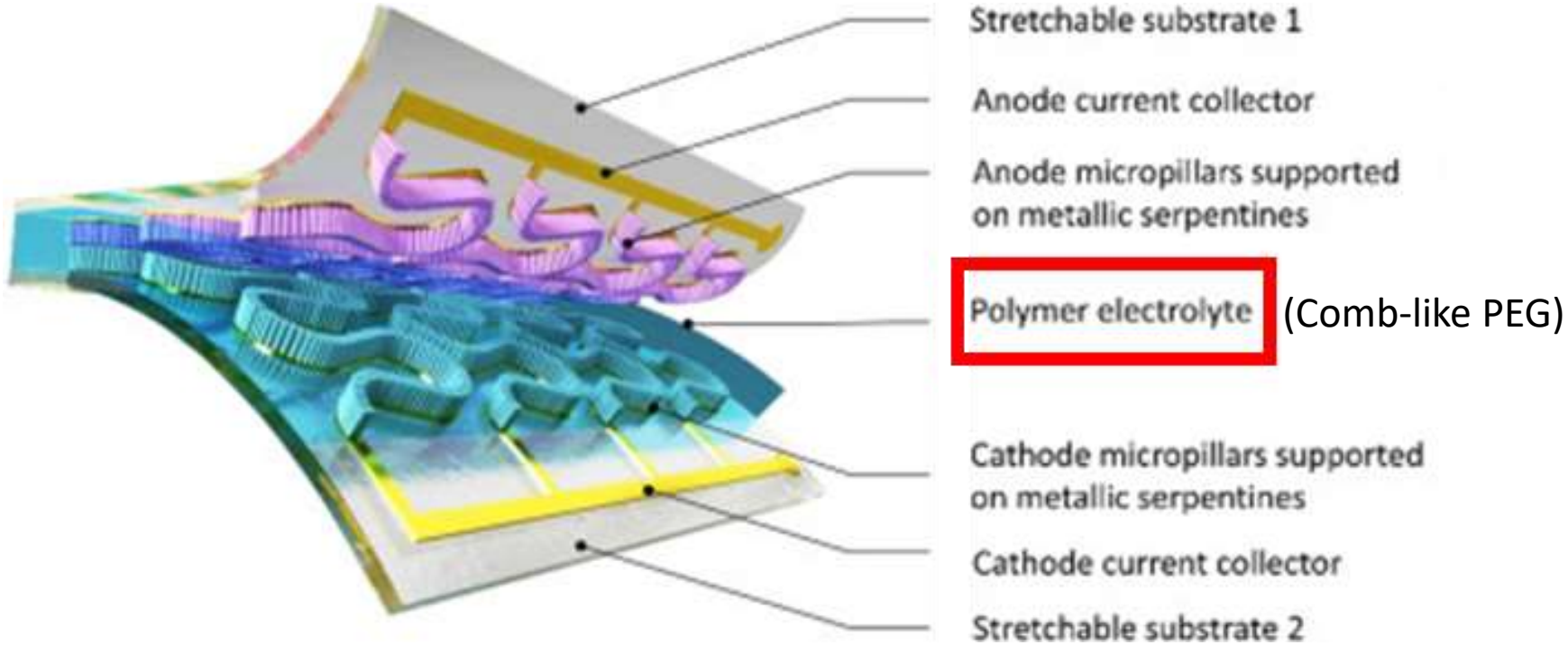
body conformable electronic bracelet with biological sensors powered by the stretchable microbattery

J. Hayward, Wearables Technology in 2021, A summary of Key Market Data and Trends, 2021

High Performance Stretchable Li-ion Microbatteries

Previous work: Stretchable substrate carrying micropillar electrodes separated by a polymer electrolyte



MINES Saint-Étienne

Thierry Djenizian

38APS

M. Nasreldin, R. Delattre, C. Calmes, M. Ramuz, V. A. Sugiawati, S. Maria, J.-L. de Bougrenet de la Tocnaye and T. Djenizian l (2020), Energie Storage Materials, 33, 108-15

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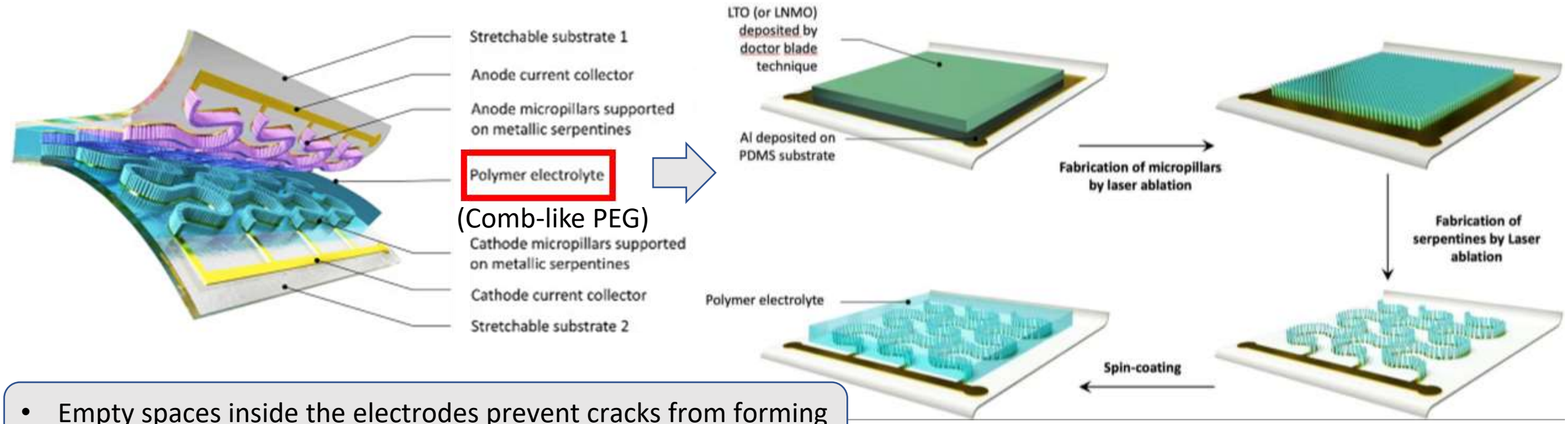

- Empty spaces inside the electrodes prevent cracks from forming
- 3D electrodes increase energy and power density

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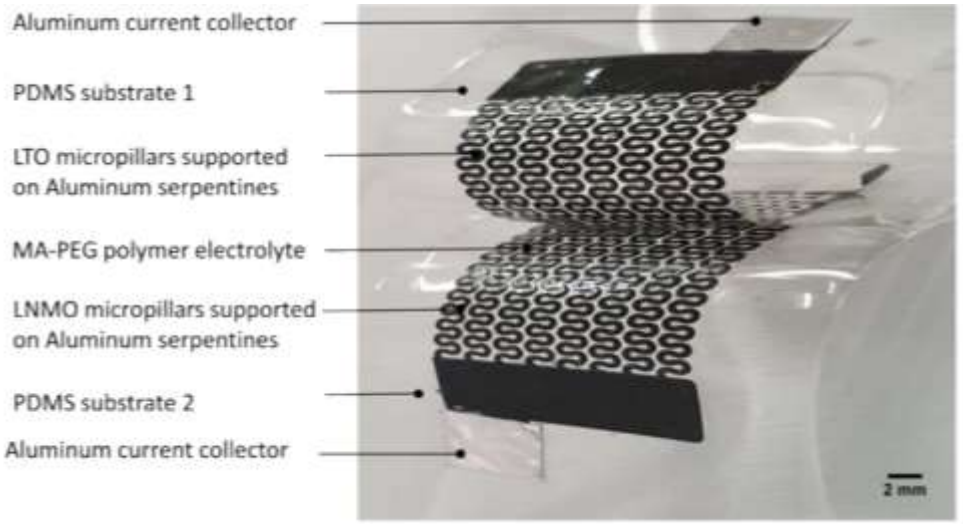

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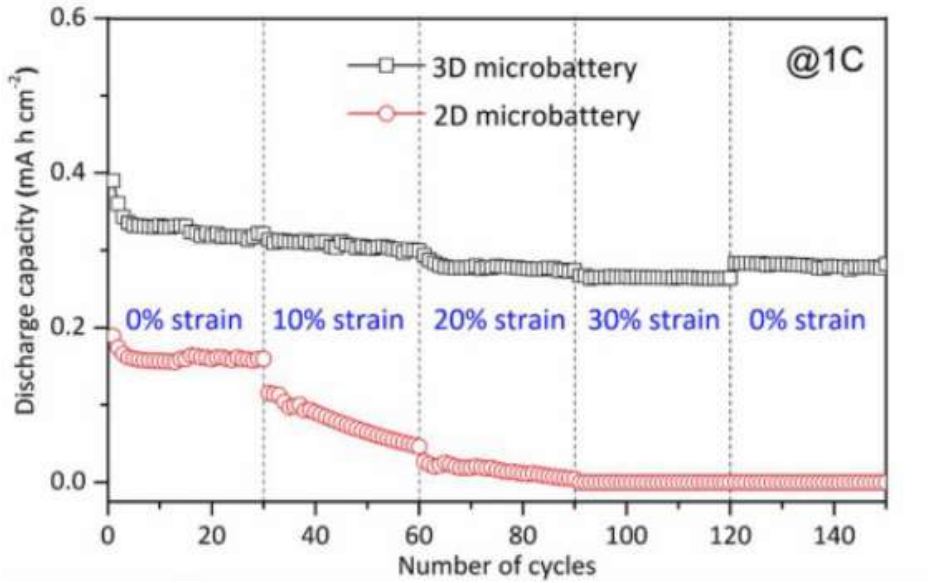
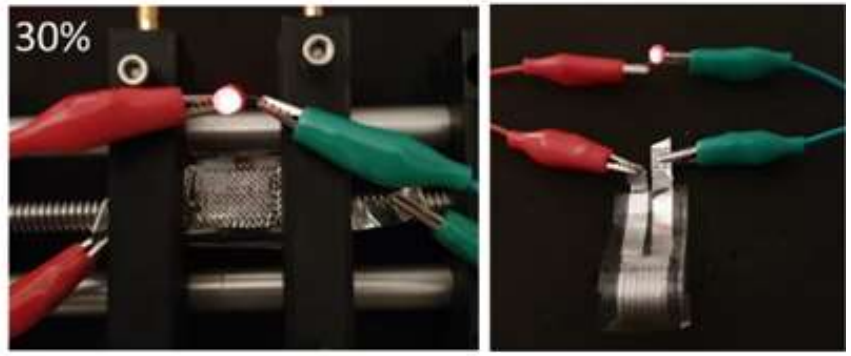


Electrochemical performance of 3D and 2D under different tensile stress at 1C



LED lights up when microbattery is stretched or bent

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High Performance Stretchable Li-ion Microbatteries

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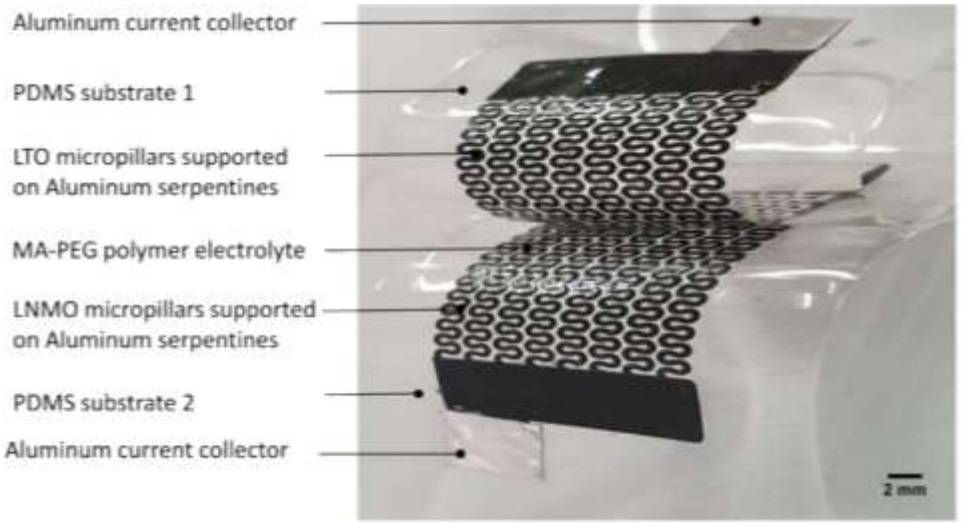
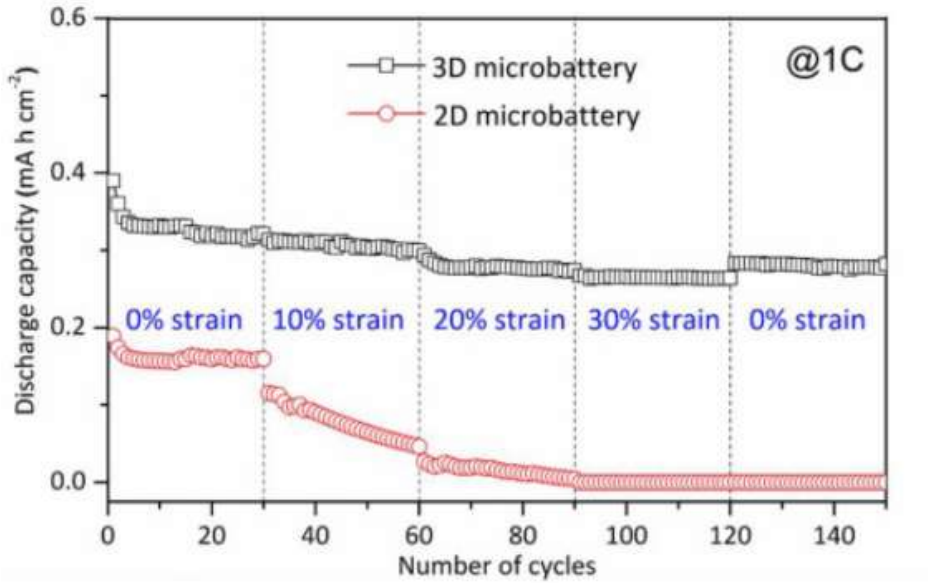
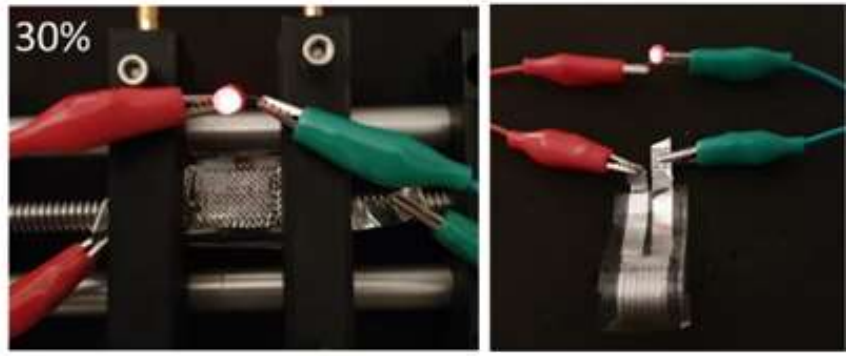




Electrochemical performance of 3D and 2D under different tensile stress at 1C

- Empty spaces inside the electrodes prevent cracks from forming
- 3D electrodes increase energy and power density

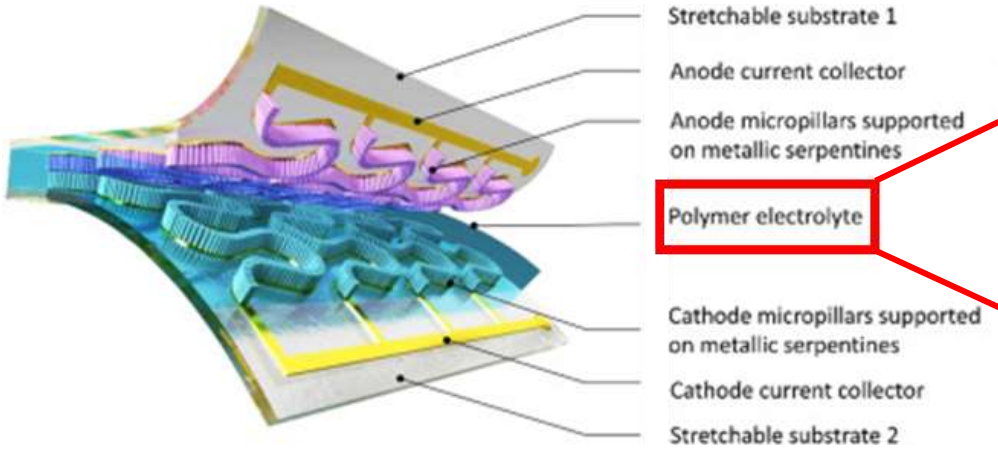
Stretchable Self-healing electrolyte to heal microcracks and improve electrolyte/electrode interface



Lightening of red diode in stretch and bend

High Performance Stretchable Li-ion Microbatteries

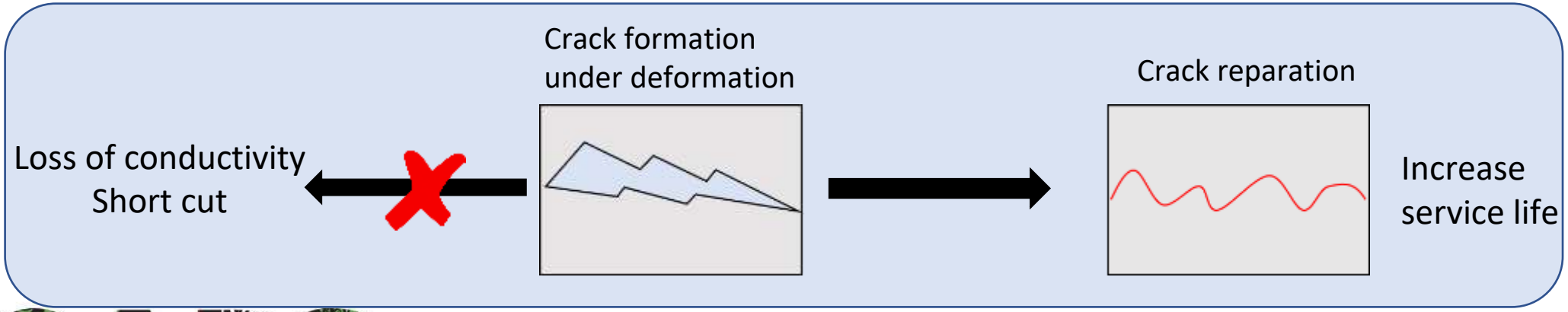
Stretchable substrate carrying micropillar electrodes separated by a stretchable self-healing polymer electrolyte



Technical specifications

- Good ionic conductivity : *~ 0,1 mS/cm*
- Electrochemical stability : *at 4 V vs Li/Li⁺*
- Stretchability *: full strain recovery after 100% deformation*
- Autonomous self-healing : *90 % recovery of mechanical and electrochemical in few hours*
- Safe : *non flammability and no leak risk*
- Good affinity with electrodes

Self-healing interest



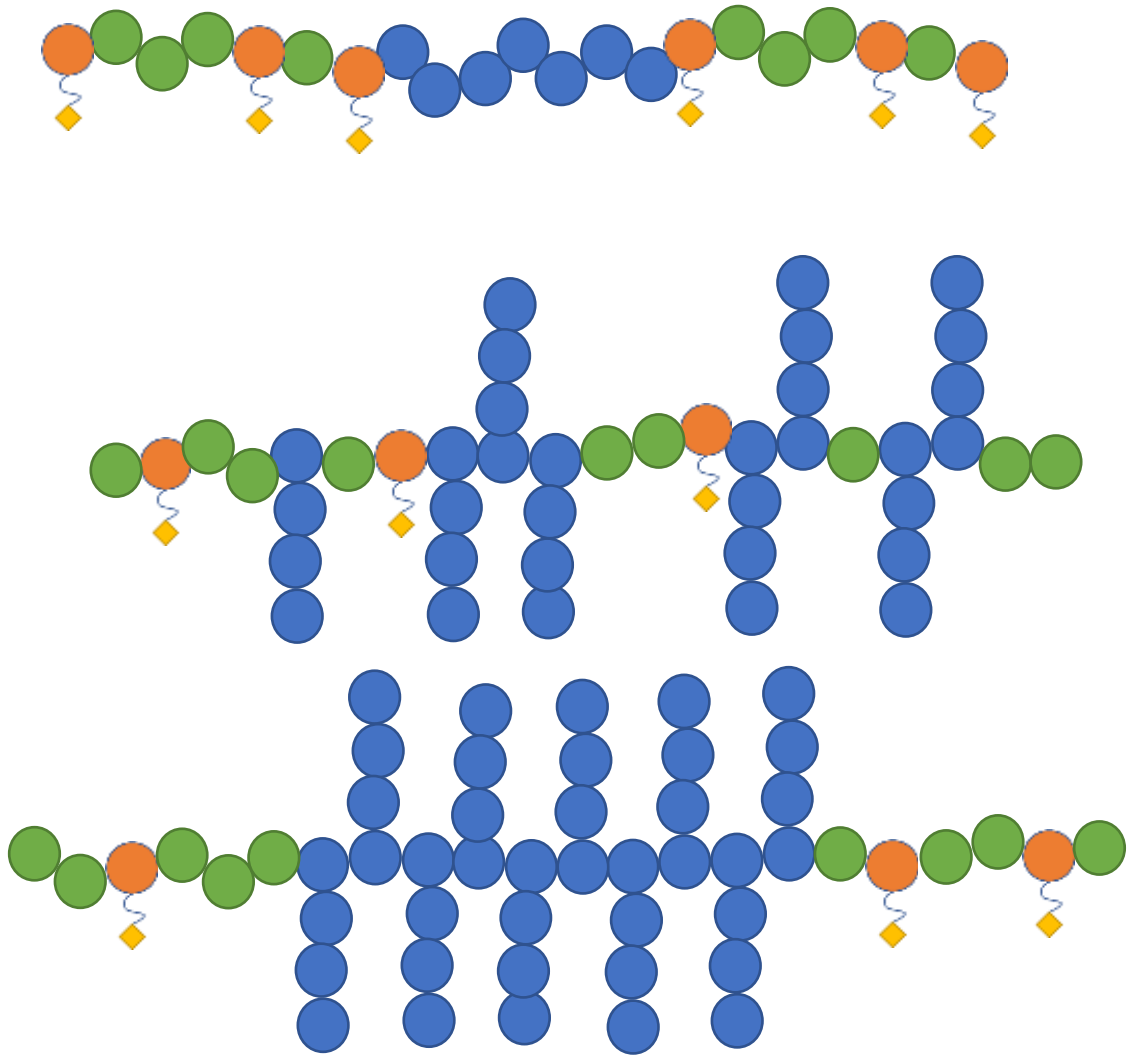
Strategies

Ethylene oxide (ionic conductivity)

Self-healing monomer

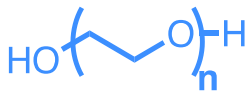
H-bonding

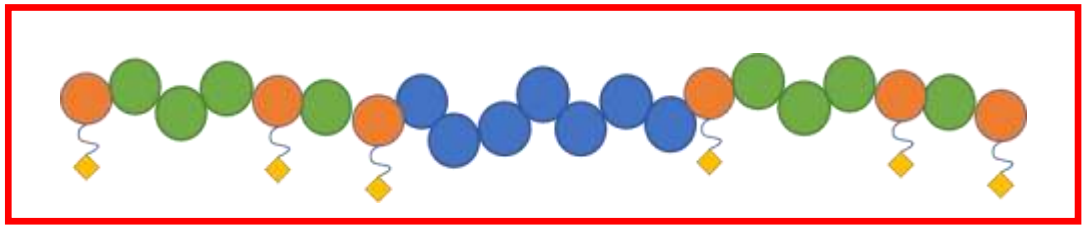
Monomer affording mechanical and/or electrochemical properties



Linear triblock copolymer by NMP

Ethylene oxide (ionic conductivity)





5 eq.

R. Bouchet, S. Maria et al. Nat. Mat., **2013,** 12, 452-457

Linear triblock copolymer by Nitroxide Mediated Polymerization (NMP)

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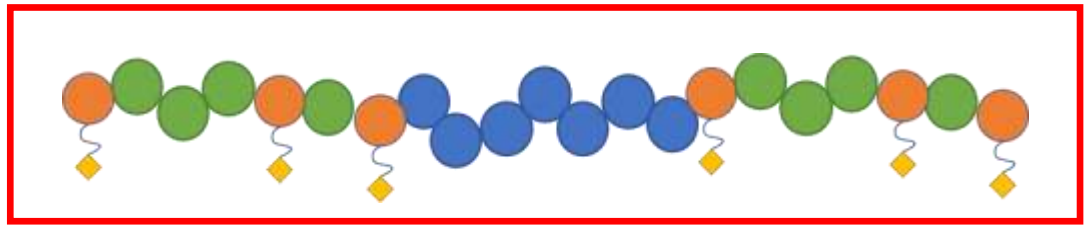

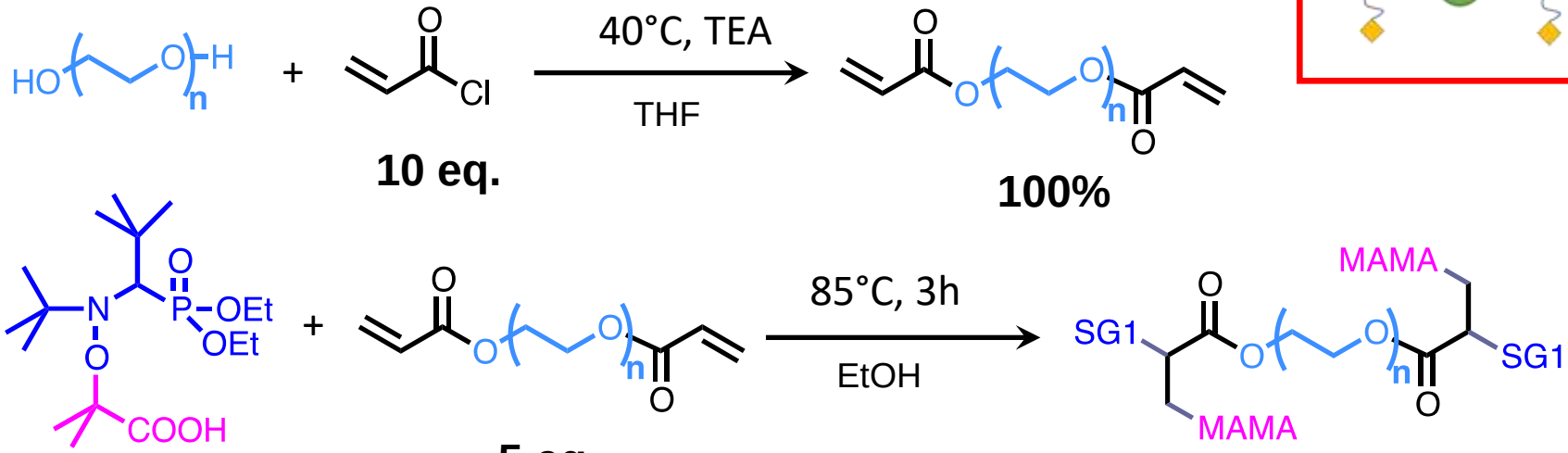

MAMA–SG1

(or BlocBuilder®)

PEO-diSG1

100%

R. Bouchet, S. Maria et al. Nat. Mat., **2013,** 12, 452-457
Didier Gigmes et al., Polymer Chemistry **2011**, *2*, 1624.

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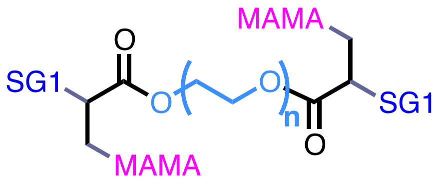
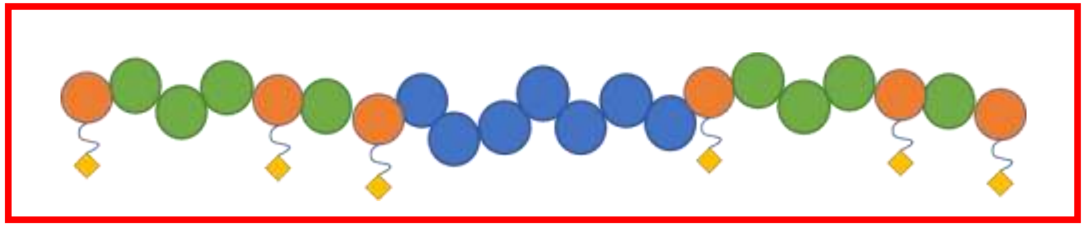


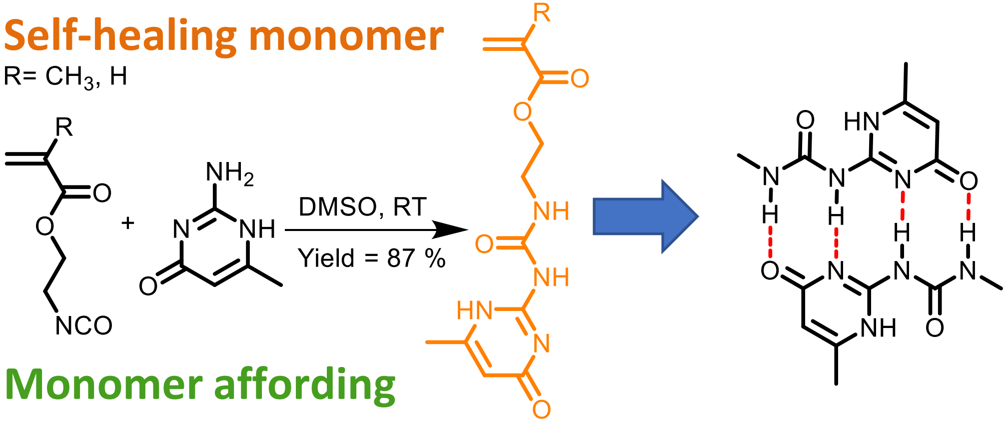
Linear PEO functionalized for NMP polymerization (4, 10, 35 kg/mol)



Nitroxide mediated polymerization in DMF at 120°C

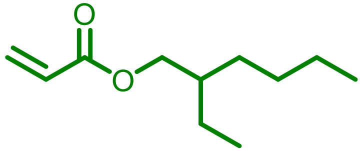
Self-healing monomer

R= CH_3, H



Ureidopyrimidinone (meth)acrylate ((M)AUPY)

Monomer affording mechanical properties



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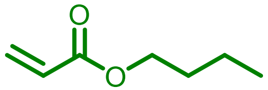

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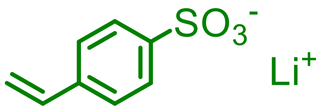

2-ethylhexyl acrylate Homo polymer Tg = -70°C	Butyl acrylate Homo polymer Tg = -60°C	Styrene sulfonate Homo polymer Tg = 152°C

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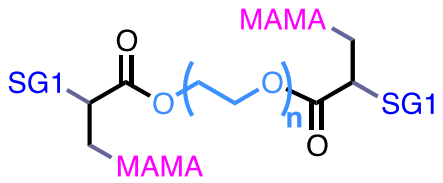

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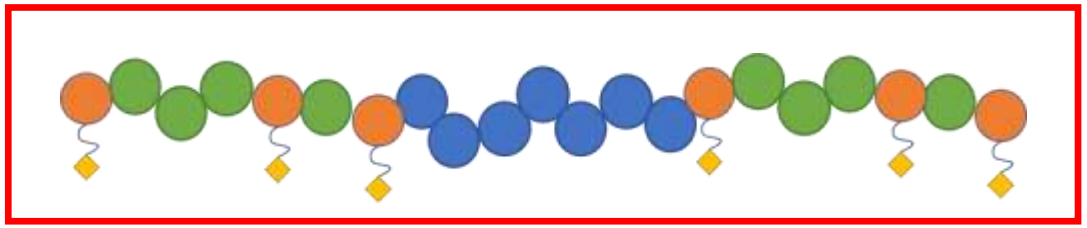

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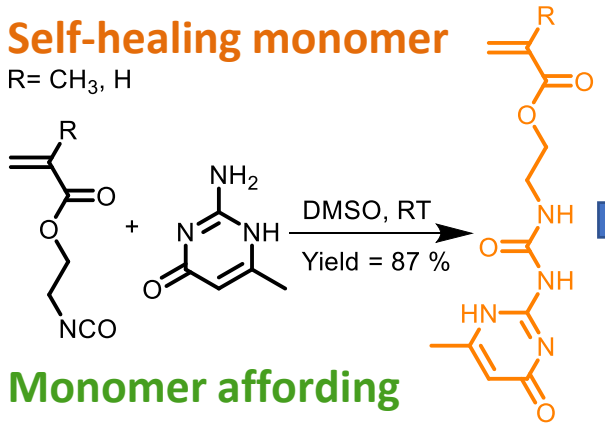
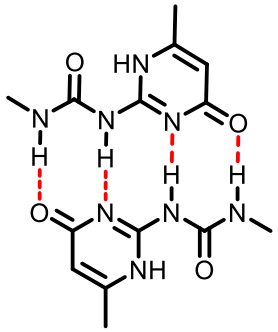
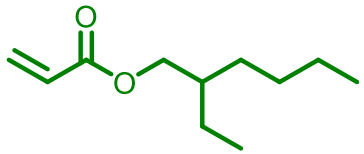




Ureidopyrimidinone (meth)acrylate ((M)AUPY)

Monomer affording mechanical properties



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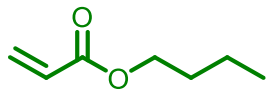

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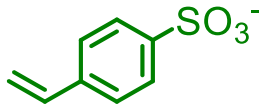

2-ethylhexyl acrylate
Homo polymer Tg = -70°C

Butyl acrylate
Homo polymer Tg = -60°C

Styrene sulfonate
Homo polymer Tg = 152°C

Single-ion strategy to increase Lithium transport number t_{Li+} (improve power) + ionic interaction for self-healing

R. Bouchet, S. Maria et al. Nat. Mat., **2013,** 12, 452-457
B. Zhou et al., J. Mater. Chem. A, 6, 11725-11733 (2018)

Linear triblock copolymer by Nitroxide Mediated Polymerization (NMP)

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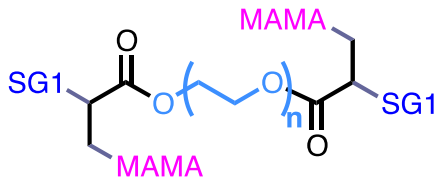

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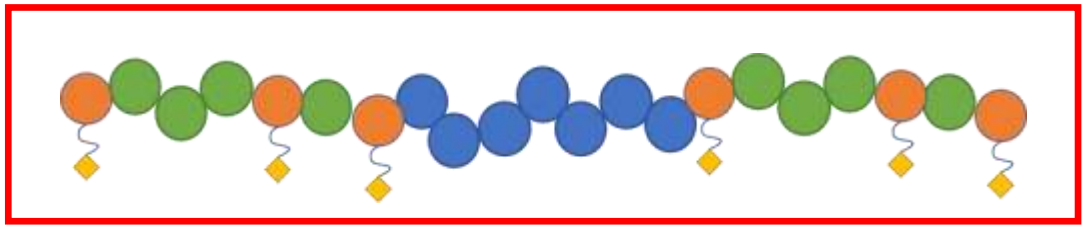

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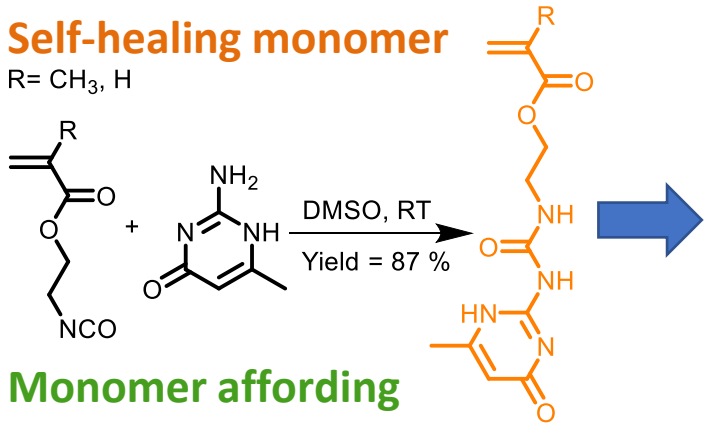

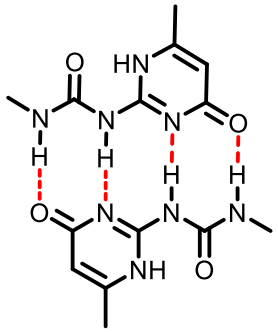

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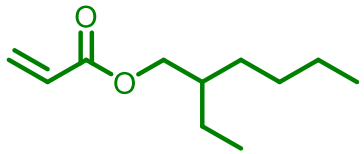

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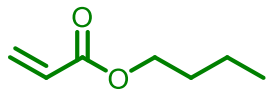

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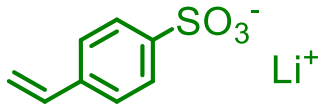


2-ethylhexyl acrylate
Homo polymer Tg = -70°C

Butyl acrylate
Homo polymer Tg = -60°C

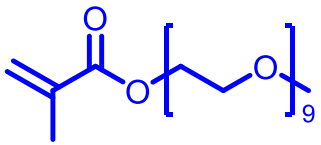
Styrene sulfonate
Homo polymer Tg = 152°C

- No self-healing properties at RT
- Brittle material : stress-strain test impossible to achieve (crystallinity ~ 40%)
- Partial degradation of self-healing monomer during polymerization (high T°)

R. Bouchet, S. Maria et al. Nat. Mat., **2013,** 12, 452-457
B. Zhou et al., J. Mater. Chem. A, 6, 11725-11733 (2018)

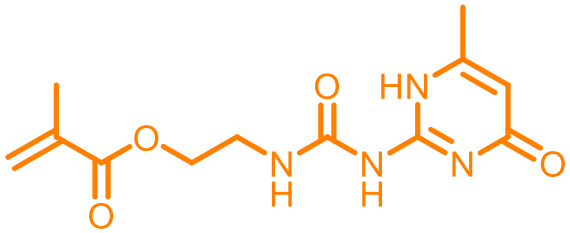
Comb-like PEG copolymer by free radical polymerization

Ethylene oxide (ionic conductivity)



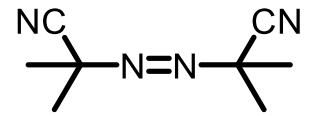
Comb-like PEO

Self-healing monomer



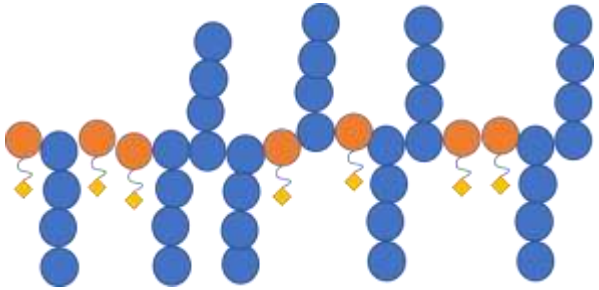
- Self-healing at RT in few hours
- Extremely soft material

Need to increase mechanical properties



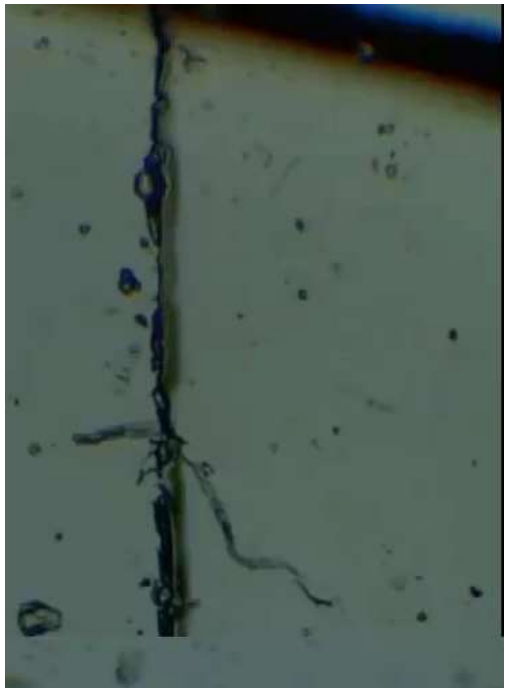
AIBN

DMF, 70°C, 24h



MAPEG/MAUPy =5/1

(purification by dialysis)



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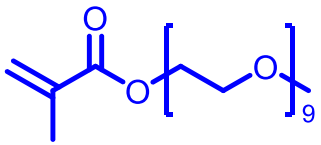
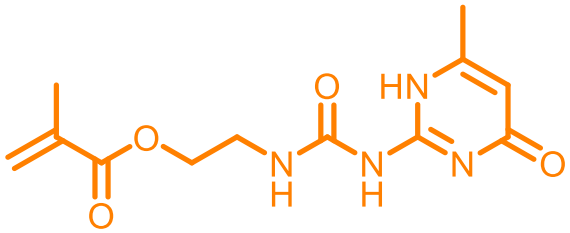


Self-healing monomer



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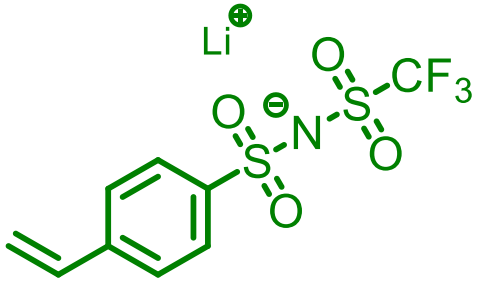
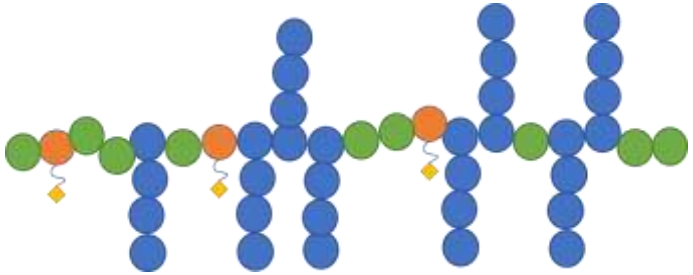


4-styrene sulfonyl(trifluoromethylsulfonyl)imide) Lithium salt (STFSI)

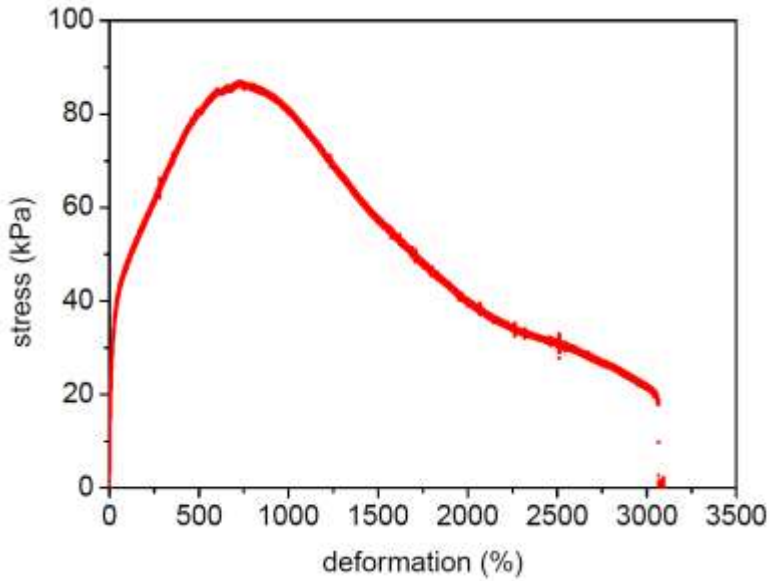
AIBN

DMF, 70°C, 24h



MAPEG/MAUPy/STFSI=7/1/3,5

(purification by dialysis)



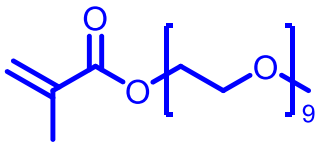
Stress-strain test 10 mm/min

Soft material extremely strechable with a deformation up to 3000 % and a Young Modulus of 230 kPa

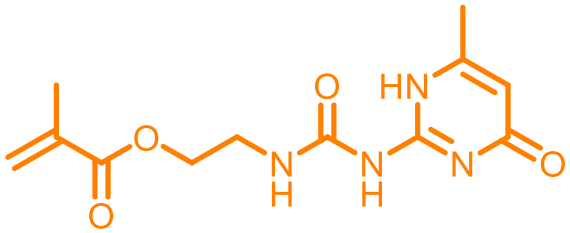
Marc Ramuz

RAFT mediated block copolymer synthesis

Ethylene oxide (ionic conductivity)

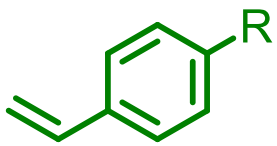


Self-healing monomer

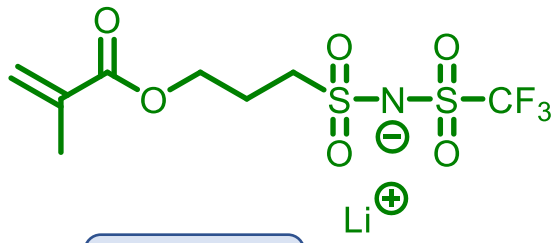


Monomer affording mechanical properties

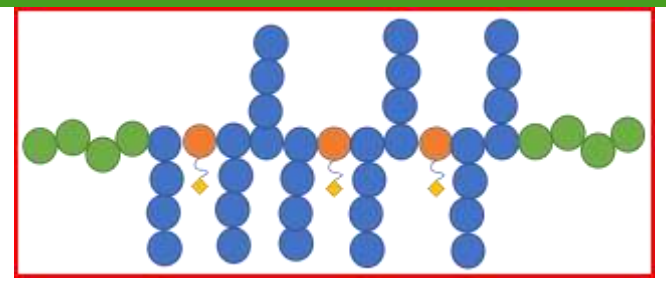
R=H, LiTFSI



Styrene or STFSI



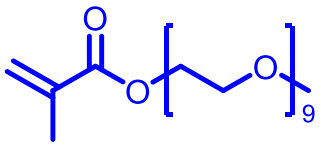
MATFSI



R. Bouchet, S. Maria et al. Nat. Mat., **2013,** 12, 452-457
T. N. T. Phan, A. Ferrand, H. T. Ho, L. Liénafa, M. Rollet, S. Maria, R. Bouchet, D. Gigmes, Polymer Chemistry, 2016, 7, 6901

RAFT mediated block copolymer synthesis

Ethylene oxide (ionic conductivity)



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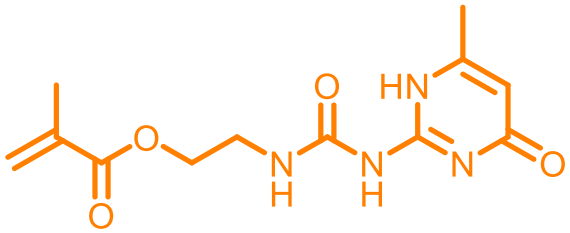

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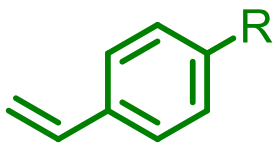

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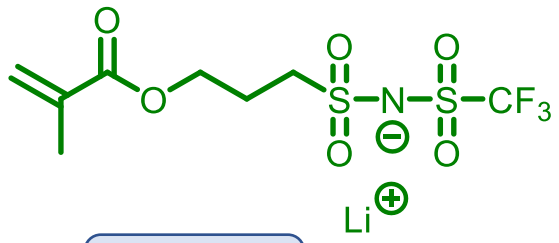
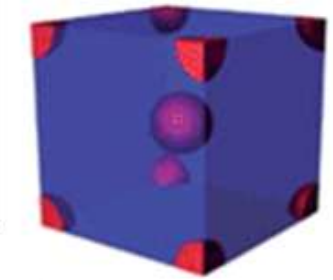
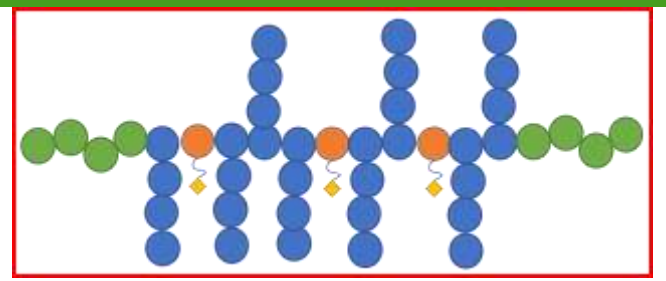


MATFSI





Block copolymer design to obtain **nano-structuration** :

- increase **mechanical properties** (hard domains)
- keeping **self-healing** (soft domains)

Yulin Chen et al. *Nature Chemistry* **4**, 467–472 (2012)

RAFT mediated block copolymer synthesis

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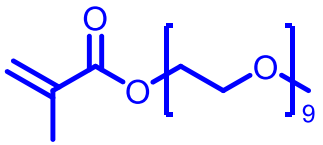
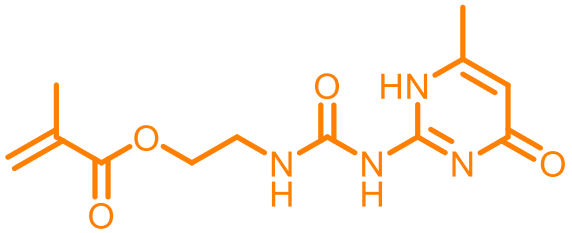
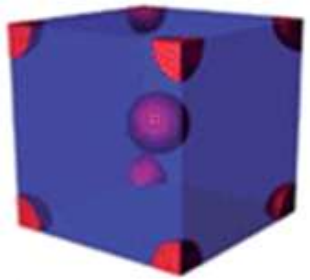
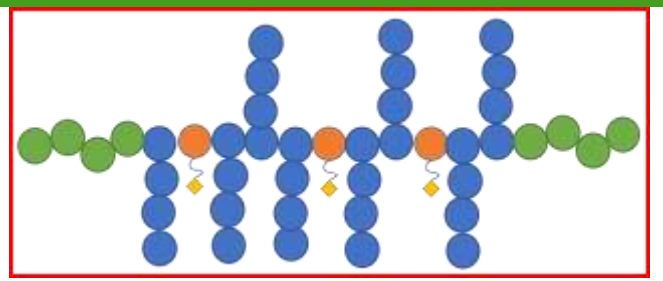


Self-healing monomer







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Need of controlled polymerization operating at low temperature (< 80°C)

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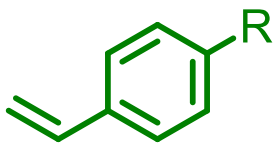

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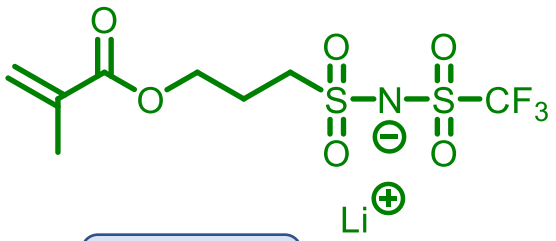

MATFSI

RAFT mediated block copolymer synthesis

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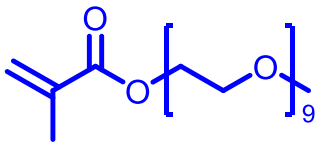

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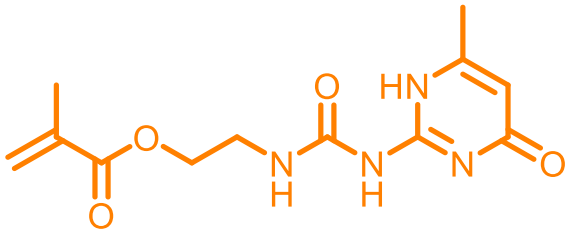

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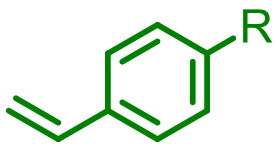

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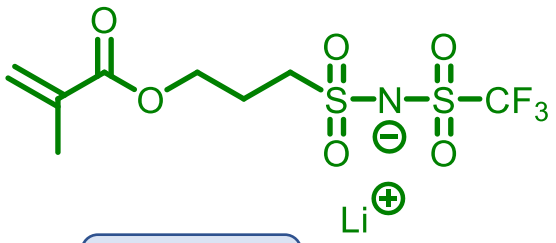

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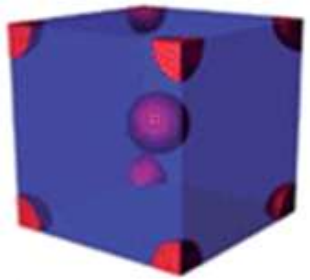

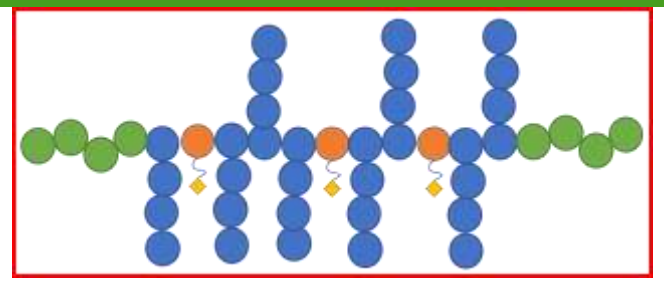

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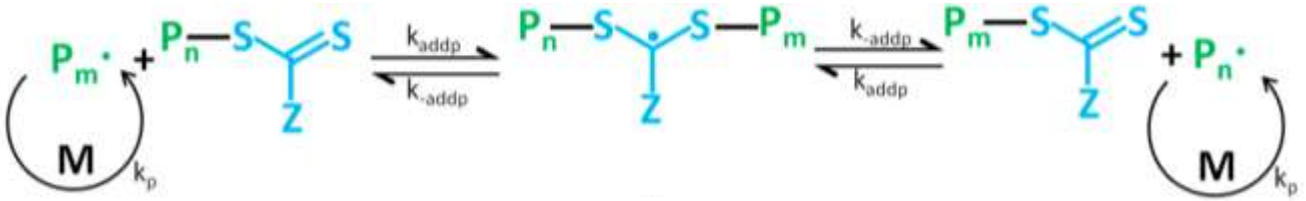
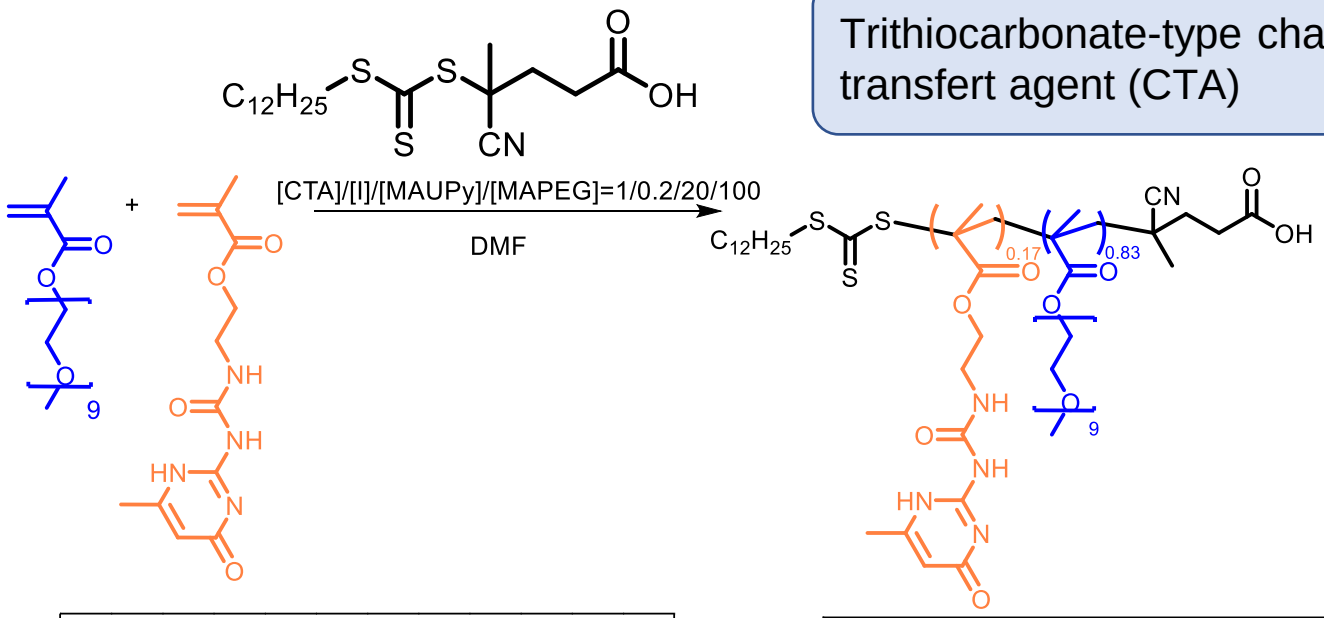
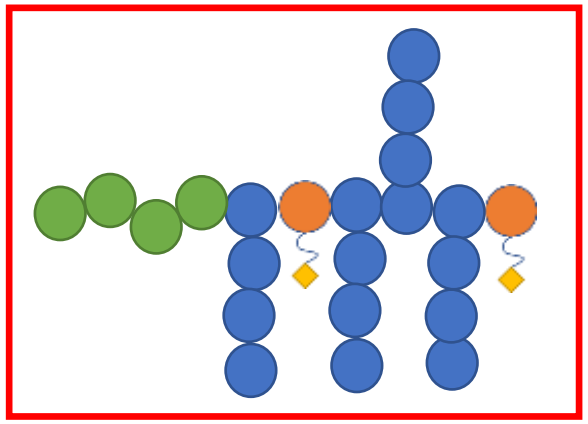


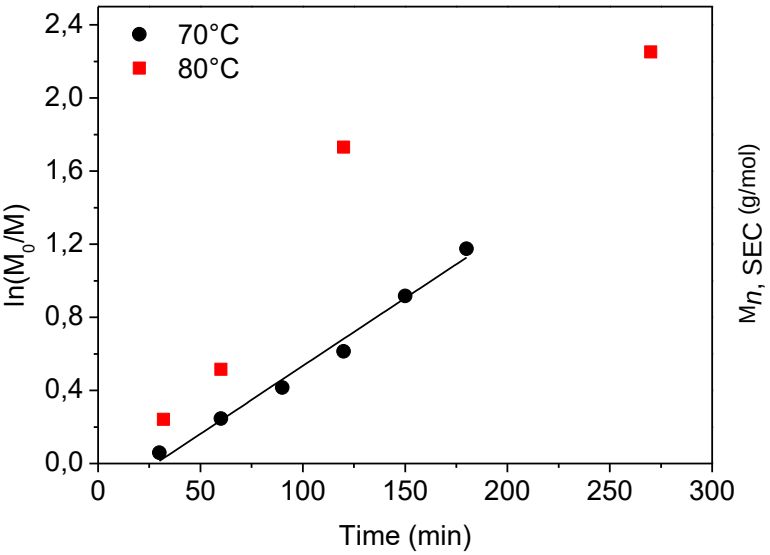
Reversible Addition-Fragmention chain Transfert (RAFT) process

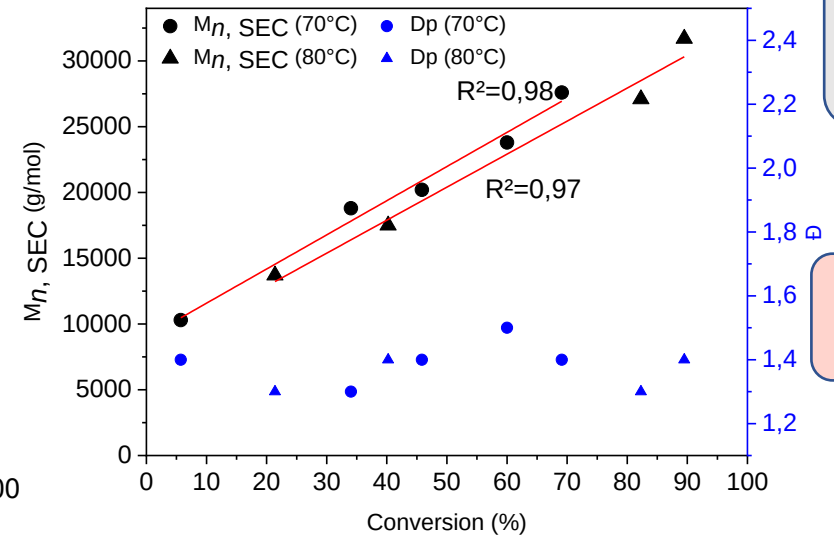
RAFT mediated diblock synthesis

Trithiocarbonate-type chain transfert agent (CTA)







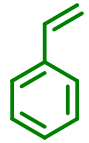


- First order kinetics at 70°C
- Linear evolution of average molar masses at 70°C and 80°C

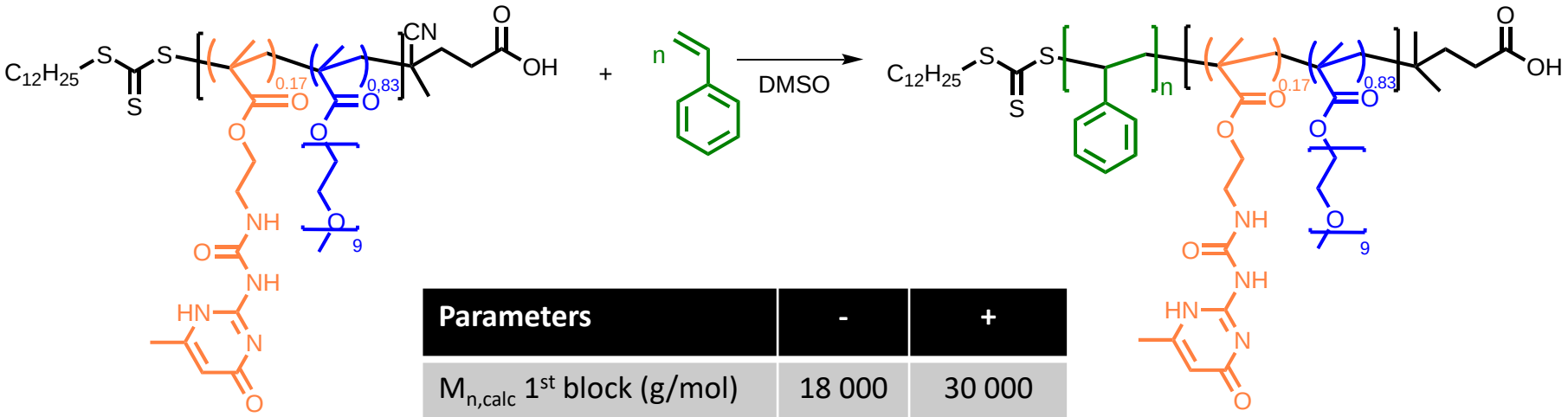
Well-defined and controlled first block with low dispersity

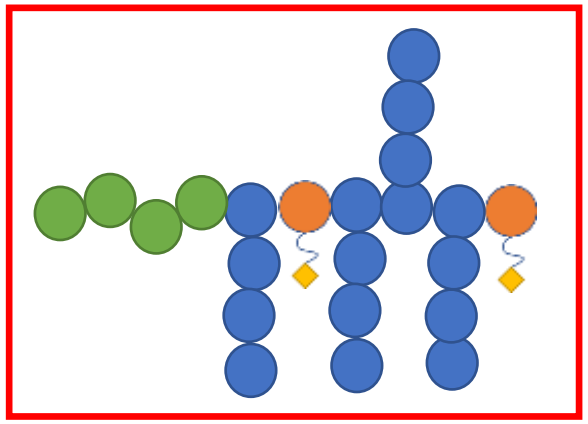
RAFT mediated diblock synthesis

Block extension in solution



- Well known model monomer
- Increase of mechanical properties

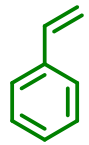




Parameters	-	+
$M_{n,calc}$ 1st block (g/mol)	18 000	30 000
T(°C)	70	80
[S]/[macroCTA]	200	2000
%wt S_i	10	30

RAFT mediated diblock synthesis

Block extension in solution



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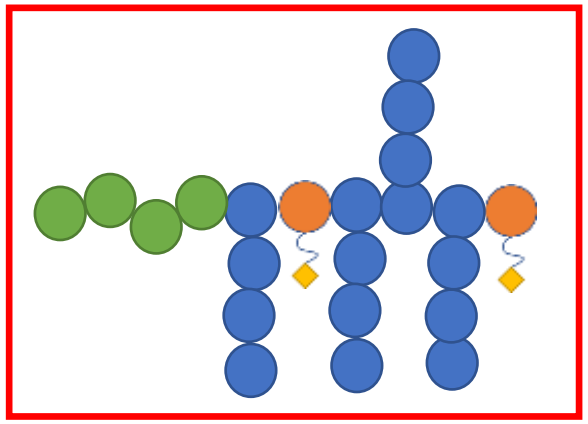
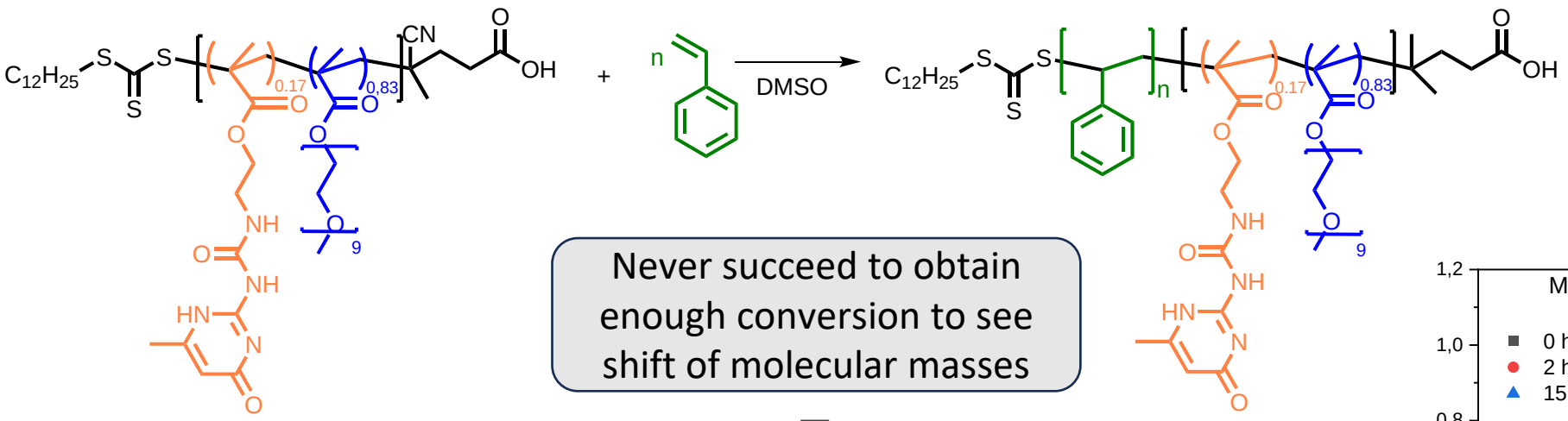
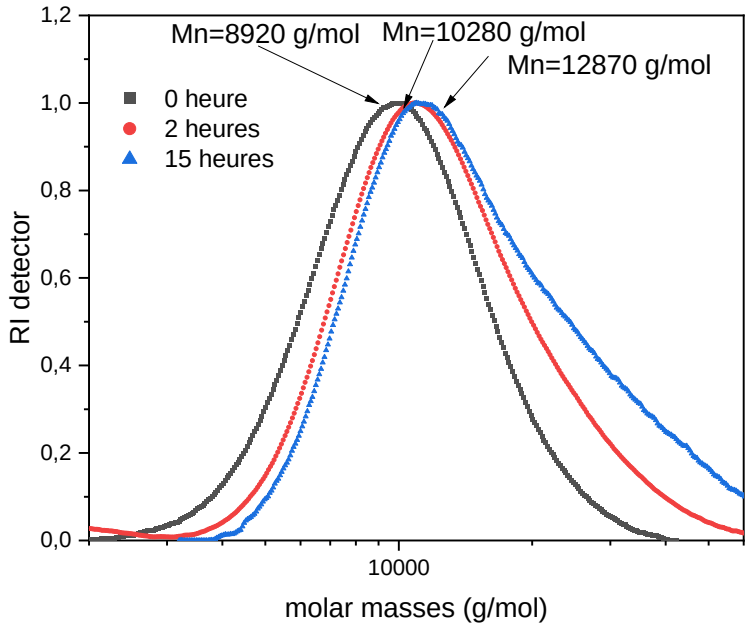




Never succeed to obtain enough conversion to see shift of molecular masses

Possible degradation of macroRAFT over **long polymerization time** (reddening of the solution)

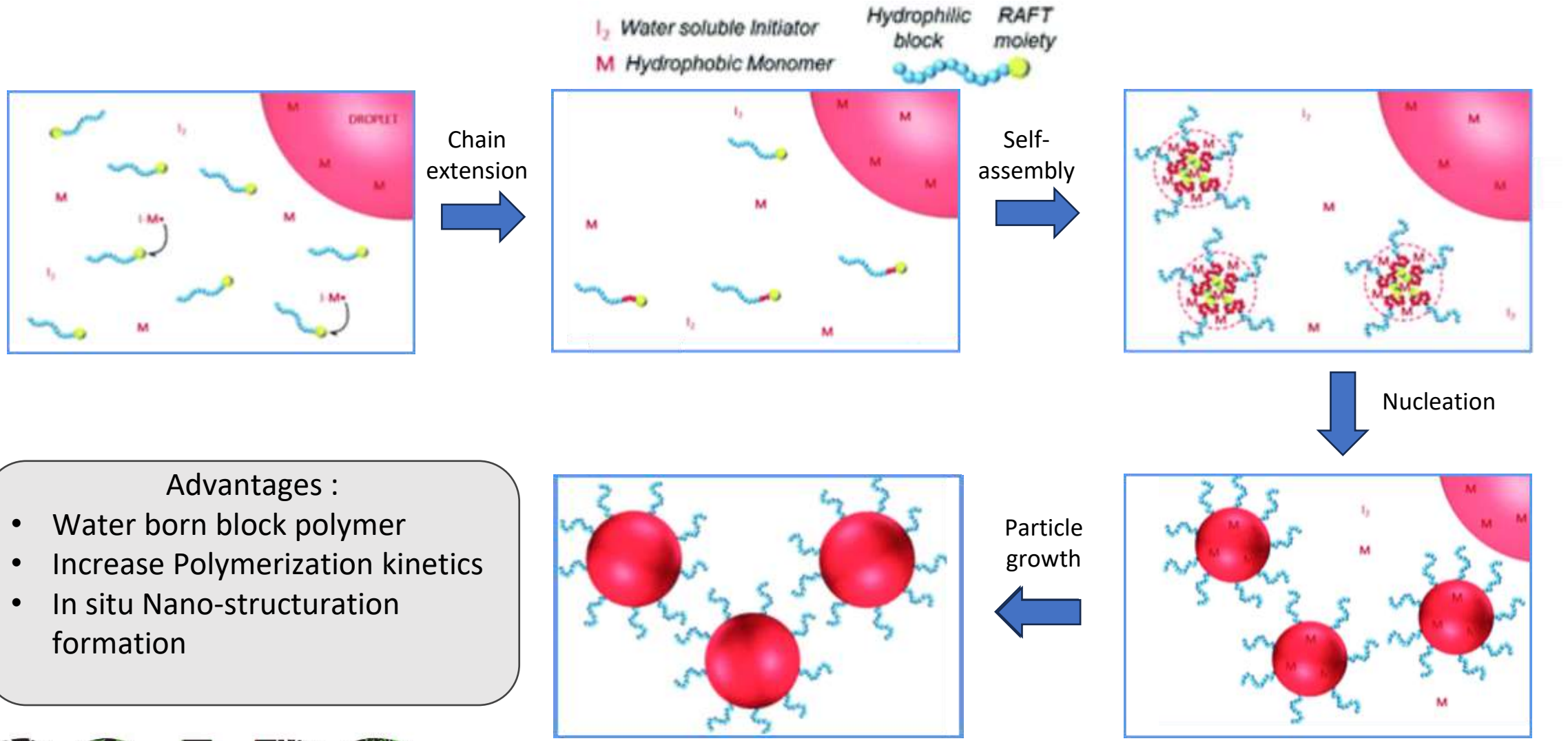
Need to increase polymerisation kinetics



200 eq of styrene , $M_{n,calc}$ 1st block 18 kg/mol at 80°C

Diblock synthesis by RAFT-PISA

RAFT-PISA: RAFT-mediated polymerization-induced self-assembly

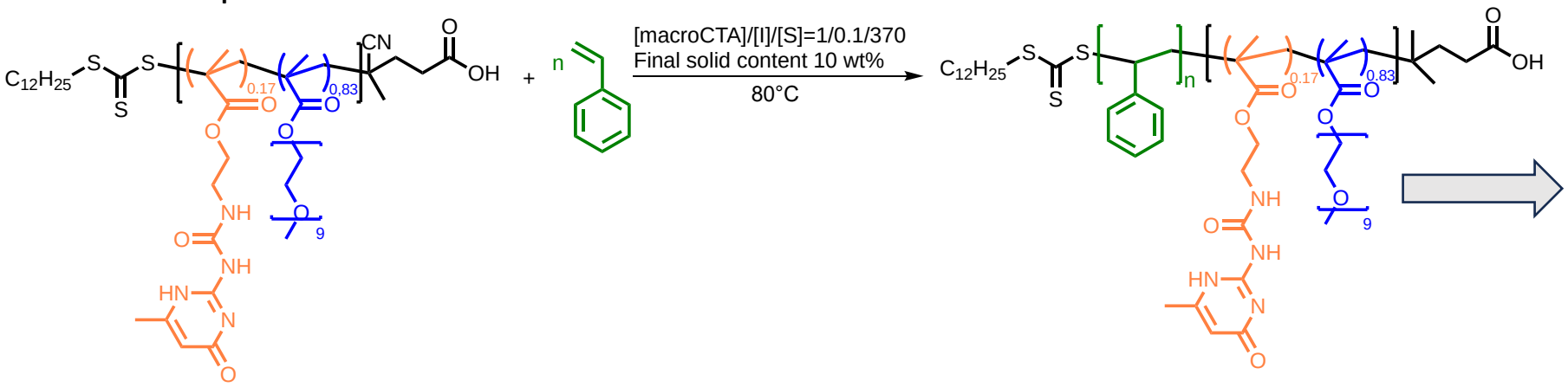


Advantages :

- Water born block polymer
- Increase Polymerization kinetics
- In situ Nano-structuration formation

Diblock synthesis by RAFT-PISA

First attempts



I: 4,4-Azobis(4-cyanovaleric acid), (ACVA)

Polymer precipitation after addition of few Styrene units

Hypothesis : agglomeration because intermicellar hydrogen bonding?

J.-F. Xu et al. Org. Lett., 16, 4016−4019, 2014

Diblock synthesis by RAFT-PISA

First attempts

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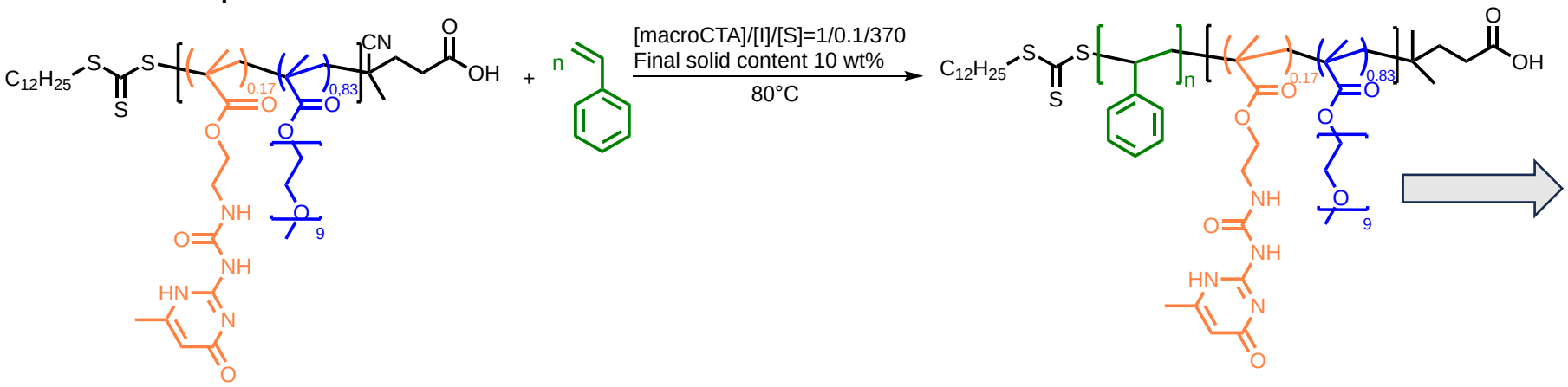
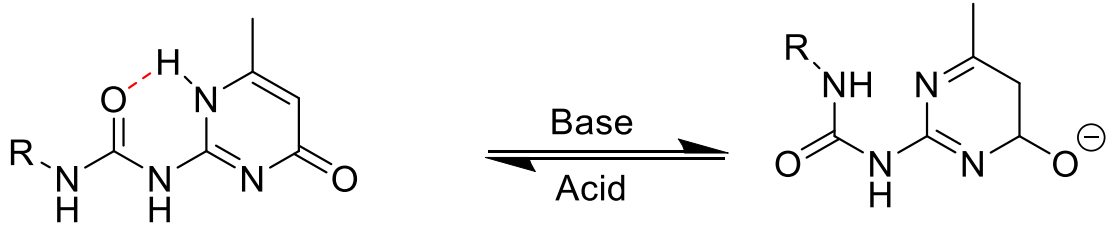


Polymer precipitation after addition of few Styrene units

Hypothesis : agglomeration because intermicellar hydrogen bonding?

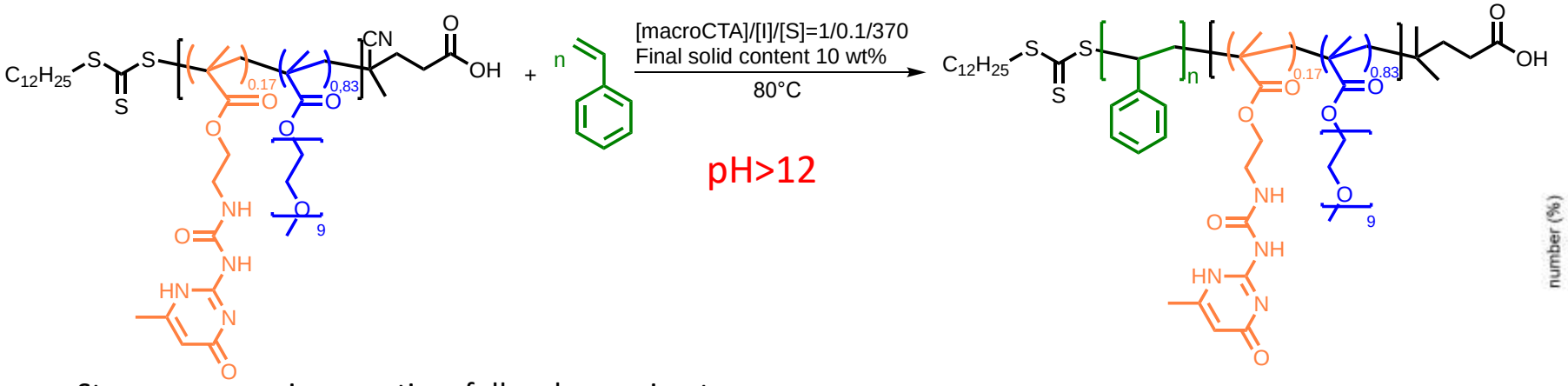
Increasing pH reduces hydrogen bonding:

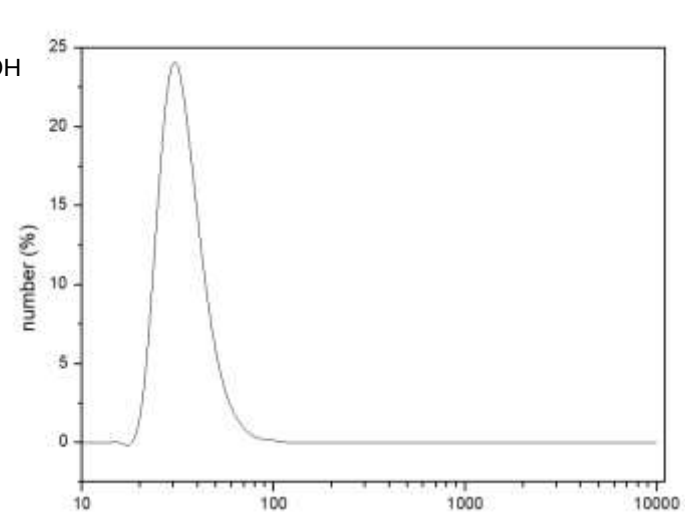


DDAA system

ADAA system

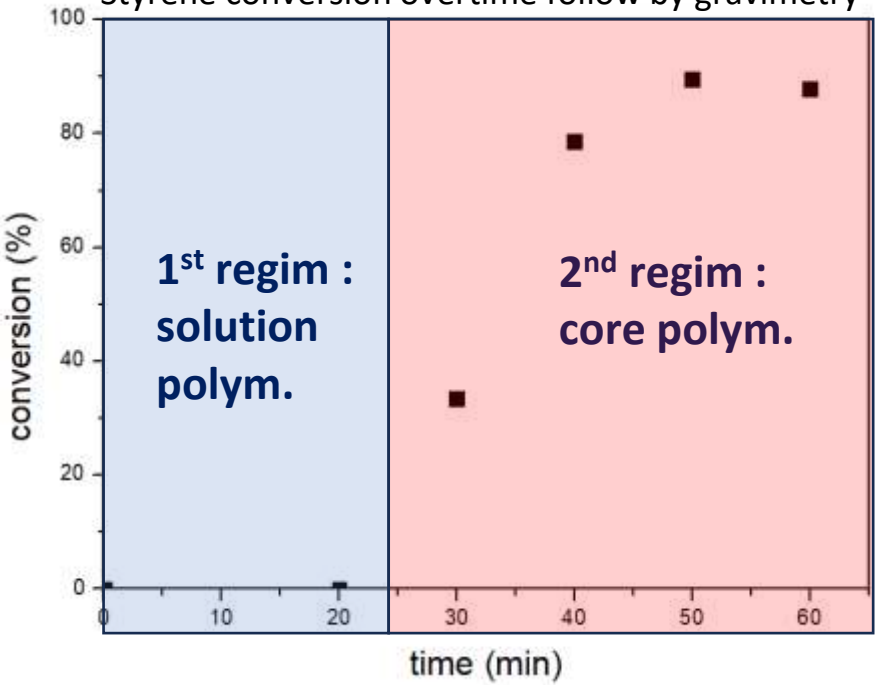
Diblock synthesis by RAFT-PISA

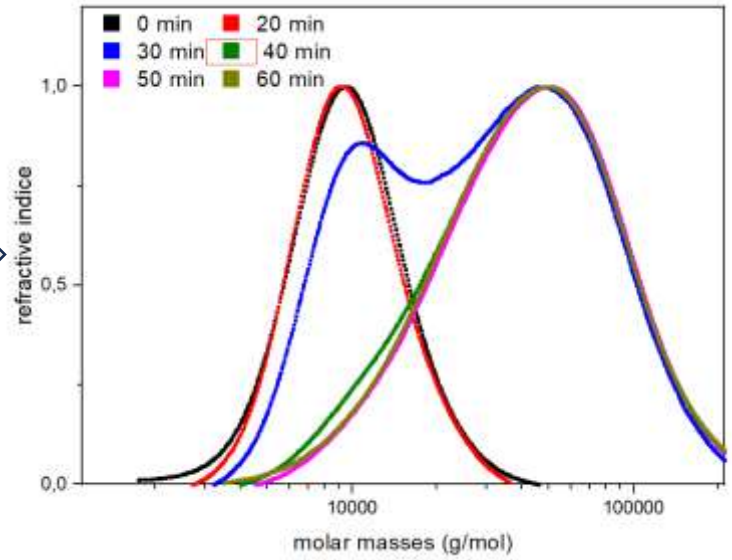




Particle size distribution by DLS at the end of the polymerization. Average diameter 70 nm.

Styrene conversion overtime follow by gravimetry



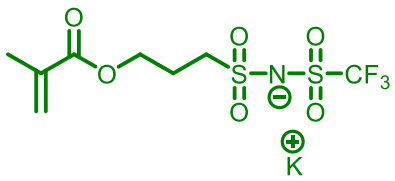


- Fast polymerization rate
- Bimodale distribution during regim transition ?
- Observation of nanoparticles formation

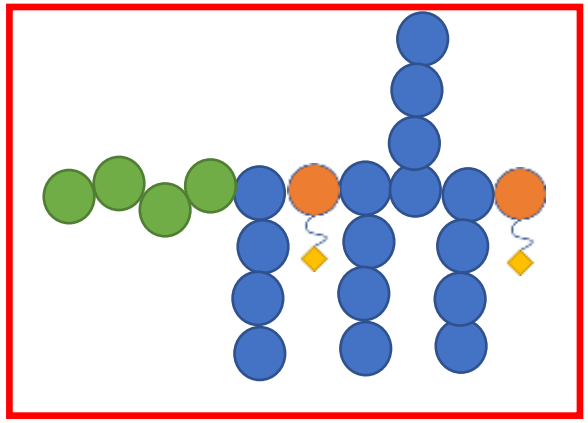
Tan, J. et al. *Polym. Chem.* **2016**, *7* (13), 2372–2380.
D'Agosto, F. et al. *Angewandte Chemie International Edition* **2020**, *59* (22), 8368–8392.

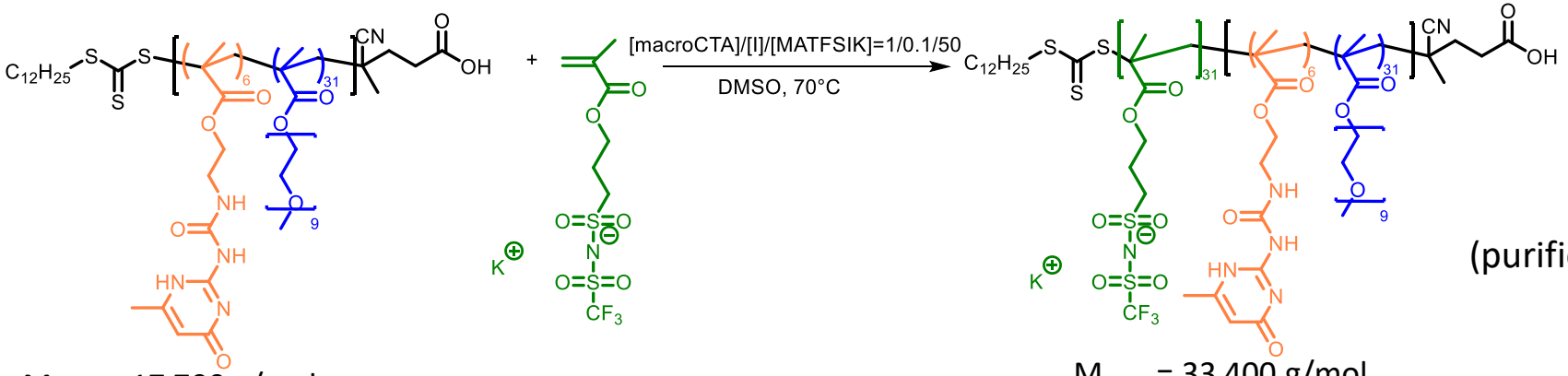
RAFT mediated diblock synthesis

Block extension in solution



- Single-ion strategy : increase t_{Li+}
- Increase of mechanical properties

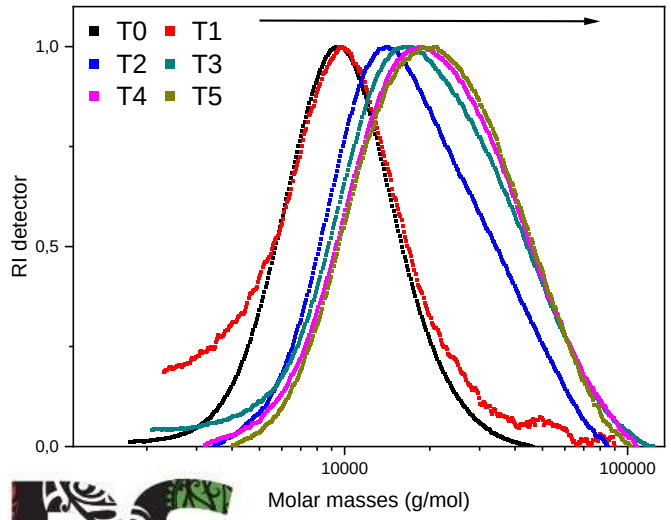




$M_{n,calc}$= 17 700 g/mol

$M_{n,calc}$= 33 400 g/mol
42 %wt MATFSIK

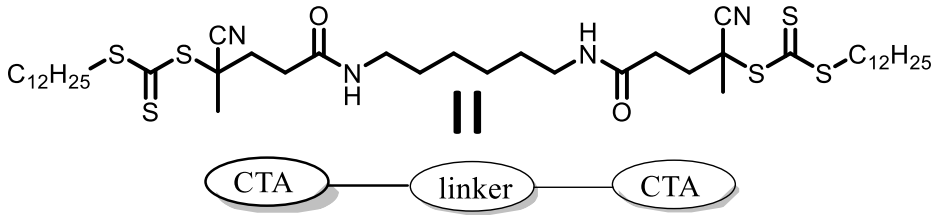
(purification and exchange K^+/Li^+ by dialysis)

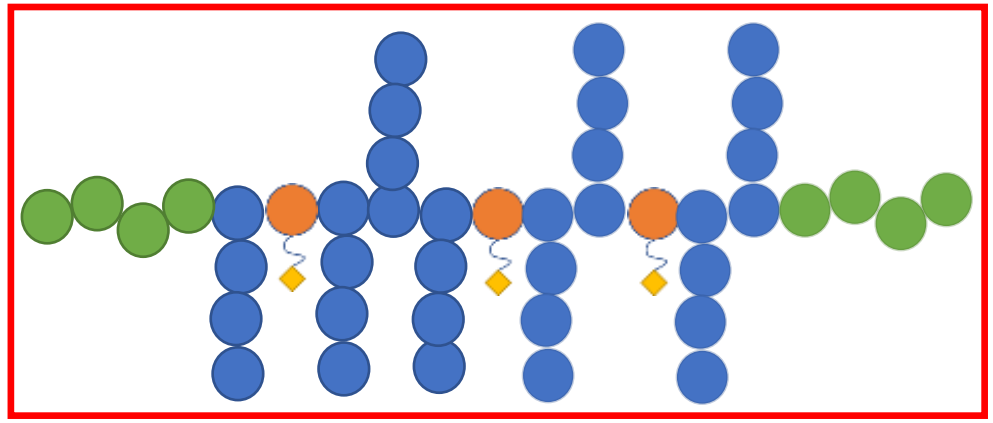


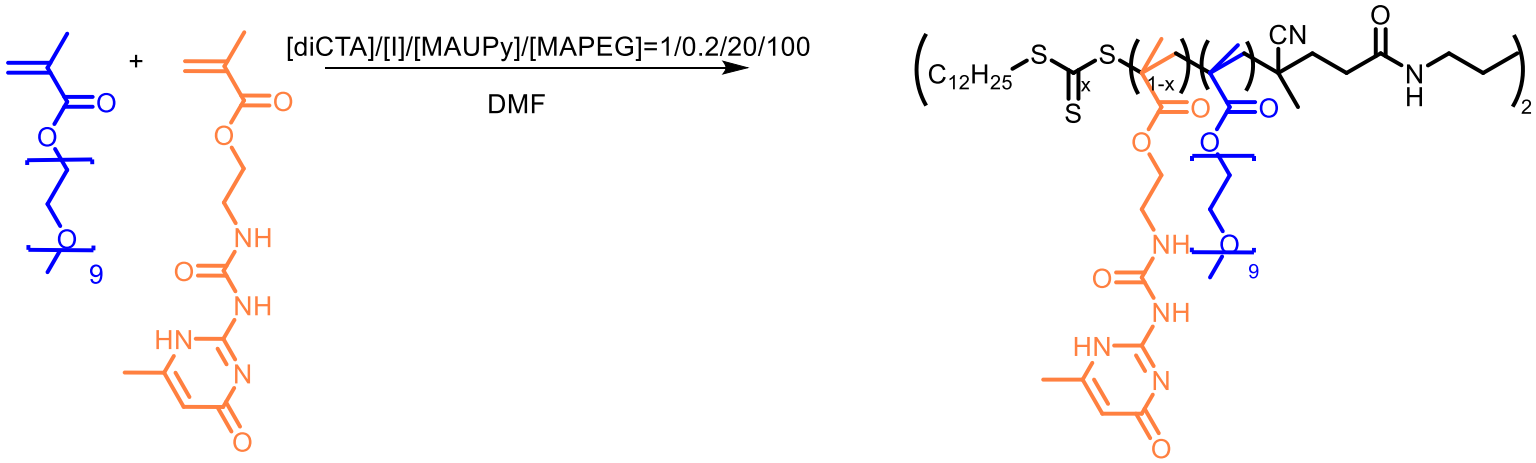
- Controlled block extension
- Low dispersity (Đ<1,4)
- Succeed to obtain diblock with **10,20,30 %wt** of MATFSIK by varying [MATFISK]/[macroCTA] ratio

RAFT mediated triblock synthesis

Triblock strategy : increase cohesion and mechanical properties







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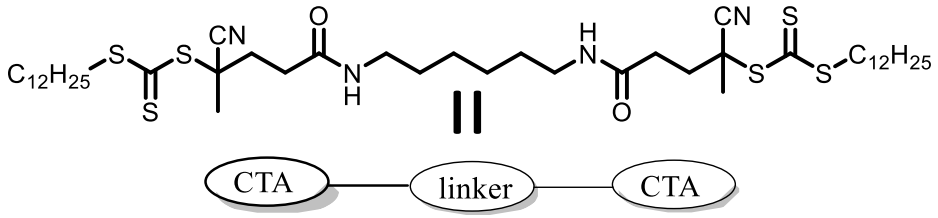
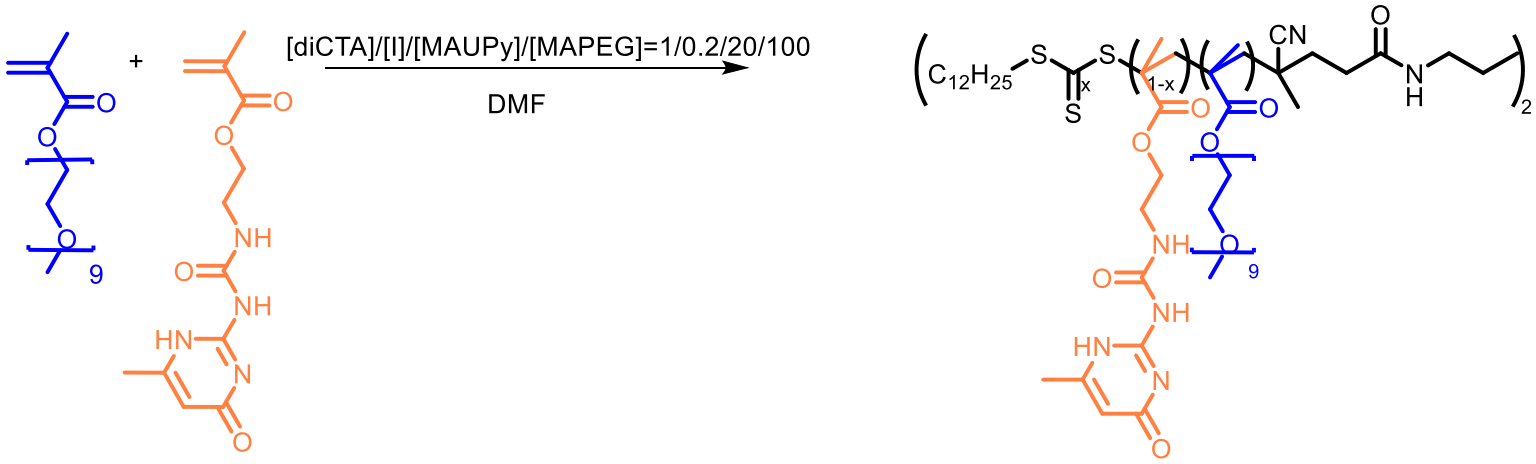
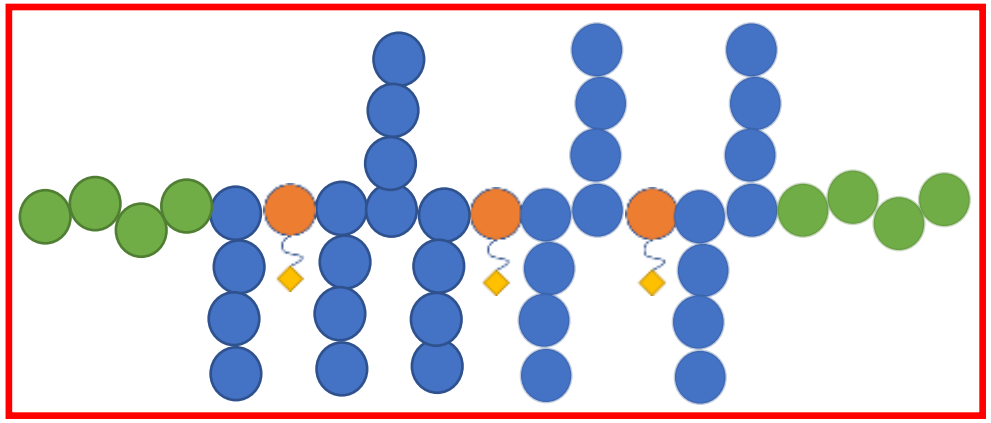
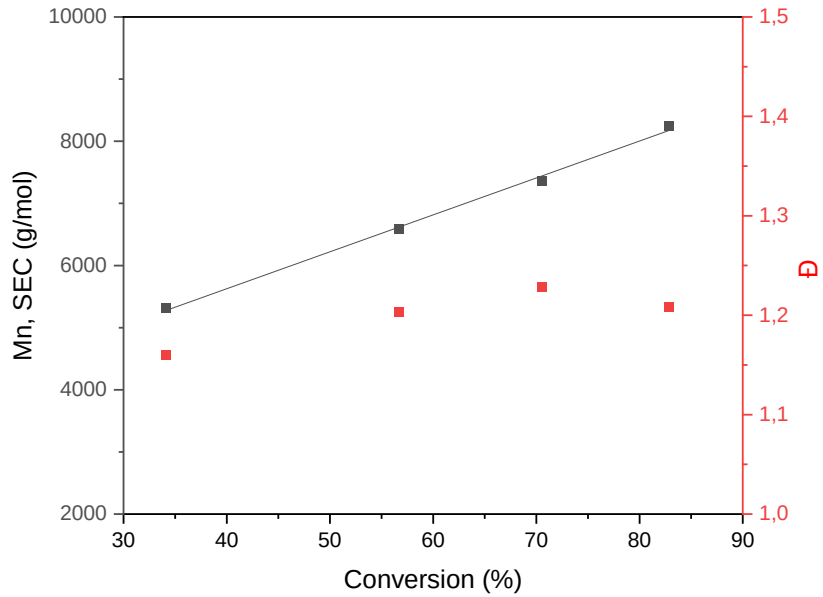


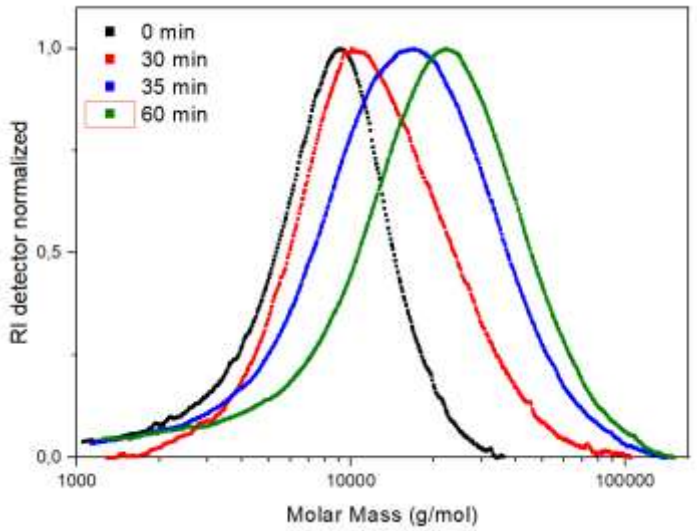


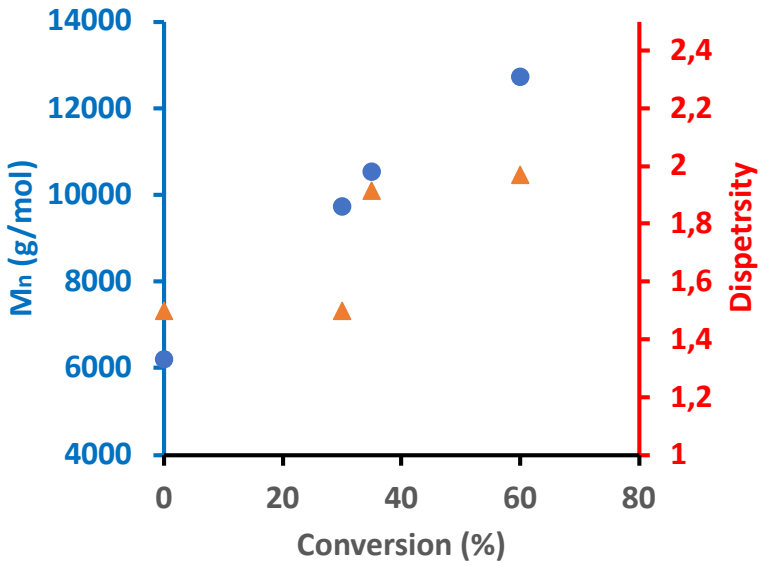


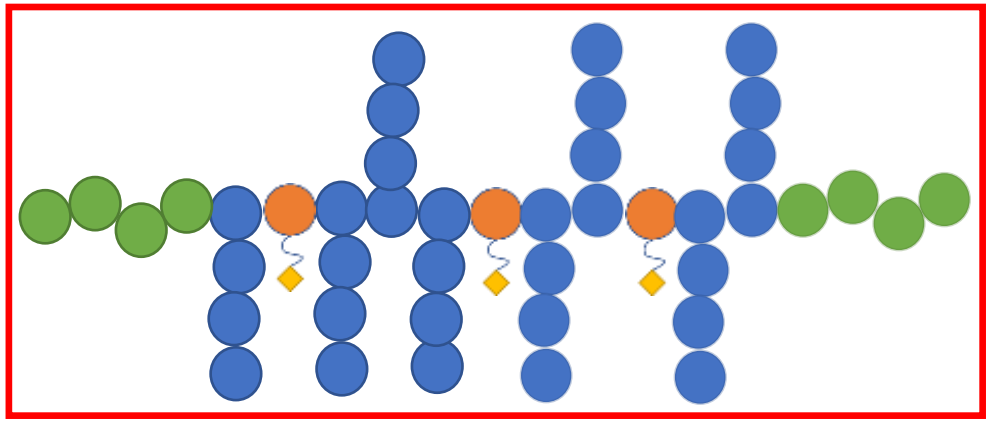


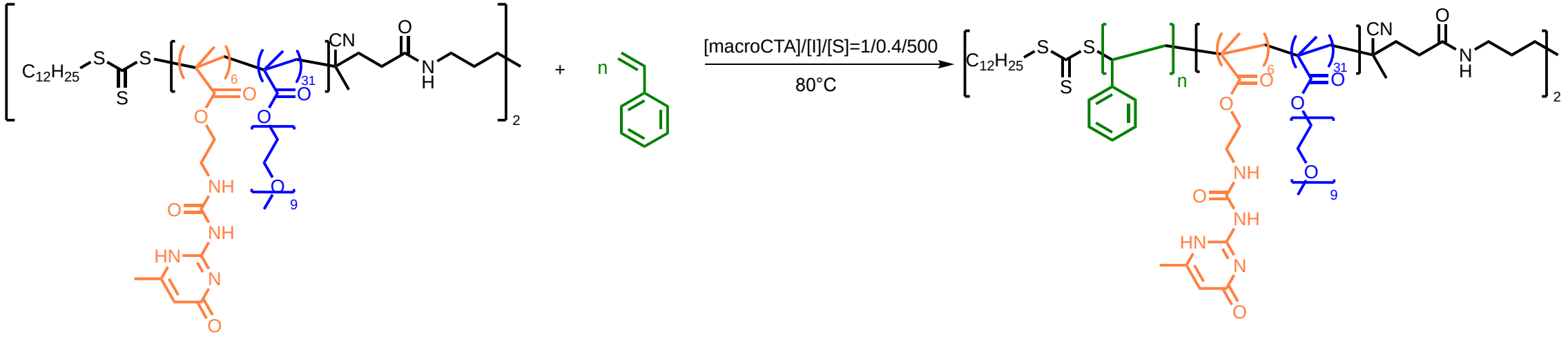
Well defined and controlled first block with low dispersity with a **difunctional RAFT agent**

RAFT-PISA mediated triblock synthesis



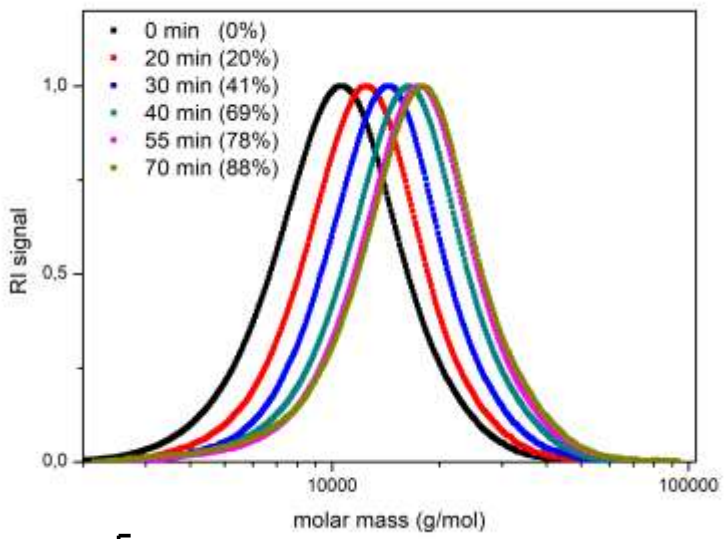


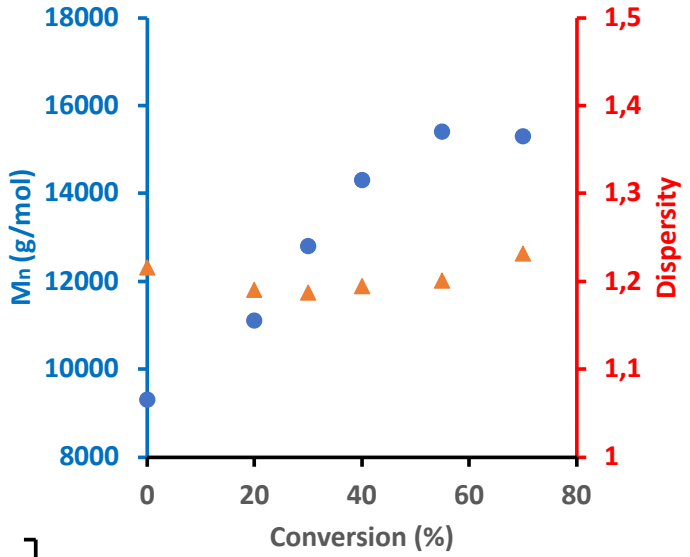


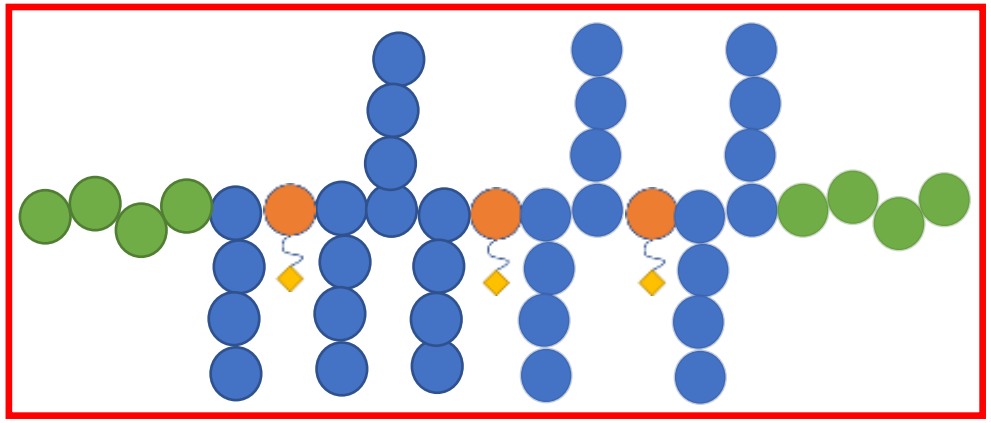


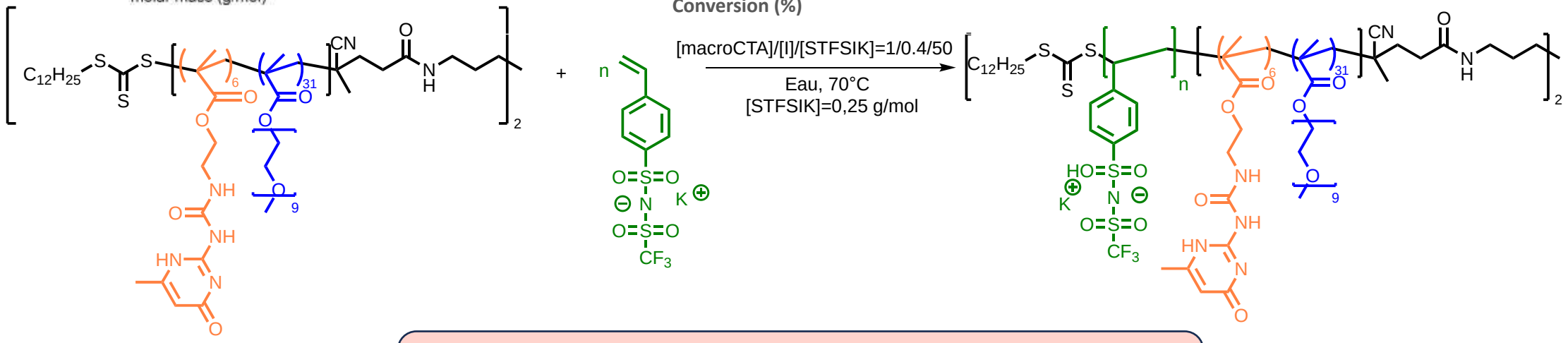
Successfull triblock synthesis by **RAFT PISA**, but high dispersity

RAFT mediated triblock synthesis





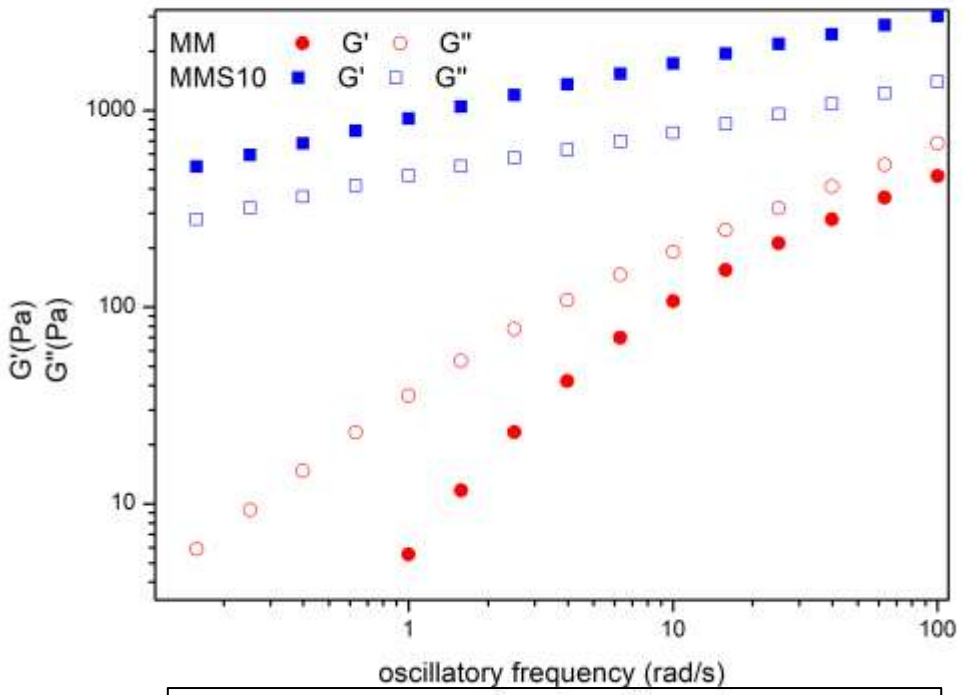




Well-defined and controlled Triblock single-ion with low dispersity with a **difunctional RAFT agent**

Mechanical characterization

Mechanical characterization: rheology



poly(MAPEG$_{0.83}$-MAUPy$_{0.17}$)-b-PS (10wt% PS)

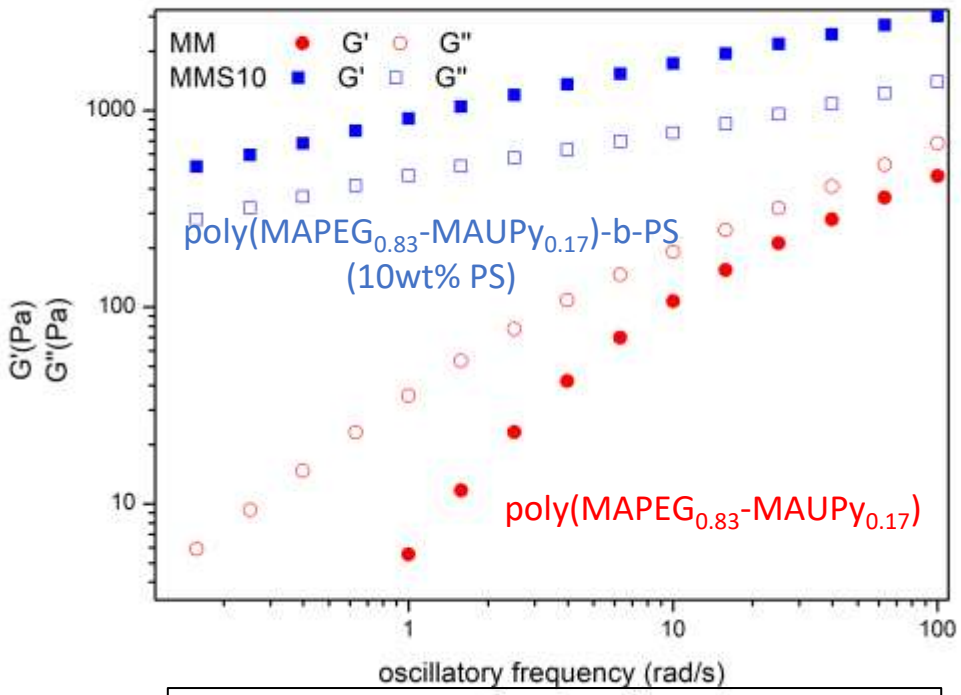
poly(MAPEG$_{0.83}$-MAUPy$_{0.17}$)

Frequency sweep from 0,1 to 100 rad/s with 1% deformation at 25°C

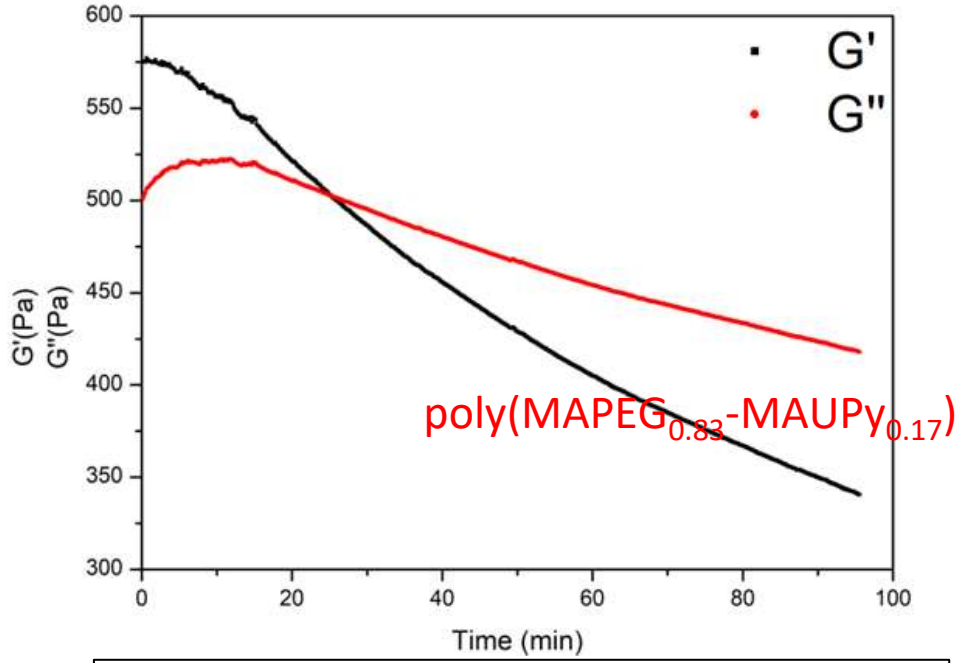
Increase of mechanical properties

Mechanical characterization

Mechanical characterization: rheology



Frequency sweep from 0,1 to 100 rad/s with 1% deformation at 25°C



Behavior of G' and G'' over time at 1% deformation and shear rate of 1 rad/s

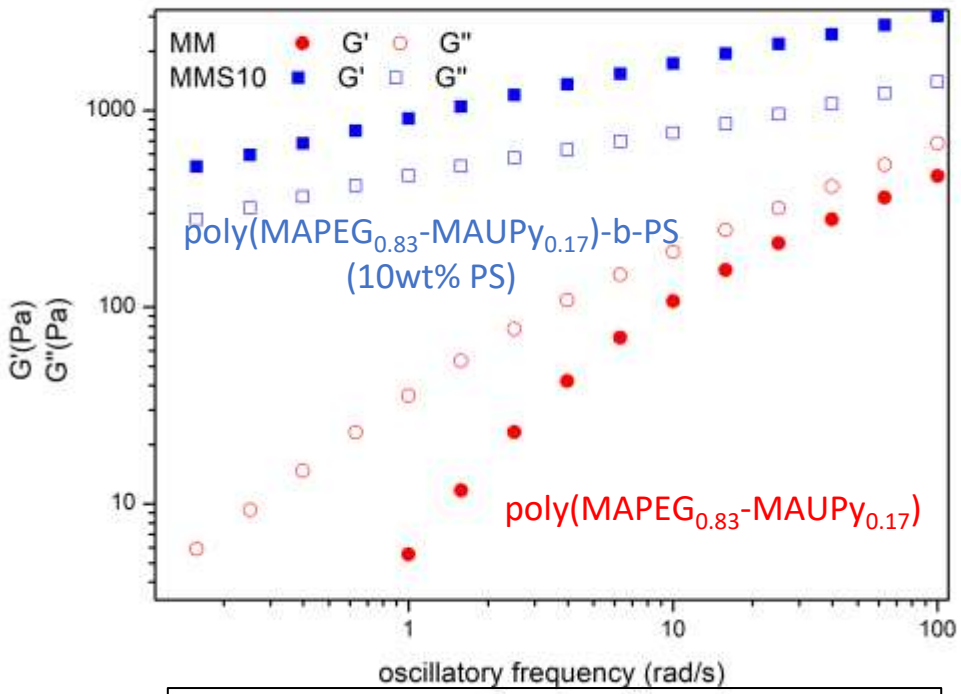
Increase of mechanical properties

Materials **highly hygroscopic** transition from soft solid to viscous liquid within few minutes

Need to perform mechanical test under controlled atmosphere

Mechanical characterization

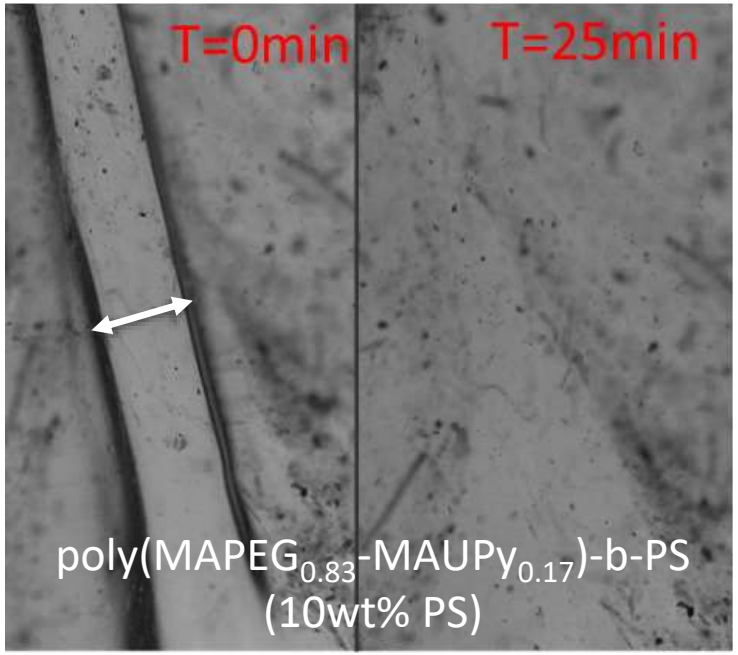
Mechanical characterization: rheology



Frequency sweep from 0,1 to 100 rad/s with 1% deformation at 25°C

Increase of mechanical properties

Self-healing properties



Microscopy picture after cuting and 25 min later film is store under vaccum between both picture

Self-healing behaviour keep under controlled atmospher

Conclusion and Outlook

- Synthesis of **well-defined** PEG **copolymer electrolytes** with different compositions (stat, diblock and triblock), architectures (linear and branched), functionalities (quadrupolar hydrogen bonding, single-ion), by different techniques (FRP, NMP, RAFT, and RAFT-PISA).
- **Self-healing** and stretchability for these materials.
- Need for **electrochemical characterization** (preliminary results: conductivity $\sigma > 10^{-5}$ S/cm at 20°C).
- Need for **Mechanical characterization** (tensile-stress) taking hygroscopy into account.
- Alternative self-healing monomers / architectures will be designed.

Aknowledgements

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Dr. Marc Ramuz

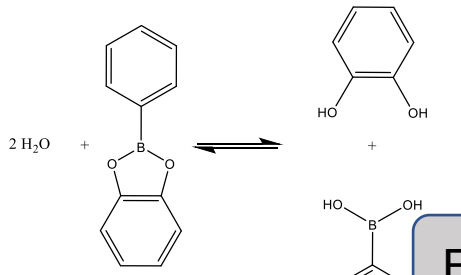
Fundings

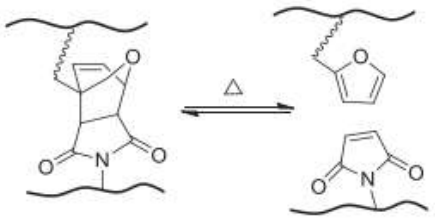
Radical Organic Chemistry and Specialty Polymers team

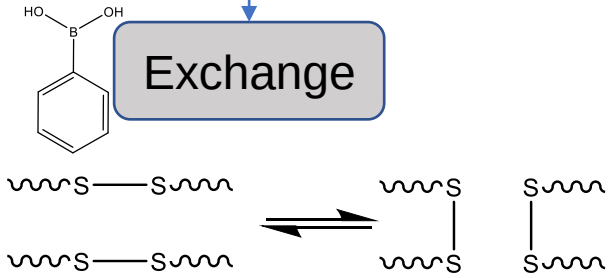
Thank you for your attention

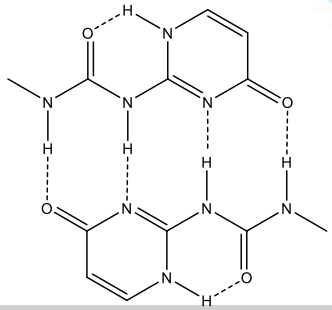
Self-healing strategies

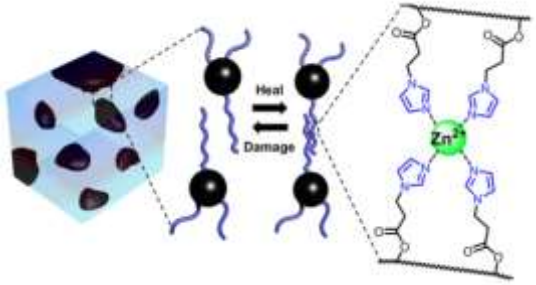
- Reversible Bond
  - covalent dynamic bond
    - Condensation
    - Addition
    - Exchange
  - Non-covalent bond
    - H-bond
    - Metal-ligand interaction
    - Ionic interaction
    - Host-guest

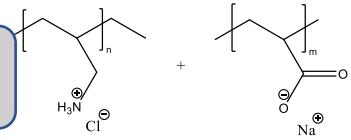










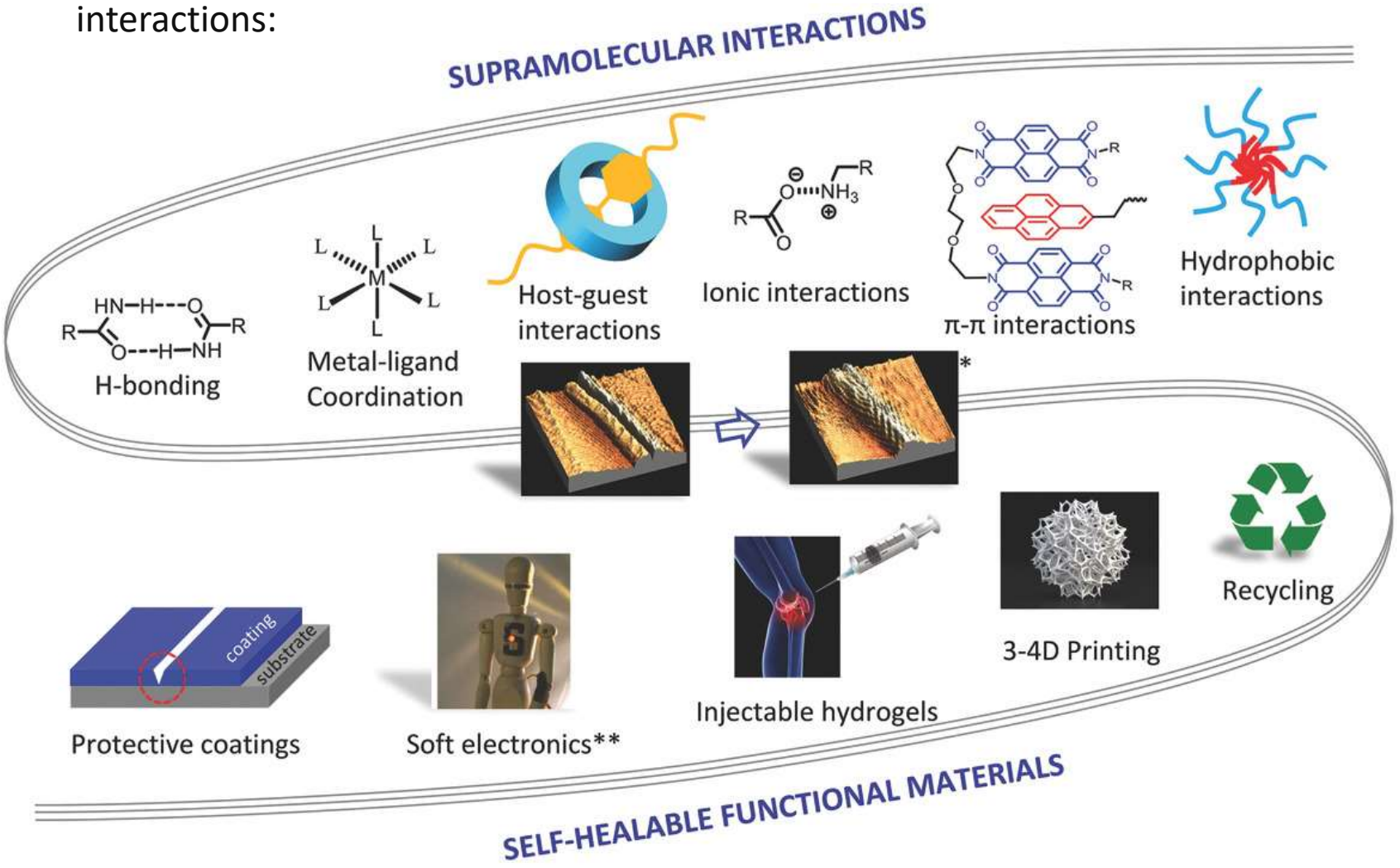


D. Mozhdehi et al. , *J. Am. Chem. Soc.*, ***2014***, *136, 46, 16218-16131*

A. Reisch et al., *Adv. Material*, ***2014***, *26, 2547*

Self-healing by supramolecular interactions

Supramolecular self-healing polymers based on various non-covalent interactions:



Intrinsic self-healing: without adding capsules of monomer for example

High Performance Stretchable Li-ion Microbatteries