Advanced Polymer Synthesis

Tutorial on Macromolecular Engineering

ENB Elite Study Program “Macromolecular Science”
Lecture on August 28, 2007

UNIVERSITÄT
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Tutorial on Macromolecular Engineering

A. Mechanisms of Living Polymerization

B. Synthesis and Properties of Block Copolymers

Literature

Mechanisms:

G. Odian: "*Principles of Polymerization*", 4th Ed., Wiley, New York 2004

Mark-Bikales-Overberger-Menges, Eds.: "*Encyclopedia of Polymer Science and Engineering*", 2nd Ed., Vol 1-17+ Suppl. , Wiley, New York, 1985-89. *Contains numerous review articles from* "Anionic Polymerization" (Vol. 2, p. 1) *via* "Living Polymer Systems" (Suppl. Vol., p. 380) *to* "Zwitterionic Polymerization" (Vol. 17, p. 1028).

G. Allen, J.C. Bevington, Eds.: "*Comprehensive Polymer Science*", Vol. 3+4: Chain Polymerization, Pergamon Press, Oxford 1989 *(very detailed review articles on mechanisms and properties)*

Macromolecular Engineering in general:

G. Allen, J.C. Bevington, Eds.: "*Comprehensive Polymer Science*", Pergamon Press, Oxford 1989; Vol. 6, chapters 8-13 (p. 227-436), Vol. 7, chapter 1, Suppl. Vol. 1 (1992); p. 83-106

H.L. Hsieh, R.P. Quirk: "*Anionic Polymerization: Principles and Practical Applications*", Marcel Dekker, New York 1996

Y. Gnanou: "*Design and Synthesis of New Model Polymers", J. Macromol. Sci.-Rev. Macromol. Chem. Phys*., **C36**, 77 (1996)

J. C. Salamone (Ed.): *Polymeric Materials Encyclopedia*, CRC Press, Boca Raton (1996)

K. Hatada, T. Kitayama, Eds.: "*Macromolecular Design of Polymeric Materials*", M. Dekker, New. York, 1997

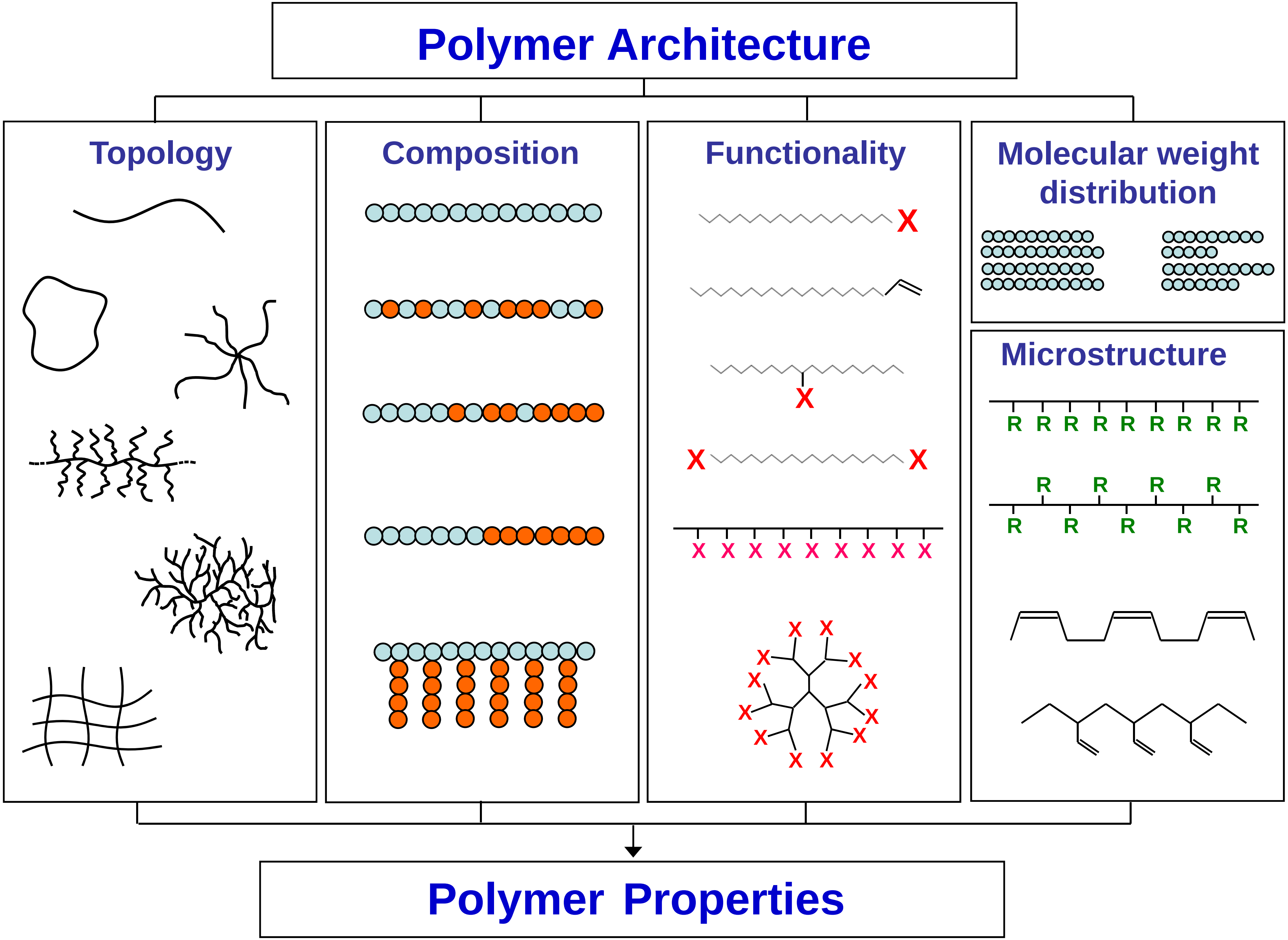
K. M. Stridsberg, M. Ryner, A.C. Albertsson: *”Controlled Ring-Opening Polymerization: Polymers with Designed Macromolecular Architecture*” Adv. Polym. Sci. **157**, 42 (2002)

Block copolymers:

I.W. Hamley, “*The Physics of Block Copolymers*”, Oxford University Press 1998

M. Pitsikalis, S. Pispas, J.W. Mays, N. Hadjichristidis, "*Nonlinear Block Copolymer Architectures*, Adv. Polym. Sci. **134**, 1 (1998)

N. Hadjichristidis, S. Pispas, G. A. Floudas, “*Block Copolymers: Synthetic Strategies, Physical Properties, and Applications*”; Wiley-Interscience, 2003



Polymer Architecture

Topology

Composition

Functionality

Molecular weight distribution

Microstructure

Polymer Properties

Part A:

Mechanisms of Living Polymerization

- **Anionic Polymerization**
- **Cationic Polymerization**
- **Ring-Opening Polymerization**
  (anionic, cationic)
- **„Living“/Controlled Radical Polymerization**

Basic Principles of Living Polymerization

Initiation: $I^* + M \xrightarrow{k_i} P_1^*$

Propagation: $P_i^* + M \xrightarrow{k_p} P_{i+1}^*$

Termination: $P_i^* \ (+ X) \xcancel{\xrightarrow{k_t}} P_i' \ (+ Y^*)$

Transfer: $P_i^* + X \xcancel{\xrightarrow{k_{tr}}} P_i' + P_1^*$

When termination and transfer are absent

$(R_t, R_{tr} << R_p)$

→ LIVING POLYMERIZATION

Conditions for a Living Polymerization (1)

1. No Termination: $k_t = 0$

The number of *active* chain-ends [P*] is constant:

Evidence:

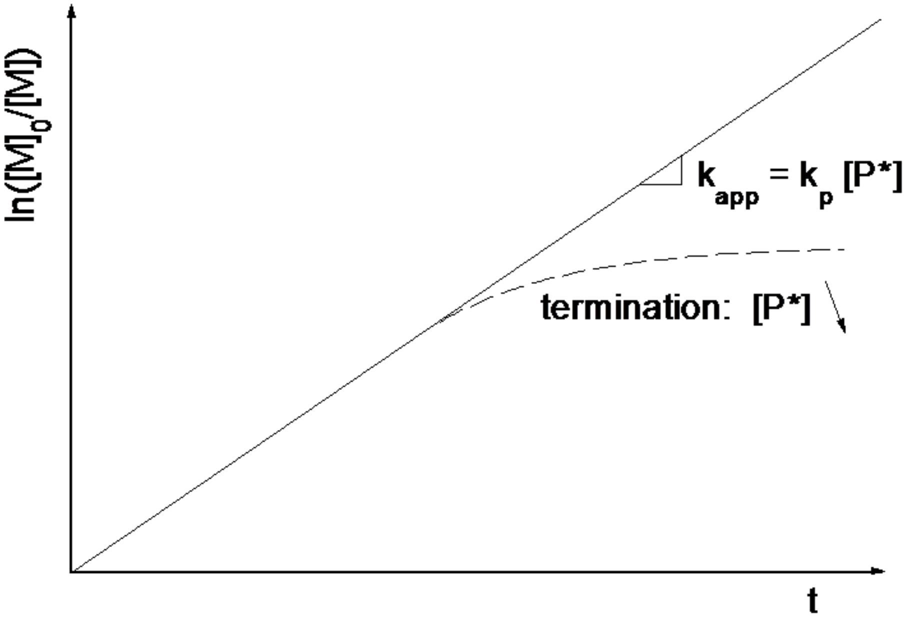
First-order **kinetics** with respect to monomer concentration:

The rate of polymerization is given by

$$R_p = -\frac{d[\mathrm{M}]}{dt} = k_p[\mathrm{M}][\mathrm{P}^*]$$

Integration renders

$$\ln\frac{[\mathrm{M}]_0}{[\mathrm{M}]} = k_p[\mathrm{P}^*]t = k_{app}\,t$$



Conditions for a Living Polymerization (2)

2. No Transfer: $k_{tr} = 0$

→ There are no new chains formed,

→ the total number of polymer chains, [P], *(including the terminated ones!)*

is constant: $[P] = [P^*] + [P_{dead}] = [I]_0$

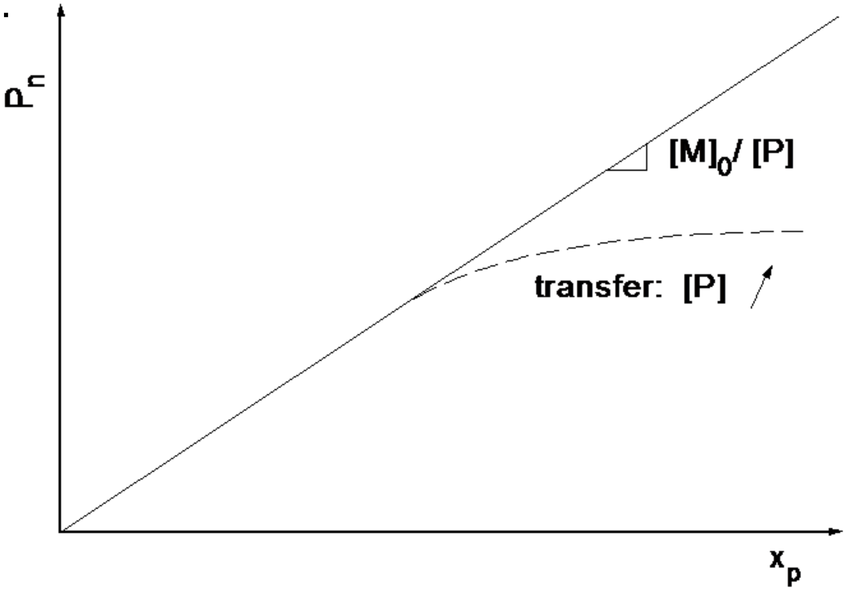
<u>Evidence:</u>

the number-average degree of polymerization,

$\overline{P}_n$,is a linear function of monomer conversion, x_p:

$$\overline{P}_n = \frac{\text{number of polymerized monomers}}{\text{number of polymer chains}}$$

$$= \frac{[M]_0 x_p}{[P]} = \frac{[M]_0 x_p}{[I]_0}$$



Molecular Weight Distribution (MWD)

Ideally, a very narrow MWD is expected, the *Poisson distribution*

(Flory, 1940).

The polydispersity index is given by

$$\frac{M_w}{M_n} = 1 + \frac{P_n - 1}{P_n^2} \approx 1 + \frac{1}{P_n} \approx 1$$

Factors leading to broader MWD's

Non-living Processes:

- termination → $M_w/M_n \leq 2$ (*important for anionic polymerization of (meth)acrylates)*
- transfer → $M_w/M_n \leq 2$ (*important in cationic polymerization of isobutylene)*

Living Processes:

- inadequate mixing:

  $t_{mix} > t_{1/2}$ → M_w/M_n can be very high
- slow initiation:

  $k_i < k_p$ → $M_w/M_n \leq 1.33$
- reversible polymerization ("scrambling"):

  → $M_w/M_n \leq 2$
- slow equilibria between species of different activity:

  $R_{ex} < R_p$ → M_w/M_n can be very high (*important for many "new" living/controlled processes*)

Controlled Polymerization

is a synthetic method to obtain polymers where:

- the number-average degree of polymerization is given by ratio of monomer over initiator:

$$\overline{P}_n = \frac{[\mathrm{M}]_0 x_p}{[\mathrm{I}]_0} = \frac{\Delta[\mathrm{M}]}{[\mathrm{I}]_0}$$

- MWD is narrow: $\overline{M}_w / \overline{M}_n$ < 1.1 or 1.2
- all chains can be functionalized: $P_i^* + X \rightarrow P_i\text{-}X$

This is obtained if:

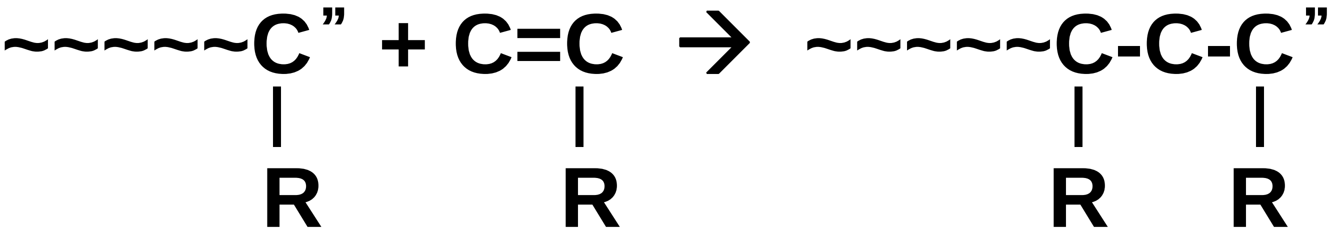
- the rate of initiation and rate of exchange reactions between various active species are fast compared to propagation ($R_{ex}, R_i > R_p$).
- chain-breaking reactions (termination or transfer) are not too strong ($R_t, R_{tr} << R_p$).

Thus a *controlled* polymerization is not necessarily *living*
(e.g. controlled/"living" radical polymerization)

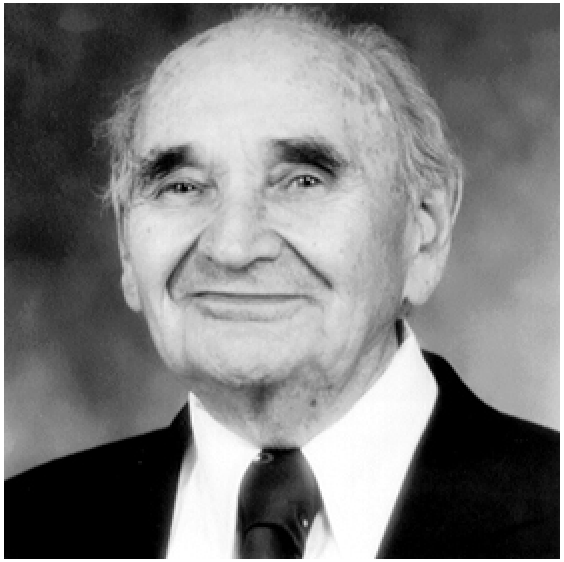
and a *living* polymerization is not necessarily *controlled*
(e.g. slow initiation, slow equlibrium)

Optimum: Living *and* controlled polymerization

Anionic Polymerization



$$\sim\sim\sim\sim\sim\sim\underset{\mathrm{R}}{\underset{|}{\mathrm{C}}}^{”} + \mathrm{C}{=}\underset{\mathrm{R}}{\underset{|}{\mathrm{C}}} \rightarrow \sim\sim\sim\sim\sim\sim\underset{\mathrm{R}}{\underset{|}{\mathrm{C}}}\text{-}\mathrm{C}\text{-}\underset{\mathrm{R}}{\underset{|}{\mathrm{C}}}^{”}$$



M. Szwarc, 1956:

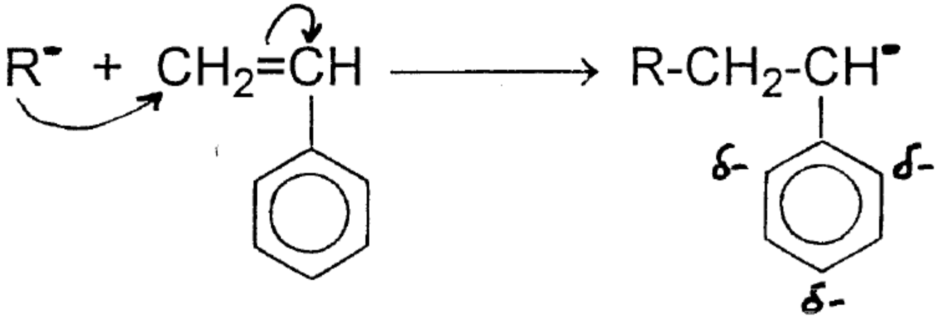
„Living Polymers“

Nature **178**, 1168 (1956)

Important Monomers

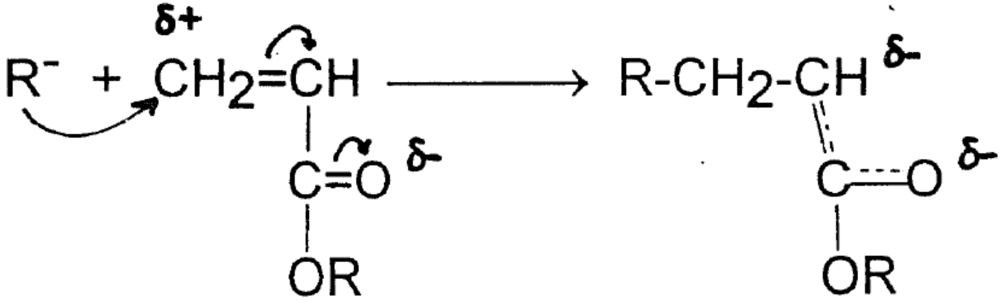
1. Non-polar vinyl compounds (with strong delocalization):

- <u>styrene</u>, α-methyl styrene
- o-, m-,p-alkyl styrenes
- vinyl naphthalene
- <u>dienes</u> (butadiene, isoprene, …)



2. Polar electrophilic vinyl compounds (with electron attracting substiuents):

- <u>vinyl pyridine</u>
- <u>(meth)acrylates</u>
- N,N-dialkyl acrylamides
- (meth)acrylonitrile



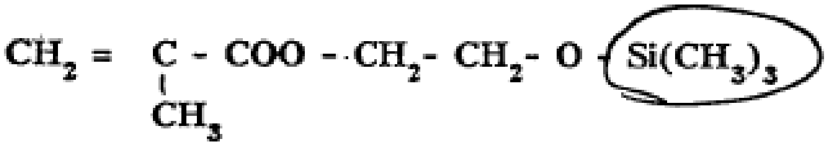
3. Cyclic Ethers, Esters, Siloxanes, ...:

→ Ring-Opening Polymerization

Protected Monomers

Monomers with acidic hydrogens need to be protected:

BY SILYLATION :

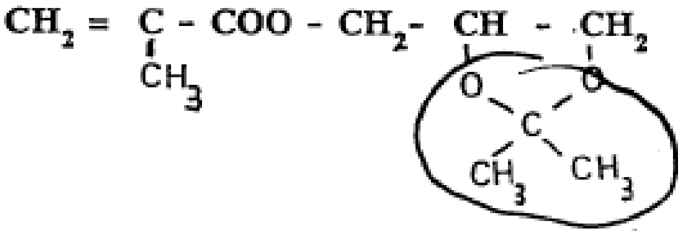


$CH_2 = \underset{CH_3}{C} - COO - CH_2 - CH_2 - O - \boxed{Si(CH_3)_3}$

or

2-hydroxyethyl methacrylate (HEMA)

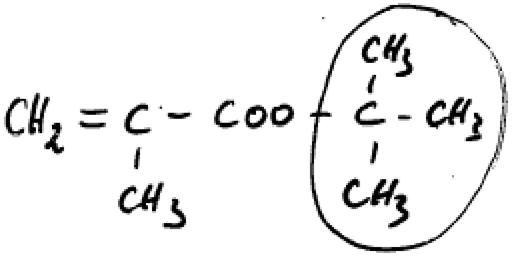
BY ACETALIZATION :



solketal methacrylate

or

AS *tert*-BUTYL ESTER:



$CH_2 = \underset{CH_3}{C} - COO - \boxed{\underset{CH_3}{\overset{CH_3}{C}} - CH_3}$

methacrylic acid

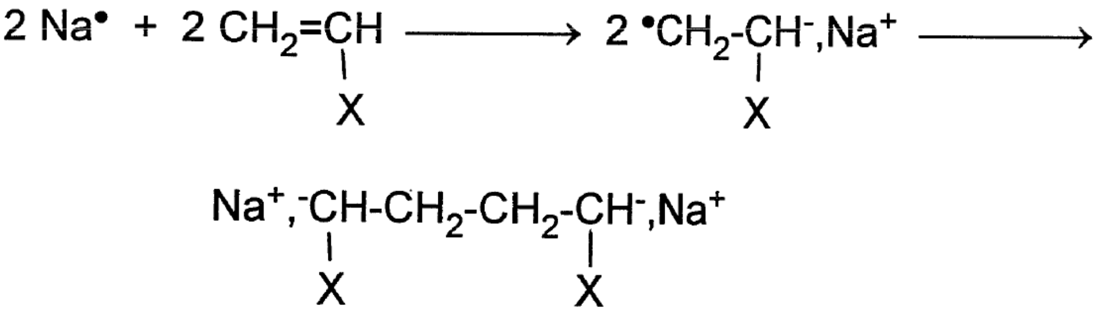
Initiators

1. **Organometallic bases** (monofunctional):

- organolithium: n-BuLi, s-BuLi, t-BuLi
- alcoholates (t-BuO-Li, t-BuO-K, ...)
- alkali salts of aromatic hydrocarbons: benzyl-Na, cumyl-K, ...

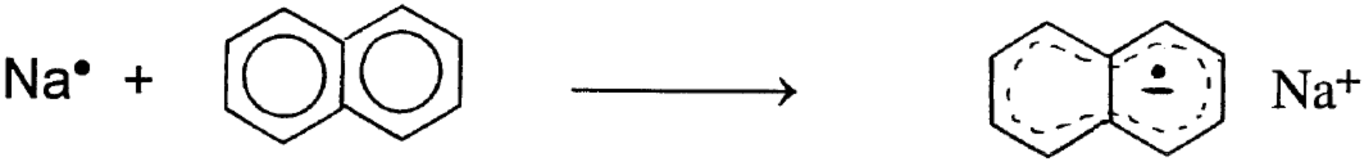
2. **Electron transfer agents** (bifunctional):

- alkali metals (heterogeneous):



$$2\,Na^{\bullet} + 2\,CH_2{=}\underset{\displaystyle X}{\underset{|}{CH}} \longrightarrow 2\,{}^{\bullet}CH_2\text{-}\underset{\displaystyle X}{\underset{|}{CH}}{}^{-},Na^{+} \longrightarrow Na^{+},{}^{-}\underset{\displaystyle X}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_2\text{-}\underset{\displaystyle X}{\underset{|}{CH}}{}^{-},Na^{+}$$

- radical anions: <u>naphthalene sodium</u> (homogeneous):



Special Considerations for Experimental Work

Due to the high nucleophilicity of the initiators (and propagating chain ends) it is absolutely necessary to avoid oxygen, water and protic impurities:

This implies

- aprotic solvents:
  polar: THF, ...
  non-polar: toluene, cyclohexane, hexane, ...
- rigorous purification of reagents
- handling of reagents in vacuum or under inert gas.

Due to the absence of termination, the concentration of active species can be much higher than in radical polymerization.
Thus, the rates sometimes can be very high
(e.g., $t_{1/2} < 1$ s for MMA in THF at room temperature).

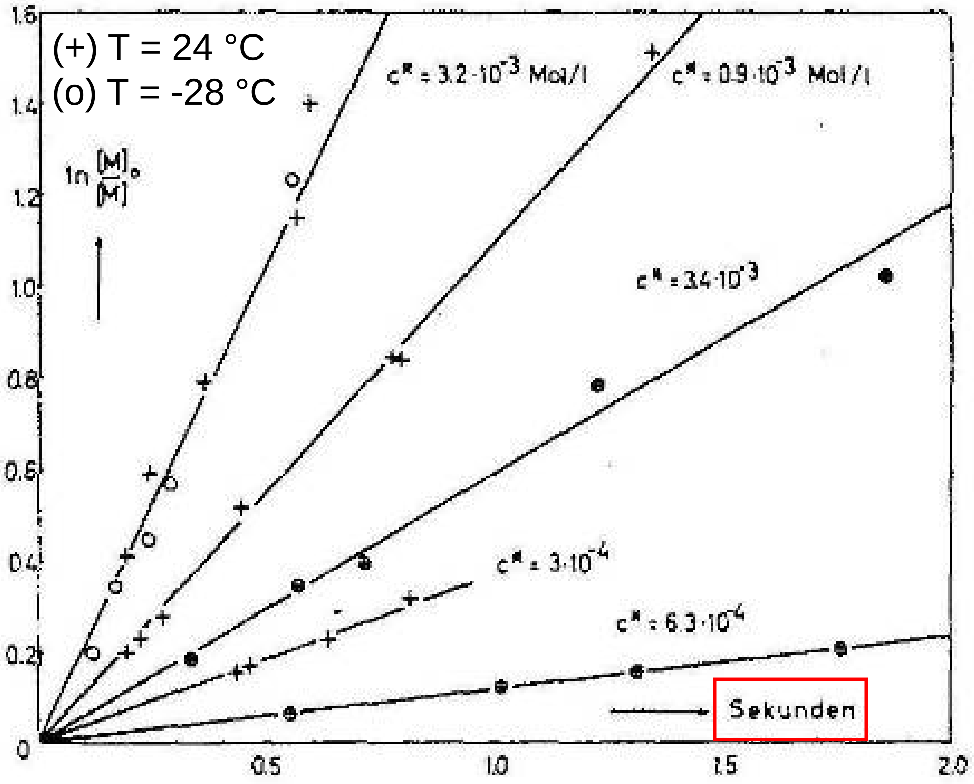
In order to control the polymerization it may be necessary to

- use specially designed reactors (fast mixing: flow tube)
- add monomer slowly (vapour phase)
- work at low temperatures (-78 °C)

Anionic Polymerizaton of Non-Polar Monomers

Polymerization of styrene with Na^+ counterion in THF

First-Order Plot of Kinetics



G.V. Schulz et al., *Makromol. Chem.* **71**, 198 (1964)

$k_{app} = k_p[P^*]$

is the slope of the first-order plot

Linear plot (constant slope)

→ [P*] = const.

→ **no termination**

→ **fast initiation**

Molecular Weight vs. Conversion

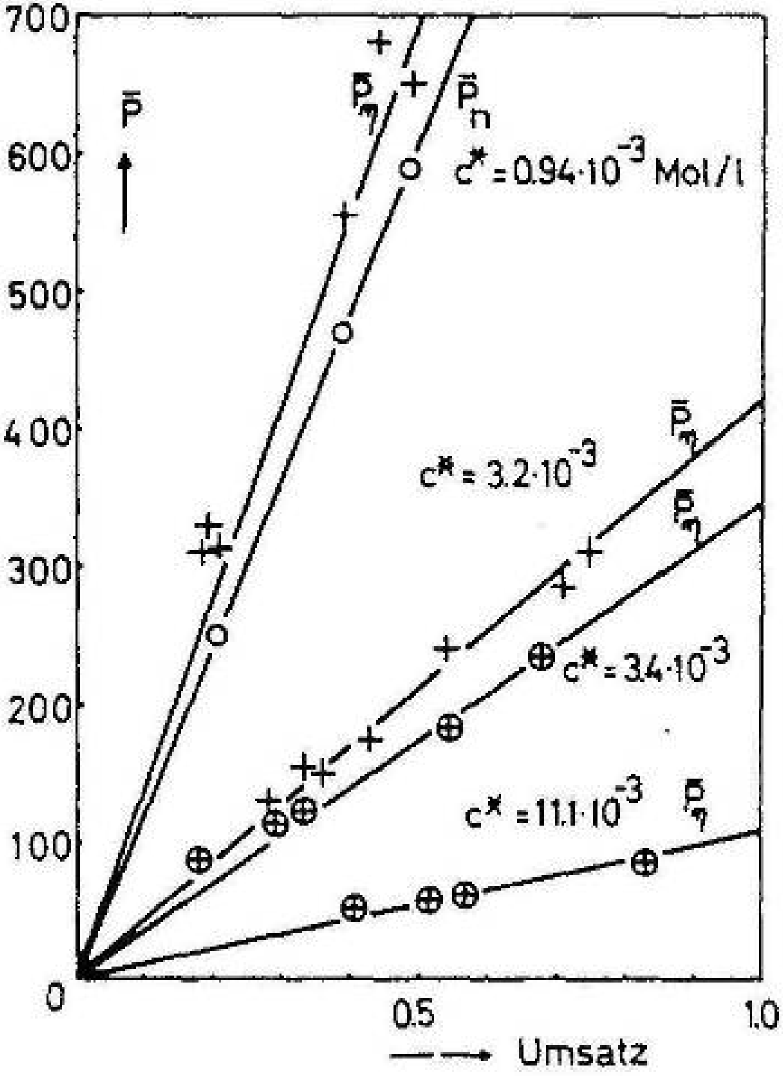
Linear plot (constant slope)

→ the number of all chains, [P], is constant

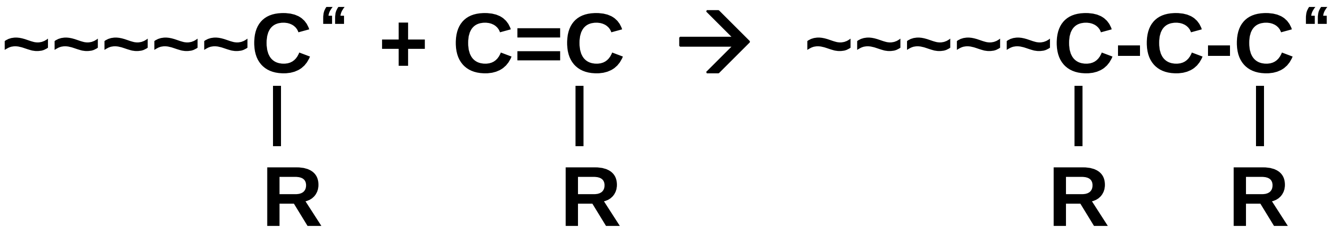
→ no transfer

→ fast initiation

→ $M_w/M_n < 1.02$



Cationic Polymerization



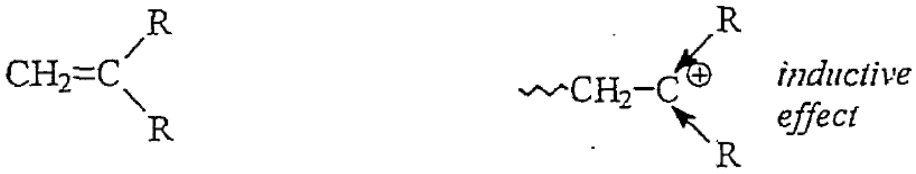
$$\sim\sim\sim\sim\sim\underset{R}{\underset{|}{C}}{}^{“} + C{=}\underset{R}{\underset{|}{C}} \rightarrow \sim\sim\sim\sim\sim\underset{R}{\underset{|}{C}}\text{-}C\text{-}\underset{R}{\underset{|}{C}}{}^{“}$$

M. Sawamoto, T. Higashimura, 1979

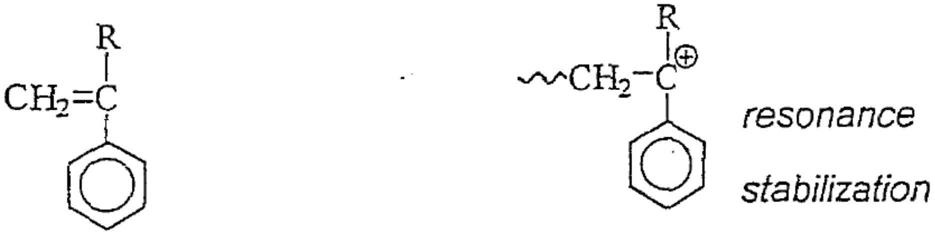
Monomers

Requirement for carbo-cationic polymerization: stabilization of carbenium ion

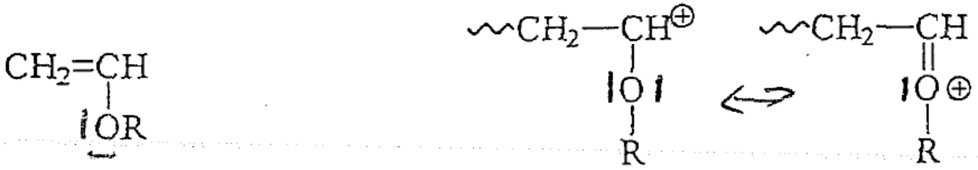
Monomer **Active species**



1,1-substituted alkenes: isobutylene (→ low T_g rubber, low permeability)



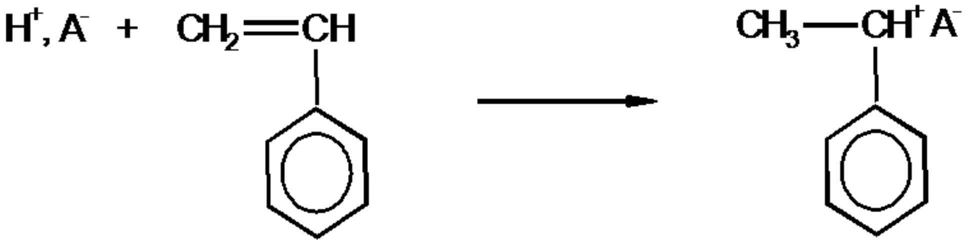
styrenics: PS-*b*-PIB-*b*-PS: excellent thermoplastic elastomer



vinyl ethers : poly(methyl vinyl ether) is water-soluble

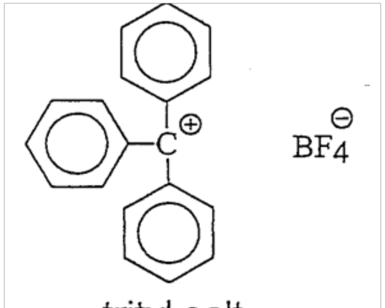
Initiators

Protic Acids: $HClO_4$, CF_3SO_3H, ...



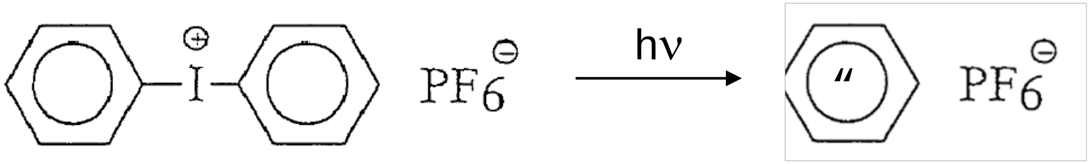
Lewis Acids: $AlCl_3$, BF_3, ….: $H_2O + BF_3 \rightleftharpoons H^{\delta+}\ldots(OH)BF_3^{\delta-}$

Stable cations

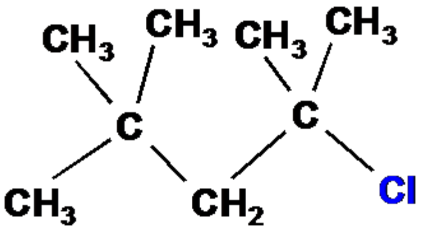


trityl salt

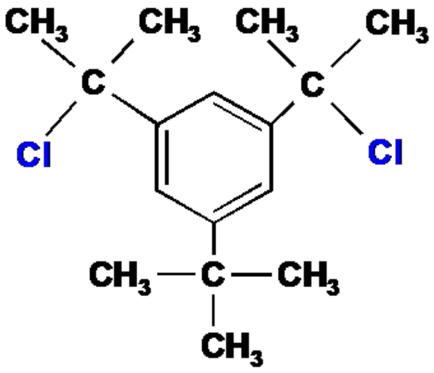
Photoinitiators



Living Polymerization Initiators

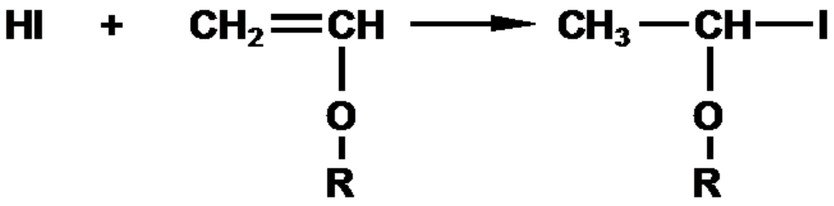


2,4,4-Trimethylpentyl-2-chloride
(TMP-Cl)
monofunctional



1,3-Di(2-chloro-2-propyl)-5-*tert*.-butylbenzene (*t*Bu-DiCum-Cl)
bifunctional

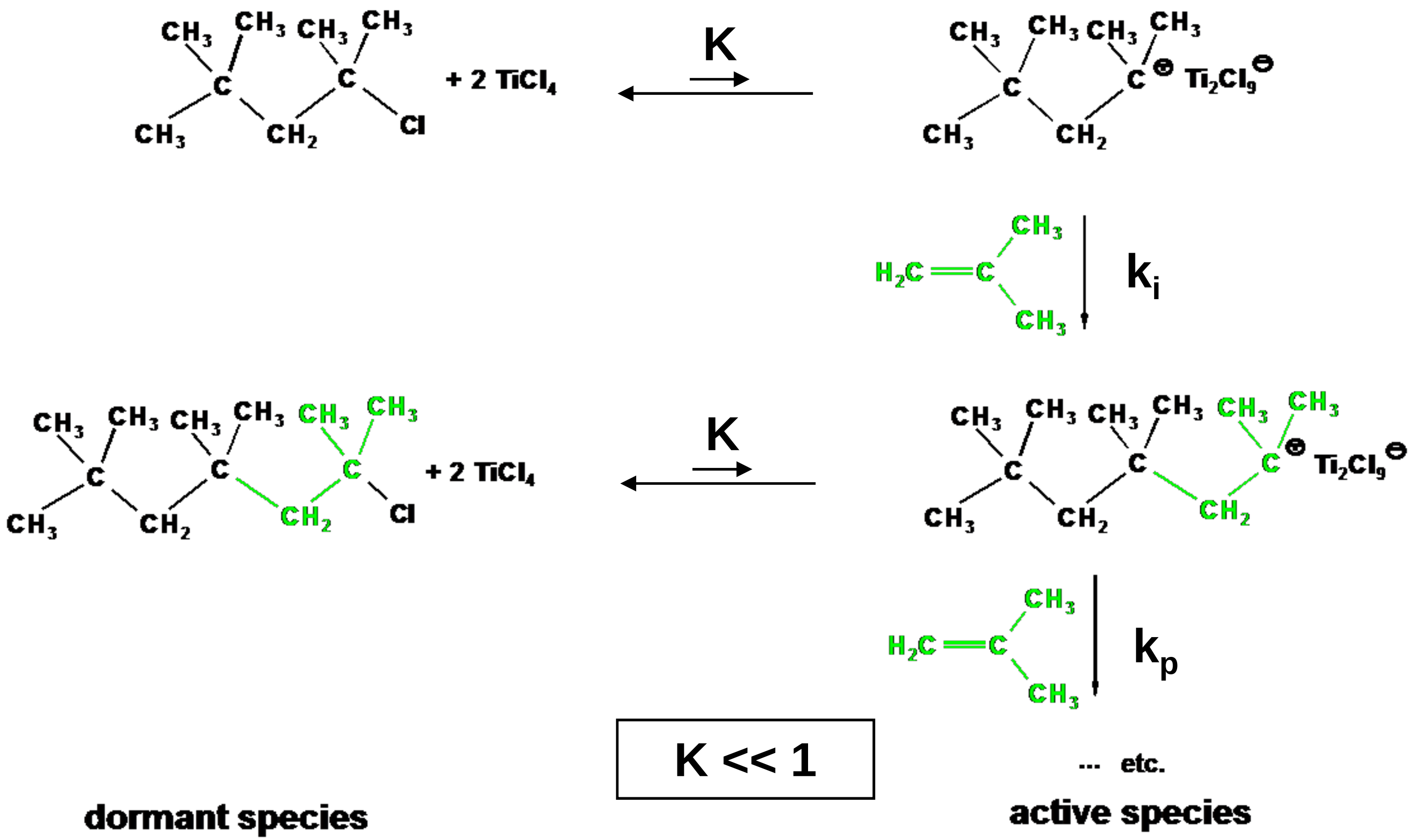
In situ generation of halides from HI and vinyl ethers:



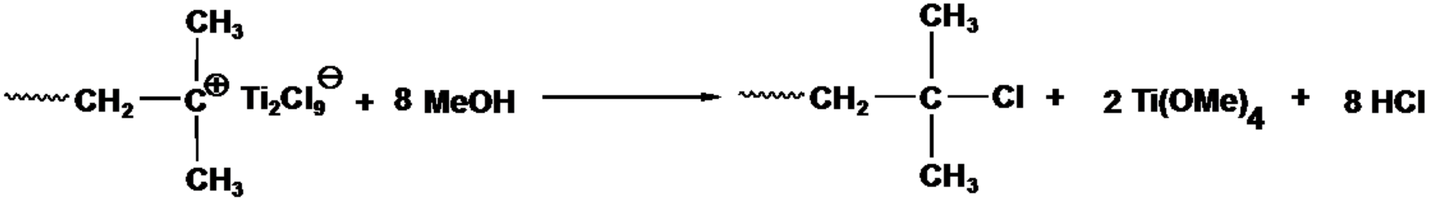
$$HI + CH_2{=}CH(OR) \longrightarrow CH_3{-}CH(OR){-}I$$

Catalyst necessary to generate cations!

Living Polymerization of Isobutylene



Termination by Protons:

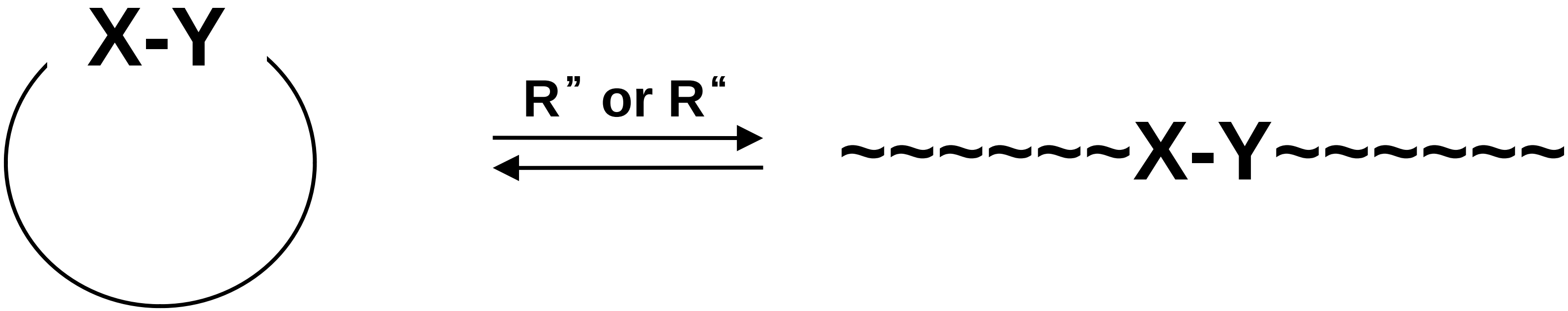


$$\sim CH_2-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}}\ Ti_2Cl_9^{\ominus} + 8\ MeOH \longrightarrow \sim CH_2-\underset{CH_3}{\overset{CH_3}{C}}-Cl + 2\ Ti(OMe)_4 + 8\ HCl$$

Conclusions: Cationic Polymerization

- “Living” cationic polymerization depends on a **catalyzed dynamic equilibrium** between “dormant” (inactive, covalent) and active species (ion pairs, free cations)
- The **rate of polymerization** is determined by the position of the dissociation and aggregation equilibria.
- “**Transfer**" (spontaneous and to monomer) is the main **side** reaction; it can be minimized by using larger counterions and highly polar solvents.

Ring-Opening Polymerization (ROP)



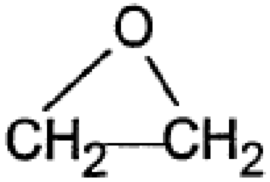
- Anionic ROP (AROP)
- Cationic ROP (CROP)
- Ring-Opening Metathesis Polymerization (ROMP)

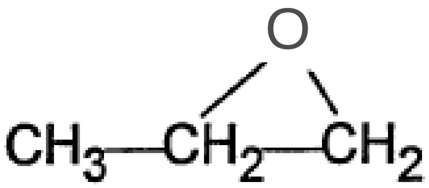
Anionic Ring-Opening Polymerization (AROP)

Monomers (1):

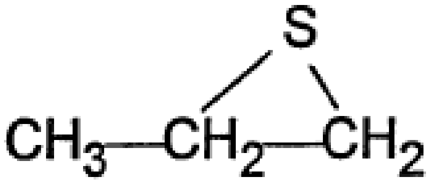
Cyclic Ethers:

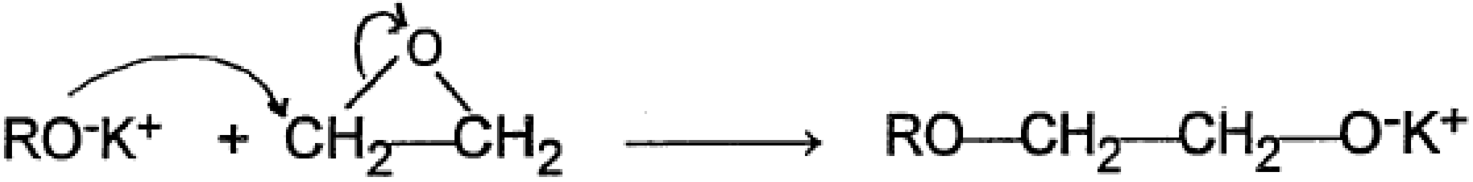
Ethylene Oxide, Propylene Oxide





Propylene Sulfide



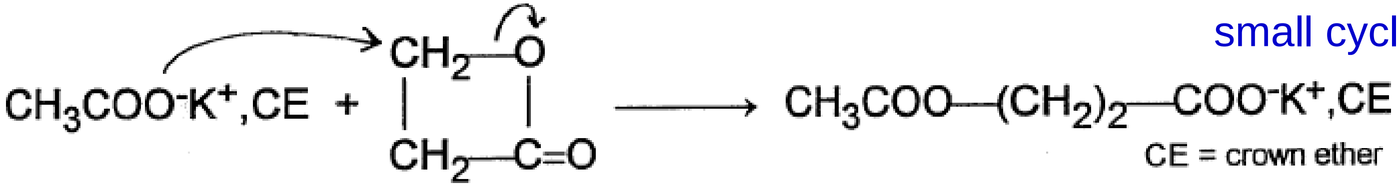


Nucleophilic Substitution → linear anionic chain end

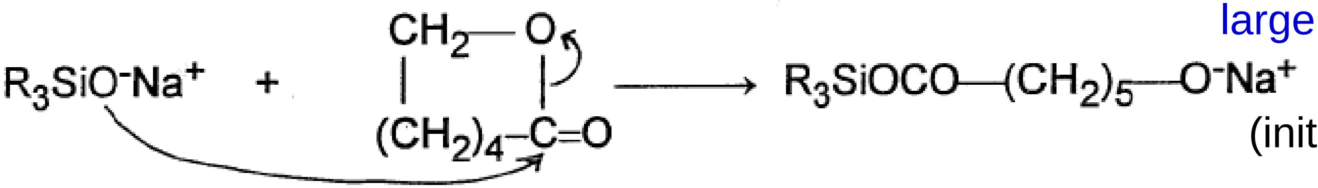
Monomers (2)

Lactones:

small cycles → “alkyl split”

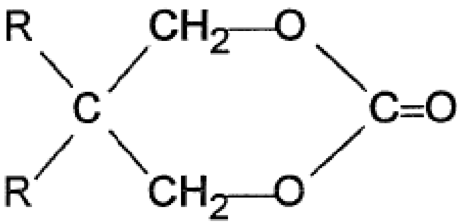


larger cycles → “acyl split”

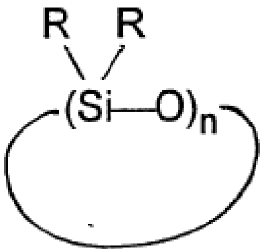


(initiation with RLi, ROLi)

Cyclic Carbonates:



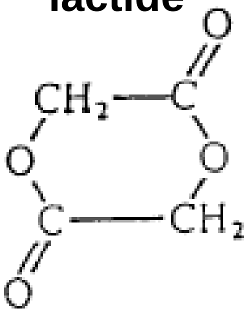
Cyclic Siloxanes:



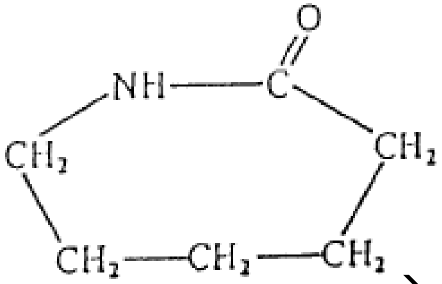
n = 3, 4, ...

→ silicones

lactide

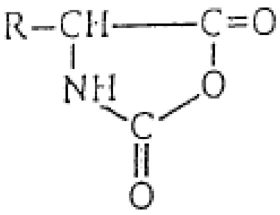


ε-caprolactam



→ Nylon 6

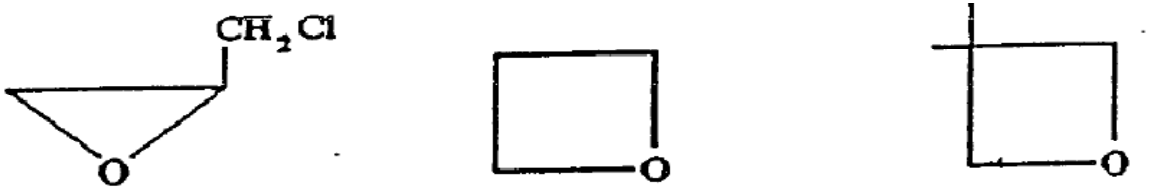
N-carboxyanhydrides

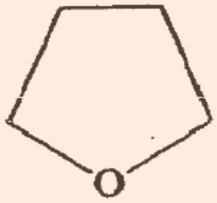


→ polypeptides

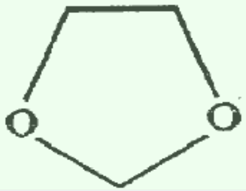
Cationic Ring-Opening Polymerization (CROP)

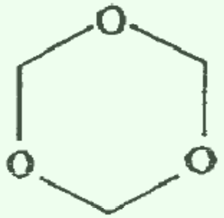
Some monomers



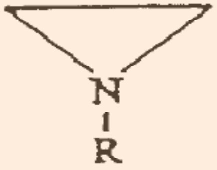


THF

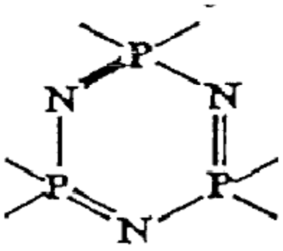




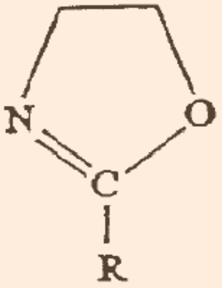
1,3-dioxolane + trioxane → POM



azridines

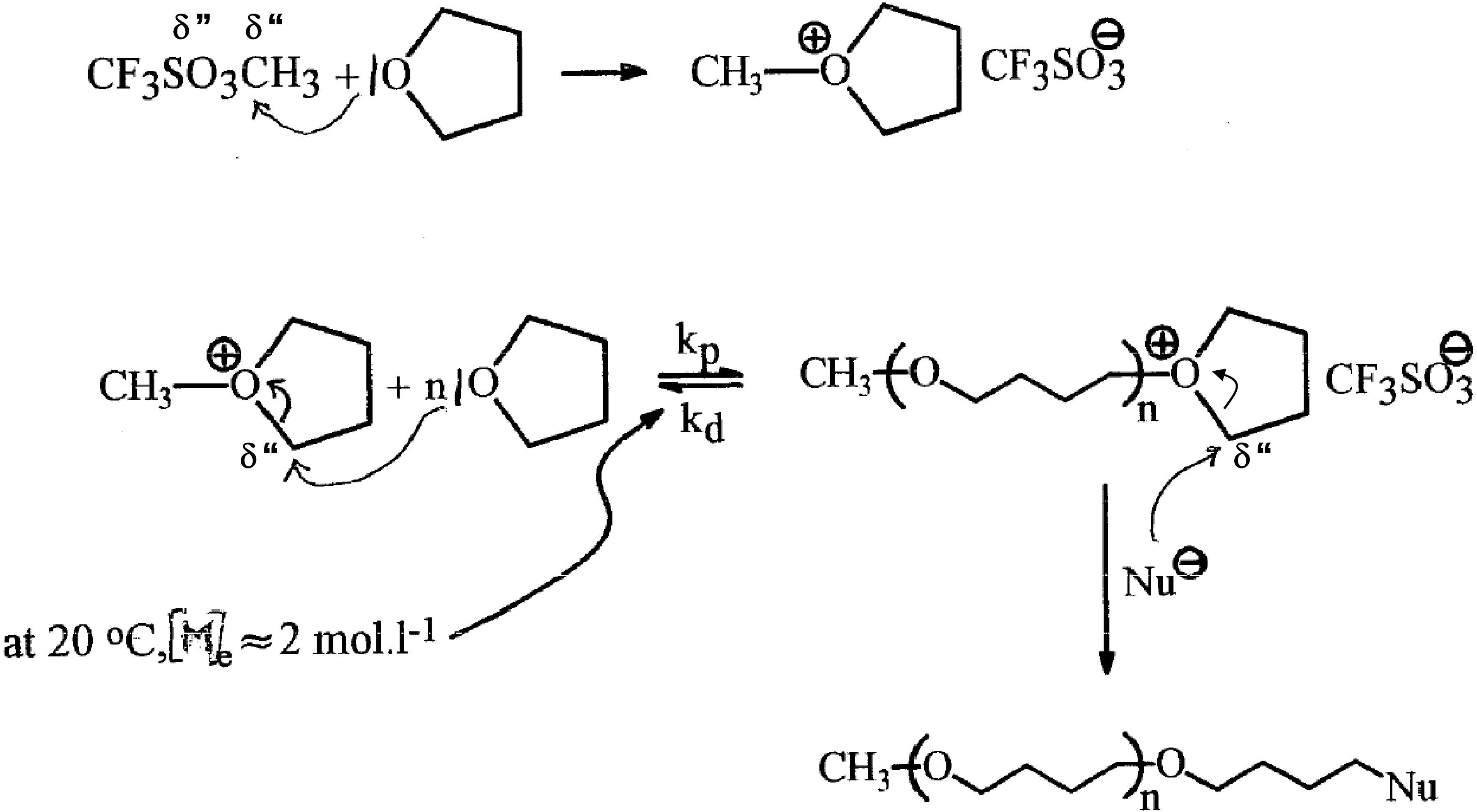


phosphazenes



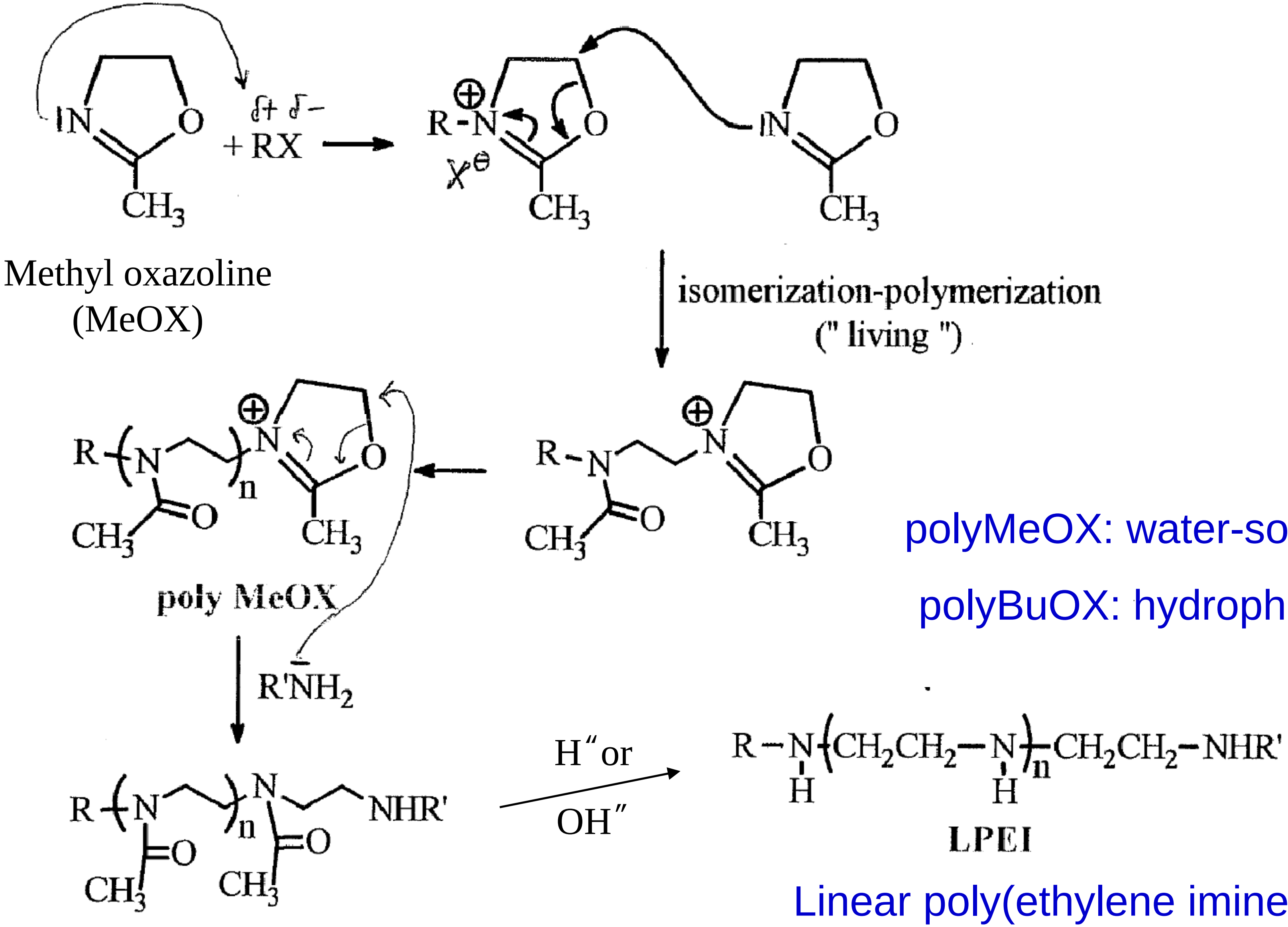
oxazolines

Mechanism of Living CROP of THF



Equilibrium polymerization!

Living CROP of Oxazolines

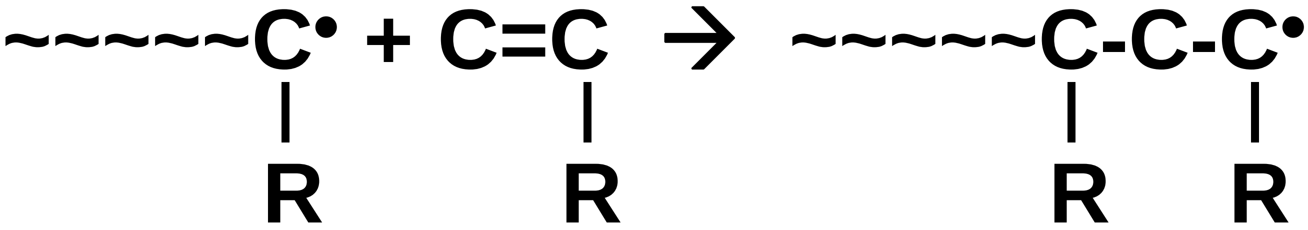


polyMeOX: water-soluble

polyBuOX: hydrophobic

Linear poly(ethylene imine)

Controlled/“Living“ Radical Polymerization



$$\sim\sim\sim\sim\sim\underset{\underset{R}{|}}{C}{}^{\bullet} + C{=}\underset{\underset{R}{|}}{C} \rightarrow \sim\sim\sim\sim\sim\underset{\underset{R}{|}}{C}\text{-}C\text{-}\underset{\underset{R}{|}}{C}{}^{\bullet}$$

- **Nitroxide-Mediated Polymerization (NMP)**
  E. Rizzardo, M. Georges 1992

- **Atom Transfer Radical Polymerization (ATRP)**
  K. Matyjaszewski, M. Sawamoto 1994

- **Reversible Addition-Fragmentation Chain Transfer (RAFT)**
  E. Rizzardo, G. Moad, S. Thang 1996

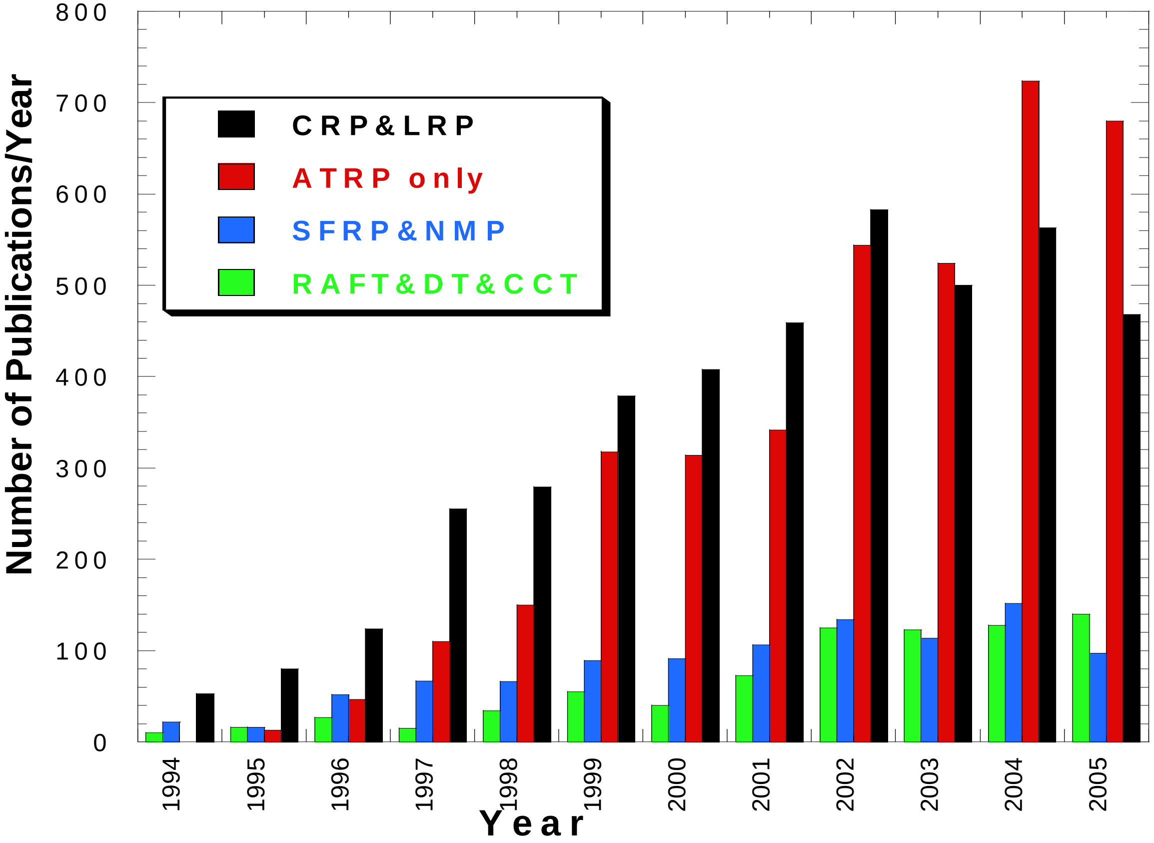
Controlled/“Living” Radical Polymerization

>5,000 papers on CRP
(>3,000 ATRP since ‘95)

>600 patents on CRP
(>400 ATRP since ‘95)

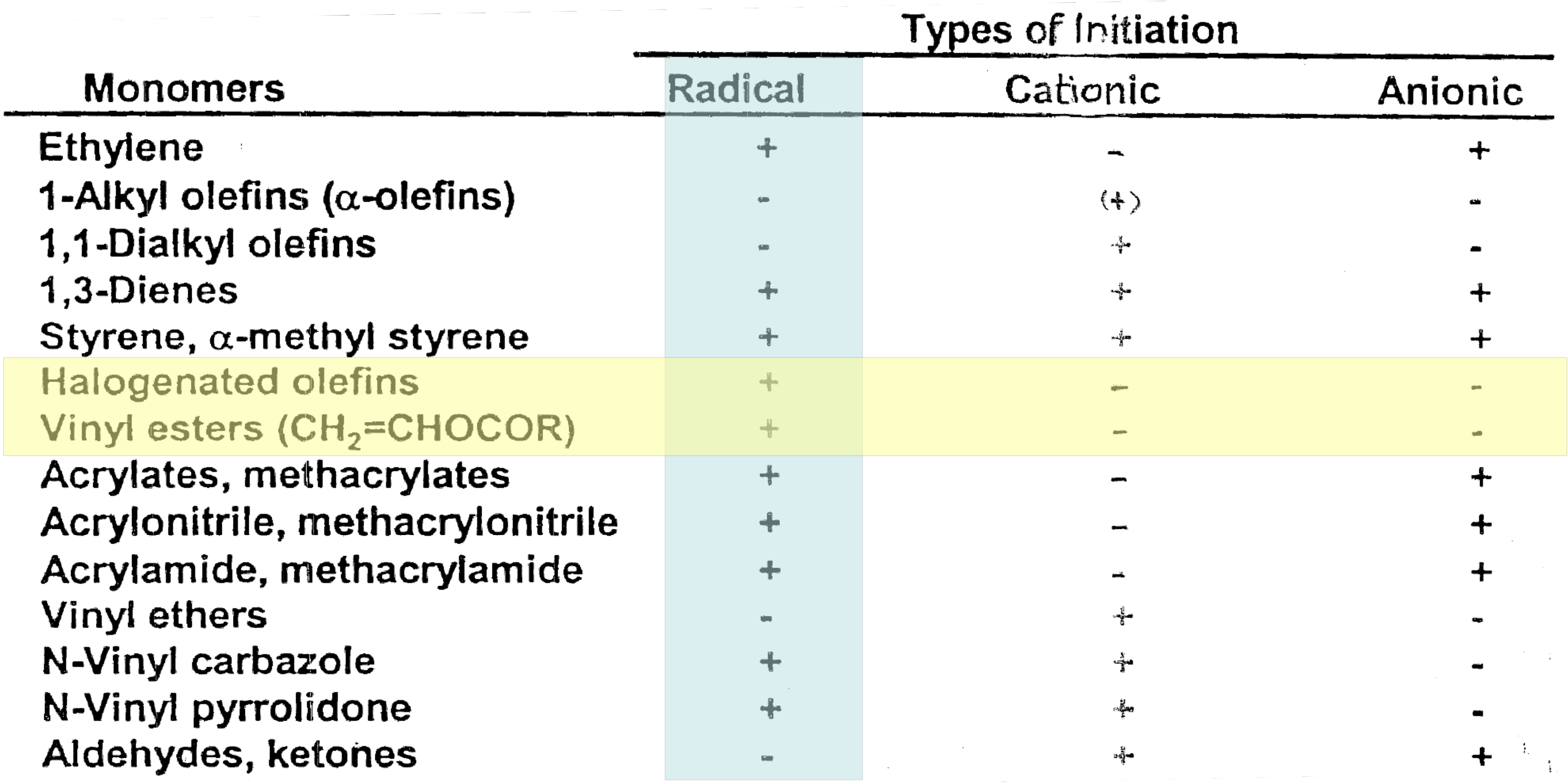
Anticipated market:
>20$billion/year
Bob Matheson (DuPont)

Applications:
coatings, adhesives, surfactants, dispersants, lubricants, gels, additives, thermoplastic elastomers, electronics, biomaterials, …
Specialties



SciFinder Scholar: September 14, 2005

Polymerizability of Monomers



Monomers	Types of Initiation		
	Radical	Cationic	Anionic
Ethylene	+	-	+
1-Alkyl olefins (α-olefins)	-	(+)	-
1,1-Dialkyl olefins	-	+	-
1,3-Dienes	+	+	+
Styrene, α-methyl styrene	+	+	+
Halogenated olefins	+	-	-
Vinyl esters (CH_2=CHOCOR)	+	-	-
Acrylates, methacrylates	+	-	+
Acrylonitrile, methacrylonitrile	+	-	+
Acrylamide, methacrylamide	+	-	+
Vinyl ethers	-	+	-
N-Vinyl carbazole	+	+	-
N-Vinyl pyrrolidone	+	+	-
Aldehydes, ketones	-	+	+

→ **Radical Polymerization works for the largest number of monomers!**

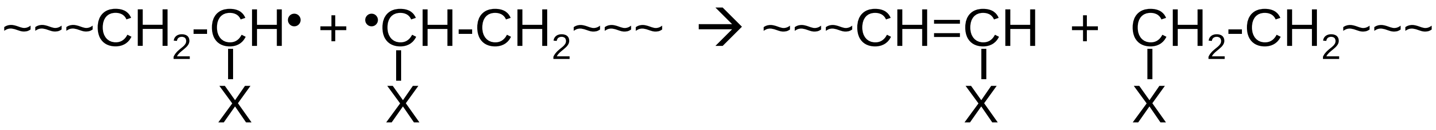
→ **Very many monomer pairs can be copolymerized**

→ **Undemanding reaction conditions (just remove oxygen)**

Problems of Conventional Radical Polymerization

1. Termination via fast bimolecular radical-radical reactions:

- Recombination: $\sim\sim\sim P_n^\bullet + {}^\bullet P_m\sim\sim\sim \rightarrow \sim\sim\sim P_{n+m}\sim\sim\sim$
- Disproportionation:

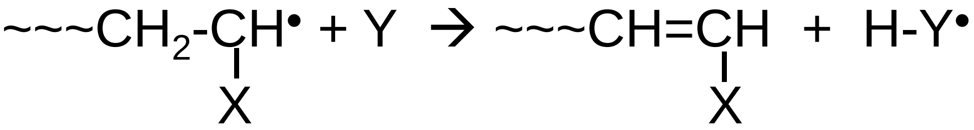


$$\sim\sim\sim \mathrm{CH_2}\text{-}\underset{\mathrm{X}}{\mathrm{CH}^\bullet} + {}^\bullet\underset{\mathrm{X}}{\mathrm{CH}}\text{-}\mathrm{CH_2}\sim\sim\sim \rightarrow \sim\sim\sim \mathrm{CH}{=}\underset{\mathrm{X}}{\mathrm{CH}} + \underset{\mathrm{X}}{\mathrm{CH_2}}\text{-}\mathrm{CH_2}\sim\sim\sim$$

Radical lifetime is in the range of milliseconds!

2. Transfer to monomer, polymer, solvent, …:

- Generates new chains:



$$\sim\sim\sim \mathrm{CH_2}\text{-}\underset{\mathrm{X}}{\mathrm{CH}^\bullet} + \mathrm{Y} \rightarrow \sim\sim\sim \mathrm{CH}{=}\underset{\mathrm{X}}{\mathrm{CH}} + \mathrm{H}\text{-}\mathrm{Y}^\bullet$$

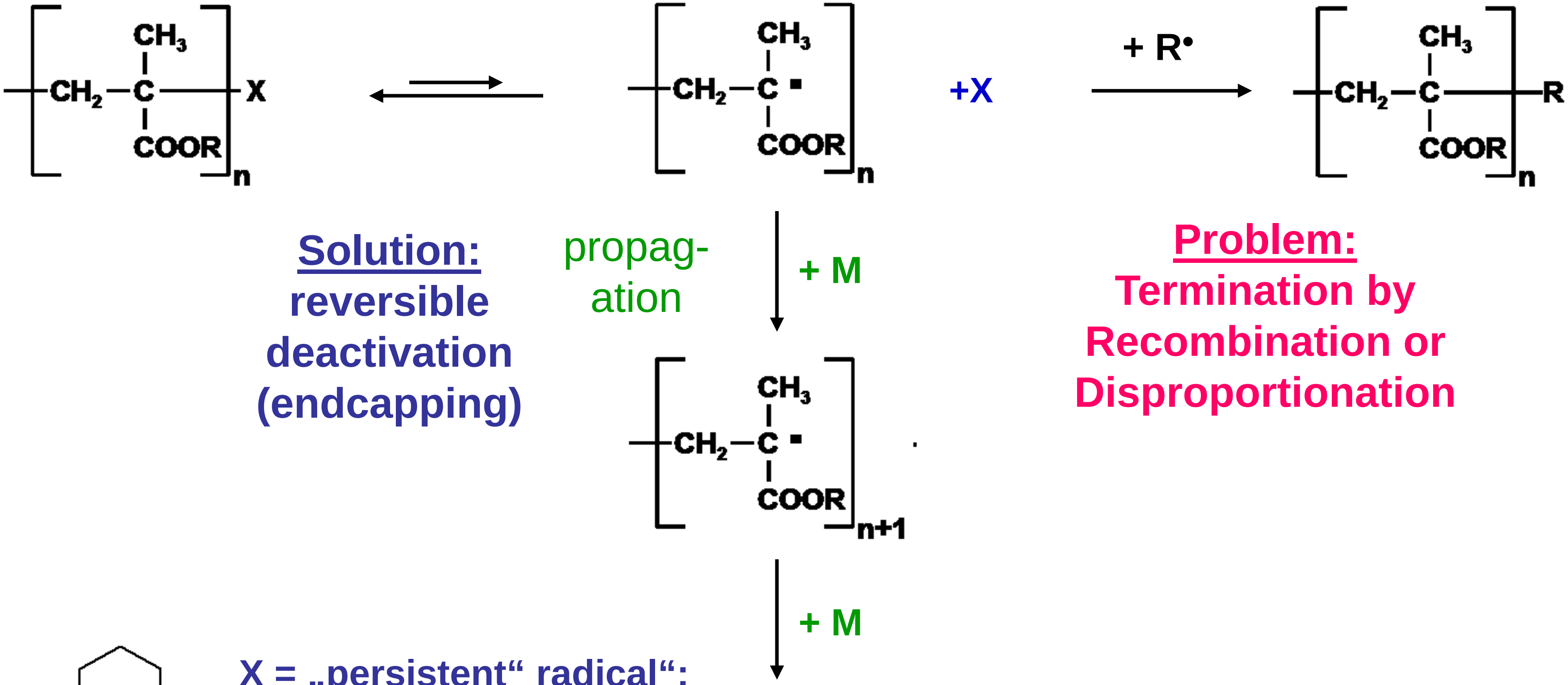
Decreasing Termination by Dilution of Chain Ends:

$$R_t = k_t\left[\mathrm{P}^*\right]^2$$

$$R_p = k_p[\mathrm{M}]\left[\mathrm{P}^*\right]$$

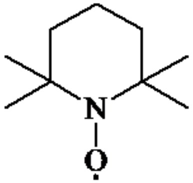
$$\Longrightarrow \quad \frac{R_t}{R_p} = \frac{k_t}{k_p}\frac{\left[\mathrm{P}^*\right]}{[\mathrm{M}]}$$

1. Reversible Deactivation of Chain Ends



Solution:
reversible deactivation (endcapping)

Problem:
Termination by Recombination or Disproportionation



X = „persistent“ radical“:

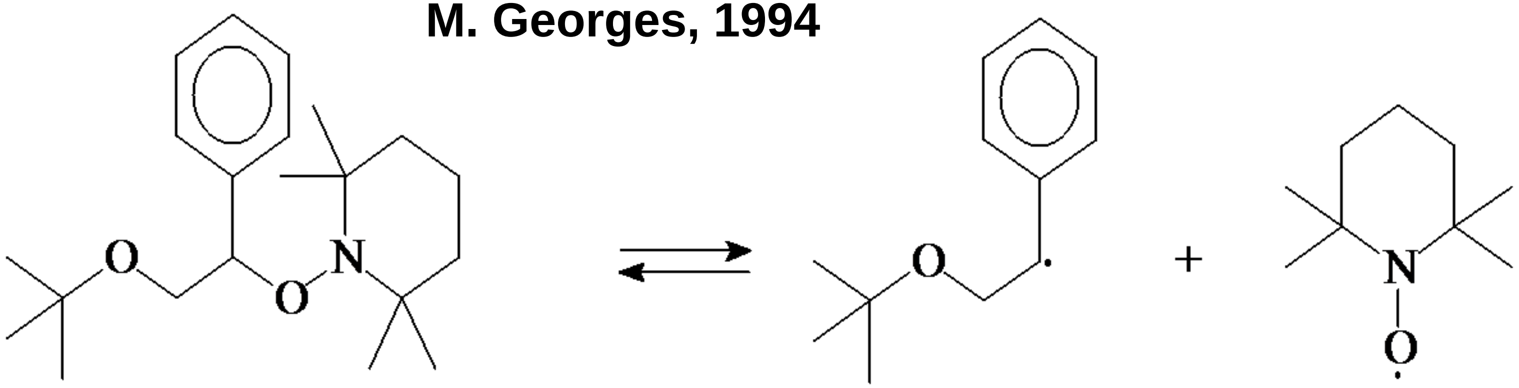
X = nitroxide, e.g., TEMPO → NMP, SFRP

X = transition metal halide, e.g. $CuBr_2$ → ATRP

→ Dynamic equilibrium between active and dormant species

Nitroxide-Mediated Polymerization (NMP)

M. Georges, 1994



alkoxyamine **radical** **persistent radical**

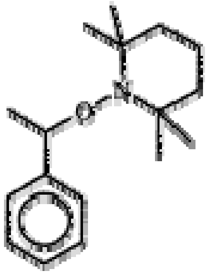
Advantages:

- Simple, many (functional) nitroxides available
- Radicals can be formed by classical initiators or from alkoxyamines
- works well in emulsion and miniemulsion
- $M_w/M_n < 1.2$ possible

Disadvantages:

- slow, high temperatures needed (> 100 °C)
- works for few monomers only (styrene, acrylates)

Partial library of alkoxyamine structures evaluated as initiators for the living radical polymerization of styrene and n-butyl acrylate.



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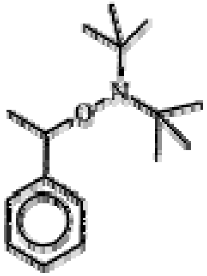

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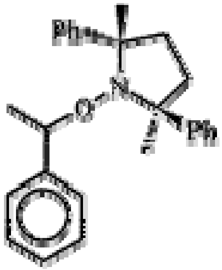

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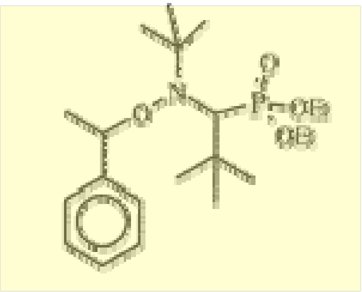
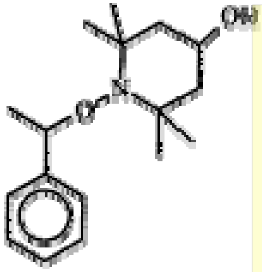


27

“SG1”
(diethylphosphonate)
Tordo, Gnanou



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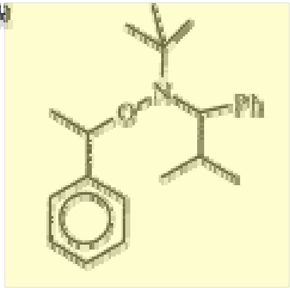

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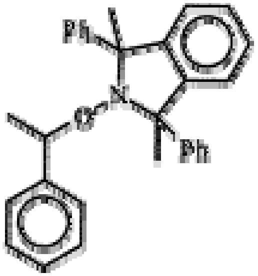
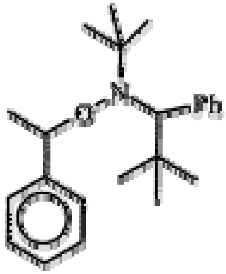


30a = cis
30b = trans



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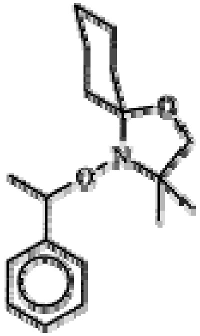

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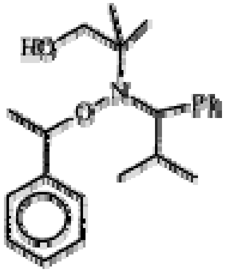

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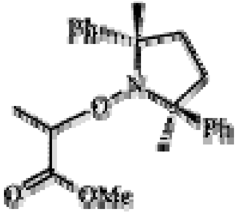

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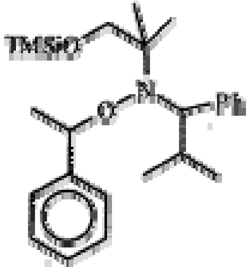


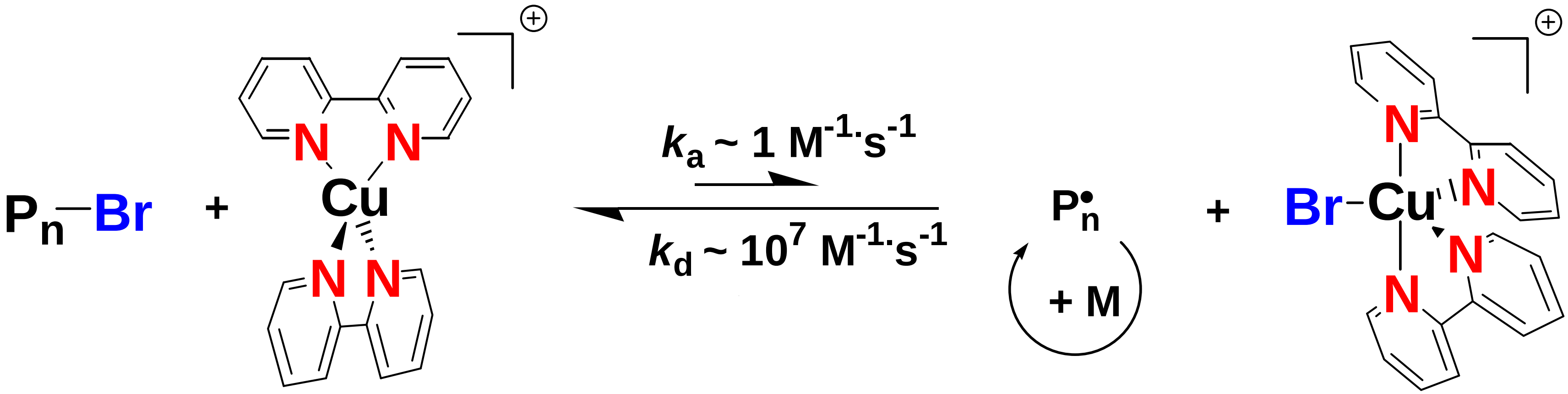
35

Braslau, Hawker

Atom Transfer Radical Polymerization (ATRP)

(Transition Metal Mediated Polymerization)

K. Matyjaszewski, M. Sawamoto, 1995



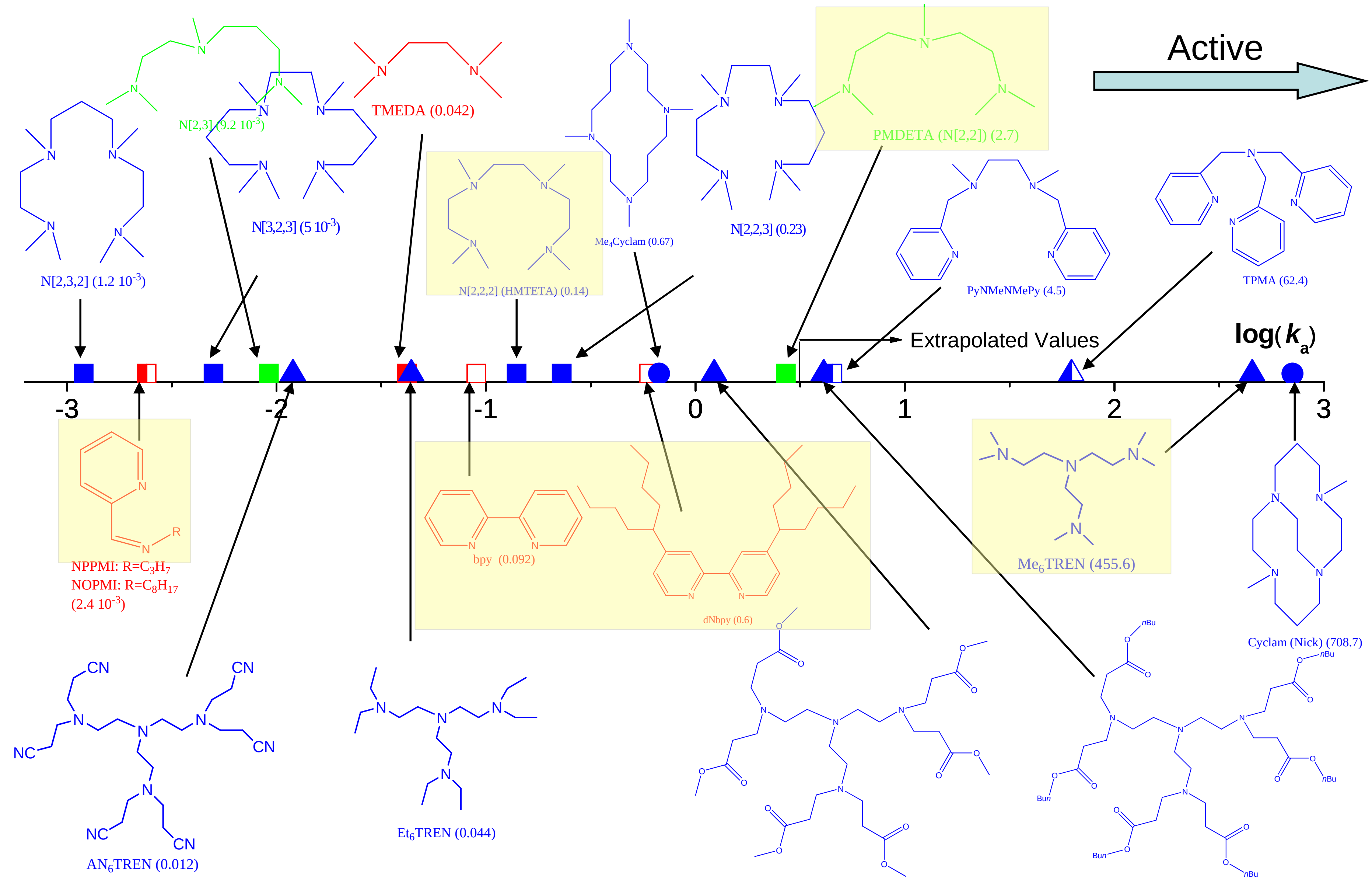
Advantages:

- Simple; many metal ions (Fe, Ni, …) and ligands available
- works for most monomers (not acrylic acid, …)
- No conventional initiator needed
- $M_w/M_n < 1.2$ possible

Disadvantages:

- removal of catalyst on large scale difficult
- does not work for monomers that complex the Mt ion (acrylic acid, …)

Some Ligands



Note: Values ($M^{-1}s^{-1}$) are measured with EtBriB/Cu(I)Br in AN at 35 ° C.

N2: red, **N3**: green, **N4**: blue; **Amine/imine**: solid, **Pyridine**: open, **Mixed**: left-half solid; **Linear**: ☐, **Branched**: ▲, **Cyclic**: ○.

Some Initiators

CCl_3Br

I-7

$F(CF_2)_6I$

I-8

$F(CF_2)_4I$

I-9

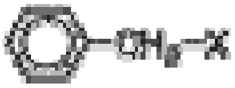
CHI_3

I-10

$CH_2{=}CH{-}CH_2{-}X$

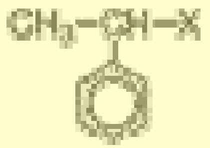
(X = Cl, Br)

I-11



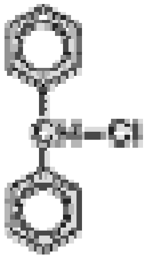
(X = Cl, Br)

I-12

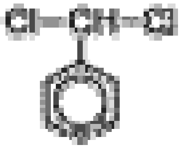


(X = Cl, Br, I)

I-13



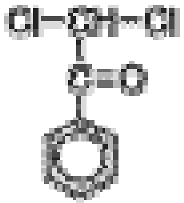
I-14



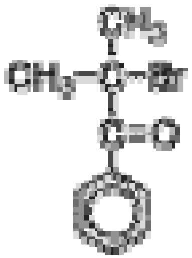
I-15

CCl_3COCH_3

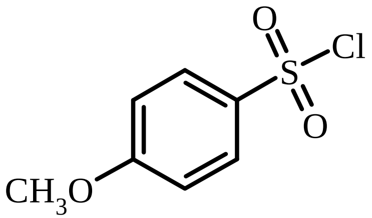
I-16

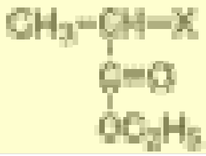


I-17



I-18

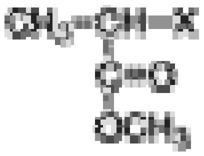




$$\begin{array}{ccc}\mathrm{CH_3}-&\mathrm{CH}&-\mathrm{X}\\ &|&\\ &\mathrm{C{=}O}&\\ &|&\\ &\mathrm{OC_2H_5}&\end{array}$$

(X = Cl, Br, I)

I-21



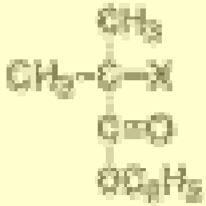
$$\begin{array}{ccc}\mathrm{CH_3}-&\mathrm{CH}&-\mathrm{X}\\ &|&\\ &\mathrm{C{=}O}&\\ &|&\\ &\mathrm{OCH_3}&\end{array}$$

(X = Cl, Br)

I-22

$$\begin{array}{ccc}\mathrm{C_2H_5}-&\mathrm{CH}&-\mathrm{Br}\\ &|&\\ &\mathrm{C{=}O}&\\ &|&\\ &\mathrm{OC_2H_5}&\end{array}$$

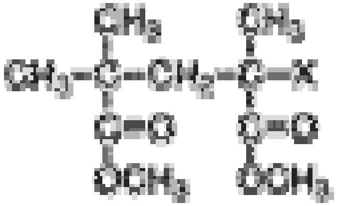
I-23



$$\begin{array}{ccc}&\mathrm{CH_3}&\\ &|&\\ \mathrm{CH_3}-&\mathrm{C}&-\mathrm{X}\\ &|&\\ &\mathrm{C{=}O}&\\ &|&\\ &\mathrm{OC_2H_5}&\end{array}$$

(X = Br, I)

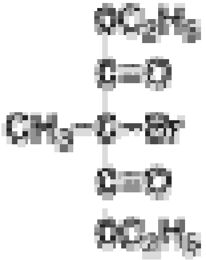
I-24



$$\begin{array}{ccccc}&\mathrm{CH_3}&&\mathrm{CH_3}&\\ &|&&|&\\ \mathrm{CH_3}-&\mathrm{C}&-\mathrm{CH_2}-&\mathrm{C}&-\mathrm{X}\\ &|&&|&\\ &\mathrm{C{=}O}&&\mathrm{C{=}O}&\\ &|&&|&\\ &\mathrm{OCH_3}&&\mathrm{OCH_3}&\end{array}$$

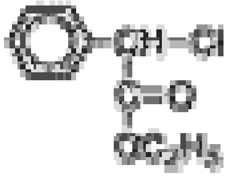
(X = Cl, Br)

I-25



$$\begin{array}{ccc}&\mathrm{OC_2H_5}&\\ &|&\\ &\mathrm{C{=}O}&\\ &|&\\ \mathrm{CH_3}-&\mathrm{C}&-\mathrm{Br}\\ &|&\\ &\mathrm{C{=}O}&\\ &|&\\ &\mathrm{OC_2H_5}&\end{array}$$

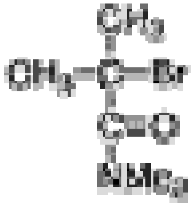
I-26



I-27

$$\begin{array}{ccc}\mathrm{CH_3}-&\mathrm{CH}&-\mathrm{Br}\\ &|&\\ &\mathrm{C{=}O}&\\ &|&\\ &\mathrm{NMe_2}&\end{array}$$

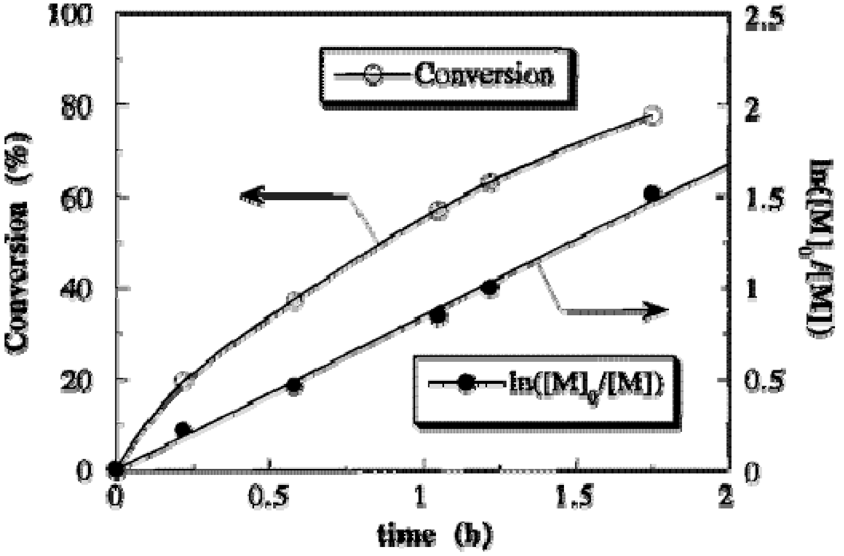
I-29

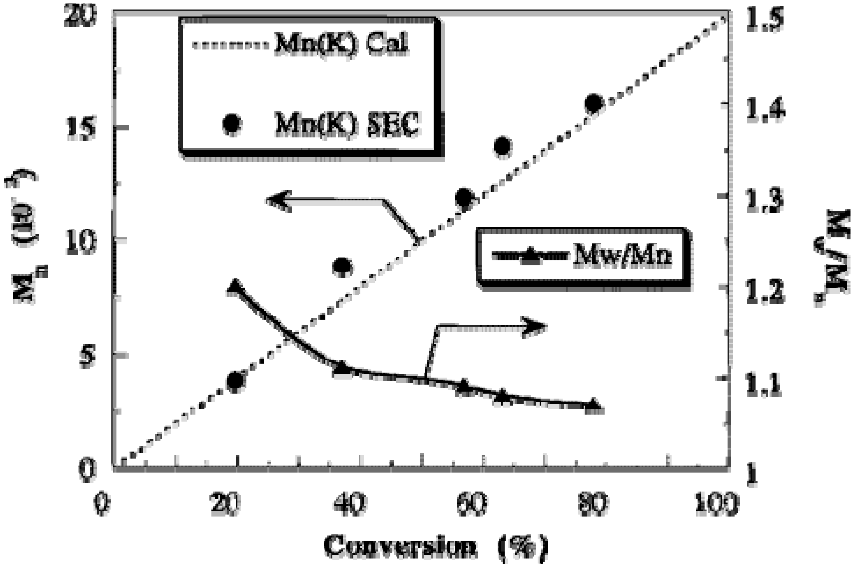


$$\begin{array}{ccc}&\mathrm{CH_3}&\\ &|&\\ \mathrm{CH_3}-&\mathrm{C}&-\mathrm{Br}\\ &|&\\ &\mathrm{C{=}O}&\\ &|&\\ &\mathrm{NMe_2}&\end{array}$$

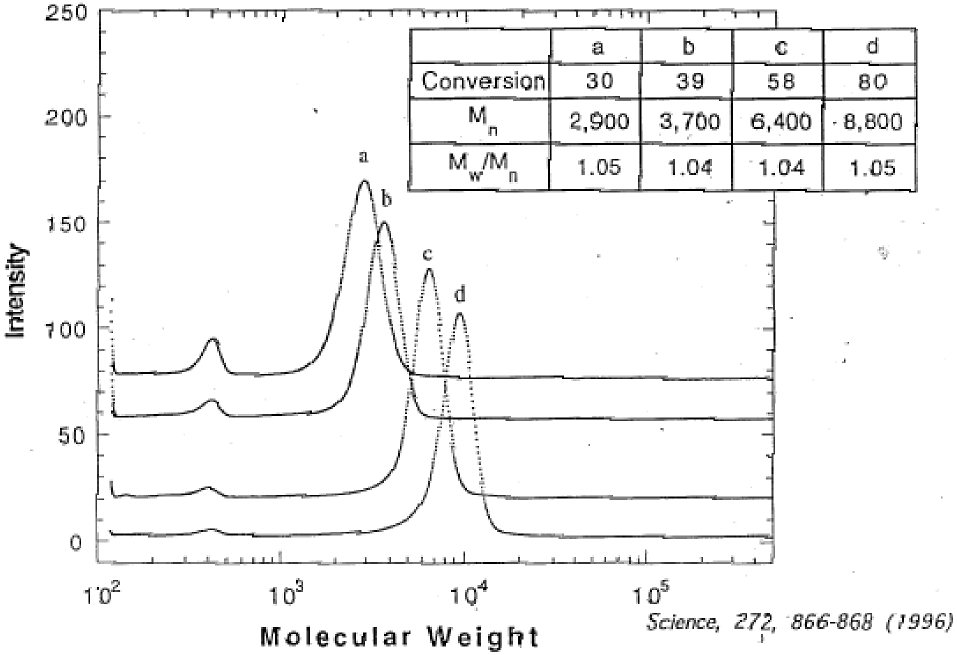
I-30

Bulk ATRP of Styrene





$[M]_o=8.7M$; $[1\text{-PhEt-Br}]_o=[CuBr]_o=0.1M$; $[4,4'\text{-dHBPY}]_o=0.2M$; 110°C



	a	b	c	d
Conversion	30	39	58	80
M_n	2,900	3,700	6,400	8,800
M_w/M_n	1.05	1.04	1.04	1.05

Science, 272, 866-868 (1996)

$$R_p = k_p \cdot K \cdot [M] \cdot [RX] \frac{[Cu^I L_2]}{[X-Cu^{II} L_2]};$$

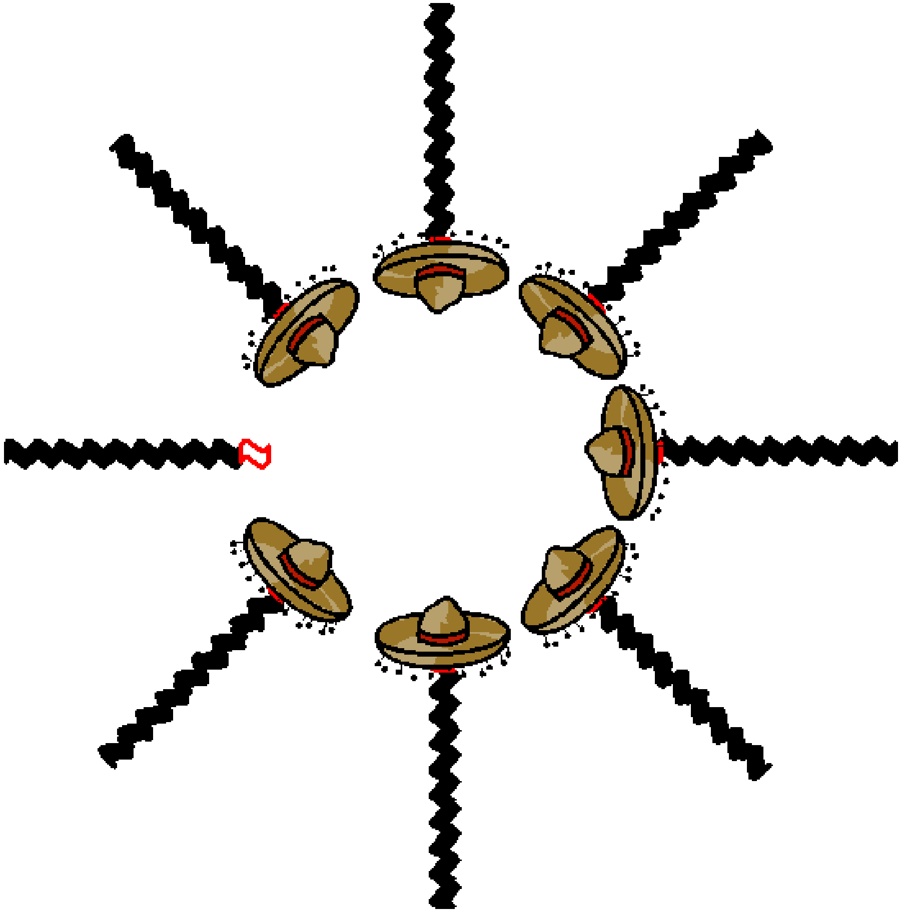
$$K = \frac{k_{act}}{k_{deact}}$$

2. Reversible Transfer

Degenerative Transfer between active and dormant chains:

$$\sim\sim\sim P_m\text{-}I + {}^\bullet P_n\sim\sim\sim \rightleftharpoons \sim\sim\sim P_m{}^\bullet + I\text{-}P_n\sim\sim\sim$$

where [P-I] >> [P •]

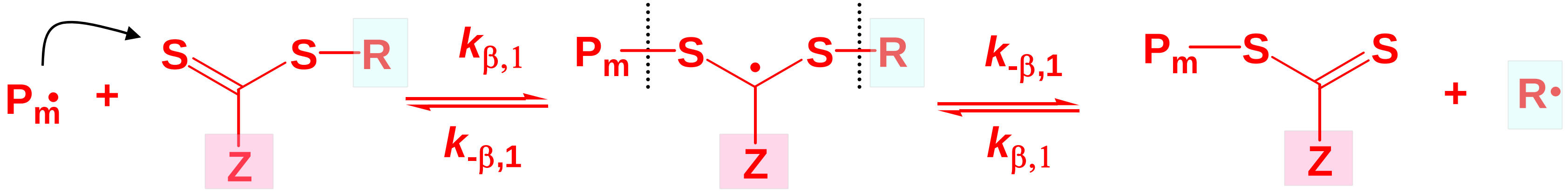


Reversible Addition-Fragmentation Chain Transfer **(RAFT)** Polymerization

Rizzardo, Moad 1998

Initiation: **initiator + monomer → $P_m^\bullet$**

Addition / fragmentation:



chain transfer agent

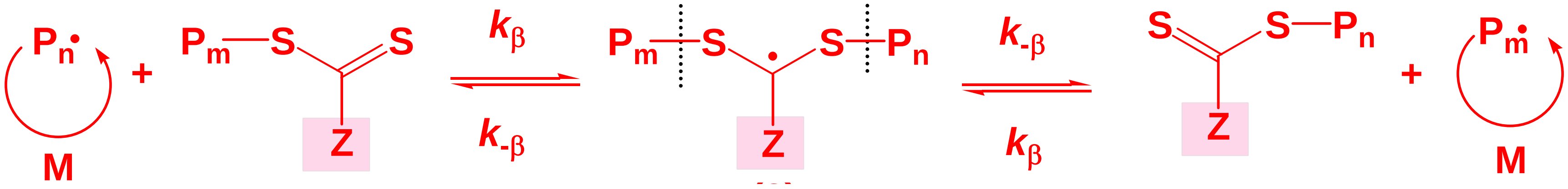
dormant

dormant

Re-inintiation: $R^\bullet \xrightarrow[k_i]{\textbf{Monomer}} P_n^\bullet$

Propagation: $P_n^\bullet \xrightarrow[k_p]{\textbf{Monomer}} P_{n+1}^\bullet$

Equilibration:



active

dormant

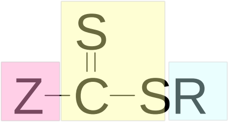
dormant

dormant

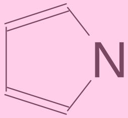
active

Chain Transfer Agents (CTAs)

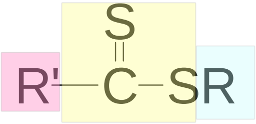
are thiocarbonylthio compounds:



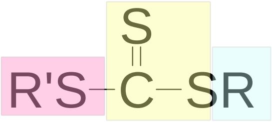
$Z-\overset{\overset{\displaystyle S}{\|}}{C}-SR$

Z = alkyl, aryl,  N, R'O-, R'S- (stabilizes radical)

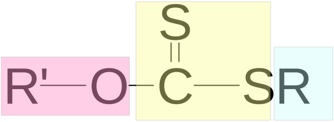
R = alkyl, aryl (leaving group): reinitiates polymerization,
can carry functional groups

dithioester 

$R'-\overset{\overset{\displaystyle S}{\|}}{C}-SR$

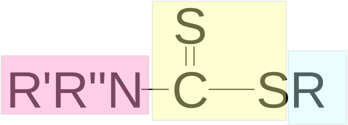
trithiocarbonate 

$R'S-\overset{\overset{\displaystyle S}{\|}}{C}-SR$

xanthate 

$R'-O-\overset{\overset{\displaystyle S}{\|}}{C}-SR$

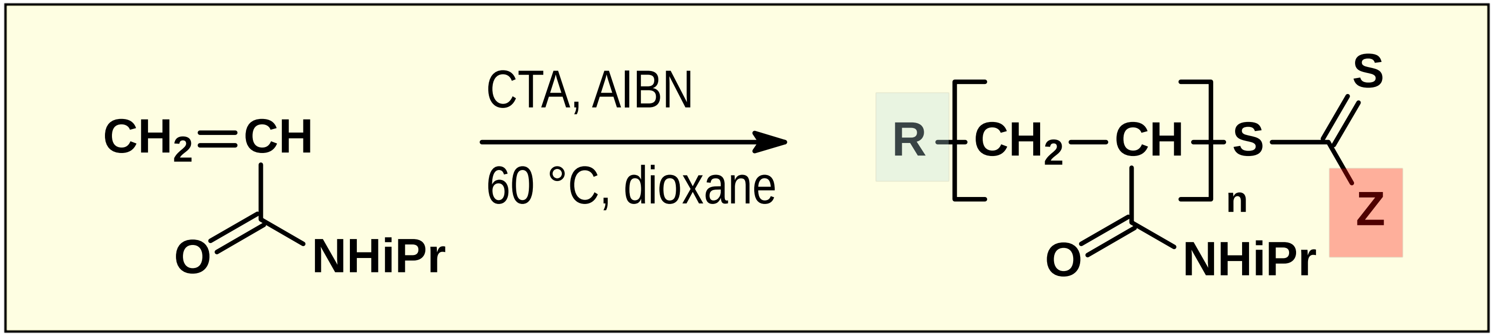
→ MADIX
(Rhodia 1999)

dithiocarbamate 

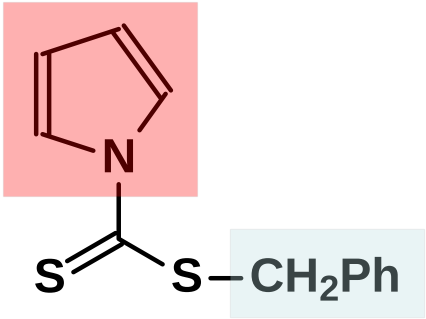
$R'R''N-\overset{\overset{\displaystyle S}{\|}}{C}-SR$

RAFT of *N*-isopropylacrylamide (NIPAAm)

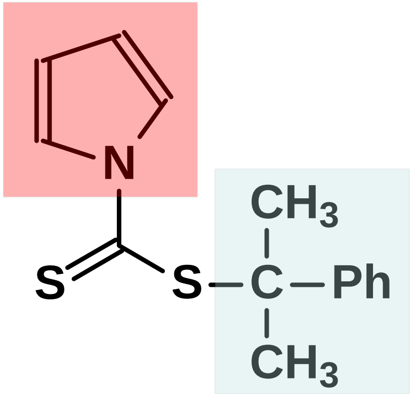
Synthesis of polyNIPAAm via RAFT with dithiocarbamates as chain transfer agents



Chain transfer agents used:



benzyl 1-pyrrolecarbodithioate



cumyl 1-pyrrolecarbodithioate

Conclusions:
Controlled Radical Polymerization

- Controlled Radical Polymerization proceeds either by **Reversible Deactivation** (NMR, ATRP) or by **Reversible Transfer** (Degenrative Transfer, RAFT).
- The rate of polymerization depends on the **position of the activation equilibrium**.
- The MWD depends on the **dynamics of the activation equilibrium**.
- **Termination** cannot be completely avoided.
- **Transfer** is not affected by CRP.

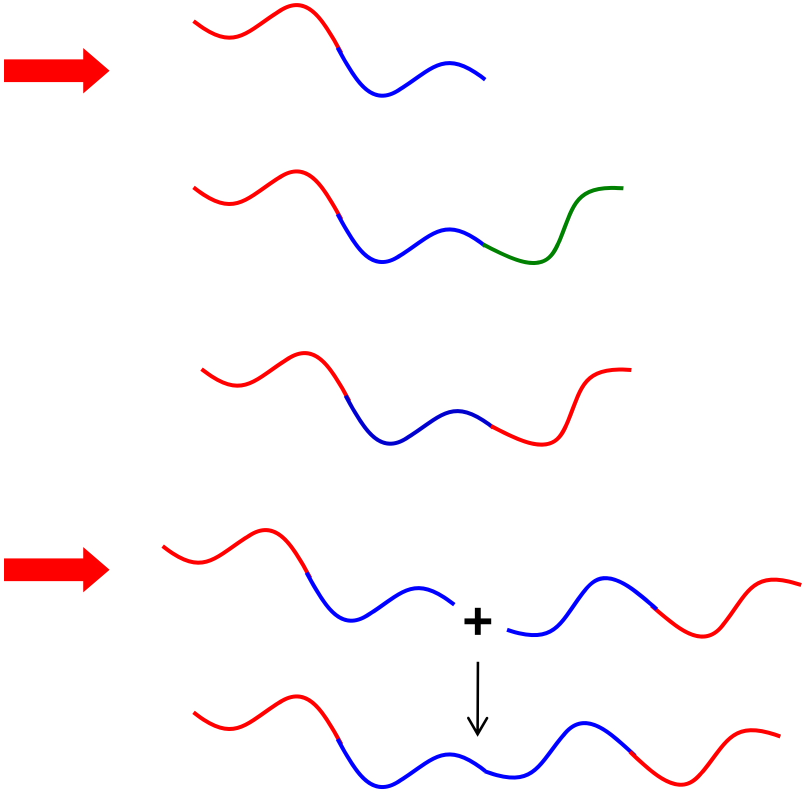
Comparison of “Living” Mechanisms

	Pro ☺	**Con ☹**
Radical	Low purity requirements (cheap) Convenient temperatures (cheap) Large variety of monomers Block copolymers Random copolymers Gradient copolymers	Expensive nitroxides, CTA’s Removal of metals difficult Very few cyclic monomers for ROP Some termination No control of transfer → low MW Little control of microstructure
Ionic	No (little) termination or transfer Block copolymers High MW ROP possible Some control of microstructure	Termination or transfer (some cases) High purity, low T (expensive) Choice of monomers restricted Random copolymers difficult

Part B

Synthesis and Properties of Block Copolymers

Synthesis of linear block copolymers



Sequential monomer addition

AB

ABC

ABA

Polymer-polymer coupling

2 x AB

ABA

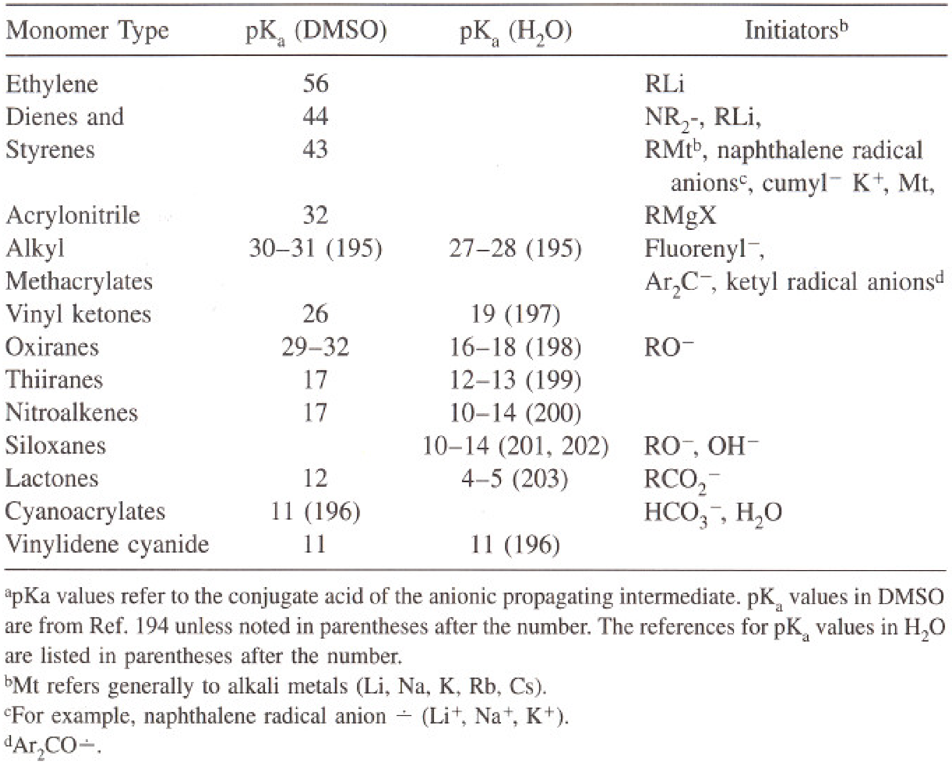
Problem: low coupling efficiencies

Sequential monomer addition

$$I^- \xrightarrow{M_A} I\sim\sim\sim\sim M_A^- \xrightarrow{M_B} I\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim M_B^- \xrightarrow{M_C} I\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim M_C^-$$

macroinitiator

Good blocking efficiency when the reactivity of the first block is higher or comparable to that of the second block.



Monomer Type	pK_a (DMSO)	pK_a (H_2O)	Initiators[b]
Ethylene	56		RLi
Dienes and	44		NR_2^-, RLi,
Styrenes	43		RMt[b], naphthalene radical anions[c], cumyl$^-$ K^+, Mt,
Acrylonitrile	32		RMgX
Alkyl Methacrylates	30–31 (195)	27–28 (195)	Fluorenyl$^-$, Ar_2C^-, ketyl radical anions[d]
Vinyl ketones	26	19 (197)	
Oxiranes	29–32	16–18 (198)	RO^-
Thiiranes	17	12–13 (199)	
Nitroalkenes	17	10–14 (200)	
Siloxanes		10–14 (201, 202)	RO^-, OH^-
Lactones	12	4–5 (203)	RCO_2^-
Cyanoacrylates	11 (196)		HCO_3^-, H_2O
Vinylidene cyanide	11	11 (196)	

[a] pKa values refer to the conjugate acid of the anionic propagating intermediate. pK_a values in DMSO are from Ref. 194 unless noted in parentheses after the number. The references for pK_a values in H_2O are listed in parentheses after the number.

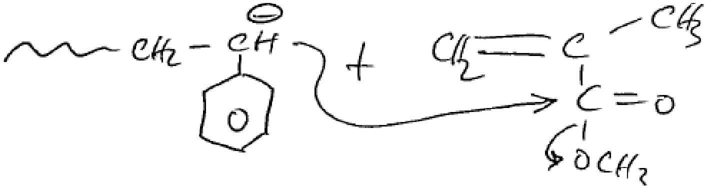
[b] Mt refers generally to alkali metals (Li, Na, K, Rb, Cs).

[c] For example, naphthalene radical anion $\dot{-}$ (Li^+, Na^+, K^+).

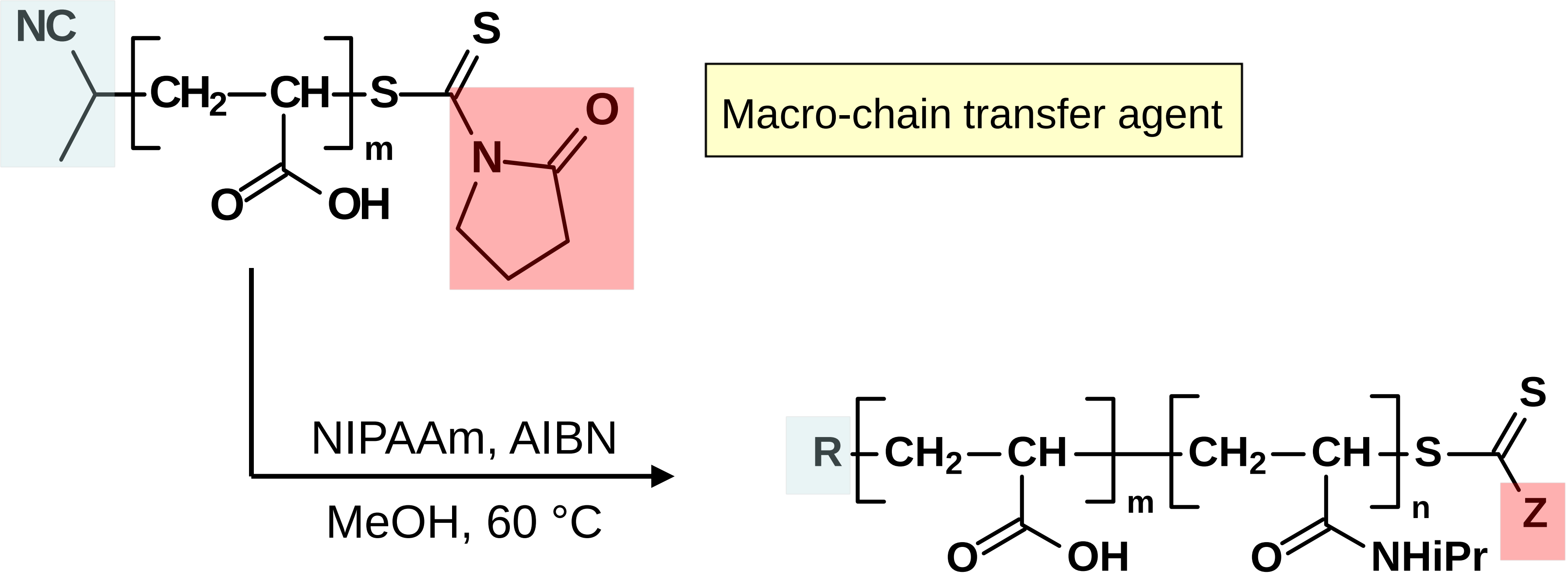
[d] $Ar_2CO\dot{-}$.

Attenuation of the reactivity of the first block may be necessary in order to avoid side reactions in the cross-over step.

$$\begin{tikzcd} PS^- + DPE \arrow[r] & PS\text{-}DPE^- \arrow[d, "MMA"] \\ & PS\text{-}PMMA \end{tikzcd}$$

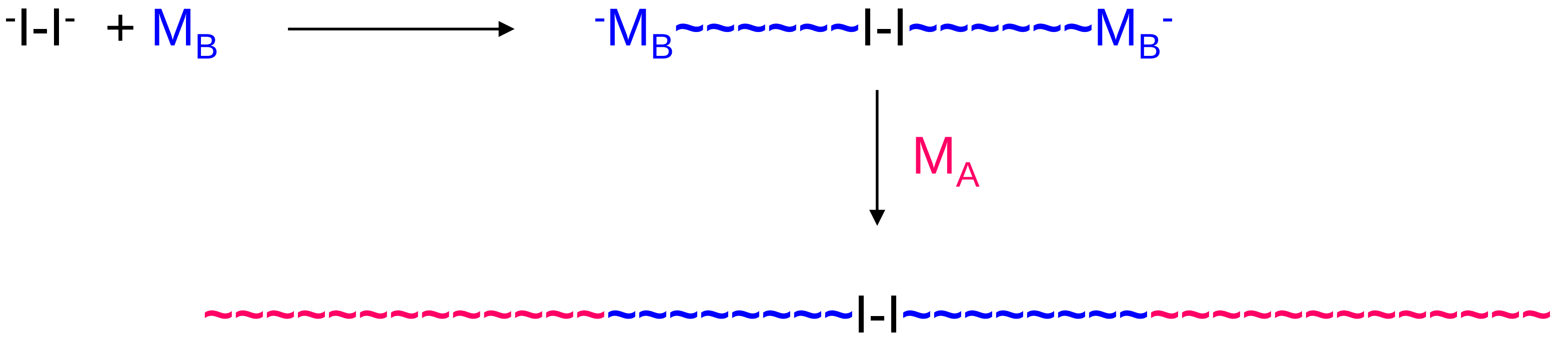


Special Case: RAFT



Macro-chain transfer agent

Bifunctional initiation



$$^{-}I\text{-}I^{-} + M_B \longrightarrow {}^{-}M_B\sim\sim\sim\sim\sim\sim\sim I\text{-}I\sim\sim\sim\sim\sim\sim\sim M_B^{-}$$

$$\downarrow M_A$$

$$\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim I\text{-}I\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim$$

Problem: Bifunctional initiators are not well soluble in hydrocarbon solvents (due to aggregation)

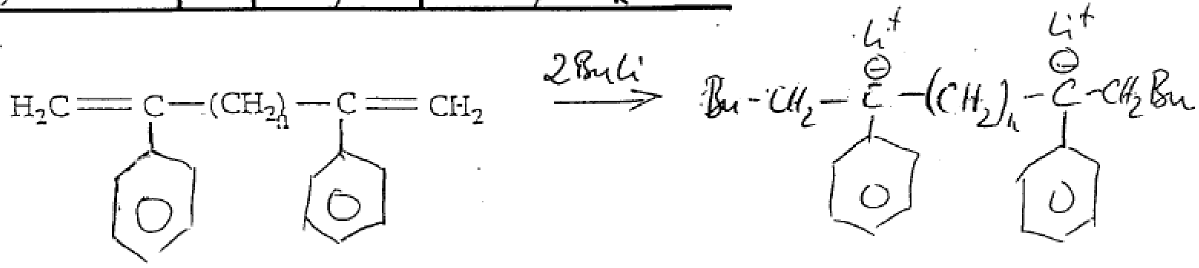
Most important properties: Microphase separation in bulk
Micelle formation in solution

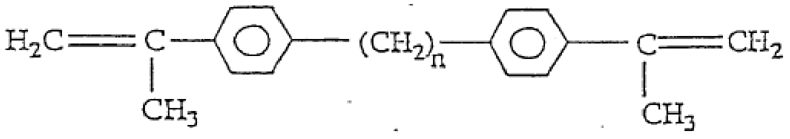
Most important applications: SBS, thermoplastic elastomers (Kraton®)
PPO-PEO-PPO, amphiphilic copolymers (Pluronics®)

Anionic bifunctional initiators for non-polar solvents

1) α,ω–bis(phenylvinylidenyl)alkanes

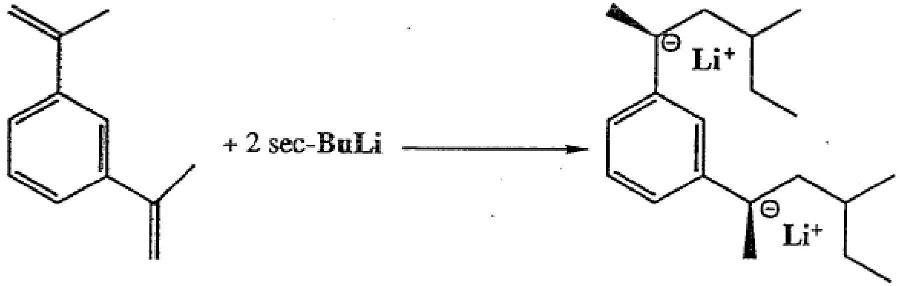
α,ω-diisopropenyldiphenylalkanes



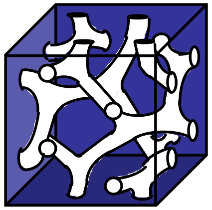


(n ≥ 2)

2) Diisopropenylbenzenes

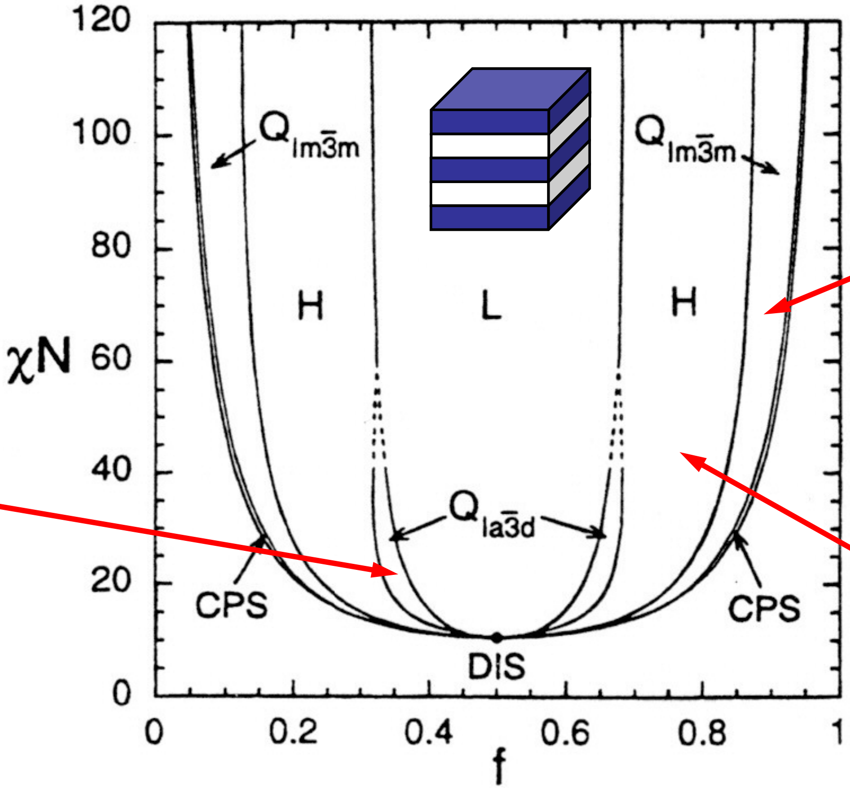


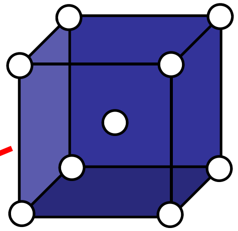
Phase diagram and topology of diblock copolymers in bulk



Gyroid

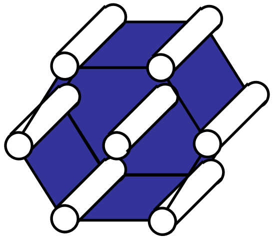
($Q_{Ia\bar{3}d}$)





BCC spheres

($Q_{Im\bar{3}m}$)

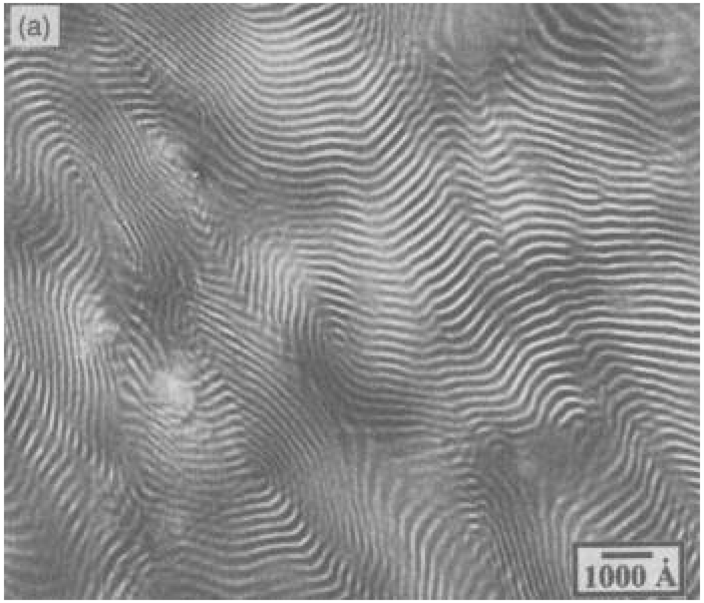


Hexagonal cylinders

(H)

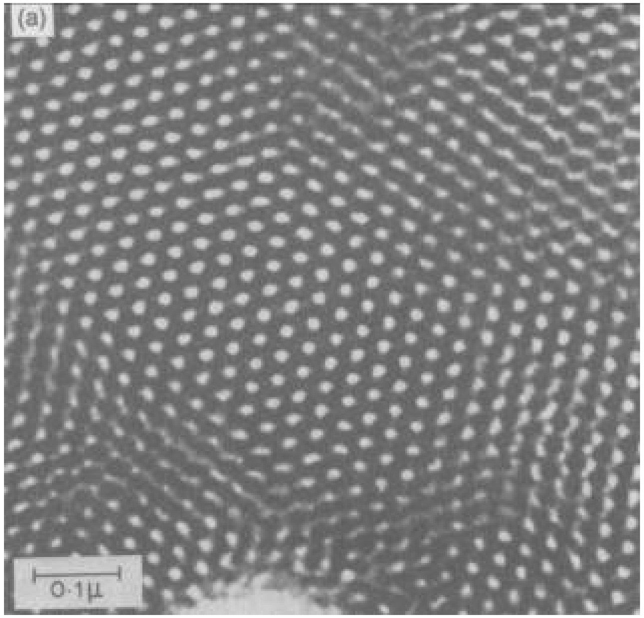
PS-b-PI lamellar morphology

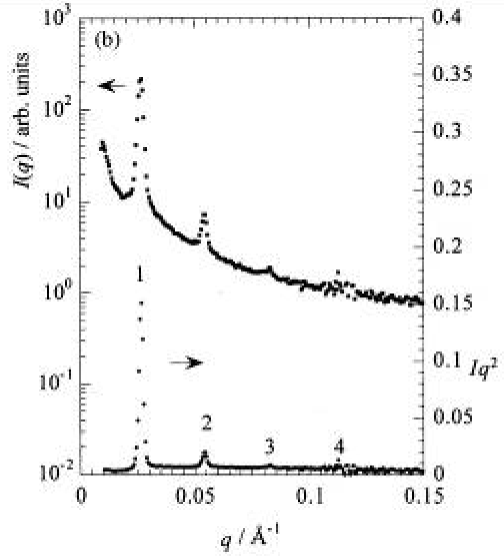
PS-PB-PS cubic (spherical) morphology



TEM

OsO_4





SAXS

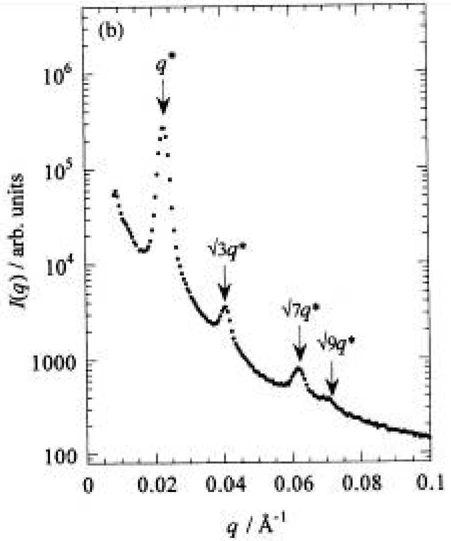
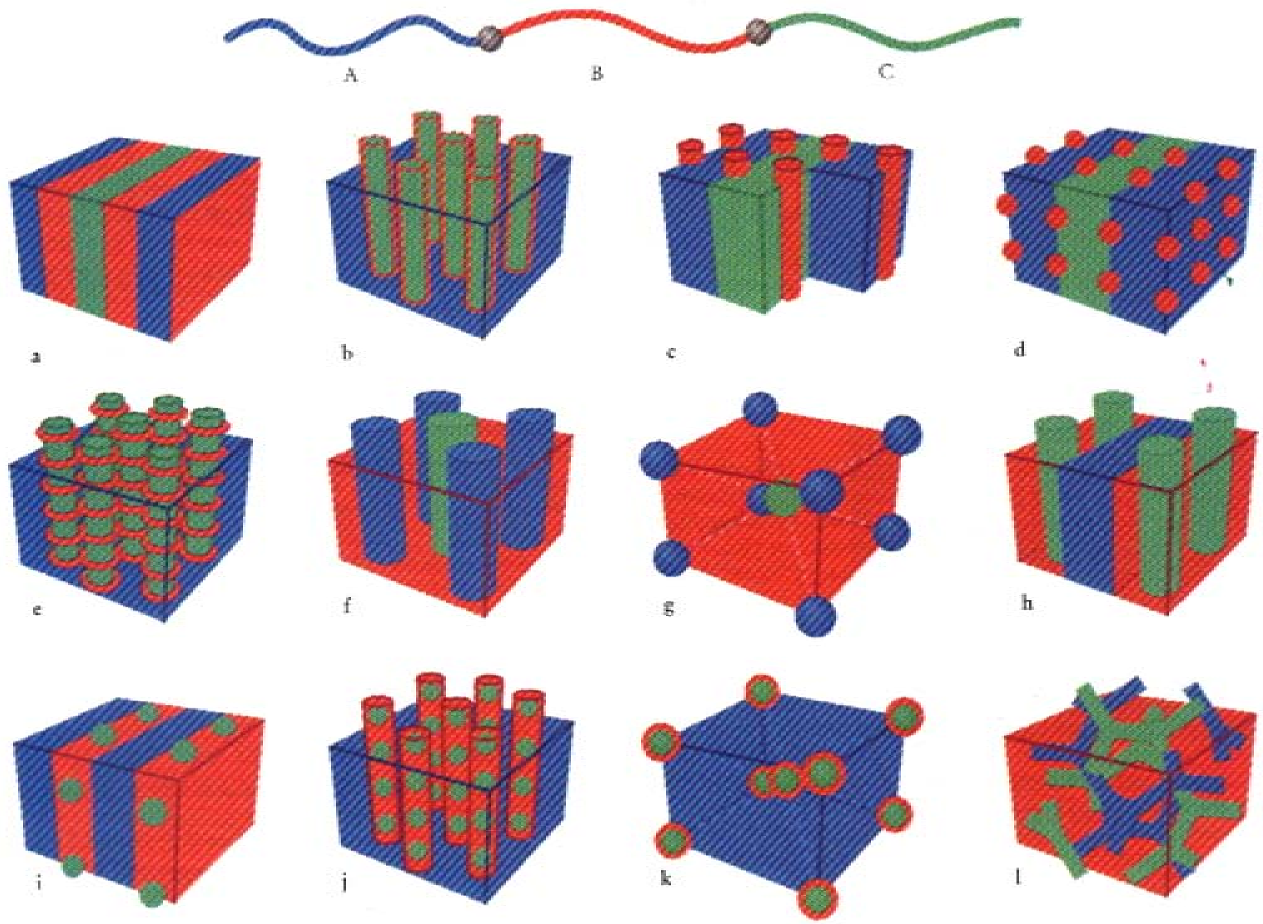


Fig. 2.6 (a) The lamellar microstructure of a PS–PI diblock with f_{PS} = 0.64 and M_n = 39 kg mol^{-1} shown by TEM where the PI is stained dark (Khandpur *et al.* 1995); (b) SAXS powder pattern from the same material.

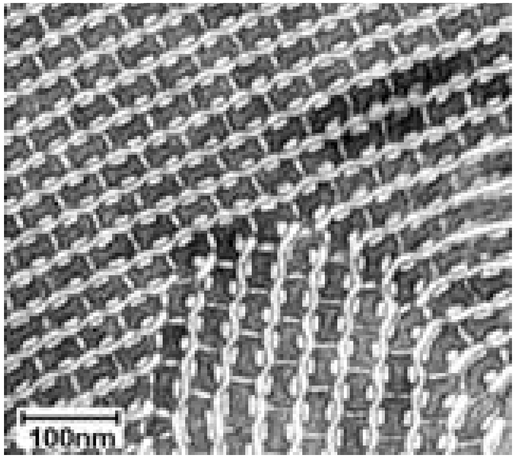
Fig. 2.9 (a) TEM micrographs from the hexagonal morphology in Kraton TR1102, a PS–PB–PS block copolymer with $f_{PS} \approx 0.24$ (Dlugosz *et al.* 1970; Keller and Odell 1985). (b) SAXS powder pattern from Kraton TR1102 (Ryan and Hamley 1997).

Morphologies of triblock terpolymers

(found with S-B-M)



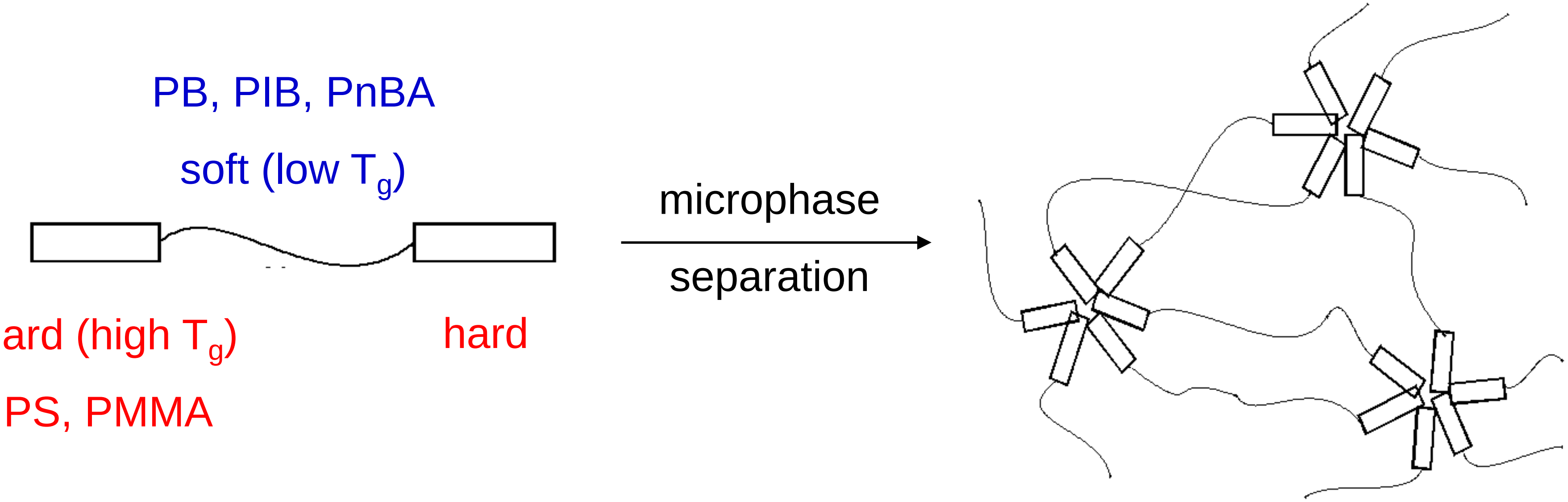
S-EP-M



“knitting pattern”

R. Stadler et al.

Thermoplastic elastomers based on ABA bock copolymers



PB, PIB, PnBA

soft (low T_g)

hard (high T_g)

PS, PMMA

hard

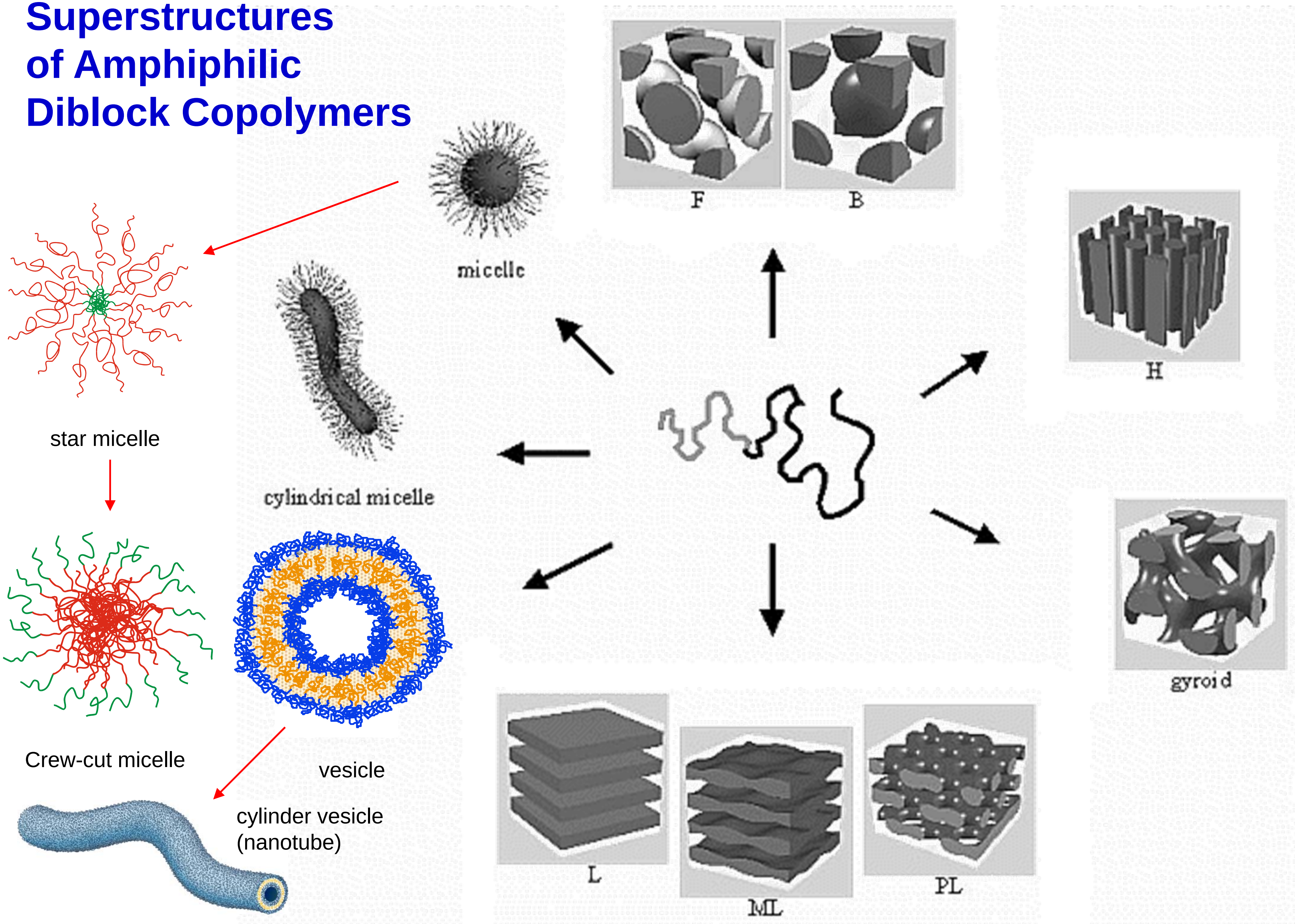
microphase

separation

physical cross-linking

reversible!

Superstructures of Amphiphilic Diblock Copolymers



star micelle

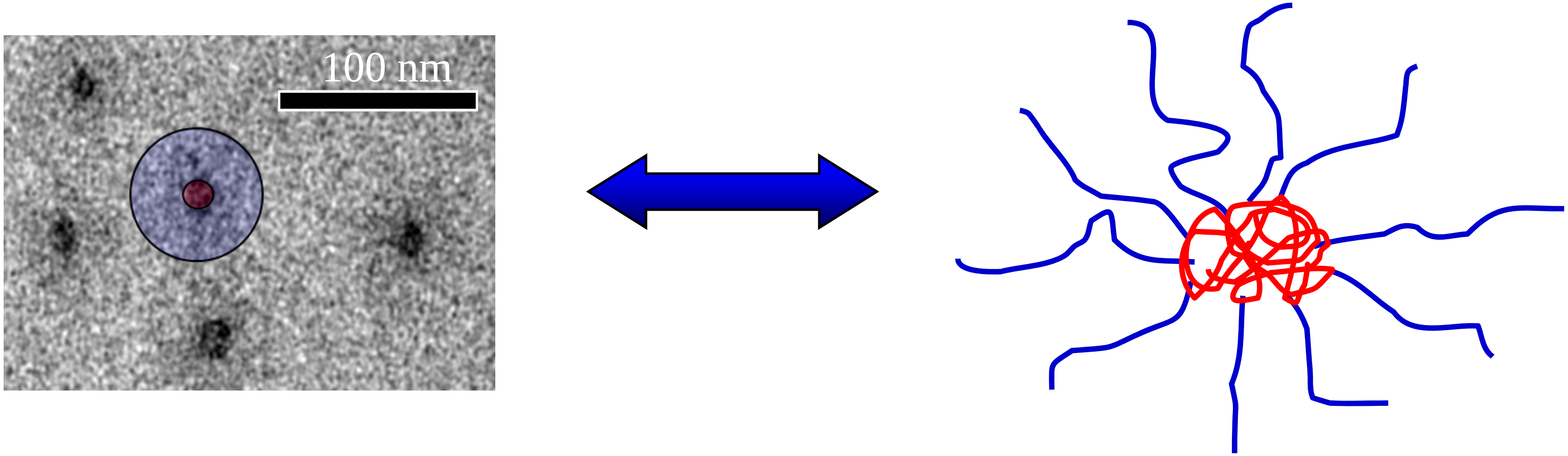
Crew-cut micelle

vesicle

cylinder vesicle
(nanotube)

Cryo-TEM of micelles at high pH

$\text{PnBA}_{90}\text{-}b\text{-PAA}_{300}$



R_{core} ~ 5 nm

$R_{micelle}$ ~ 30 - 50 nm (?)

R_h ~ 50 nm (DLS)

$L_{contour}$ (PAA) = 75 nm

Collapsed core surrounded by an extended corona