Polymer (PE) synthesis

Dr. Christophe Detrembleur

Center for Education and Research on Macromolecules (CERM)
University of Liège, Sart-Tilman B6a
4000 Liège, Belgium

Plan

1- Controlled radical polymerization vs conventional radical polymerization

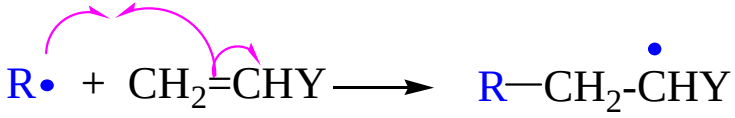
2- 1st CRP mechanism: Reversible Termination

3- 2nd CRP mechanism: Atom Transfer Radical Polymerization

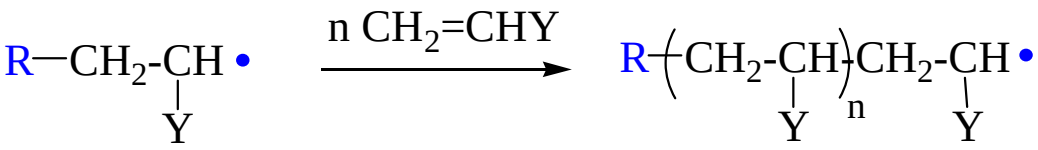
4- 3rd CRP mechanism: Degenerative Transfer (DT)

Classical radical polymerization

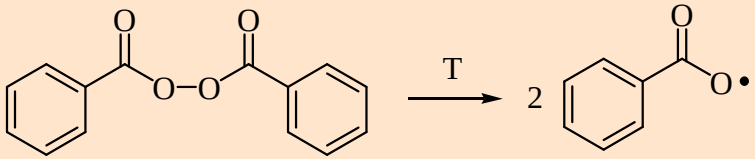
1- Initiation



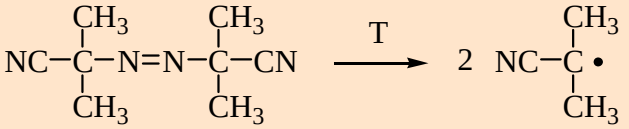
2- Propagation



Some free-radical initiators (R-R):

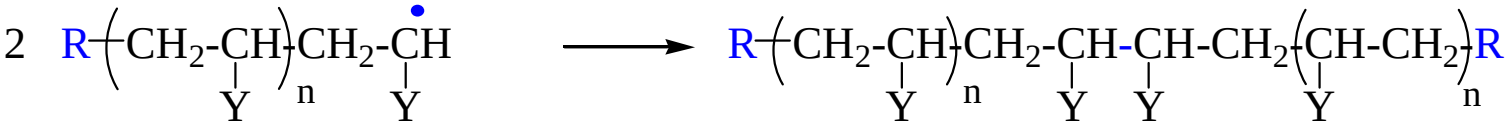


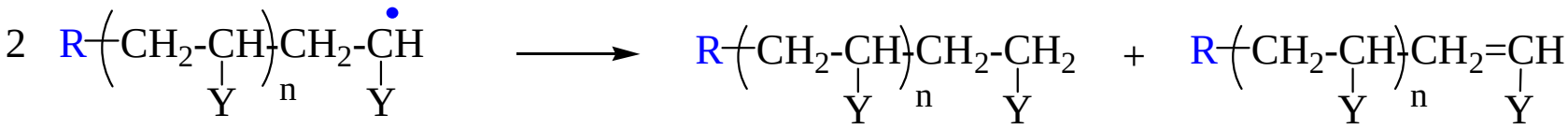
Benzoyl peroxide
(BPO)



Azobisisobutyronitrile
(AIBN)

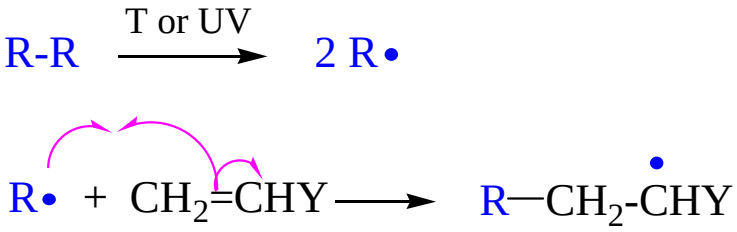
3- Terminations

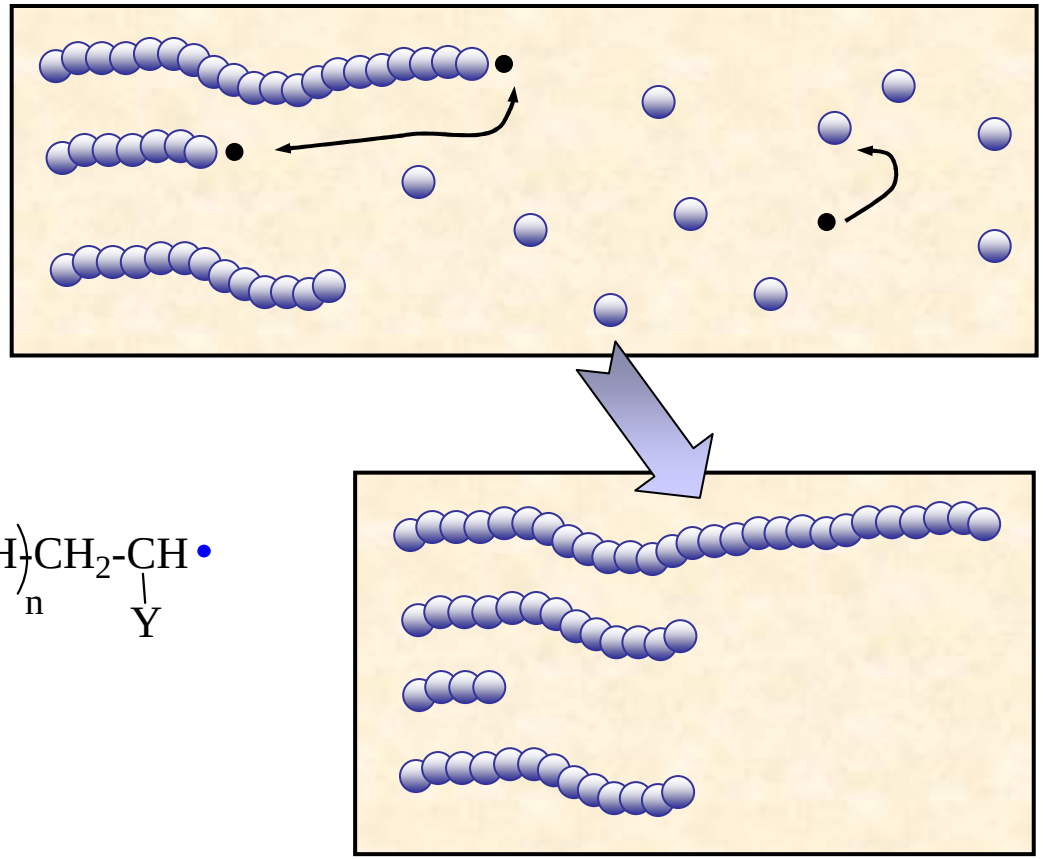




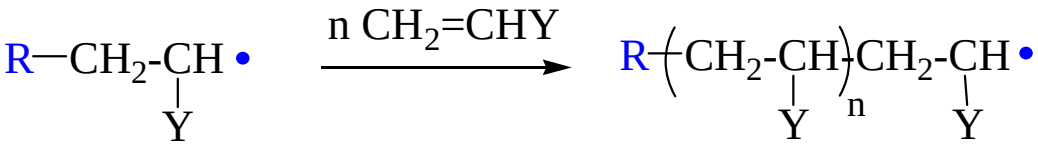
Classical radical polymerization

1- Initiation

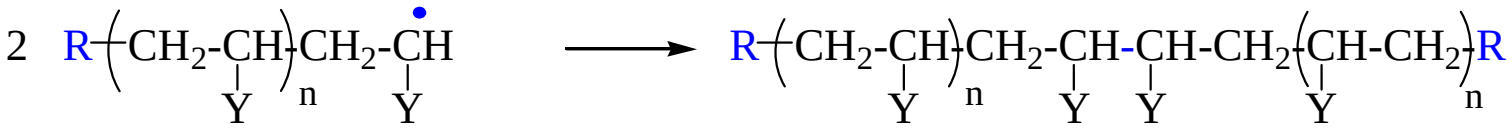


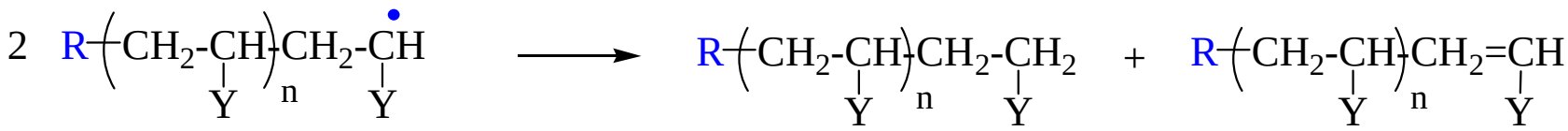


2- Propagation

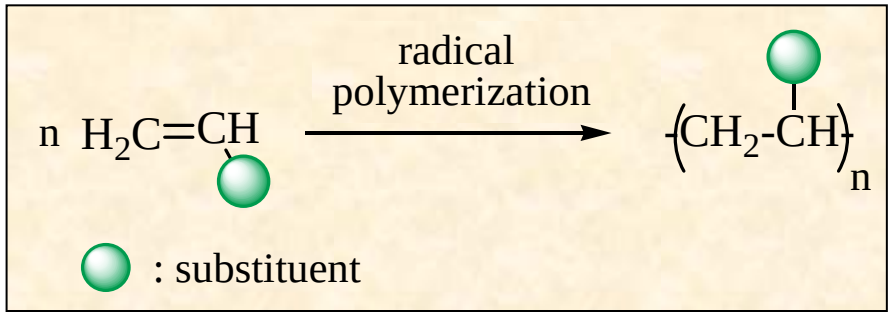


3- Terminations





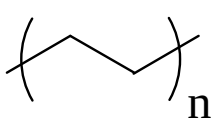
Importance of the « classical » radical polymerization



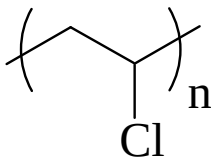
Radical polymerization is

- tolerant towards numerous functions (-COOH, -OH, -NH_2,…).
- applicable to a broad range of vinyl monomers
- can be applied to aqueous media (suspension, emulsion, miniemulsion)
- highly reproducible (tolerant to impurities)

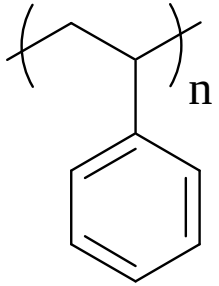
Some examples of polymers produced by this technique:



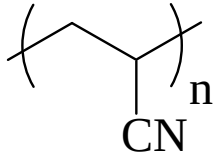
poly(ethylene)



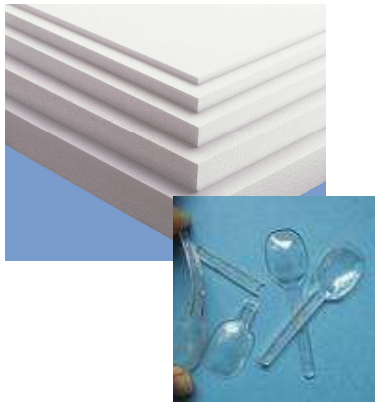
poly(vinyl chloride)



poly(styrene)

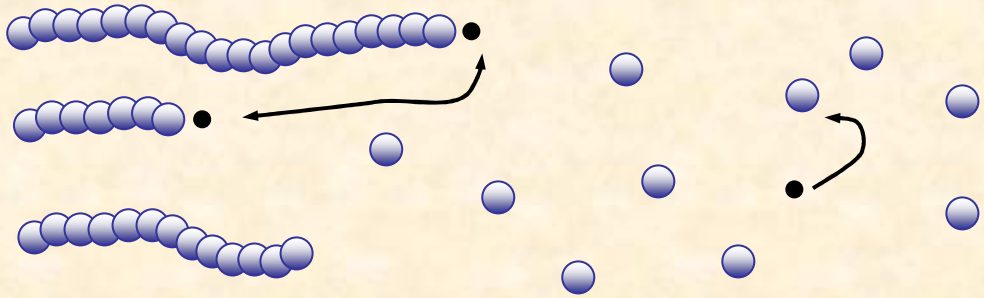


poly(acrylonitrile)



Controlled radical polymerization

Conventional radical polymerization



1- Initiation

2- Propagation : $v_p = k_p [P°] [M]$

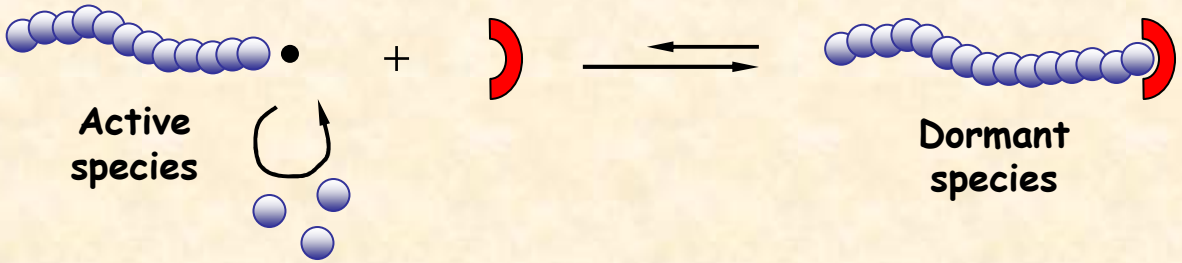
3- Occurrence of irreversible termination reactions: $v_t = k_t [P°]^2$

Controlled radical polymerization

NO irreversible termination reactions, only initiation and propagation.

How to avoid the occurrence of irreversible termination reaction ?

[P°] has to decrease $\rightarrow \mathbf{v_p/v_t} \Uparrow$

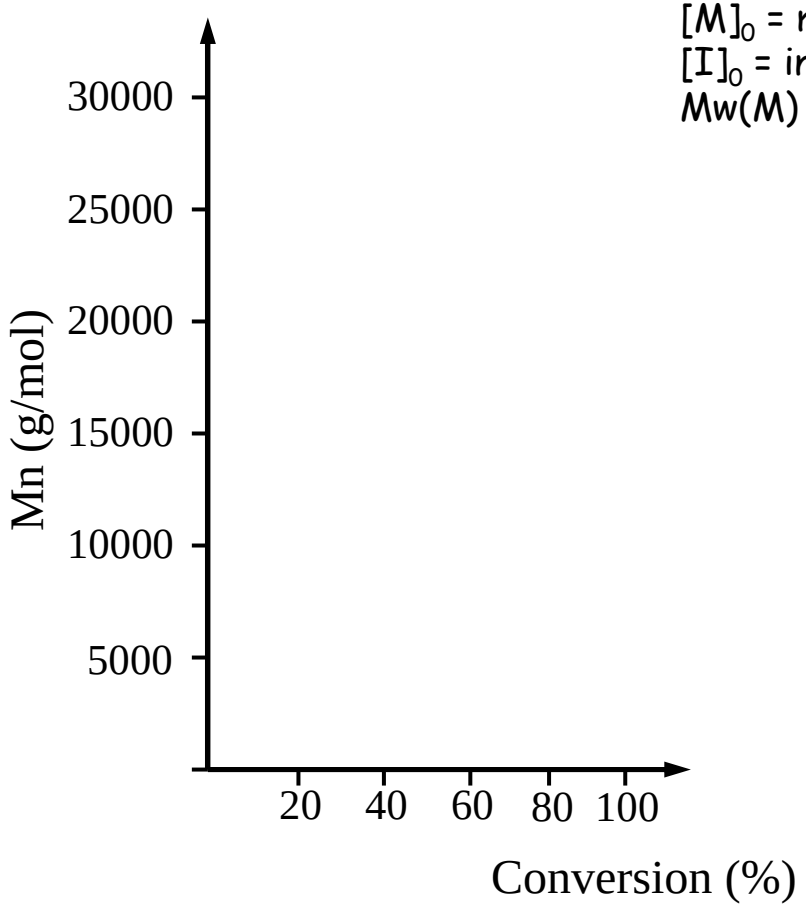


Criteria for a controlled radical polymerization

1- Control of the molecular weight

$$\mathbf{Mn} = ([M]_0/[I]_0) \times Mw(M) \times conv$$
$$= (m_M/n_I) \times conv$$

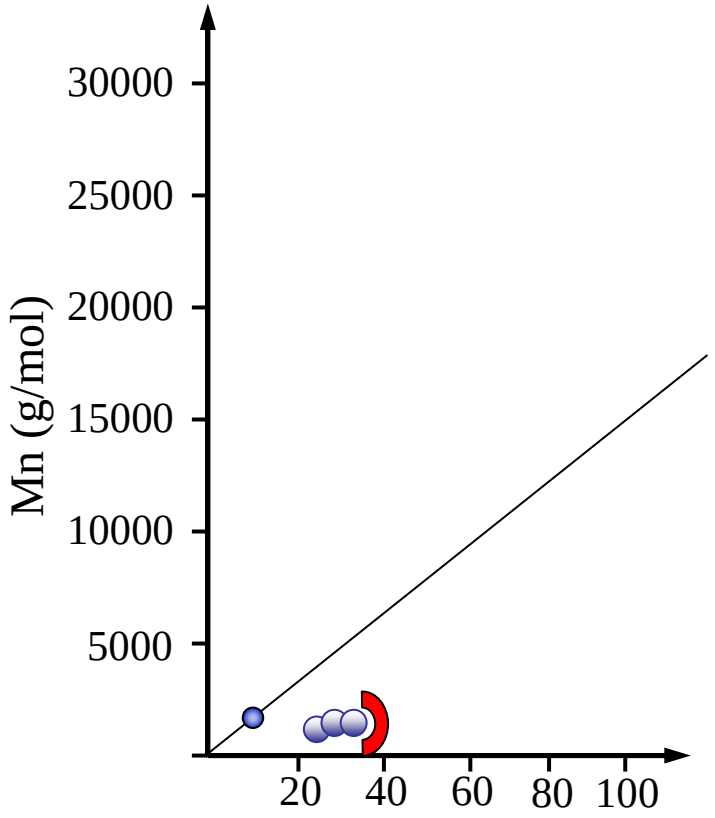
$[M]_0$ = monomer concentration at the initial stage
$[I]_0$ = initiator concentration at the initial stage
Mw(M) = molecular weight of the monomer

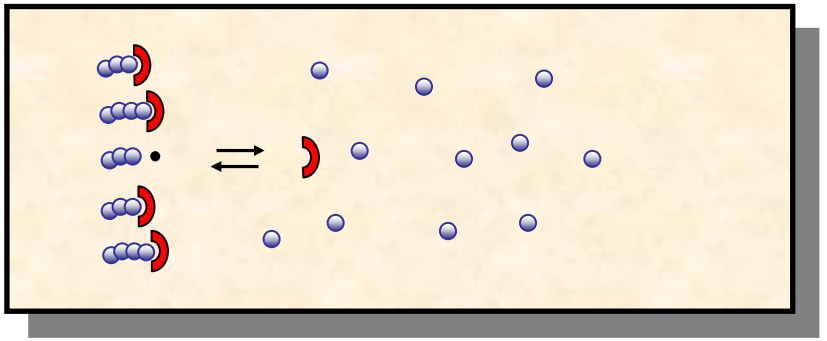


Criteria for a controlled radical polymerization

1- Control of the molecular weight

$$\mathbf{Mn} = ([M]_0/[I]_0) \times Mw(M) \times conv$$
$$= (m_M/n_I) \times conv$$

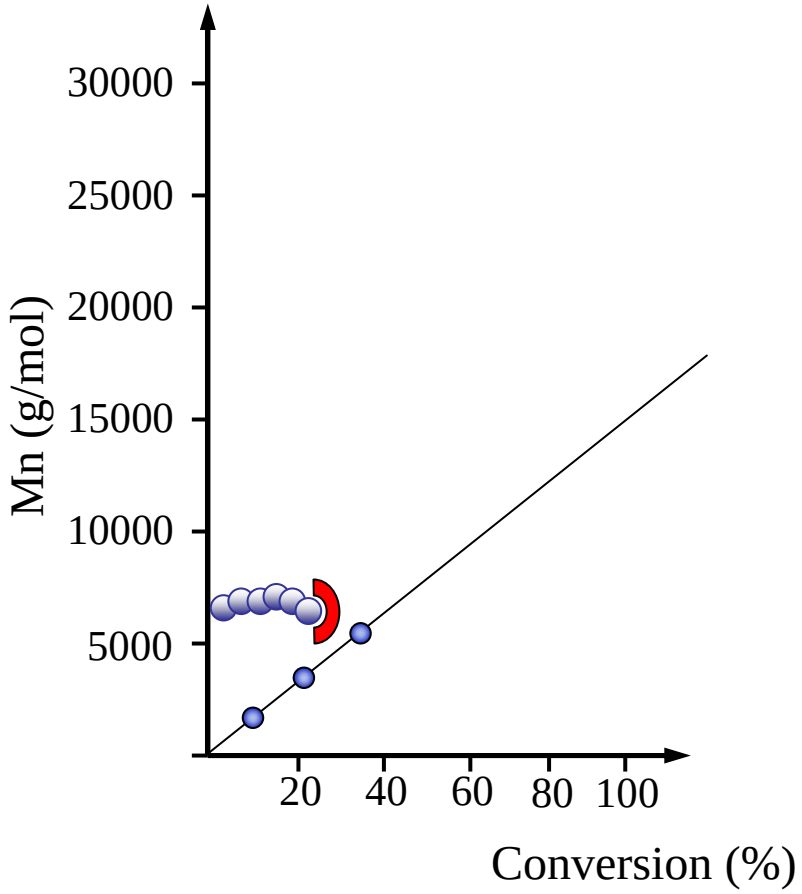




Criteria for a controlled radical polymerization

1- Control of the molecular weight

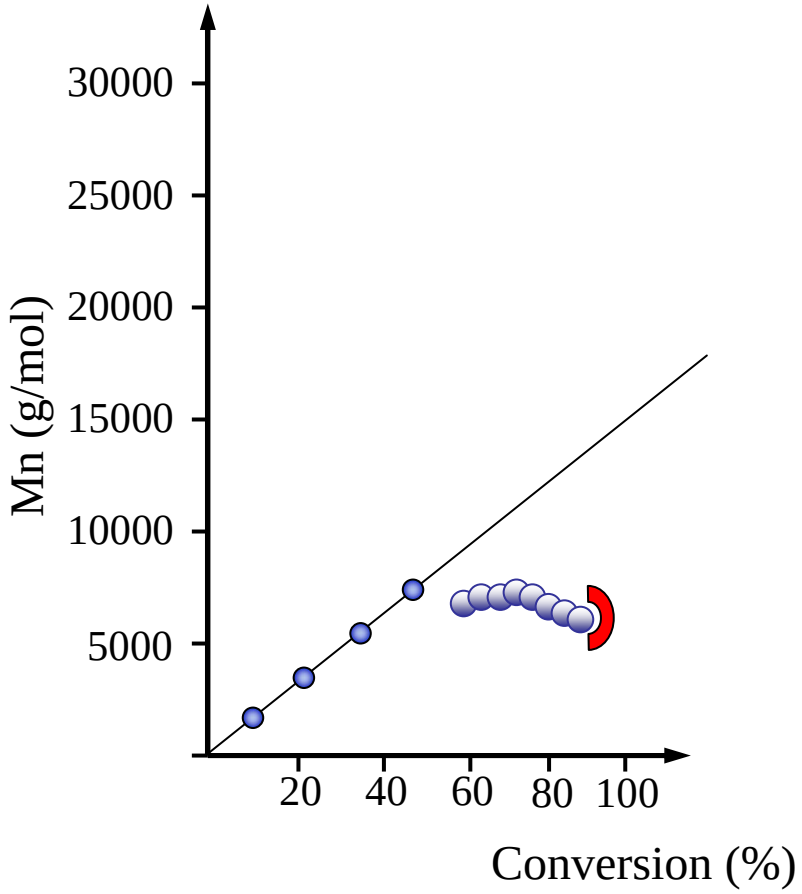
$$\mathbf{Mn} = ([M]_0/[I]_0) \times Mw(M) \times conv$$
$$= (m_M/n_I) \times conv$$



Criteria for a controlled radical polymerization

1- Control of the molecular weight

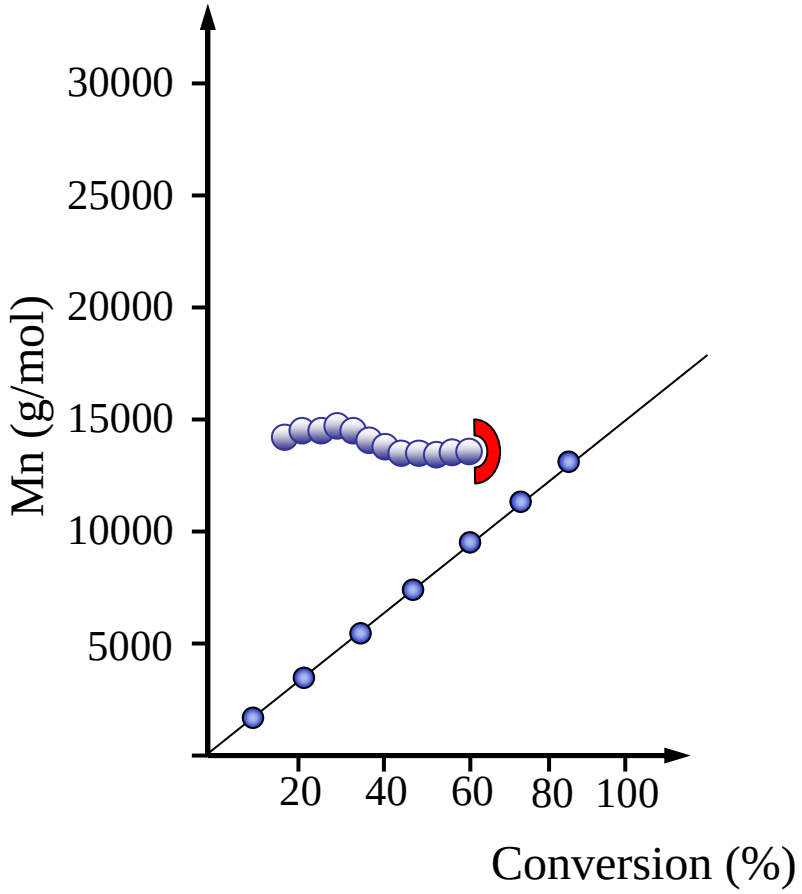
$$\mathbf{Mn} = ([M]_0/[I]_0) \times Mw(M) \times conv$$
$$= (m_M/n_I) \times conv$$



Criteria for a controlled radical polymerization

1- Control of the molecular weight

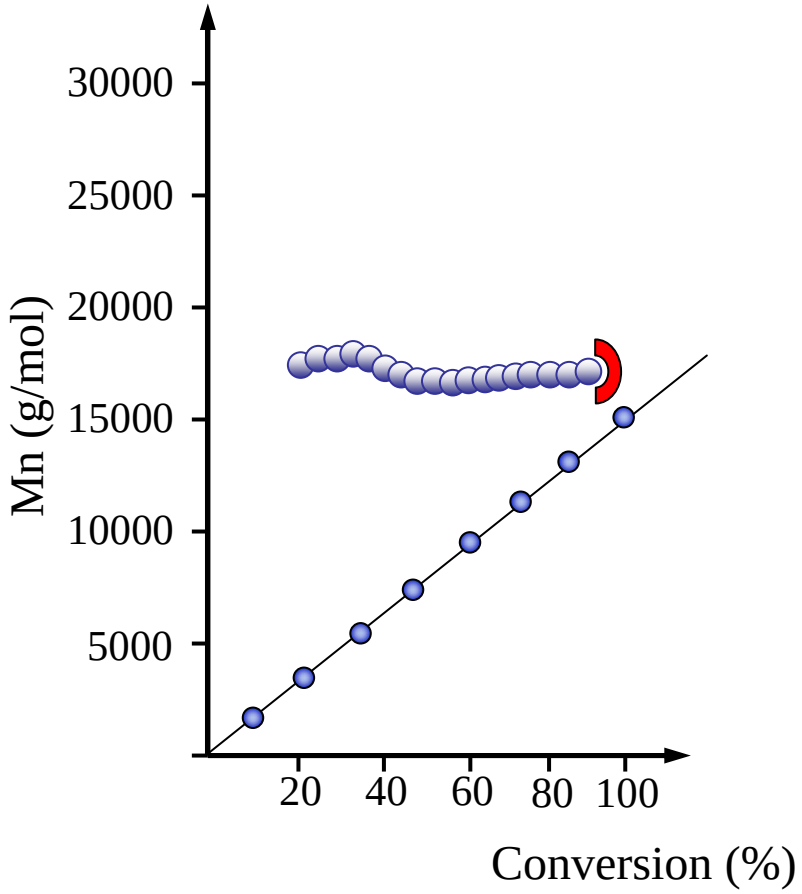
$$\mathbf{Mn} = ([M]_0/[I]_0) \times Mw(M) \times conv$$
$$= (m_M/n_I) \times conv$$



Criteria for a controlled radical polymerization

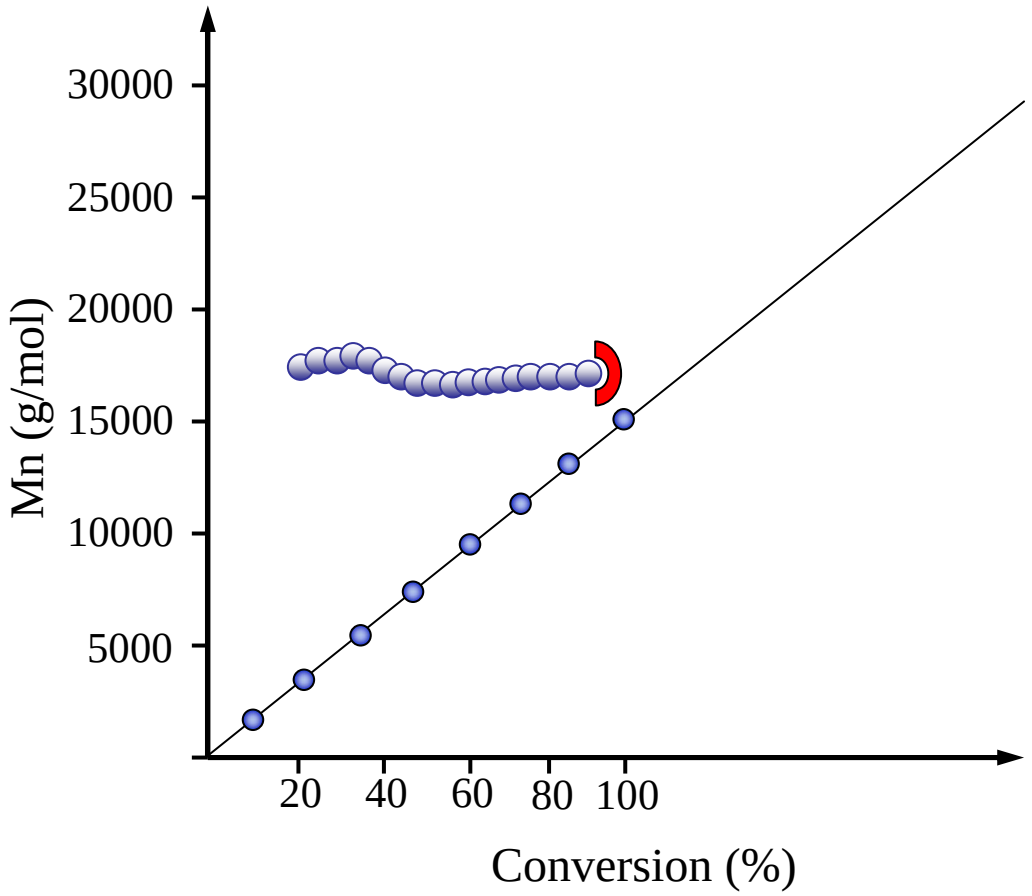
1- Control of the molecular weight

$$\mathbf{Mn} = ([M]_0/[I]_0) \times Mw(M) \times conv$$
$$= (m_M/n_I) \times conv$$



2- Resumption of the polymer chains

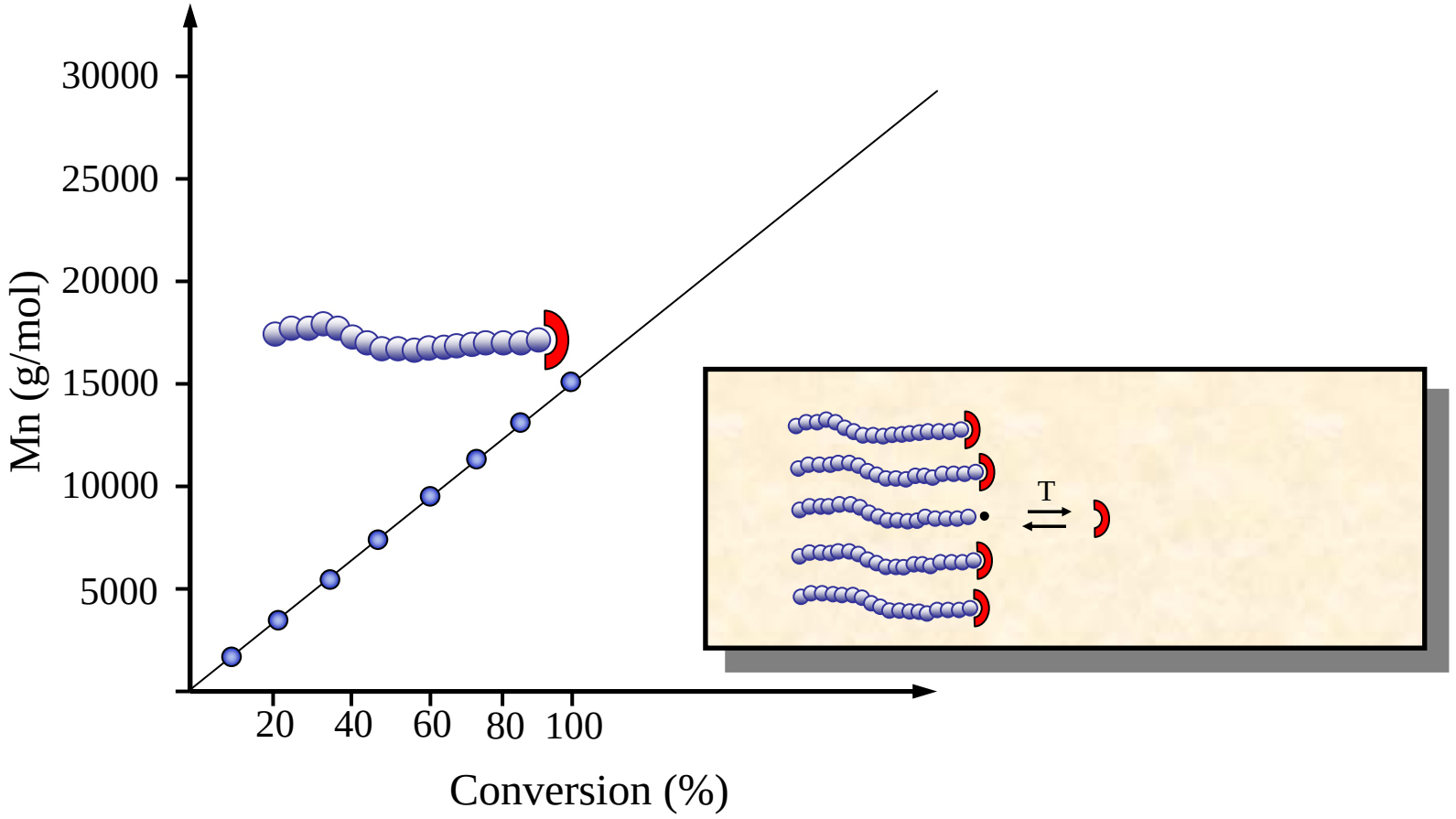
At the end of the polymerization, the chains are end-capped by the controlling agent



2- Resumption of the polymer chains

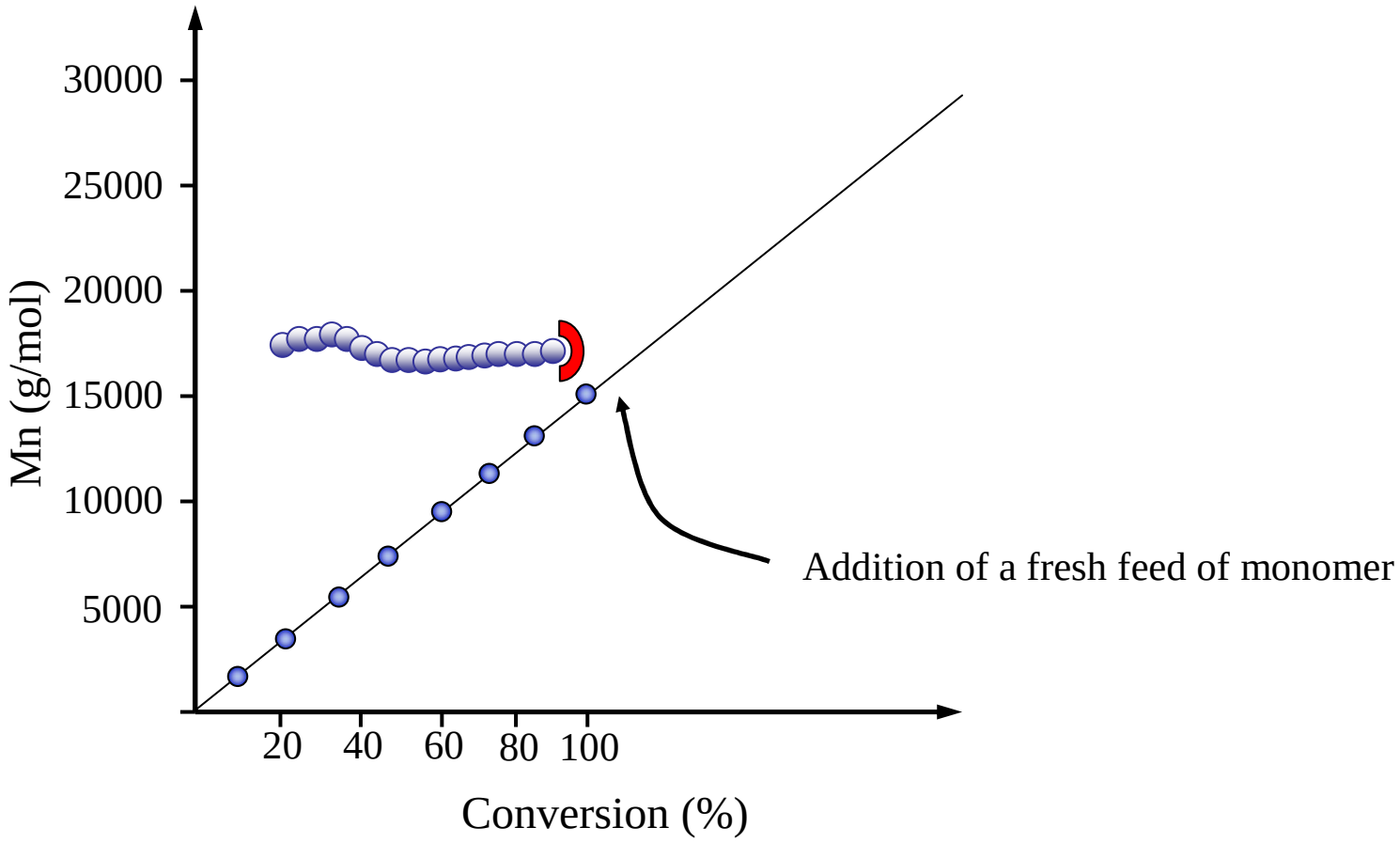
At the end of the polymerization, the chains are end-capped by the controlling agent

⇒ The chains can be reactivated and initiate the polymerization of a vinyl monomer

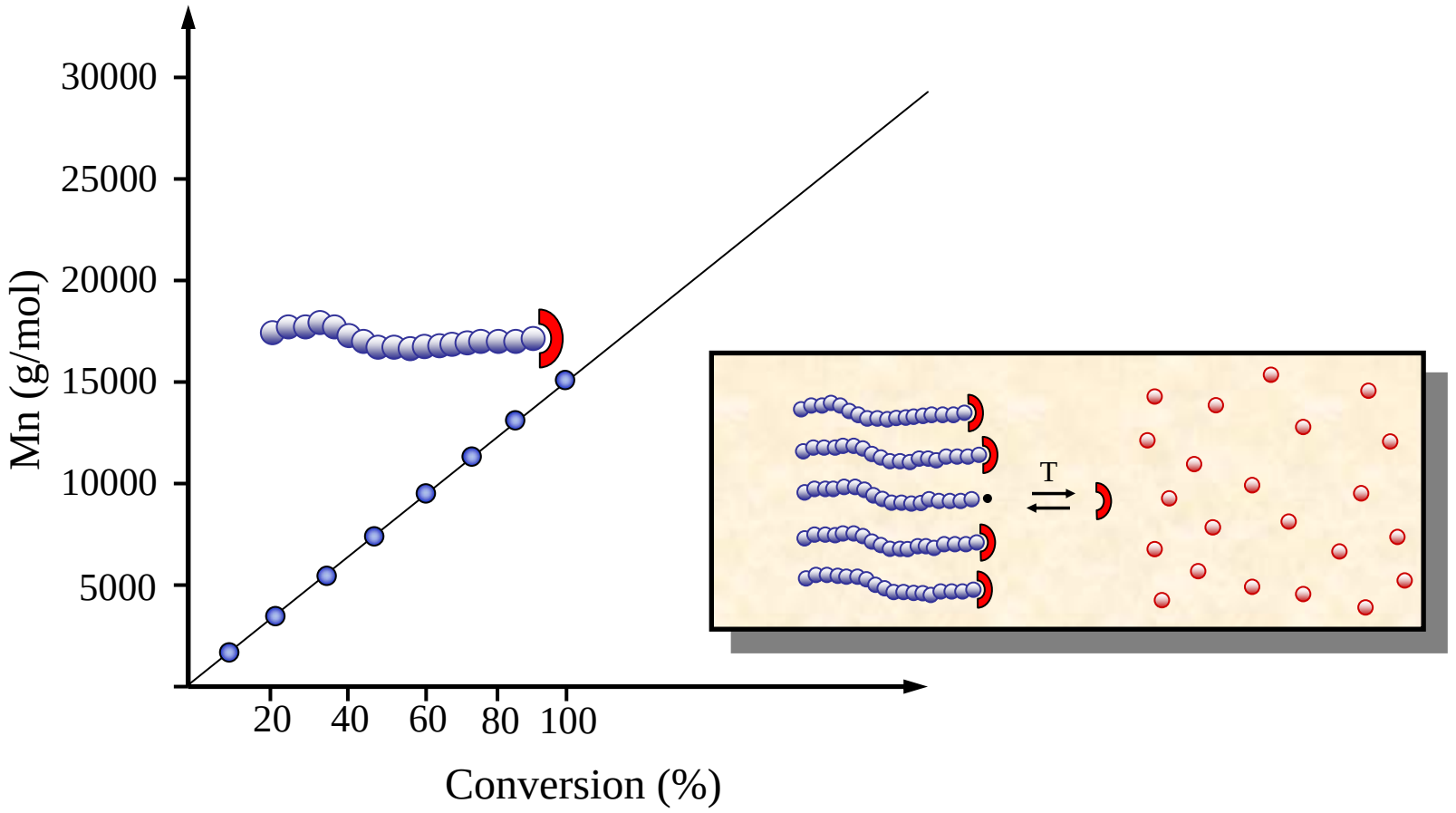


Criteria for a controlled radical polymerization

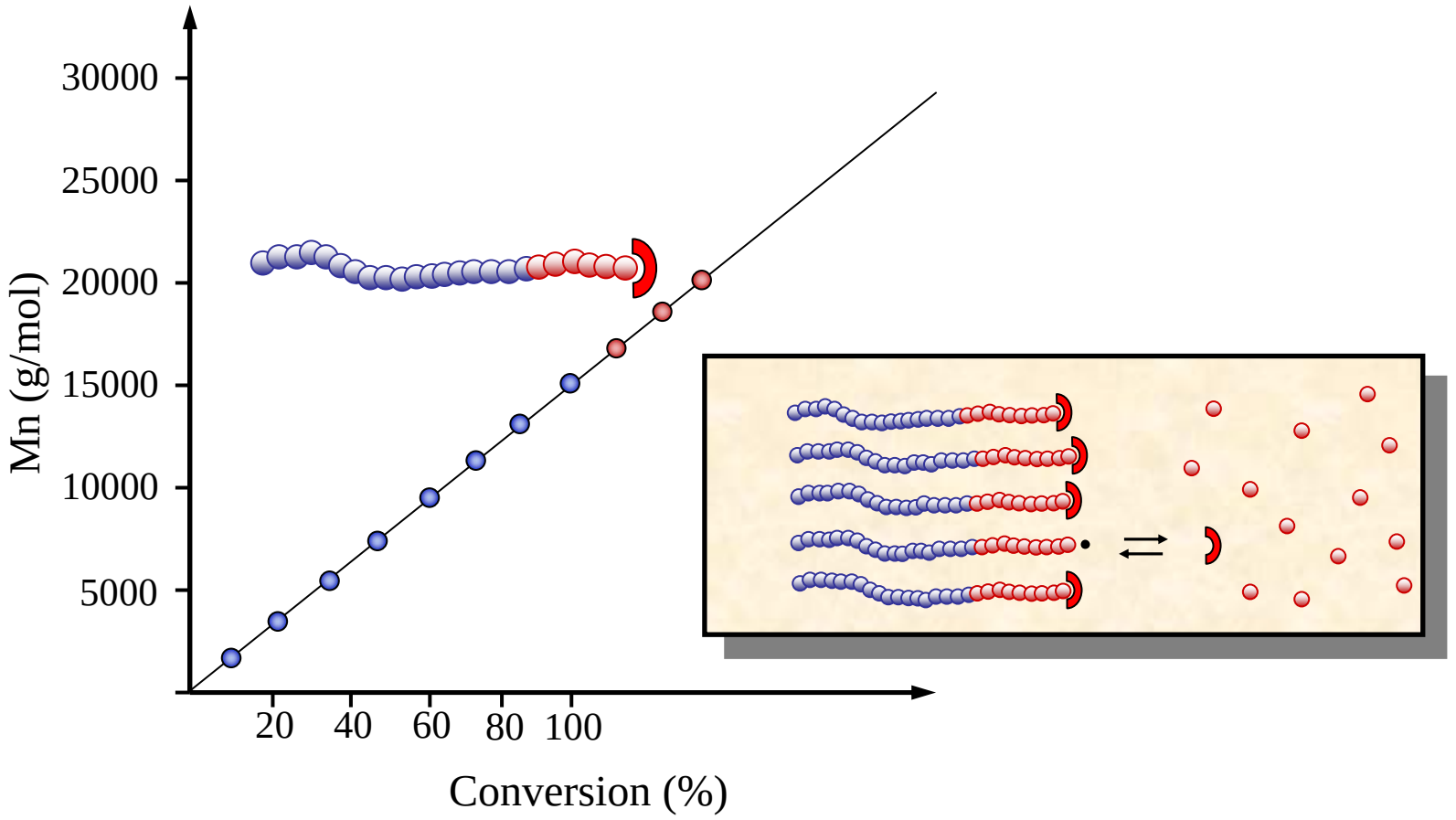
2- Resumption of the polymer chains



2- Resumption of the polymer chains

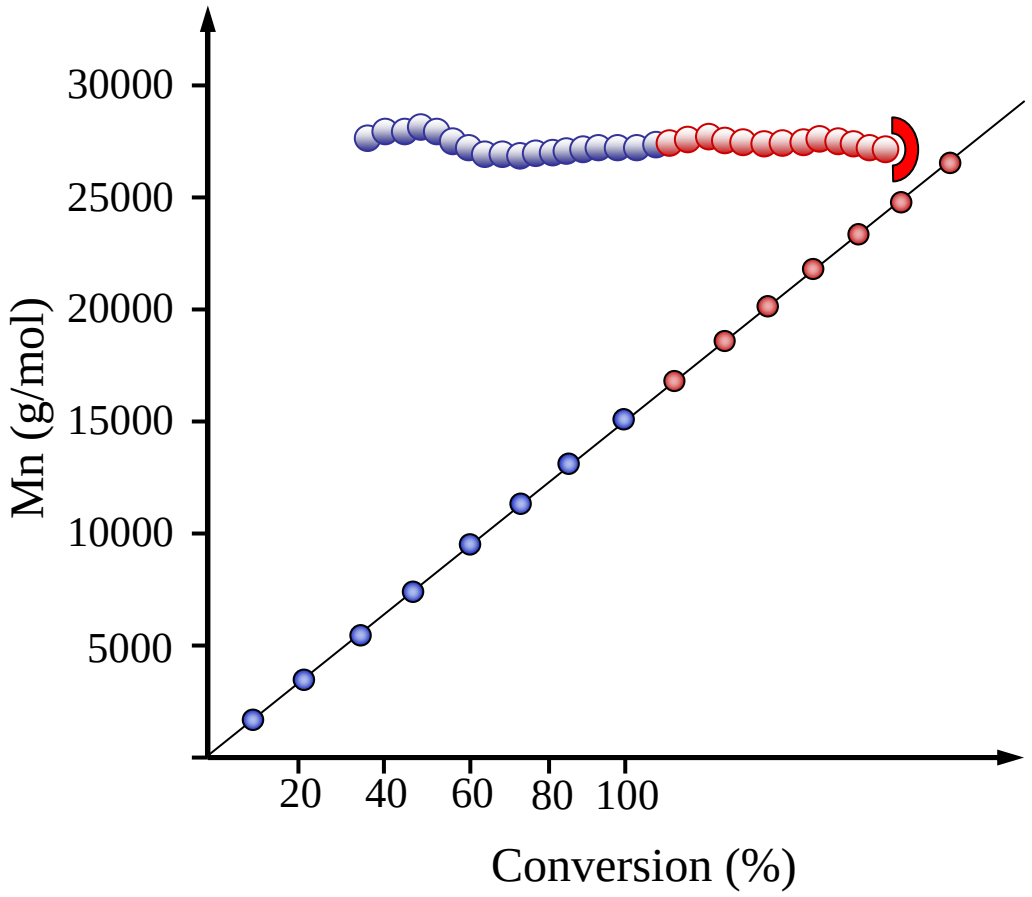


2- Resumption of the polymer chains



Criteria for a controlled radical polymerization

2- Resumption of the polymer chains



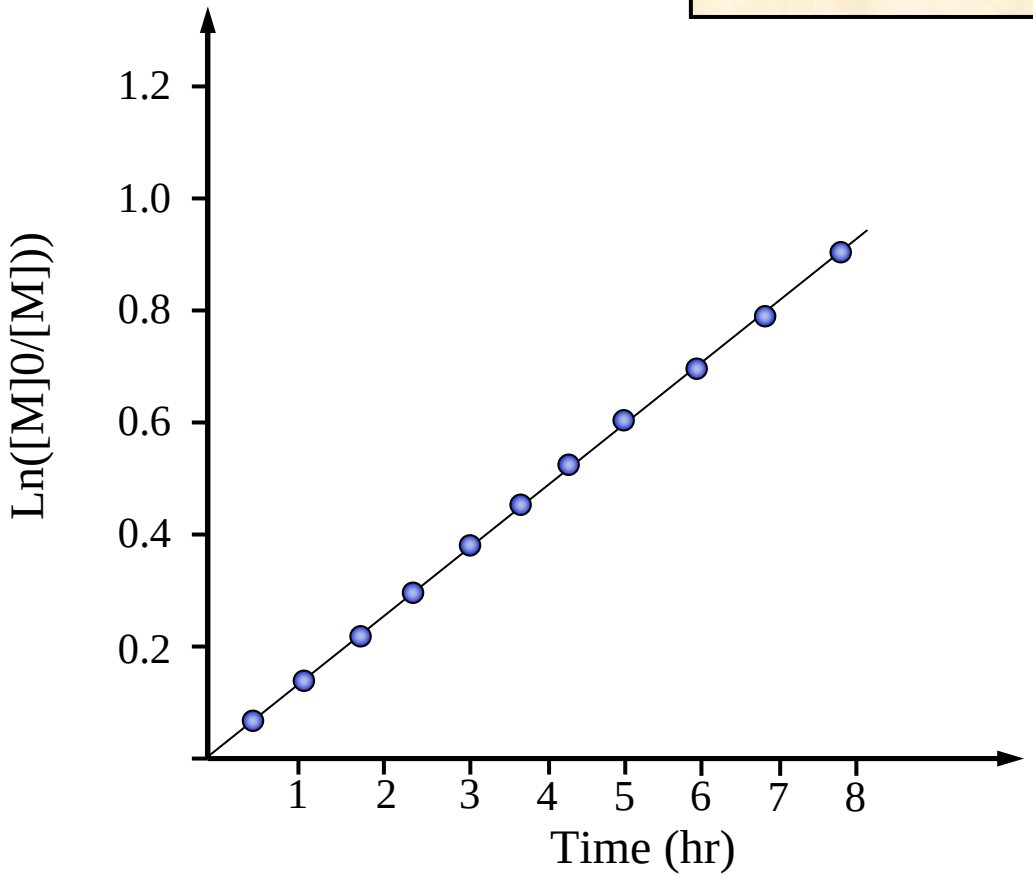
Criteria for a controlled radical polymerization

3- Kinetics is first order in monomer

$V_p = -d[M]/dt = k_p \times [M] \times [P^\circ]$

By integration of v_p:

$$Ln([M]_0/[M]) = k_p \times [P^\circ] \times t$$

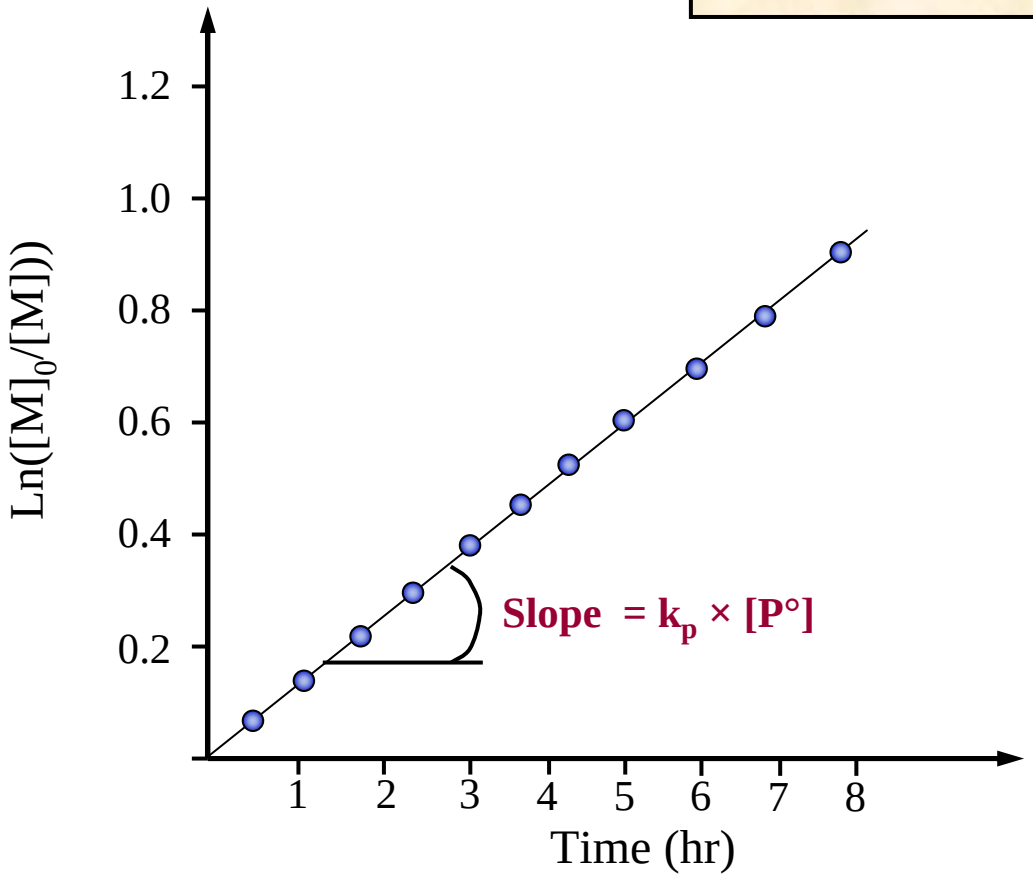


3- Kinetics is first order in monomer

$V_p = -d[M]/dt = k_p \times [M] \times [P°]$

By integration of v_p:

$$Ln([M]_0/[M]) = k_p \times [P°] \times t$$



Polydispersity: a criterium for CRP ?

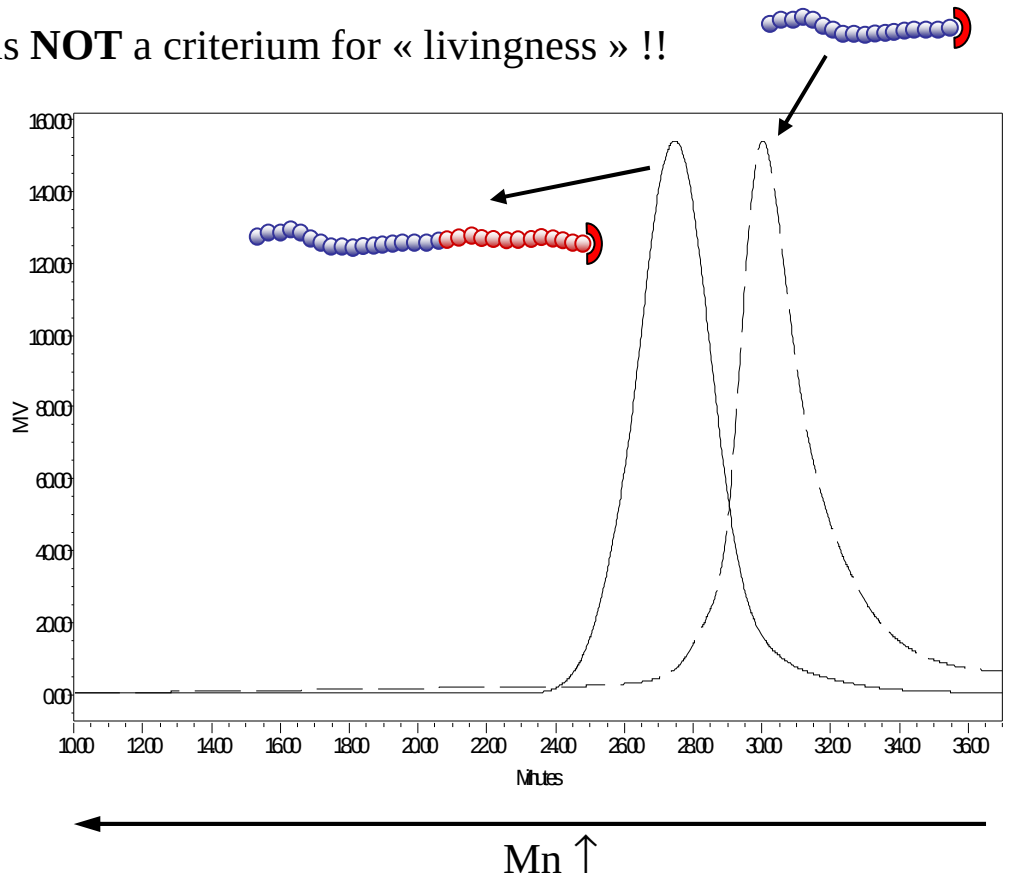
Polydispersity = Mw/Mn = size distribution of the polymer chains.

For most of living and controlled polymerization processes, **Mw/Mn → 1**.

If Mw/Mn = 1: all the polymer chains have the same length.

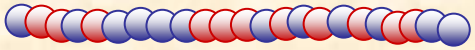
Mw/Mn → 1: **ONLY** if the initiation rate is faster than the propagation rate !!

A narrow polydispersity is **NOT** a criterium for « livingness » !!

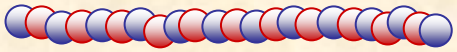


CRP: a way to the macromolecular engineering

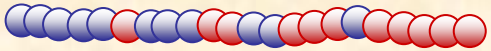
Homopolymer



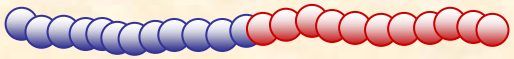
Statistical copolymer



Alternated copolymer



Gradient copolymer



Block copolymer

1- Control of Mn

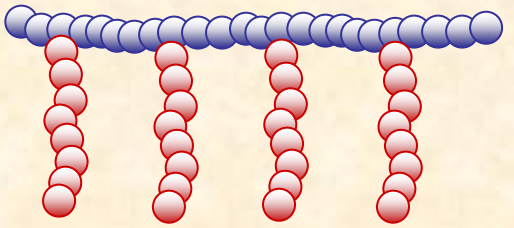
Mn =

$([M]_0/[I]_0) \times Mw(M) \times conv.$

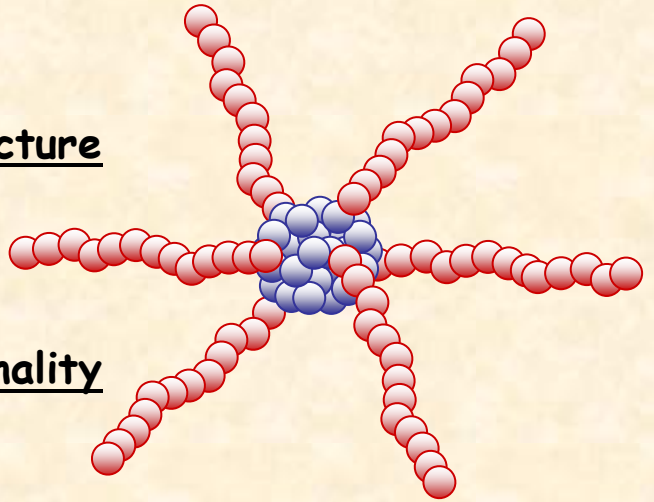
2- Control of the copolymer composition

3- Control of the architecture

4- Control of the functionality



Grafted (co)polymer



Star-shaped (co)polymer

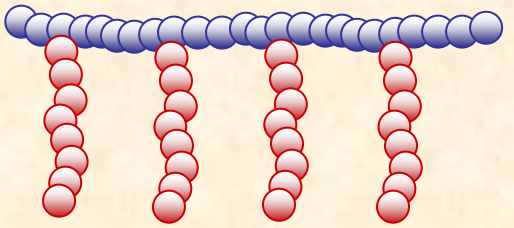
CRP: a way to the macromolecular engineering

Homopolymer

1- Control of Mn

Mn =

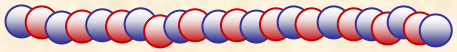
$([M]_0/[I]_0) \times Mw(M) \times conv.$



Grafted (co)polymer

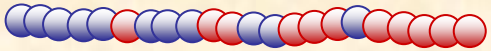
Statistical copolymer

2- Control of the copolymer composition



Alternated copolymer

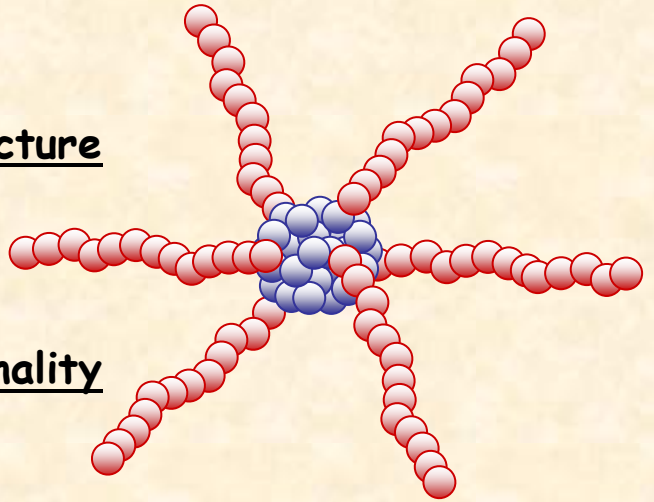
3- Control of the architecture



Gradient copolymer

4- Control of the functionality

Block copolymer

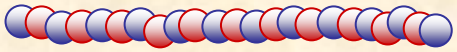


Star-shaped (co)polymer

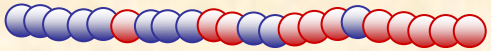
CRP: a way to the macromolecular engineering

Homopolymer

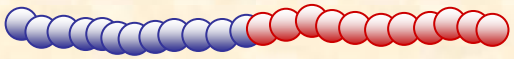
Statistical copolymer



Alternated copolymer



Gradient copolymer



Block copolymer

1- Control of Mn

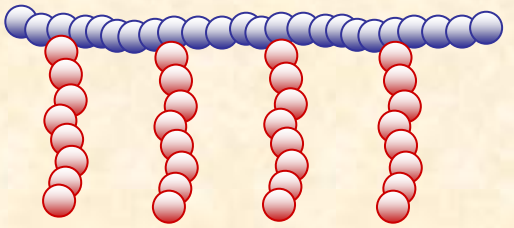
Mn =

$([M]_0/[I]_0) \times Mw(M) \times conv.$

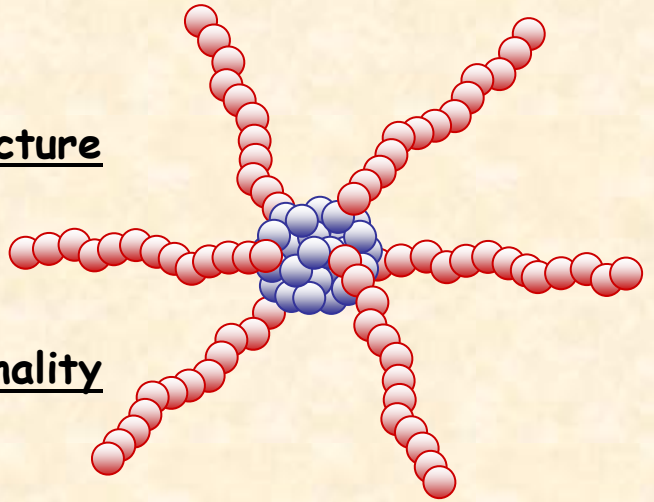
2- Control of the copolymer composition

3- Control of the architecture

4- Control of the functionality



Grafted (co)polymer



Star-shaped (co)polymer

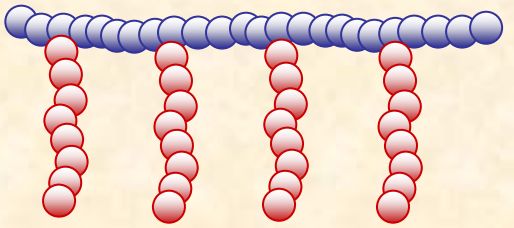
CRP: a way to the macromolecular engineering

Homopolymer

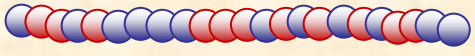
1- Control of Mn

Mn =

$([M]_0/[I]_0) \times Mw(M) \times conv.$

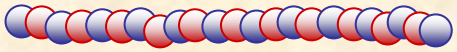


Grafted (co)polymer



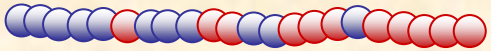
Statistical copolymer

2- Control of the copolymer composition



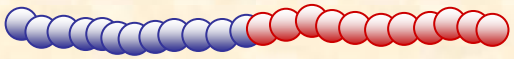
Alternated copolymer

3- Control of the architecture

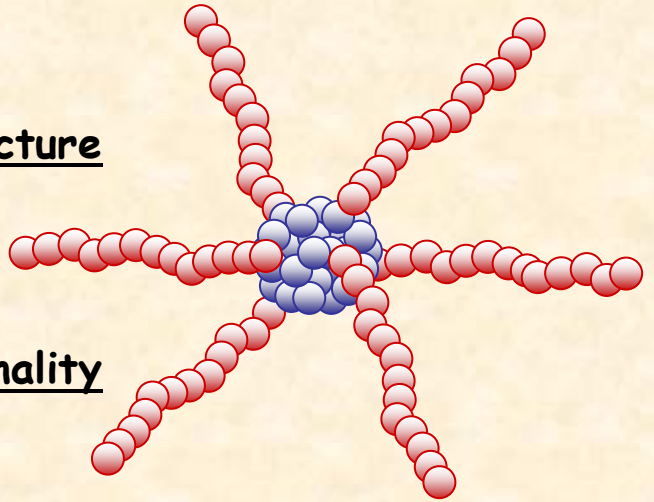


Gradient copolymer

4- Control of the functionality

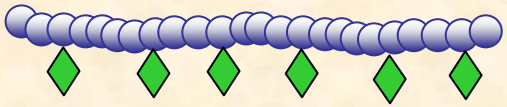


Block copolymer



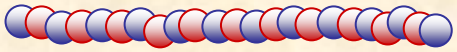
Star-shaped (co)polymer

CRP: a way to the macromolecular engineering

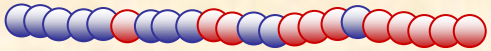


Homopolymer

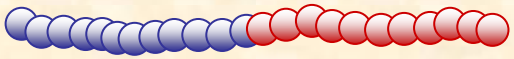
Statistical copolymer



Alternated copolymer



Gradient copolymer



Block copolymer

1- Control of Mn

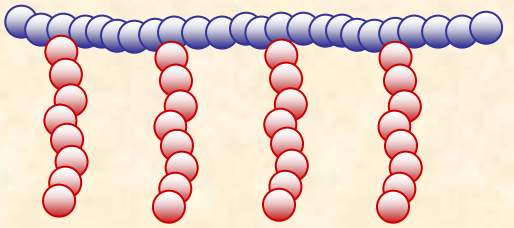
Mn =

$([M]_0/[I]_0) \times Mw(M) \times conv.$

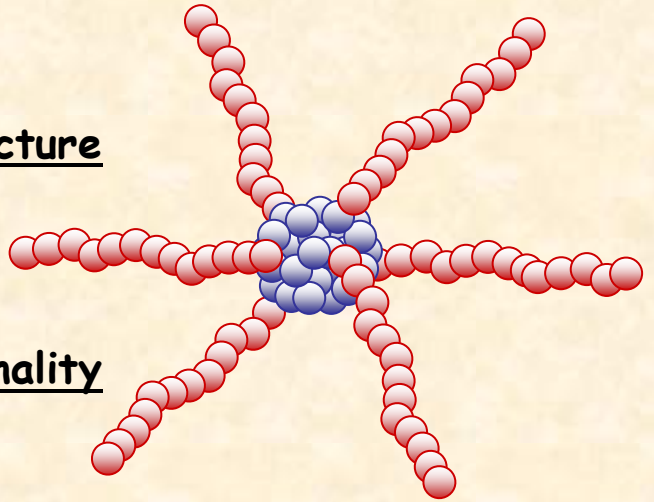
2- Control of the copolymer composition

3- Control of the architecture

4- Control of the functionality



Grafted (co)polymer

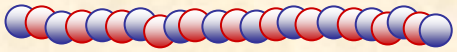


Star-shaped (co)polymer

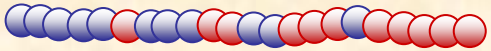
CRP: a way to the macromolecular engineering

Homopolymer

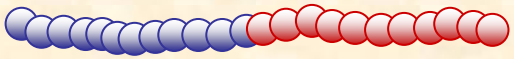
Statistical copolymer



Alternated copolymer



Gradient copolymer

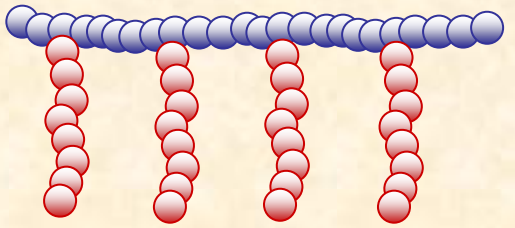


Block copolymer

1- Control of Mn

Mn =

$([M]_0/[I]_0) \times Mw(M) \times conv.$

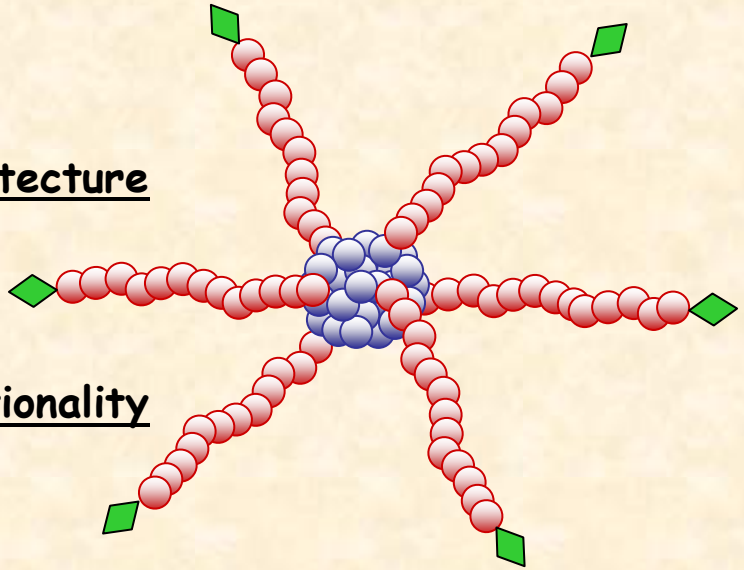


Grafted (co)polymer

2- Control of the copolymer composition

3- Control of the architecture

4- Control of the functionality



Star-shaped (co)polymer

Macromolecular engineering by CRP

Homopolymer

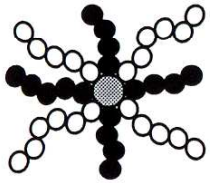
Block copolymer

Random copolymer

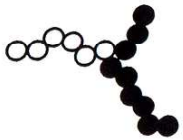
Gradient copolymer

Graft copolymer

A_n star-shaped polymer



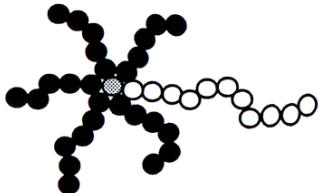
A_nB_m star-shaped copolymer

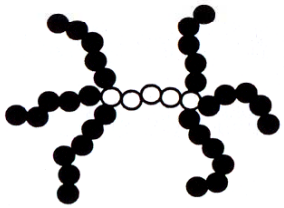


A_2B star-shaped copolymer

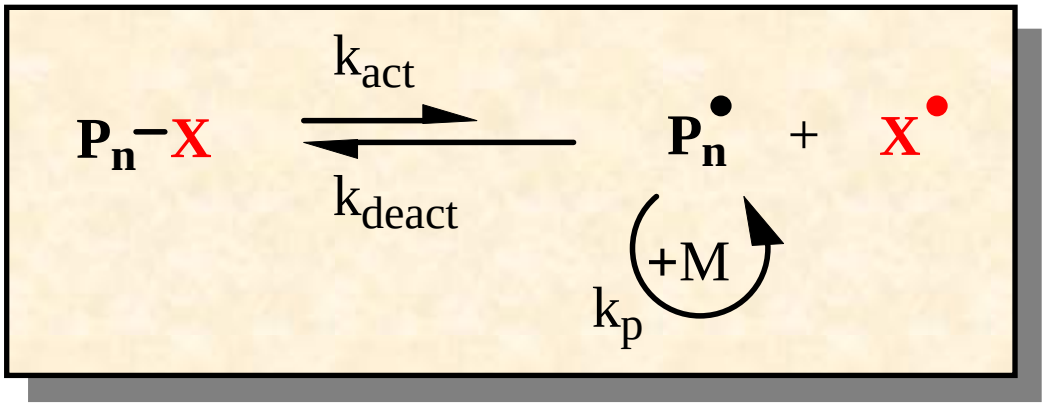
ABC star-shaped copolymer

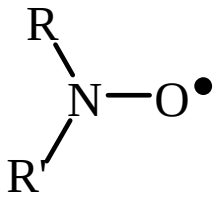
More complex architectures:



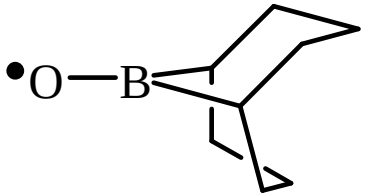


1st CRP mechanism: reversible termination





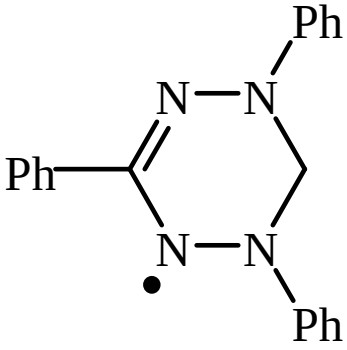
nitroxide radicals



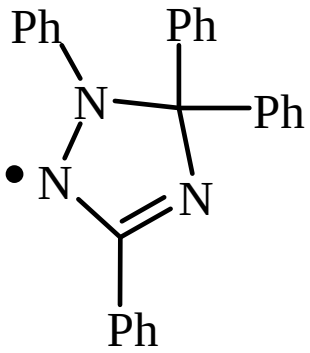
borinate radical

(TMP)Co•

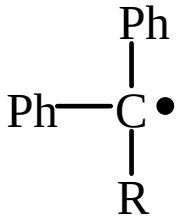
organocobalt porphyrin complexes



verdazyl radicals



triazolinyl radicals



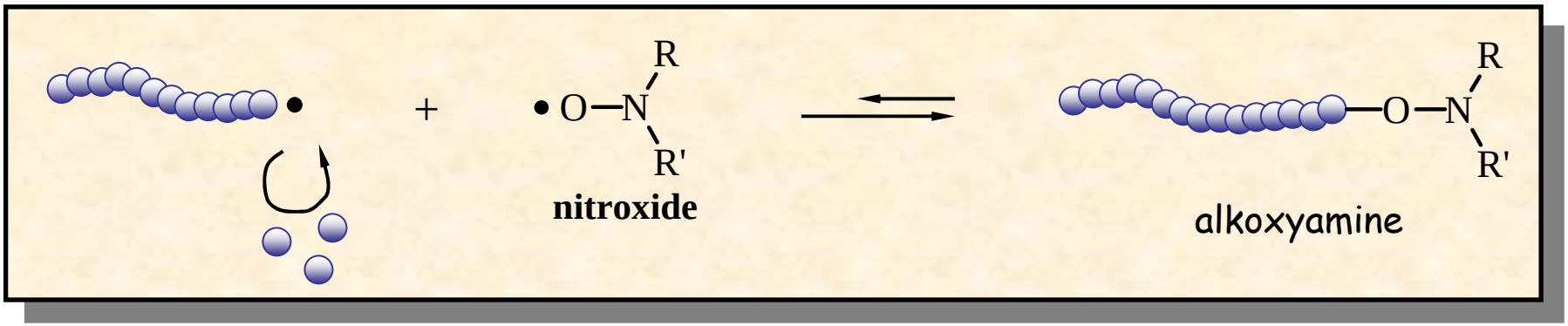
R = Ph, CN, CO_2Me,...

di- or triarylmethyl radicals

$Co(acac)_2$

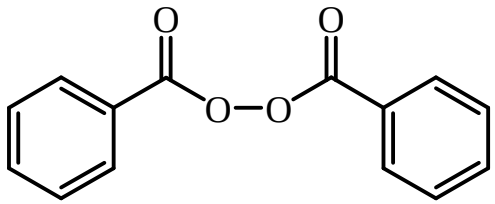
cobalt(II) acetylacetonate

The Nitroxide-Mediated Radical Polymerization (NMP)



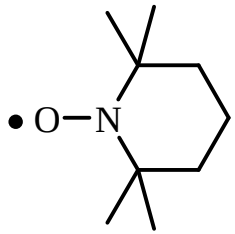
Two main approaches for NMP:

Bimolecular system:
free radical initiator + nitroxide



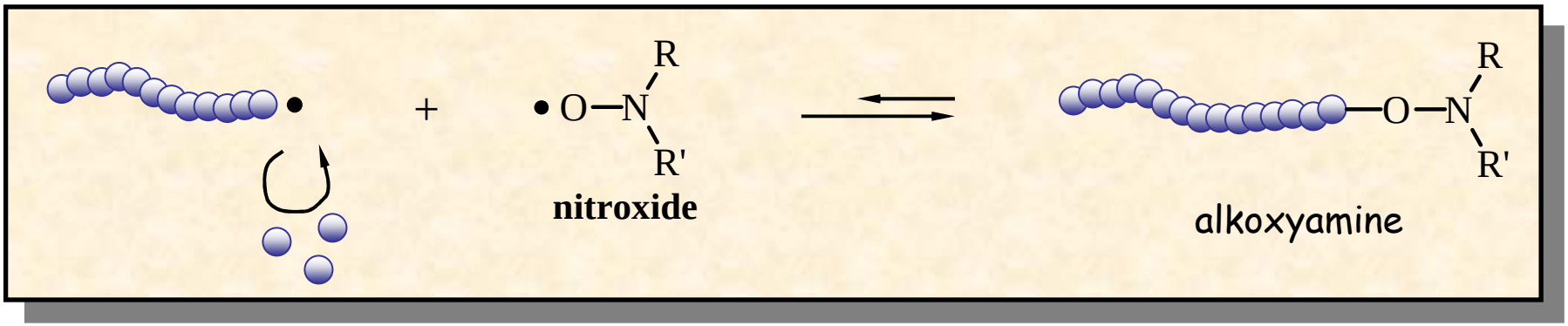
BPO

+



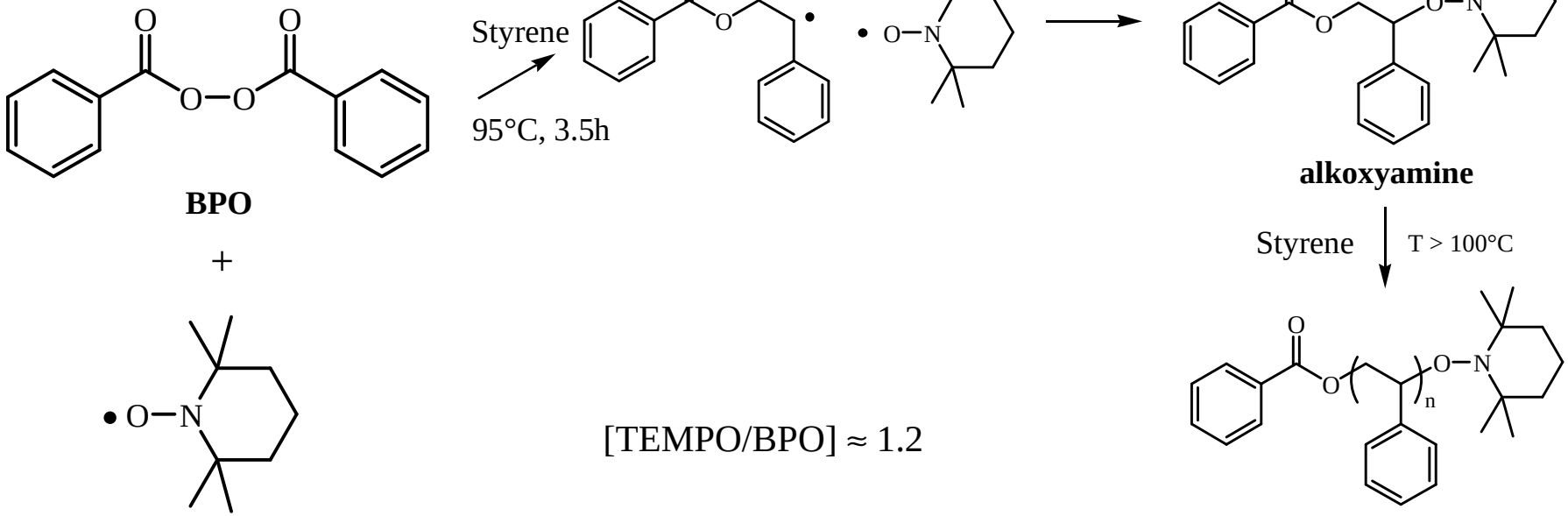
TEMPO

The Nitroxide-Mediated Radical Polymerization (NMP)



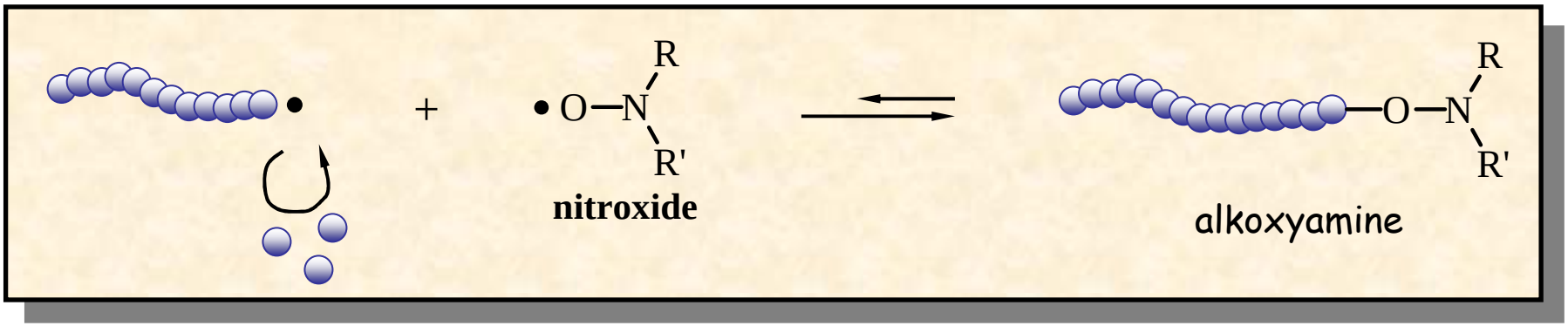
Two main approaches for NMP:

Bimolecular system:
free radical initiator + nitroxide



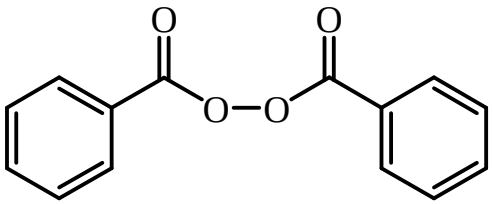
[TEMPO/BPO] ≈ 1.2

The Nitroxide-Mediated Radical Polymerization (NMP)



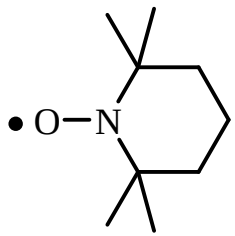
Two main approaches for NMP:

Bimolecular system:
free radical initiator + nitroxide



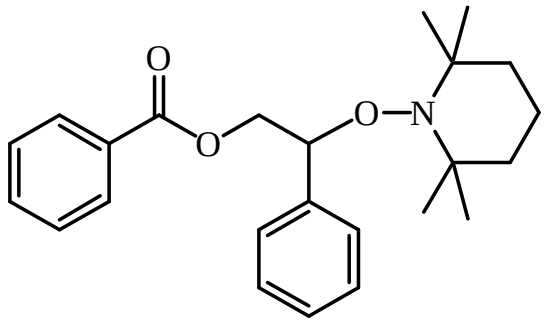
BPO

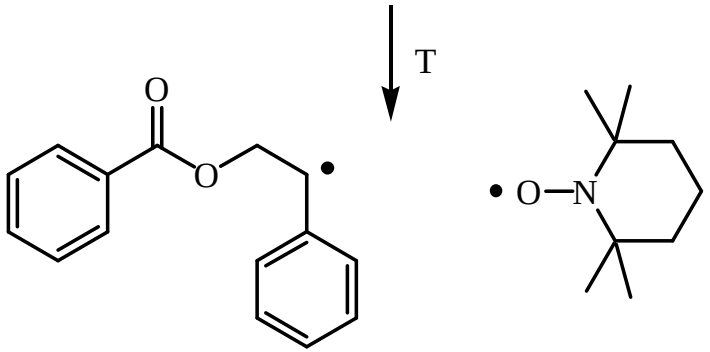
+



TEMPO

Unimolecular system: use of alkoxyamines

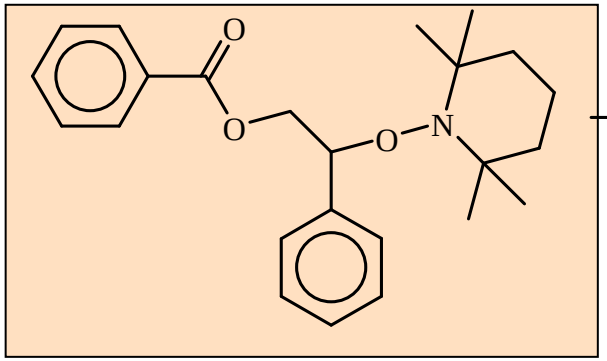




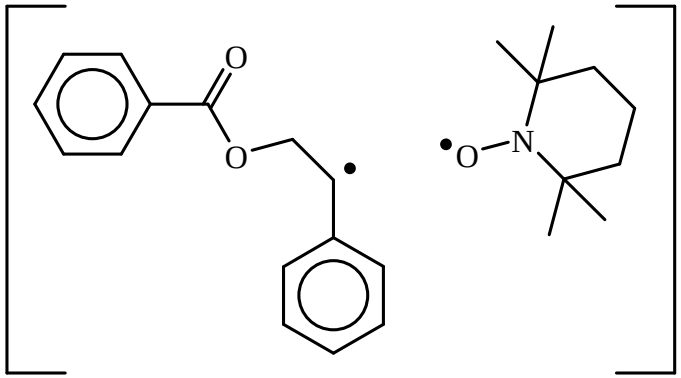
initiator

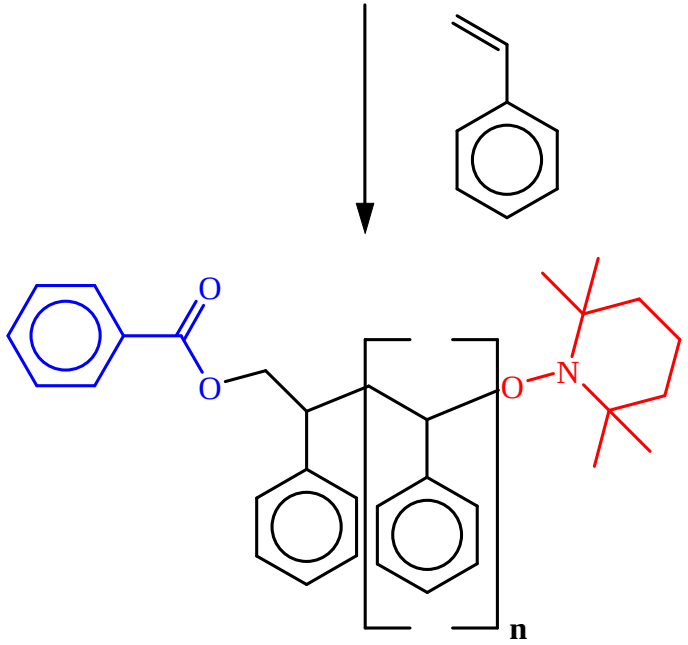
nitroxide

Unimolecular system



>100°C





Alkoxyamine

=

Initiator and control agent

Advantage of the unimolecular system:

⇒ improved initiator efficiency

⇒ control of the chain-ends structure

Molecular weight calculation:

$$M_{n,\,th.} = \frac{[M]_0}{[Alk]_0} \times MW_M \times conv$$

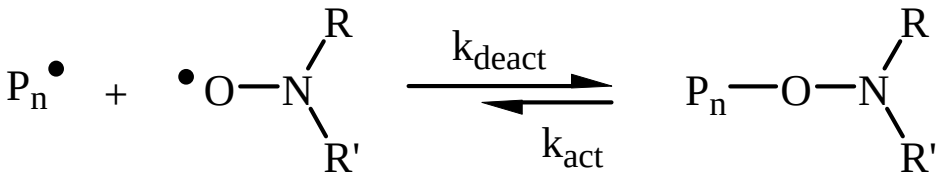
$$= (m_M/n_{Alk}) \times conv$$

where m_M is the weight (g) of monomer; and n_{Alk} is the moles number of alkoxyamine

Conditions: in the bulk at 123°C

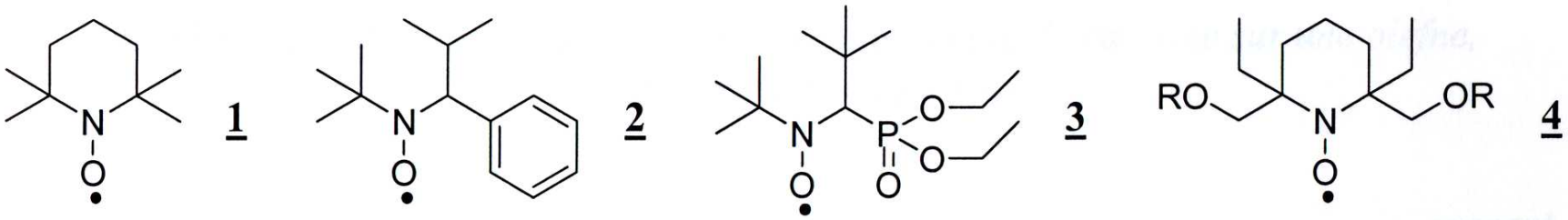
Hawker et al. J. Am. Chem. Soc. 1994, 116, 11185

Importance of the nitroxide structure

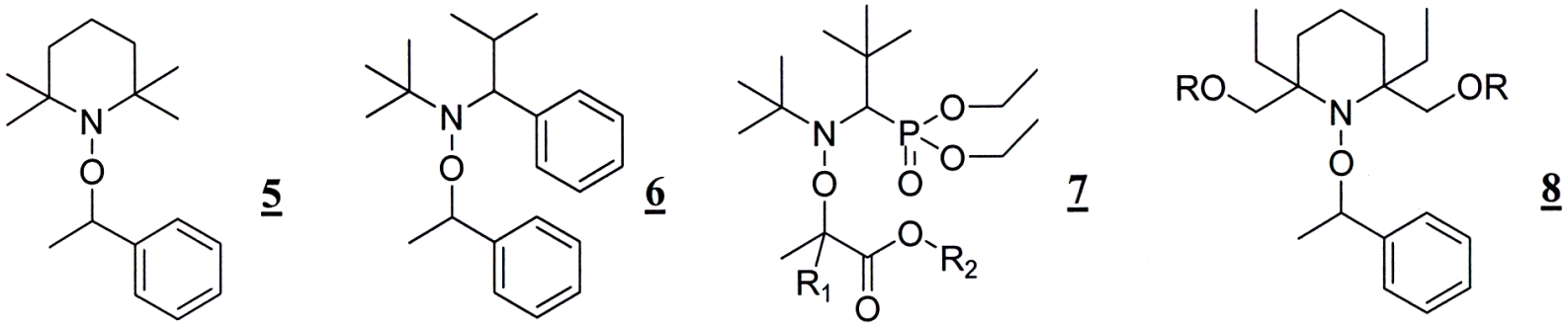


R and R' govern the stability and reactivity of the nitroxide, but also k_{deact} et k_{act}, and consequently, the equilibrium active/dormant species.

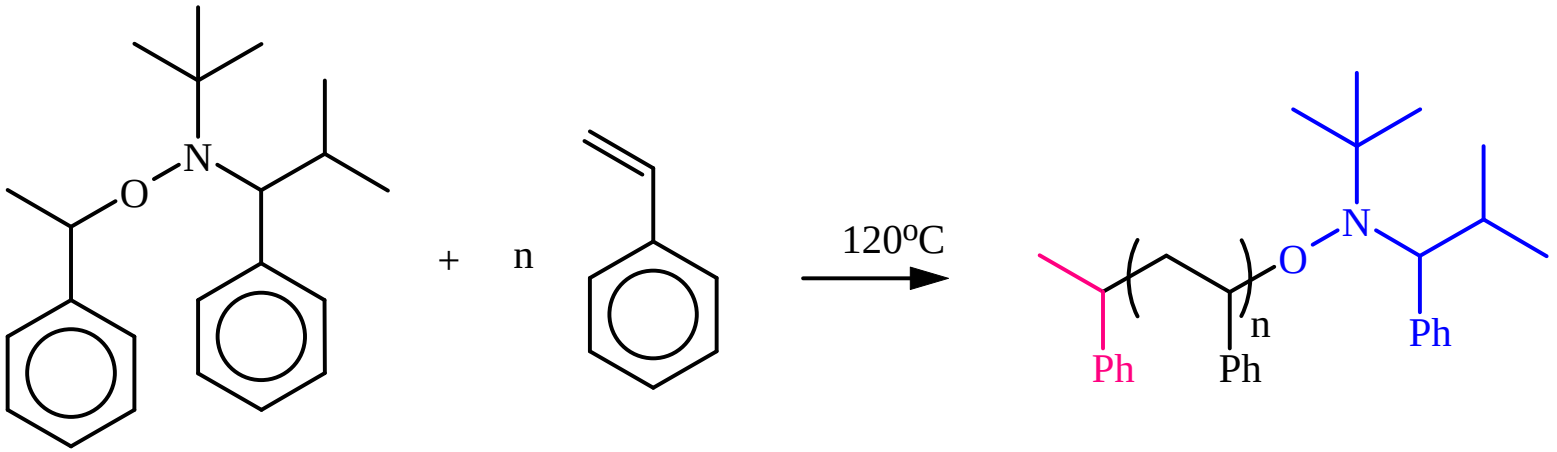
Some important nitroxides active in NMP:



Some alkoxyamines active in NMP:

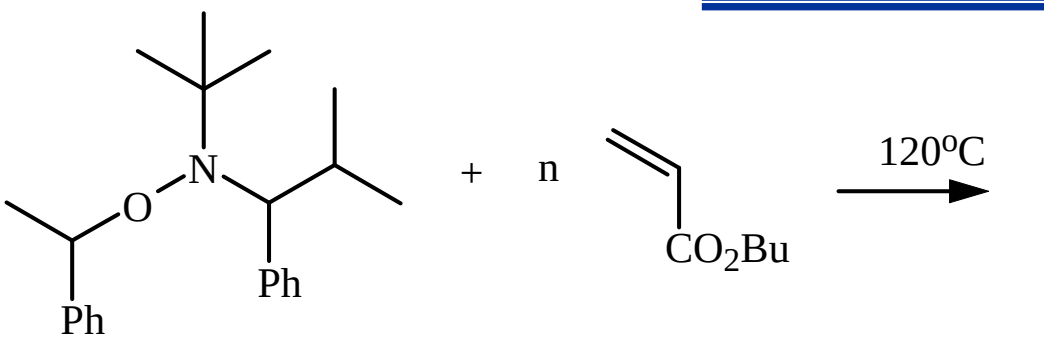


Styrene polymerization



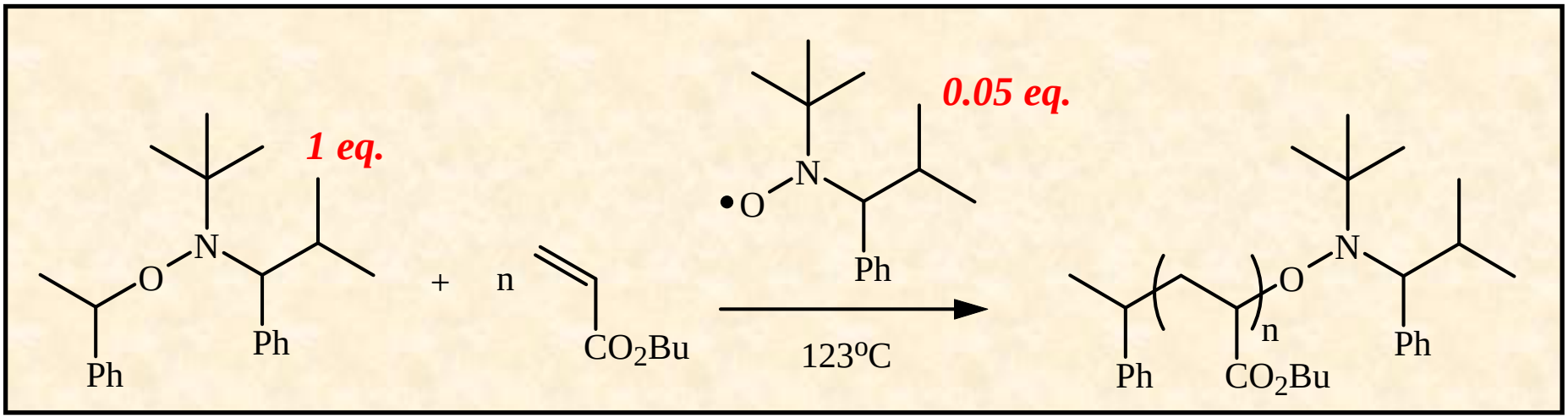
- Polymerization time: 4-18 h
- M_n controlled up to 200000 g/mol
- $M_{n,exp} \approx M_{n,th}$
- M_w/M_n : < 1.1 until Mn ~ 75000 g/mol and 1.2-1.25 until Mn ~ 200000 g/mol

Butyl acrylate polymerization



Poor control (fast polymerization and $M_w/M_n \approx 1.5\text{-}2.2$).

How to improve the control ?

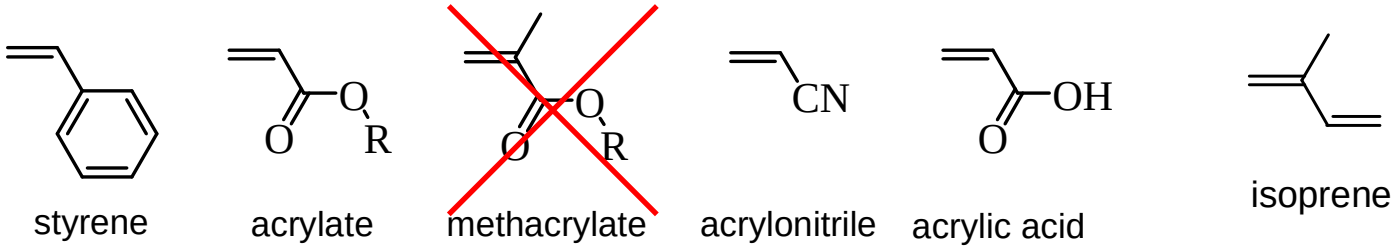


- Polymerization time : 16h at 123°C et 48h at 95-100°C.
- M_n until 150000 g/mol
- $M_{n,exp} \approx M_{n,th}$
- M_w/M_n : ≈ 1.05-1.30

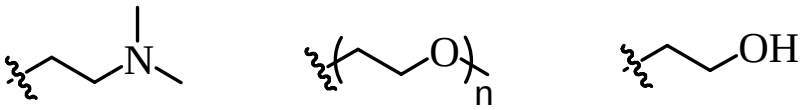
A slight excess of free nitroxide is needed !

Monomers

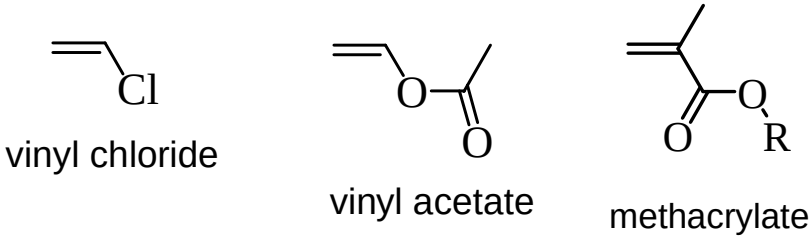
- styrenes, acrylates, acrylonitrile, (meth)acrylic acid, isoprene,…



where R =



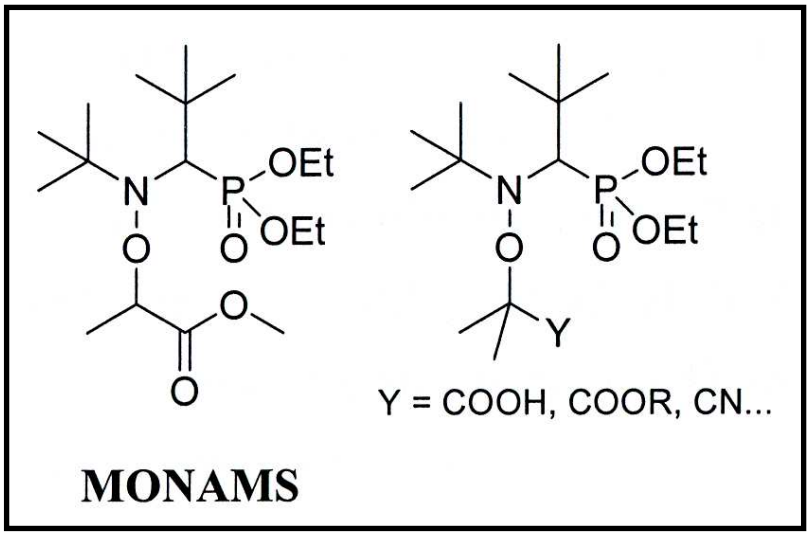
- NMP inefficient with vinyl chloride, vinyl acetate (and methacrylates)

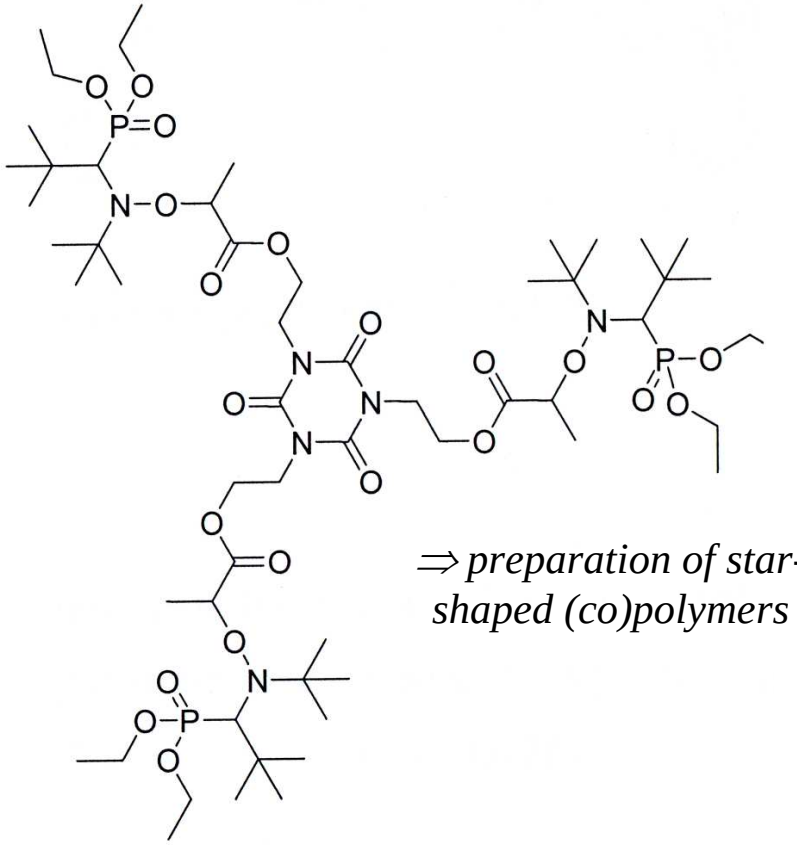


Solvents

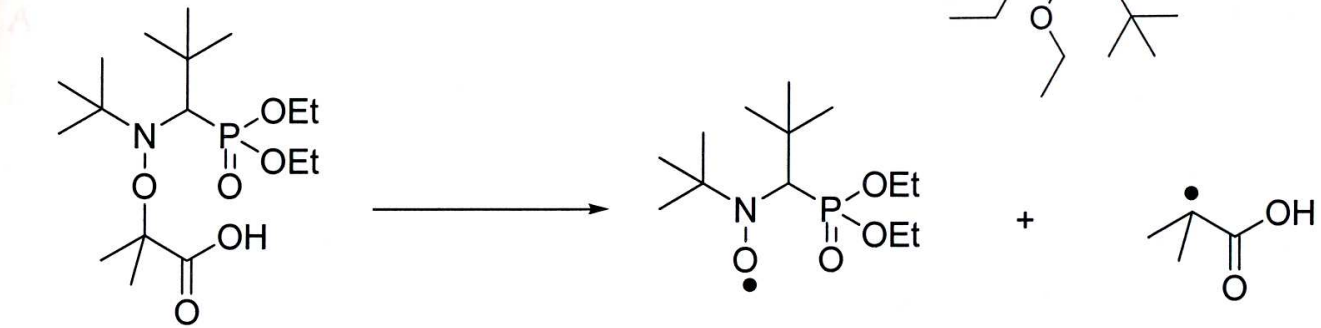
- Most often, the polymerizations are carried out in the bulk (T > 100°C)
- Non polar solvents (xylene, toluene,…) with a low transfer constant.
- Aqueous media (suspension, miniemulsion, emulsion)

SG1 based alkoxyamines





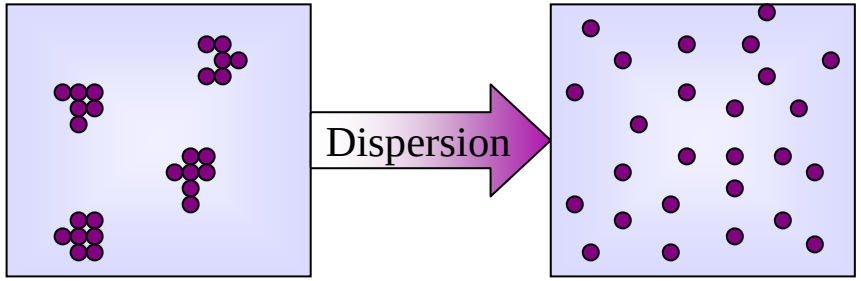
⇒ *preparation of star-shaped (co)polymers*



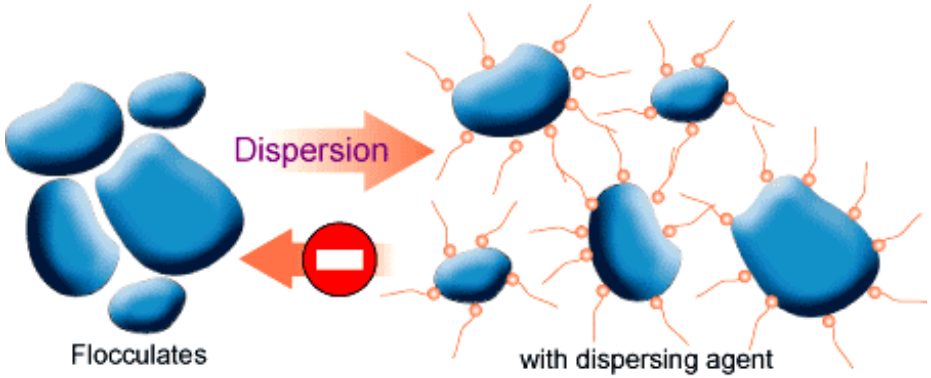
Alcoxyamine MAMA-SG1 — Nitroxyde SG1 — Radical 1-carboxy-1-méthyléthyle

Efficient for styrene and acrylate polymerizations without the use of excess nitroxides

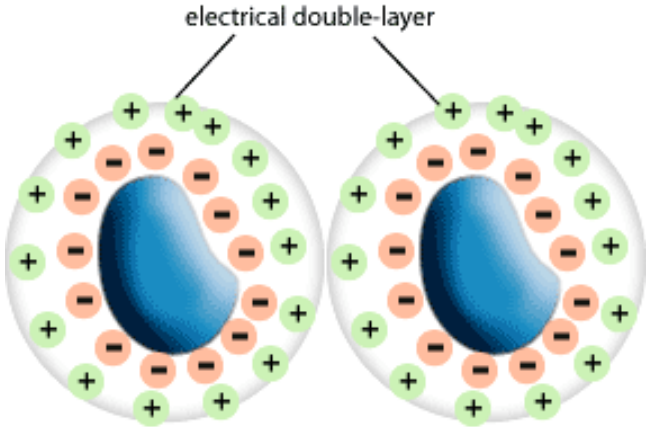
Application: pigments stabilization



Bad pigment dispersion Good pigment dispersion

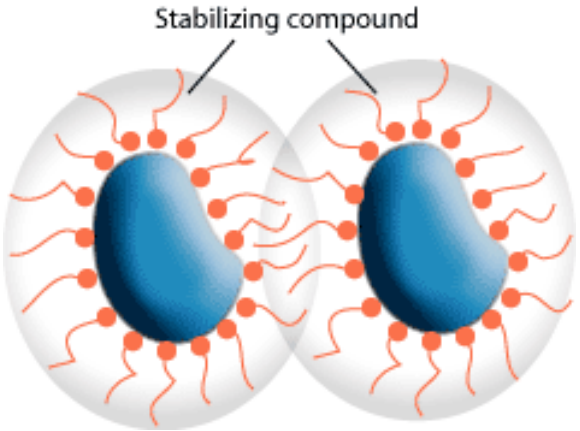


Electrostatic stabilisation



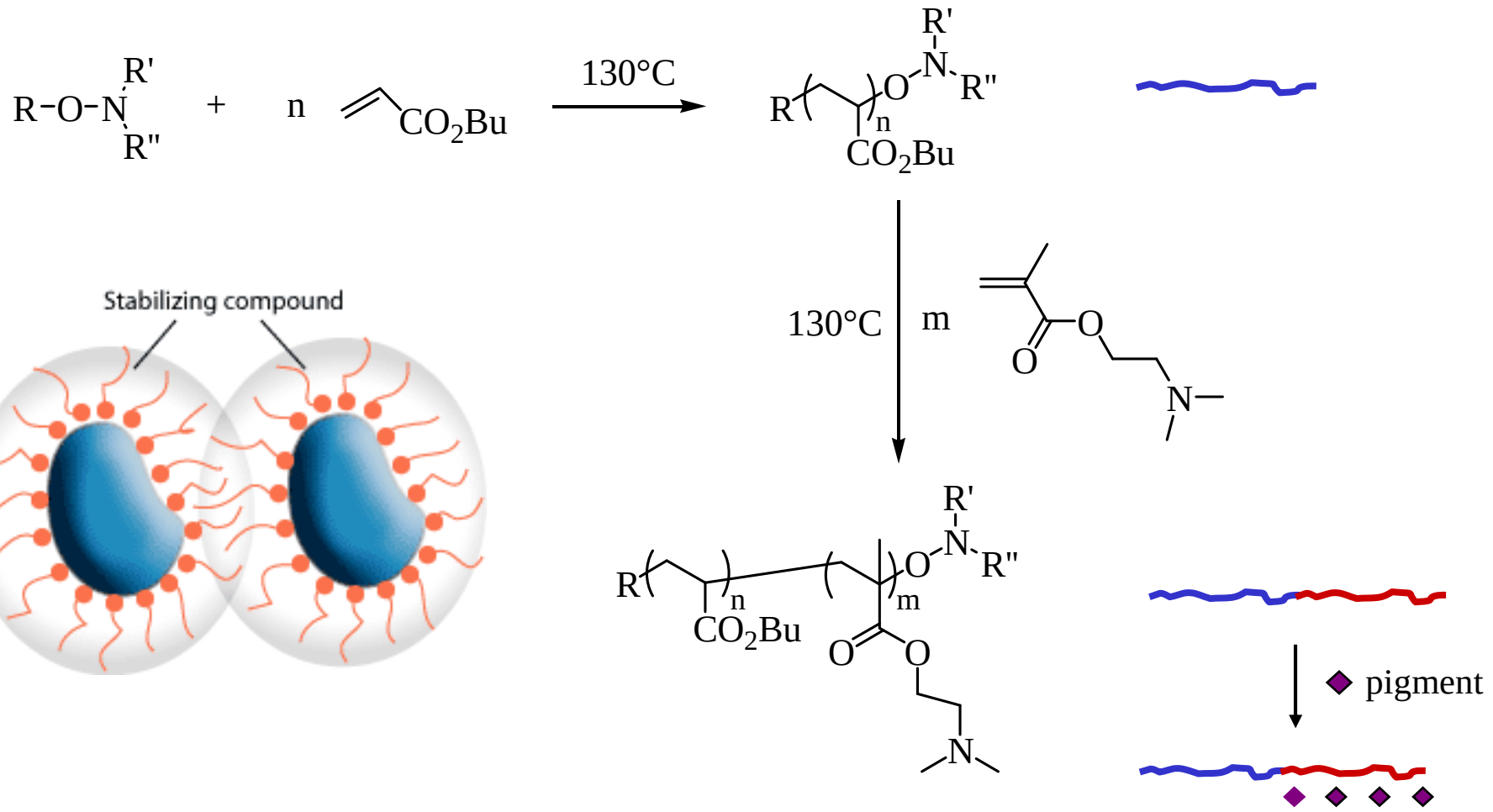
Use of polyelectrolytes
(polyphosphates, poly(carboxylic acids),…)

Steric stabilisation



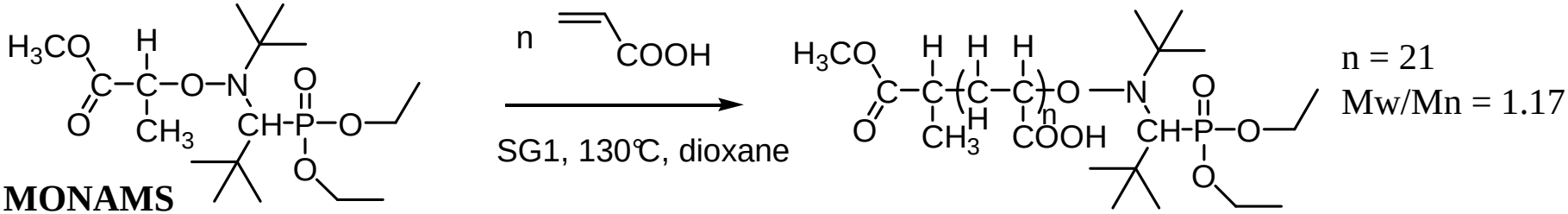
Utilisation de (co)polymères

Application: pigments stabilization



Emulsion polymerization without any surfactant

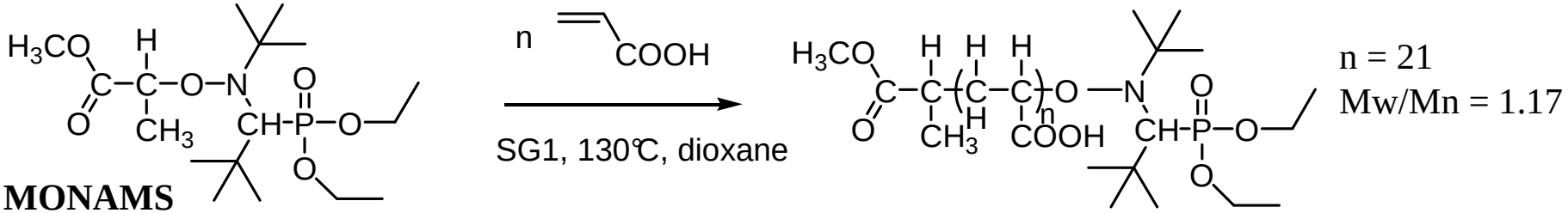
1- Preparation of PAA



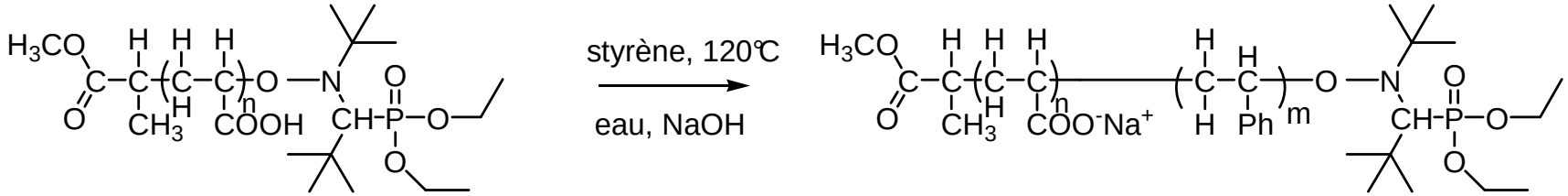
ChemComm 2005, 5, 614

Emulsion polymerization without any surfactant

1- Preparation of PAA



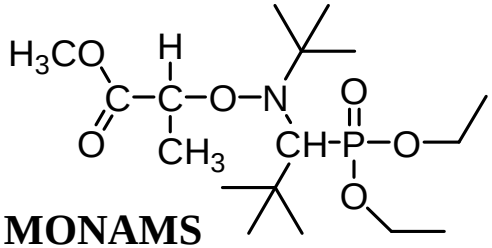
2- Preparation of PAA-b-PS
(and PAA-b-PnBuA) in emulsion



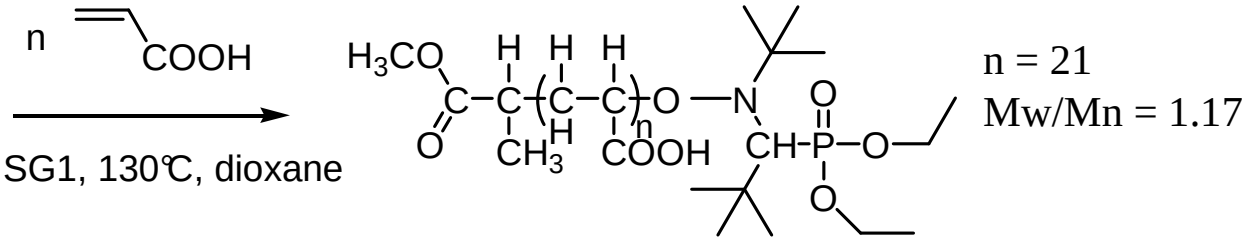
ChemComm 2005, 5, 614

Emulsion polymerization without any surfactant

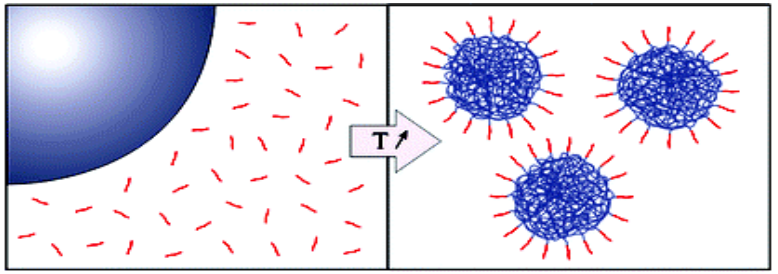
1- Preparation of PAA

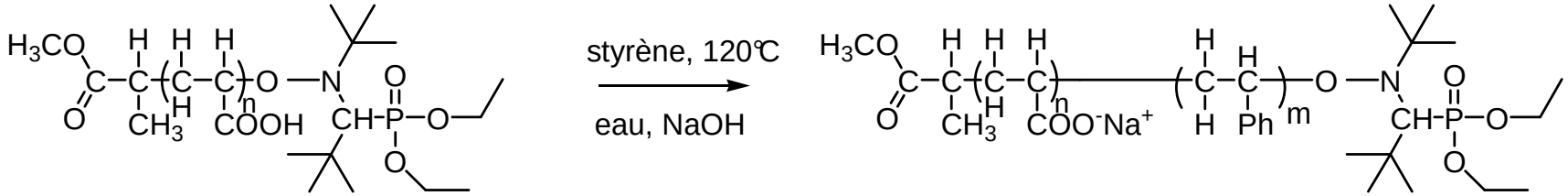


MONAMS



2- Preparation of PAA-b-PS (and PAA-b-PnBuA) in emulsion

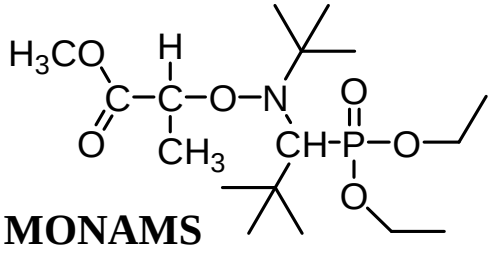




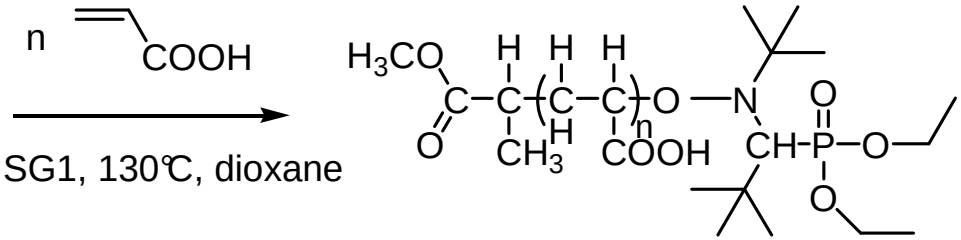
ChemComm 2005, 5, 614

Emulsion polymerization without any surfactant

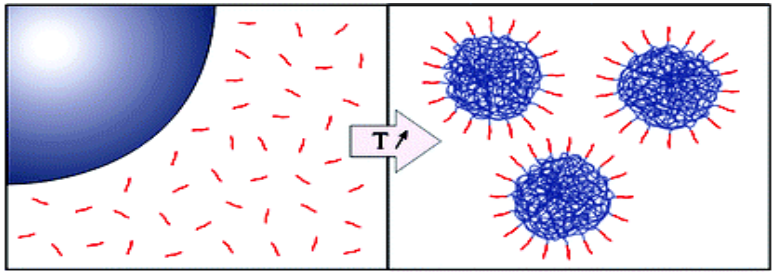
1- Preparation of PAA

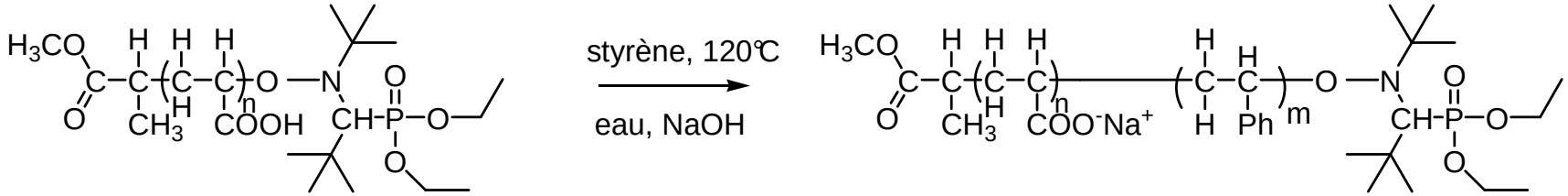


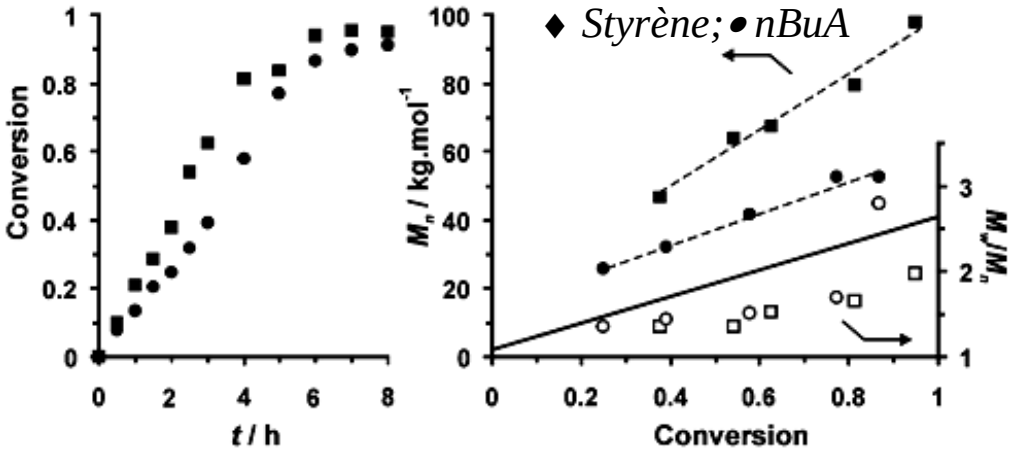
MONAMS

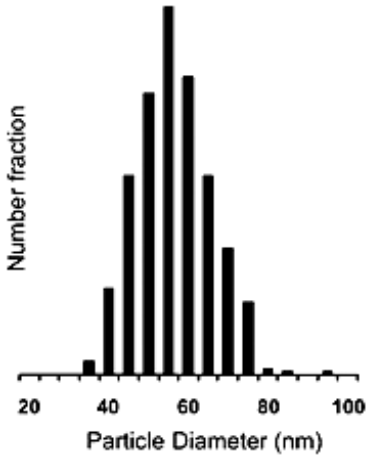


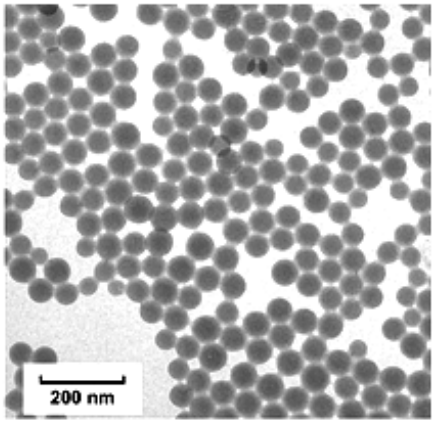
2- Preparation of PAA-b-PS
(and PAA-b-PnBuA) in emulsion





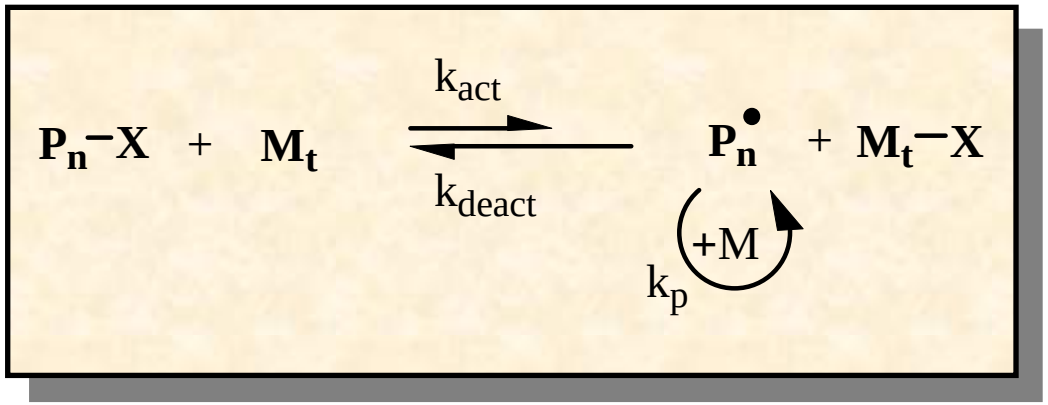






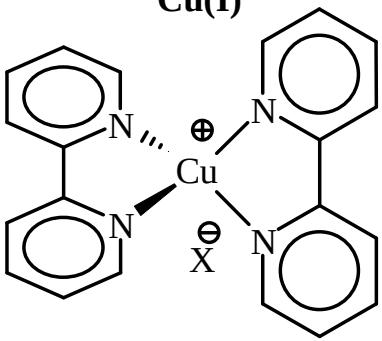
ChemComm 2005, 5, 614

2nd CRP mechanism: Atom Transfer Radical Polymerization



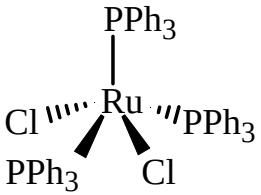
Mt:

Cu(I)

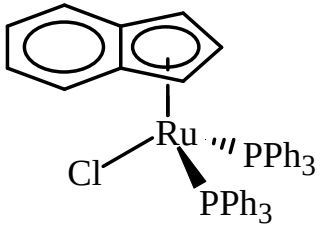


(X = Cl, Br)

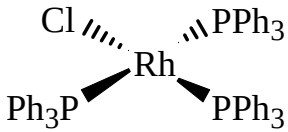
Ru(II)



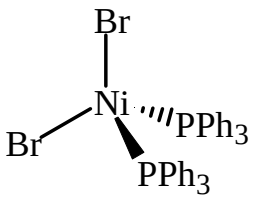
Ru(II)



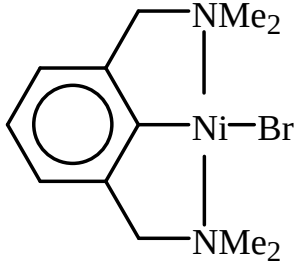
Rh(I)



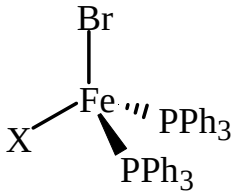
Ni(II)



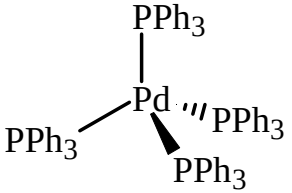
Ni(II)



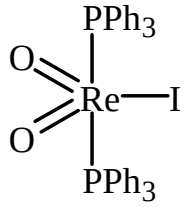
Fe(II)



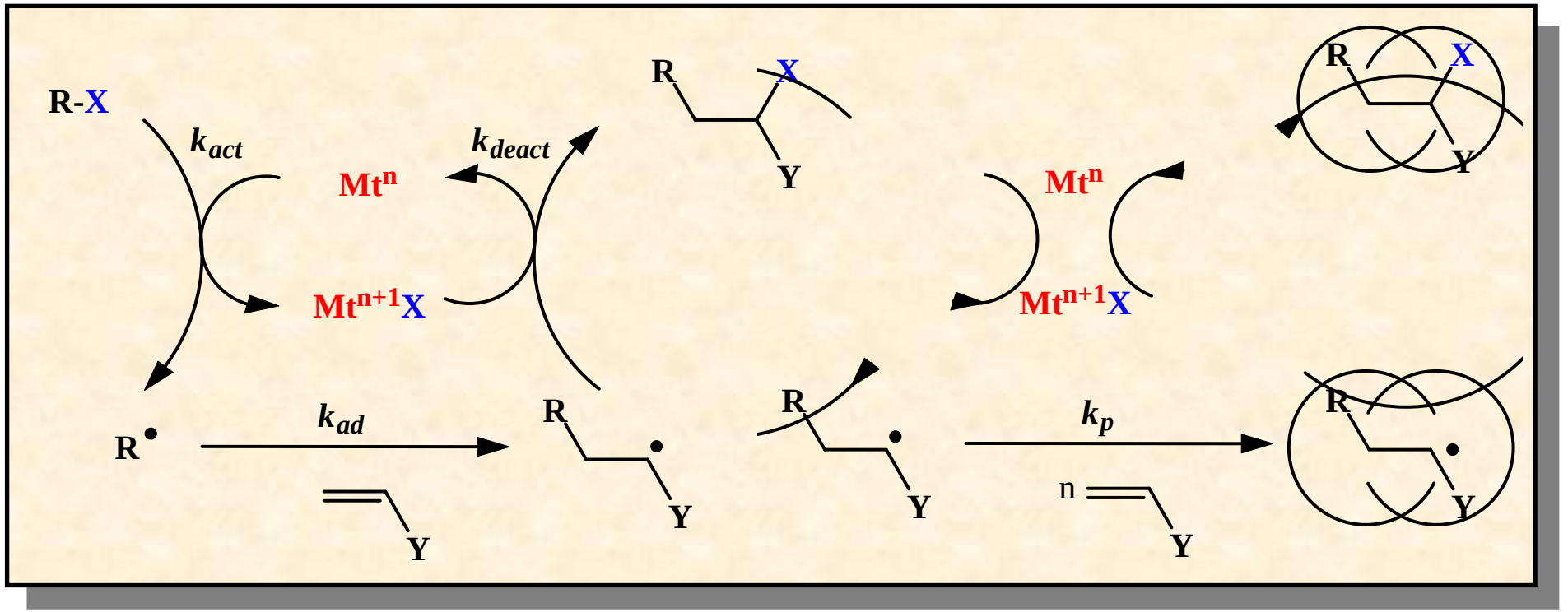
Pd(0)



Re(V)



Atom Transfer Radical Polymerization (ATRP)



Overall reaction: R-X + n CH_2=CHY $\xrightarrow{Mt^n}$ R-(CH_2-CHY)$_n$-X

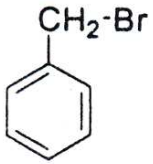
How to carry out an ATRP experiment ?

R-X + Mt + ligand + monomer → ATRP

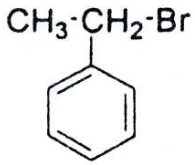
[RX]/[Mt-L] = 1/1

ATRP initiators

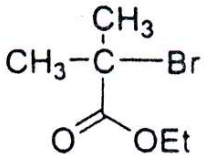
ATRP initiators = activated halogenoalcanes: α-haloketones, α-haloesters, α-nitriles, sulfonyl chlorides,…



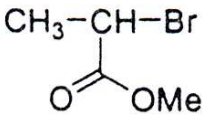
BzBr



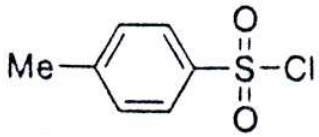
PEBr

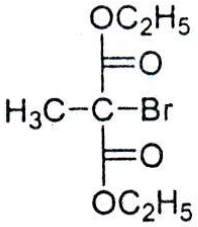


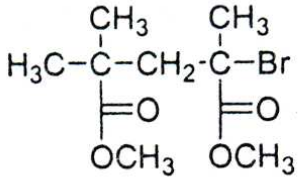
EBriB



MBP

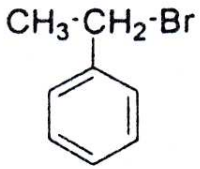




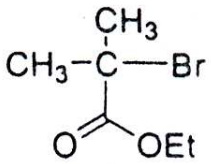


Generally, use of initiators which mimic the structure of the dormant chains:

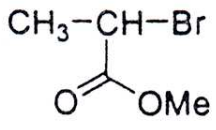
BzBr



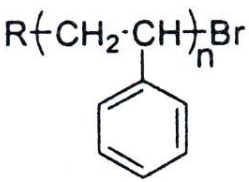
PEBr



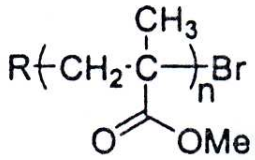
EBriB



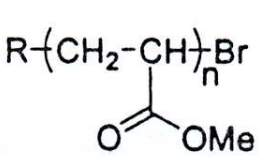
MBP



pSt-Br



pMMA-Br



pMA-Br

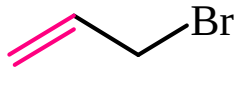
Molecular weight calculation:

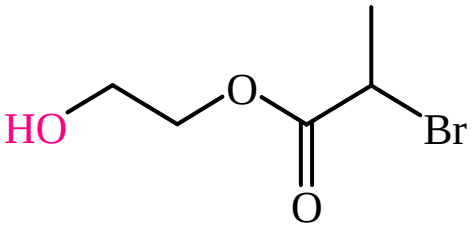
$$M_{n,\,th.} = \frac{[M]_0}{[RX]_0} \times MW_M \times conv$$

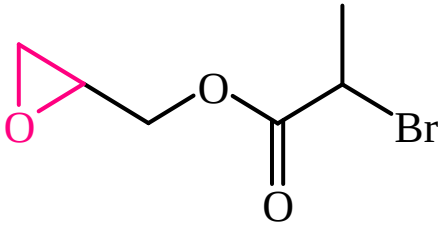
$$= (m_M/n_{RX}) \times conv$$

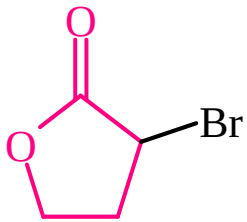
where m_M is the weight (g) of monomer; and n_{RX} is the moles number of initiator

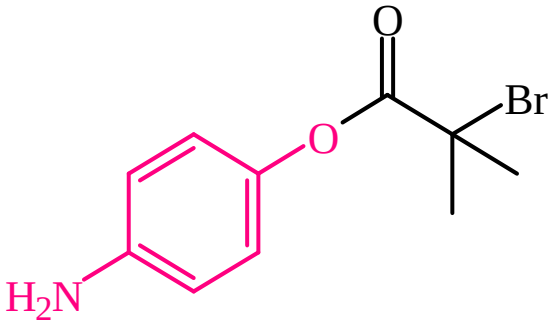
Some ATRP functional initiators

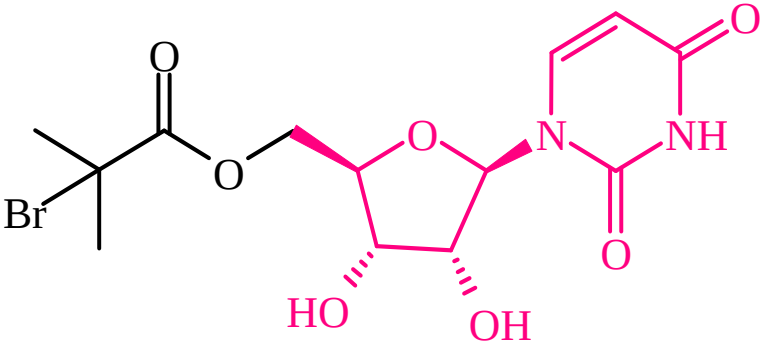


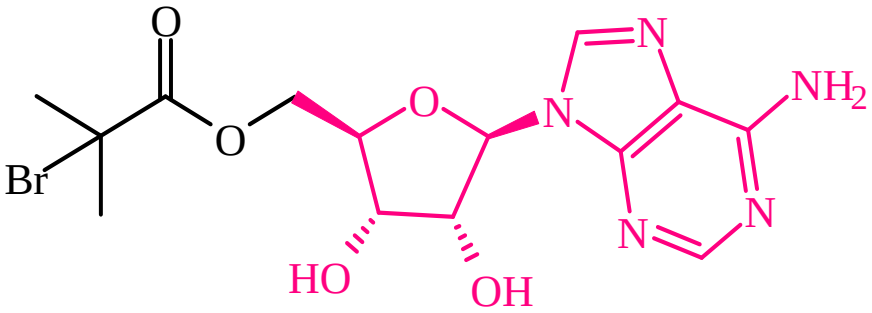




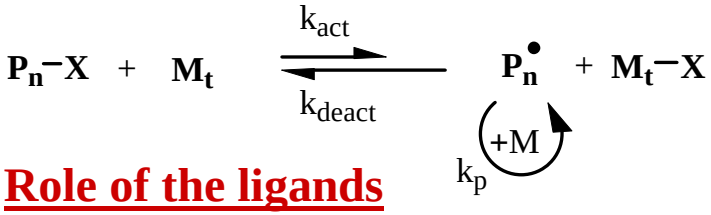








Ligands for ATRP



Role of the ligands

1- Metal solubilisation in organic media

2- Adjusting the position and dynamics of the active/dormant species equilibrium

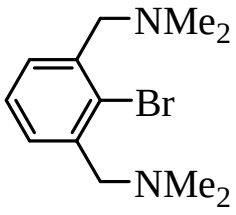
Types of ligands

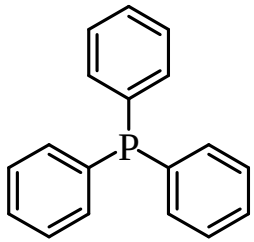
Cu: bipyridines, iminopyridines, polyamines

Ru: triarylphosphines, carbènes

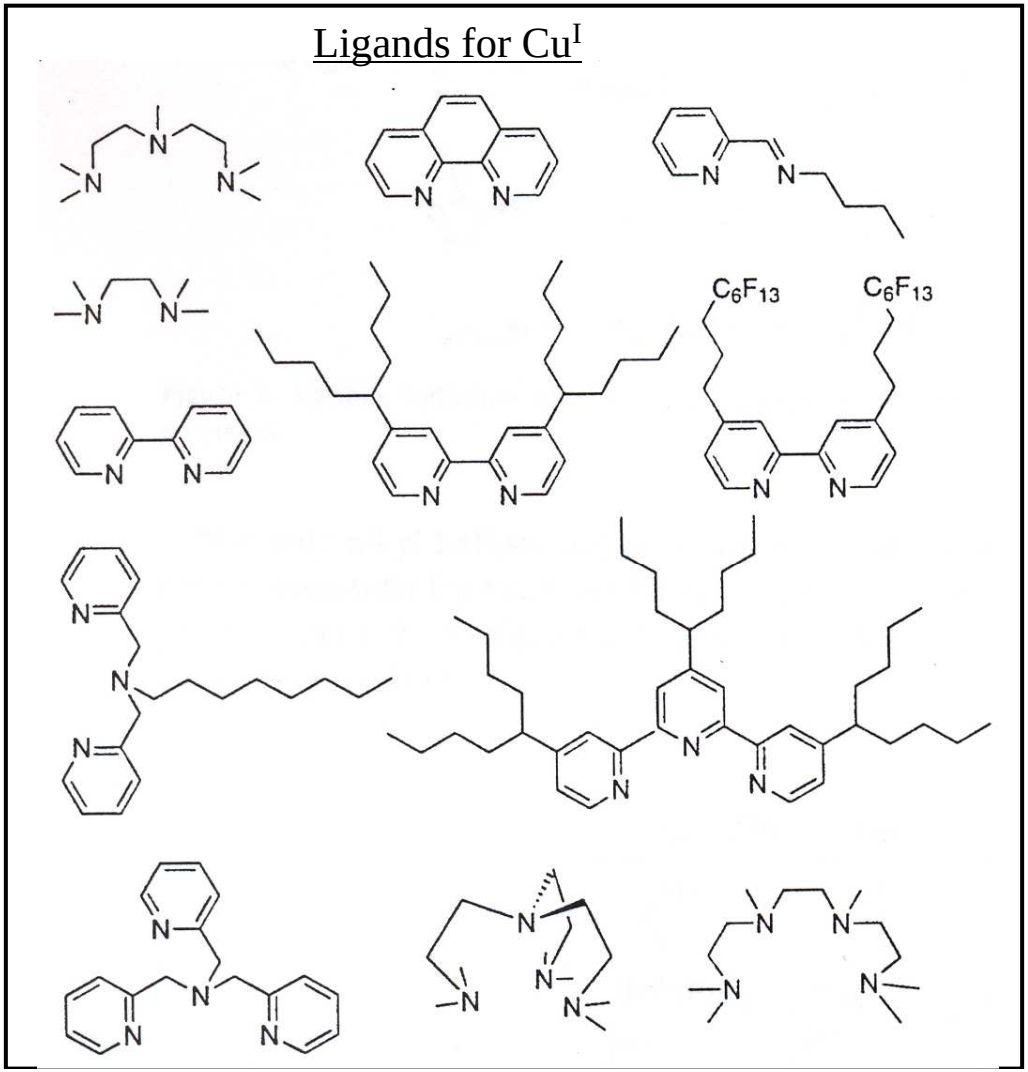
Ni: triarylphosphine, Granel

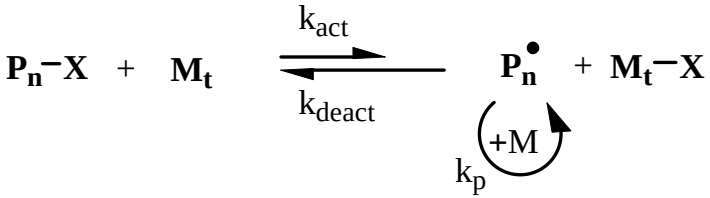
Fe: trialkylphosphine, trialkylamine





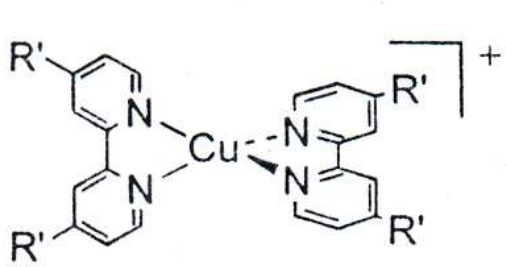
Ligands for Cu^I



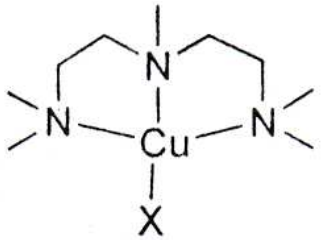


Ligands for ATRP

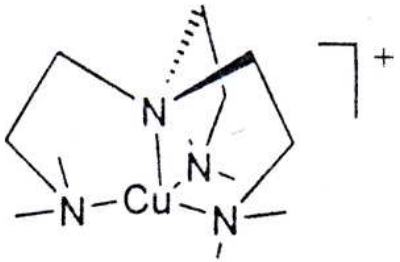
Some important Cu^{I} (CuBr et CuCl) complexes



1/2



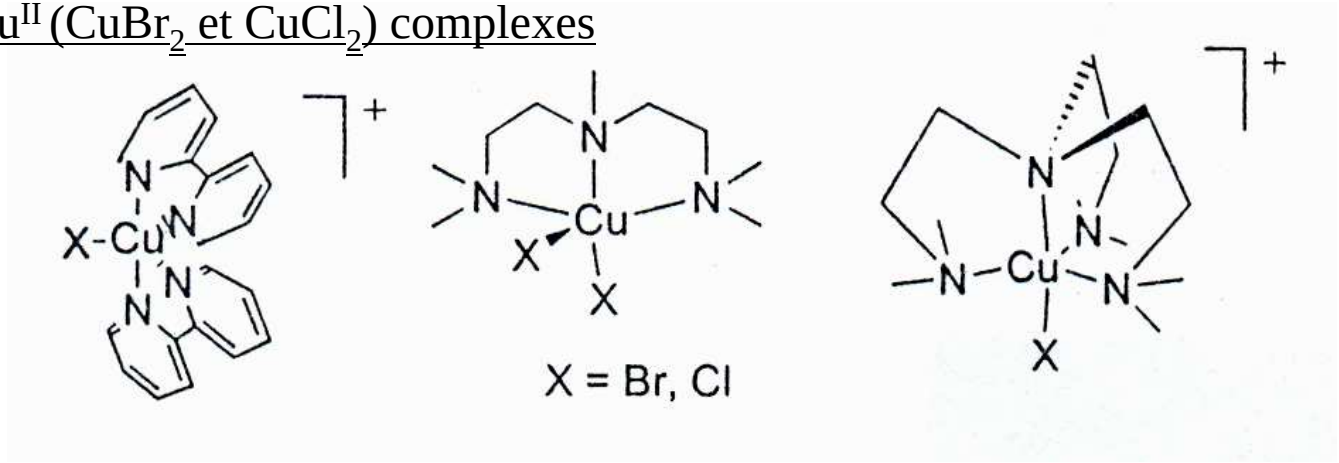
1/1



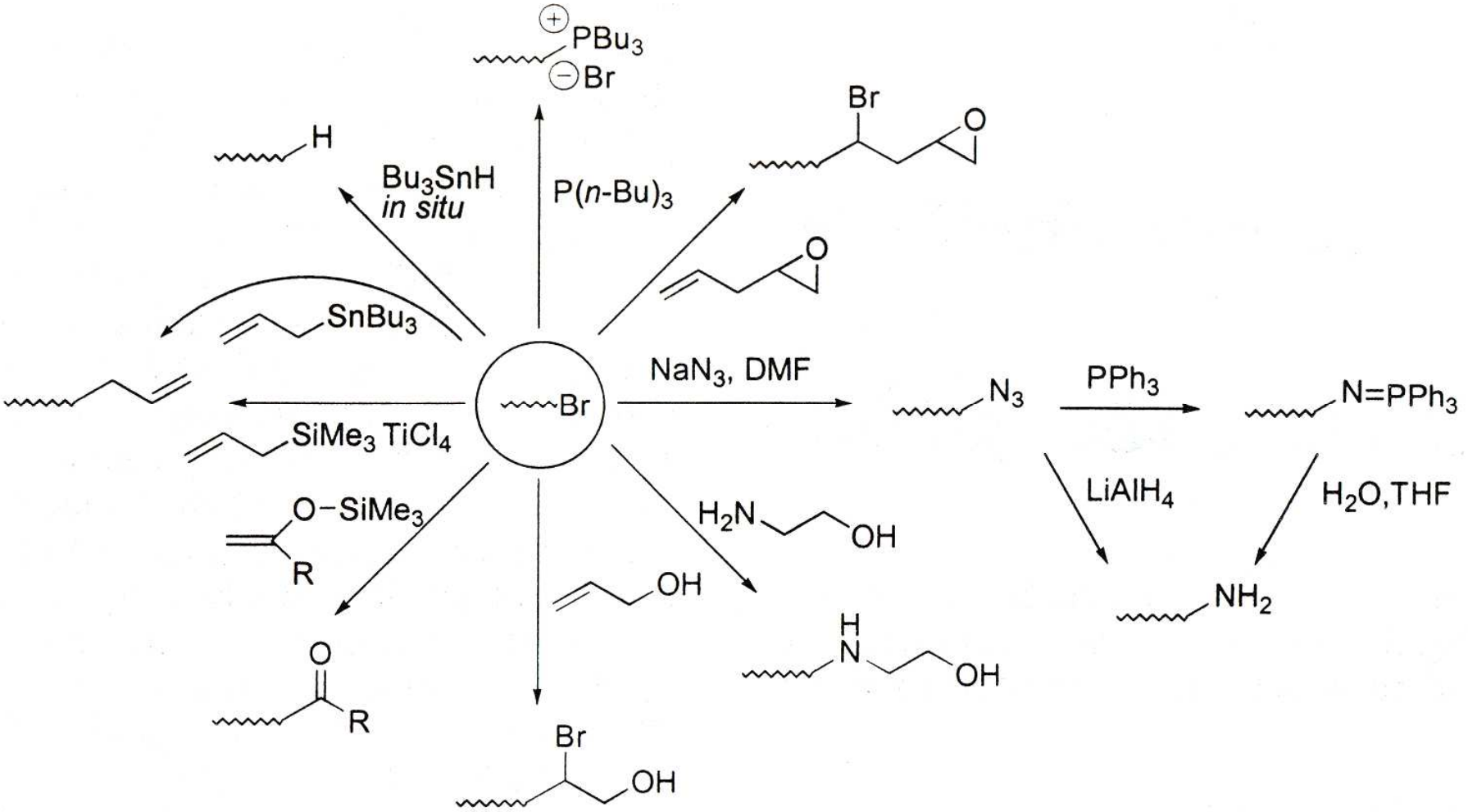
1/1

Cu(I)/Ligand molar ratios:

…and Cu^{II} ($CuBr_2$ et $CuCl_2$) complexes



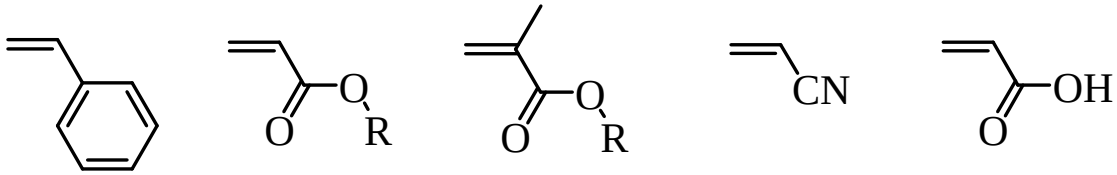
ω-chain end functionalization



Chem. Rev. 2001, 101, 2921

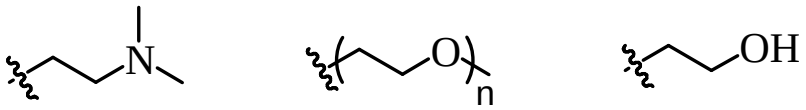
Monomers

- styrenes, acrylates, methacrylates, acrylonitrile, (meth)acrylic acid,…

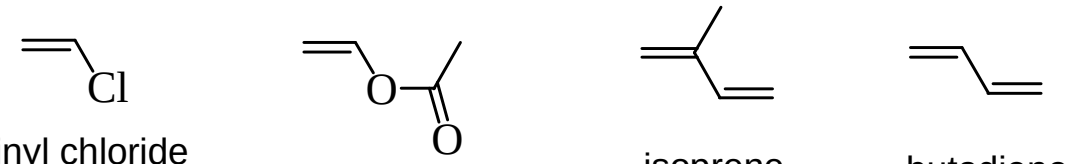


styrene acrylate methacrylate acrylonitrile acrylic acid

where R =



- ATRP inefficient with vinyl chloride, vinyl acetate and dienes because the radical is too reactive and poorly stabilized ⇒ C-X bond at the ω-chain-end is too stable.

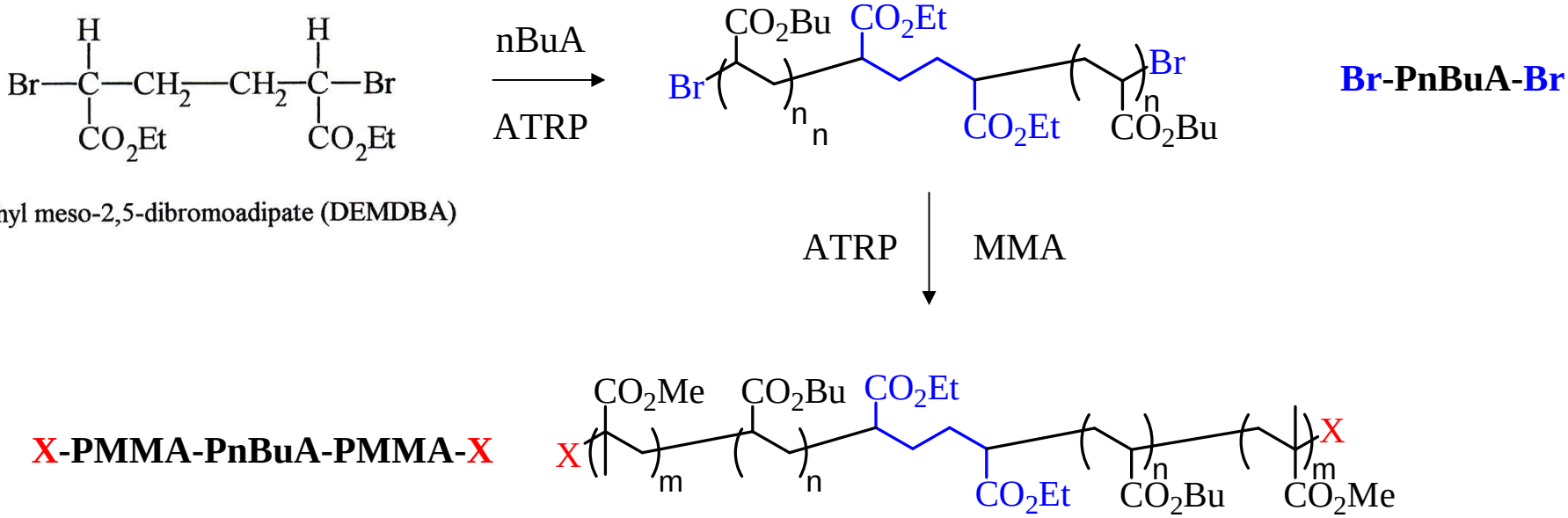


vinyl chloride vinyl acetate isoprene butadiene

Solvents

- Most often, the polymerizations are carried out in the bulk
- Non polar solvents (xylene, toluene,…) with a low transfer constant.
- Aqueous media (suspension, miniemulsion, emulsion)
- Alcohols

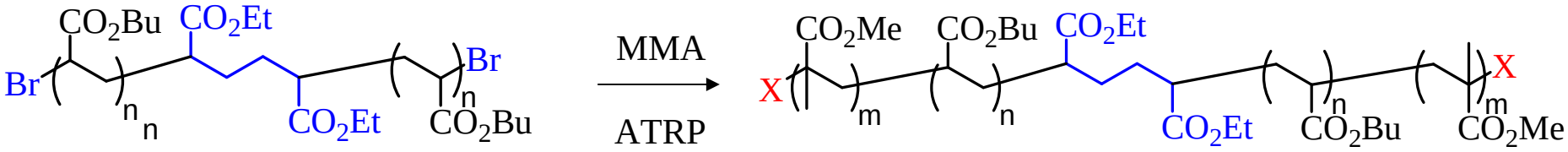
Halogen exchange in ATRP



Diethyl meso-2,5-dibromoadipate (DEMDBA)

For preparing such copolymer, the halogen exchange is required.
Optimal conditions for the MMA polymerization: CuCl + $CuCl_2$ (10mol%)

Halogen exchange in ATRP



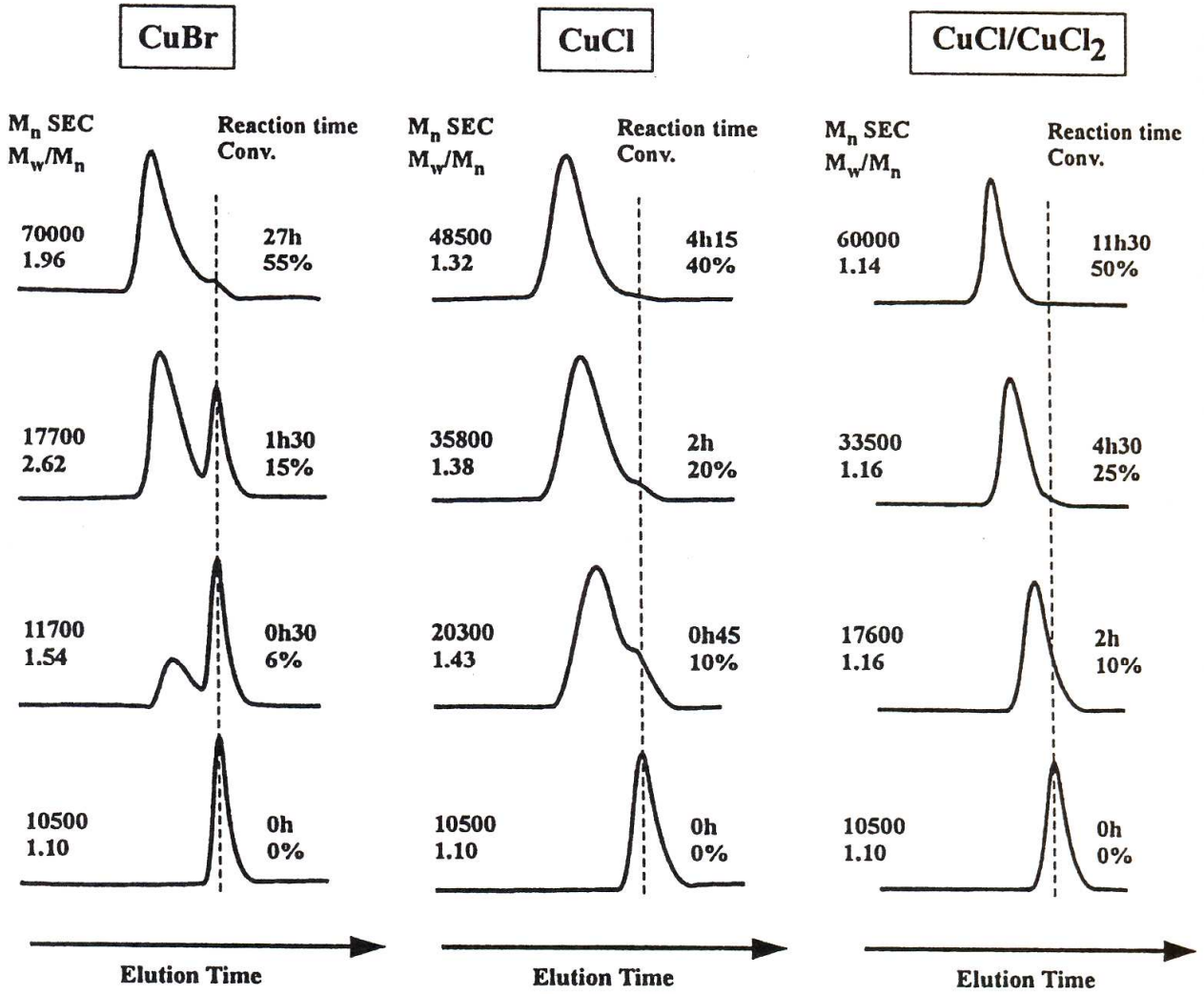
Conditions:

toluene, 85°C,

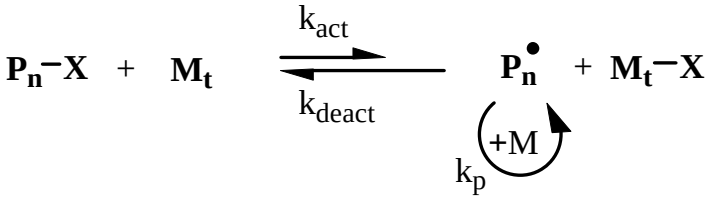
[MMA] = 4.67M,

[Br-PnBuA-Br] = 4mM,

[catalyseur] = 4mM

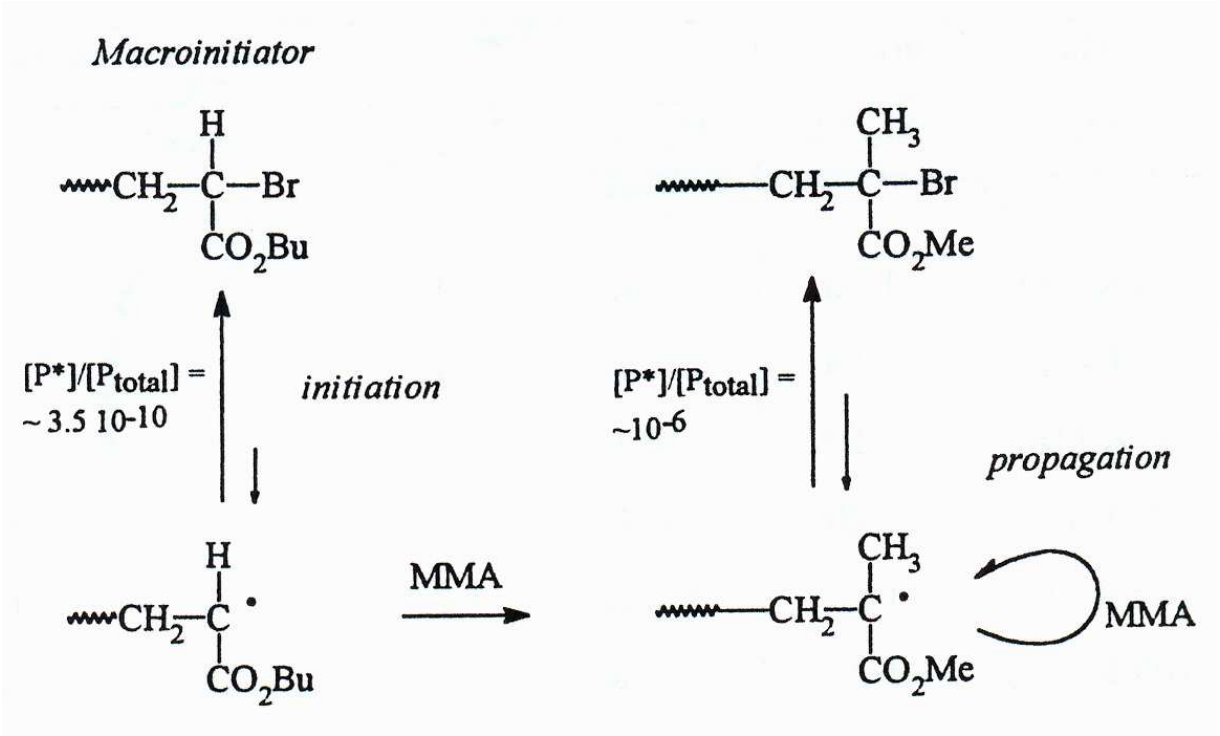


Halogen exchange in ATRP

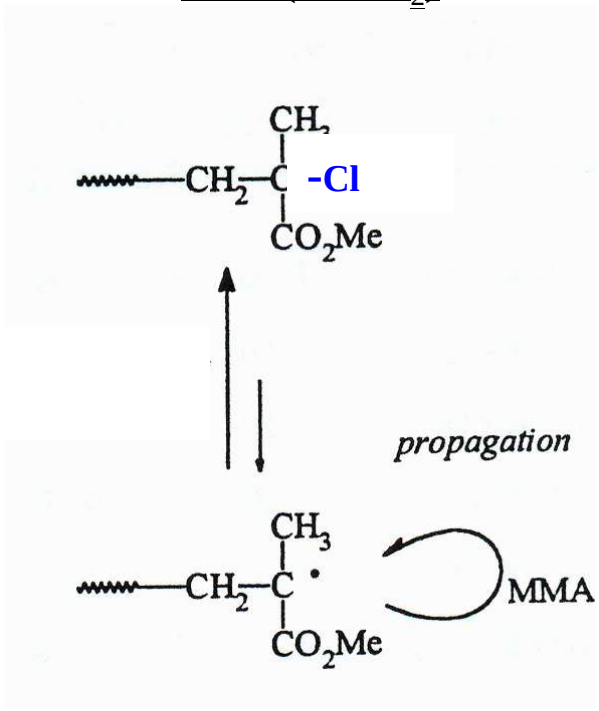


Why is this halogen exchange useful ?

CuBr



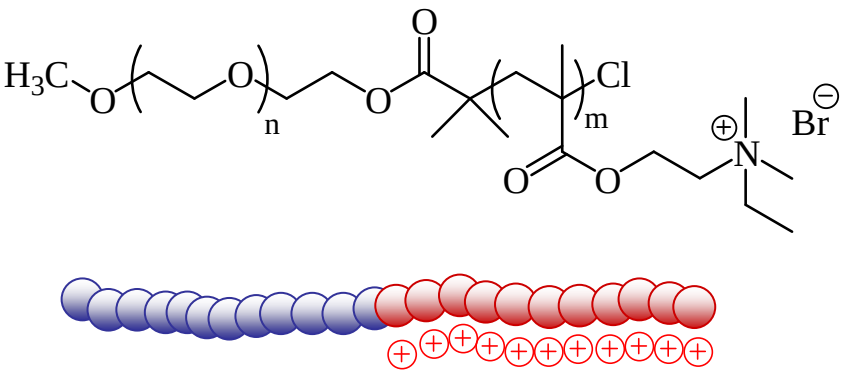
CuCl (+$CuCl_2$)

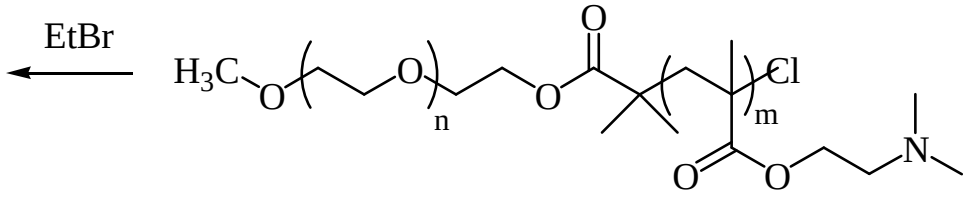


Without halogen exchange, MMA propagation is fast compared to initiation. Unreacted macroinitiator will thus be left at the end of the MMA polymerization.

With halogen exchange (Cl in place of Br), MMA propagation is decreased because C-Cl bond at the ω-chain end of PMMA is more stable than the C-Br bond. Initiation would thus be favoured compared to propagation.

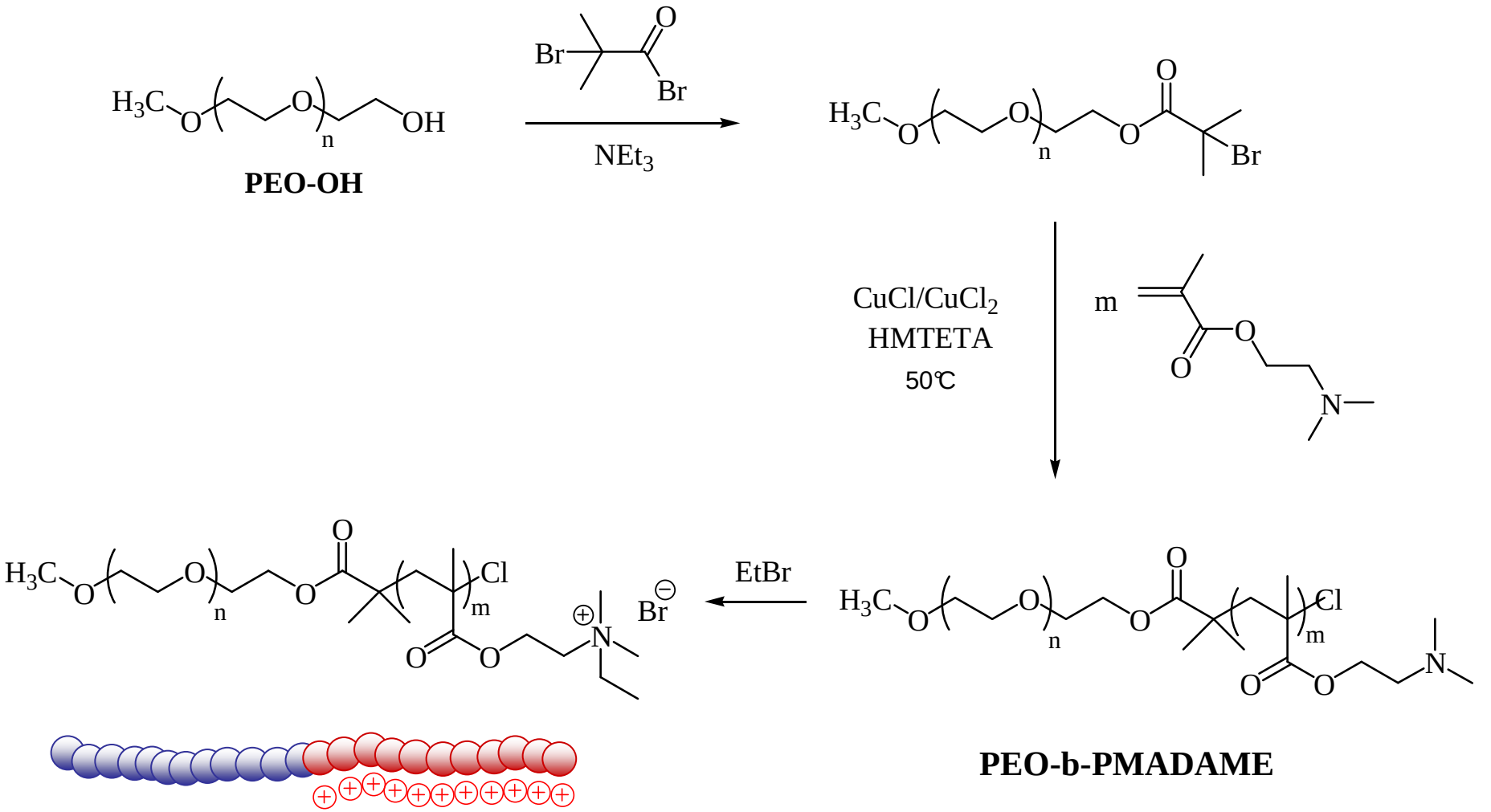
Preparation of hydrosoluble block copolymers





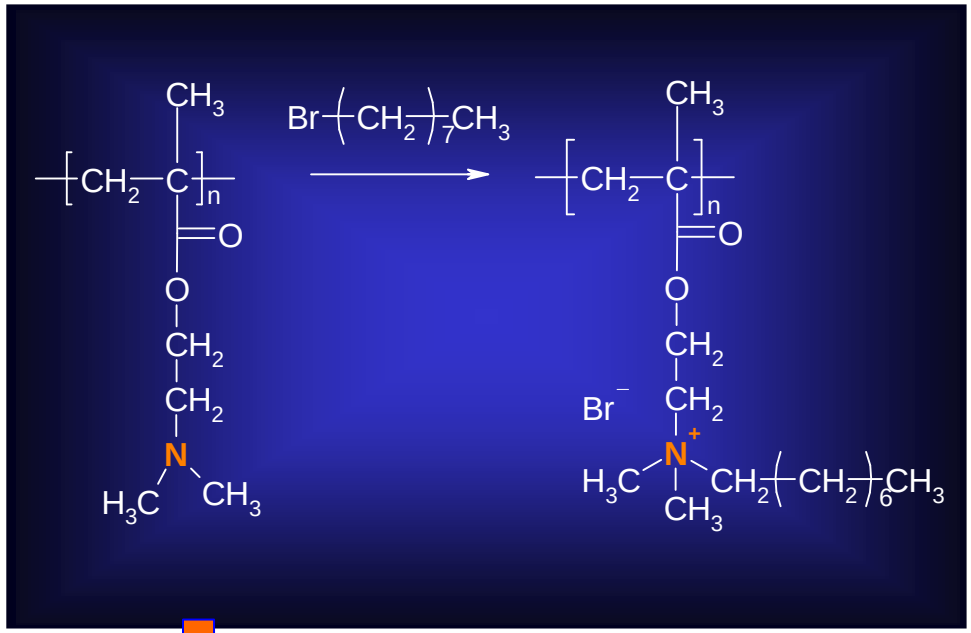
PEO-b-PMADAME

Preparation of hydrosoluble block copolymers

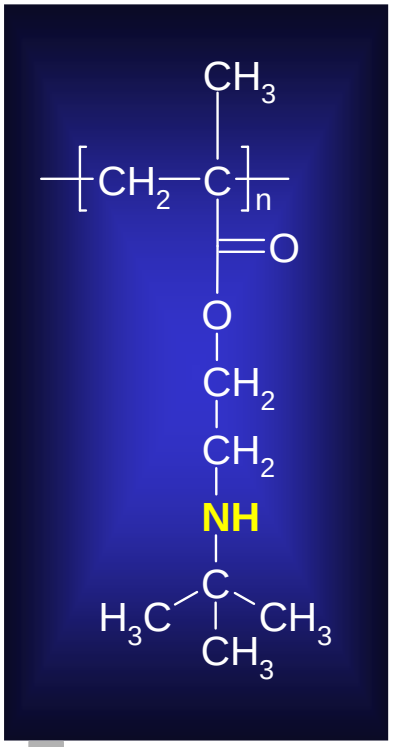


Antibacterial copolymers

Some exemples

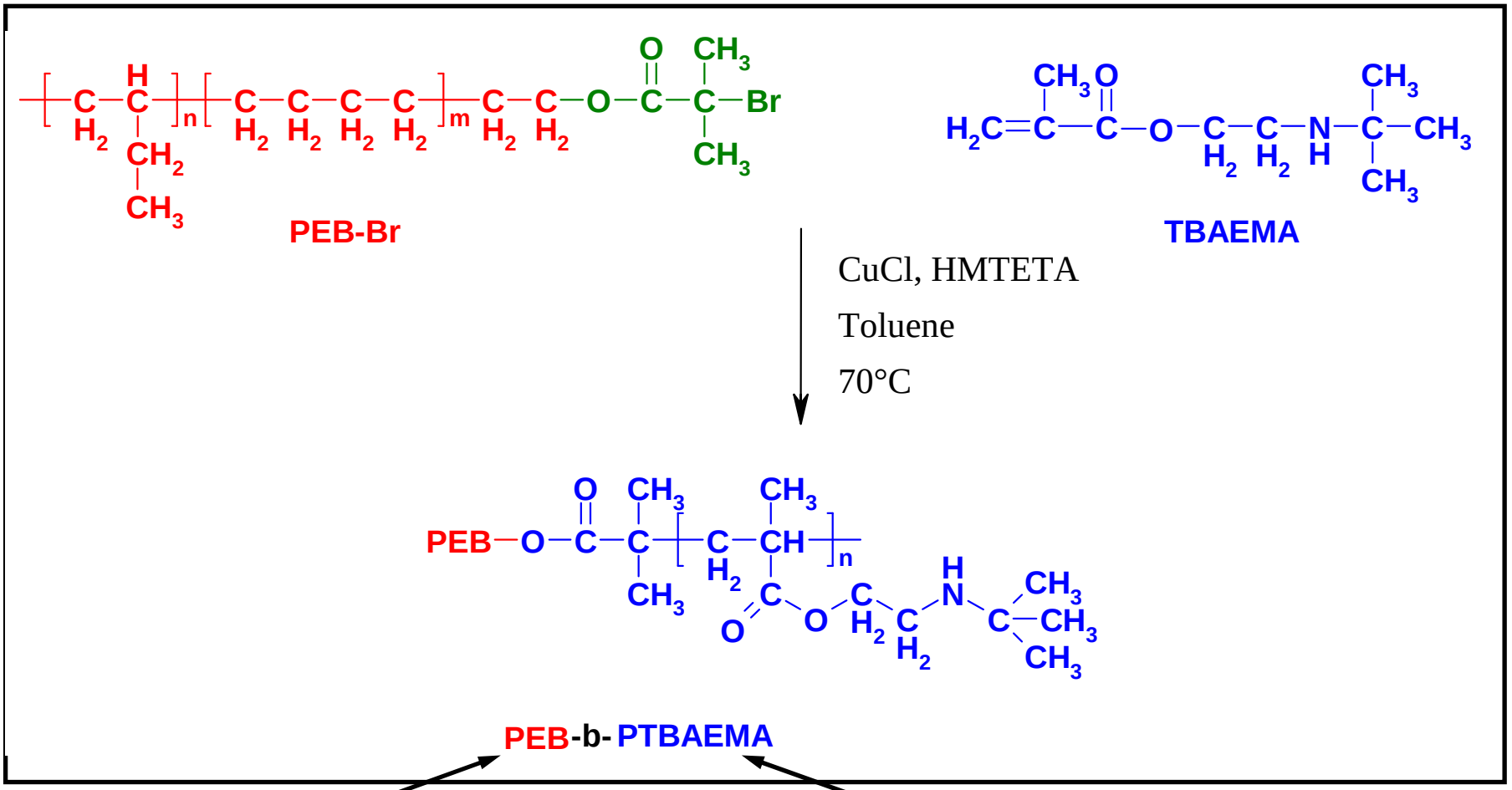


Quaternized poly(DMAEMA)



Poly(TBAEMA)

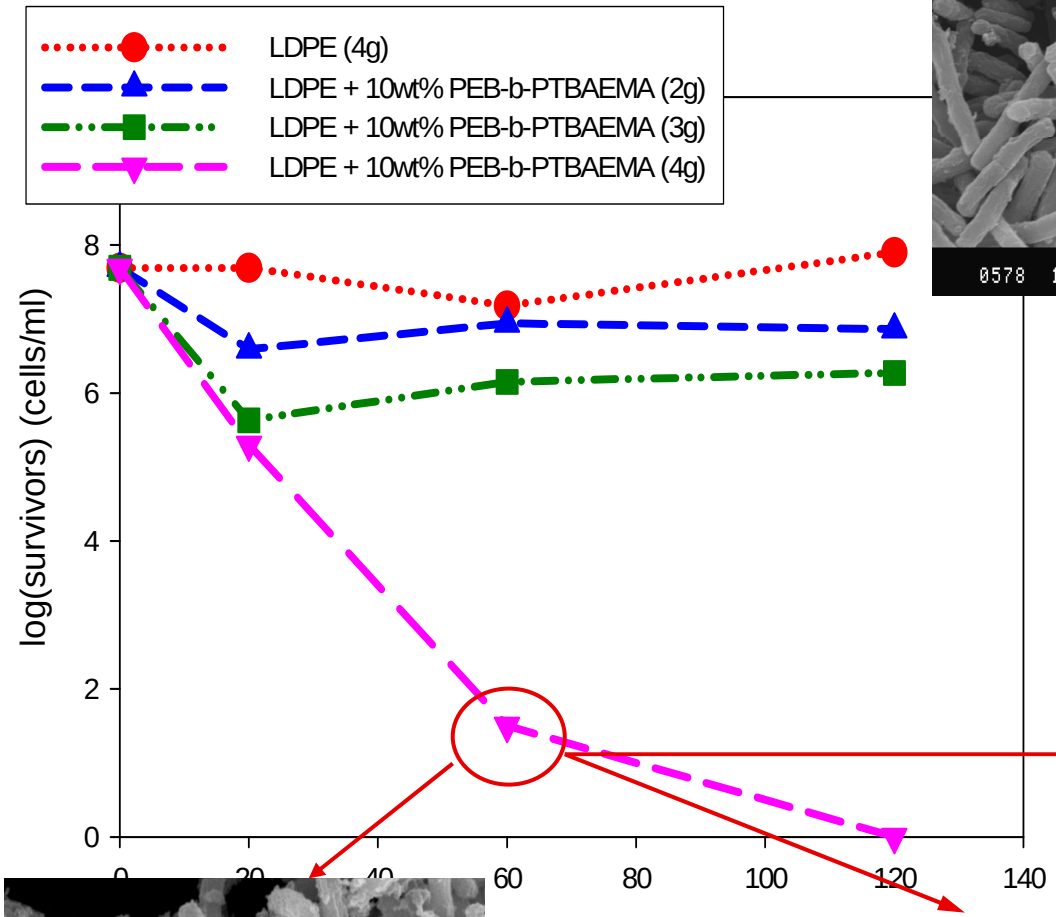
Antibacterial copolymers for LDPE

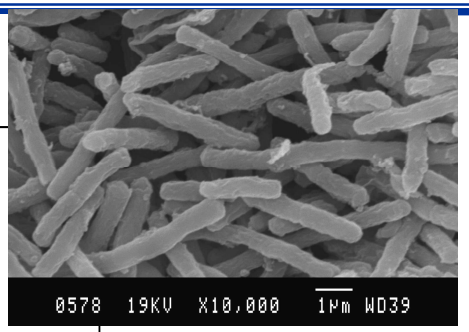


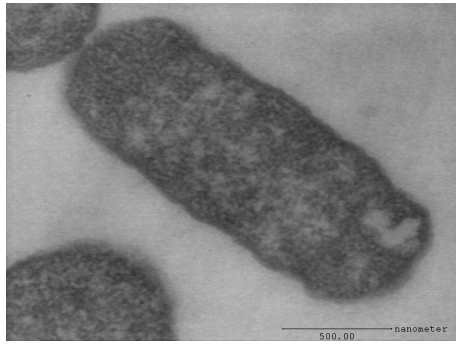
Miscible with LDPE
⇒ Anchoring block to the LDPE matrix

Antibacterial block

Antibacterial testings of LDPE bottels containing PEB-b-PTBAEMA







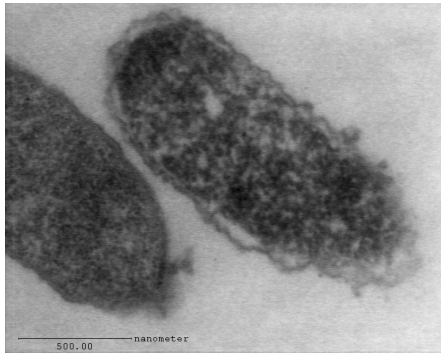
Control:

LDPE, 4g, 0.5 cm × 0.5 cm pieces

Antibacterial LDPE:

LDPE+ 10 % PEB-b-PTBAEMA,
4 g, 0.5 cm × 0.5 cm pieces
3g, 0.5 cm × 0.5 cm pieces
2g, 0.5 cm × 0.5 cm pieces

TEM images



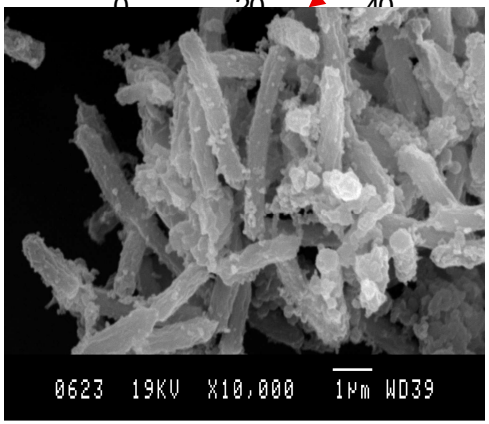
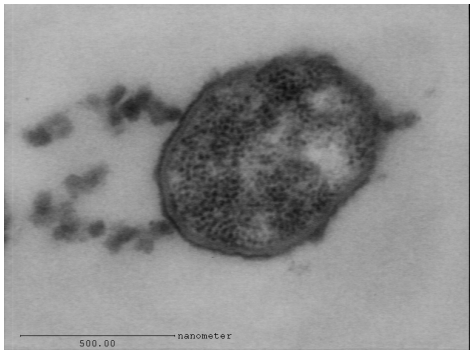
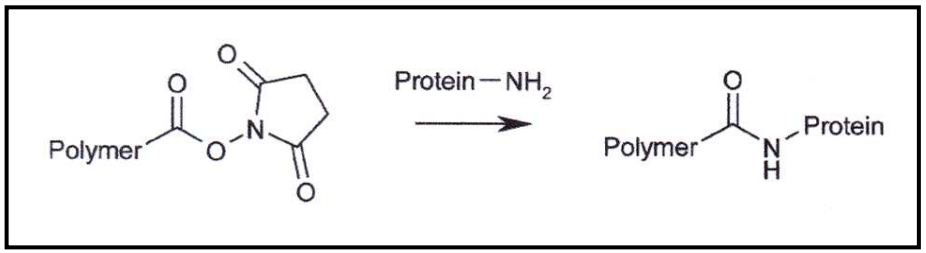


Image SEM



Biomacromolecules 2006, 7(8), 2291-2296

Polymer/biomolecules biohybrides



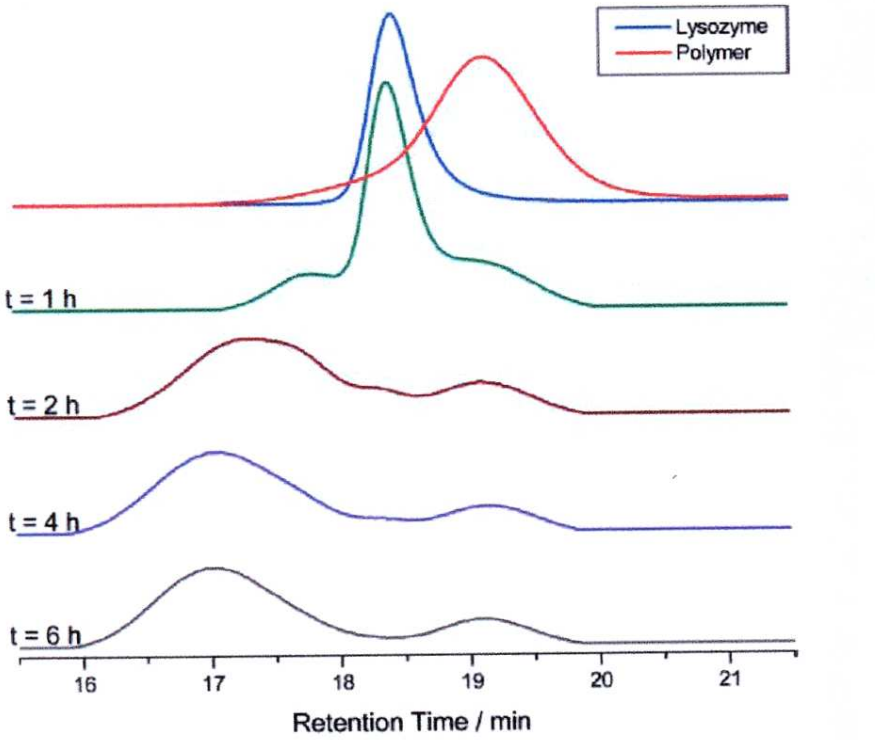
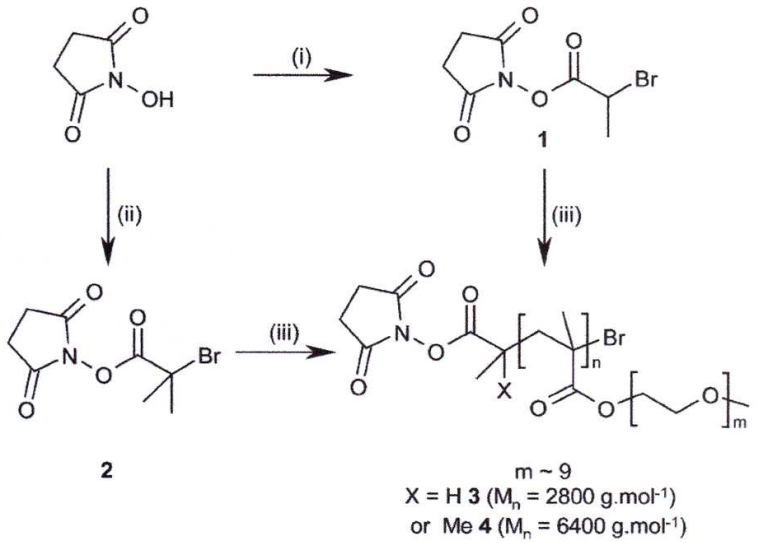


Fig. 2 SEC HPLC traces following the reaction of *N*-succinimidyl esters functionalised Poly(mPEGMA) (M_n = 6400 g mol^{-1}, M_w/M_n = 1.11) with lysozyme.

Chem. Comm. 2004, 2026



Scheme 2 Reagents and conditions: (i) 2-Bromopropionic acid, dicyclohexylcarbodiimide, CH_2Cl_2; (ii) 2-bromo-2-methylpropionyl bromide, triethylamine, CH_2Cl_2; (iii) Cu(I)Br, *N*-(ethyl)-2-pyridylmethanimine, poly(ethylene glycol) methyl ether methacrylate, toluene 50% v/v; [PEGMA]:[initiator]:[Cu(I)Br]:[ligand] = 5:1:1:2.

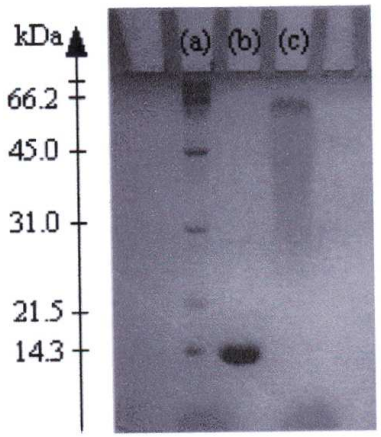
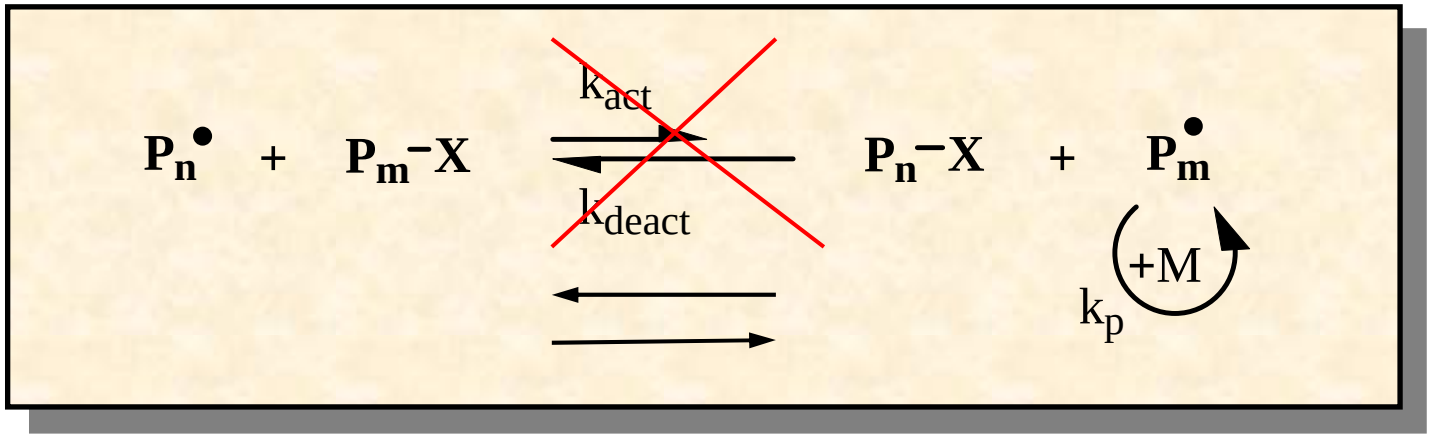


Fig. 3 SDS-PAGE for the conjugation of lysozyme with **3**. (a) Protein standards. (b) Lysozyme. (c) Protein–polymer bioconjugate.

6-7 polymer chains grafted onto lysozome

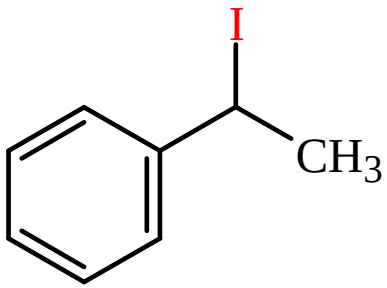
3rd mechanism: degenerative transfert (DT)

An atom or group of atoms is rapidly and reversibly transfered from a dormant chain to an active chain. During this transfer, the dormant chain becomes active, and the active chain becomes dormant.

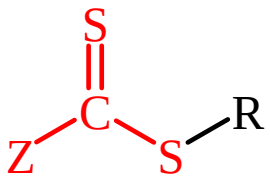


For the polymerization to be controlled, the transfer has to be fast compared to propagation !

Some exemples of DT reagents:



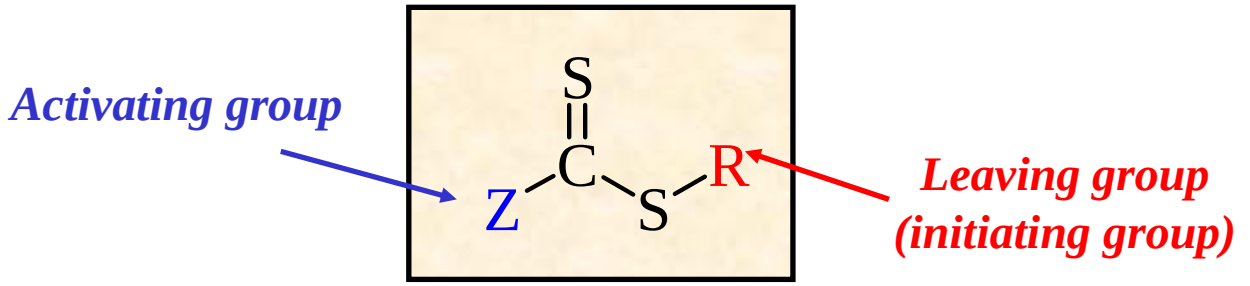
1-phenyl ethyl iodide



Z = Ph
R = CH_2Ph

thiocarbonylthio compounds

Reversible Addition-Fragmentation chain Transfer (RAFT)



a Z = Ph, R = $C(CH_3)_2Ph$

b Z = Ph, R = $CH(CH_3)Ph$

c Z = Ph, R = CH_2Ph

d Z = Ph, R = $C(CH_3)(CN)CH_2CH_2CO_2Na$

e Z = Ph, R = $C(CH_3)_2CN$

f Z = CH_3, R = CH_2Ph

g Z = Ph, R = $C(CH_3)(CN)CH_2CH_2CH_2OH$

h Z = Ph, R = $C(CH_3)(CN)CH_2CH_2CO_2H$

How to carry out a RAFT experiment ?

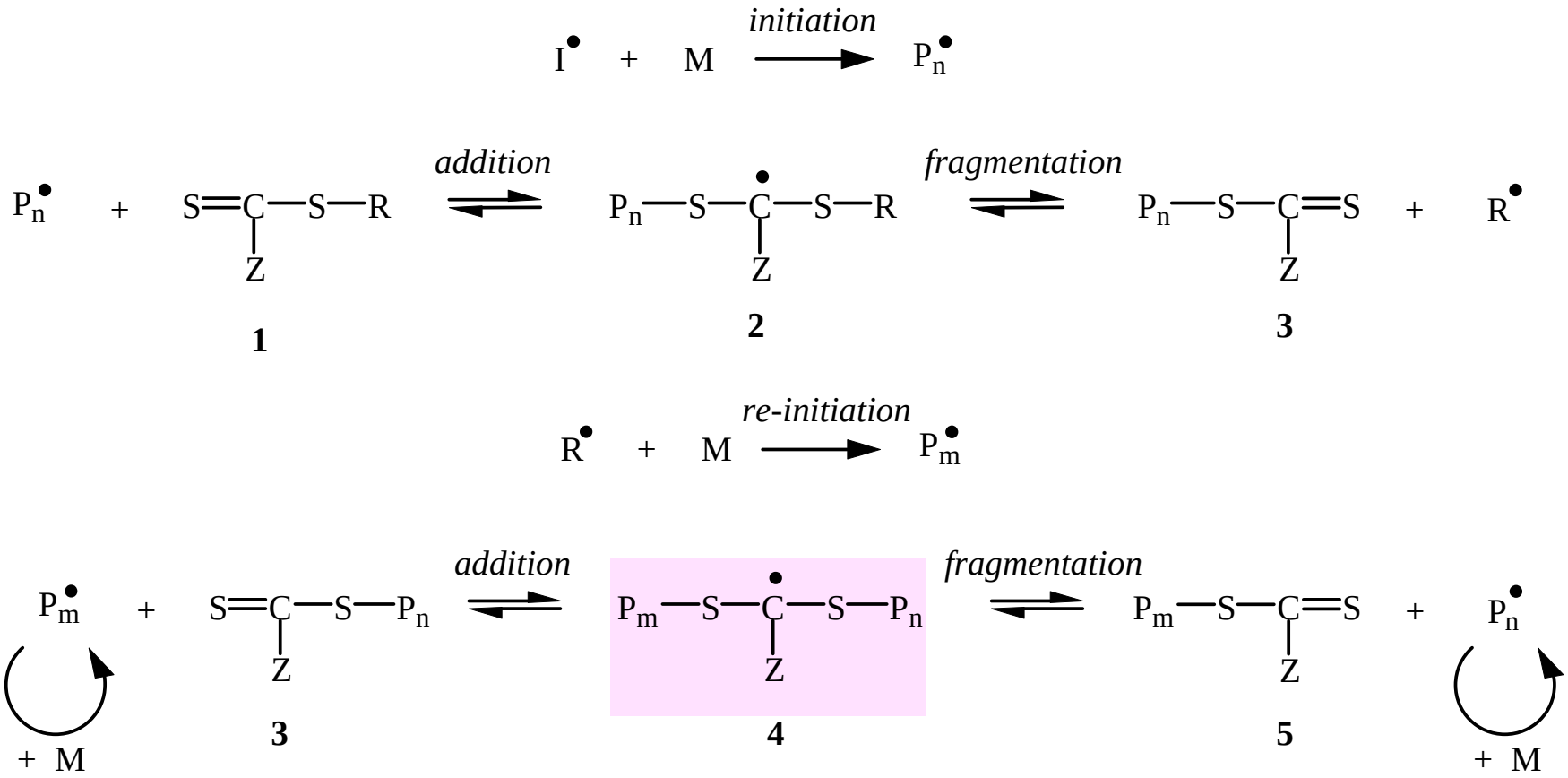
RAFT agent + free radical initiator + monomer $\xrightarrow{\Delta}$ ***RAFT***

Advantages:

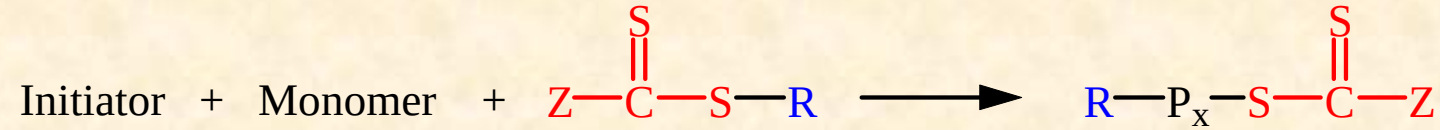
[RAFT agent]/ [free radical initiator] = 10/1 to 5/1

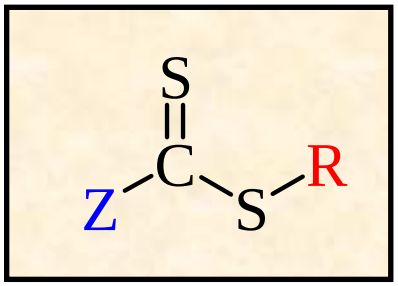
- Only organic reagents
- A wide range of monomers: methacrylates, acrylates, styrene, *styrene sulfonate*, vinyl benzoate, *2-hydroxyethyl methacrylate, acrylic acid, dimethylaminoethyl methacrylate, acrylamides, …*
- T: 60-100°C; polymerizations in bulk, solutions and aqueous (dispersed) media

RAFT mechanism



Overall process

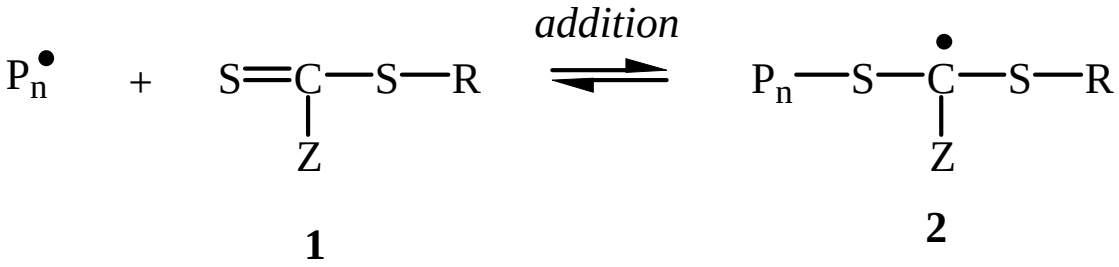




How to choose the RAFT agent ?

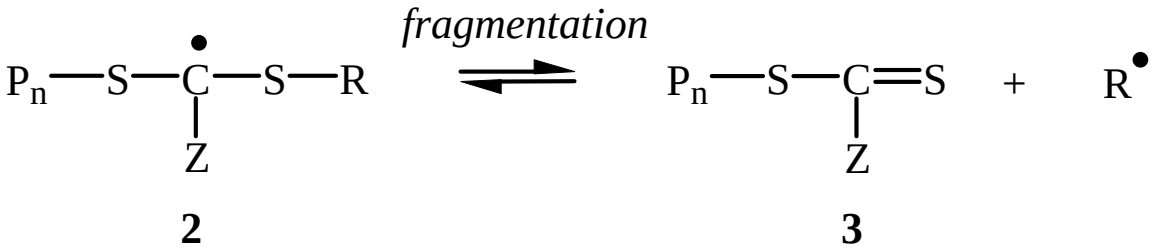
1) Importance of Z and R groups

Z = activating group ⇒ has to activate the RAFT agent for the addition of radicals



1 **2**

R = leaving group ⇒ has to be a good leaving “radicalar” group in order to promote the fragmentation in the good direction

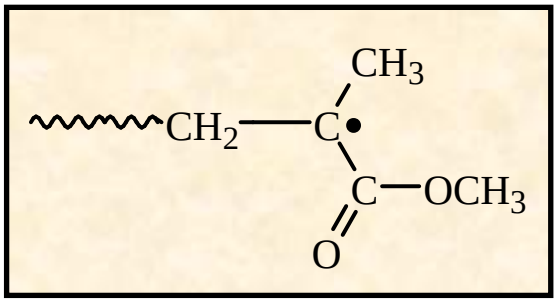


2 **3**

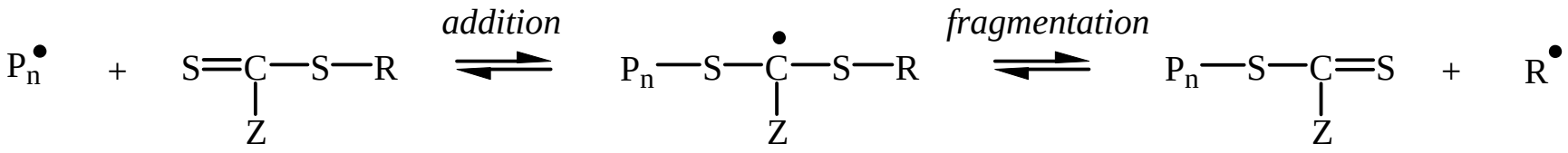
2) Choice of the RAFT agent = f(monomer)

How to choose the RAFT agent ?

Methacrylates

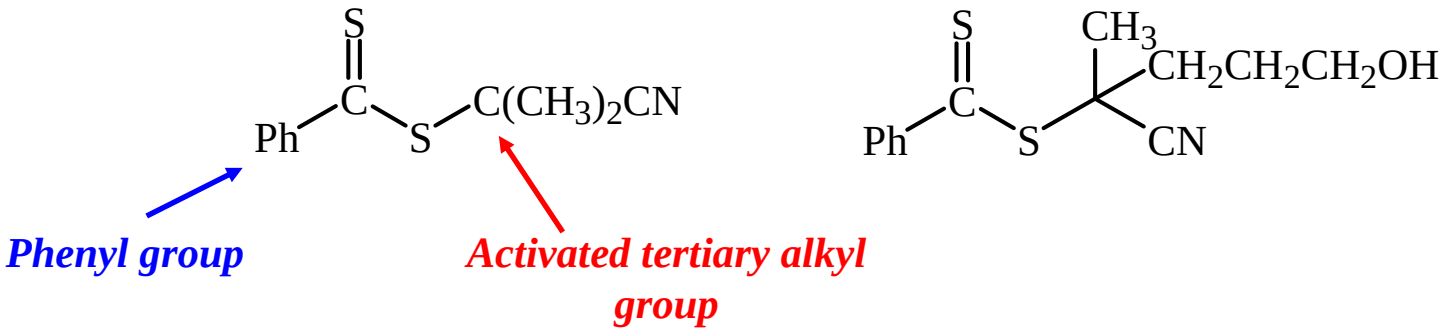


Sterically hindered propagating radical with a moderate reactivity



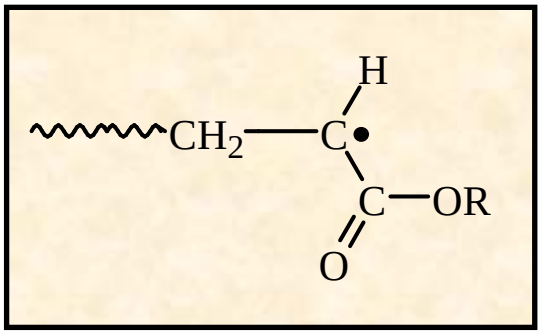
1 **2** **3**

In order to transform the active chain **Pn°** into dormant chain **3**, the S-R bond (intermediate **2**) has to break. If this S-R bond is too stable compared to S-P_n bond, the dormant species **3** will not form. No control will be observed.

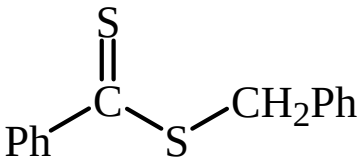


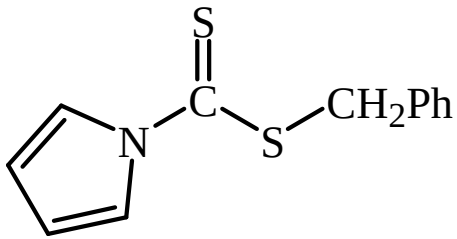
How to choose the RAFT agent ?

Acrylates et acrylic acid

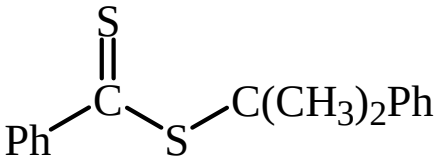


Low steric hindrance and high reactivity of the propagating radical



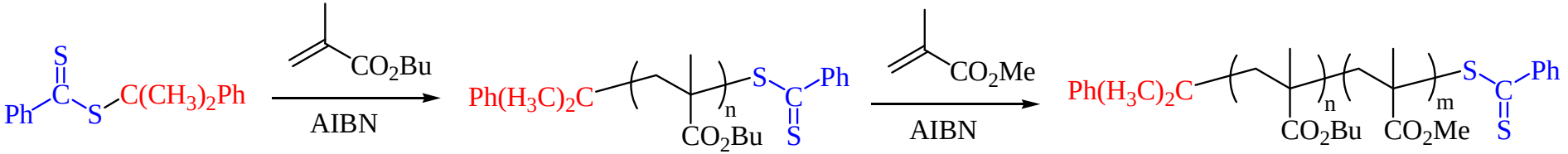


Acrylamides



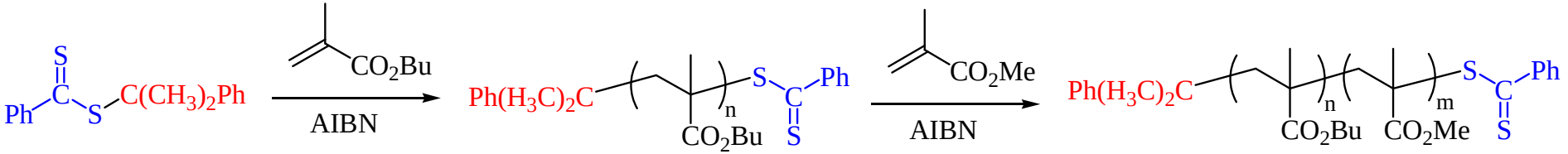
How to prepare block copolymers by RAFT ?

1- Monomers with similar reactivities

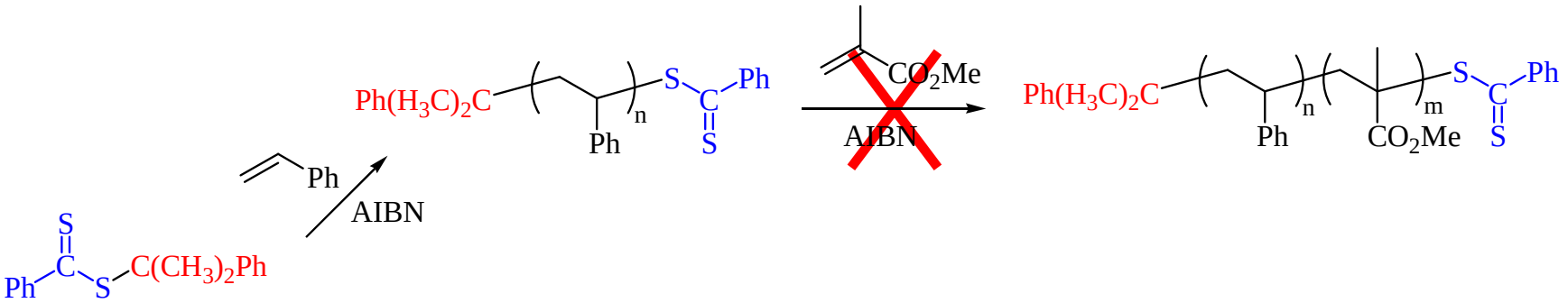


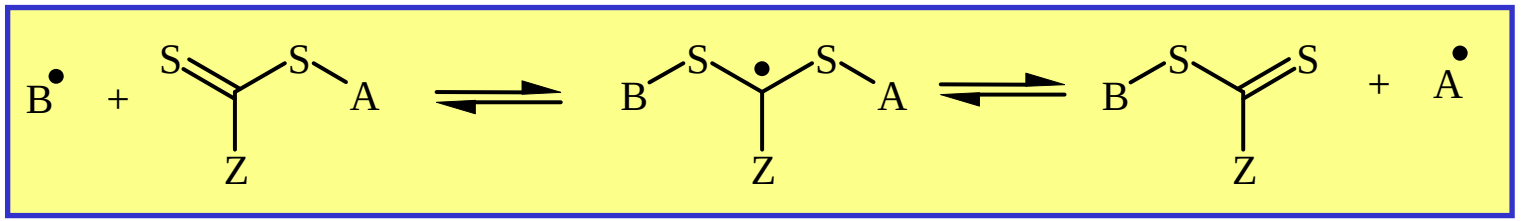
How to prepare block copolymers by RAFT ?

1- Monomers with similar reactivities



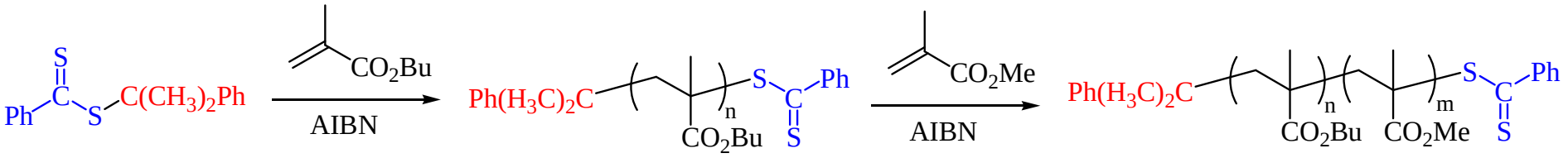
2- Monomers with different reactivities



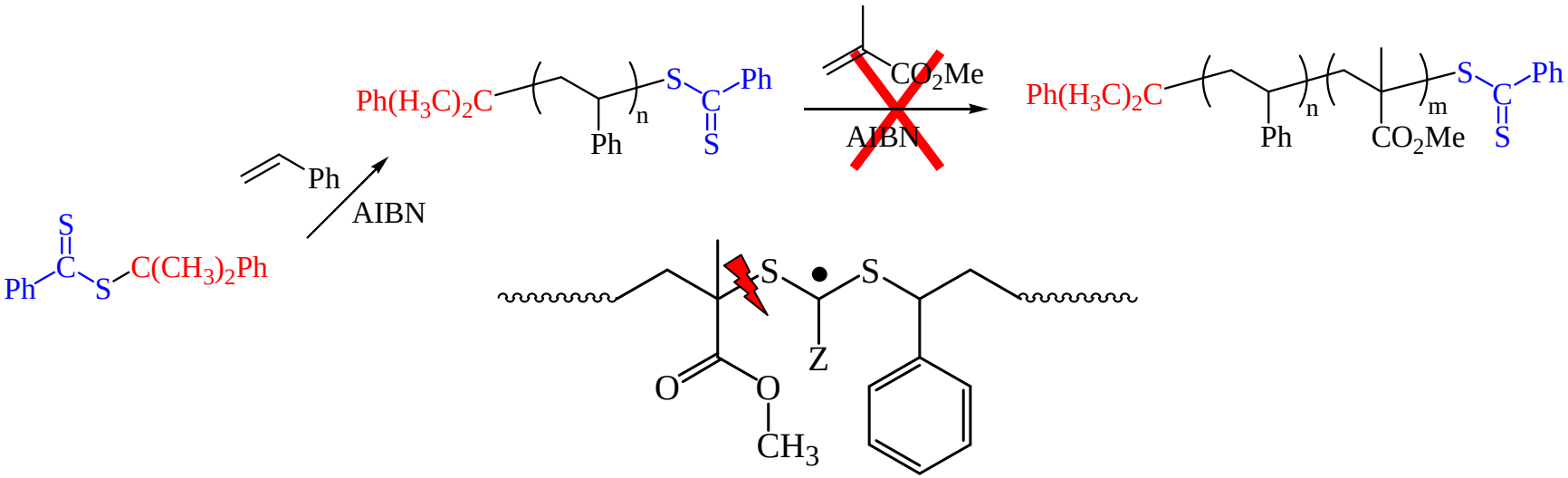


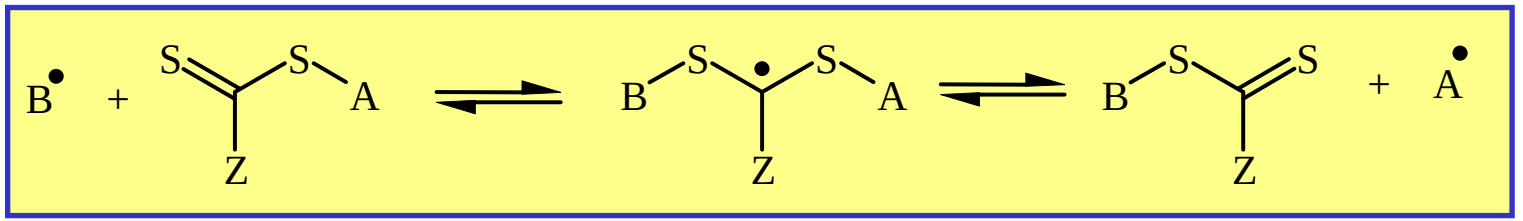
How to prepare block copolymers by RAFT ?

1- Monomers with similar reactivities



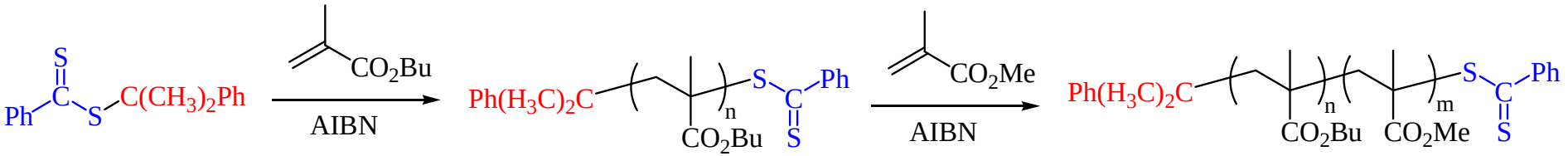
2- Monomers with different reactivities



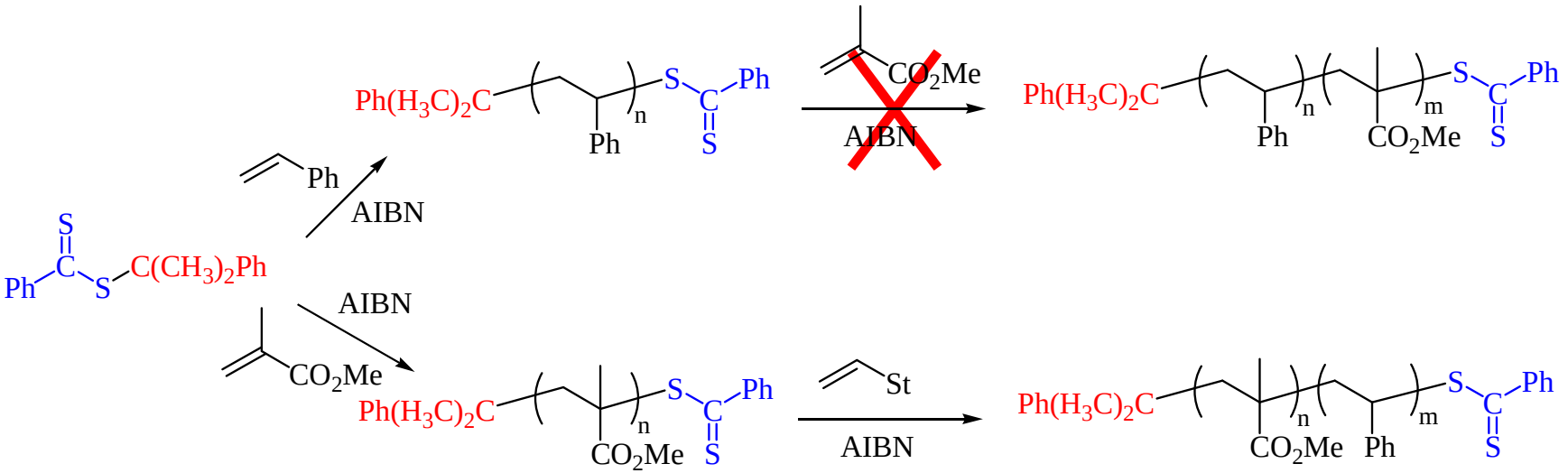


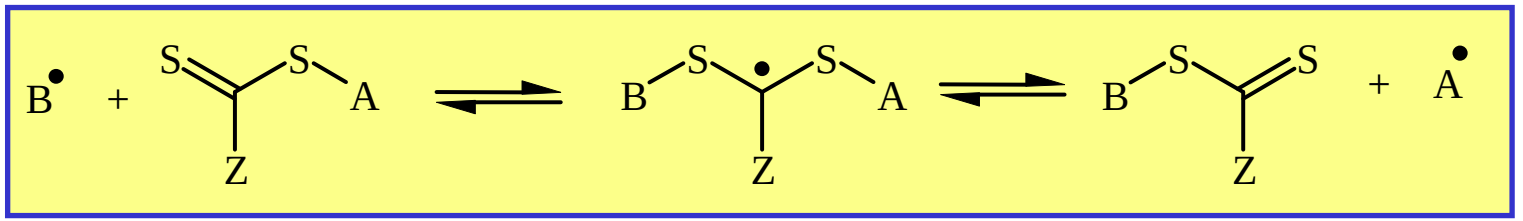
How to prepare block copolymers by RAFT ?

1- Monomers with similar reactivities

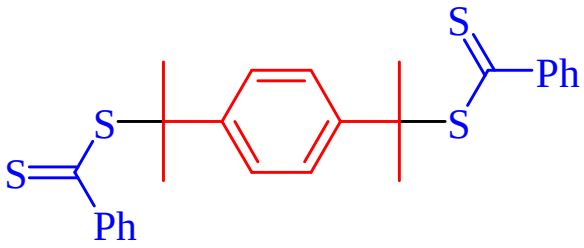


2- Monomers with different reactivities

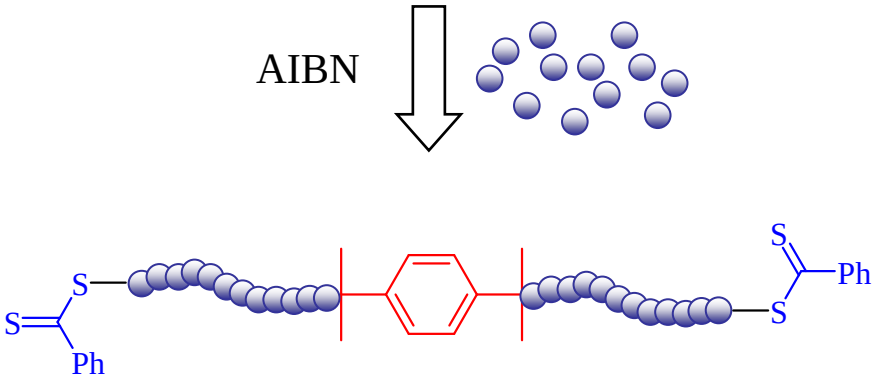


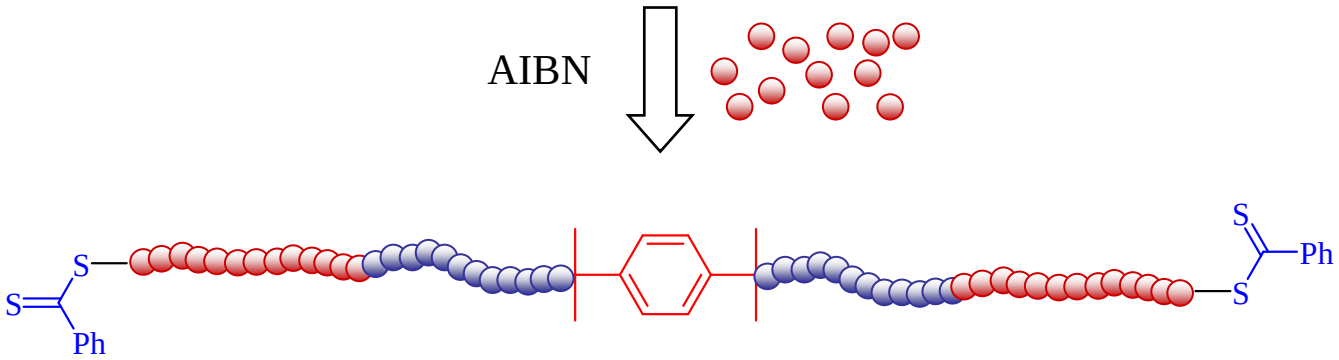


Other architectures by RAFT

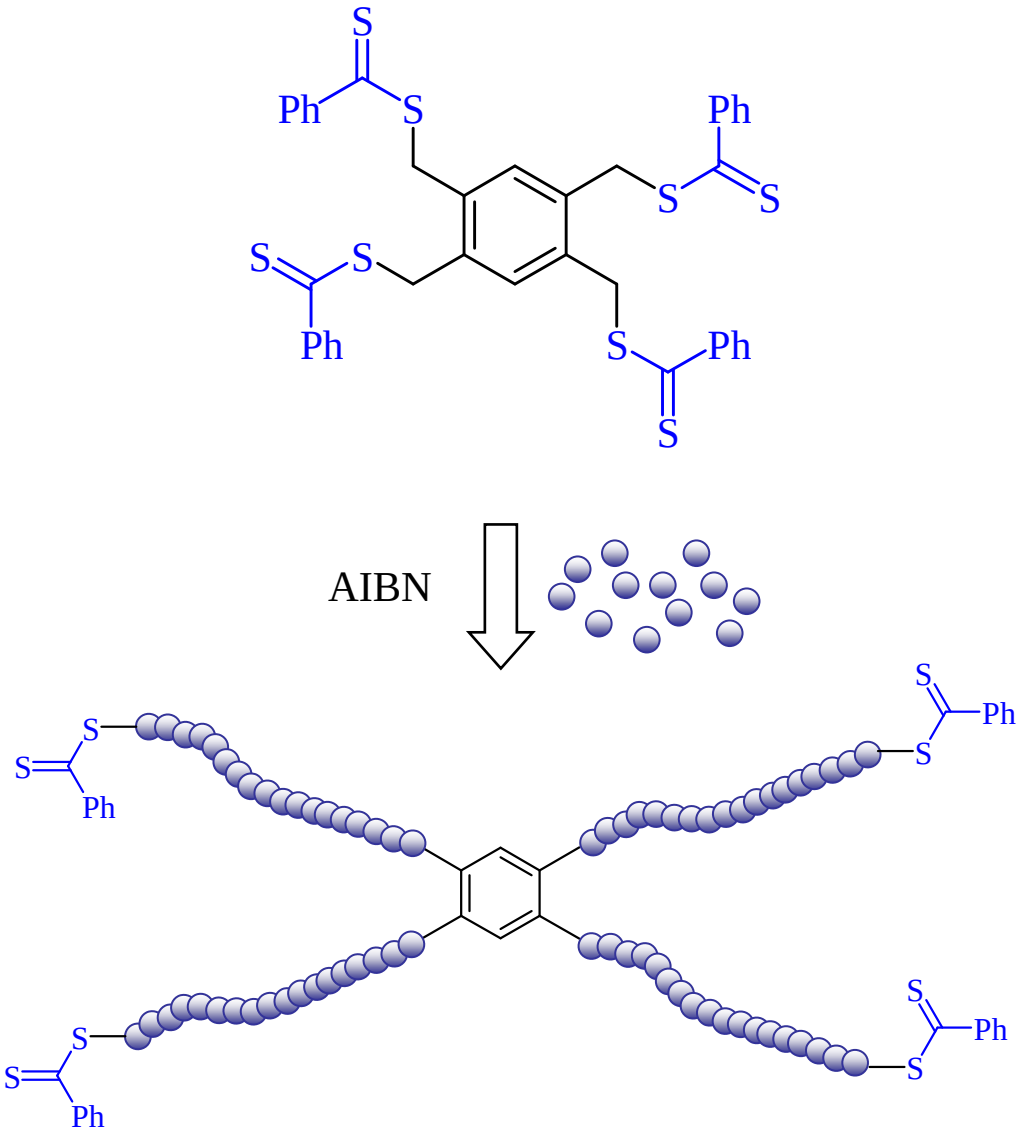


Difunctional RAFT agent

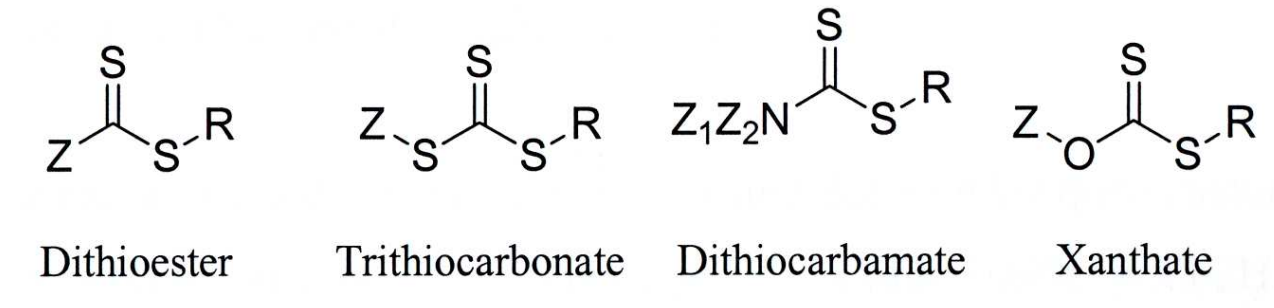




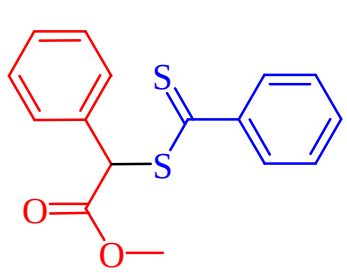
Other architectures by RAFT



RAFT agents et MADIX agents

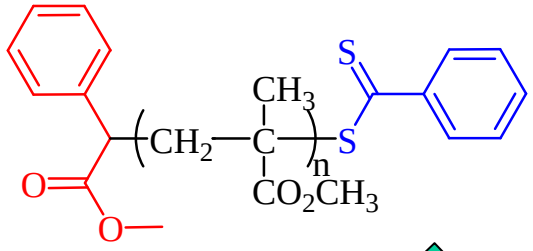


End-functionalization of (co)polymers



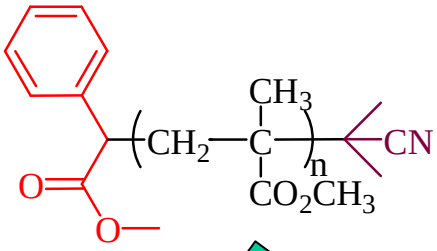
MMA

AIBN, 60°C, 8h



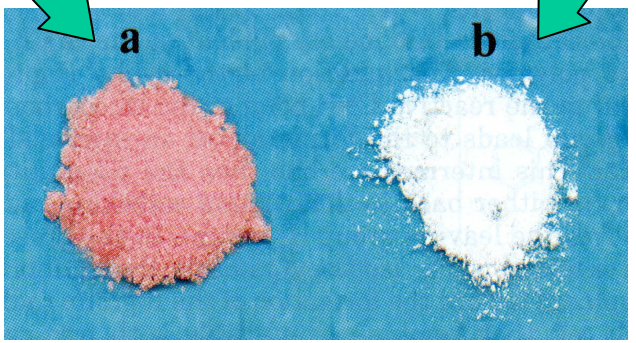
Toluene

AIBN **in excess**
80°C, 2.5 h

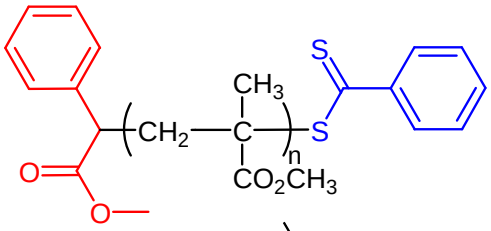


MMA/ RAFT agent /AIBN = 500/**1/0.1**

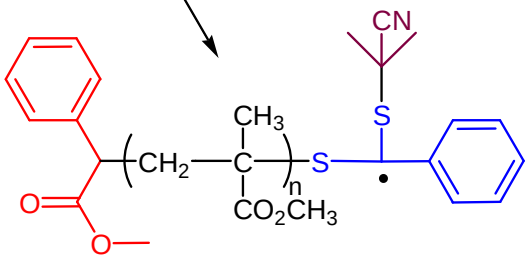
Mn = 13500
Mw/Mn = 1.18
34 % conversion

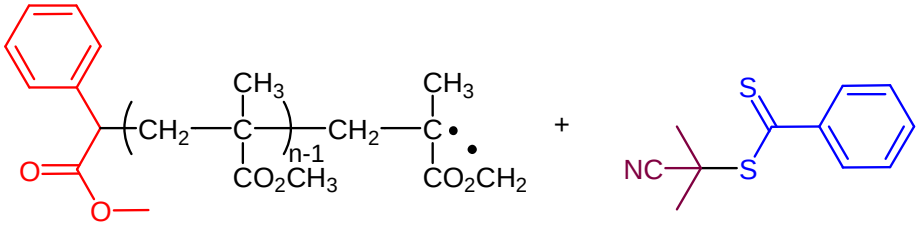


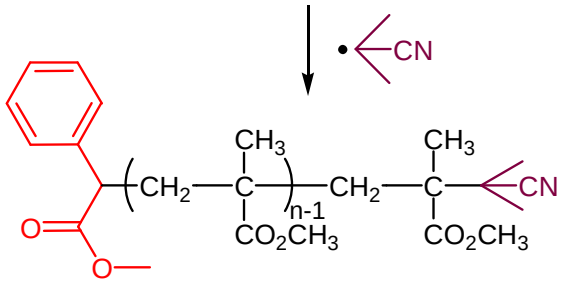
Mechanism of ω-chain end functionalization:



AIBN en excès

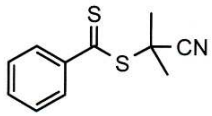
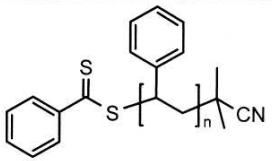
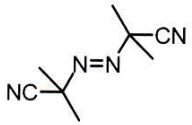
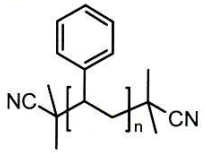
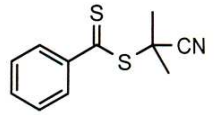
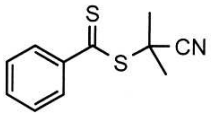
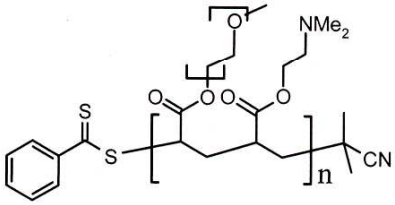
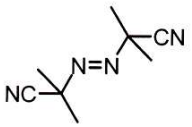
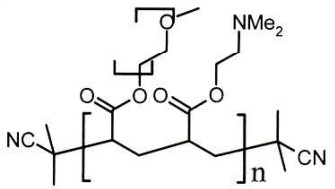
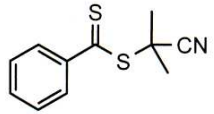
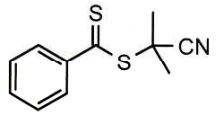
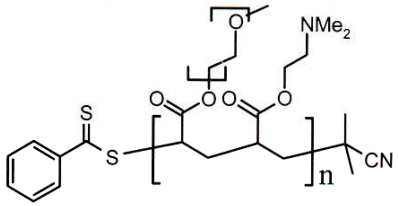
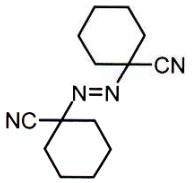
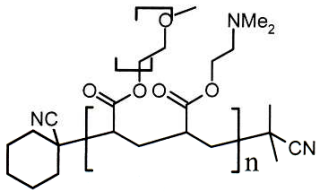
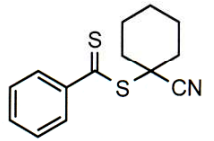
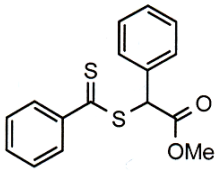
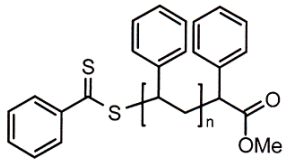
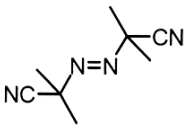
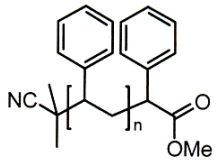
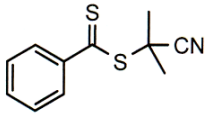
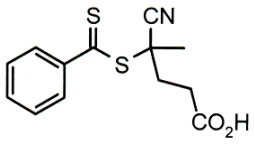
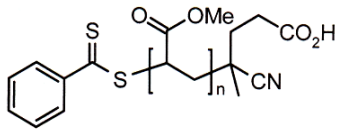
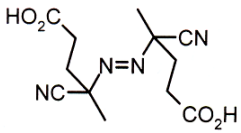
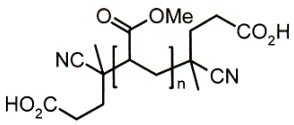
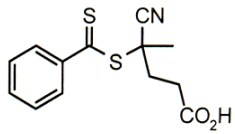




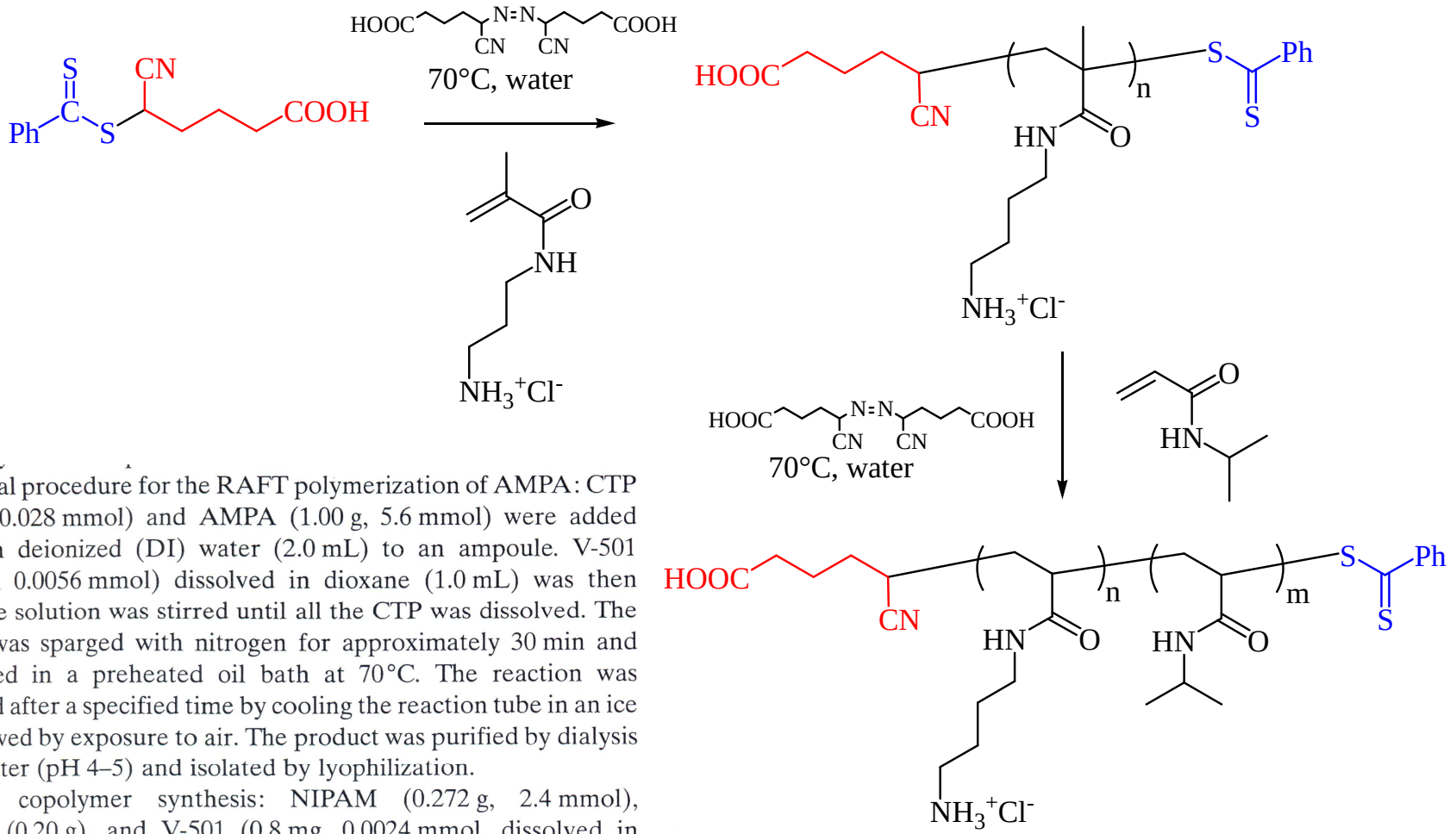


Macromolecules 2005, 38, 2033

End-functionalization of (co)polymers

CTA	Polymer	Cleavage initiator	Modified Polymer	Recycled CTA
	 Mn = 19 750, PDI = 1.18		 Mn = 19 700, PDI = 1.17	
	 Mn = 36 000, PDI = 1.23		 Mn = 35 700, PDI = 1.23	
	 Mn = 36 000, PDI = 1.23		 Mn = 35 900, PDI = 1.23	
	 Mn = 12 800, PDI = 1.10		 Mn = 12 700, PDI = 1.08	
	 Mn = 34 700, PDI = 1.26		 Mn = 32 600, PDI = 1.27	

Preparation of polyelectrolytes

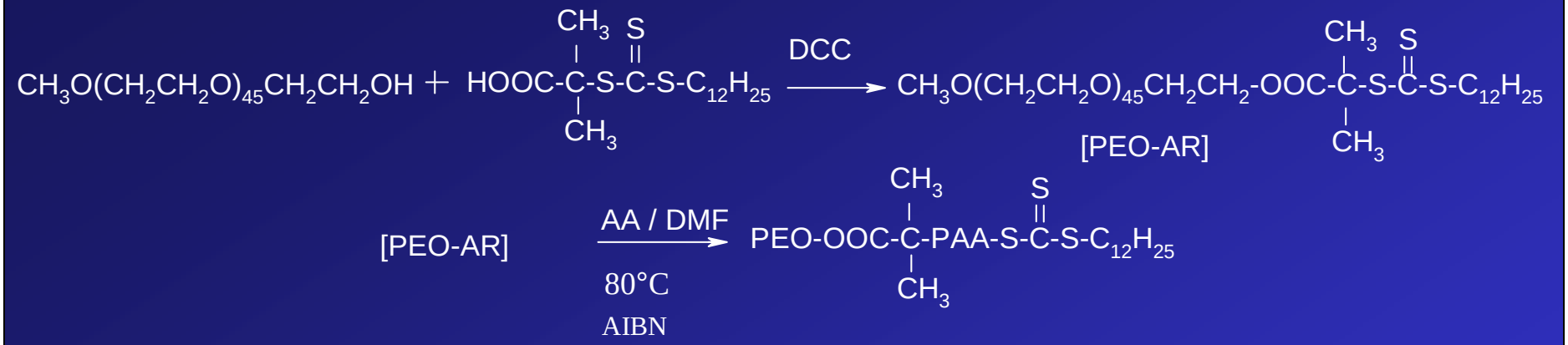


General procedure for the RAFT polymerization of AMPA: CTP (0.0078 g, 0.028 mmol) and AMPA (1.00 g, 5.6 mmol) were added along with deionized (DI) water (2.0 mL) to an ampoule. V-501 (0.00156 g, 0.0056 mmol) dissolved in dioxane (1.0 mL) was then added. The solution was stirred until all the CTP was dissolved. The ampoule was sparged with nitrogen for approximately 30 min and then placed in a preheated oil bath at 70 °C. The reaction was terminated after a specified time by cooling the reaction tube in an ice bath followed by exposure to air. The product was purified by dialysis against water (pH 4–5) and isolated by lyophilization.

Block copolymer synthesis: NIPAM (0.272 g, 2.4 mmol), $PAMPA_{88}$ (0.20 g), and V-501 (0.8 mg, 0.0024 mmol, dissolved in 0.6 g dioxane) were added along with DI water (0.8 mL) to an ampoule. After sparging with nitrogen for 30 min, the reaction was allowed to proceed at 70 °C for 2 h. The reaction was quenched by cooling the reaction vessel in an ice bath and exposure to air. The product was purified by dialysis against deionized water and isolated by lyophilization.

Angew. Chem. Int. Ed. 2006, 45, 5792

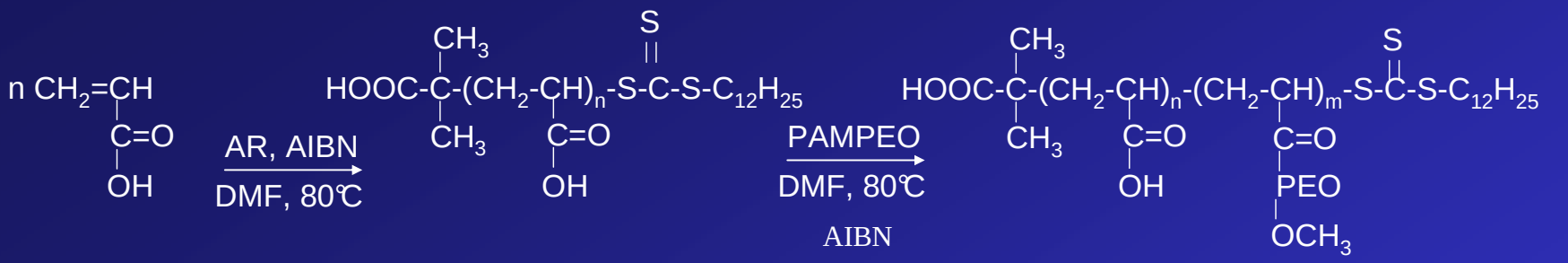
Synthesis of PEO-b-PAA

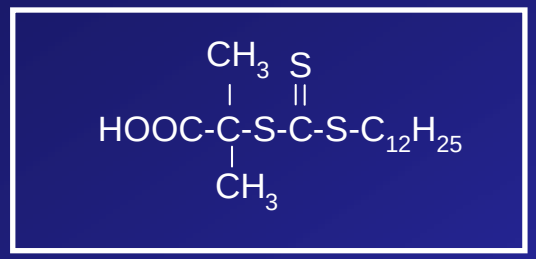


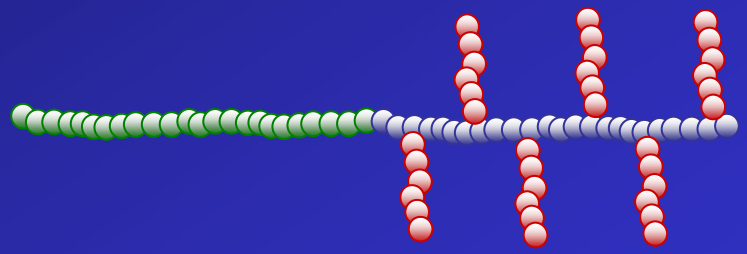
Polymerization conditions : [RAFT agent] : [AIBN] = 40: 1
[AA] = 4 M in DMF at 80°C.

CODE	Ligand	DP (NMR)	IP (GPC)
E21-1	PAA-PEO	48-45	1.19
E21-2	PAA-PEO	83-45	1.16

Synthesis of PAA-b-PAMPEO



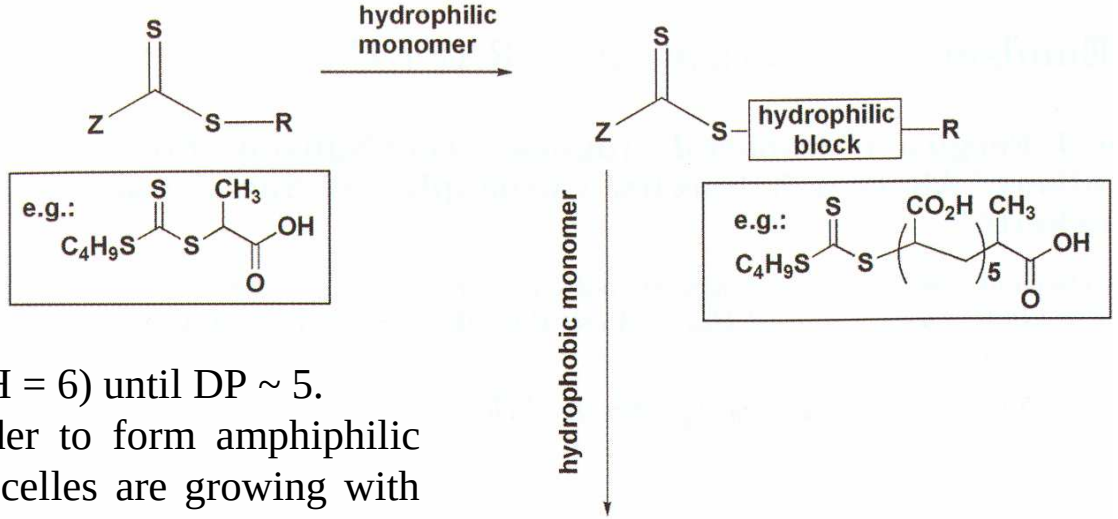




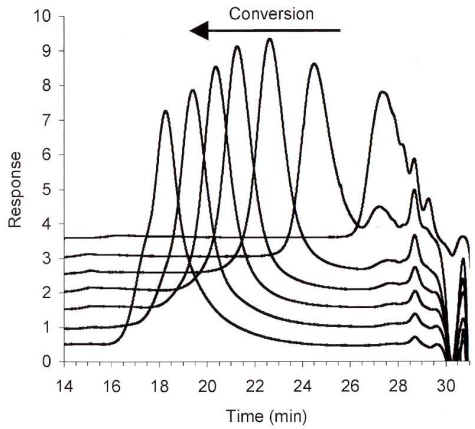
Polymerization condition : [RAFT agent] : [AIBN] = 80: 1
[AMPEO] = 0.5 M in DMF at 80°C.

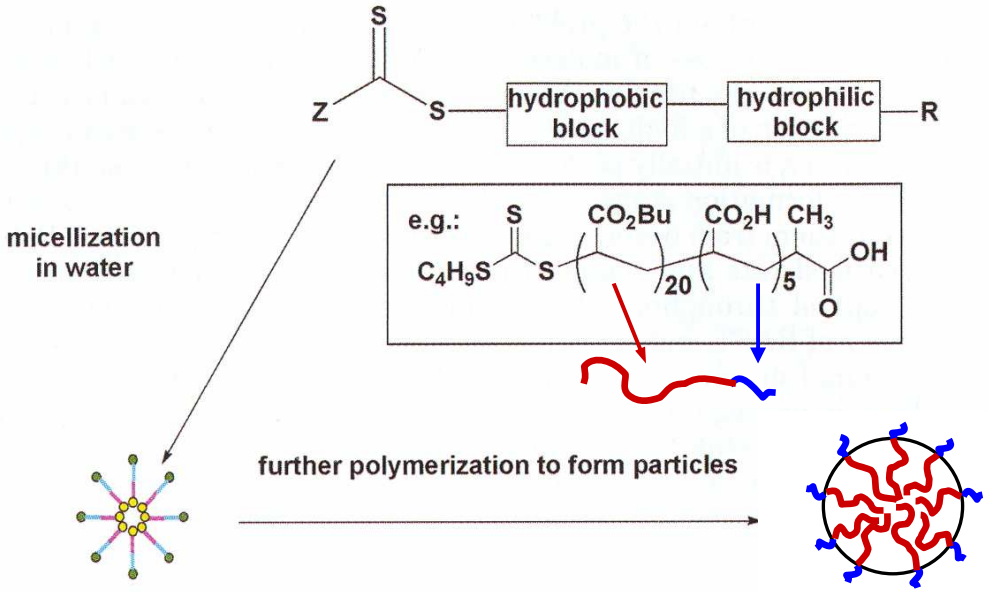
CODE	Ligand	DP(RMN)	IP(GPC)
E21-10	PAA-PAMPEO	61-11	1.25
E21-11	PAA-PAMPEO	61-21	1.51
E21-23	PAA-PAMPEO	34-110	1.35
E21-24	PAA-PAMPEO	34-66	1.30

Application to coatings



1- Acrylic acid is polymerized in water (pH = 6) until DP ~ 5.
2- Butyl acrylate is slowly added in order to form amphiphilic PAA-b-PnBuA which forms micelles. Micelles are growing with the monomer conversion to form the latex.





Advantages:
- Control of Mn
- No free surfactant ⇒ no migration of surfactant out of the coating
- Functionnalization of the latex particles possible
- No organic solvent

Macromolecules 2005, 38, 2191

Some criteria for the use of CRP at the industrial scale

Cheap CRP system

✓Cheap and readily available starting products

✓Fast polymerization

Use of the existing reactors and lines

Same conditions as for conventional technique

No purification and treatment of the final polymers

✓ Odorless polymers

✓ Colorless polymers

Stability of the polymer during processing

Polymers not contaminated by toxic residues