INITIAL TRAINING NETWORK

Introduction to Polymer Synthesis

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Soft Matter and Chemistry

ESPCI PARIS

ÉCOLE SUPÉRIEURE DE PHYSIQUE ET DE CHIMIE INDUSTRIELLES DE LA VILLE DE PARIS

Polymers: Classification

Thermoplastics

Long chains

☺ Can flow:
Processing, recycling, healing

☹ Chemical resistance / soluble

☹ Dimensional stability @ high T

Thermosets

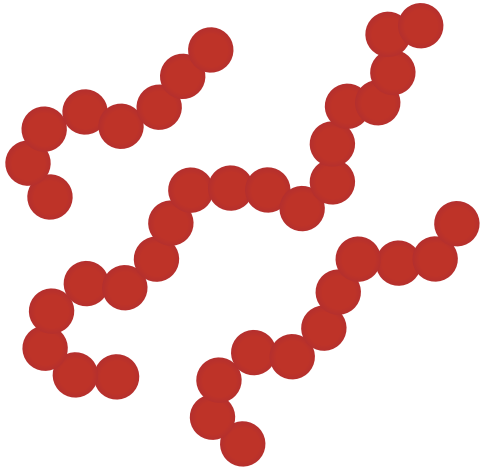
Chemical Networks

☺ Insoluble

☺ Mechanical properties

☺ Recyclability, Processability

Molar Masses



Average molar masses ⇔ distribution

Number average molar mass: M_n

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

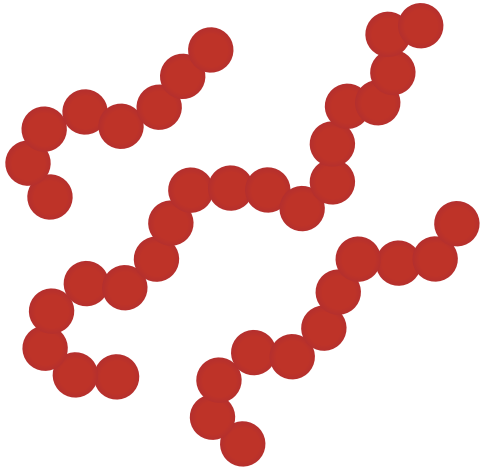
N_i number (moles) of molecules with a molar mass M_i

Mass average molar mass: M_w

$$M_w = \frac{\sum_i W_i M_i}{\sum_i W_i} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

W_i mass of molecules of molar mass M_i ($W_i = N_i \times M_i$)

Molar Masses



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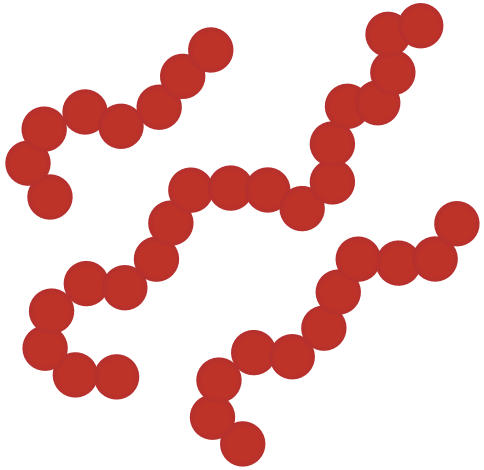
$$M_w = \frac{\sum_i W_i M_i}{\sum_i W_i} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

Distribution => Dispersity: *Đ*

$$Đ = \frac{M_w}{M_n} \geq 1$$

Molar Masses



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$$M_w = \frac{\sum_i W_i M_i}{\sum_i W_i} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

Number average degree of polymerization: DP_n

$$DP_n = \frac{M_n}{M_{r.u.}}$$

Mass average degree of polymerization: DP_w

$$DP_w = \frac{M_w}{M_{r.u.}}$$

Polymers: Classification

Type of chain growth

Step-growth polymerization :

Any molecules can react with all other molecules

monomers + monomers

monomers + growing polymers

growing polymers + growing polymers

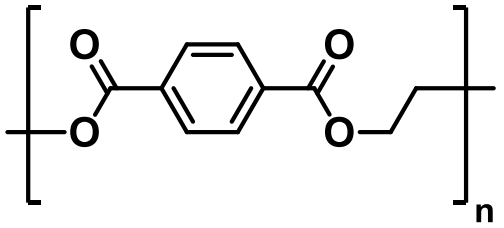
Chain-growth polymerization :

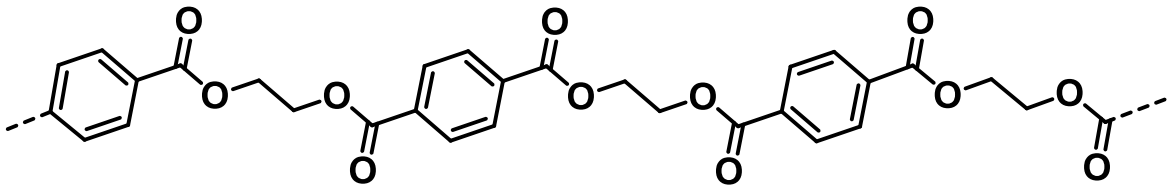
Monomers only react with growing polymers

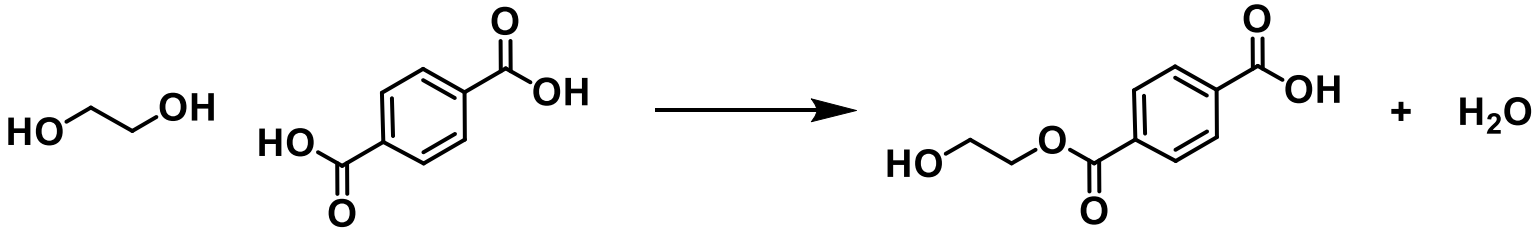
~~monomers + monomers~~

Step-Growth Polymerization

Poly(ethylene terephthalate) (PET)

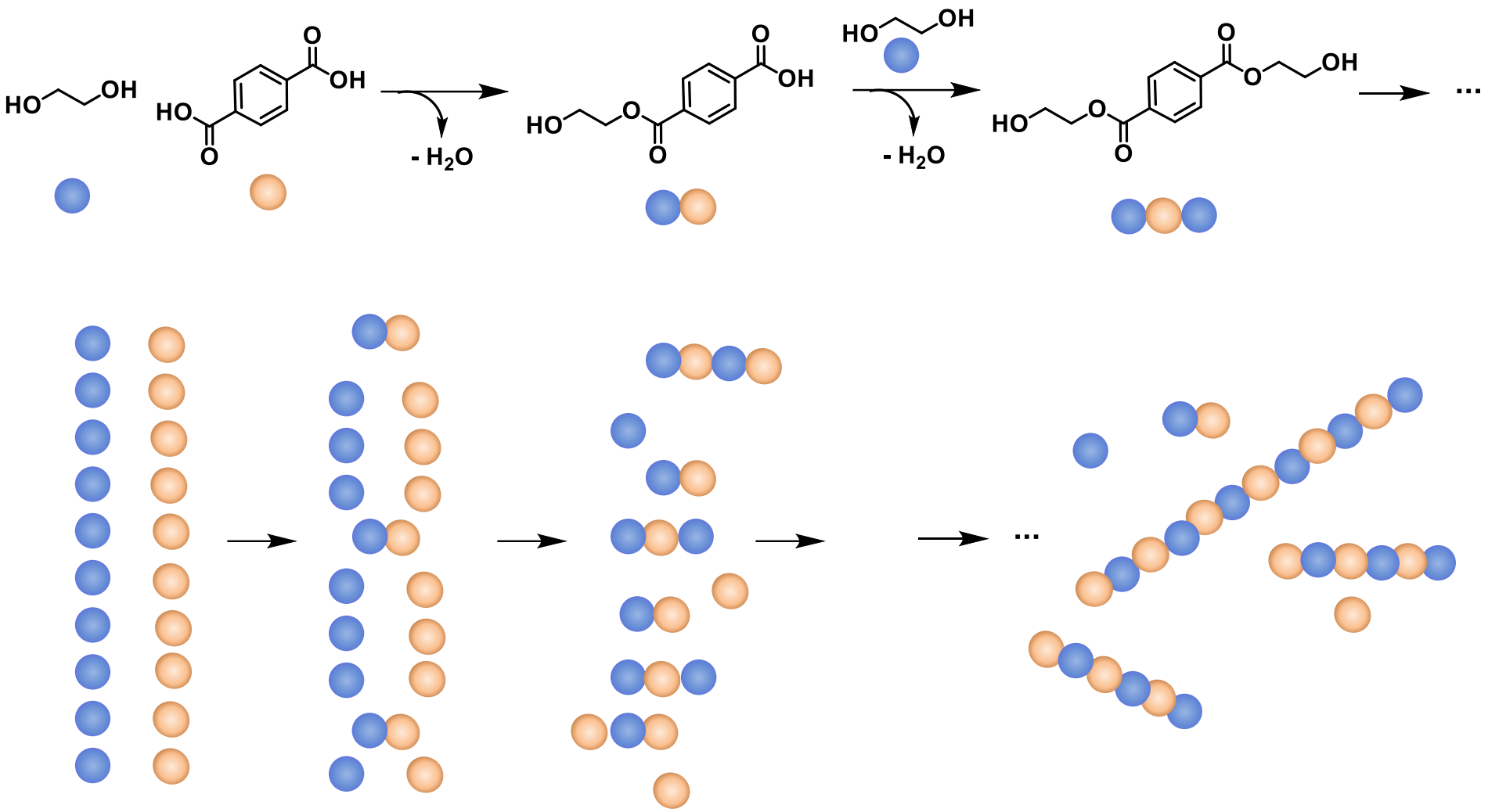




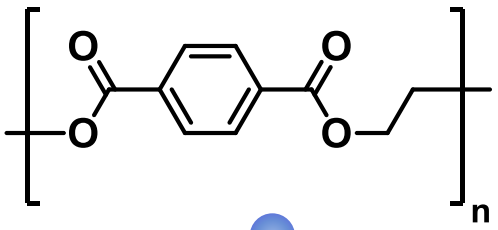


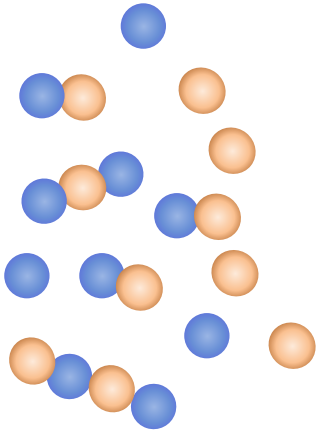
Condensation => Polycondensation

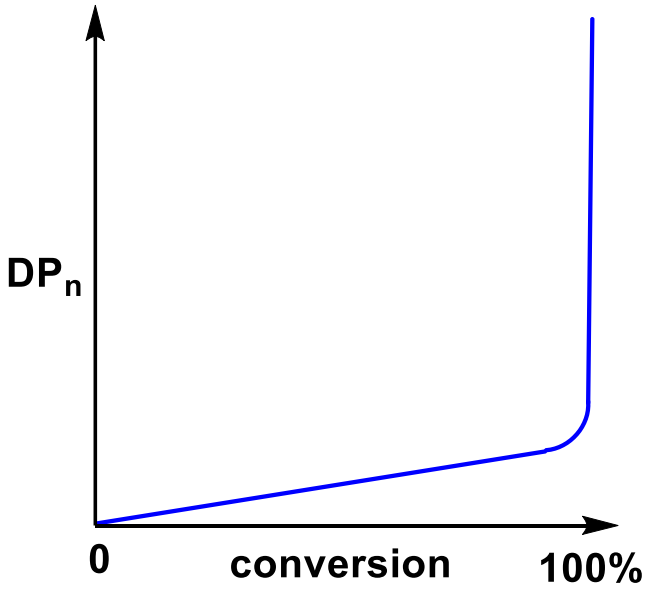
Step-Growth Polymerization



Step-Growth Polymerization





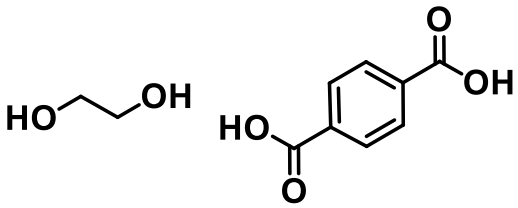


Stoichiometry between A and B

$$\overline{DP_n} = \frac{1}{1 - x}$$

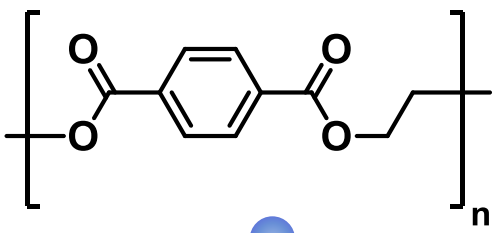
$DP_n = 20 \Leftrightarrow x = 0{,}95$

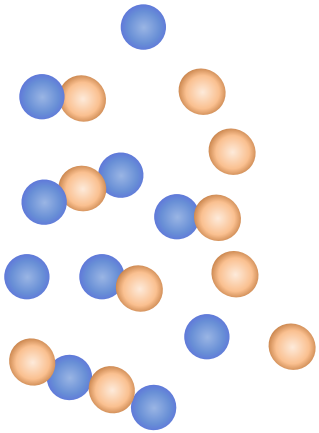
$DP_n = 200 \Leftrightarrow x = 0{,}995$

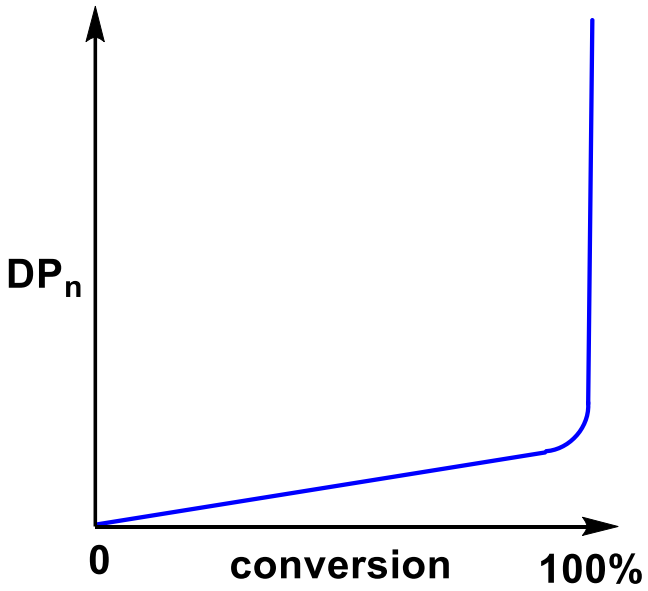


$$\text{Conversion : } x = \frac{\text{Nbr of functions that reacted}}{\text{Initial nbr of functions}}$$

Step-Growth Polymerization







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$$\overline{DP_n} = \frac{1}{1 - x}$$

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$DP_n = 200 \Leftrightarrow x = 0{,}995$

- Difunctional monomer(s)

  A-A +B-B ; A-B

- Very high conversion

- Excellent yields

$COOH + OH / NH_2$ => ester / amide

OH + NCO => urethane

…

Step-Growth Polymerization

Effect of the Equilibrium Constant on the Extent of Reaction

$$K = \frac{[COOR][H_2O]}{[COOH][OH]} = \frac{(p[M]_0)^2}{([M]_0(1-p))^2} = \frac{p^2}{(1-p)^2}$$

$$p = \frac{\sqrt{K}}{1+\sqrt{K}}$$

[ ] in function !!!

Effect of the Equilibrium Constant on the Extent of Reaction and Degree of Polymerization in a Closed System

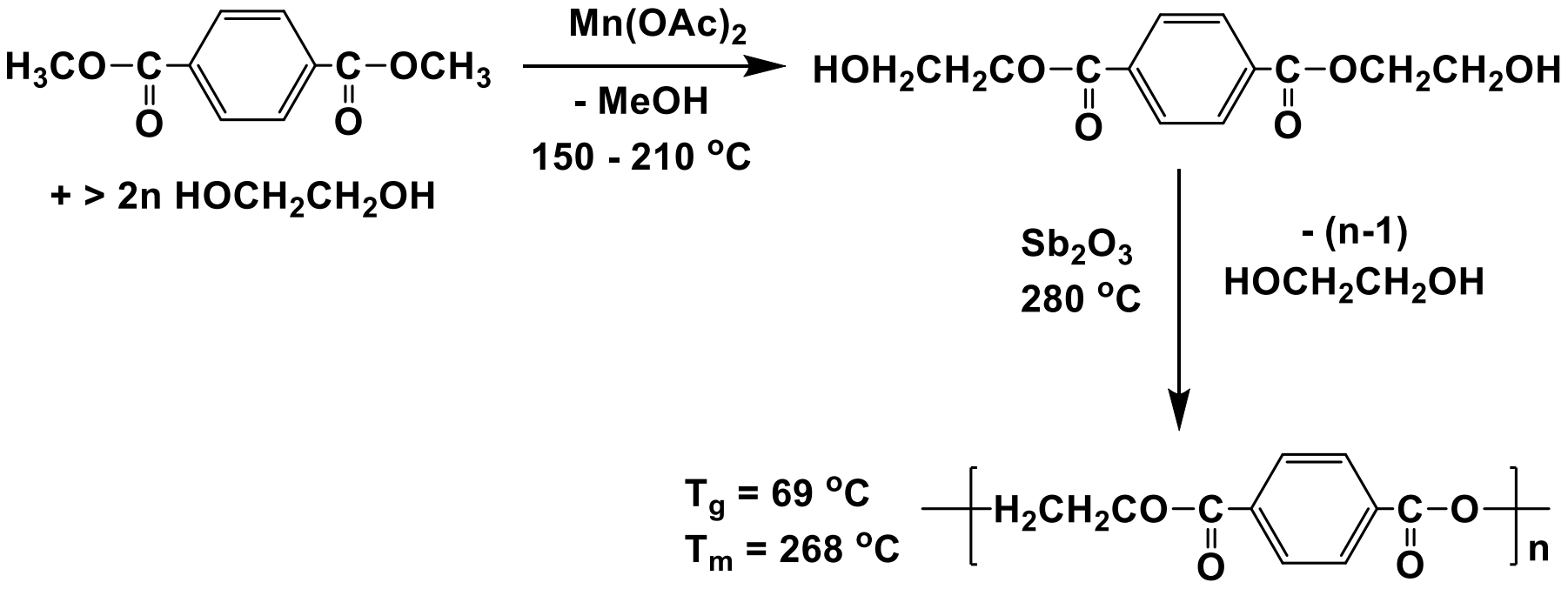
Equilibrium Constant (K)	p	X_n
1	0.500	2
16	0.800	5
81	0.900	10
361	0.950	20
9,800	0.990	100
39,600	0.995	200
249,000	0.998	500

$$DP_n = \frac{1}{1-p}$$

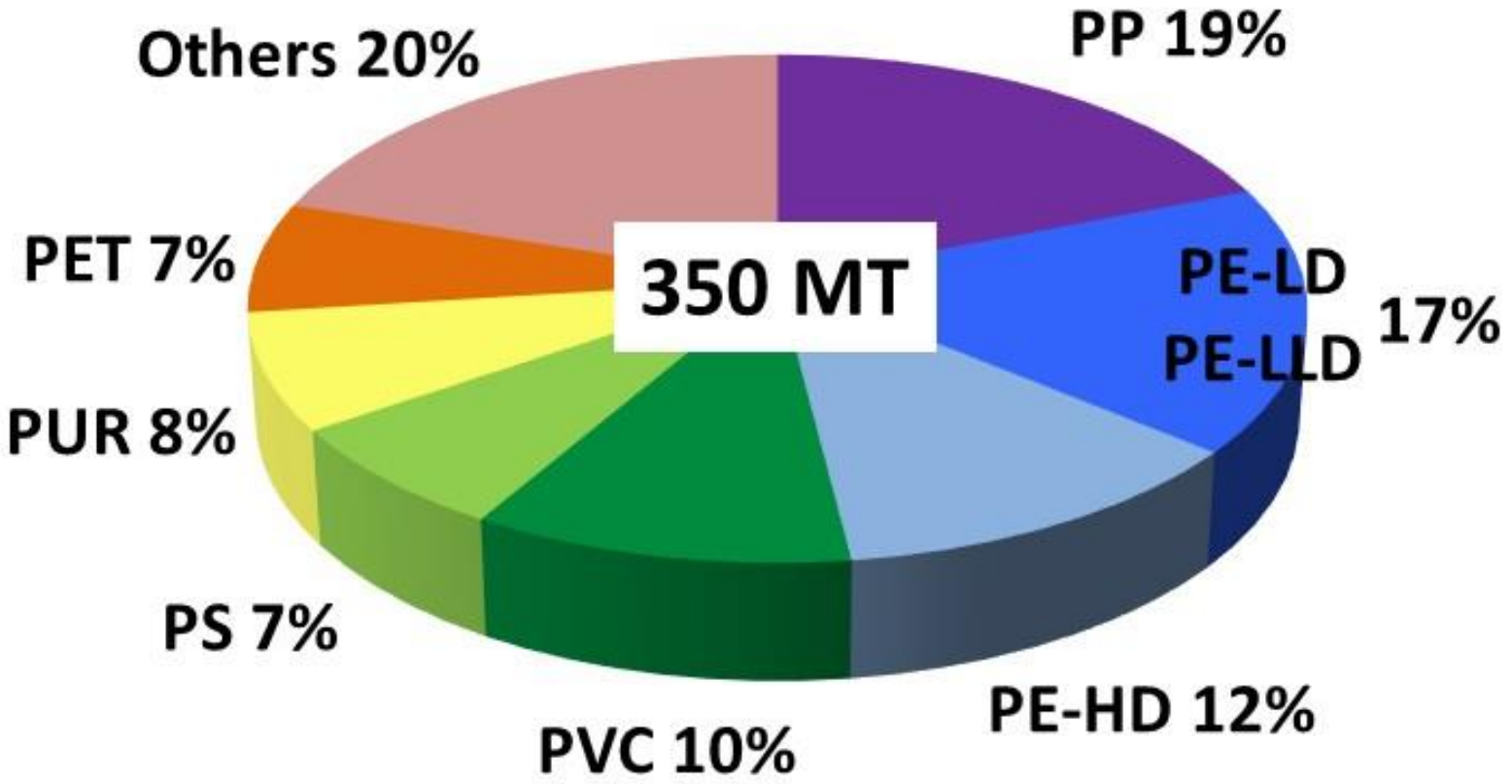
The co-product of the condensation must be removed to actually make a polymer !

Step-Growth Polymerization

Industrial Synthesis of PET

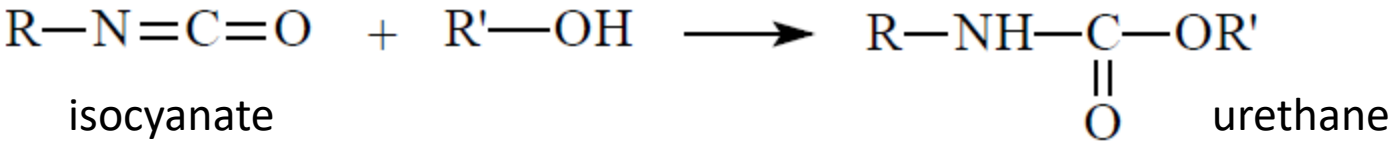


Step-Growth Polymerization



Step-Growth Polymerization

Polyurethanes



Addition => Polyaddition

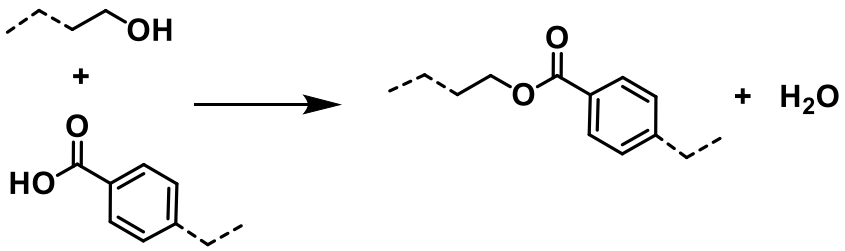
Applications : elastomers, adhesives, fibers (Lycra®), foams, paintings …

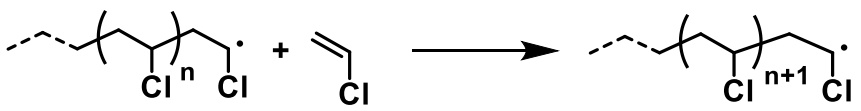
Polymers: Classification

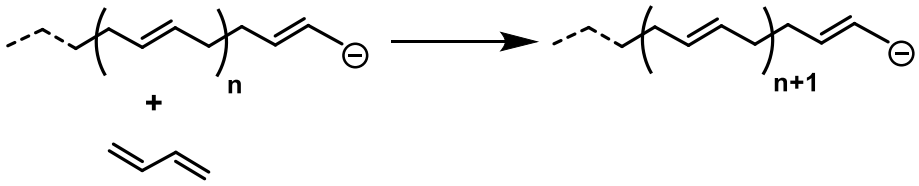
Type of chain growth

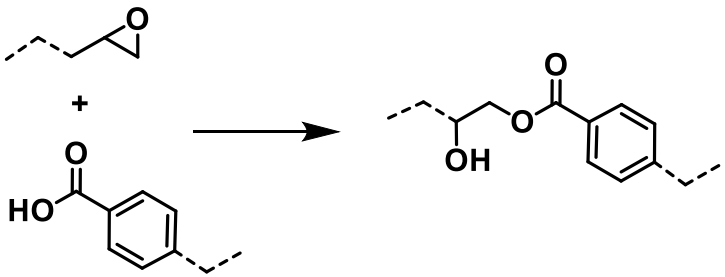
Step-growth polymerization :
Polycondensation, polyaddition

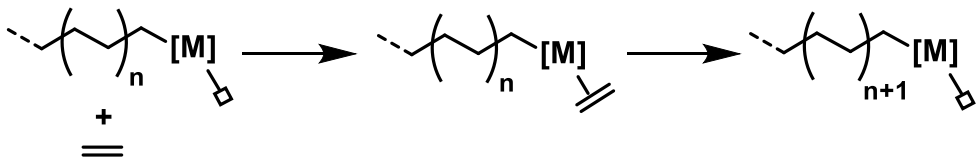
Chain-growth polymerization:
radical, ionic, coordination





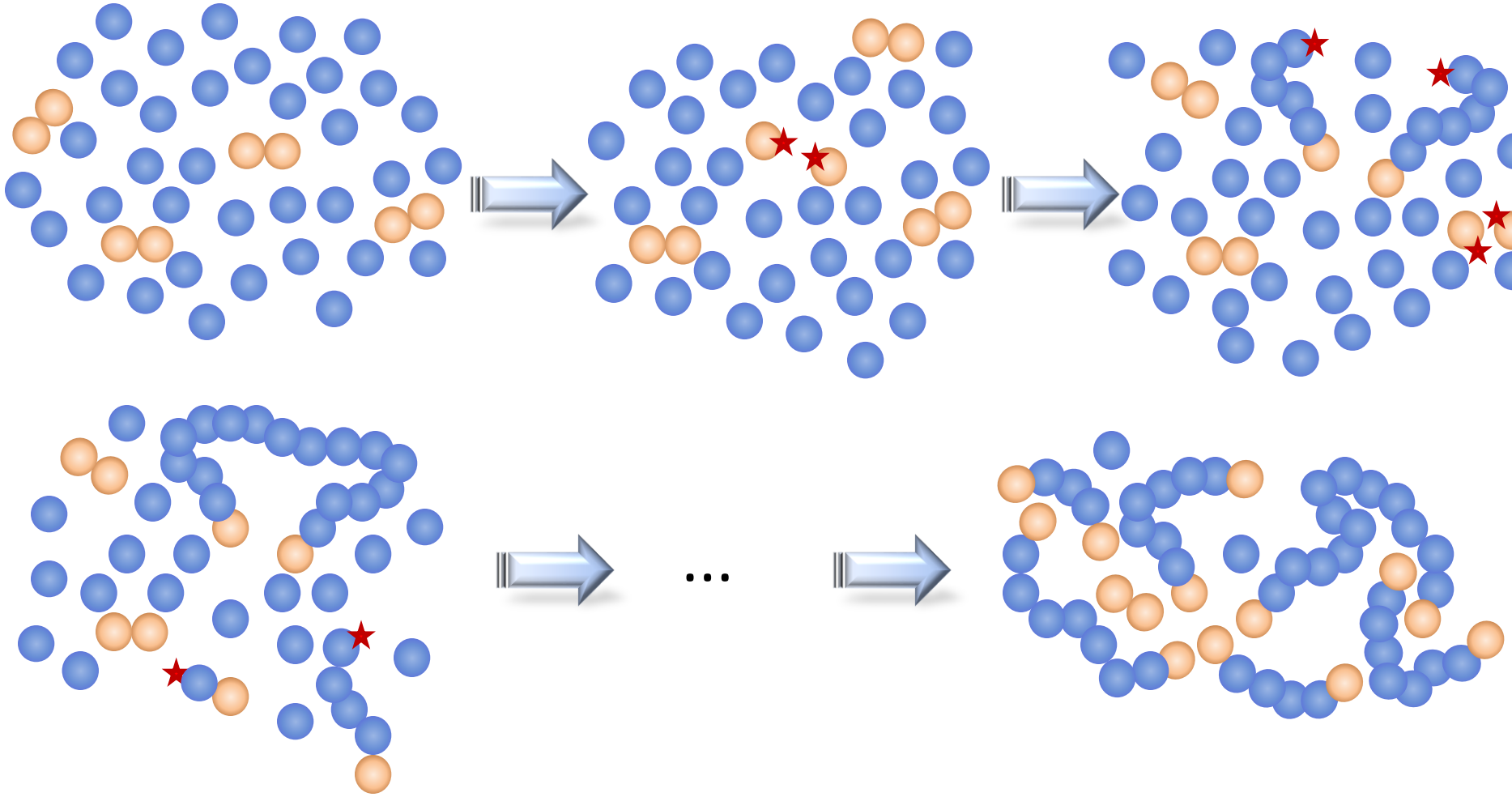






I. Overview

Free Radical Polymerization



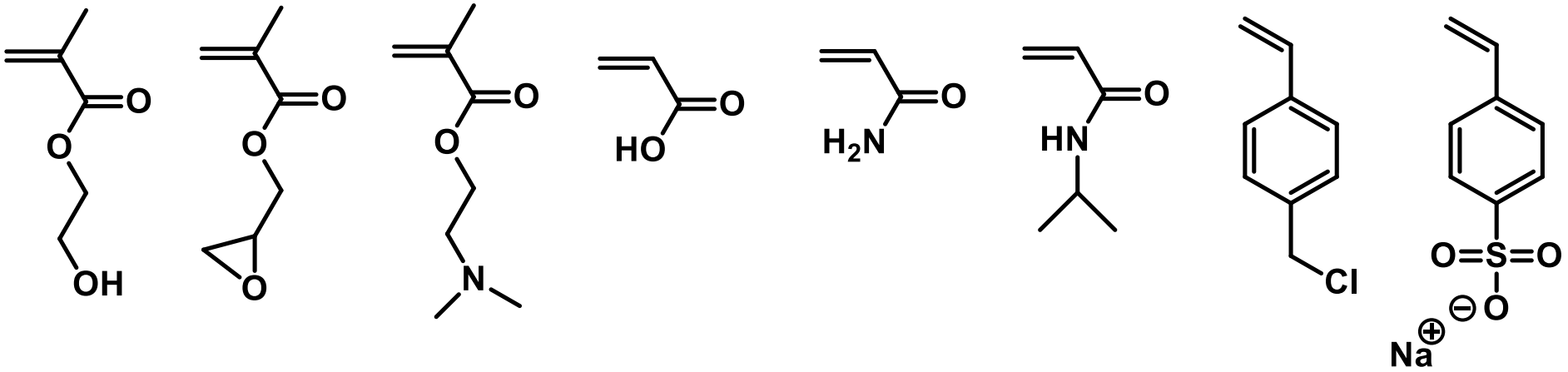
Around 50 % of synthetic polymers ⇔ radical process

- ✓ Monomers: C=C => large range of polymerizable monomers

Free Radical Polymerization

Around 50 % of synthetic polymers ⇔ radical process

- ✓ Experimental conditions (RT to 100 °C and +, AP or high pressure, water)
- ✓ Minimal purification of monomers and solvents (deoxygenating)
- ✓ Compatible with a large number of functional groups



=> solubility, proprieties, functionalization, crosslinking, ….

Free Radical Polymerization

Around 50 % of synthetic polymers ⇔ radical process

- ✓ Experimental conditions (RT to 100 °C and +, AP or high pressure, water)
- ✓ Minimal purification of monomers and solvents (deoxygenating)
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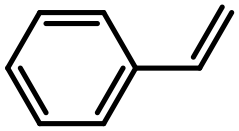
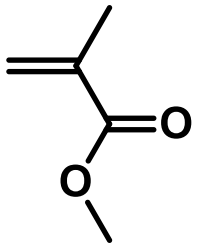
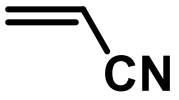
Standard Conditions *(to reach ~90% conv.)*



A. Styrene, bulk, N_2
125 °C, 1-2 days, $M_n \approx 100{,}000$



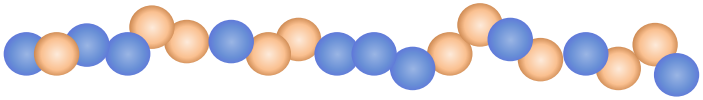
B. Methyl Methacrylate (MMA), solution, 0.5 % AIBN, N_2
1 day, 60 °C, $M_n \approx 100{,}000$



C. Acrylonitrile (AN), emulsion, H_2O, N_2, surfactant
$K_2S_2O_8/NaHSO_3$, 35 °C, 20 h, $M_n \approx 50{,}000$

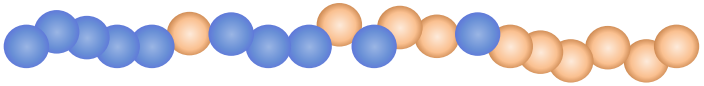
Copolymerization

- ✓ Monomers: C=C => large range of polymerizable monomers
- ✓ Compatible with a large number of functional groups
- ✓ Easy Copolymerization



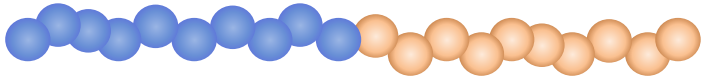
Statistical copolymer

FRP and CRP



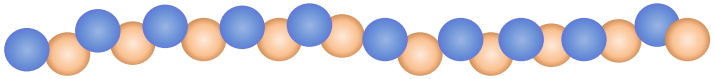
Gradient copolymer

CRP



Block copolymer

CRP (and FRP)



Alternating copolymer

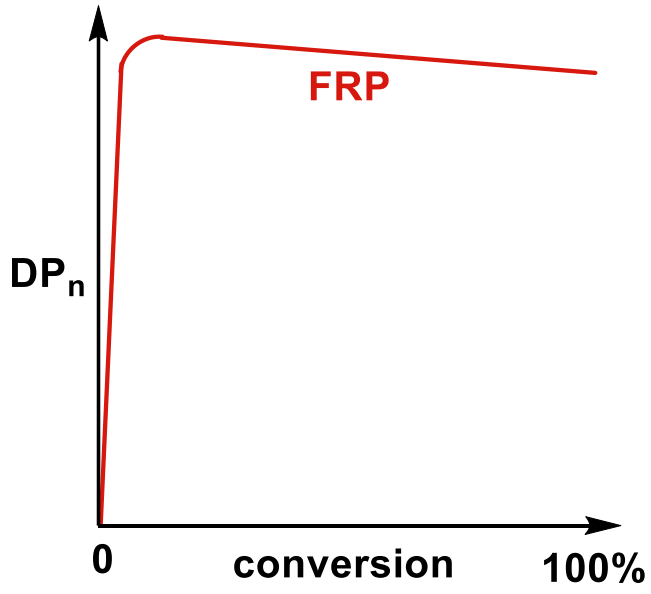
FRP and CRP

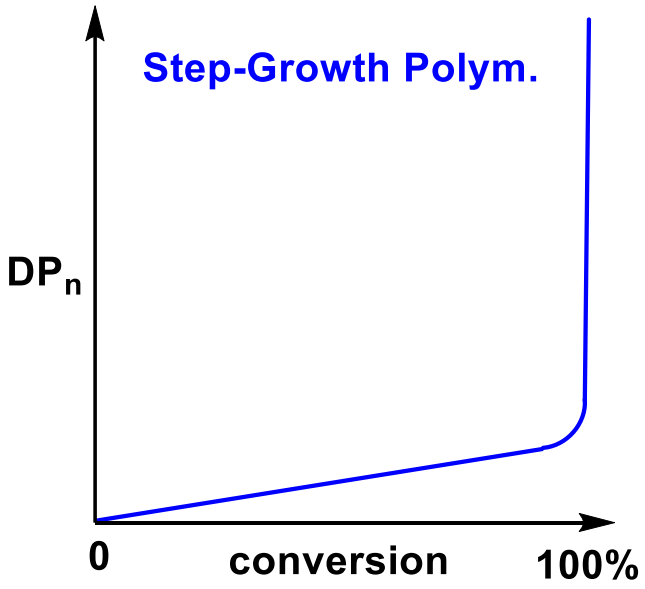
Free Radical Polymerization (FRP)

Controlled Radical Polymerization (CRP)

Free Radical Polymerization

- ✓ High molar masses from the very beginning (≠ step-growth polymerization)

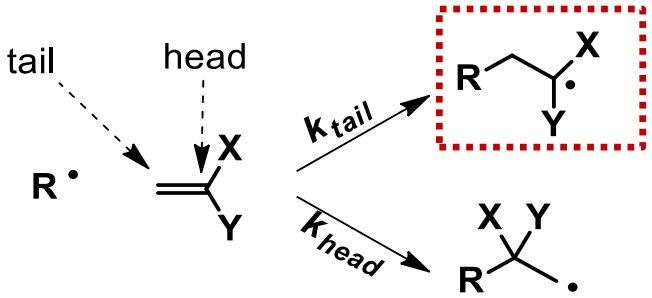




II. Radical Reactions & Reactivity

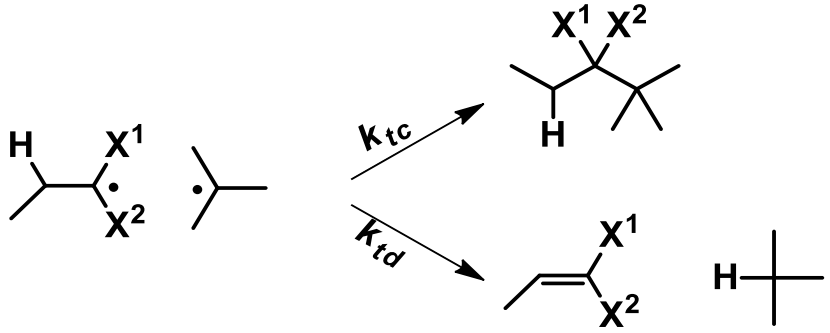
Elementary Radical Reactions

✓ Addition onto a carbon-carbon double bond *(initiation and propagation)*

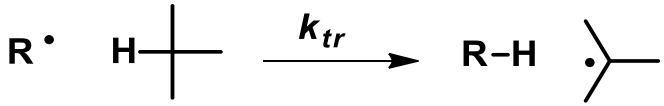


Vast majority

✓ Reaction between two carbon radicals *(termination)*



✓ Atom transfer, *e.g.* hydrogen *(chain transfer)*



Radicals' Reactivity

Which parameters influence the reactivity of the radicals?

✓ The stability of the radicals always increases with the degree of substitution

For example, alkyl radicals' stability : primary < secondary < tertiary

- One single exception : a fluorine substituent in α ou β position of a radical

(destabilization by electron-withdrawing inductive effect)

Radicals' Reactivity

Which parameters influence the reactivity of the radicals?

✓ Groups allowing the delocalization of the free spin stabilizes the radical

Most important criteria

adjacent π-bond >> heteroatoms with a lone pair of e-

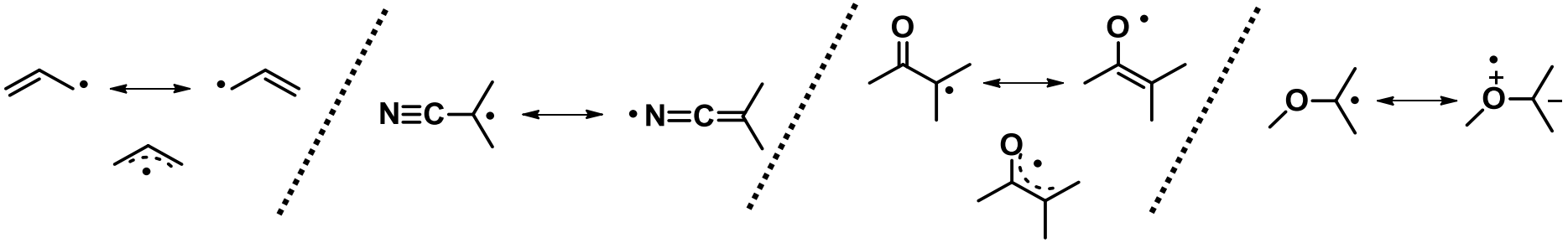
C=C, Ph, CN, COR >> N, O, Cl, …

- Valid for radicals carried by a saturated carbon (π radicals)

- Not valid for radicals carried by a saturated carbon (σ radicals)

Radicals' Reactivity

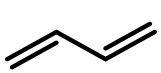
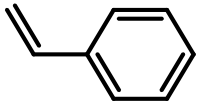
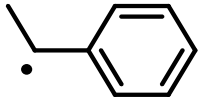
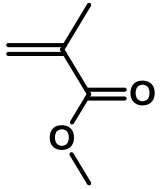
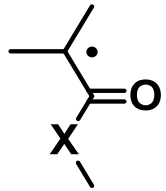
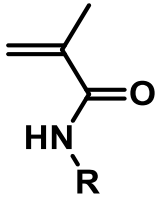
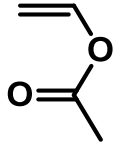
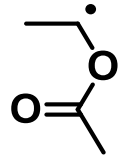
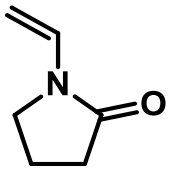
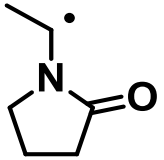
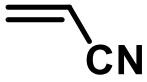
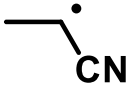
- Valid for radicals carried by a saturated carbon (π radicals)



- Not valid for radicals carried by a saturated carbon (σ radicals)

σ Radicals => no stabilization through delocalization on the π-system =>highly reactive radicals

Radicals' Reactivity: Polymerization

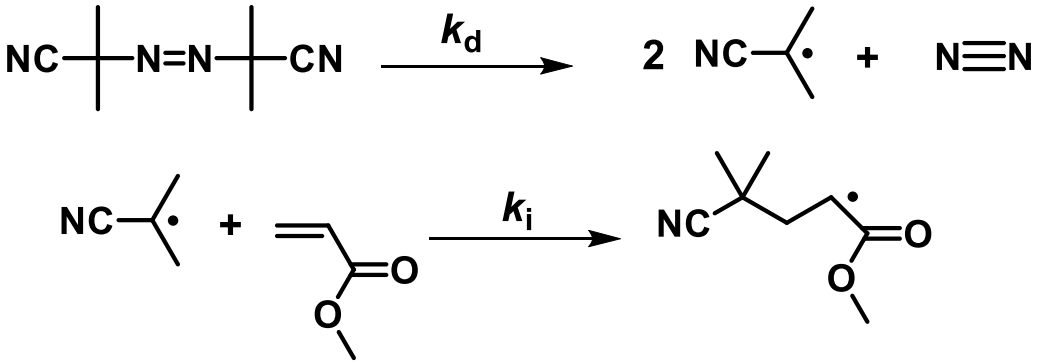
Monomers	Active species
1,3-Dienes	 
Styrene	 
Acrylates, methacrylates	 
Acrylamides, methacrylamides	
Vinylic esters	 
***N*-Vinylpyrrolidone**	 
Acrylonitrile	 

III. The Polymerization

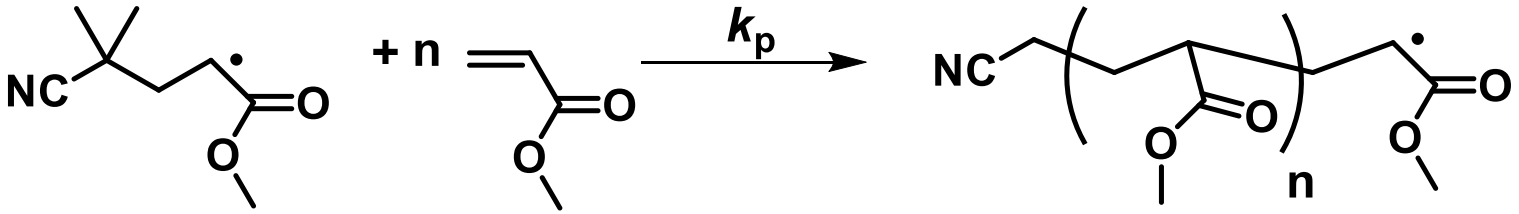
Free Radical Polymerization

Methyl acrylate polymerization initiated by AIBN

Initiation



Propagation

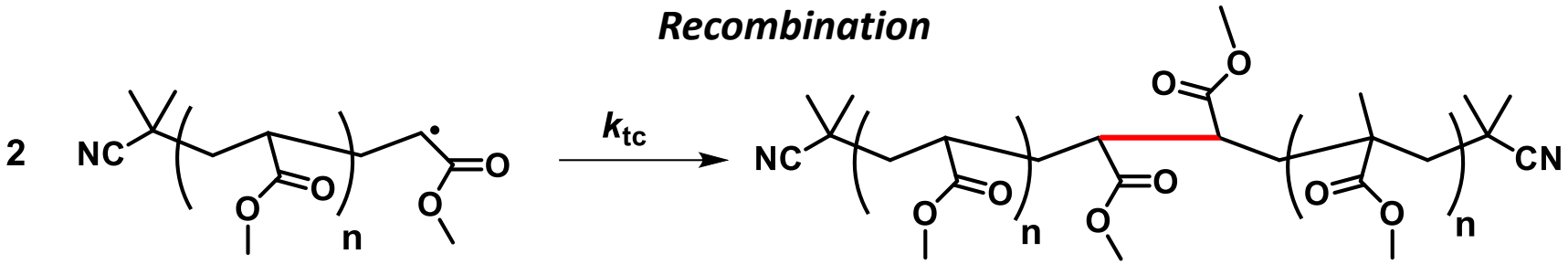


All these reactions take place during the entire process !

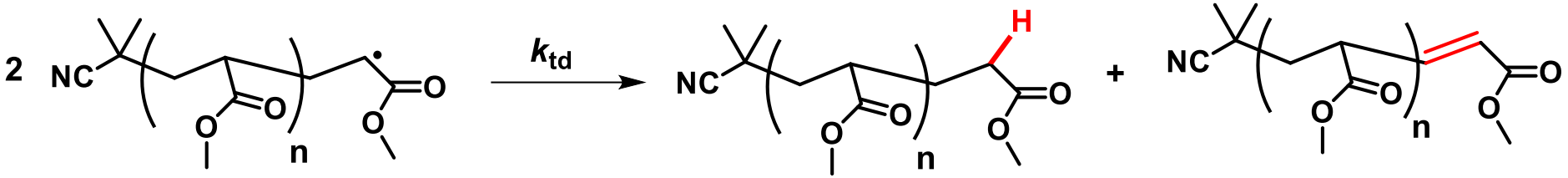
Free Radical Polymerization

Termination

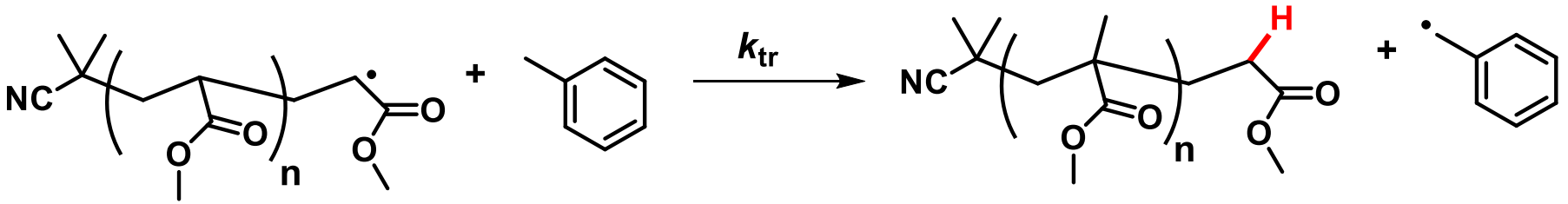
Recombination



Dismutation



Chain transfer: **not always and to different extent !**



All these reactions take place during the entire process !

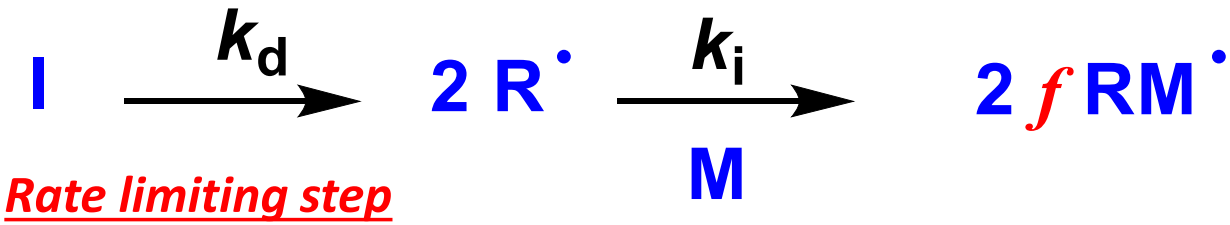
Initiation

$$I \xrightarrow{k_d} 2\,R^{\bullet}$$

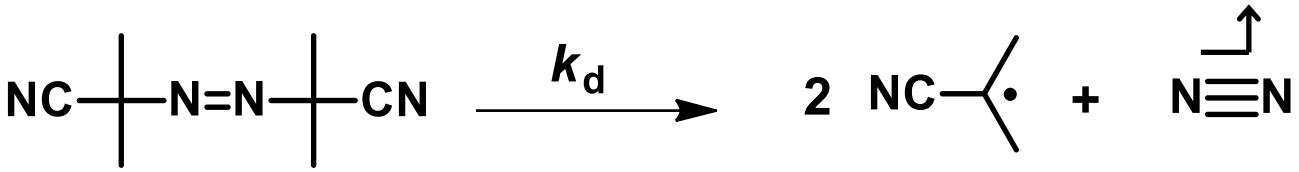
$$R^{\bullet} + M \xrightarrow{k_i} RM^{\bullet}$$

$$I \xrightarrow{k_d} 2\,R^{\bullet} \xrightarrow[M]{k_i} 2\,f\,RM^{\bullet}$$

Initiation: Radicals Formation



Exemple :



$$\frac{1}{2}\frac{d[R^\bullet]}{dt} = \frac{-d[I]}{dt} = k_d[I] \quad \Rightarrow \quad \ln\frac{[I]_0}{[I]_t} = k_d\ t$$

k_d ([s^{-1}]): decomposition rate constant;

Arrhenius's Law: $k_d = A\ e^{(\frac{-Ea}{RT})}$

Initiation: Radicals Formation

Polymerization : few hours

Initiation during the entire process

Half-lif time, $\tau_{1/2}$

$\tau_{1/2}$ = time after which half of the initiator has been decomposed

$\tau_{1/2}$ = 10 h

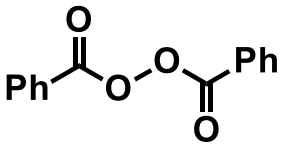
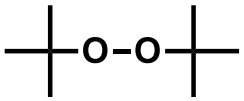
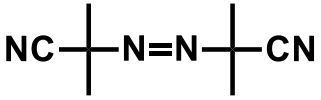
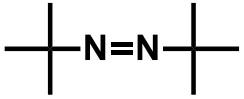
- 10 h, 50% of the initiator has been consumed
- 20 h, 75% of the initiator has been consumed
- 30 h, 87.5% of the initiator has been consumed

$$\ln \frac{[I]_0}{[I]_t} = k_d \, t$$

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

Initiation: Radicals Formation

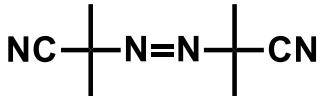
Few examples of thermal initiators

Initiator	Typical operation temperature (°C)	k_d (60°C) (s^{-1})	E_a (60°C) (kJ mol^{-1})	A (x 10^{-15}) (s^{-1})	$\tau_{1/2}$ = 10 h (°C)
	70-90	1.5 x 10^{-6}	139	9.34	78
	110-135	2.5 x 10^{-9}	152.7	2.16	125
	50-80	9.6 x 10^{-6}	131.7	4.31	65
	150-180	5.0 x 10^{-12}	180.4	91.7	161

Initiation: Radicals Formation

Effect of the temperatures on the rate of decomposition

AIBN

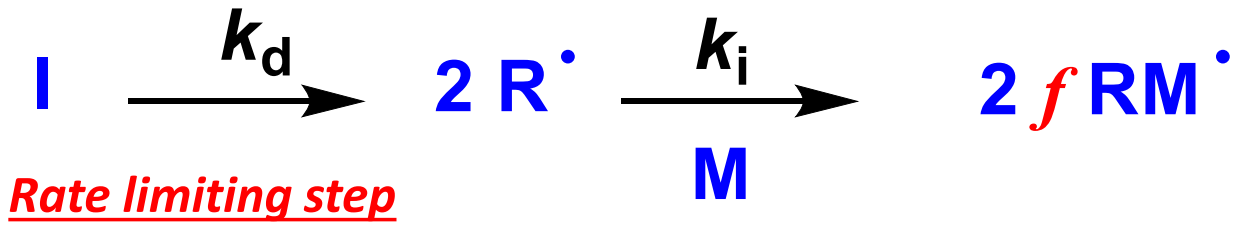
Amorceur	Température d'utilisation (°C)	k_d (60°C) ($M^{-1}s^{-1}$)	E_a (60°C) (kJ mol^{-1})	A (x 10^{-15}) (s^{-1})	$\tau_{1/2}$ = 10 h (°C)
	50-80	9.6×10^{-6}	131.7	4.31	**65**

AIBN : - **80 °C ; $t_{1/2}$ = 1h22 (94 % of the initiator has decomposed after 5h30)**

- **100 °C ; $t_{1/2}$ = 7min25sec (94 % of the initiator has decomposed after 30 min)**

- **45 °C ; $t_{1/2}$ = 8j (94 % of the initiator has decomposed after 32 days)**

Initiation: Radical Addition onto M



f : efficiency factor

Proportion of radicals generated by the initiator that actually initiate a polymer chain

$0 \leq f \leq 1$

Typically : $f = 0{,}3 - 0{,}8$ (cage effect)

Efficiency Factor depends on: initiator, M, T, solvent, conversion,…

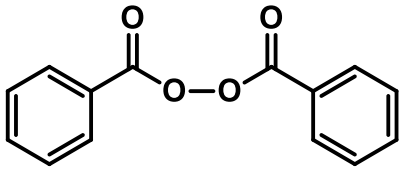
Rate of Initiation

$$v_i = \frac{d[RM^\bullet]}{dt} = 2 f \; k_d[I]$$

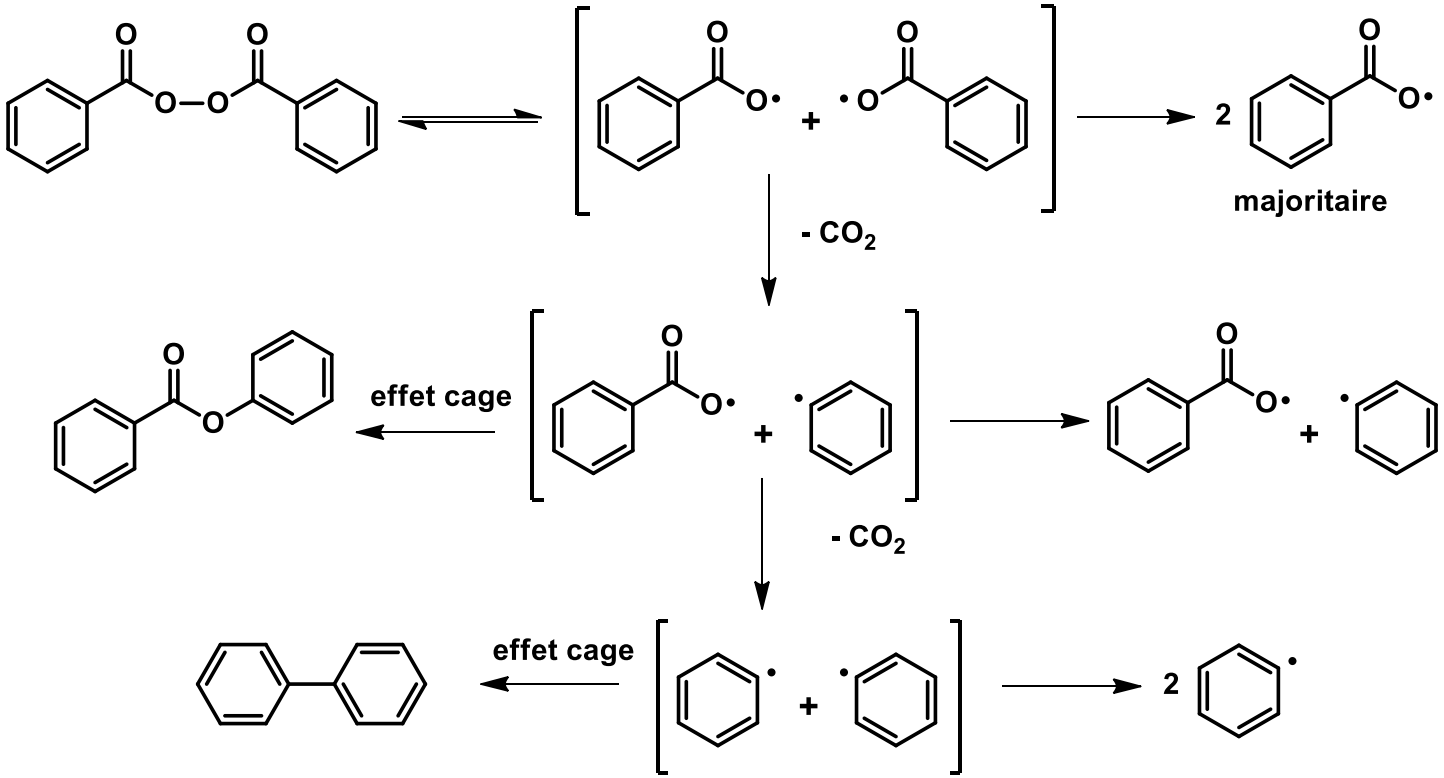
[mol/(L.s)]

Thermal Initiator - Peroxides

Benzoyle Peroxide
T_{10H} = 78 °C

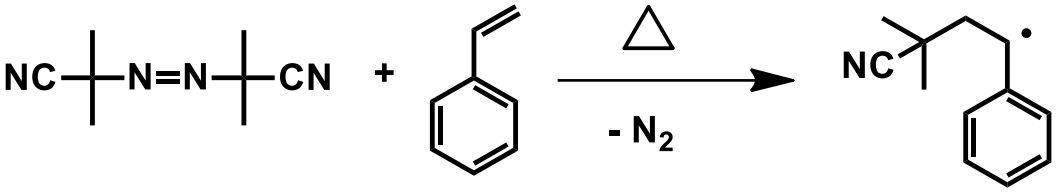


Thermal decomposition mechanism: cage effect



Thermal Initiator - Azo

Efficiency Factor= f (initiator, M, T, solvent, conversion,…)



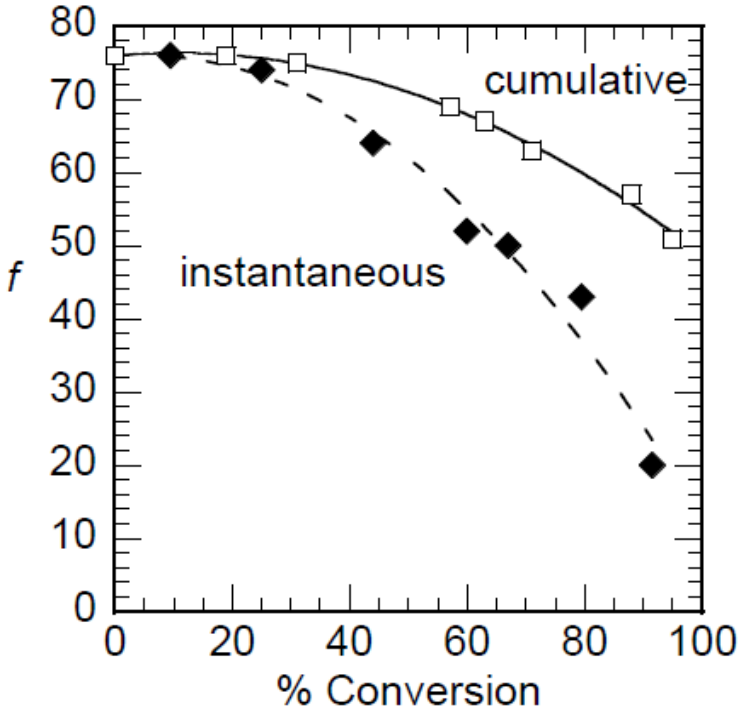
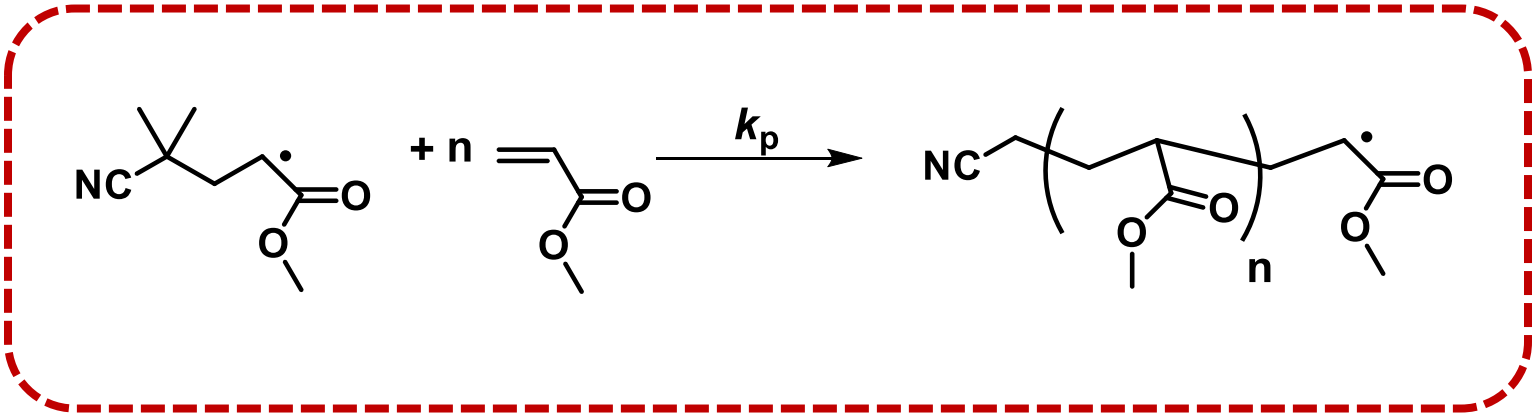


Figure 3.3 Cumulative (□) and instantaneous (◆) initiator efficiency (*f*) of AIBN as initiator in S polymerization (50% v/v toluene, 70 °C) as a function of monomer conversion (lines are a polynomial fit to the datapoints).[1,32]

G. Moad, D. H. Solomon, *The Chemistry of Radical Polymerization, 2nd edn 2006 (Elsevier: Oxford)*

Free Radical Polymerization: Propagation

Propagation

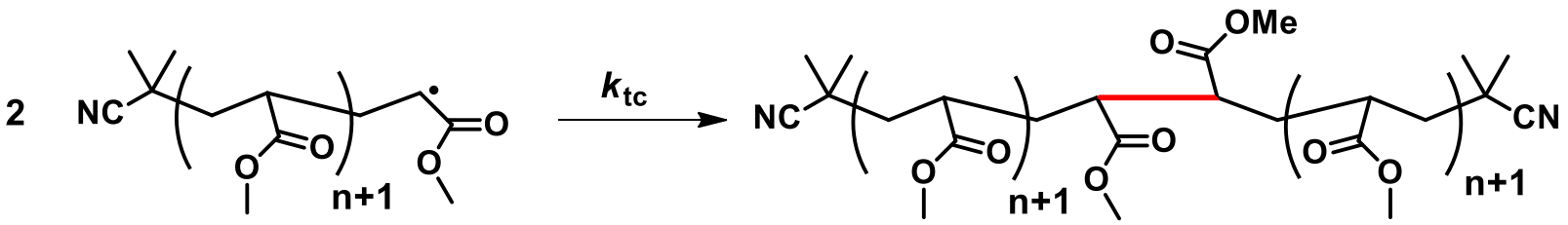


$$v_p = \frac{-d[\mathrm{M}]}{dt} = k_p\,[\mathrm{RM}^{\bullet}][\mathrm{M}] \qquad \text{[mol/(L.s)]}$$

Free Radical Polymerization: Termination

Termination reactions : diffusion control

✓ Recombination

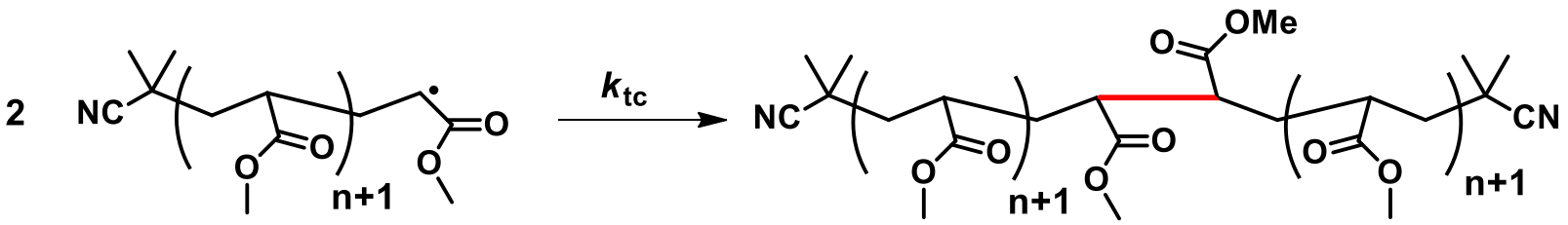


✓ Dismutation

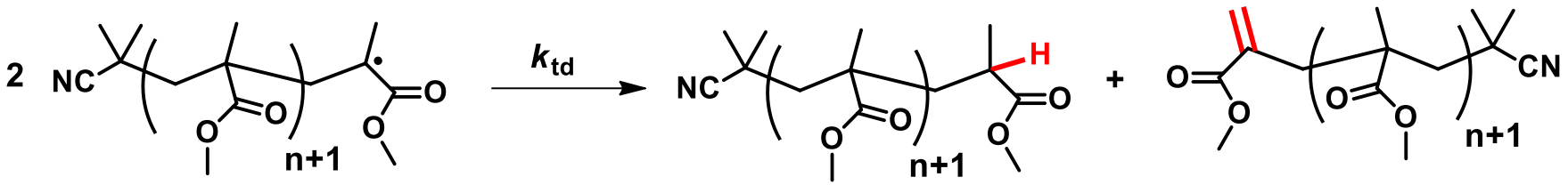
Free Radical Polymerization: Termination

Termination reactions : diffusion control

✓ Recombination



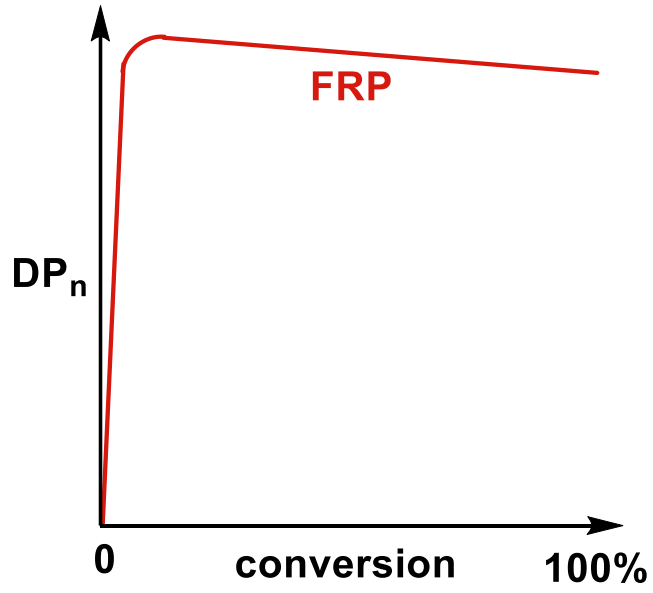
✓ Dismutation



$$v_t = \frac{-d[RM^\bullet]}{dt} = 2\,k_t\,[RM^\bullet]^2 \quad \text{[mol/(L.s)]}$$

Free Radical Polymerization

- ✓ High molar masses from the very beginning (≠ step-growth polymerization)



$$P = \frac{v_p}{v_p + v_t + v_{tr}} \qquad DP_n = \frac{1}{1 - P}$$

- ✓ **Termination reactions: diffusion control**
- ✓ **Average lifetime of propagating radicals (i.e. of a growing chain) ~1s**
- ✓ **Rate of addition: a propagating radical reacts with a monomer every ~1ms**
- ✓ **DP ~ 1 000 ⇔ M_n ≈ 100 000 g/mol => polymer size limited and poorly controlled**

Free Radical Polymerization: Steady-state

1. Initiation

$$I \xrightarrow{k_d} 2\,R^{\bullet}$$

$$R^{\bullet} + M \xrightarrow{k_i} RM^{\bullet}$$

2. Propagation

$$RM^{\bullet} + M \xrightarrow{k_p} RM_2^{\bullet}$$

$$RM_2^{\bullet} + n\,M \xrightarrow{k_p} RM_{n+2}^{\bullet}$$

3. Termination

$$R_n^{\bullet} + R_p^{\bullet} \xrightarrow{k_t} R_{n+p}$$

$$R_n^{\bullet} + R_p^{\bullet} \xrightarrow{k_t} R_n^{//} + R_p^{H}$$

✓ **Steady-state: [R •] = const. => $R_i = R_t$**

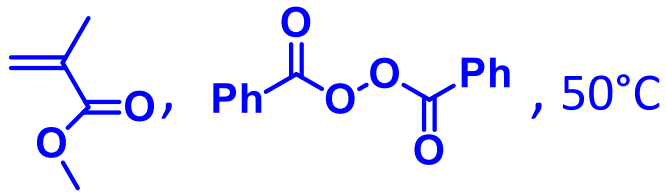
$$v_i = \frac{d[RM^{\bullet}]}{dt} = 2\,f\,k_d[I] \qquad v_t = \frac{-d[RM^{\bullet}]}{dt} = 2\,k_t\,[RM^{\bullet}]^2$$

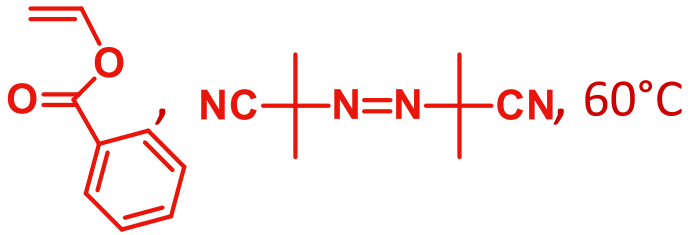
$$2\,f k_d[I] - 2k_t[RM^{\bullet}]^2 = 0 \quad \Rightarrow \quad [RM^{\bullet}] = \sqrt{\frac{2\,f\,k_d[I]}{2k_t}}$$

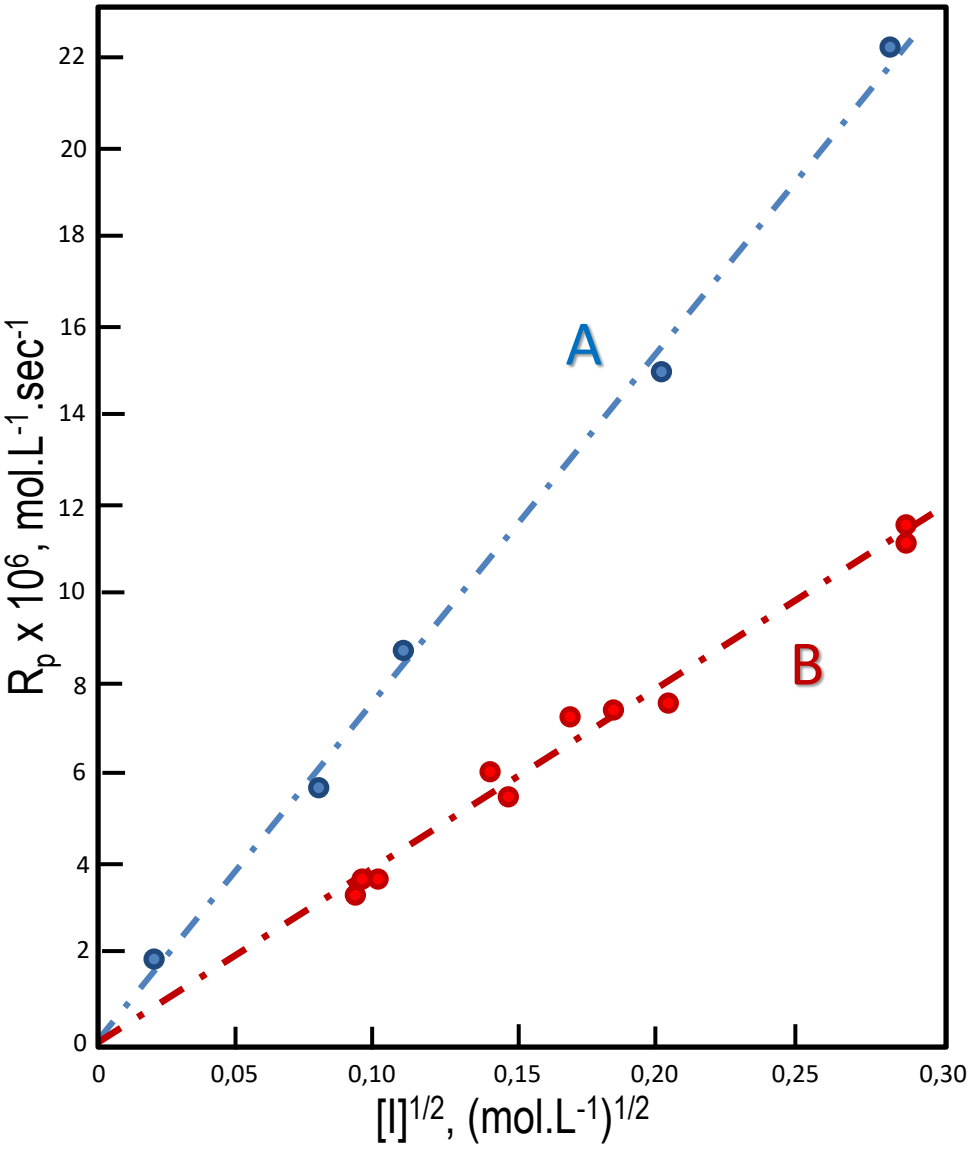
$$v_p = \frac{-d[M]}{dt} = k_p\,[RM^{\bullet}][M] = k_p \sqrt{\frac{2\,f\,k_d[I]}{2k_t}}[M]$$

Free Radical Polymerization: Steady-state

$$v_p = \frac{-d[M]}{dt} = k_p\,[M]\sqrt{\frac{2f\,k_d[I]}{2k_t}}$$

A :  , 50°C

B :  , 60°C



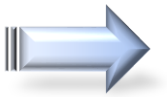
G. Odian, *The Chemistry of Radical Polymerization, 4th edn 2004 (John Wiley & Sons Inc)*

Degree of Polymerization (in the absence of transfer)

DP_n : number-average degree of polymerization

DP_n = Average number of monomer unit per chain

$$DP_n = \frac{\text{total number of m.u. polymerized}}{\text{total number of macromolecules formed}}$$



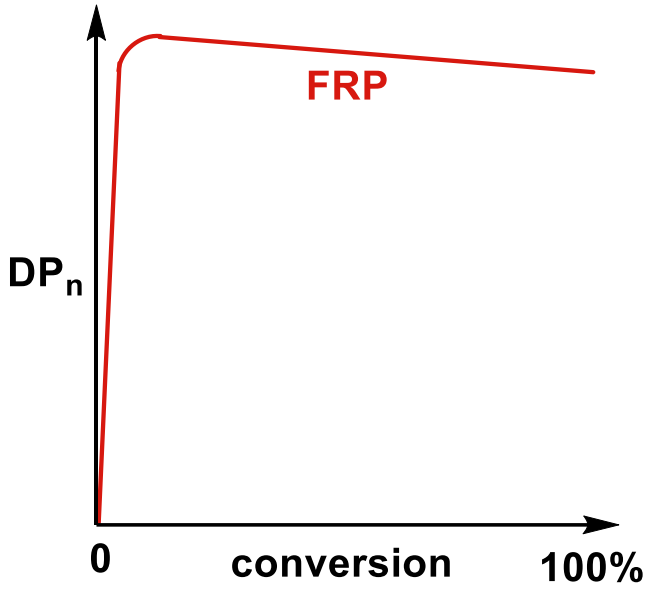
$$M_n = DP_n . M_M$$

DP_0 : number-average degree of polymerization in the absence of transfer reactions

$$DP_0 = \frac{[M]_0 . x(t)}{(2) f ([I]_0 - [I]_t)} = \frac{[M]_0 . x(t)}{(2) f [I]_0 (1 - e^{-k_d . t})}$$

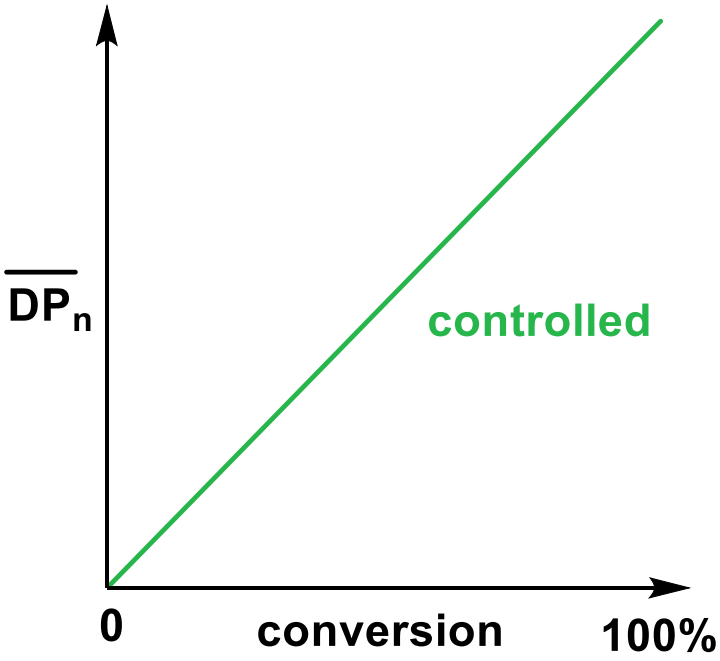
- factor 2 if termination by dismutation

From Free to Controlled Radical Polymerization



$$P = \frac{v_p}{v_p + v_t + v_{tr}} \qquad DP_n = \frac{1}{1 - P}$$

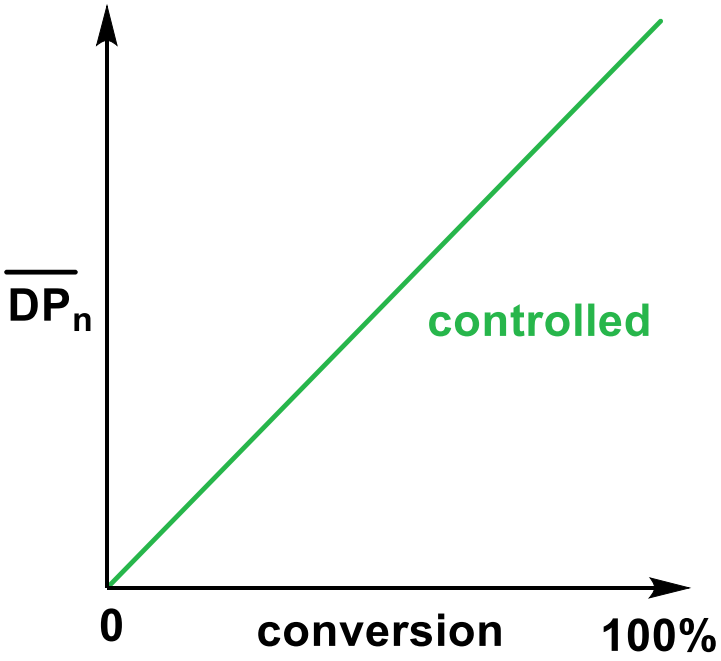
$$\overline{DP}_n = \frac{[M]_0 \, conv.}{[I]}$$



From Free to Controlled Radical Polymerization

- Fast and quantitative initiation at the early stage of the polymerization
  - ✓ $V_i \geq V_p$
- Constant number of growing polymer chains
  - ✓ $[I]_0 = [I]_t$ = concentration of growing chains
- Limit termination reactions
  - ✓ low [P•]

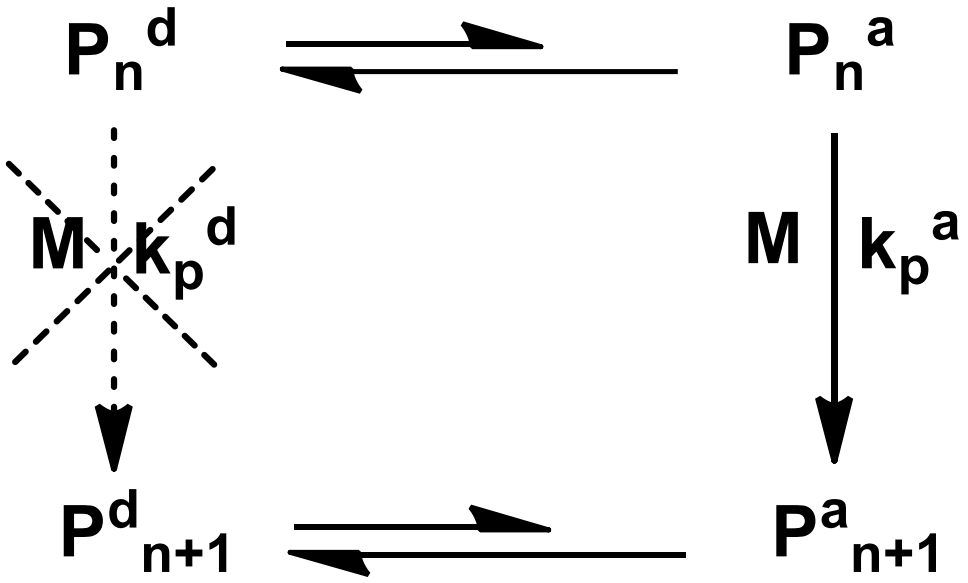
$$\overline{DP}_n = \frac{[M]_0 \, conv.}{[I]}$$



Controlled Radical Polymerization

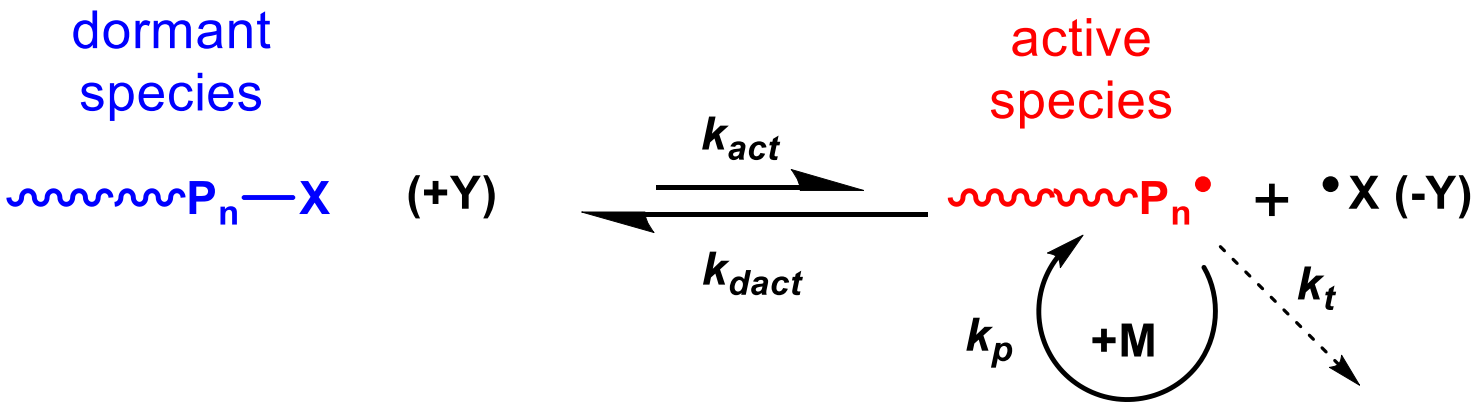
2 types of polymer chains in equilibrium:

dormant and active species



[Polymer chains] = [dormant polymer chains] + [active polymer chains]

Controlled Radical Polymerization



Thermodynamics

$$K = \frac{k_{act}}{k_{dact}} \approx 10^{-5} - 10^{-8}$$

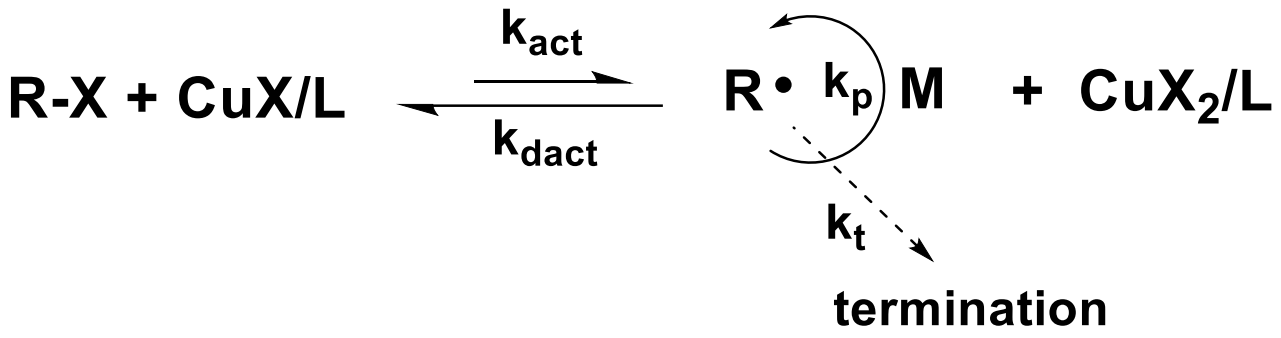
Limit termination reactions

Kinetics

Fact equilibrium (as compared to propagation)

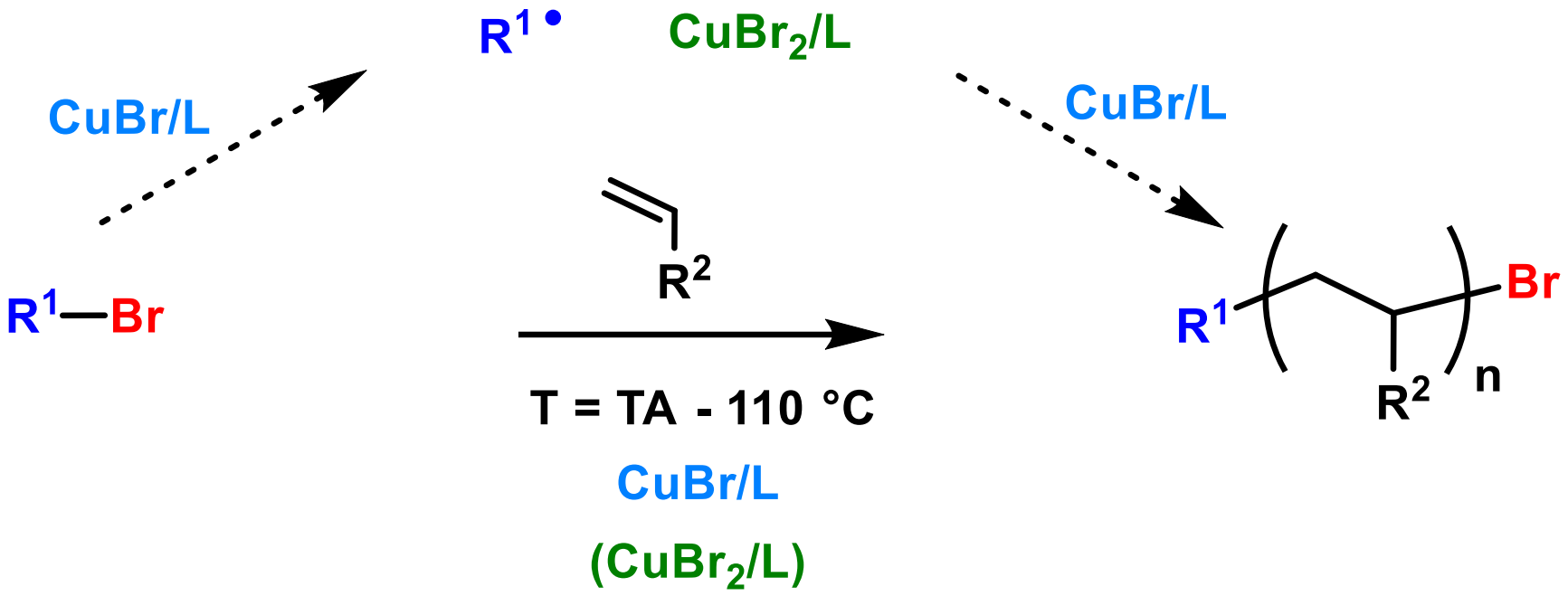
Homogeneous growth of all polymer chains

Atom Transfer Radical Polymerization (ATRP)



Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* 1995, *117*, 5614
Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, *28*, 1721

Atom Transfer Radical Polymerization (ATRP)



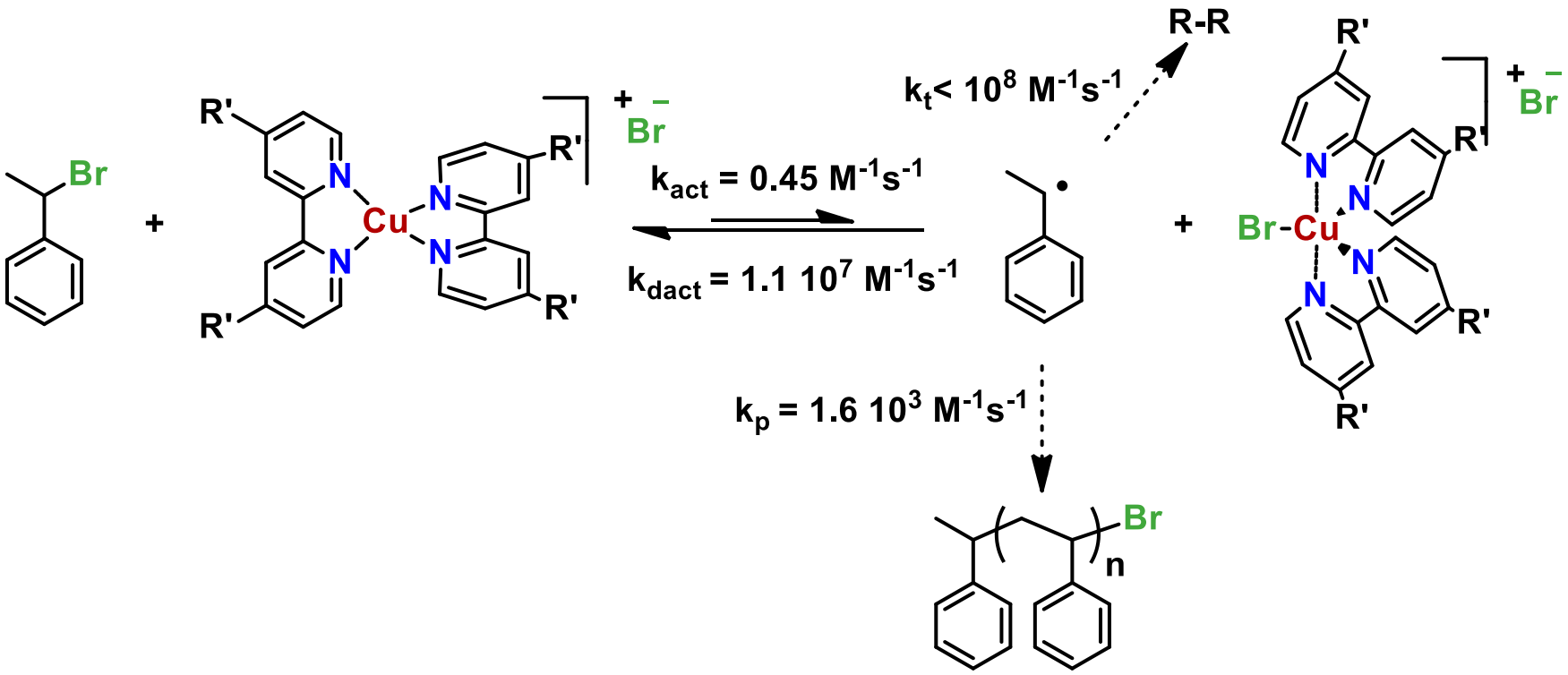
$$DP_n = \frac{[M]_0 \times conv}{[RX]_0}$$

$$M_n = M_{RX} + \frac{[M]_0 \times conv}{[RX]_0} \times M_M$$

Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* 1995, *117*, 5614

Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, *28*, 1721

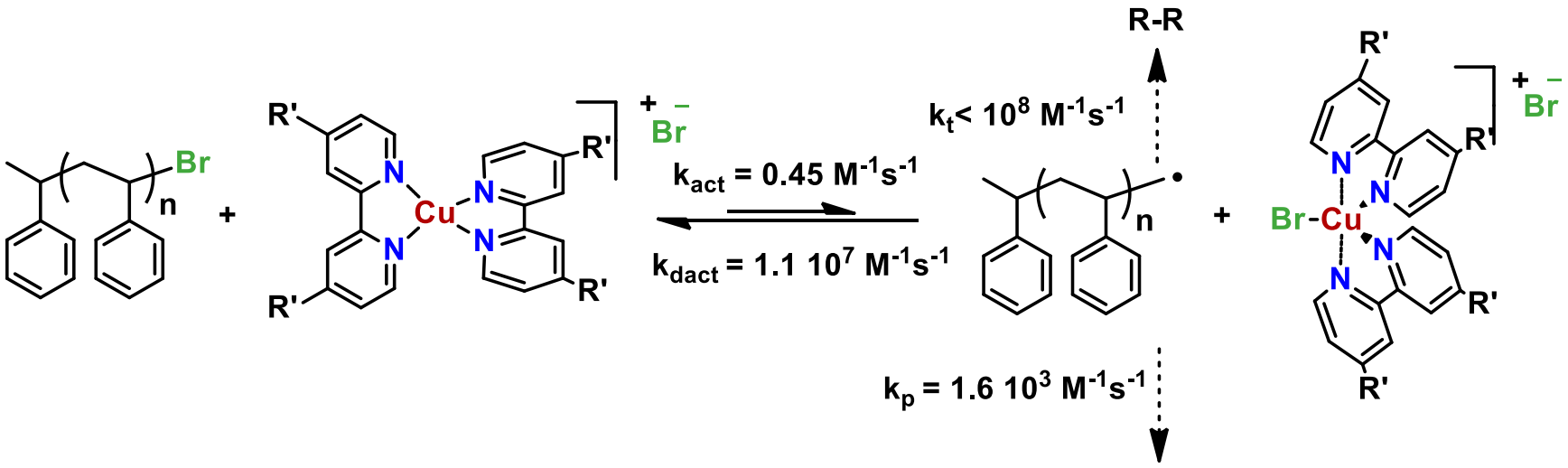
ATRP: Styrene, CuBr/dNby, 110 °C, in bulk



- St/PEtBr/CuBr/dNbpy = 100:1:1:2 =>$[Cu(II)]_{st}$ ≈ 5%
- Polystyrene: M_n ≈ 10,000 g/mol; M_w/M_n ≈ 1.05; P_n-Br » 95%

Matyjaszewski, K. et al. *J. Am. Chem. Soc. 1997,* 119, 674; *Macromolecules 1998,* 31, 548; *Macromolecules 1998,* 31, 2699

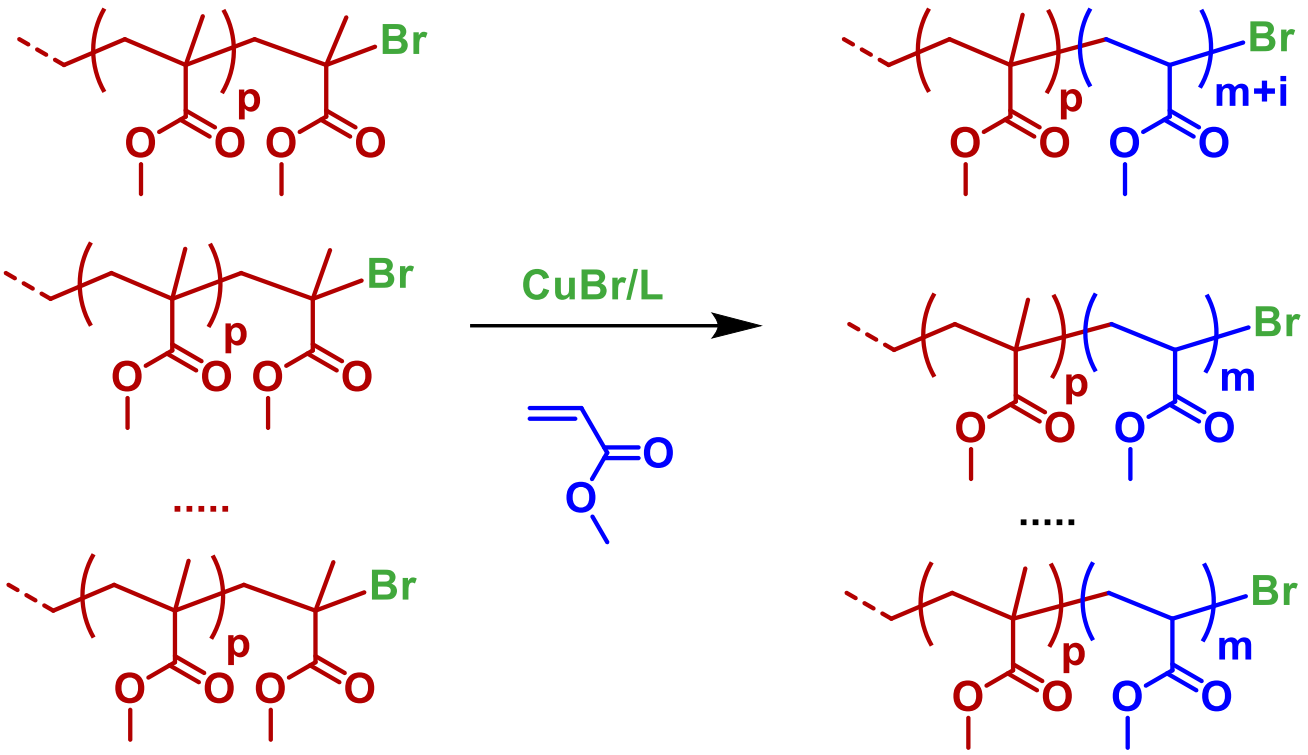
ATRP: Styrene, CuBr/dNby, 110 °C, in bulk



- Frequency of molecular events at chain end; $\tau = 1/(k\,[C])$
  - activation: τ = **22** s
  - propagation: τ = 0.12 ms
  - deactivation: τ = 0.018 ms (**~6** times faster than propagation !)
  - termination: τ = 0.1 s (**~ 800** times slower than propagation !)
- Thus, chain wakes up every **20 s**, adds monomer only every 120 s (**2 min**; i.e. 3 h needed for DP=100) & dies after 100,000s (**30 h**)

ATRP: Block Copolymers

Successive polymerization of two monomers

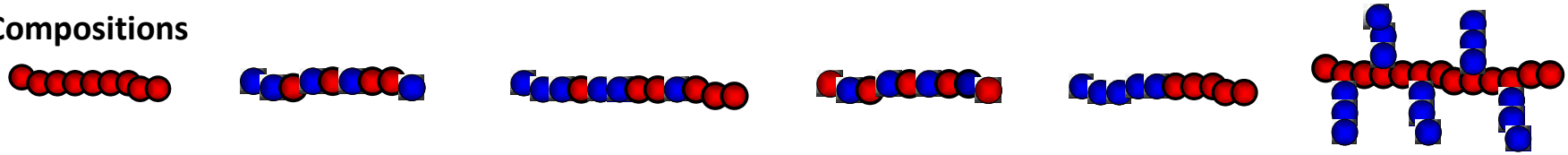


Macromolecular Engineering

Size and distribution : **$200<M_n<10^6$ (or more if needed) ; $1.01<M_w/M_n<$**

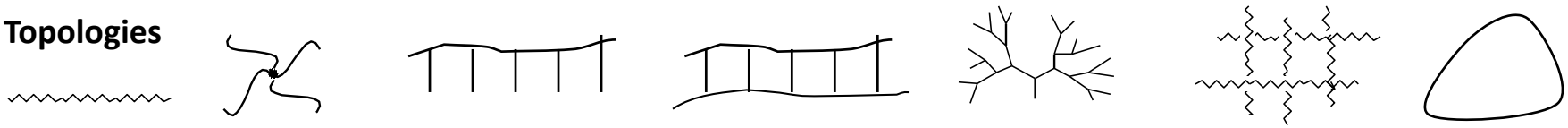
Tacticity : **isotactic, syndiotactic, atactic => crystallinity**

Compositions



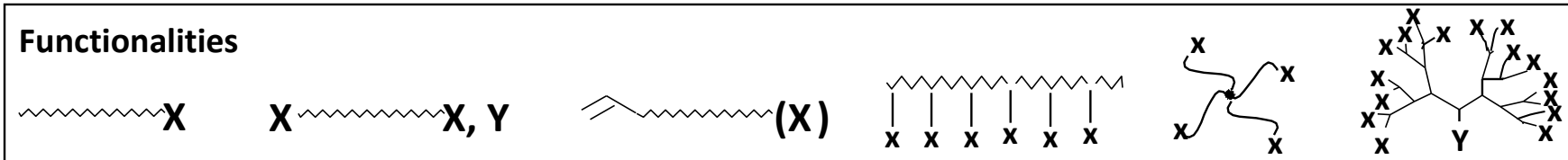
Homopolymer | Statistical copolymer | Gradient copolymer | Alternated copolymer | Block copolymer | Grafted copolymer

Topologies



Linear | Star | Brush | Ladder | Hyperbranched Dendrimer | Network/Gel | Cyclic

Functionalities



Monofunctional | Homo/Hetero T elechelic | Macromonomer | Functional Brush | Functional Star | Functional Hyperbranched

Systems: **bulk, solution (org., H_2O, CO_2), emulsion, suspension**