

Polymerization of ethylene: from free radical homopolymerization to hybrid radical/catalytic copolymerization

An “ideal” polymer: PE

- Advantages of PE:

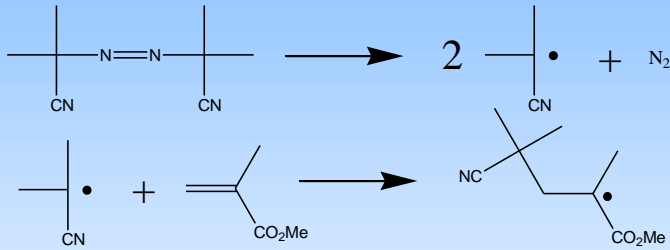
- Efficient and low cost industrial processes
- Easy to work up
- Different materials (HDPE, LDPE, LLDPE)
- Interesting properties
 - Due to a balance between crystalline and amorphous part
 - Chemical inertia
 - Water impermeability

An “ideal” polymer: PE

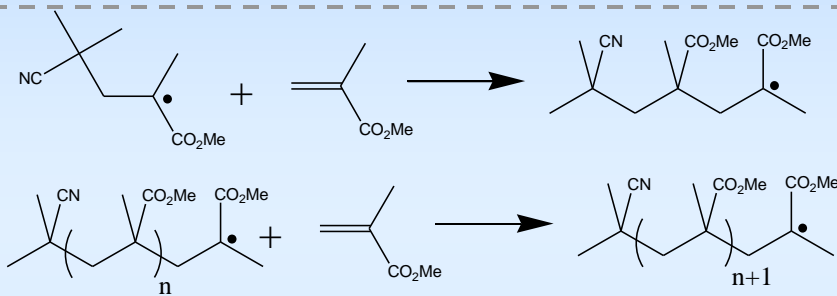
- Disadvantage of PE
 - Polyethylene is a non-polar material
 - Low interaction with inks, dyes, fillers ...
- How to solve this issue? → material has to contain some polar functions
 - Post-treatment step
 - Copolymerization

Incorporation of polar function via a radical copolymerization

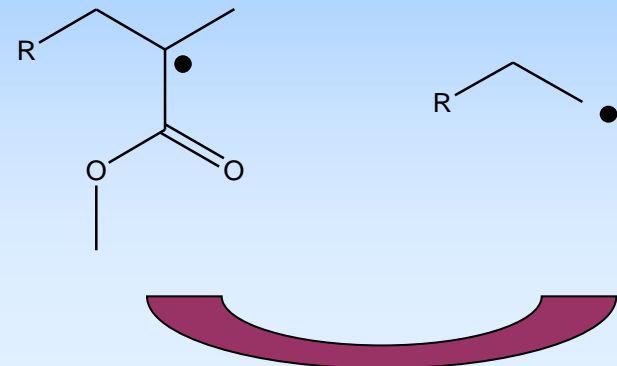
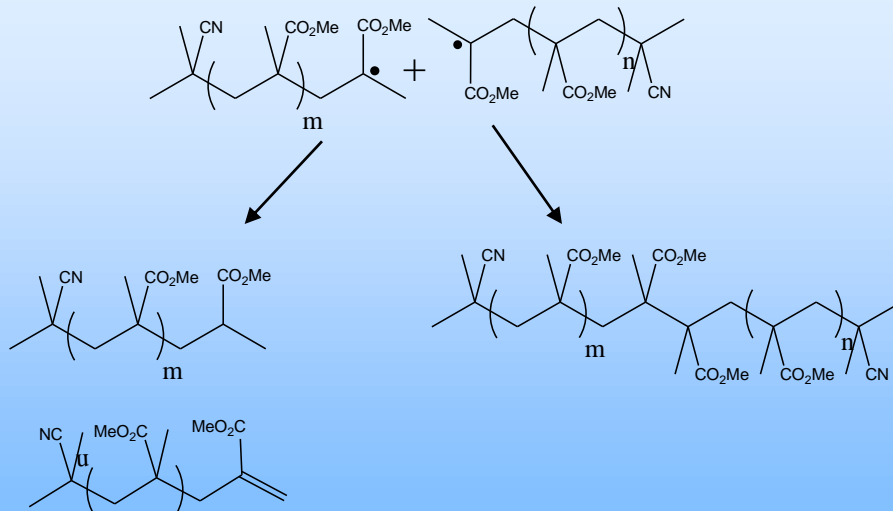
initiation



propagation



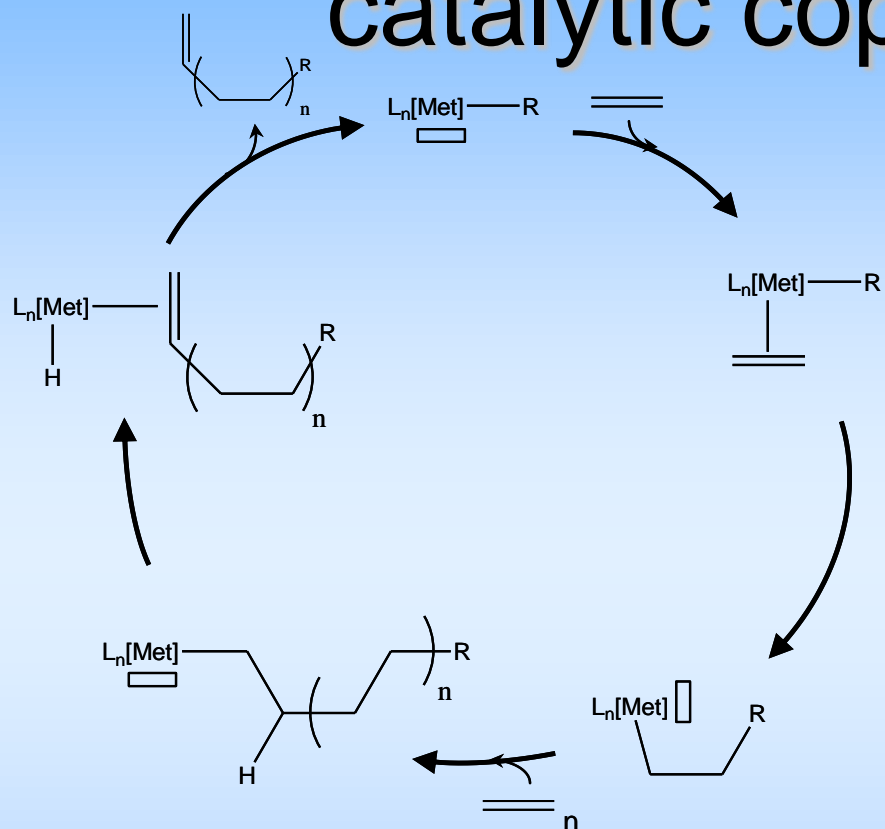
termination



Two distinct reactivities

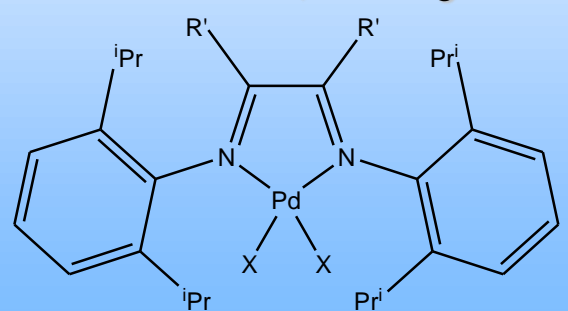
Efficient copolymerization only under severe experimental conditions ($P > 500$ bar, $T > 100^\circ\text{C}$)

Incorporation of polar function via a catalytic copolymerization

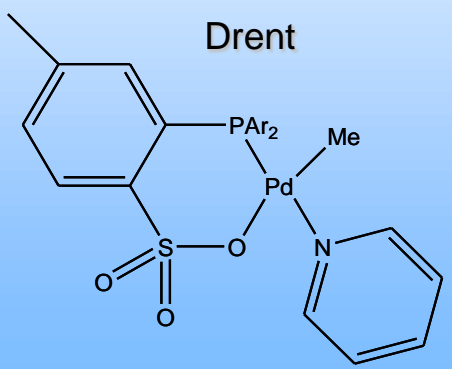


Most catalysts are totally deactivated in presence of polar comonomer

Brookhart, Mecking



Drent

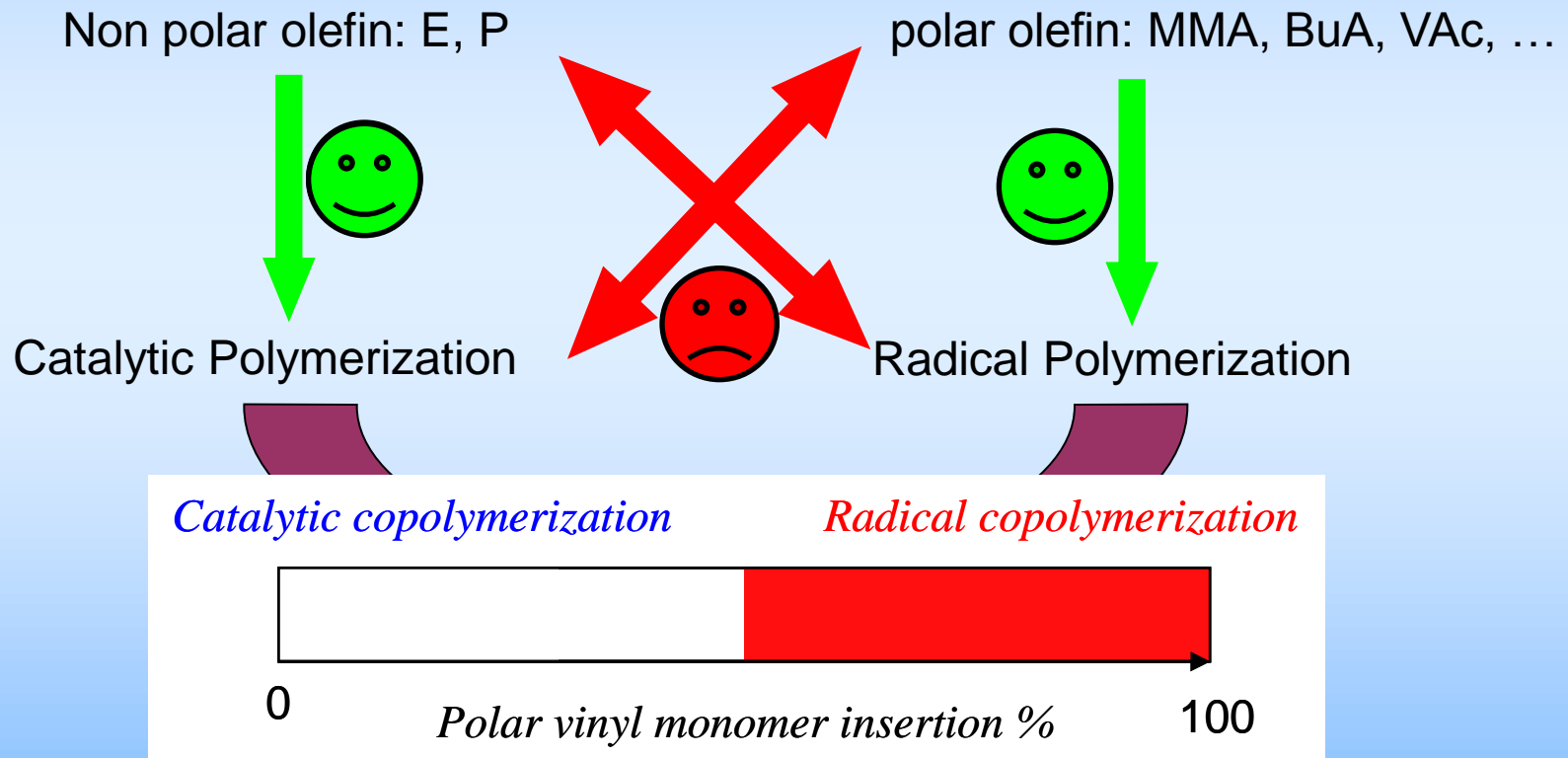


Some results have been obtained using specific catalysts

PhD Defense

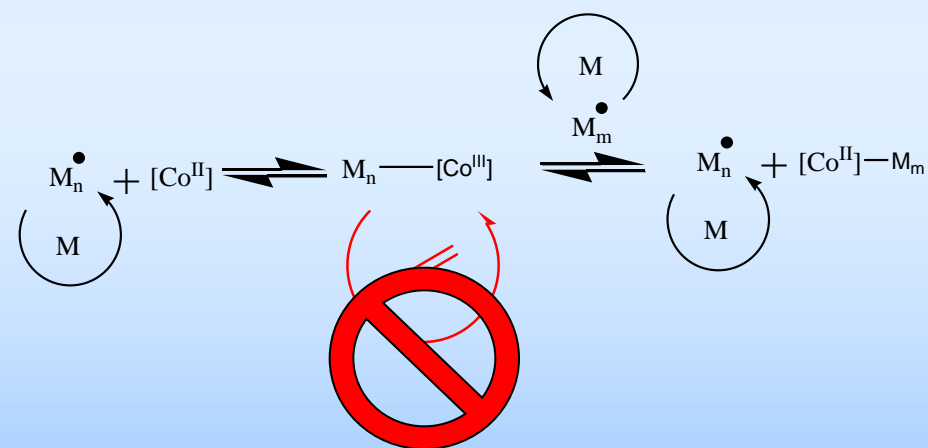
What is the purpose of these three years of study?

Synthesis of copolymers of non polar/polar olefins under mild conditions ($T < 100^\circ\text{C}$ and $P < 100$ bar)

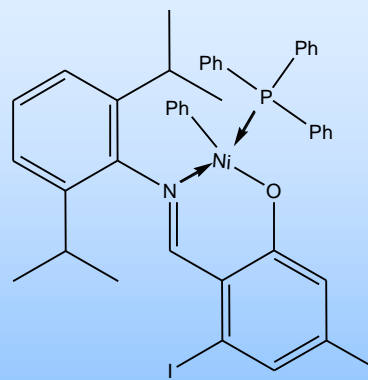
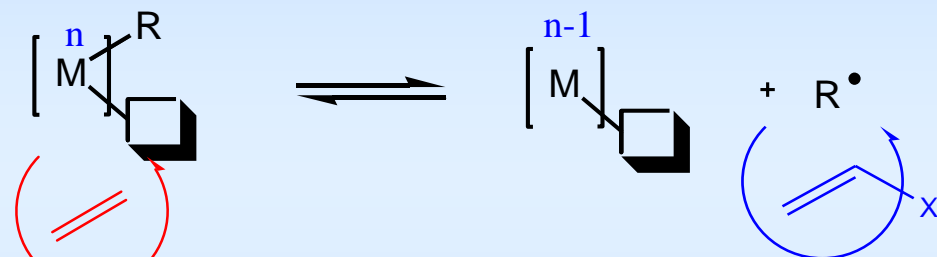


Interactions between radical and organometallic compounds already observed

Organometallic specie which traps radical



Pioneering work done by Alexandra LEBLANC at the LCPP (2005-2008)



- Catalytic polymerization of ethylene
- Radical polymerization of MMA, Sty and BuA

First results on ethylene/MMA copolymerization

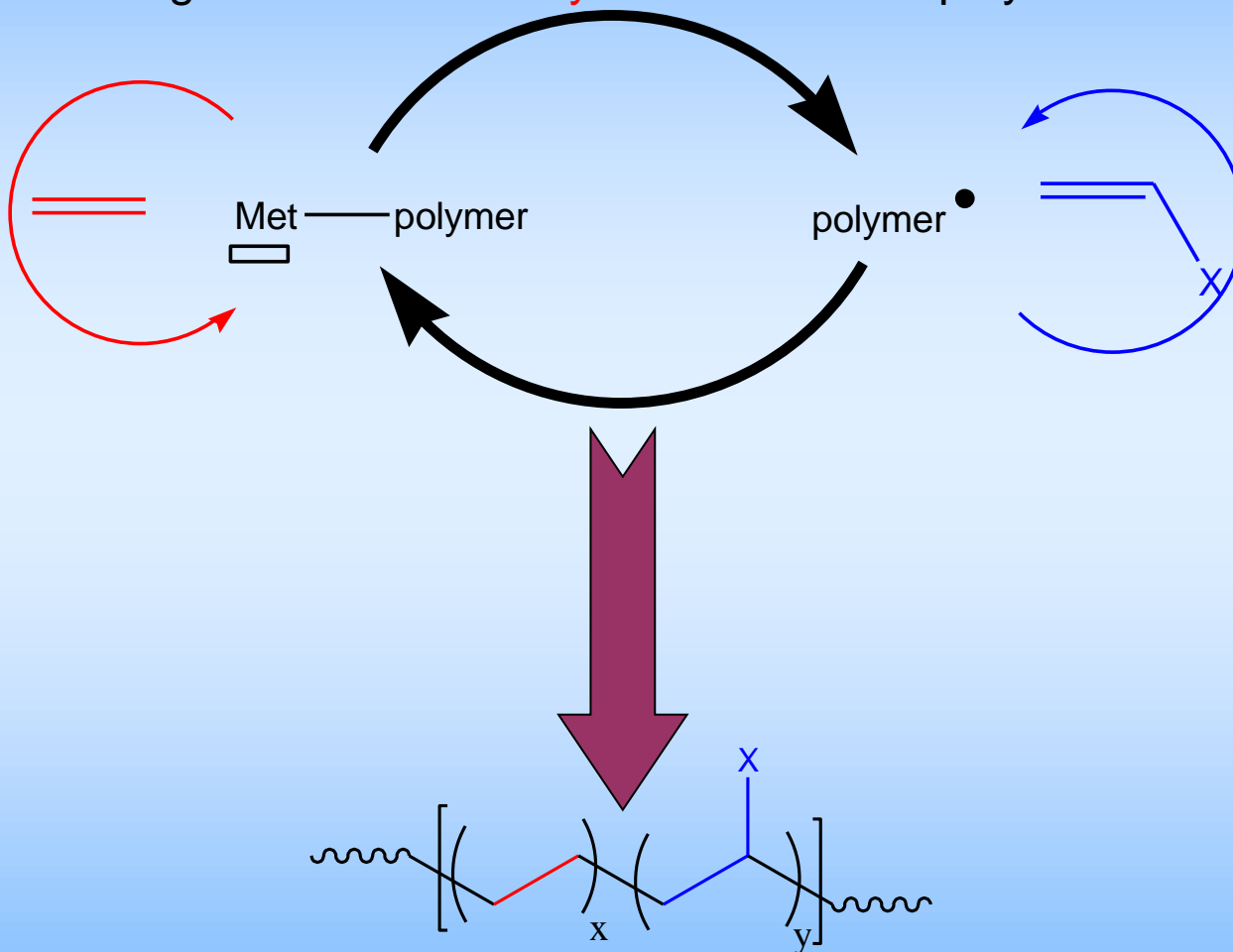
WO 2010049633

Outlook of the presentation

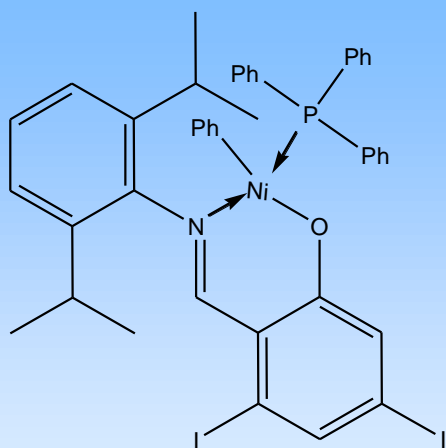
- Development of the hybrid copolymerization
 - Efficiency of the system
 - Investigation of the mechanism
- Study of free radical polymerization
 - Copolymerization
 - Ethylene radical polymerization

Hybrid copolymerization

Exchange between a **catalytic** and a **radical** polymerization

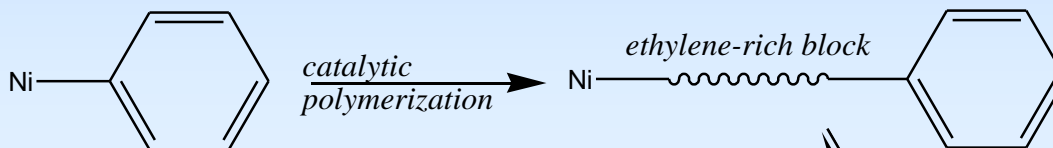


The NiNO system

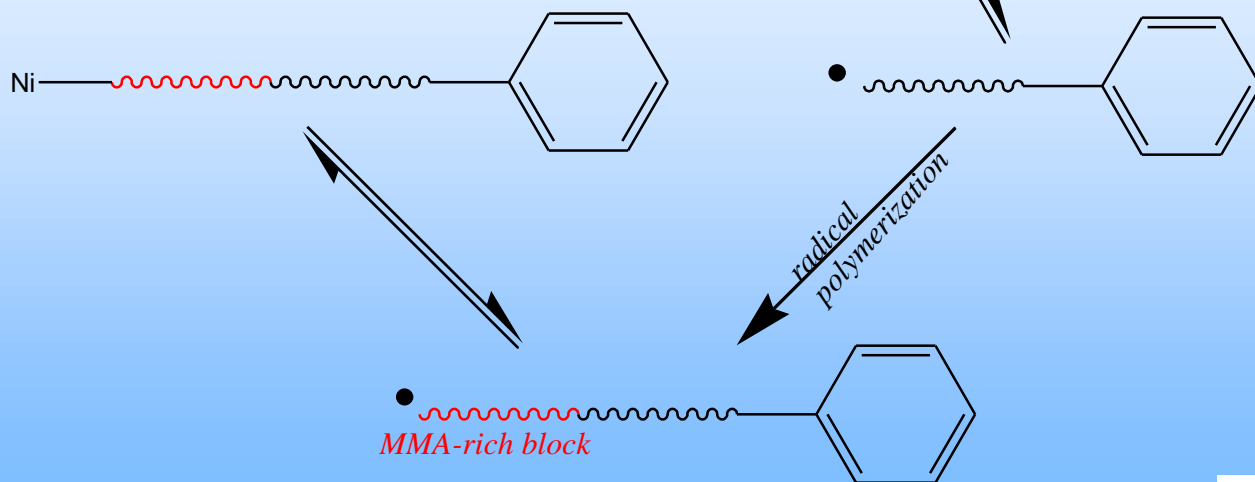


NiNO

Mono-component catalyst → no alkylating agent
Relatively low oxophilicity

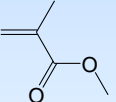
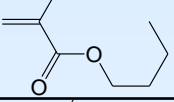
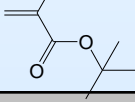
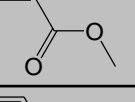
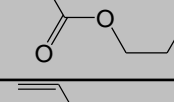
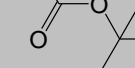


Hybrid mechanism expected



Is the hybrid system efficient?

NiNO alone

Comonomer		Yield (g)	Comonomer molar insertion (%)
MMA		2.8	4.3
BuMA		5.5	3.3
tBuMA		6.3	4.5
MA		0.02	nd
BuA		0.05	95
tBuA		0.1	97



High yield



Low polar monomer insertion

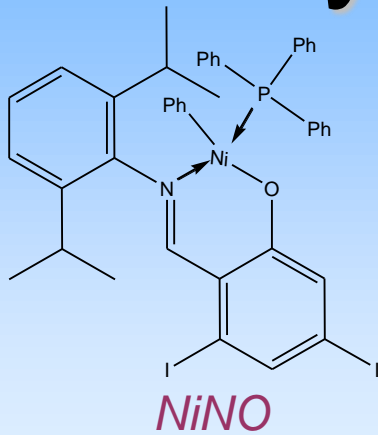


Almost inefficient

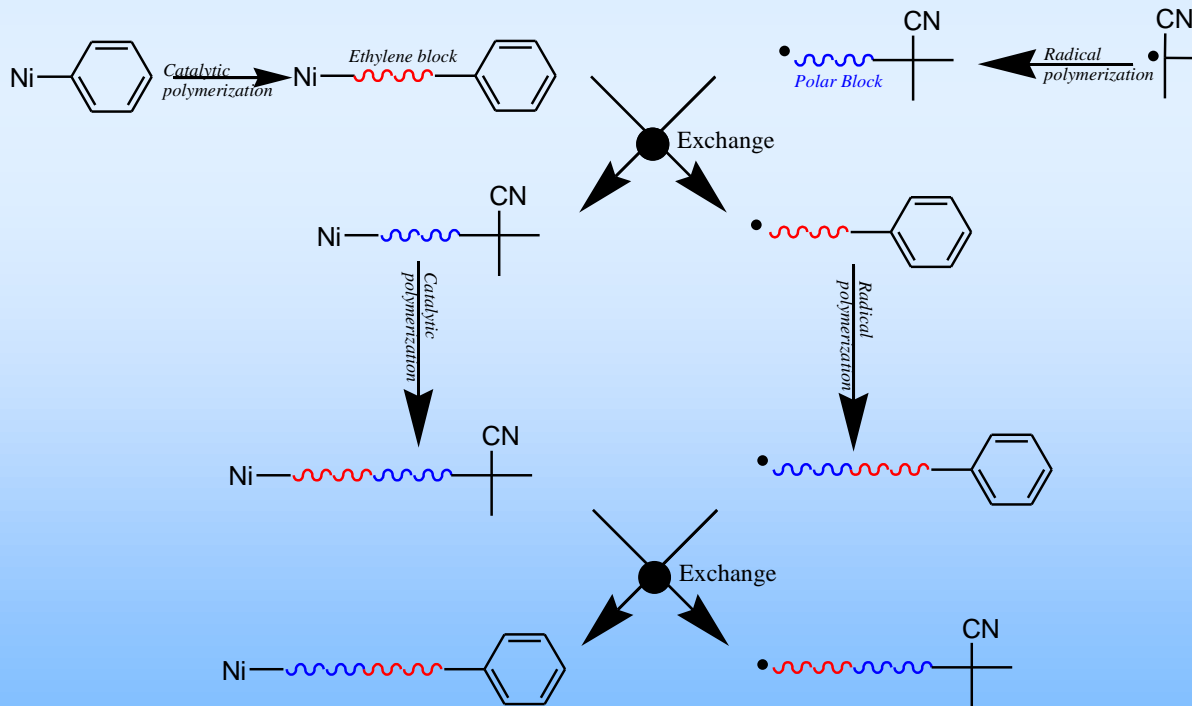
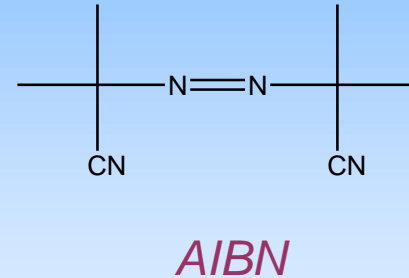
Polymerizations are performed during 12 hours with 50 mg of NiNO at 70°C in 250 mL of toluene with 25 g of comonomer under **20 bar of ethylene pressure**

Could be due to an inefficient exchange between mechanisms

“Full” hybrid system: NiNO + AIBN



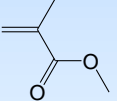
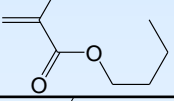
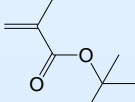
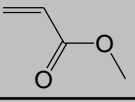
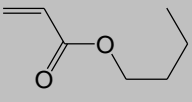
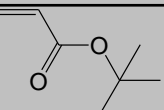
← Higher exchange frequency →



Is the full hybrid system efficient?

NiNO alone

NiNO + ½ AIBN

Comonomer		Yield (g)	Comonomer molar insertion (%)	Yield (g)	Comonomer molar insertion (%)
MMA		2.8	4.3	12	60
BuMA		5.5	3.3	12.7 +	54
tBuMA		6.3	4.5	17.3	35
MA		0.02	nd	12	88
BuA		0.05	95	16 ++	75
tBuA		0.1	97	15.5	51

Polymerizations are performed during 12 hours with 50 mg of NiNO and ½ molar equivalent of AIBN at 70°C in 250 mL of toluene with 25 g of comonomer under **20 bar of ethylene pressure**

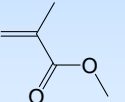
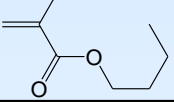
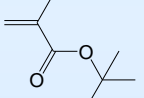
IT WORKS

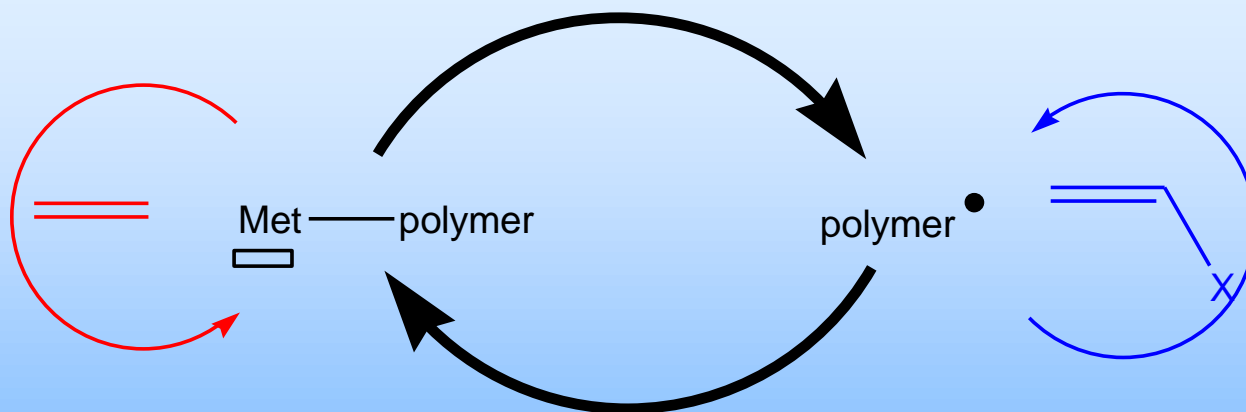


Is the hybrid system efficient?

NiNO alone

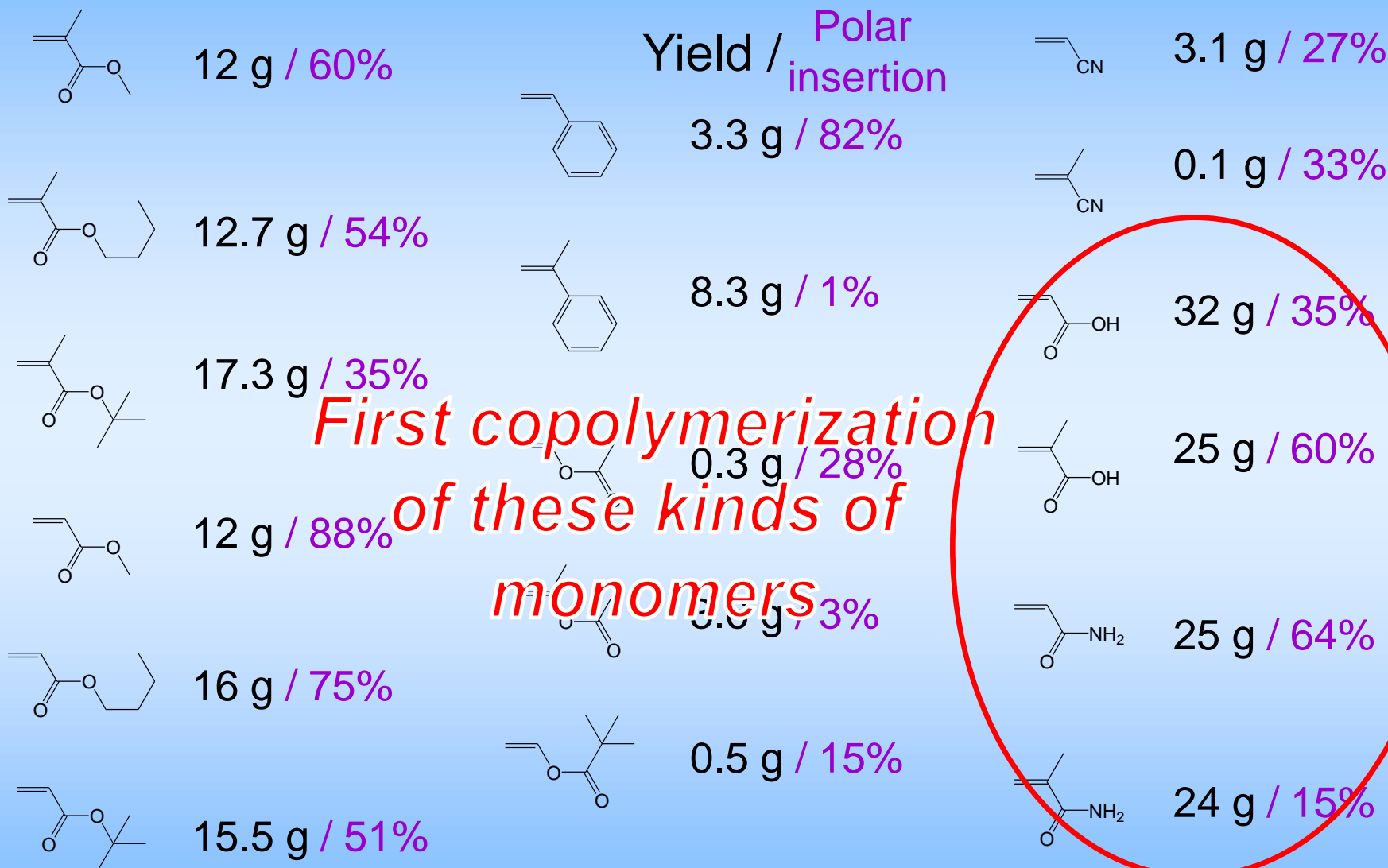
NiNO + 1/2 AIBN

Comonomer		Yield (g)	Comonomer molar insertion (%)	Yield (g)	Comonomer molar insertion (%)
MMA		2.8 ↓	4.3 ↓	12 ↓	60 ↓
BuMA		5.5 +	3.3 ≈	12.7 +	54 -
tBuMA		6.3 ↓	4.5 ↓	17.3 ↓	35 ↓



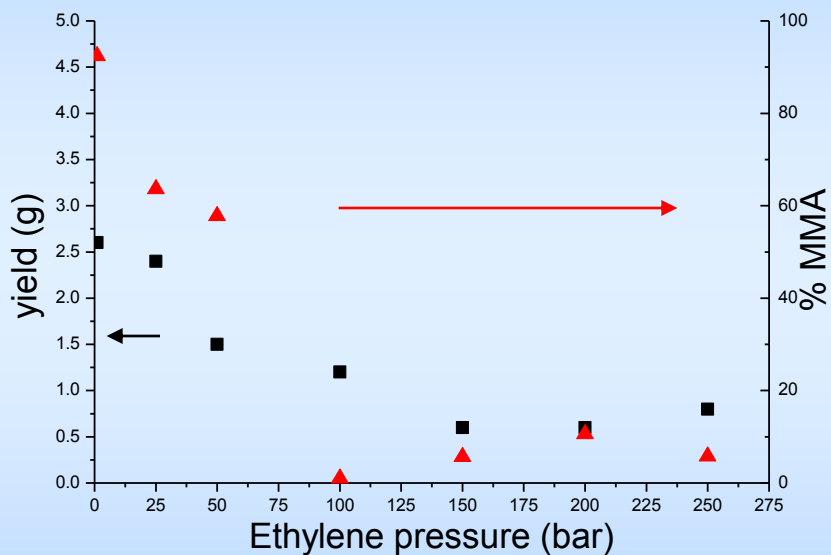
Exchange less efficient with bulky monomer

It works with various comonomers

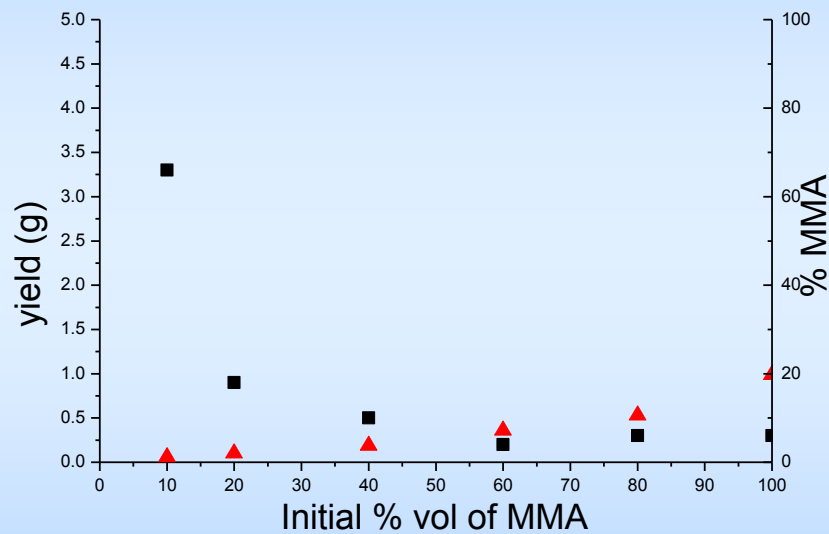


Efficient and tunable system

Variation of ethylene concentration



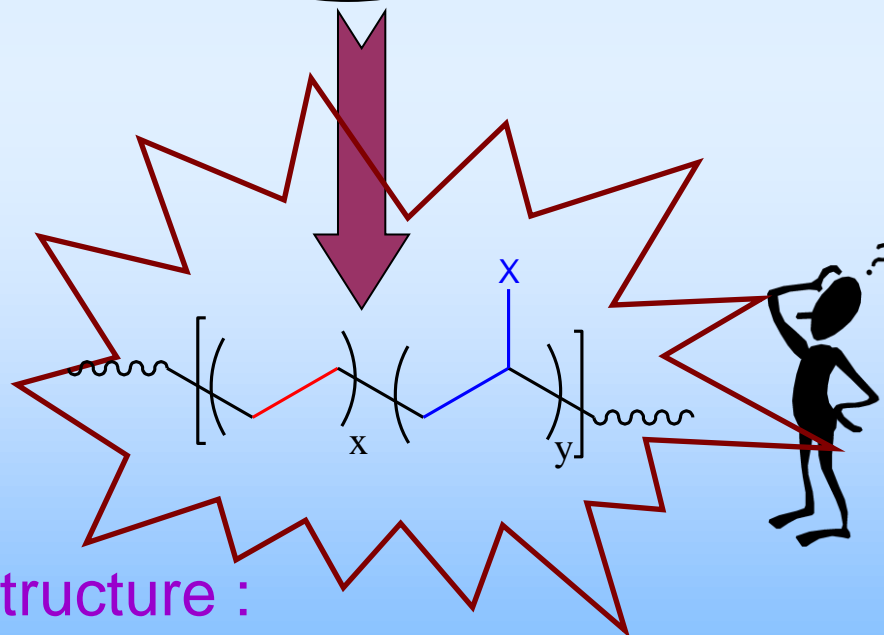
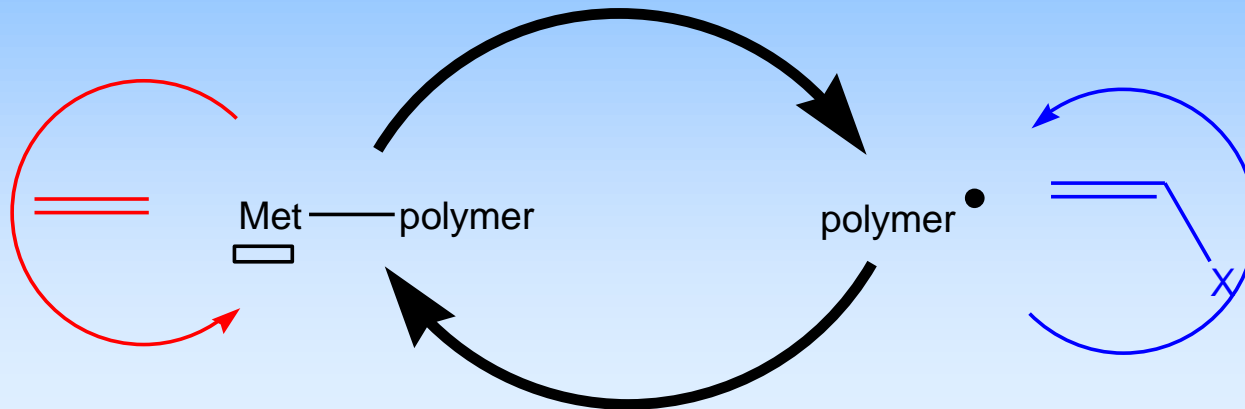
Variation of MMA concentration



Two simple ways to control the Ethylene/Polar monomer ratio in copolymer

So it works

But, how does it work?



Copolymer microstructure :

Are the synthesized copolymers multiblock?

Copolymer microstructures

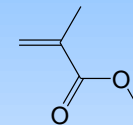
- SEC analysis
 - Monomodal distribution in molecular weight
- Thermal analysis
 - T_m & crystallinity remain even at high polar content
- Extractions by solvent
 - No homopolymer
- LC-CC in collaboration with DKI Darmstadt
 - Monomodal distribution in polar content
- NMR
- Amphiphilic properties analysis

Copolymers are synthesized

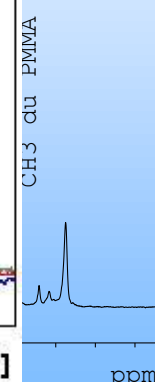
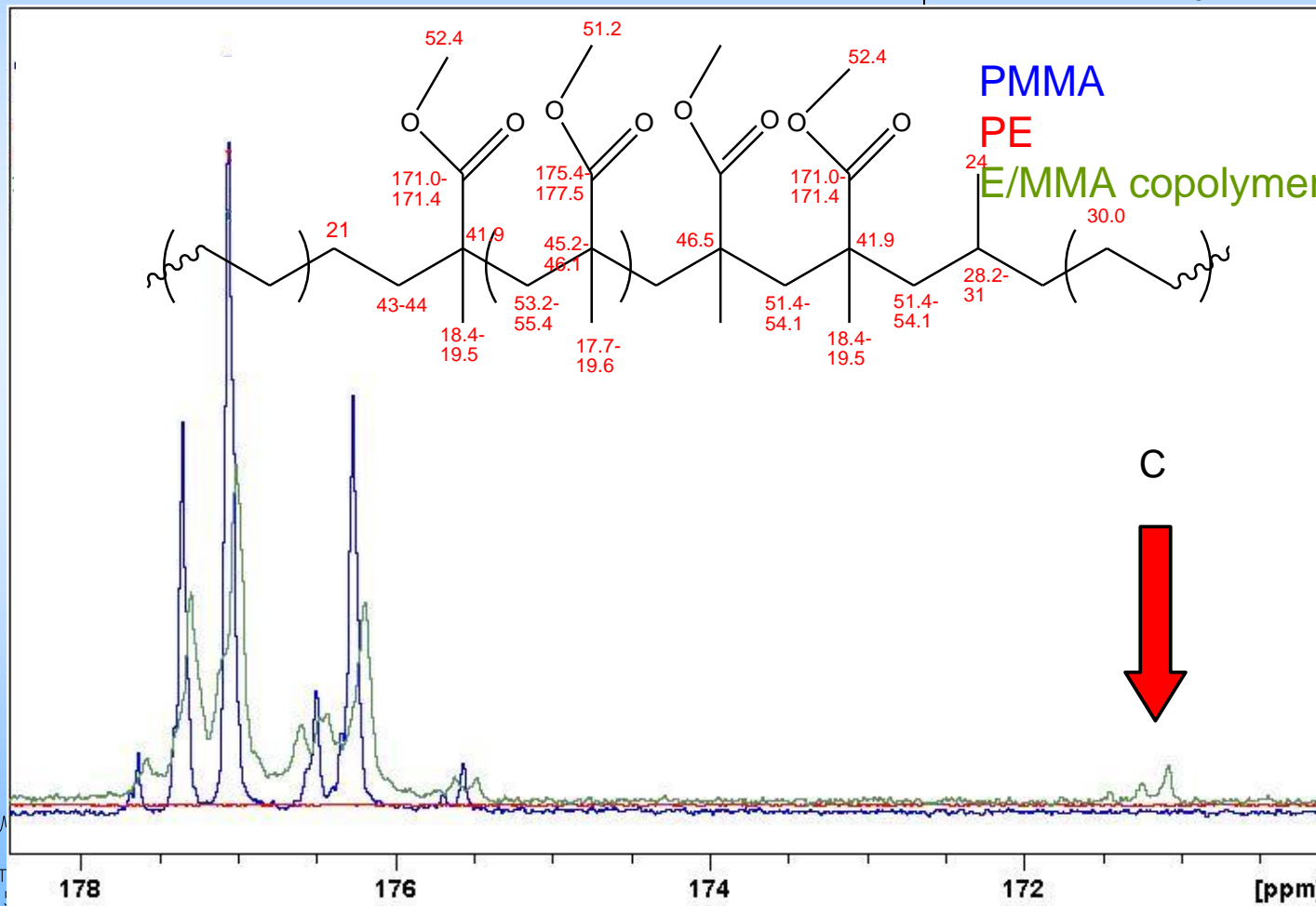
E/MMA copolymer microstructure

Polymers are multiblocks

^{13}C NMR new signals



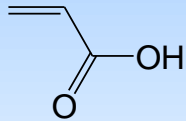
Yield 12 g
MMA 60%



Copolymer microstructure

Polymers are multiblocks

Case of ethylene/acrylic acid copolymer



Yield 32 g

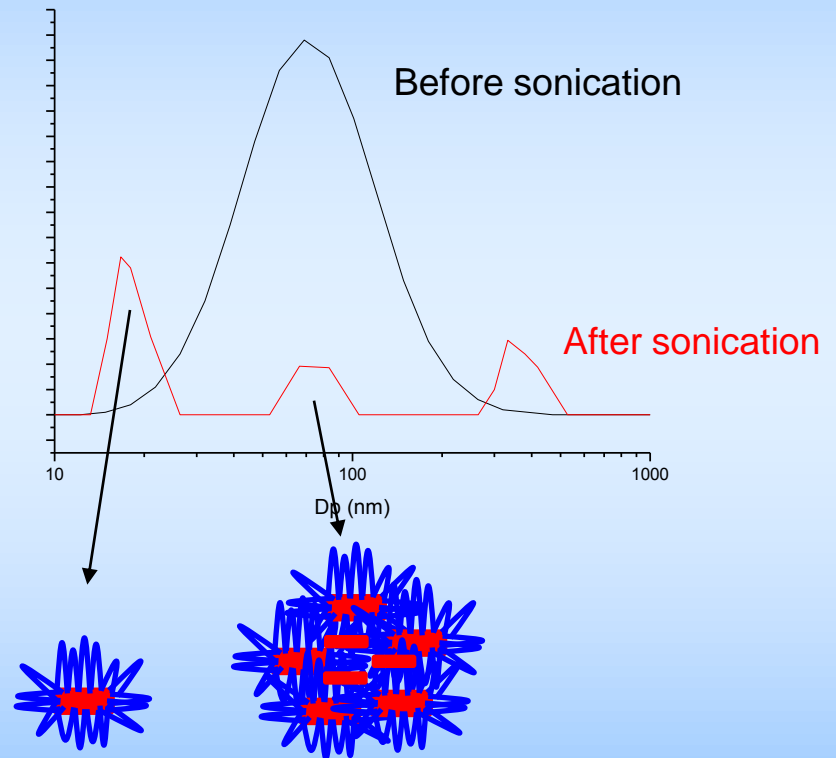
Ethylene content 65%

Contain ethylene units

And are *water dispersible*

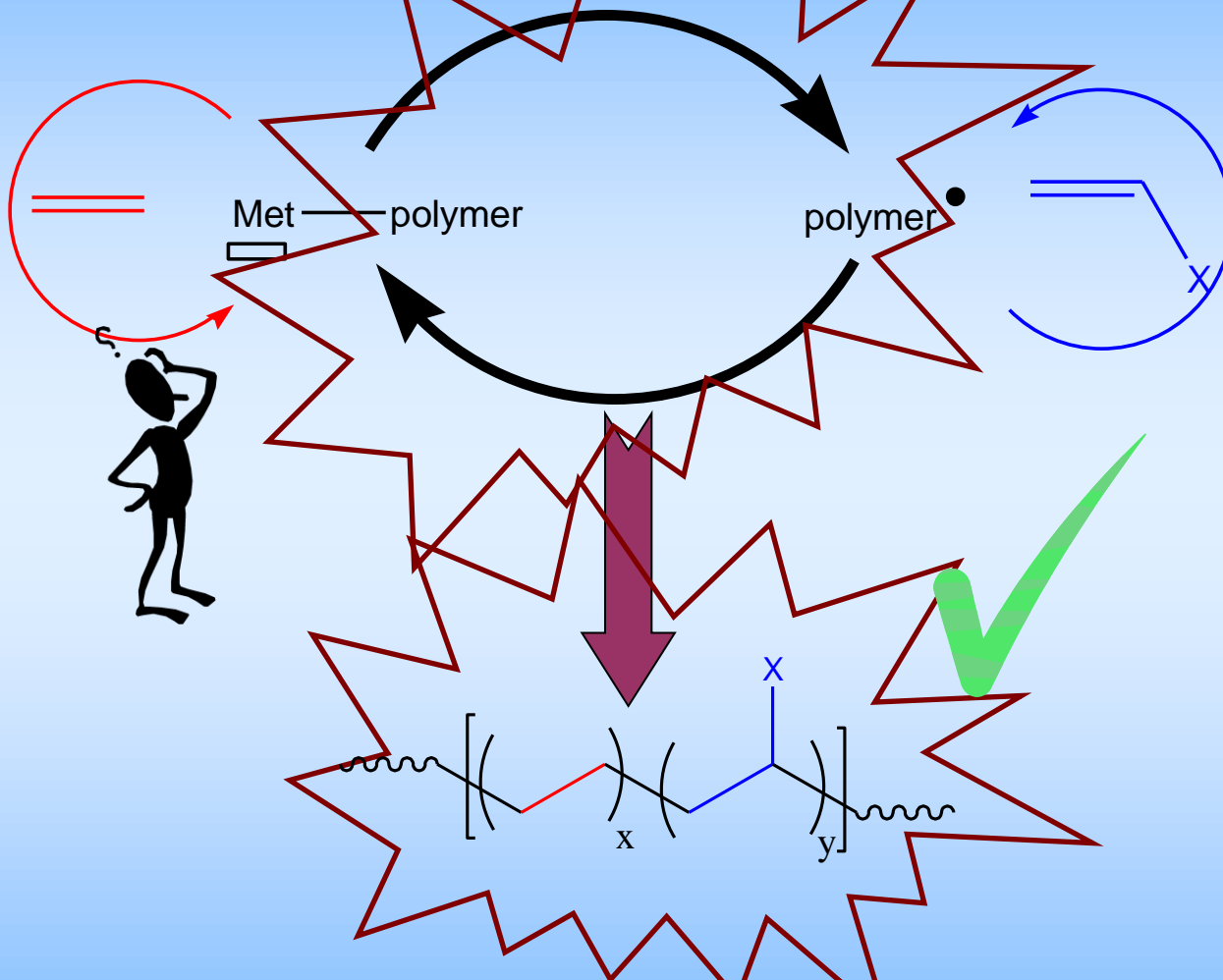


Nano-objects



So it works

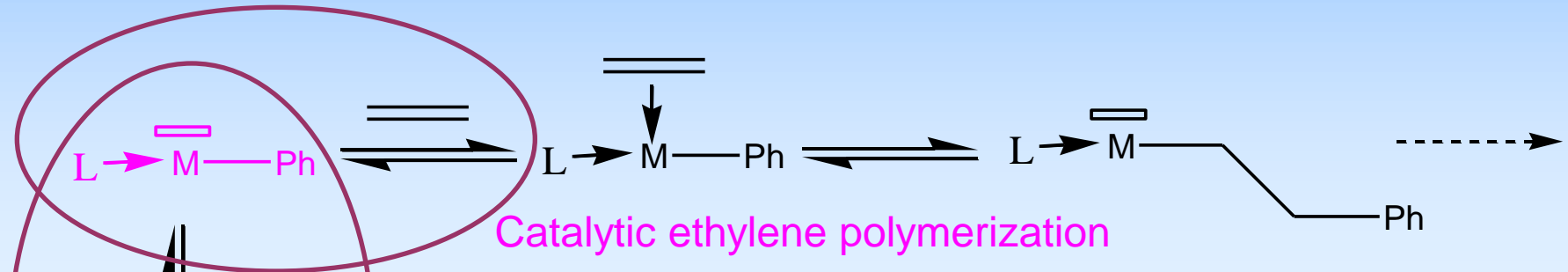
But, how does it work?



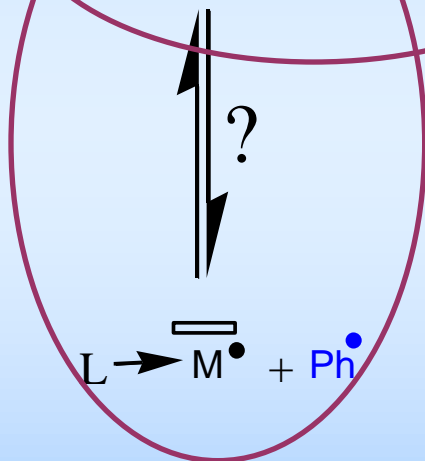
Exchange between radical and catalytic polymerization

Investigations on the exchange mechanism

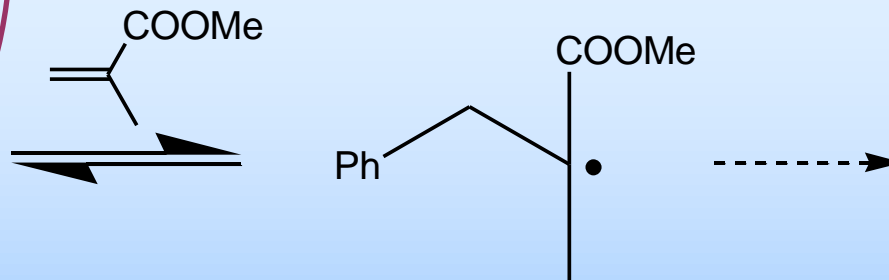
Catalyst



Catalytic ethylene polymerization



Initiator

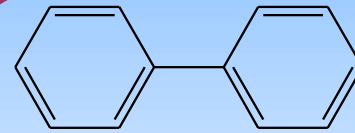


Radical polymerization

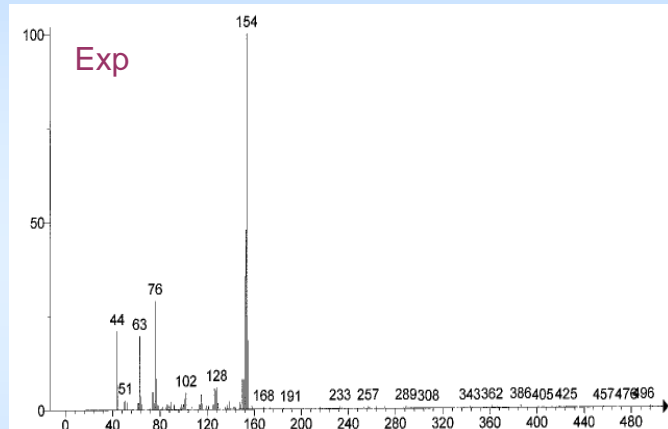
Experimental proof of the homolytic cleavage of Ni-C bond



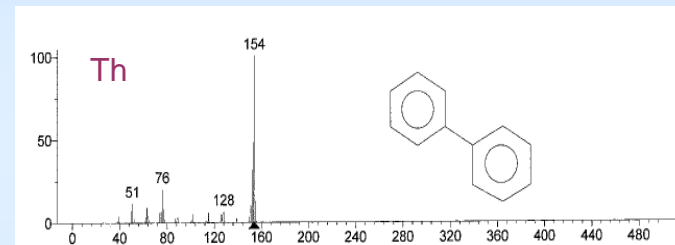
5 ml Toluene, 70°C, 12h



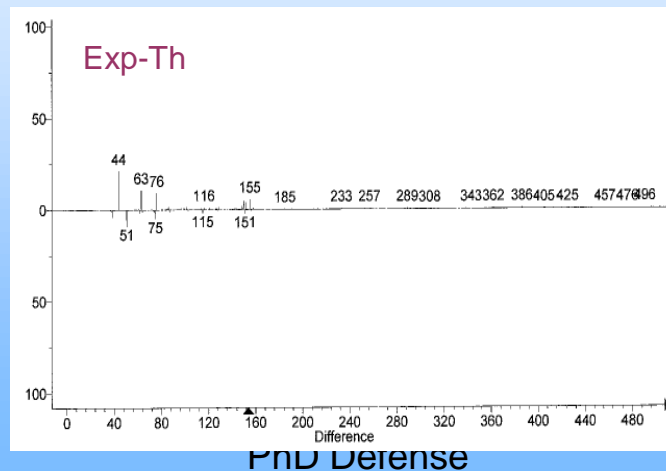
Coupling product of phenyl radical



Identified by GC-MS



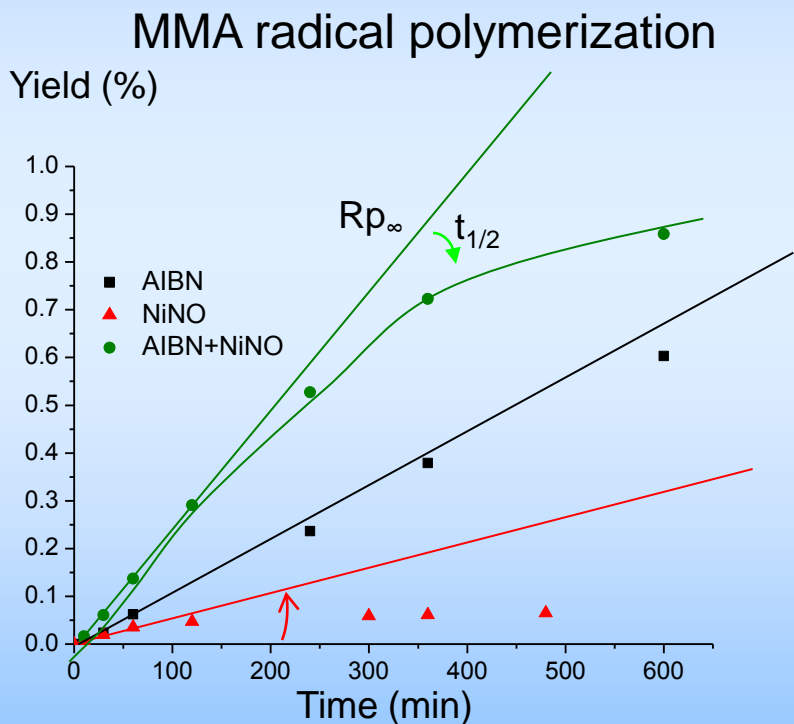
==



Synergy effect between AiBN and NiNO

MMA radical polymerization

50 mg NiNO and/or 10 mg AiBN (1/2 eq)
 10 mL MMA
 40 mL Toluene
 70°C



NiNO = (poor) initiator
 Synergy between AiBN and NiNO

Ethylene catalytic polymerization

100 mg NiNO and/or 20 mg AiBN (1/2 eq)
 20 bar Ethylene pressure
 250 mL Toluene
 70°C 1h

NiNO Catalyst	1/2 eq AIBN	activity (g/mmol/h)
yes	no	95
no	yes	0
yes	yes	135

Reactivation of dead catalyst by AiBN

$$Rp_{\infty} = k_p \sqrt{\frac{2fk_d[I]_0}{k_t}} = X \sqrt{k_d}$$

$$t_{1/2} = \frac{\ln 2}{k_d}$$

If k_p and k_t cst

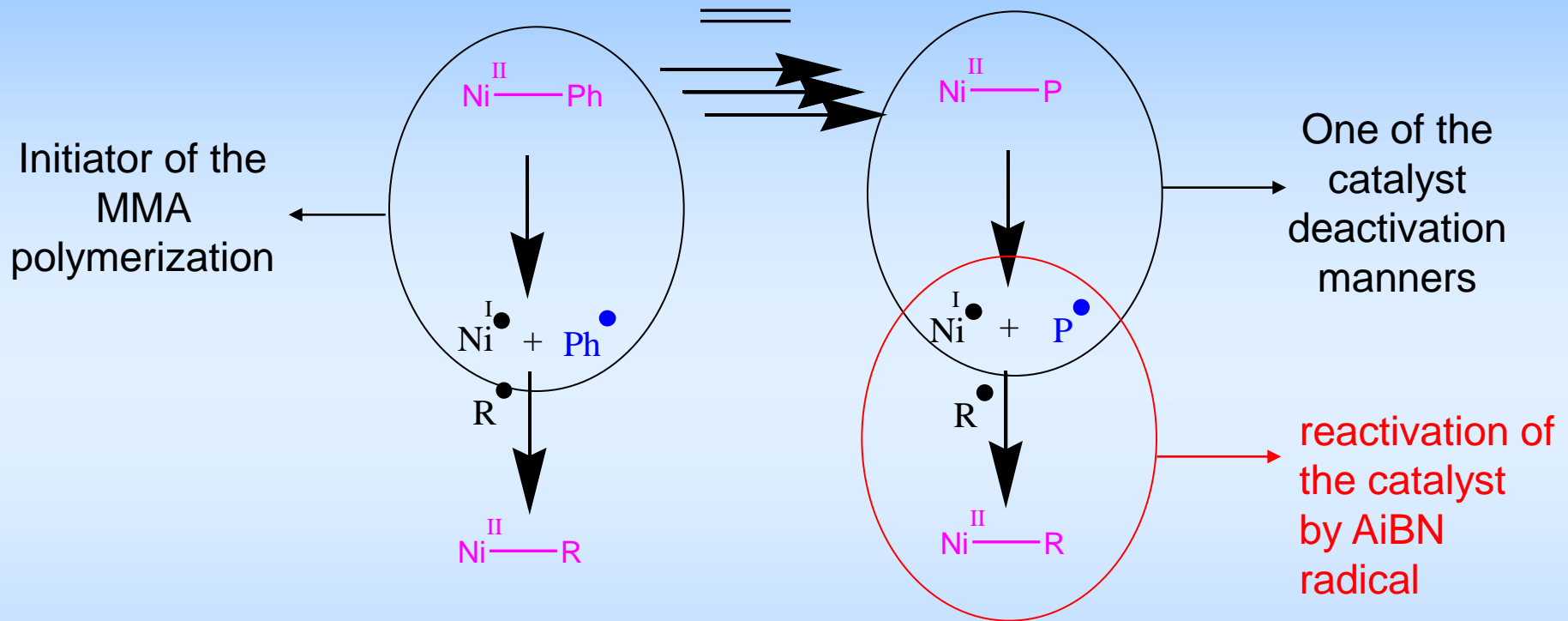
$$f[I]_{NiNO} = 0.15[NiNO]$$

$$t_{1/2} = 200 \text{ min}$$

$$Rp_{\infty_{AIBN+NiNO}} > Rp_{\infty_{AIBN}} + Rp_{\infty_{NiNO}}$$



Versatility of the NiNO complex



Doesn't explain the synergy observed

$$R_{p_{\infty, AIBN+NiNO}} > R_{p_{\infty, AIBN}} + R_{p_{\infty, NiNO}}$$

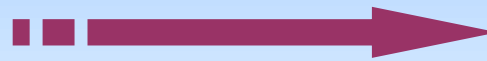


What is the interaction between NiNO and AiBN?

$$R_{p\infty_{AIBN+NiNO}} > R_{p\infty_{AIBN}} + R_{p\infty_{NiNO}} \quad f[NiNO]=0.15[NiNO] \quad R_{p\infty_{AIBN+NiNO}} = R_{p\infty_{AIBN}} + R_{p\infty_{NiNO}} \quad f[NiNO]=[NiNO]$$

$$f[I]_{NiNO} = 0.15[NiNO]$$

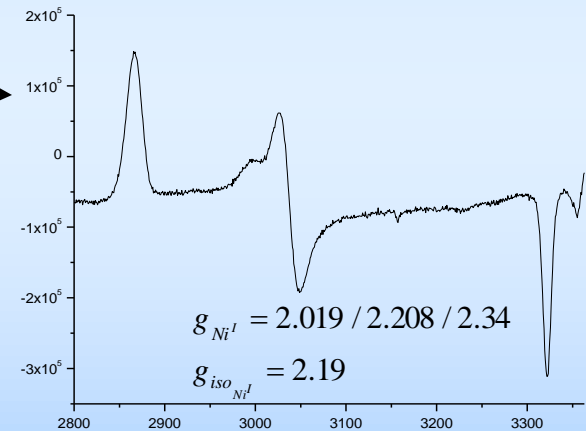
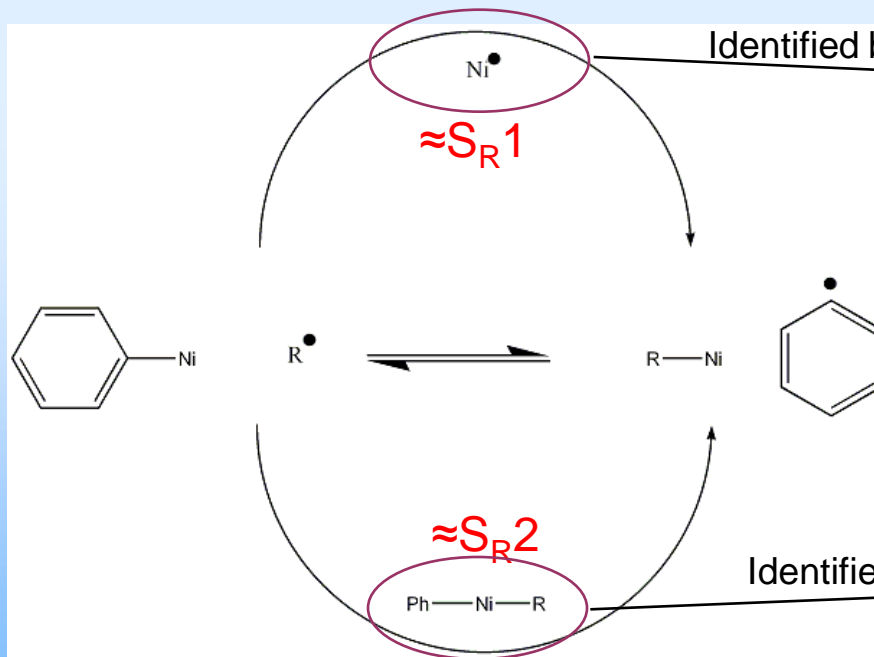
Without AiBN



$$f[I]_{NiNO} = [NiNO]$$

With AiBN

AiBN increases the efficiency of the NiNO initiation

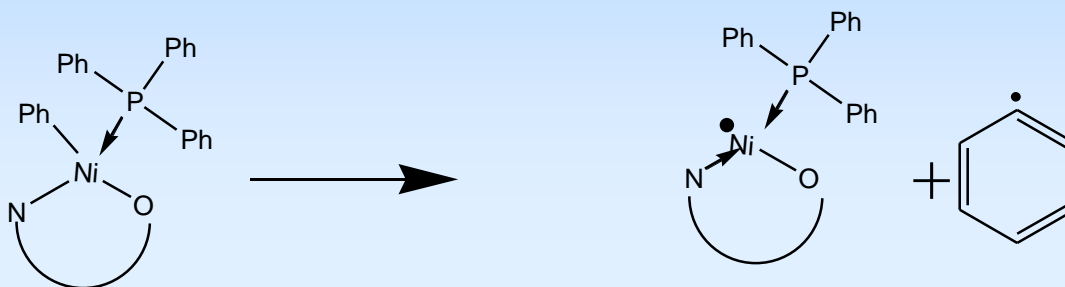


$$g_{Ni^{III}} = 2.070$$

Both S_{R1} and 2 take place

Study of the S_R1 : ligand effect

- How to tune the kinetics of the reaction?



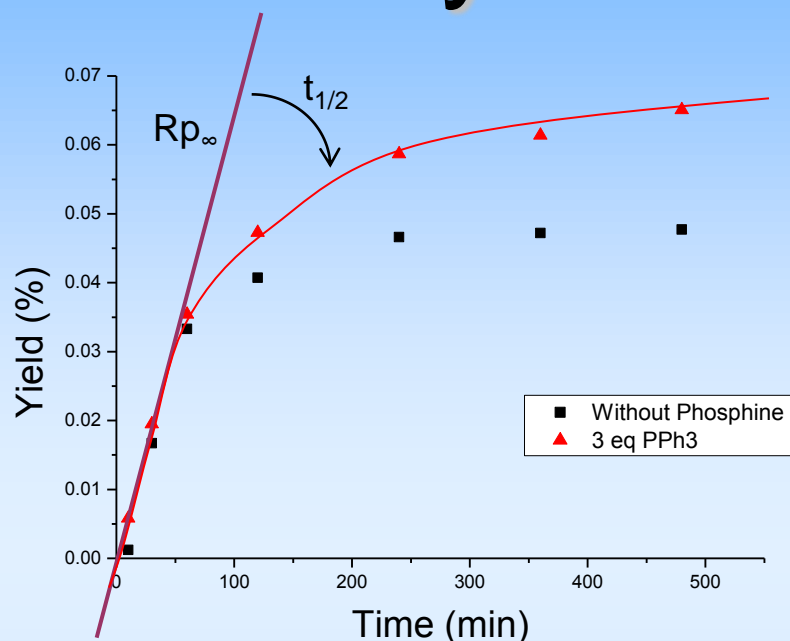
- Possible control of the length of the non-polar bloc

 High k_d

 Low k_d

- Additionnal ligand can favor or disfavor the process

Polymerization of MMA

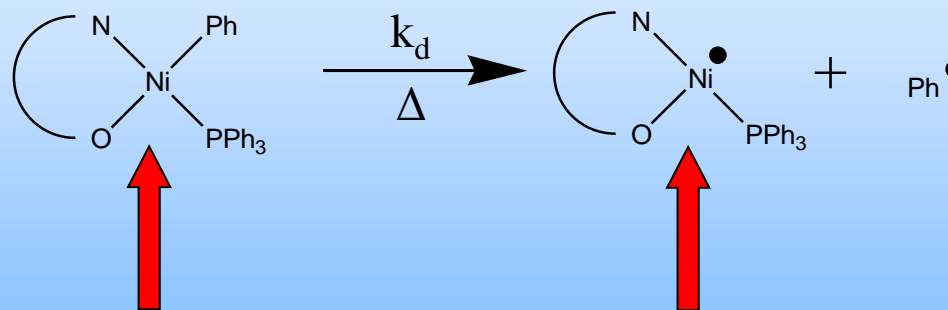


50 mg NiNO
 (3eq phosphine)
 10 mL MMA
 40 mL Toluene
 70°C

$$Rp_{\infty} = k_p \sqrt{\frac{2fk_d[I]_0}{k_t}} = X \sqrt{k_d}$$

$$t_{1/2} = \frac{\ln 2}{k_d}$$

Phosphine effect : ↗ Kinetic with PPh₃



axial coordination of the phosphine
 → weakening of Ni-C bond

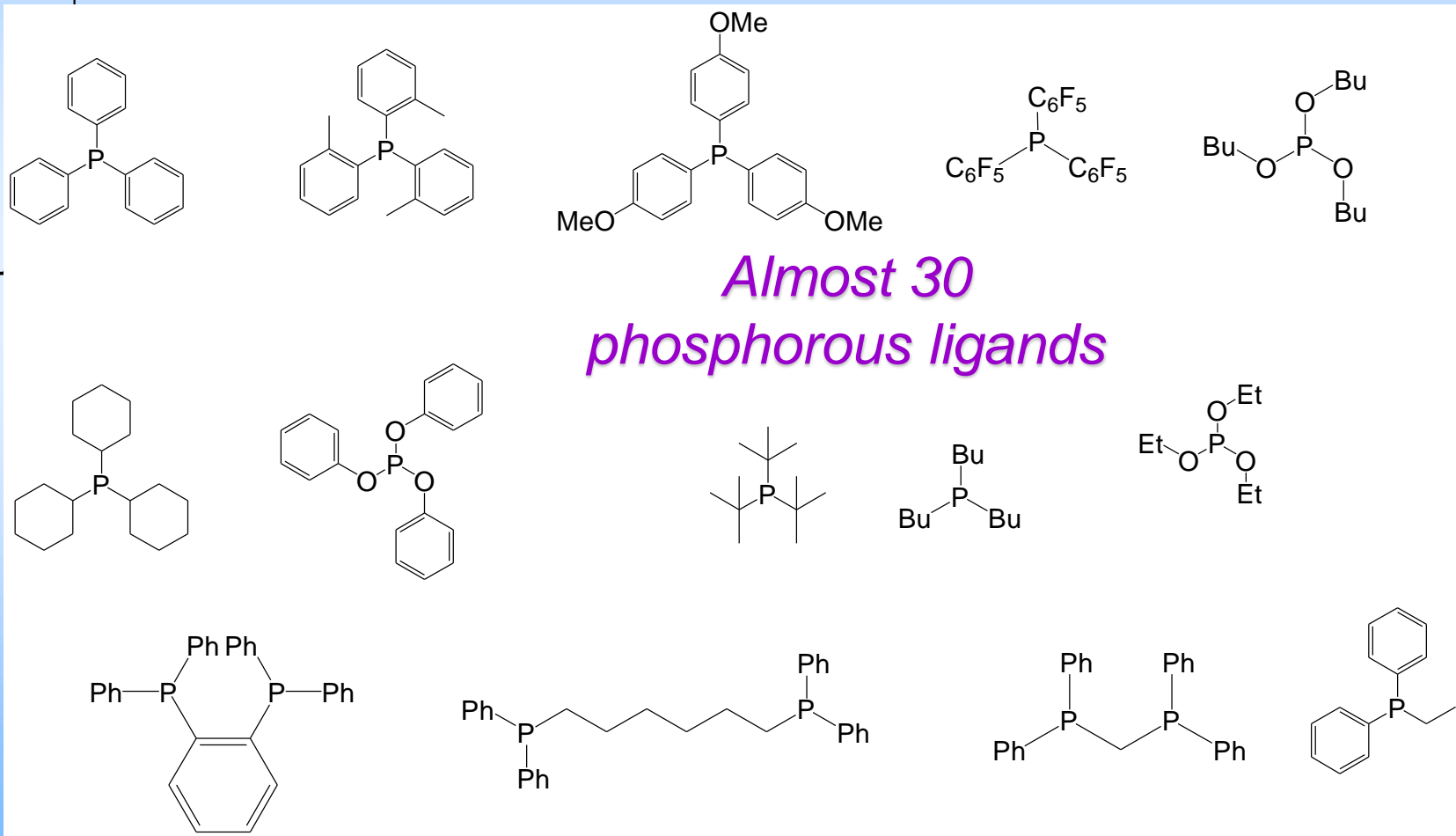
phosphine coordination
 → stabilization of Ni^I

Quantification of the phosphine effect

$$i^* \chi d + j^* (\theta - \theta_{st}) + k^* E_{ar} + l^* \pi p = t_{1/2} \text{ or } X$$

i^* χd j^* $(\theta - \theta_{st})$ k^* E_{ar} l^* πp

σ -donation Tolman's angle Aryl effect π retro-donation



Summary – multiple role for NiNO compound

- NiNO = catalyst
 - Reactivated by free radical

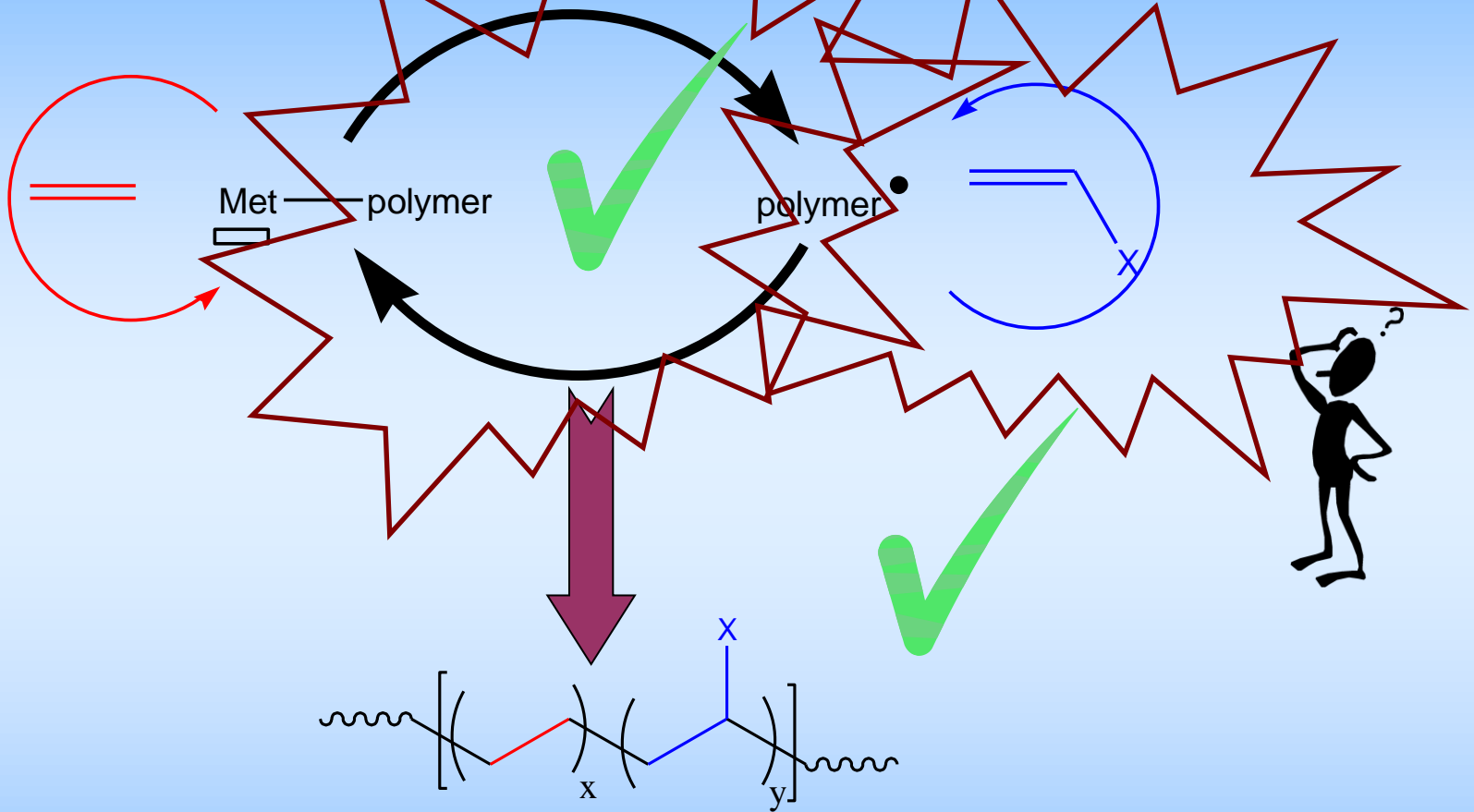
- NiNO = initiator
 - Synergy with free radical
 - Both S_{R1} and S_{R2} exist

Can be tuned by phosphorous ligand

- NiNO = radical trap (S_{R1}), transfer agent (S_{R2})

So it works

But, how does it work?



Influence of ethylene on radical polymerization of the polar monomer

Radical copolymerization ethylene-polar vinyl monomers

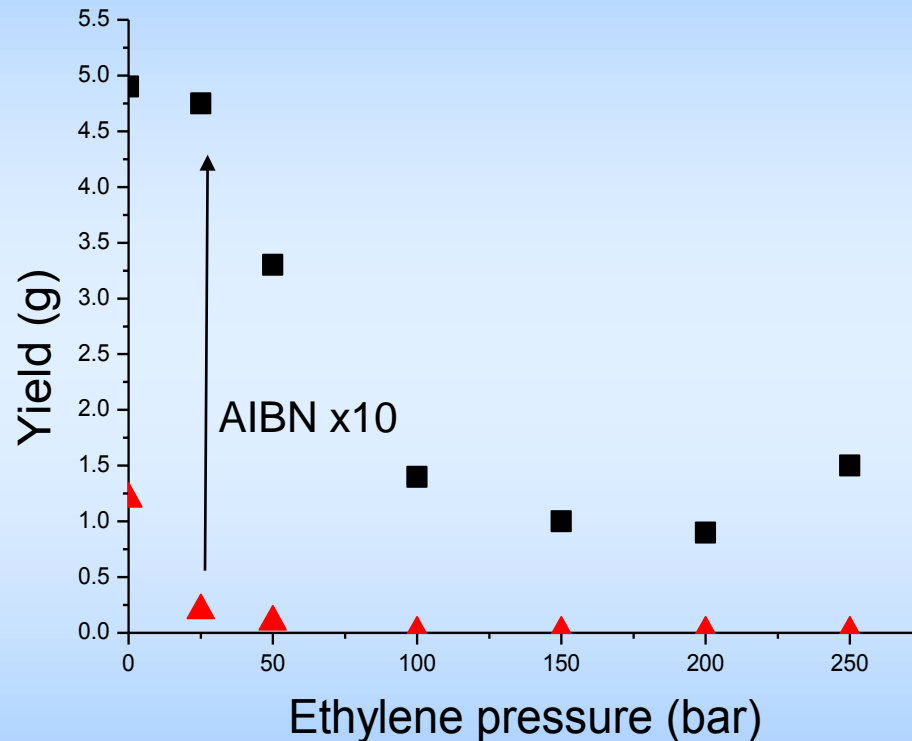
Experimental conditions:

Toluene 40 mL

10 mL of MMA

AIBN **16** or **160** μmol

4 hours at 70°C

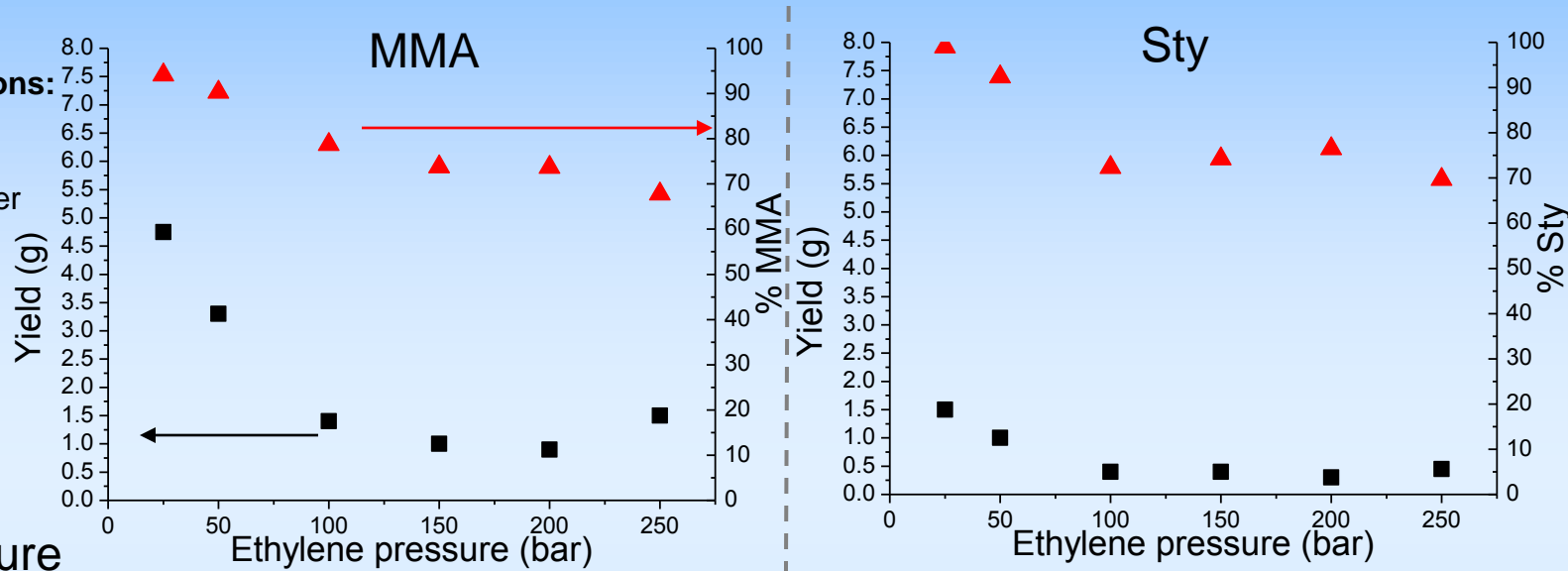


*Free radical copolymerization only efficient at
higher AIBN concentration*

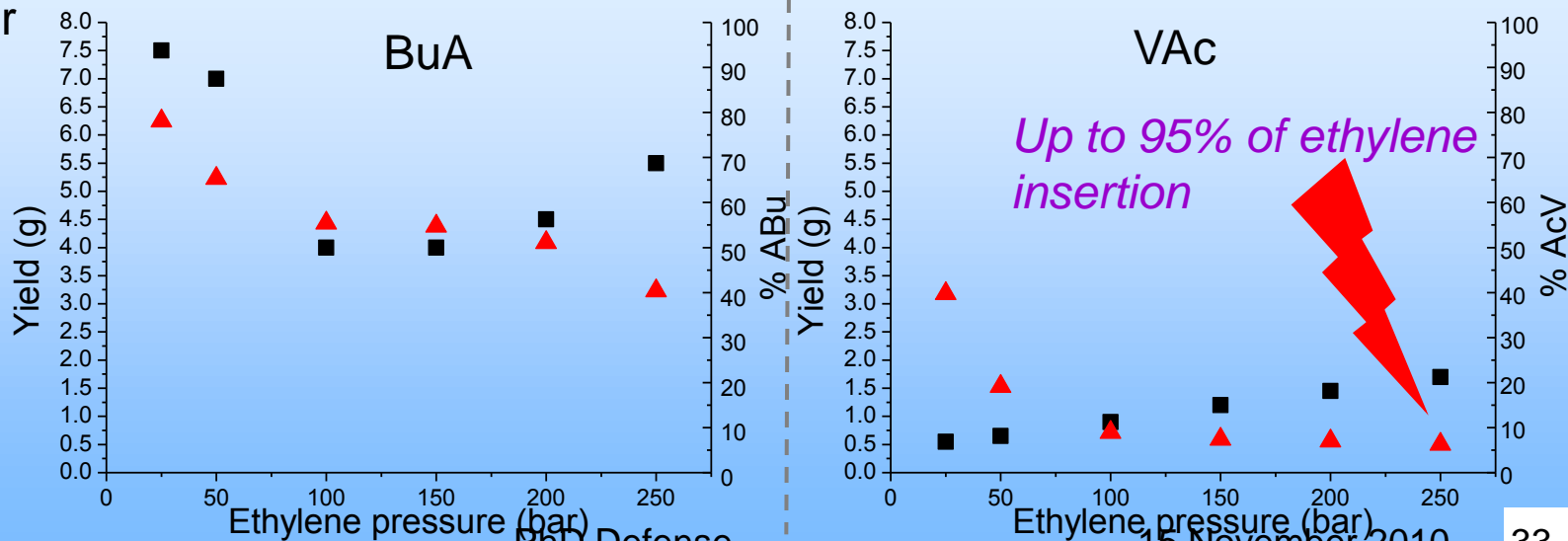
Radical copolymerization ethylene-polar vinyl monomers

Experimental conditions:

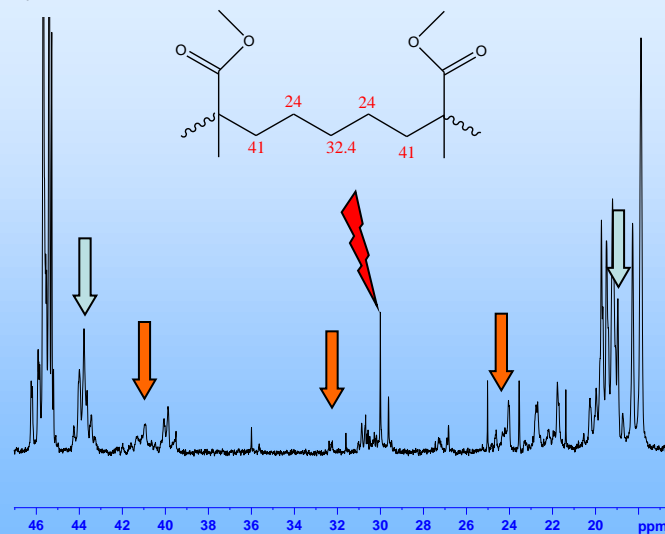
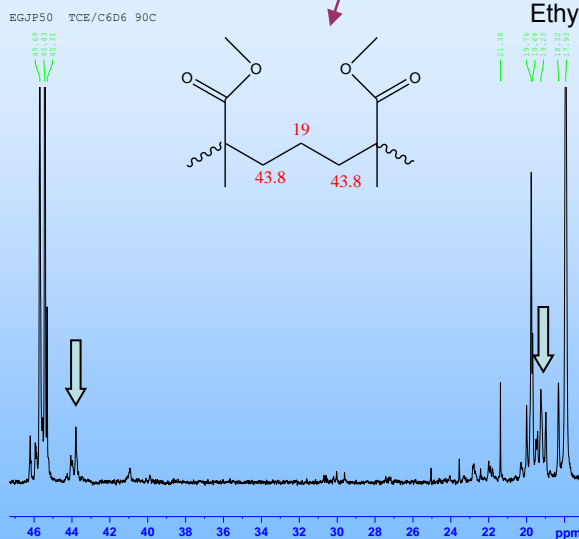
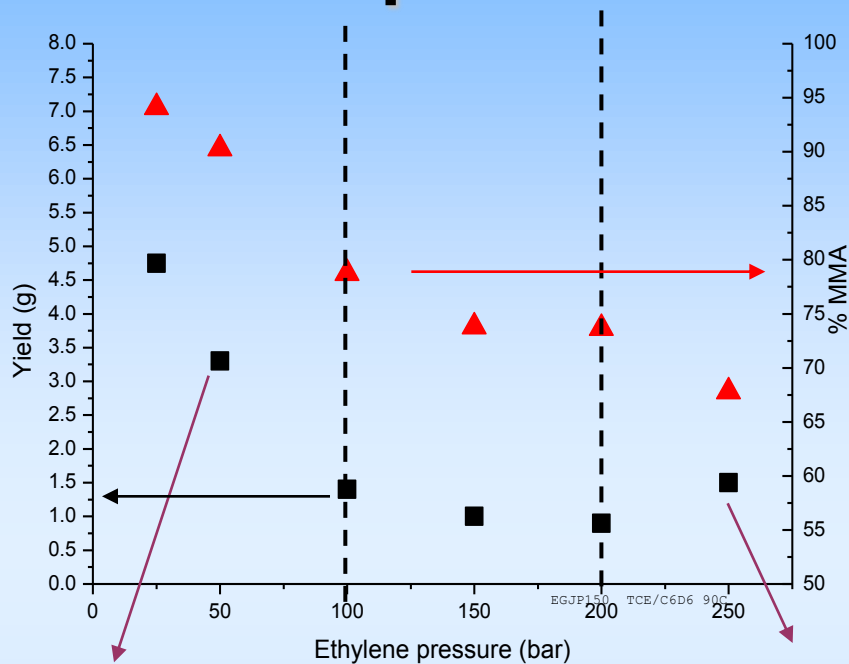
- Toluene 40 mL
- 10 mL polar monomer
- AIBN 160 μmol
- 4 hours at 70°C



Ethylene pressure
up to 250 bar

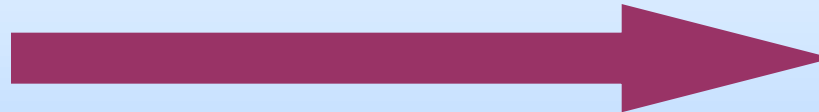
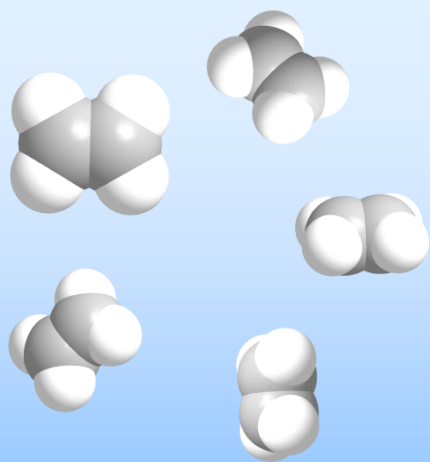


Ethylene sequences analysis

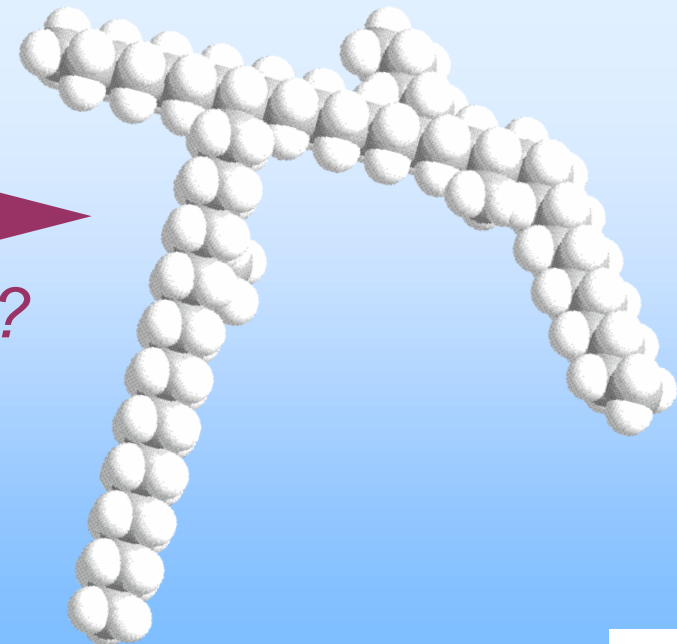


Can ethylene be polymerized by free radical polymerization under these mild conditions?

Consecutive ethylene units
High ethylene content
even at medium pressure

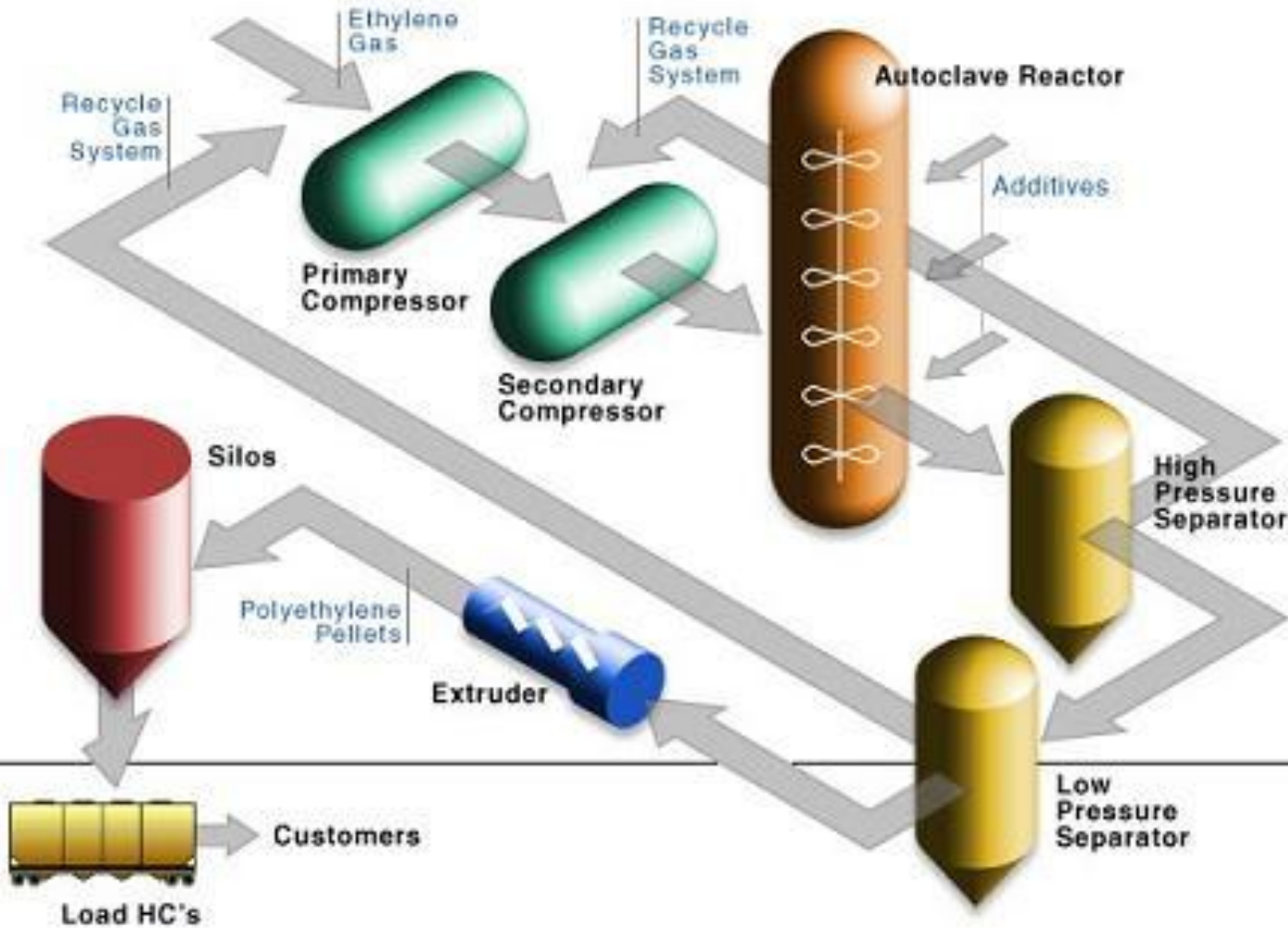


Radical polymerization?

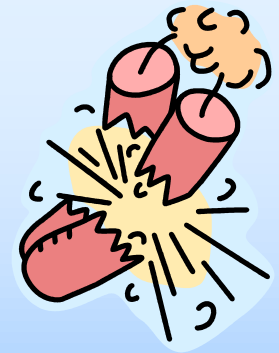


Standard radical LDPE process

Low Density Polyethylene Production Process
(Antwerp Polymers Plant)



Severe conditions:
200-300°C
Over 2000 bar
In bulk



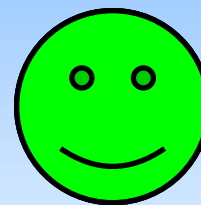
Ethylene homopolymerization

Experimental conditions:

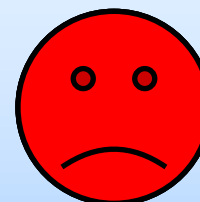
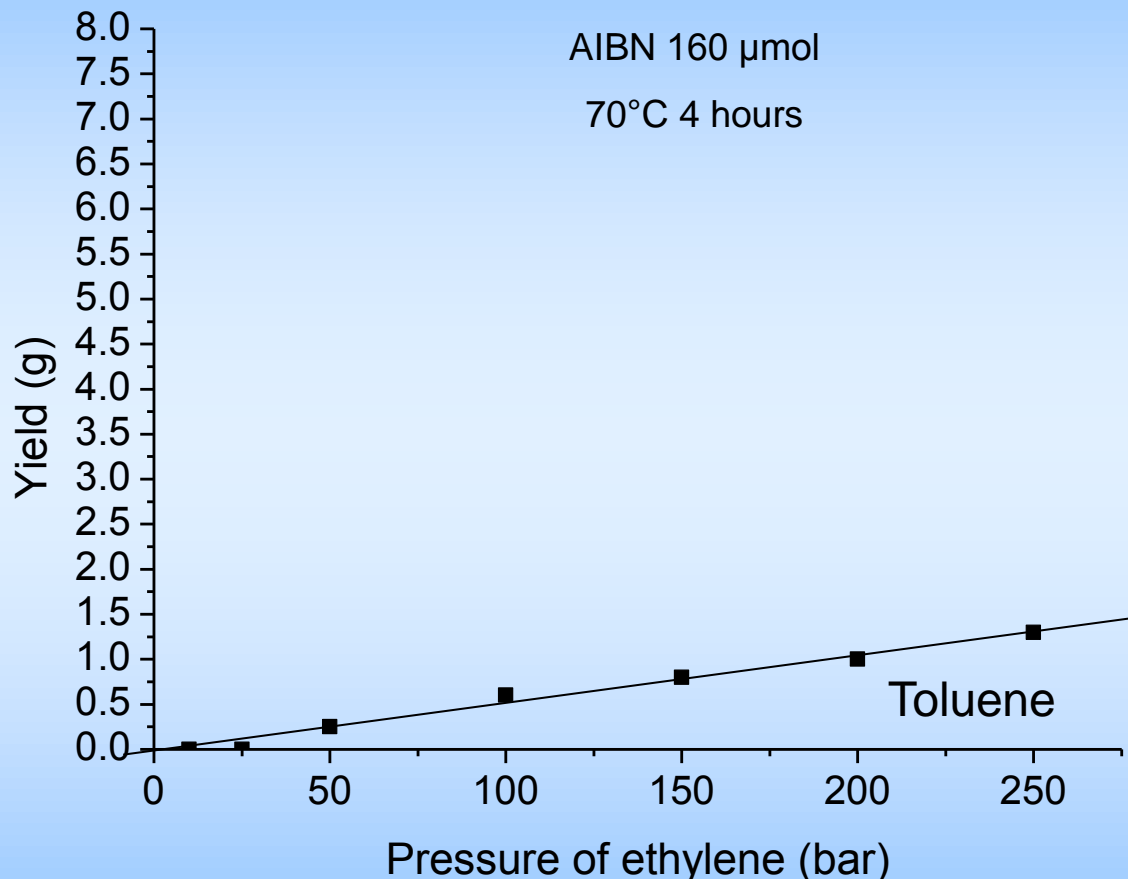
Toluene 50 mL

AIBN 160 μmol

70°C 4 hours



Polyethylene synthesis under low temperature and pressure.



Conversion < 3%

Can we increase significantly the yield?

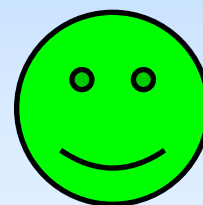
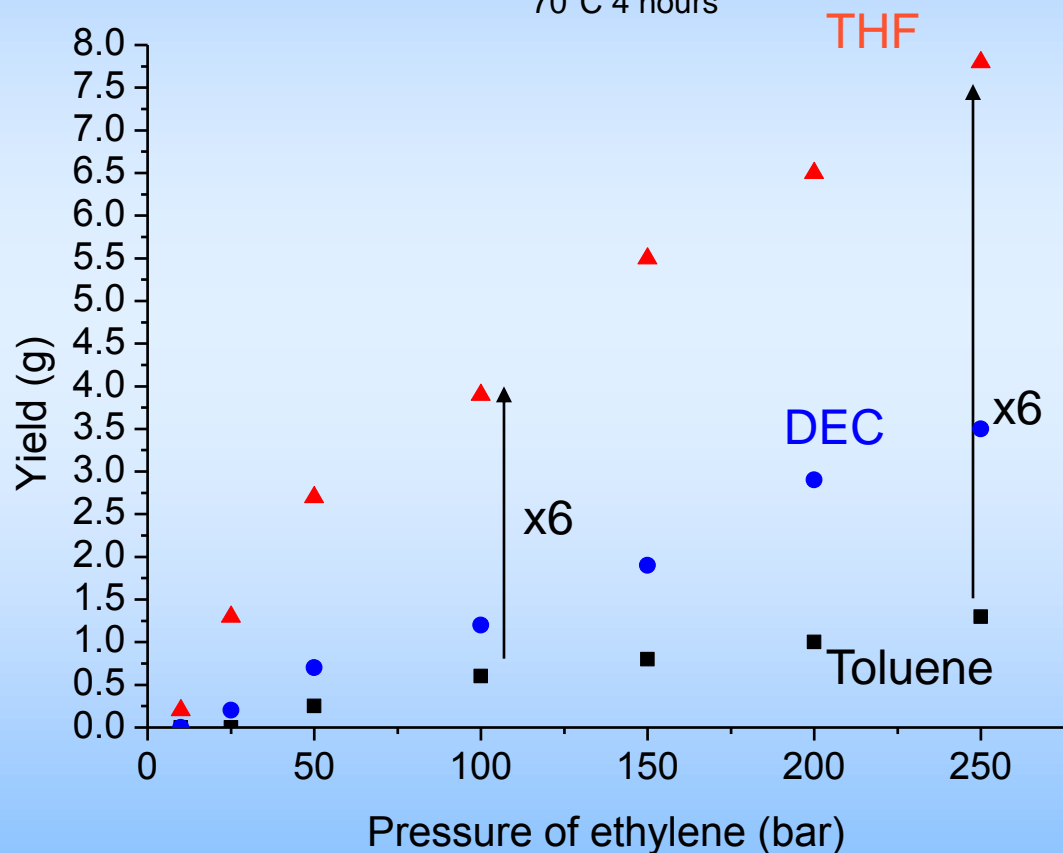
Effect of other solvents

Experimental conditions:

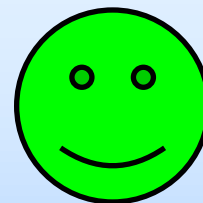
Toluene, THF or DEC 50 mL

AIBN 160 μmol

70°C 4 hours



Polymerization in THF is 6 times more efficient



Conversion \approx 18%

WHY ?



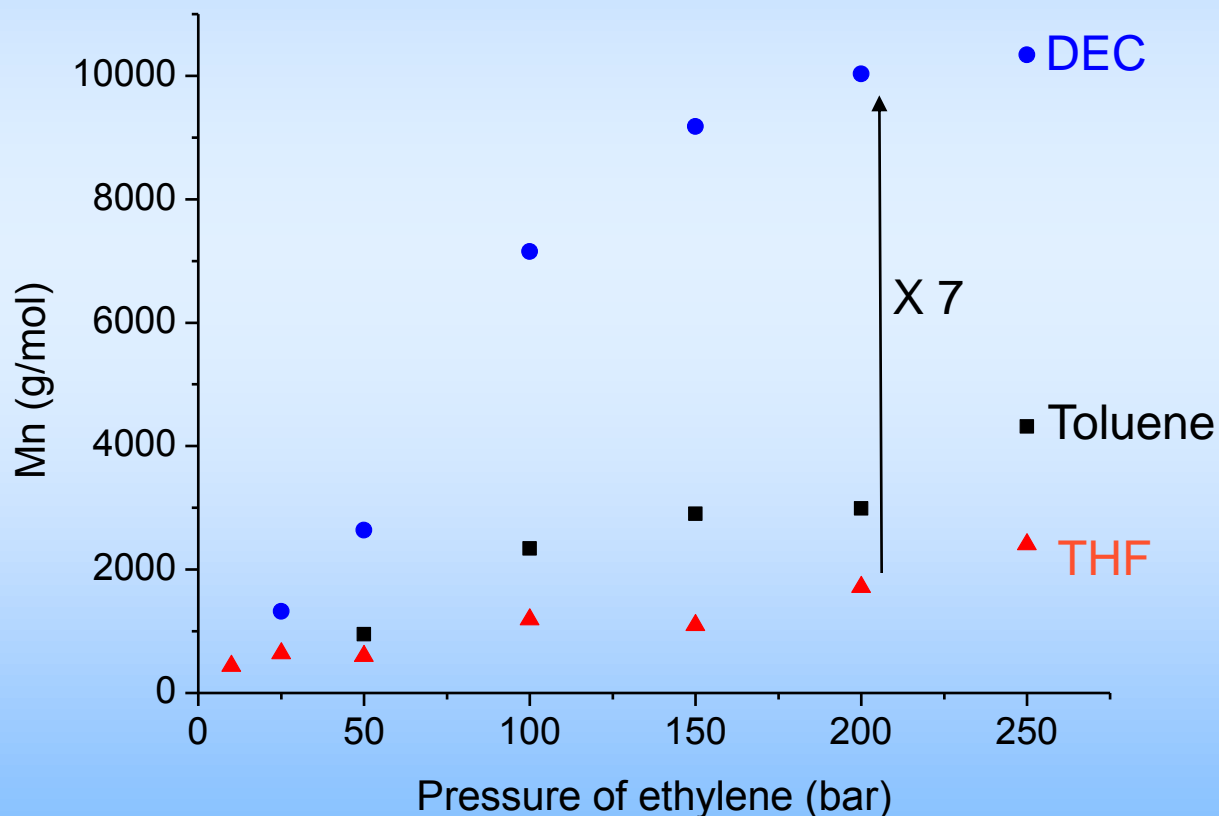
Influence of solvents on MWD

Experimental conditions:

Toluene, THF or DEC 50 mL

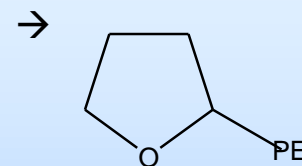
AIBN 160 μmol

70°C 4 hours



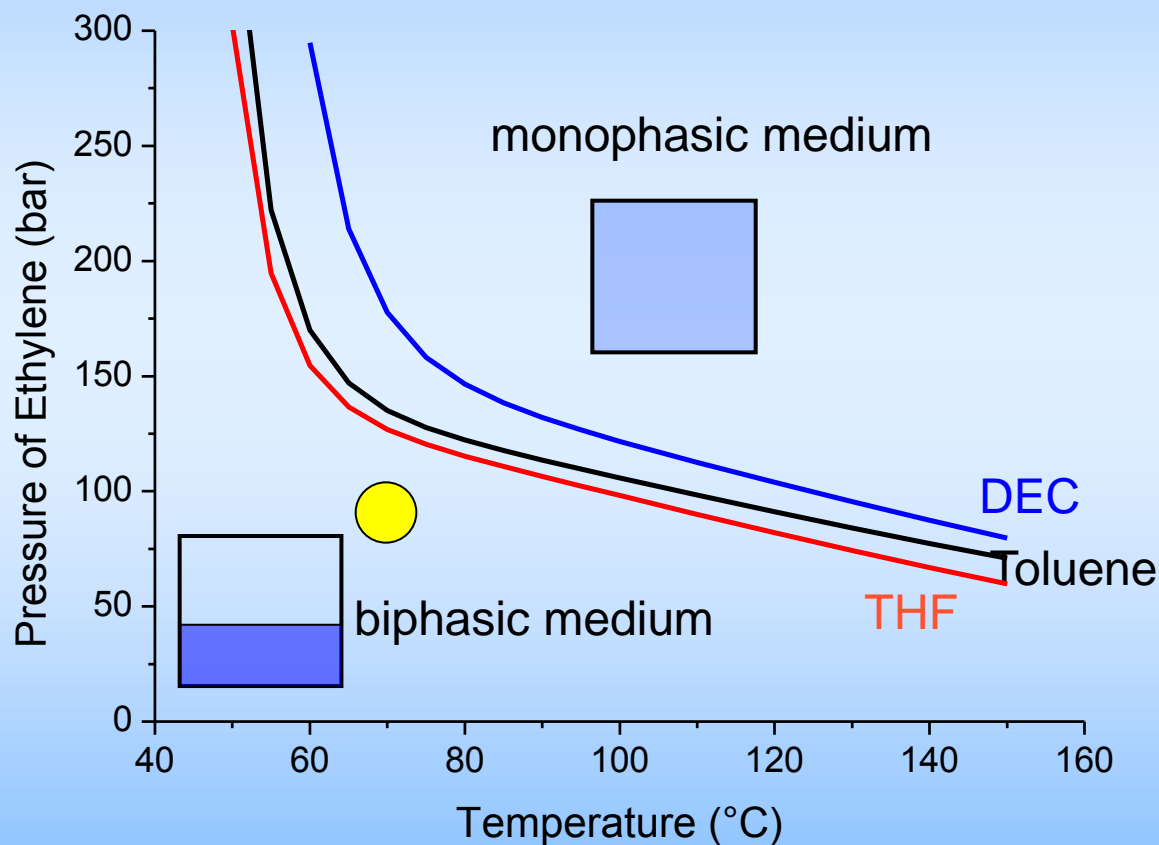
- Higher Mn in DEC
→ Up to 10000 g/mol

- Lower Mn in THF



Is it a physical effect ?

THF > DEC > toluene



At 100 bar 70°C 50 mL

Biphasic medium

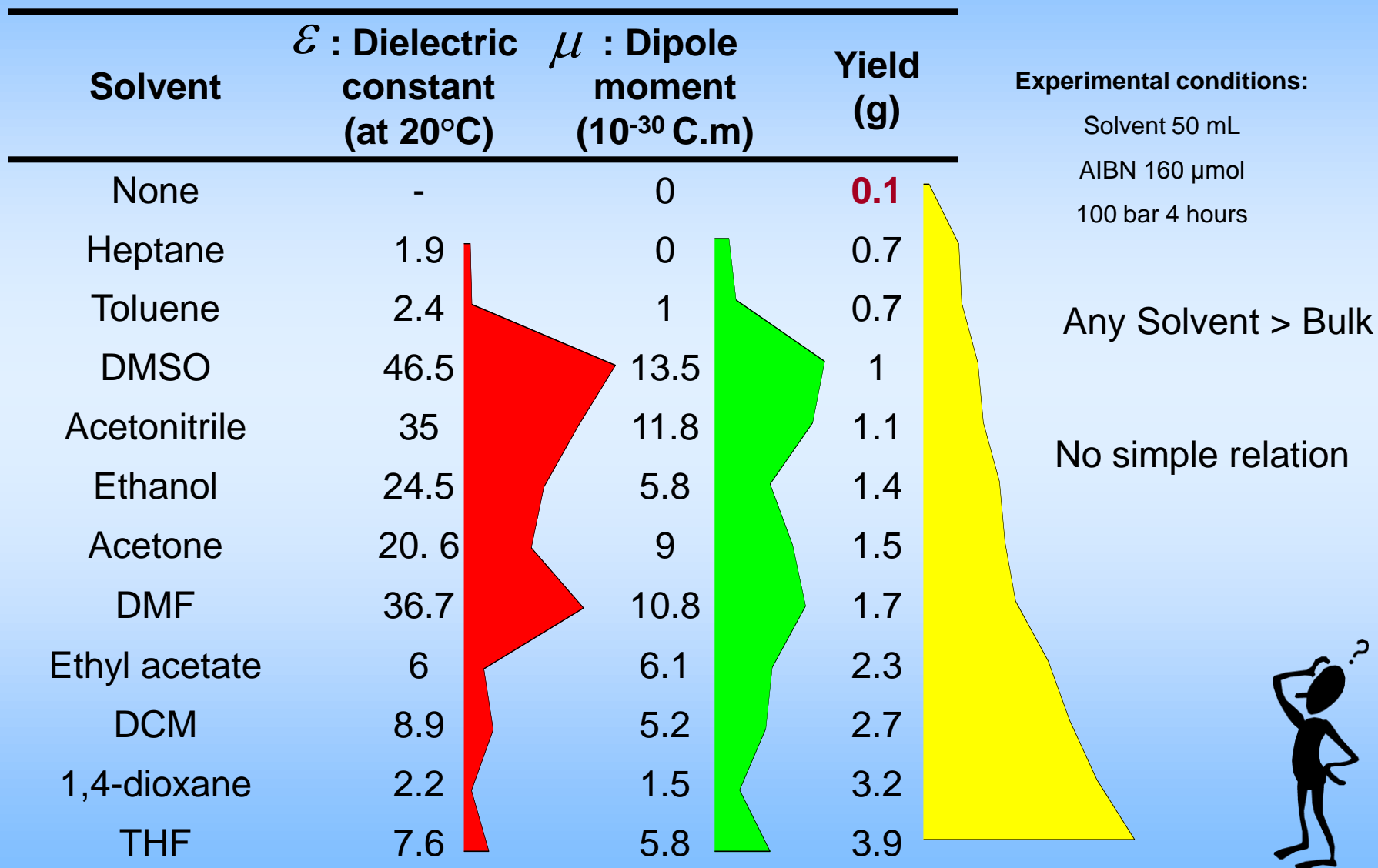
Almost the same phase transition

→ Not an effect of the medium

Activator effect of THF is a solvent effect



The route to the optimum solvent



How to predict the solvent effect?

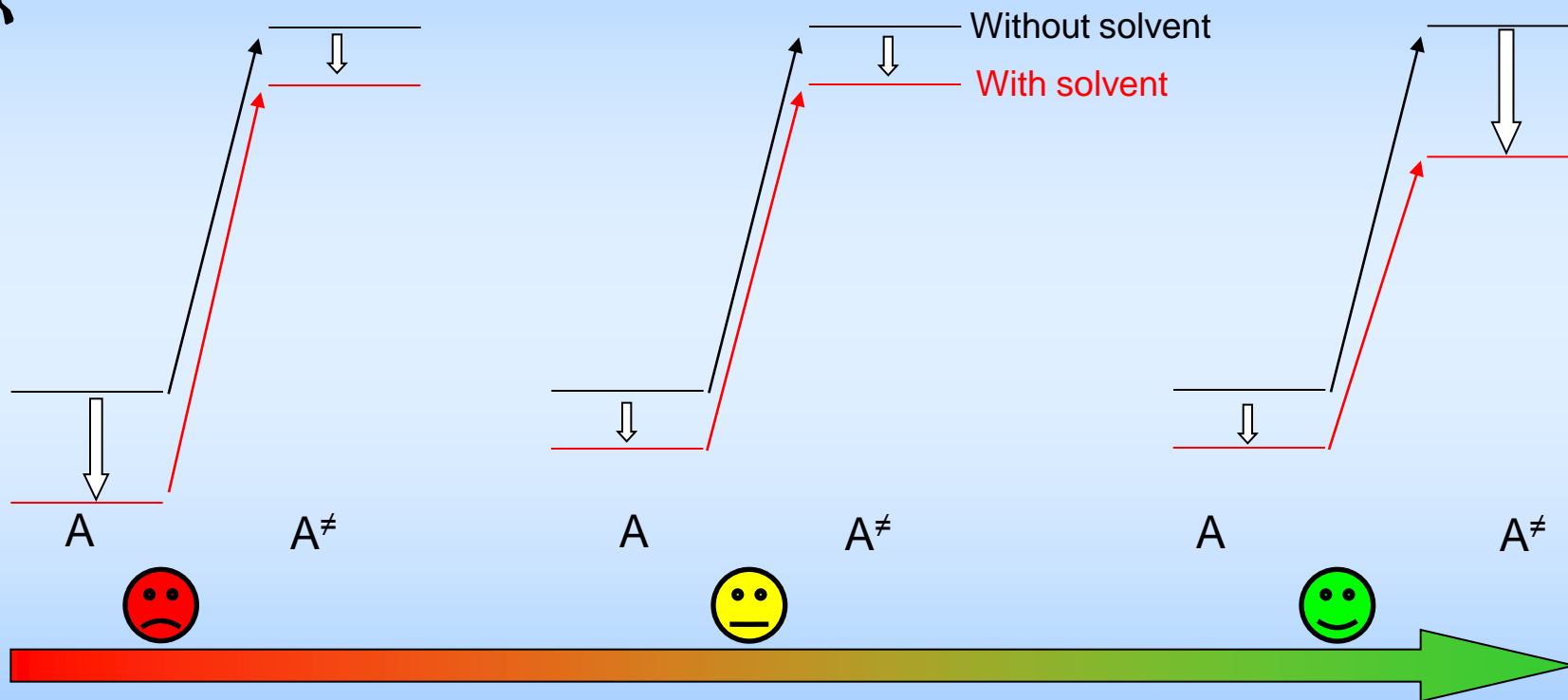


Hughes-Ingold theory:

Better solvation of the initial state

Same solvation

Better solvation of the activated state



How to quantify the solvent effect?

Activated state theory:
$$\ln k = \ln k_0 - \frac{1}{RT} (\Delta G_{A,solv} - \Delta G_{(A)^\ddagger,solv})$$

Rationalization of the solvent effect

Activated state theory

$$\ln k = \ln k_0 - \frac{1}{RT} (\Delta G_{A,\text{solv}} + -\Delta G_{(A)^\ddagger,\text{solv}})$$

+



Radical polymerization kinetic law

$$\ln k \propto \left(\frac{\mu}{\varepsilon}\right)^2 + \frac{1}{1-x} \frac{\partial x}{\partial t} = k_p \sqrt{\frac{2fk_d[I]}{k_t}}$$

Van der Waals interaction

$$E_{Debye} = -\frac{1}{r^6} \left[\frac{\mu_1^2 \cdot \alpha_2 + \mu_2^2 \cdot \alpha_1}{(4\pi \cdot \varepsilon_0 \cdot \varepsilon)^2} \right]$$

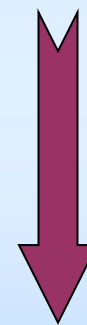
~~Dipole - Induced dipole~~

$$E_{London} = -\frac{1}{r^6} \left[\frac{3}{4} \cdot \frac{h \cdot \nu \cdot \alpha_1 \cdot \alpha_2}{(4\pi \cdot \varepsilon_0)^2} \right]$$

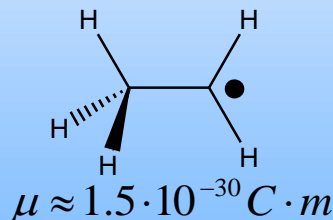
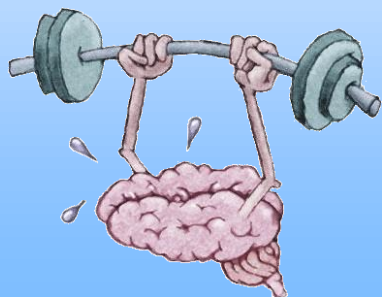
~~Instantaneous Dipole - Induced dipole~~

$$E_{keesom} = -\frac{1}{r^6} \left[\frac{\mu_1^2 \cdot \mu_2^2}{3(4\pi \cdot \varepsilon_0 \cdot \varepsilon)^2 kT} \right]$$

Dipole - Dipole

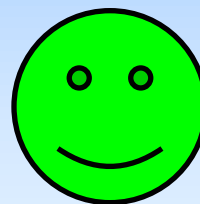
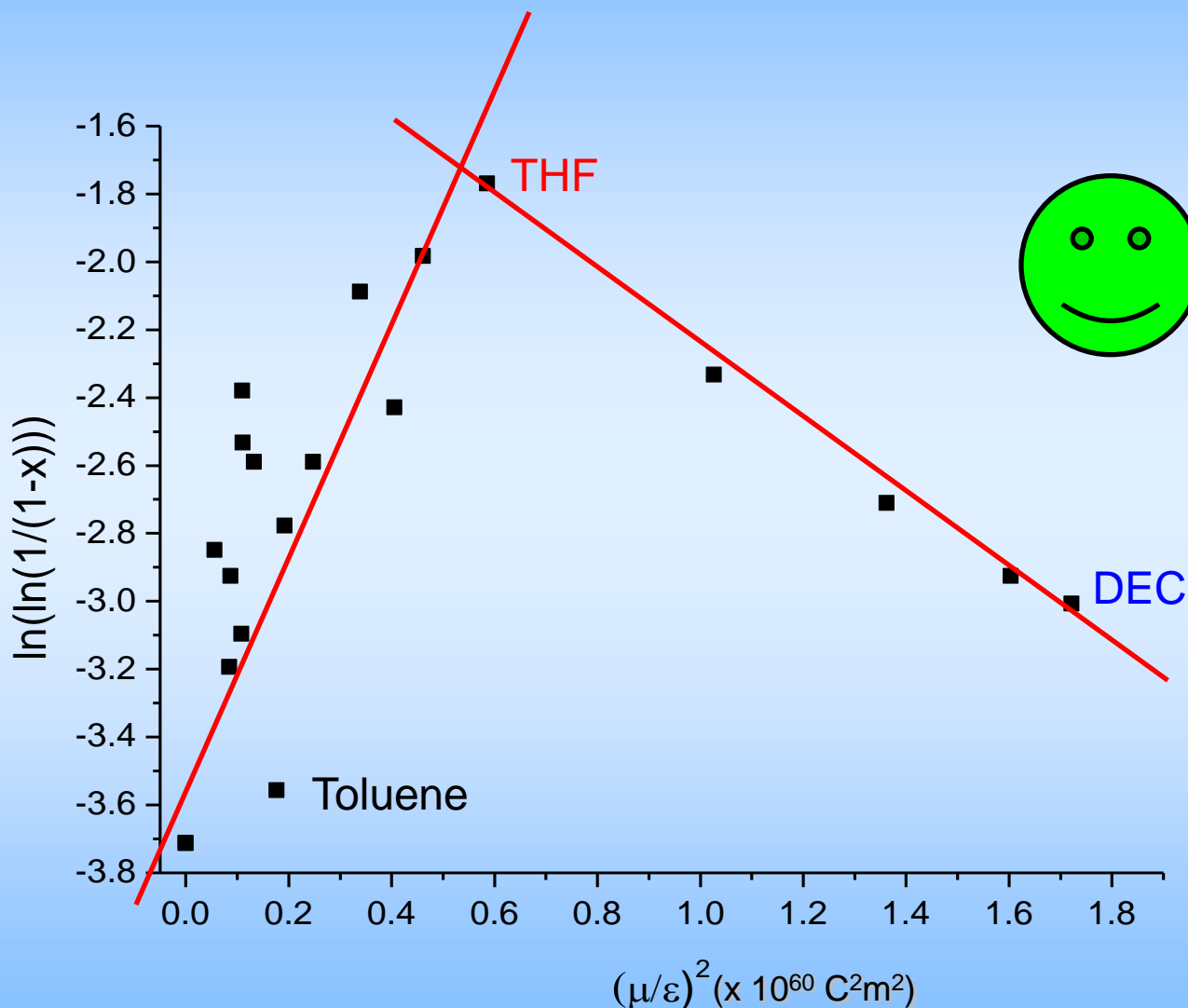


$$\ln \left(\ln \left(\frac{1}{1-x} \right) \right) \propto \left(\frac{\mu}{\varepsilon} \right)^2$$



x = conversion
 μ = dipole moment
 ε = dielectric constant
 α = polarizability

Rationalization of the solvent effect



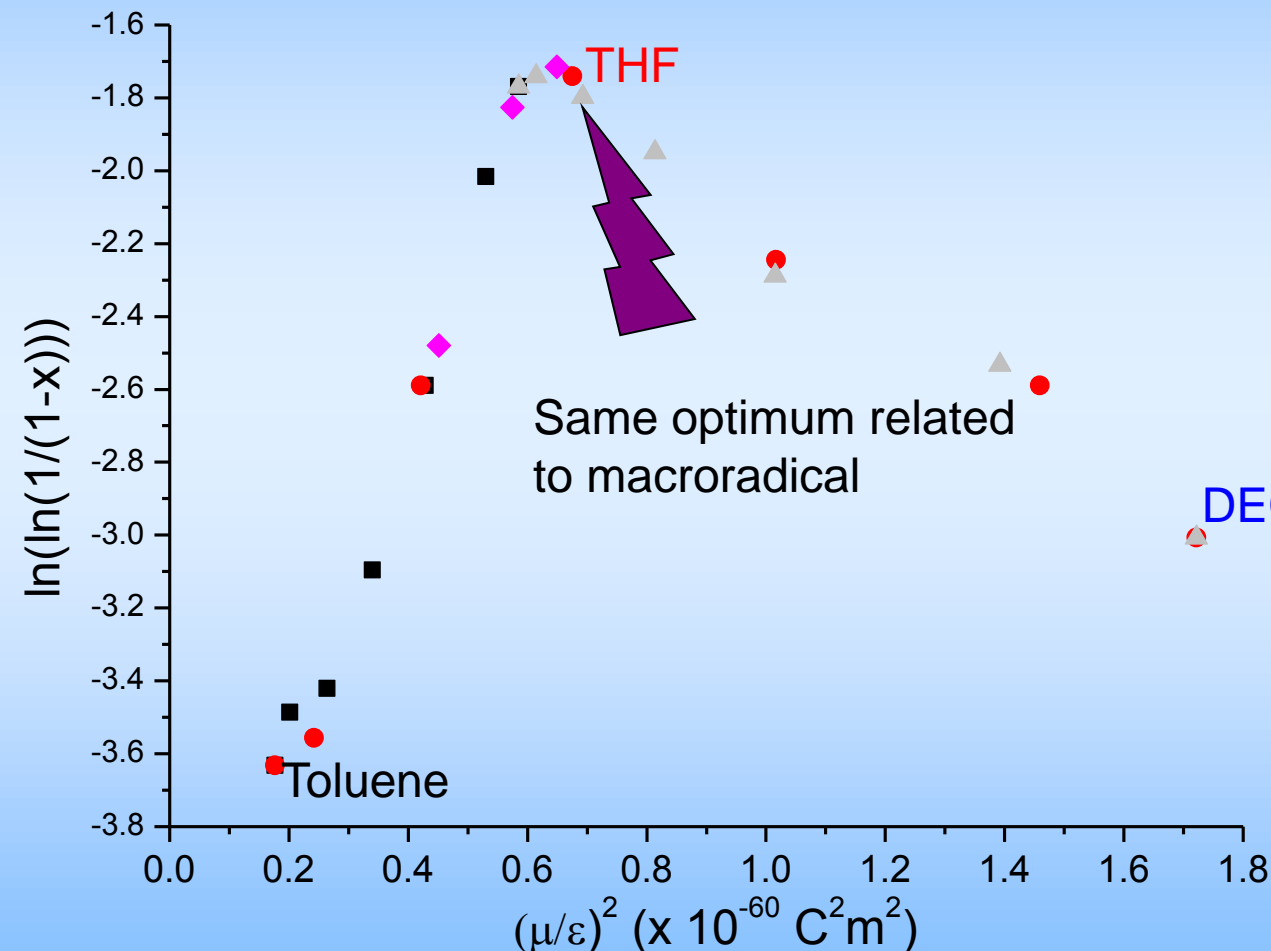
Good agreement

Also valid with hexene and VAc radical polymerization

Solvent optimum $\left(\frac{\mu}{\epsilon}\right)^2 \approx 0.6$

Micro- or macroscopic effect

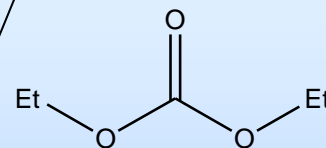
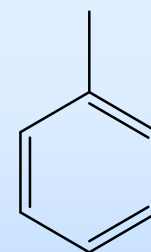
Similar experiments conducted using mixtures of THF
toluene and DEC



Solvent effect is due to the overall μ and ϵ

Same $(\mu/\epsilon)^2$

DEC

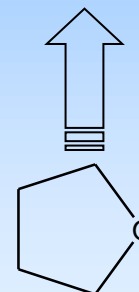


Yield 4g

Mn=3200 g/mol

Yield 3.9g

Mn=1200 g/mol



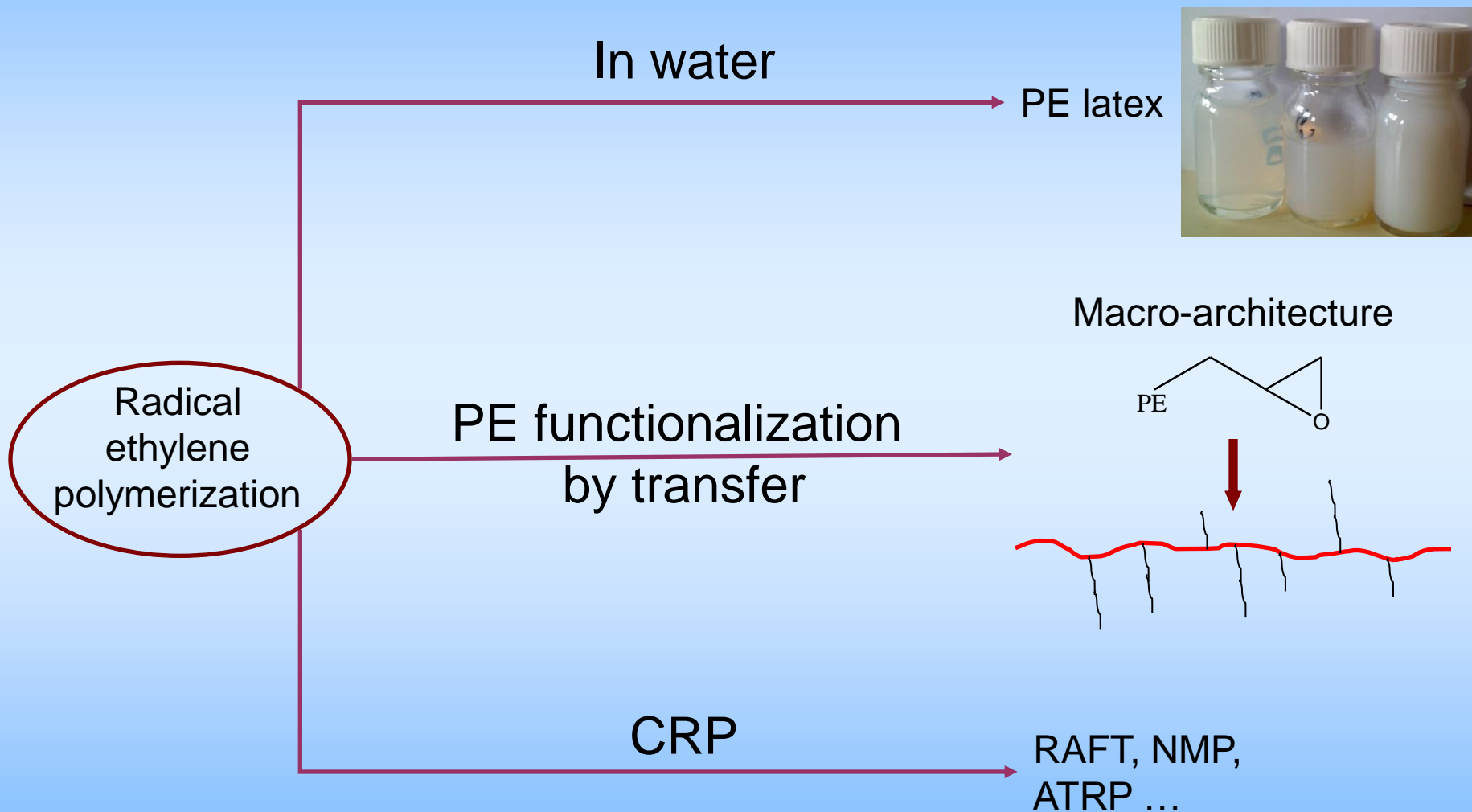
Summary - on free radical polymerization of ethylene

Polyethylene synthesis under mild conditions

- 50-90°C / 0-250 bar
- Conversion up to 40% in 4 hours
- New kind of PE LDPE < T_m, crystallinity < HDPE
- Low M_n < 20000 g/mol

- Fundamental description and understanding of the solvent effect
- Determination of the phase transition
- Highest yield $\rightarrow \left(\frac{\mu}{\varepsilon}\right)^2 \approx 0.6 \cdot 10^{-60} \text{ C}^2 \cdot \text{m}^2$
 \rightarrow nearest to the phase transition

Opened research topics



Polymerization in water

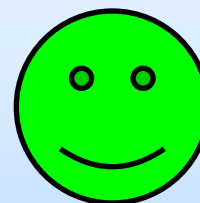
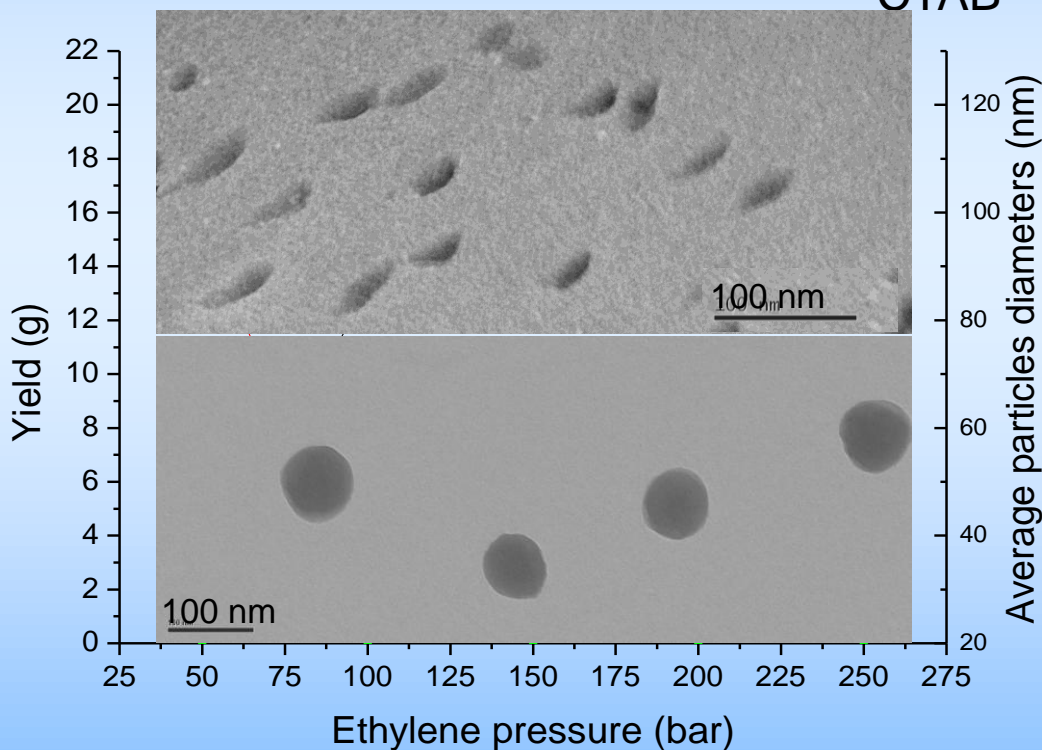
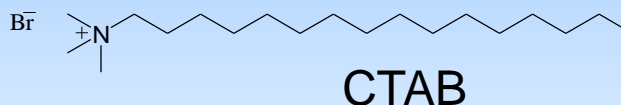
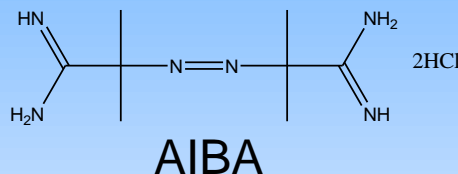
Experimental conditions:

Water 50 mL

— CTAB 1 g/L

— AIBA 160 μmol

70°C 4 hours



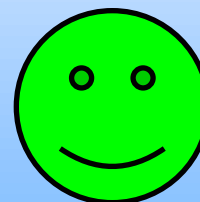
Polymerization of ethylene can be done in water

Stable latex

high Sc (up to 40%)

$M_n = 10^4 - 10^6$ g/mol

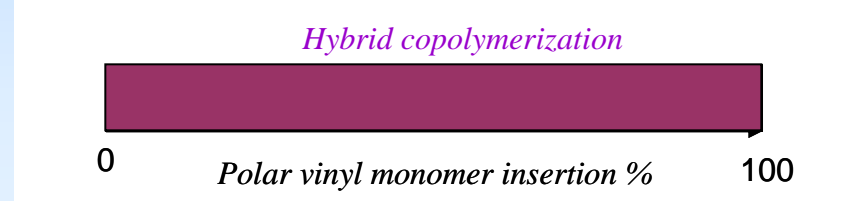
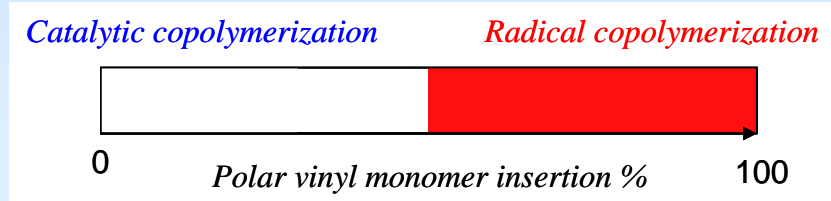
Original morphology



E. Grau, P-Y Dugas, J.-P. Broyer, C. Boisson, R. Spitz, V. Monteil, *Angewandte Chemie*, **2010**, 49, 6810.

Final conclusion

- Development of hybrid catalytic/radical polymerization



- First efficient copolymerization system
- Control of exchange mechanism via radical addition (or phosphorous ligand)
- New kinds of multiblock copolymers

Final conclusion

- Investigation of radical copolymerization
 - Polymerization in solution and emulsion
 - With VAc, Ethylene content up to 95%
 - With MMA, Sty and BuA up to 60%
 - Dual role of polar monomer as solvent and comonomer (not detailed in this presentation)

Final conclusion

- Study of free radical homopolymerization of ethylene
 - Synthesis of new kinds of PE
 - Efficient polymerization in water
 - Fundamental understanding of solvent effect
 - Promising results toward CRP of ethylene

Some perspectives

- Hybrid copolymerization
 - New catalysts
 - Copolymerization of propylene, styrene
 - Fine characterization of copolymers produced
- Free radical homopolymerization of ethylene
 - Theoretical investigation of solvent effect
 - Controlled radical polymerization of ethylene
 - Architectures based on polyethylene

Thank you for your attention

Dr. Vincent MONTEIL



Dr. Roger SPITZ



Dr. Christophe BOISSON



Jean-Pierre BROYER



Pierre-Yves DUGAS for TEM

Dr. Pierre-Antoine ALBOUI, LPS, for X-Rays

Dr. Medhi ZEGHAL, LPS, for Latex-SSNMR

Dr. Christophe CHASSENIEUX, PCI, for SLS

David ALBERTINI, INL, for AFM

Xavier JAURAND, CT μ , for Tomo-TEM

Dr. Laurent BONNEVIOT and Dr. Belen ALBELA, ENS, for EPR

Dr. Fernande BOISSON and Annick WATON, for NMR

Dr. Vincent LEDENTU, LCTMM, for DFT/MM calculations

Dr. Robert BRULL and Chitta RAJESH, DKI, for HT-LC-CC

Olivier BOYRON for HT-SEC

Dr. Christian GRAILLAT

Dr. Alexandra LEBLANC

Last but not least all project students:

Nérime LAGGOUNE, Christoph FISCHER, Alexandre FAURIE

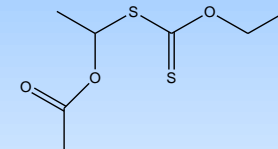
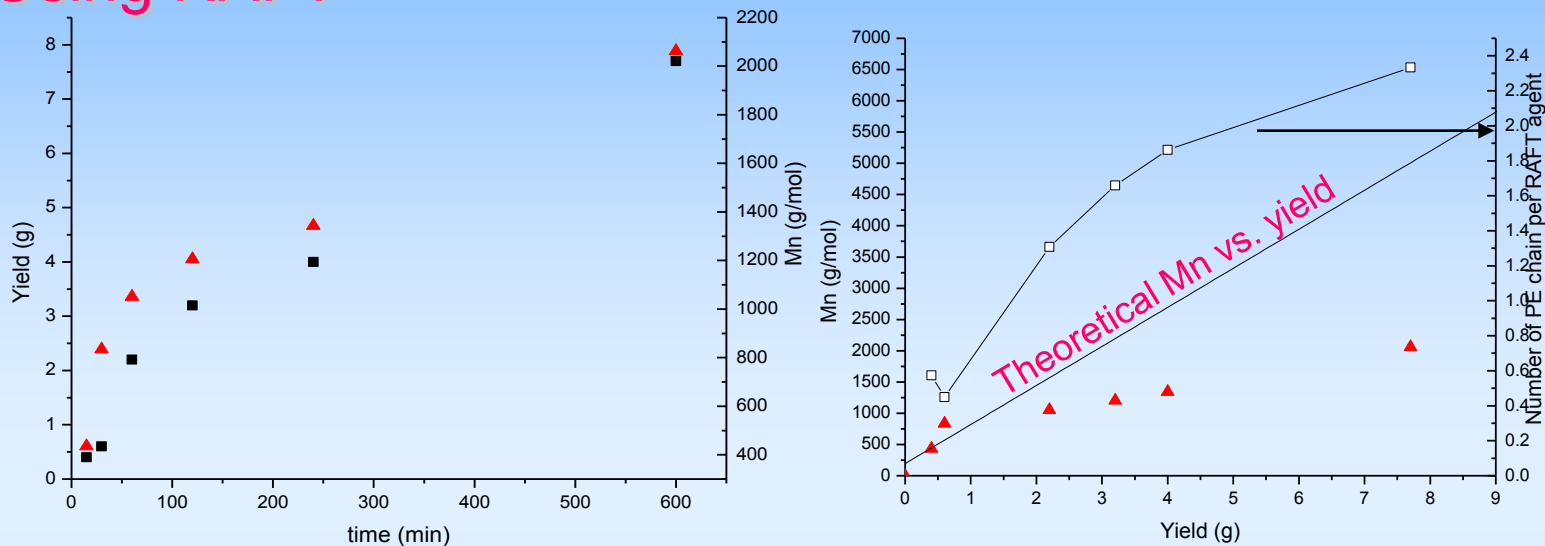
Clément CID, Cédric DOMMANGET, Alexandra TCHERNOOK

All « microprojet » students

Any Questions?

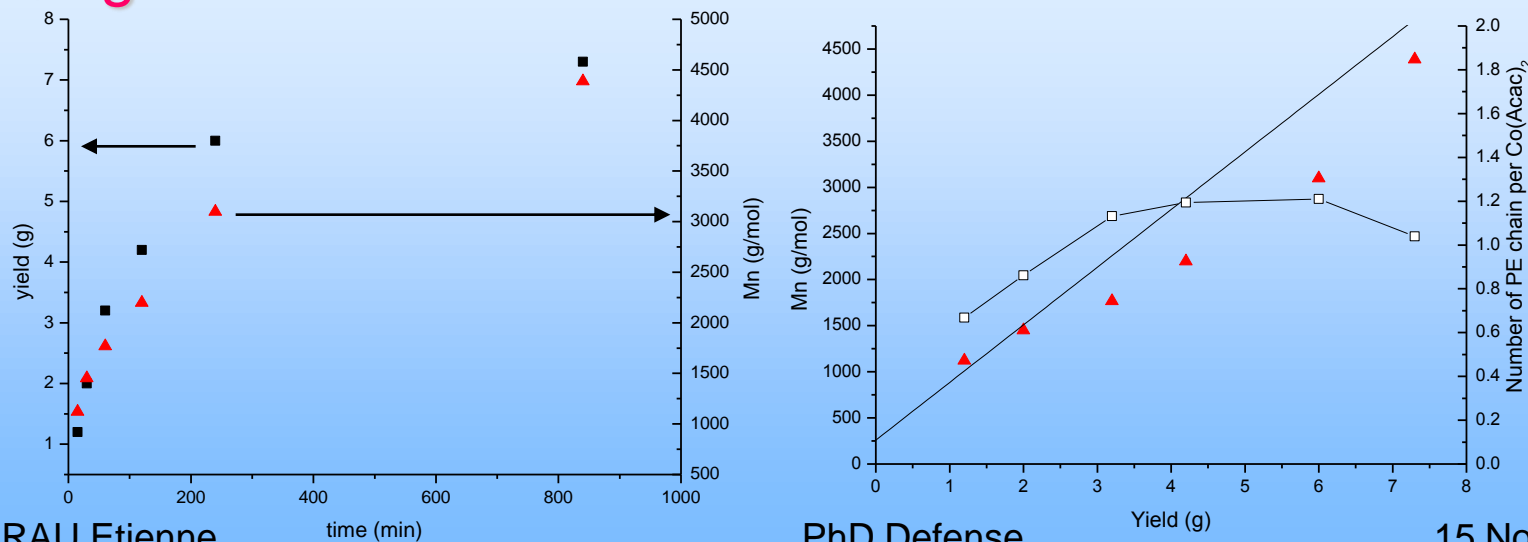
Toward CRP of ethylene

Using RAFT



50 mg of AIBN
 10 eq of RAFT agent
 100°C
 250 bar
 50 mL of THF

Using CMRP

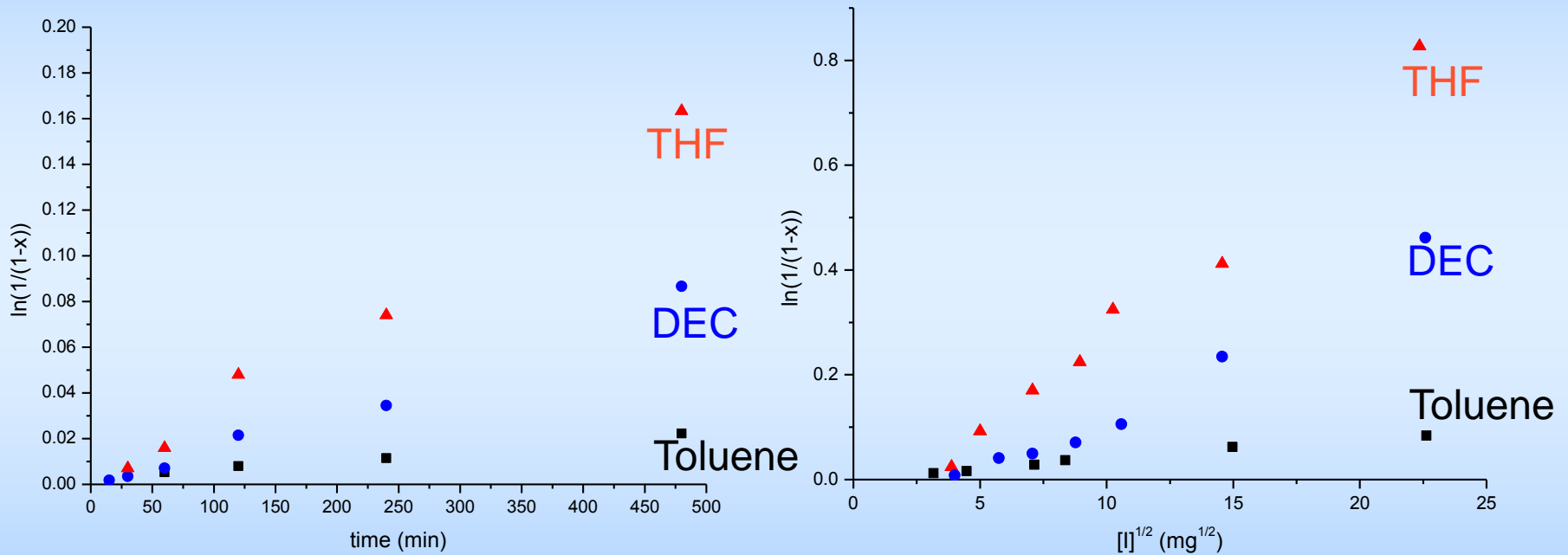


50 mg of AIBN
 10 eq of Co(Acac)₂
 90°C
 250 bar
 50 mL of THF

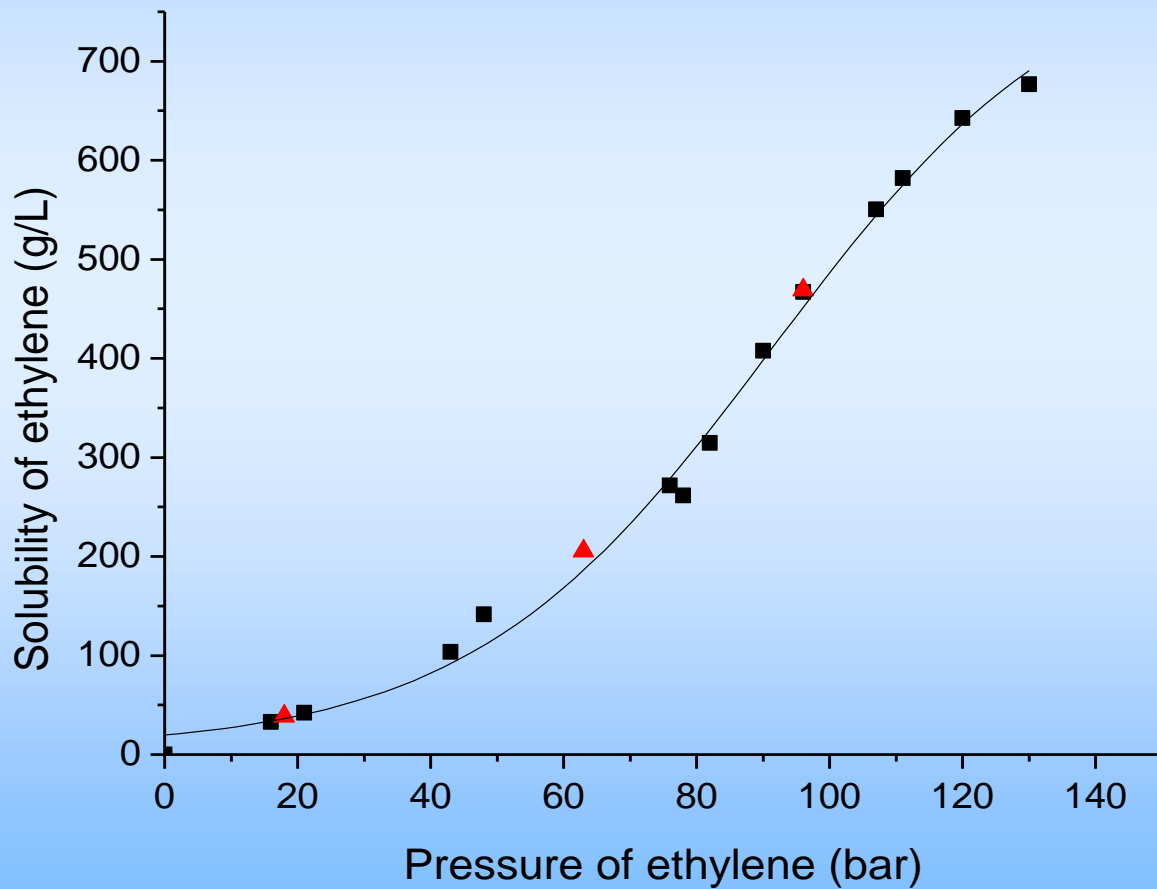
Free radical polymerization of ethylene

$$\frac{1}{1-x} \frac{\partial x}{\partial t} = k_p \sqrt{\frac{2fk_d[I]}{k_t}}$$

Under 100 bar of ethylene pressure



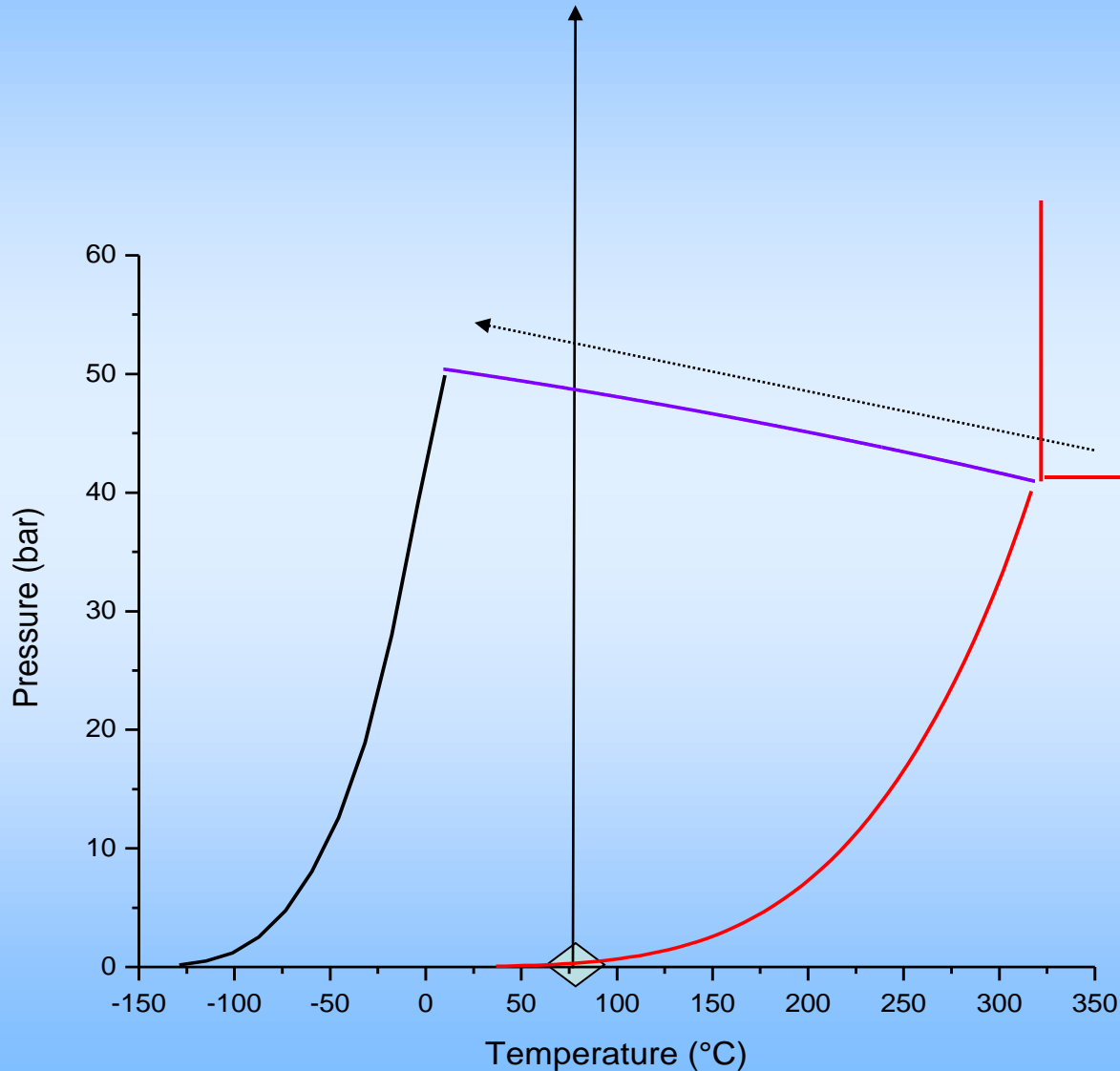
Solubility measurement



Same solubility in both solvent

Solubility = 3* ethylene density

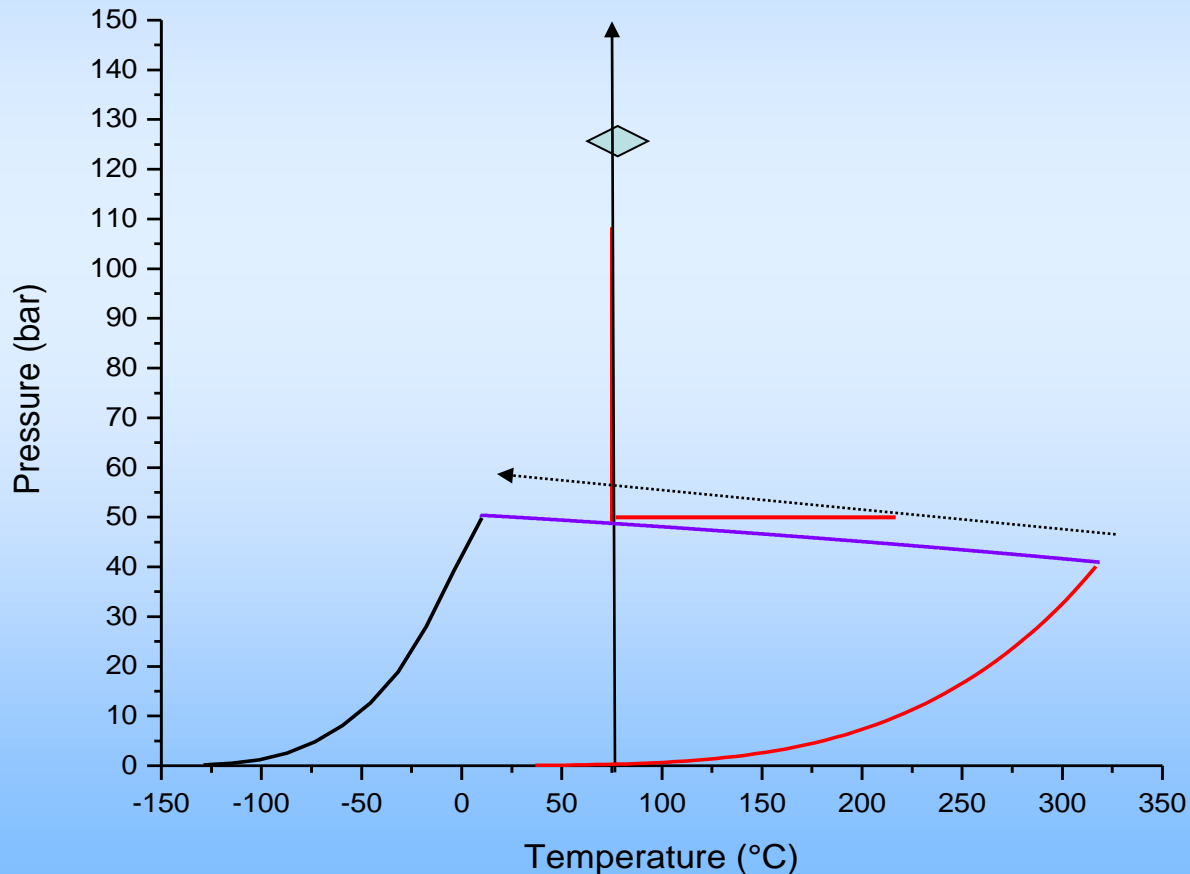
Methodology



Virtual experience:
 T_{c_m} is linked to P_{exp}

$T_{c_m} = T_{exp} \rightarrow$ Phase transition

Methodology



Virtual experience:

T_{c_m} is linked to P_{exp}

$T_{c_m} = T_{exp} \rightarrow$ Phase transition

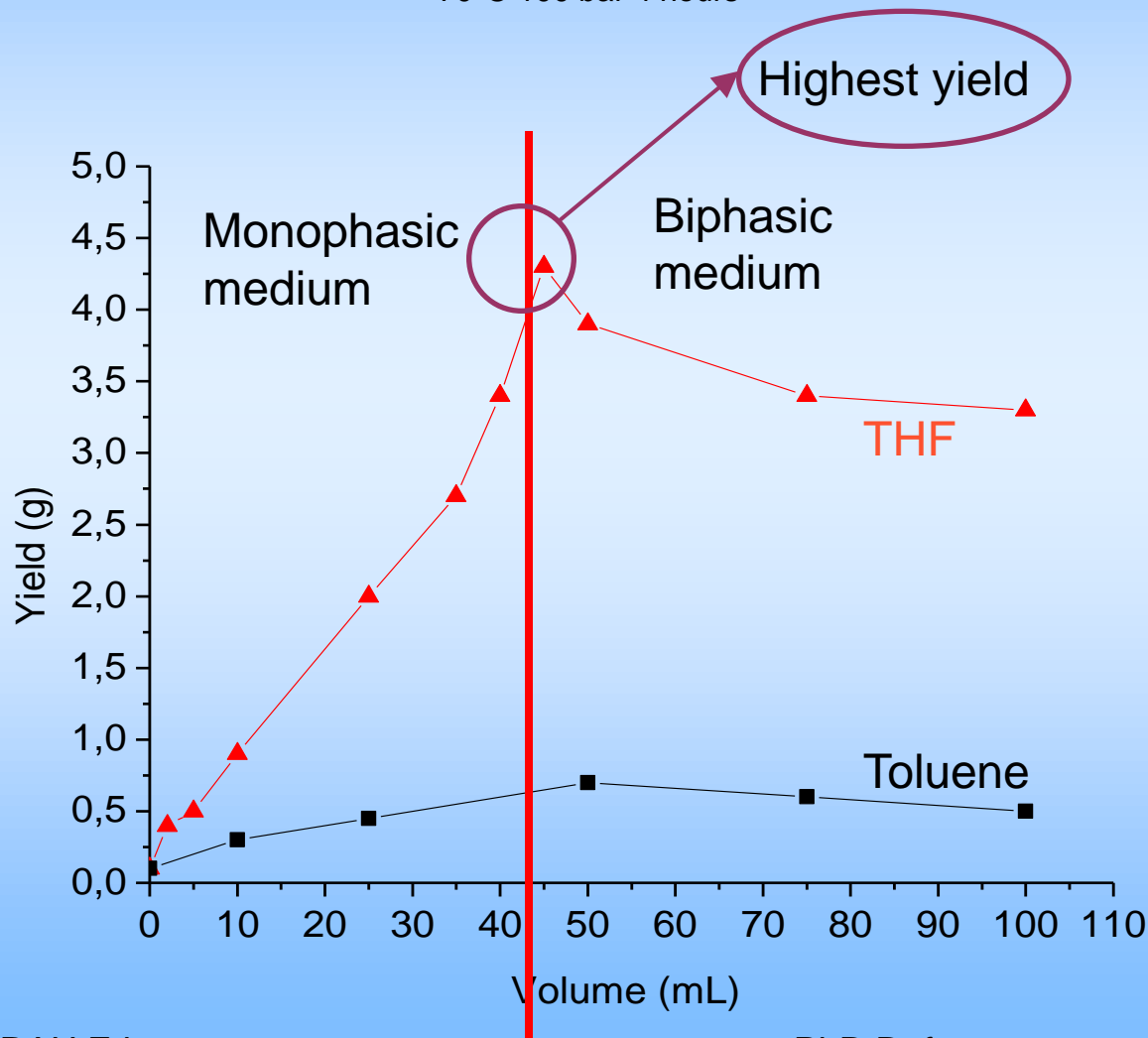
Here phase transition when $P_{exp} = 125$ bar

Monophasic or biphasic?

Experimental conditions:

AIBN 160 μmol

70°C 100 bar 4 hours



Transition between 40-45 mL

Over 45 mL

- $[E]=\text{cst}$

- $[I] \searrow$

→ yield \searrow

Below 40 mL

- $[I]=\text{cst}$

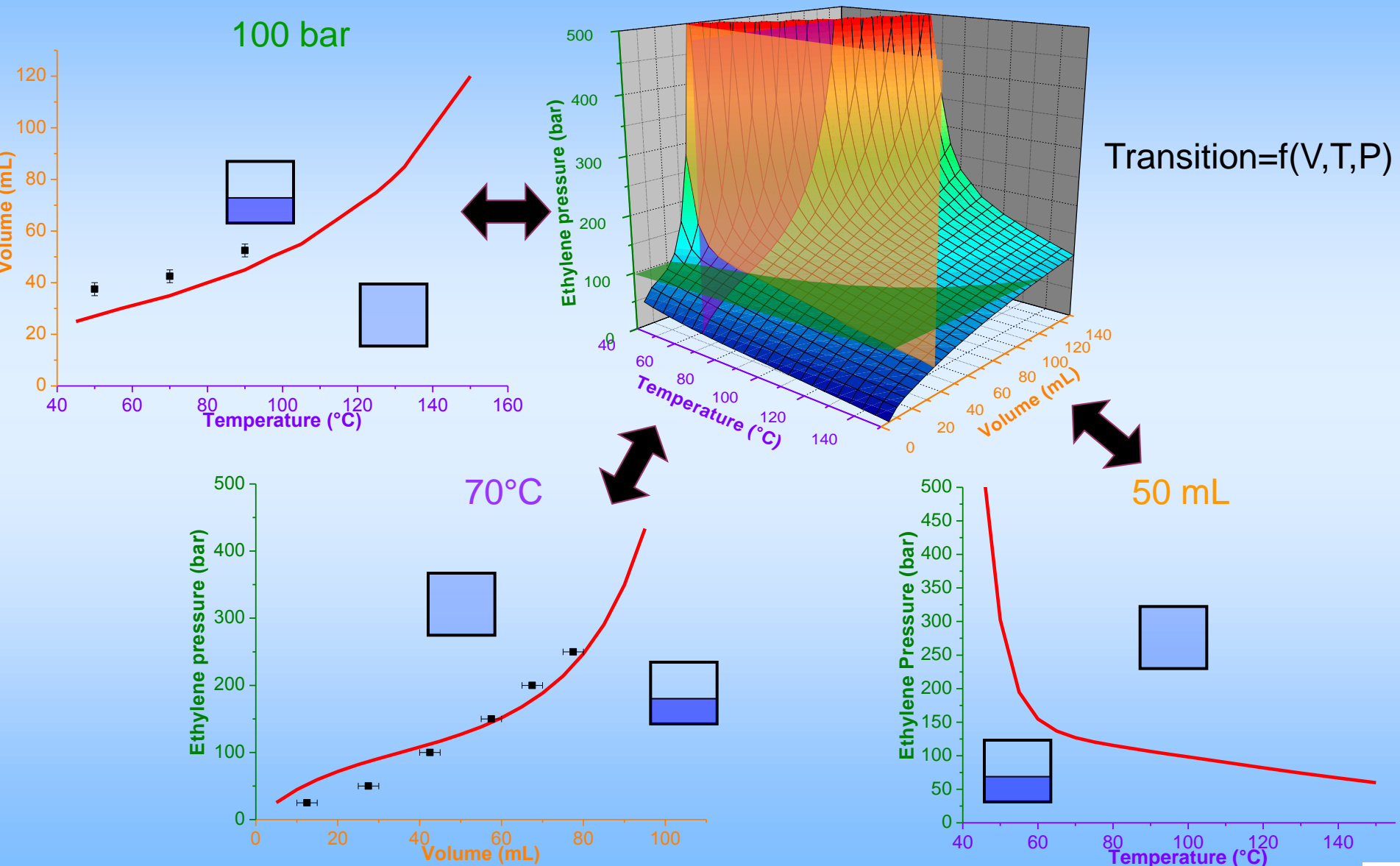
- $[E] \searrow P=P_E+P_{\text{THF}}$

- $[\text{Solvent}] \nearrow$ } It's a solvent effect !!!

→ Yield \nearrow

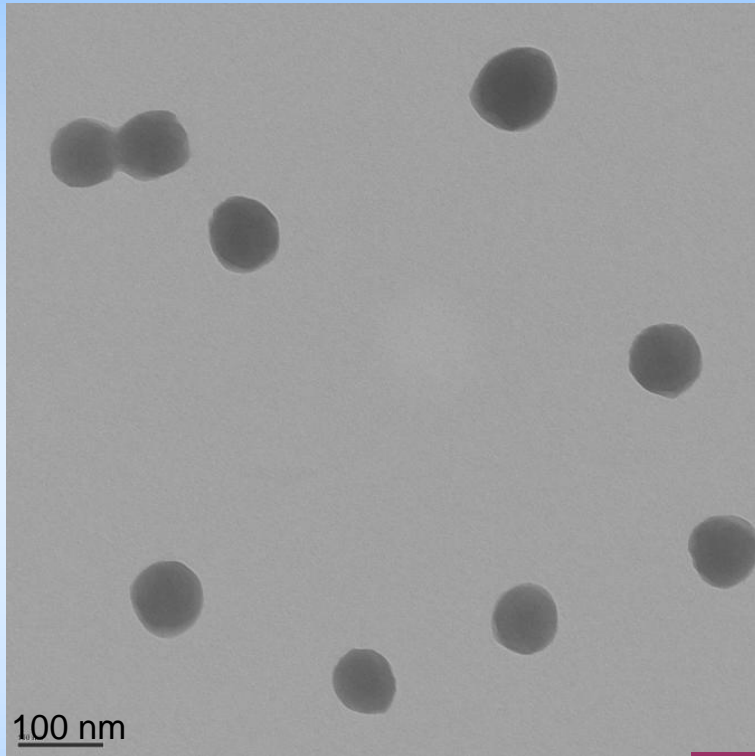
Mixed with medium effect?

THF/Ethylene phase diagrams



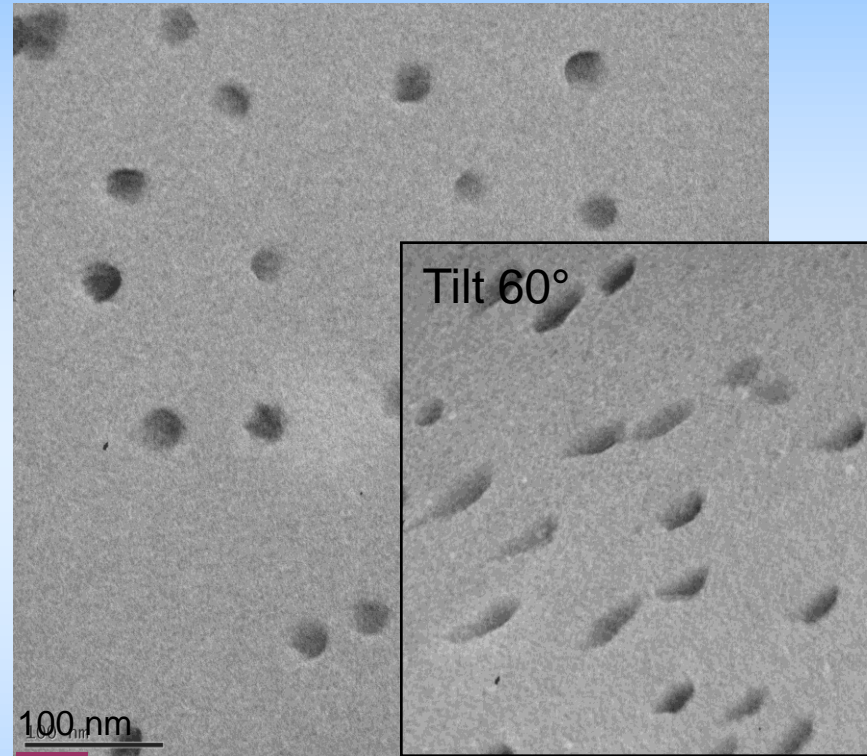
TEM pictures of PE particles

Without CTAB



Sphere-like
Facets due to PE lamella

With 1 g/L CTAB

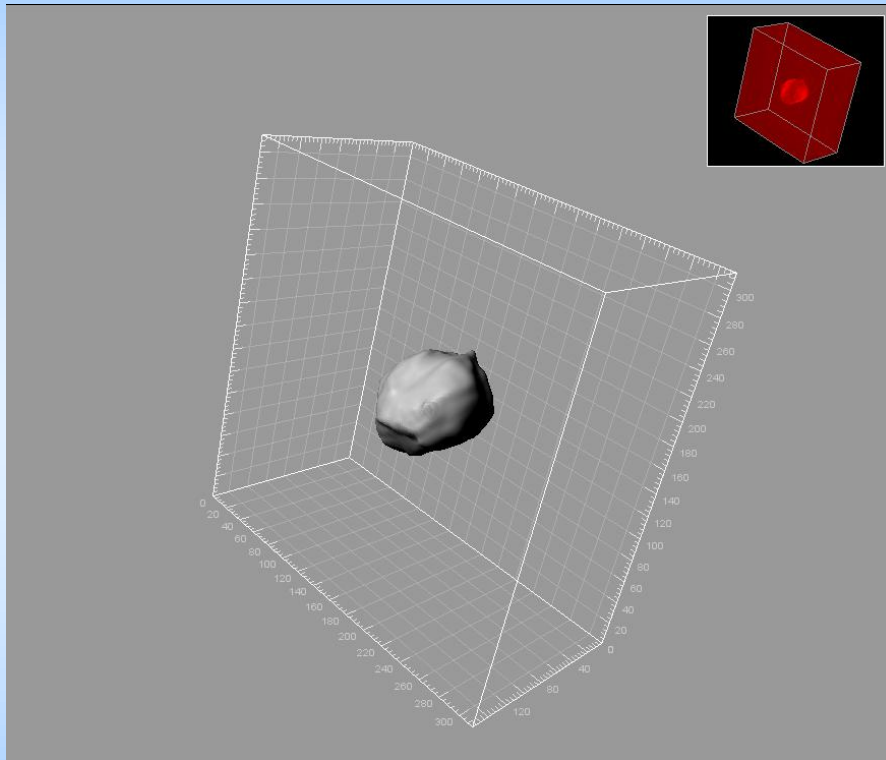


~~Sphere like~~
+ low contrasted
Disk-like

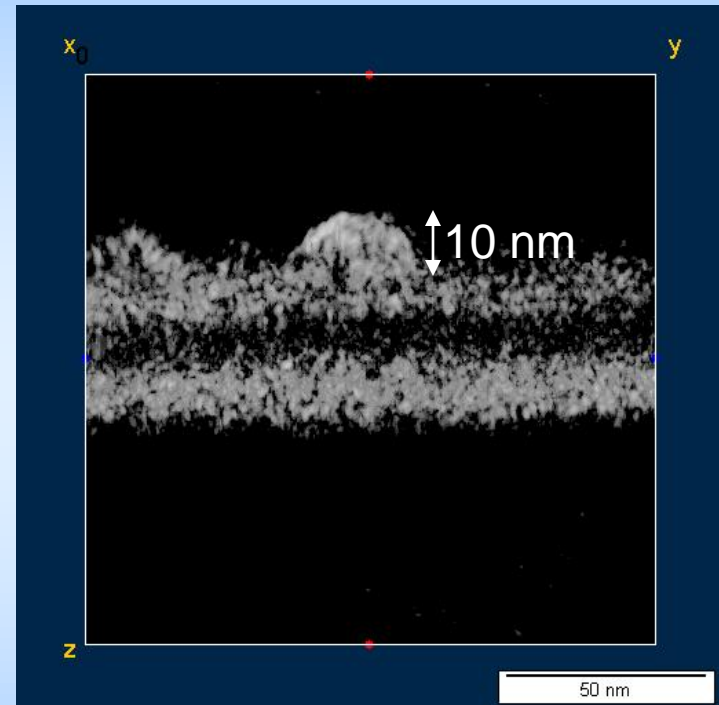
Identical surface
As CTAB = 80\AA^2

Tomographes of PE particles

Without CTAB



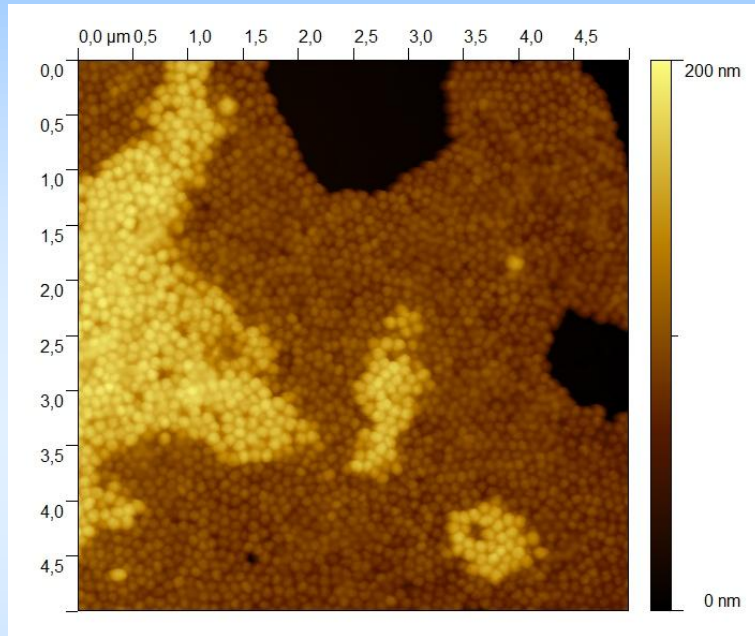
With 1 g/L CTAB



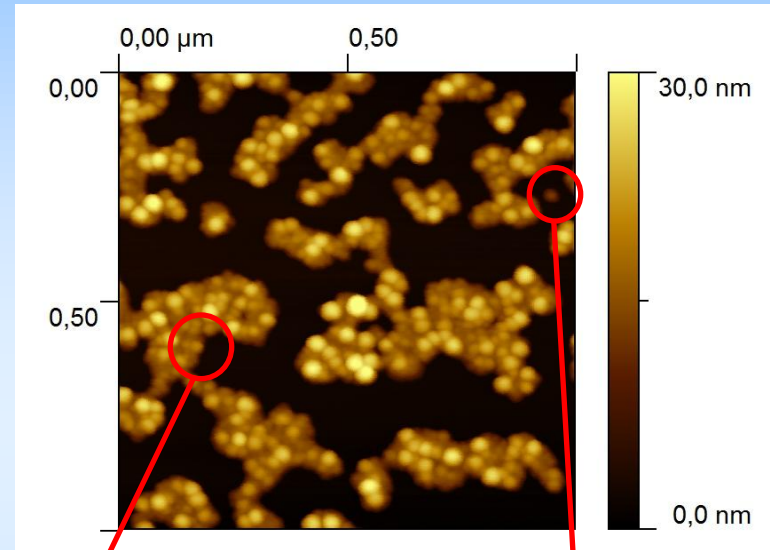
Confirm morphology but only for one particle

AFM of PE particles

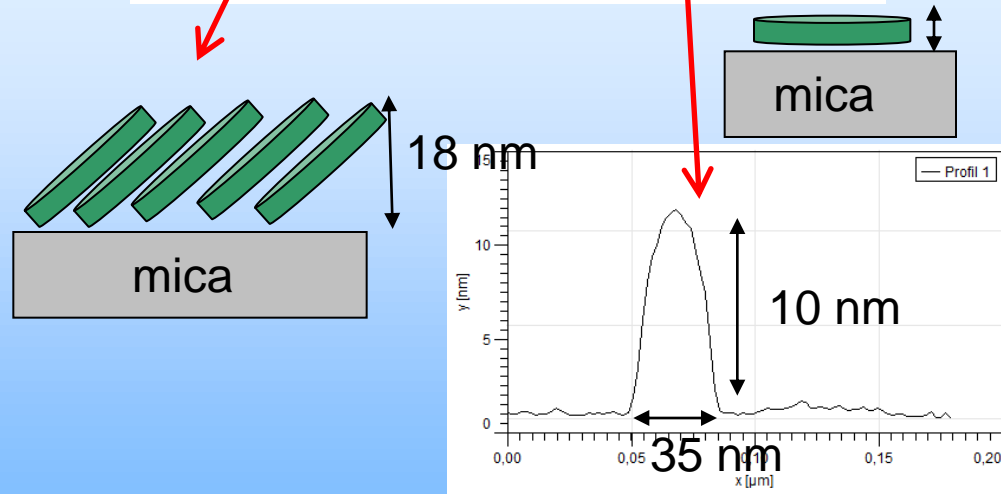
Without CTAB



With 1 g/L CTAB

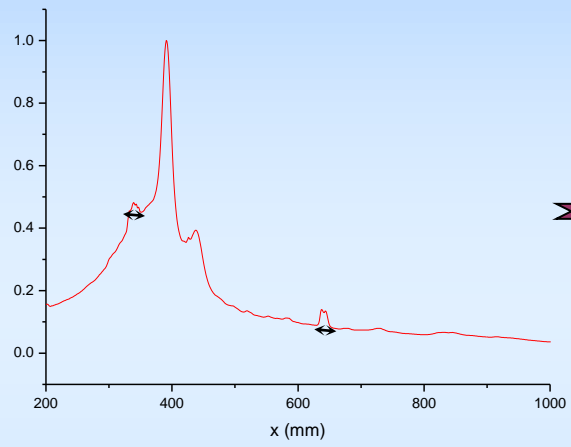
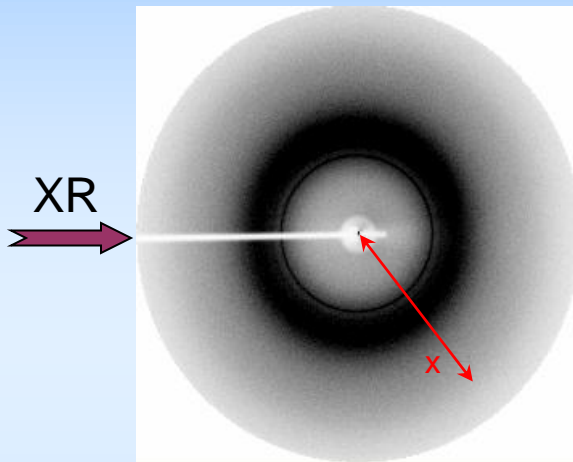


Particles diameters 82.3 ± 1.6 nm
1st layer 76.5 ± 1.6 nm
2nd layer 66.8 ± 9.1 nm

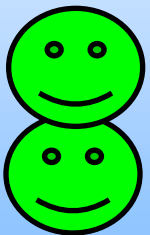


X-Ray analysis

PE is semi-crystalline



Crystallite dimension
+ crystallinity



1 facet = 1 crystallite

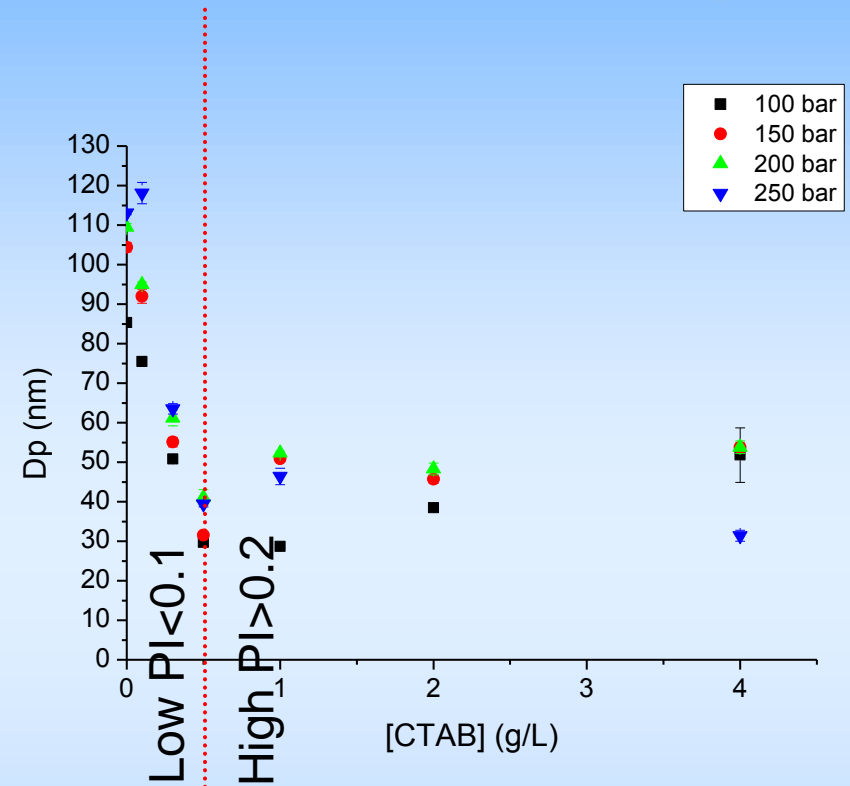
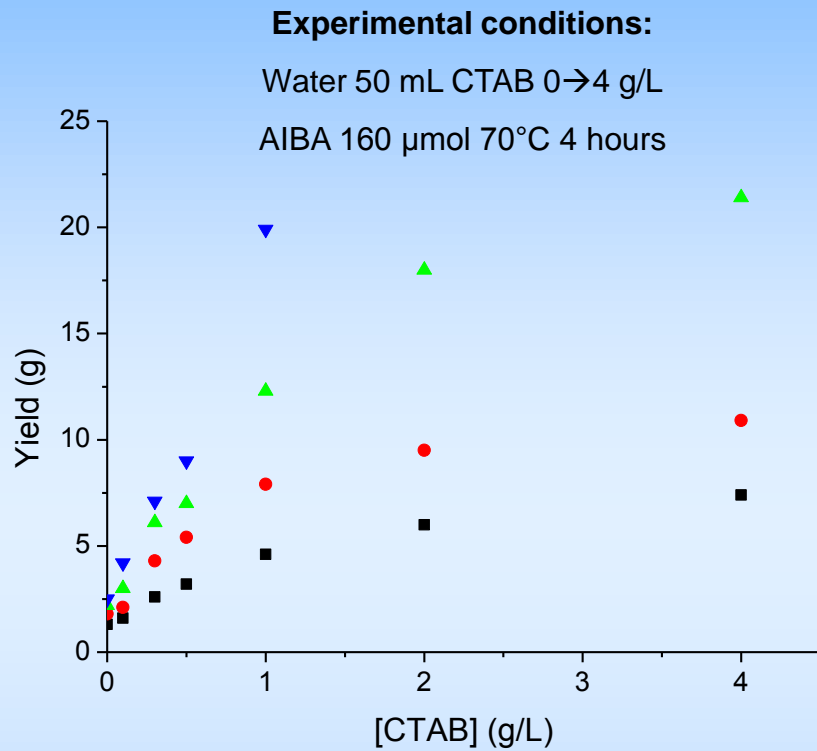
1 particles = 1 crystallite

Particles diameters	Crystallite diameters	Native Crystallinity in particles	Crystallinity in bulk
82 nm	18 nm	25%	35%
36 nm	32 nm	21%	30%

Without CTAB

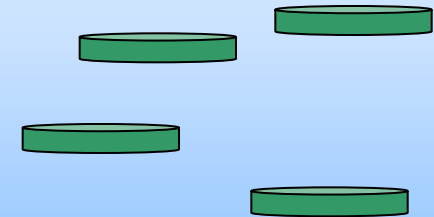
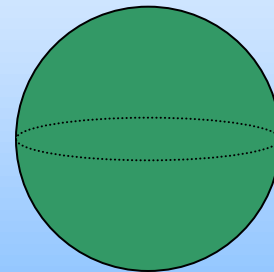
1 g/LCTAB

CTAB effect on particles morphologie



Below CTAB cmc N_p cst vs pressure

Over cmc N_p \nearrow with pressure

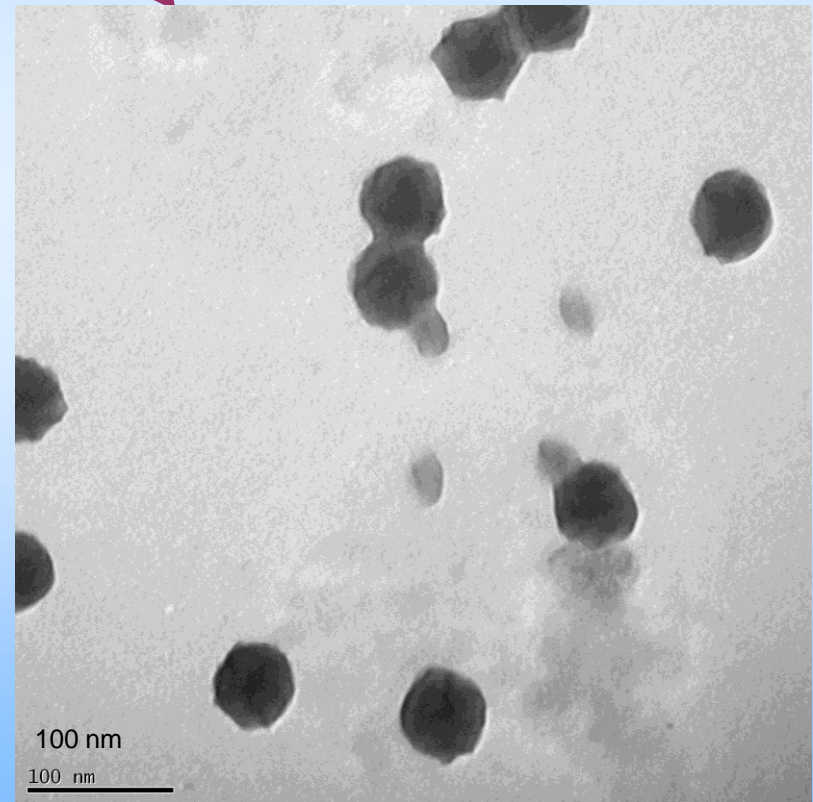
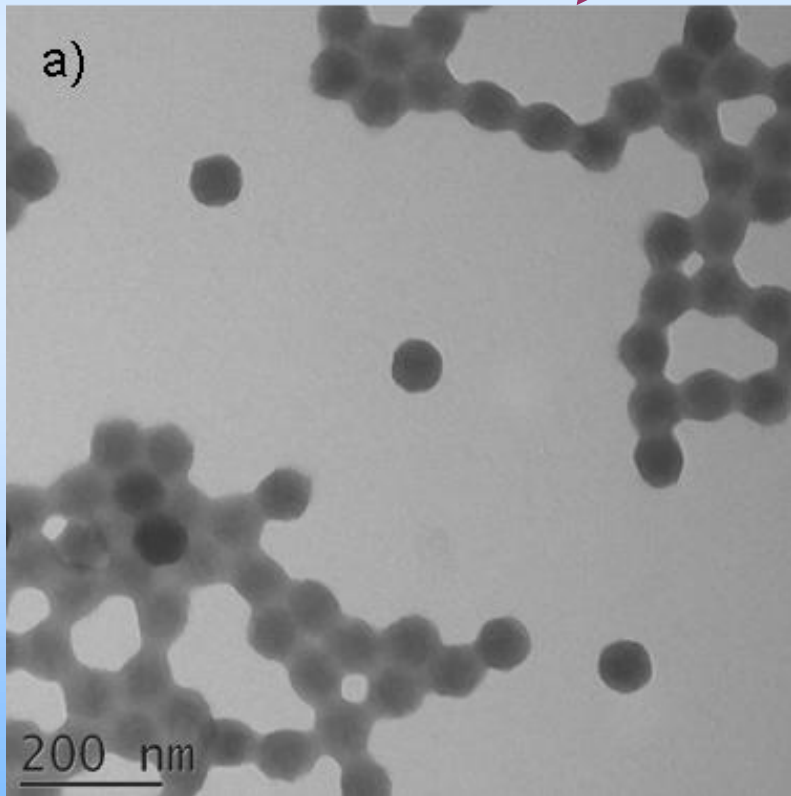


Can spheres turn into disks ?

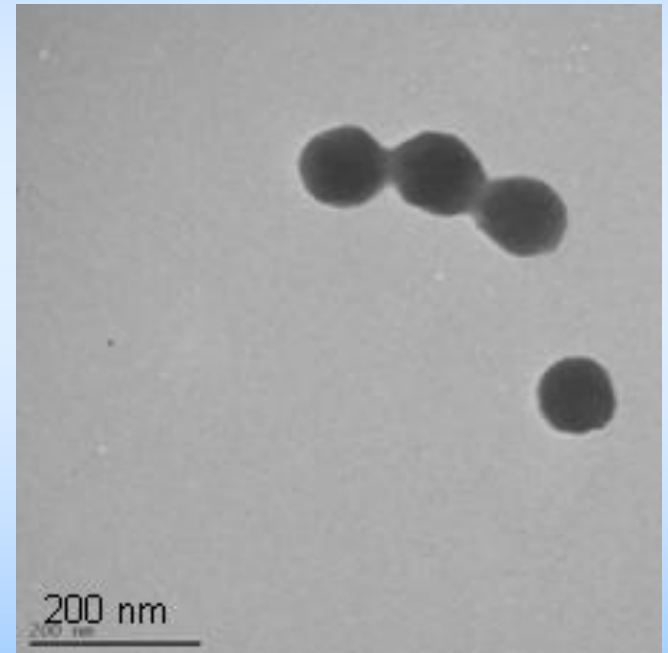
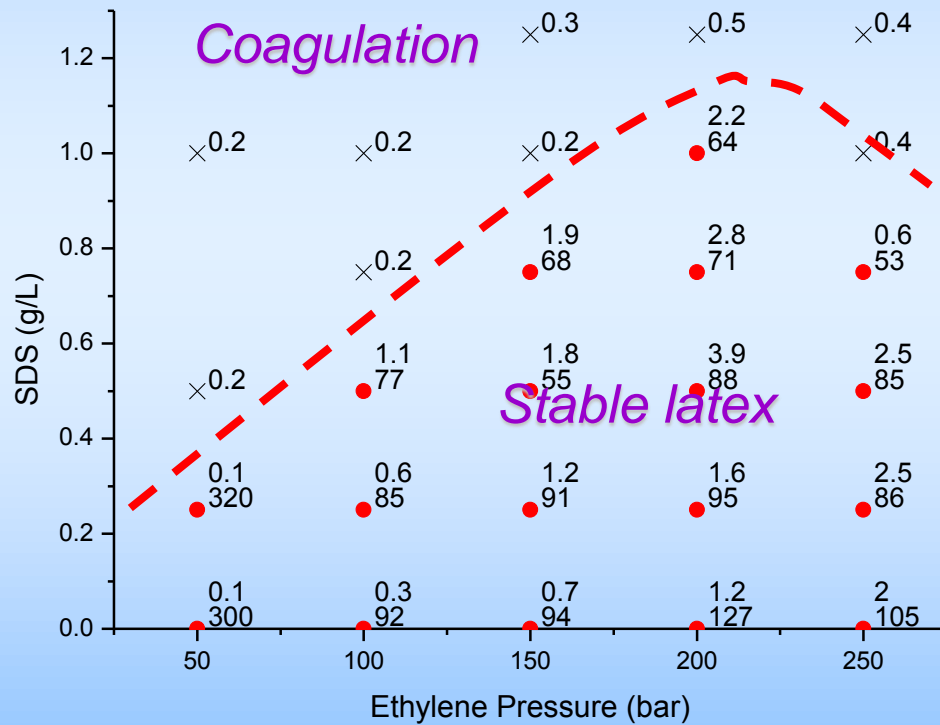
Latex without CTAB

4h 70°C

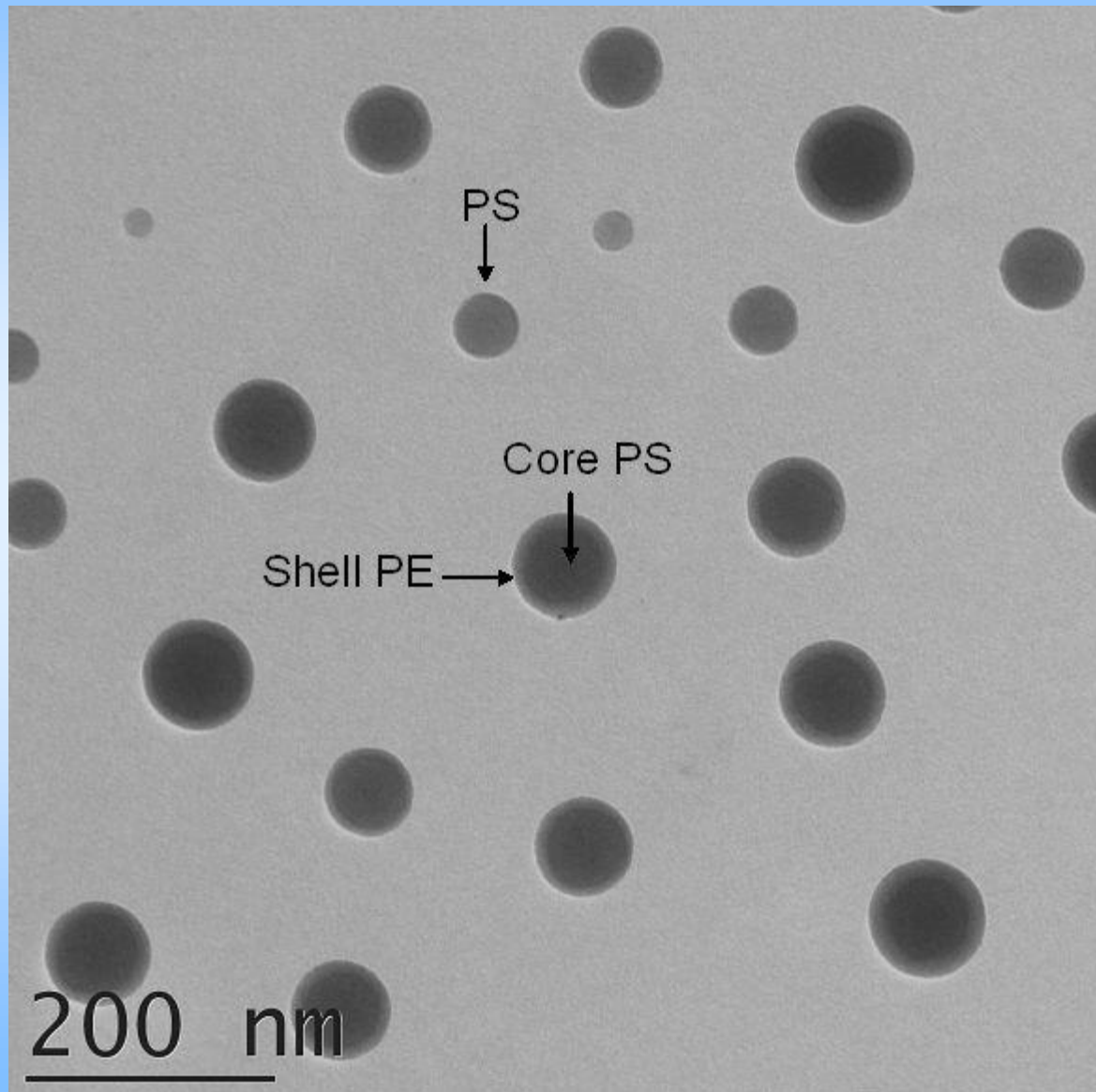
4h 70°C +1 g/L CTAB



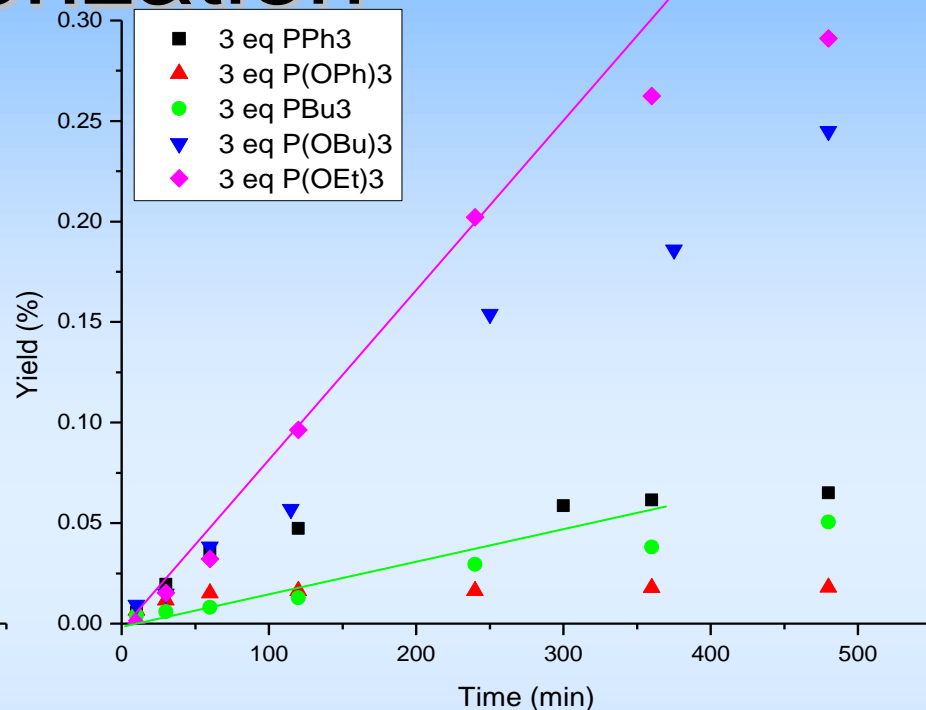
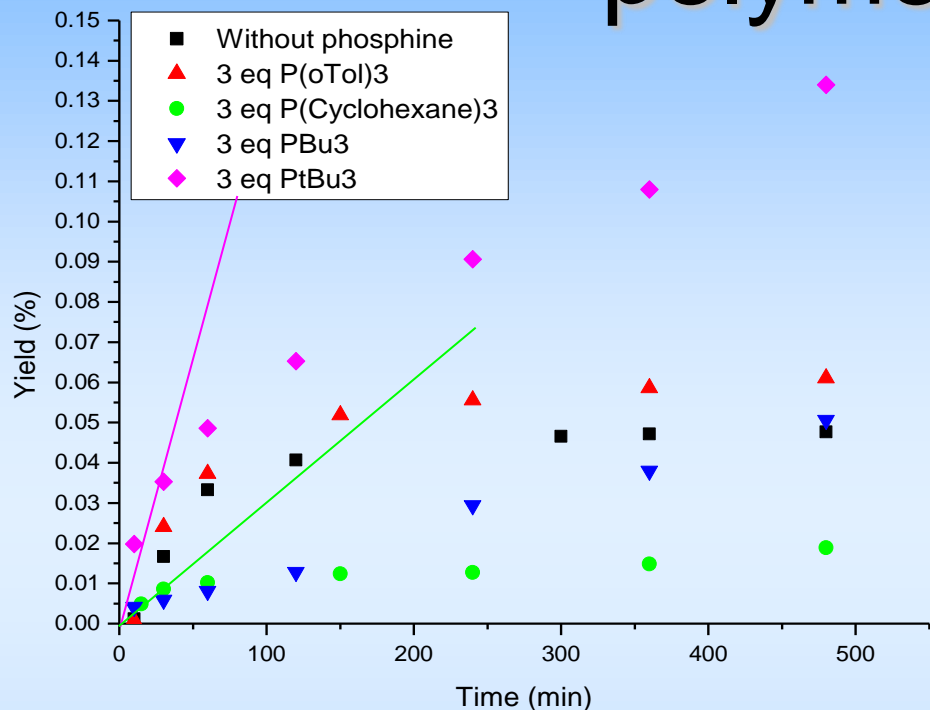
Polymerization initiate by APS



PS core / PE shell



Phosphine effect on MMA polymerization



	cd	q	Ear	pp
PPh3	13.25	145	2.7	0
P(oTol)3	10.65	178	2.7	0
PCy3	1.4	170	0	0
PBU3	5.25	136	0	0
PtBu3	0	182	0	0

	cd	q	Ear	pp
PPh3	13.25	145	2.7	0
P(OPh)3	23.6	128	1.3	4.1
PBU3	5.25	136	0	0
P(OBu)3	15.9	110	1.3	2.7
P(OEt)3	15.8	109	1.1	2.9

σ-donation

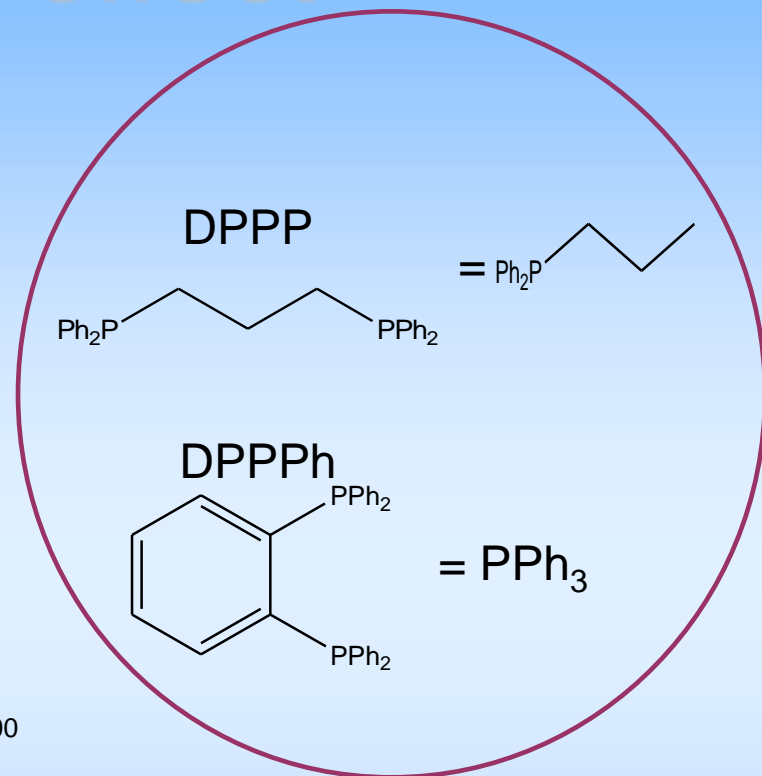
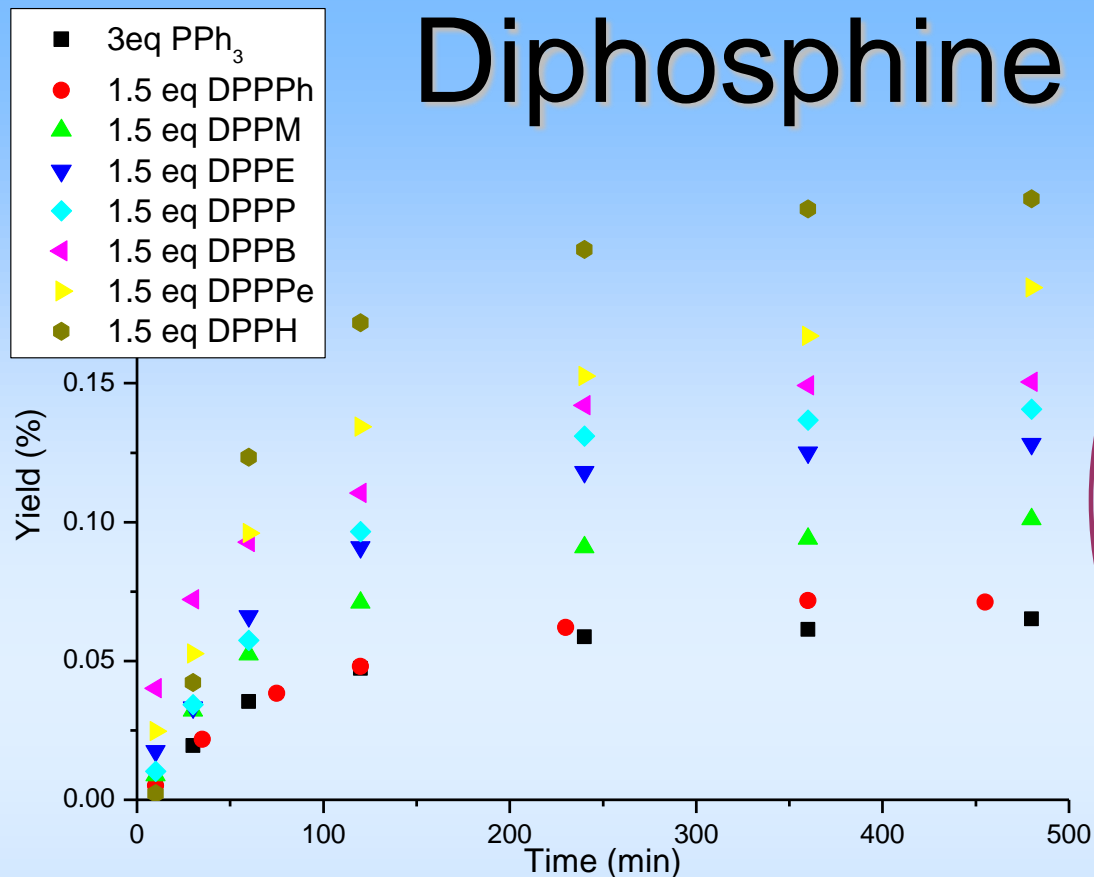
Tolman's angle

Aryl effect

π retro-donation

Yield can be tuned 1% to 30% by phosphorous ligand addition

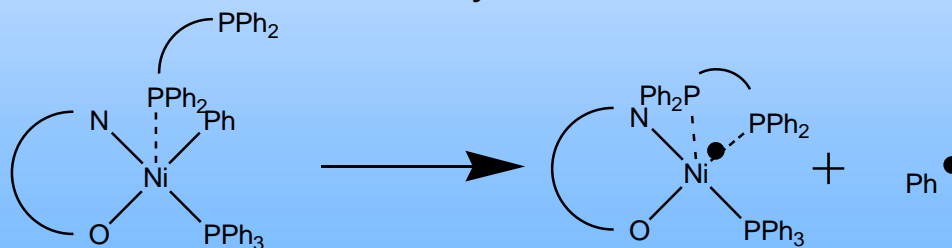
Diphosphine effect



No bidentate effect

	Bite angle
DPPPh	<110
DPPM	<80
DPPE	85
DPPP	91
DPPB	98
DPPPe	≈110
DPPH	120

Bidentate effect only with DPPH and DPPPe



Phosphine effect during catalytic polymerization

Additional phosphine	Activity (g mmol ⁻¹ h ⁻¹)	Mn (g/mol) ^b [PDI] ^b	Melting Temperature (°C) ^c
-	94.7	7150 [2.2]	117.9
PPh ₃	209	16150 [2.2]	118.1
P(o-Tol) ₃	146	14200 [1.9]	113.3
PBu ₃	1.1	nd [nd]	nd
P ^t Bu ₃	40.6	nd [nd]	118.1
PCy ₃	201	23700 [2.1]	118.0
P(C ₆ F ₅) ₃	135	10600 [2.1]	110.9
P(p-MeO-Ph) ₃	96.1	16300 [2.3]	115.6

Phosphine	Bite angle (°)	Activity (g mmol ⁻¹ h ⁻¹)	Mn (g/mol) ^b [PDI] ^b	Melting temperature (°C) ^c
-	-	94.7	7150 [2.2]	117.9
PPh ₃	-	209	16150 [2.2]	118.1
DPPPh	109	201	18200 [2.1]	115.1
PEtPh ₂	-	54.1	15794 [3.2]	119.6
DPPM	<80	117	16100 [2.3]	117.1
DPPE	85	155	12700 [2.5]	116.2
DPPP	91	120	18400 [2.2]	115.4
DPPB	98	21.7	11000 [1.9]	116.2
DPPPe	111	344	9450 [2.6]	111.8
DPPH	120	10100 [2.0]	114.4	

Polymerizations are performed during 1 hour with 20 mg of NiNO at 50°C in 250 mL of toluene under 20 bar of ethylene pressure

