

Program

1° Basic principles of anionic Polymerization

- General Reaction Scheme
- Initiators, Monomers, experimental conditions
- Aspects of living Polymerization
- Factors Affecting the Molar Mass Distribution
- Control of Microstructure : Methods and distribution of tacticity

2 Anionic Polymerization of Non-polar Monomers

- Initiation and Propagation in Polar Solvents
- Initiation and Propagation in Hydrocarbon Solvents
- Stereochemistry of Polydienes
- Association Phenomena in non Polar Solvents

Specific Problems of bifunctional Initiators

3) Anionic Polymerization of Polar Monomers

- Type of Polar Monomers**
- Potential Problems due to Polar Side Groups**
- Kinetics and Mechanisms of (Meth)acrylate (MMA) Polymerization**
- Stereoregulation in MMA Polymerization**
- Modification of Active Centres via Additives and New Initiating Systems**

4) Macromolecular Engineering by Anionic Polymerization

- Block Copolymers**
- Functional Polymers (including Macromonomers)**
- Graft copolymers (grafting from, grafting onto, grafting through)**
- Special case of Cyclic Polymers**
- Branched Polymers**

Living Polymerization Mechanism

- **Anionic Polymerization**
M. Szwarc 1956
- **Cationic Polymerization**
T. Higashimura, 1979
- **Group Transfer Polymerization**
O.W. Webster, 1983
- **Ring-opening Metathesis Polymerization**
R.H. Grubbs, 1986
- **Radical Polymerization**
(T. Otsu, 1984)
M. Georges 1993, K. Matyjaszewski 1993

Anionic Polymerization

Known for a long time:

- The Polymerization of styrene in liquid ammonia, initiated by sodium amide (NaNH_2)
- The polymerization of dienes initiated either by metallic sodium (Buna) or with butyllithium
- The ring opening polymerization of oxirane (ethylene oxide) initiated by potassium alcoholates
- The polymerization of monomers such as cyanoacrylates by weak bases in acrylic glues

- **Control of Molar Mass and Molar Mass Distribution**
- **Developement related to well-defined polymers as model for physico-chemical studies:
Relation Structure / Properties**
- **Access to functional polymers, to block copolymers to branched species... Cycles, to more complex architectures**

Still actual ?

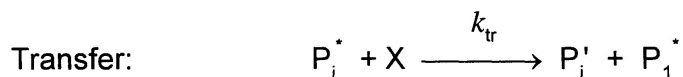
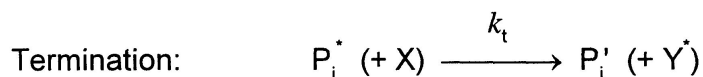
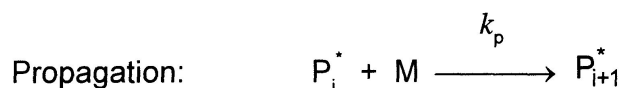
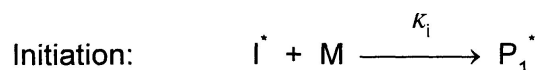
Living anionic polymerization : kinetic scheme

1) Initiation

2) Propagation (or chain growth)

No Spontaneous termination

No transfer reaction



if termination and transfer are absent ($R_t, R_{tr} \ll R_p$):

☞ **LIVING POLYMERIZATION**

- Molar mass is determined by the monomer to initiator mole ratio

- Polymolecularity is small (Poisson type distribution)

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

- Active sites remain at chain end, capable of further reactions :

- A new addition of monomer results in increase in size of the existing chains
Synthesis of block copolymers upon addition of a second suitable monomer

- Functionalization at chain end upon addition of an adequate reagent
Chain extension reactions, grafting reaction, controlled crosslinking

➡ **Life time of the anionic sites exceeds the duration of the polymerization** 5

Conditions for a living Polymerization

- Anionic polymerizations proceed via metalorganic sites: Carbanions, oxanions / Metallic counterions

NO TERMINATION

i.e. the number of *active* chain-ends $[P^*]$ is constant

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

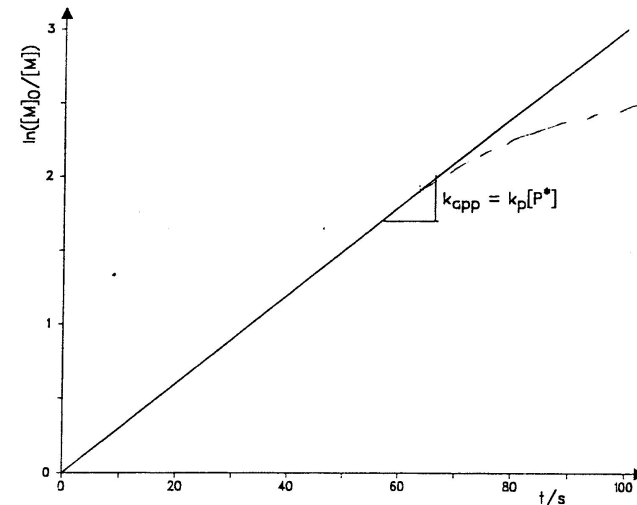
$$R_p = - \frac{d[M]}{dt} = k_p [M] [P^*],$$

$$[P^*] = \text{const.} = [I]_0$$

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

$[P^*]$ is the concentration of *living* chain-ends

Presence of **ion-pairs** and **free ions**: if a equilibrium is involved the rates of dissociation and association are fast with respect to propagation
 α , degree of ionic dissociation



$$k_p = \alpha k_{p-} + (1 - \alpha) k_+$$

Conditions for a living Polymerization

- Anionic polymerizations proceed via metalorganic sites: Carbanions, oxanions / Metallic counterions

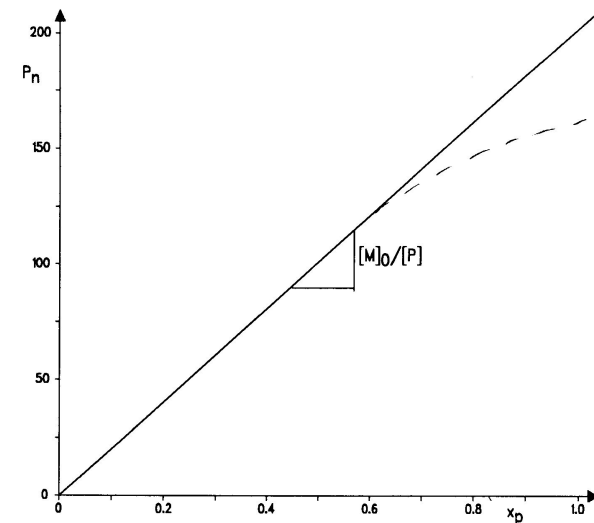
NO TRANSFER

There are no new chains formed, i.e. the total number of polymer chains, $[P]$, (*including the terminated ones*) is constant:

$$[P] = [P^*] + [P^{\text{dead}}] = [I]_0$$

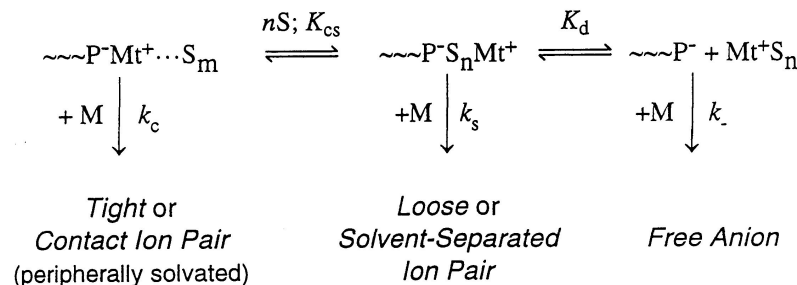
Evidence: the number-average degree of polymerization, P_n , is a linear function of monomer conversion, x_p :

$$P_n = \frac{\text{number of polymerized monomers}}{\text{number of polymer chains}} = \frac{[M]_0 x_p}{[P]} = \frac{[M]_0 x_p}{[I]_0}$$



Active sites:**Contact and Solvent-Separated Ion Pairs**

These two findings are both related to the coexistence of two kinds of ion pairs in solvents of higher polarity, i.e. contact and solvent-separated ion pairs.

Three-State Mechanism

Due to the higher interionic distance, solvent-separated ion-pairs are more reactive than contact ion pairs ($k_- > k_s \gg k_c$).

At lower temperatures the solvating power of the solvent increases (solvation is exothermic). This increases the fraction of the more reactive solvent-separated ion pairs. This more or less compensates the decrease of rate constants at lower temperatures.

Smaller counterions (Li^+ , Na^+) more easily form solvent-separated ion-pairs than larger counterions. Thus, PS-Li and PS-Na are more reactive than PS-Cs in THF and DME.

The Three-State-Mechanism is a part of the "**Winstein Spectrum**" of ionicity which also includes covalent species.

Deviation for living character: Factors leading to broader MWDs

Non-living processes : termination, transfer

- inadequate mixing

$$t_{\text{mix}} > t_{1/2}$$

- slow initiation

$$k_i < k_p \quad M_w / M_n < 1.35$$

- reversible polymerization

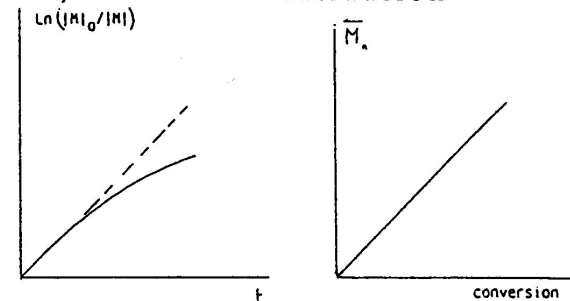
« scrambling »

M_w / M_n lower or equal to 2

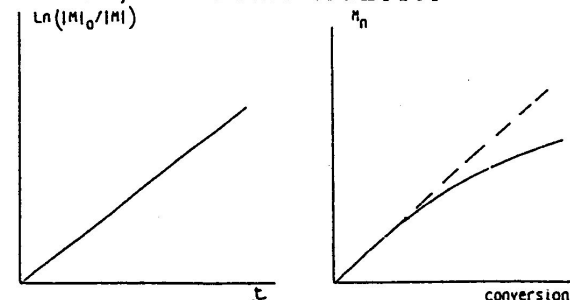
- Slow equilibria between species of different activities

$$R_{\text{ex}} < R_p$$

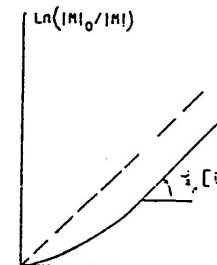
No transfer, but some termination



No termination, but some transfer



Slow initiation, but no transfer and no termination



Special consideration for experimental work

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

This implies

Aprotic solvents polar THF

non polar toluene, cyclohexane (rigorous purification of reagents)

Handling of reagents in vacuum or under inert gas

- Due to the absence of termination, the concentration of active species is much higher than in radical polymerization.

- Thus the rates sometimes can be very high ($t_{1/2} < 1\text{s}$)
- 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

Why is industry interested in living polymerization ?

- **Controlled Polymerization Process**

 - Predictable Molar Mass

 - Narrow Molar Mass Distribution

 - 100% Monomer Conversion

 - Monomer-free Products (Health, Environment)

- **Designed Polymer Architecture**

 - Topology linear, cyclic, Star-block copolymers

 - Composition : block, graft, star-block copolymers

- **Designed Combination of Structural Elements**

 - Monomers :**

 - Hydrophobic / hydrophilic (amphiphilic copolymers)

 - high / low T_g (thermoplastic elastomers)

 - Functional Groups (terminal or internal)

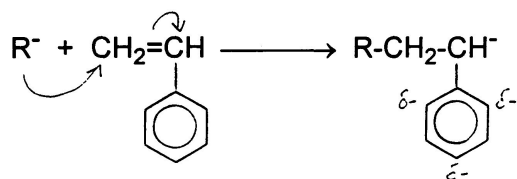
 - Macromonomers

 - Telechelics

 - Labels

Monomers: A monomer can be polymerized anionically if the sites derived therefrom are capable to induce chain growth

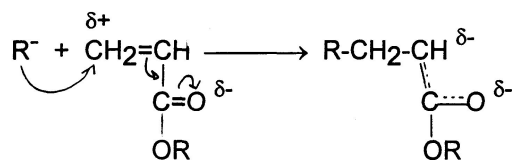
- Limited number of monomers to be polymerized anionically
vinyl monomers : -electronic substituant No functions that could deactivate the sites
- Monomers with deactivating functions (protonic, electronic) Polymerizable anionically
protection/ Polymerization/deprotection
- Ring-opening polymerization of heterocyclic monomers
(no general routes, cationically /anionically)



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

Styrene, α -methyl styrene
o-, m-, p-alkyl styrenes
vinyl (isoprenyl) naphthalene
butadiene, isoprene, cyclohexadiene,....

2. Polar electrophilic vinyl compounds (with electron attracting substituents)



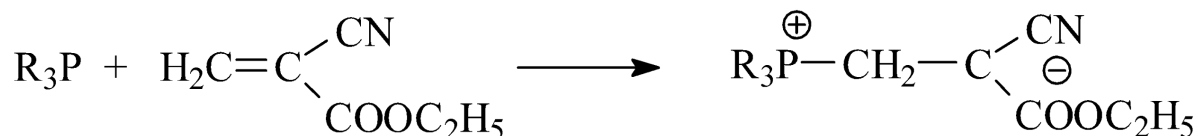
Vinyl (isoprenyl) pyridine
(meth)acrylates
vinyl (isoprenyl) ketones
(meth)acrolein
(methacrylonitrile)

3. Isocyanates, $R-N=C=O$, Isocyanides, $R-N^+ \quad C^-$

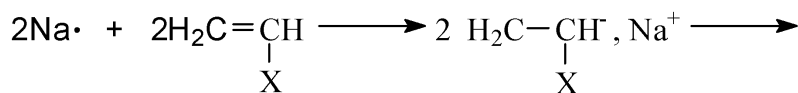
4. Cyclic Ethers, Esters, Siloxanes Ring Opening Polymerization

Initiators

- **Organometallic bases monofunctional**
 - alcoholates (t-BuOLi, t-BuO-K
 - amides
 - organolithium BuLi....
 - alkali salts of aromatic hydrocarbons
 - Grignard reagents, R-Mg-Br
 - alkaline earth –and aluminium-organic compounds
 - transition-metal compounds
 - (ester) enolates, picolyl salts
- **Lewis Bases : Zwitterionic Polymerization**



- **Electron transfer agents : bifunctional**



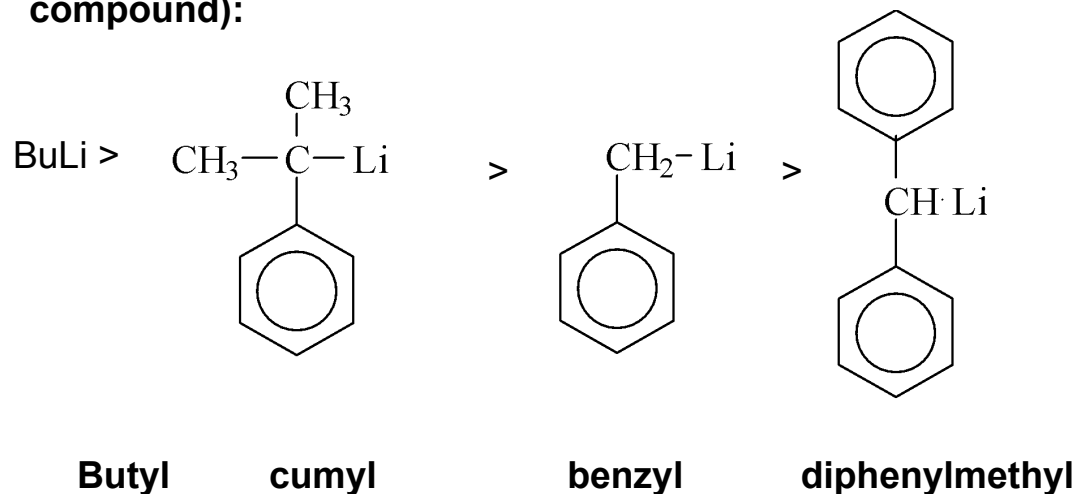
- **Radical anions: naphthalene sodium, (homogeneous)**



- **Living Polymers : formation of block copolymers**

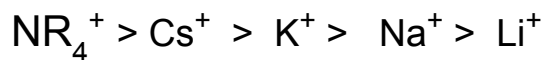
The reactivity of an initiator depends on

- The nucleophilicity of the anion (roughly correlates with the pKa value of the non-metalated compound):



Fluorenyl Li, methyl propionate, t-butoxide

- The ionic radius of the counterion :



- The polarity of the solvent

THF > toluene, Pb of transfer



The nucleophilicity of the initiator must be equal or higher than the electrophilicity of the monomer (pKa of the « hydrogenated » monomer

Scale of Initiator Efficiency with respect to monomer

INITIATOR		Rapid quantitatif	MONOMER	
↑ INCREASING NUCLEOPHILICITY	CUMYL POTASSIUM	→	P-DIMETHYLAMINOSTYRENE	↑ INCREASING ELECTROAFFINITY
			A-METHYLSTYRENE	
	BENZYL K		STYRENE	
			BUTADIENE (isoprene)	
	DIPHENYLMETHYL K		VINYLNAPHTALENE	
			VINYLPYRIDINE	
	FLUORENYLPOTASSIUM		METHYLMETHACRYLATE	
	K BUTOXYDE		OXIRANE	
	KOH	→	METHYLENEMALONIC ESTERS	
			CYANOACRYLICS ESTERS	

- Monomers, Initiators, experimental conditions

Block copolymer synthesis

Monomer A	Monomer B	Method	Type
Styrene	Trimethylsilylstyrene	1	AB, BAB
Styrene	Substit. Styrenes	1	AB, BAB
Styrene	Isoprene, Butadiene	1,2	AB, BAB, ABA
Styrene	Phenylbutadiene	1,2	AB, BAB, ABA
Styrene	Vinyl Pyridine	1	AB, BAB
Styrene	Alkylmethacrylates	1	AB, BAB
Styrene	Oxirane	1,2	AB, BAB
Styrene	Caprolactame	3	AB, BAB
Styrene	Oxolane (THF)	2,3	AB, ...
Isoprene	Butadiene	1	AB, BAB, ABA
Isoprene	Alkylmethacrylates	1	AB, BAB
Isoprene	Oxirane	1	AB, BAB
Vinyl Pyridine	Oxirane	1	AB, BAB and others

Method 1 : sequential addition of monomers

Method 2 : coupling between functional Polymers

Method 3 : site transformation technique

Anionic Polymerization in Non-Polar Solvents

Specific Case of Diene Polymerization of Controlled Microstructure

- Non polar Solvents
 - Li as a counterion
 - As in classical anionic polymerization : non spontaneous termination
 - High content of 1,4- (cis) units (elasticity)
 - Microstructure can be modified by introduction of polar additives
 - Low propagation rates (increased probability of deactivation) as compared to polar solvents
 - Limited to a few number of monomers
- Diene, Styrene
- Industrial applications : Thermoplastic elastomers, Styrene butadiene rubbers

Structure and Bonding of Organolithium Compounds

- Unique compounds : Properties and Characteristics of

Covalent compounds

Ionic compounds

- Specific case of Lithium
 - Among alkali metals has the smallest radius
 - Highest ionization potential
 - Greatest electronegativity
 - unoccupied p orbitals for bonding
- Not compatible with ionic character
 - Solubility in Hydrocarbons
 - More complex bonding
 - orbital calculations
 - fractional charges

Association States of n-alkyl Organolithium Initiators

Gas phase / solid state

Nature of the solvent

Concentration of the reaction medium

Temperature

Compound	Solvent	n ^a	Method ^b
C₂H₅Li	Benzene	6	F
	Benzene	6	F
	Benzene	4.5-6.0	F
	Benzene	6.0	F
	Cyclohexane	6.0	F
	Benzene	6.1	F
	Cyclohexane	6.0	F
n-C₄H₉Li	Benzene	6.3	I
	Benzene	7	B
	Cyclohexane	6.2	I
	Benzene	6.0	F
n-C₆H₁₁Li	Benzene	6.0	V
n-C₈H₁₇Li	Benzene	6.0	V

a) Average degree of aggregation

b) Freezing point, I isopiestic, B boiling point, elevation, V vapor pressure depression

CLASSICAL ANIONIC INITIATORS IN NON POLAR SOLVENTS

- **Monofunctional**

- Soluble in classical non polar solvents
- Butyllithium (BuLi) , sec BuLi is the best
- Phenyllithium
- Diphenylmethyllithium

Preparation easy, commercially available

- **Difunctional**

- Specific case of difunctional initiators
- Association degrees , mixed association
- Problem : solubility in non polar solvents

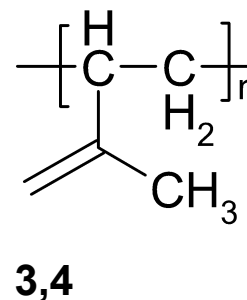
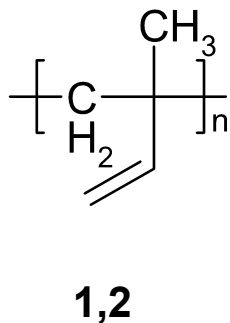
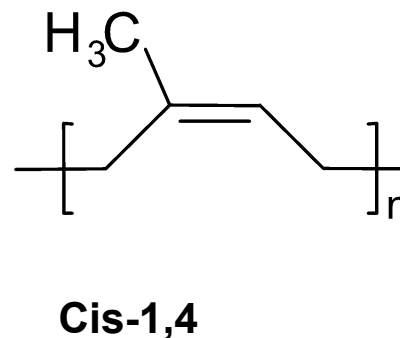
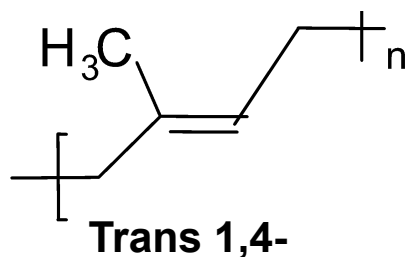
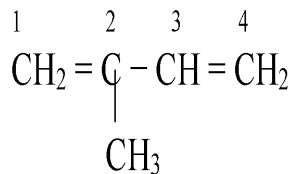
How to obtain them ?
→

Typical non-polar solvents : Benzene, toluene, ethylbenzene, xylene

Cyclohexane, n-hexane

Stereochemistry of polydienes

Conjugated dienes : can be polymerized in four modes :



Microstructure analysis can be achieved in solution or in the solid state by I.R or NMR

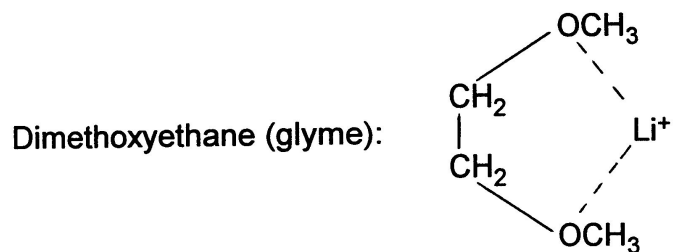
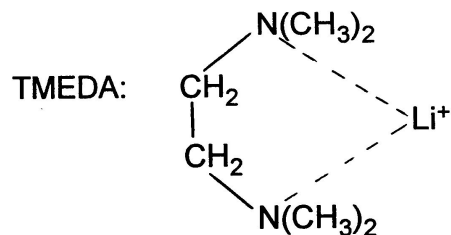
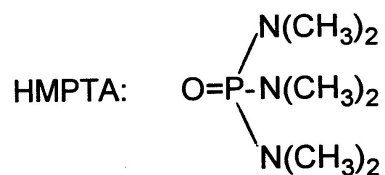
Microstructure depends on the

- Nature of the counter-ion (Li^+ , K^+ , Na^+ ..., Li^+ favours 1,4 units in non polar solvents)
- Nature of the solvent : polar $\rightarrow$ 1,2 (ex. THF), non-polar $\rightarrow$ 1,4 (ex. cyclohexane)
- Presence of polar additives (amines, ethers: $\rightarrow$ increase 1,2-content)
- Polymerization temperature, pressure, concentration of active sites

Statistical incorporation of styrene in SBRs can be controlled by:

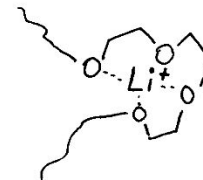
- The introduction of low amounts of ether
- The introduction of potassium alcoholates

The presence of ethers, amines increases the propagation rate

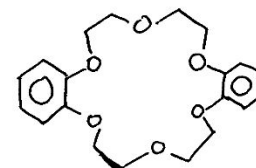
Chelating Solvent/ Agents

Sparteine

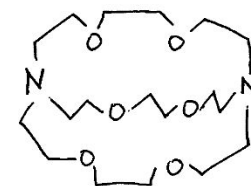
Di-, tri-, tetra-glyme,...
Poly(ethylene oxide)



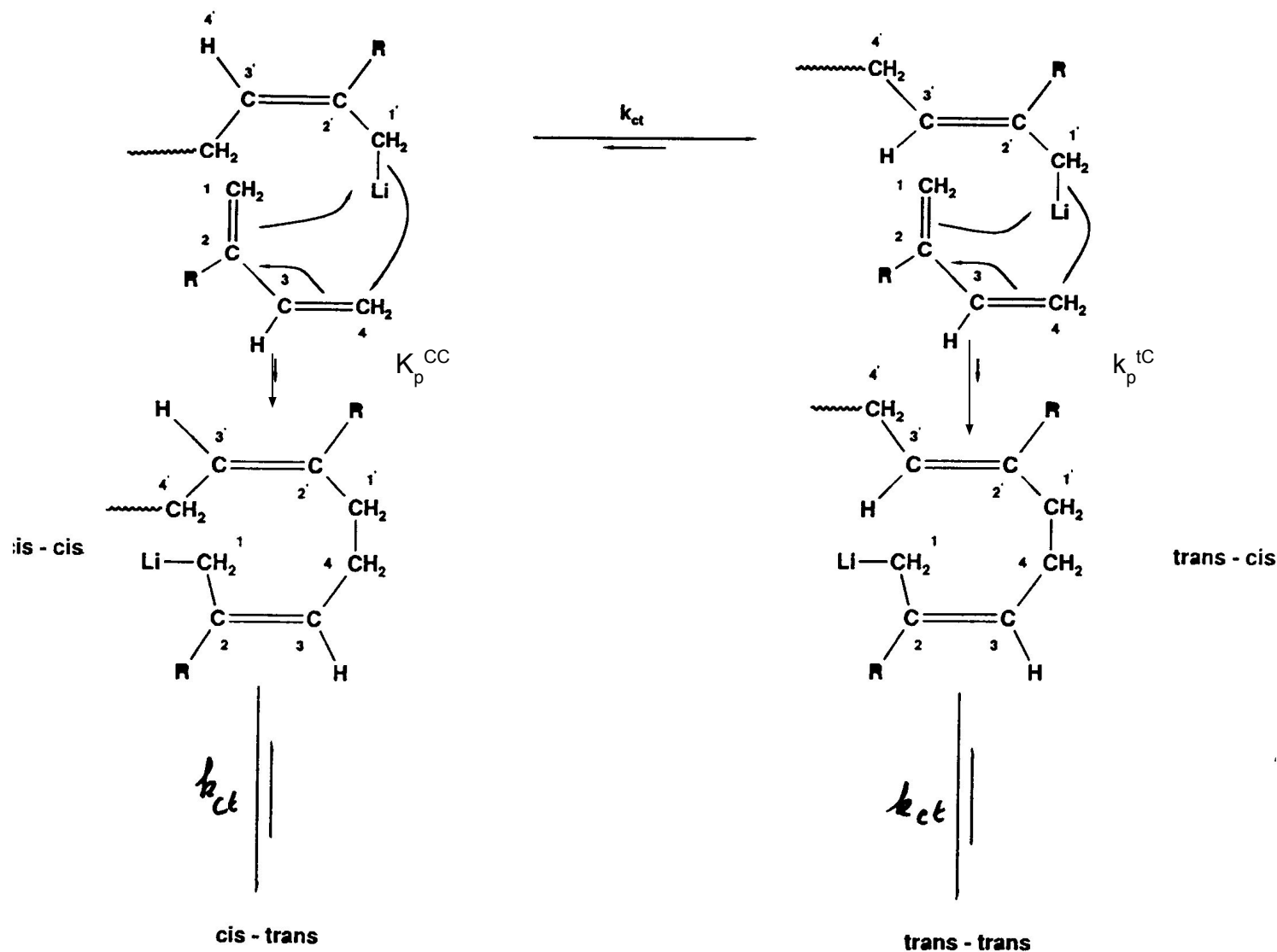
Crown ethers (*Pederson*):
(Dibenzo-18-crown-6)



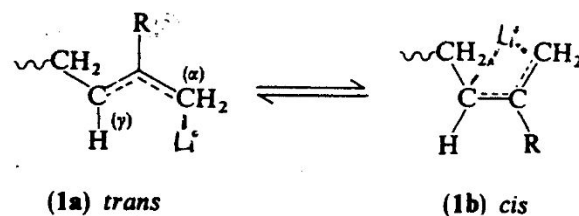
Cryptands (Lehn)
(Cryptand 2.2.2)



Thermodynamically stable form is trans in non polar solvents addition of monomer leads to a cis chain-end which slowly isomerizes to trans

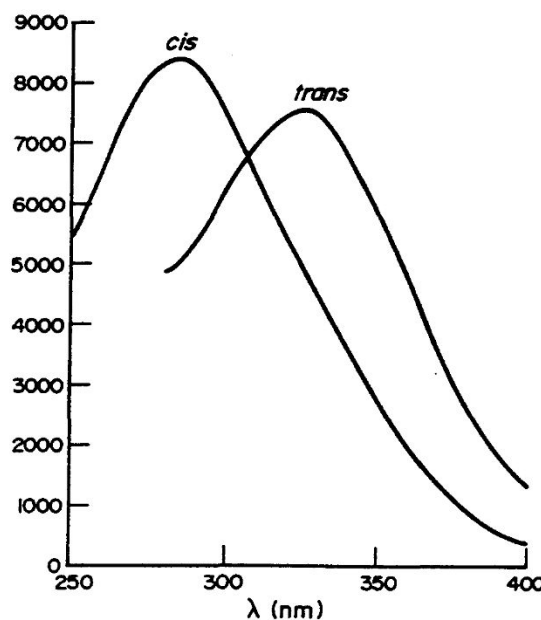


Estimated Spectra of cis and trans forms of the active centres of poly(butadienyl)lithium



Non polar
solvents
1,4 stru.

1,2 and 3,4
struc.



Polar
solvents or
Lewis Base
Ligands

Microstructure of polydienes prepared in solvating media

Solvent	Cation	Temps (°C)	Cis 1,4 %	Trans 1,4 %	3,4 %	1,2 %
Butadiene						
THF	Li	80		25		70
THF	Li	15		13		87
THF	Na	0	6	14		80
Dioxan	Na	15		15		85
	K	15		45		55
	Cs	15		59		41
Radical			25	50		21

TMEDA
Benzene
Li 60/1
Hexane
Li 1/1

Solvent	Cation	Temps °C	Cis 1,4 %	3,4 %	1,2 %
Isopren					
THF	Li	30	12	59	29
THF	Free anion	30	22	47	31
THF	Free anion	-70	10	45	45
Ethe	Li	20	35	52	13
Ethe	Na	20	17	61	22
Ethe		20	38	43	19
Ethe	C	20	52	32	16
Dioxan	Li	15	11	68	18
TMEDA	Li		30	55	15
TMEDA	Li		25	45	30
DME	Li	15			
Radical Polyme			25	6	6

Temperature

Polyisoprene^a

Temp. (°C)	[<i>s</i> -BuLi] 10 ³	Solvent	Microstructure ^b			
			Trans-1,4	Cis-1,4	3,4	1
46	.01	None	1	95	4	-
20	.01	None	1	95	4	-
0	.01	None	2	95	3	-
-25	.01	None	3	93	4	-
40	1	Hexane	18	76	6	-
25	1	Hexane	18	78	4	-

Polybutadiene^b

35	.007	None	9	85		6
20	.007	None	9	86		5
0	.007	None	7	86		5

^a Monomer = 2.5 M; ^b Via 300 MHz ¹H-NMR

Conversion

Conv. (%)	Trans-1,4	Microstructure ^b	
		Cis-1,4	3,4
13	2	93	5
29	3	92	5
40	2	92	6
46	3	92	5
48	1	95	4
86	1	95	4

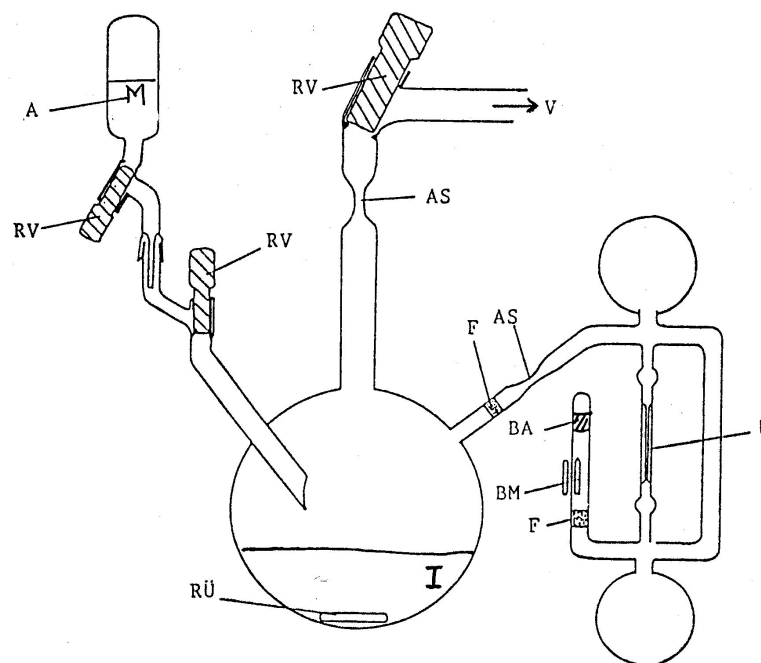
^a No solvent; polymerization temp. = 20 °C; [*s*-BuLi] = 10⁻⁵ M;

^b Via 300 MHz ¹H-NMR

Influence of pressure and initiator concentration upon
the microstructure of poly(2,3-dimethylbutadiene)

[Buli] (molar)	1,4 cis %	1,4 trans %	1,2 %
Pressure 1 bar			
0.03	42	28	30
0.09	35	40	25
0.19	35	56	9
0.25	38	54	8
Pressure 6000 bars			
0.03	47	9	43
0.09	46	15	40
0.18	47	25	28
0.25	47	29	24

HOW TO MEASURE ASSOCIATIONS DEGREES FOR LIVING POLYMERS



HOW TO MEASURE ASSOCIATION DEGREES FOR LIVING POLYMERS

- Case of benzylic -and allylic actives centres
- dimeric state of association are present for these active centres at the concentration for polymerization

Viscosimetric Method : (in the entanglement regime)

$$\eta = K M^{3.4}$$

include the concentration terme c , c remains unchanged after termination

$$\frac{\eta_a}{\eta_t} = \frac{t_a}{t_t} \left(\frac{M_{wa}}{M_{wt}} \right)^{3.4}$$

t corresponds to the polymer solution flow time a and t to active and terminated solutions

N_w weight average association number of carbanions

Other methods light scattering, viscosity (influence of concentration)

Usually PS : 2, PI : 2 or 4

PB Li > PI Li > PS Li

Mixed aggregates EthylLi / High molar PI in hexane



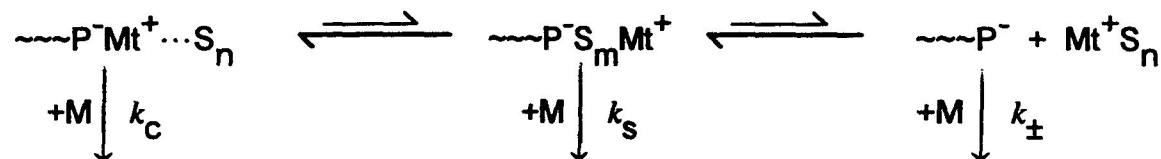
Active sites in anionic polymerization

Polar Solvents:

Contact Ion Pair

Solvent-Separated
Ion Pair

Free Anion

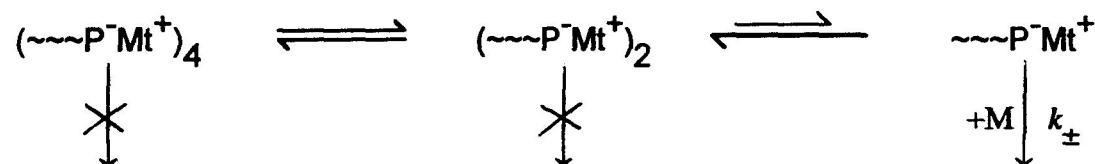


Non-Polar Solvents:

Tetrameric
Aggregates

Dimeric
Aggregates

Contact Ion Pair
(non-solvated)



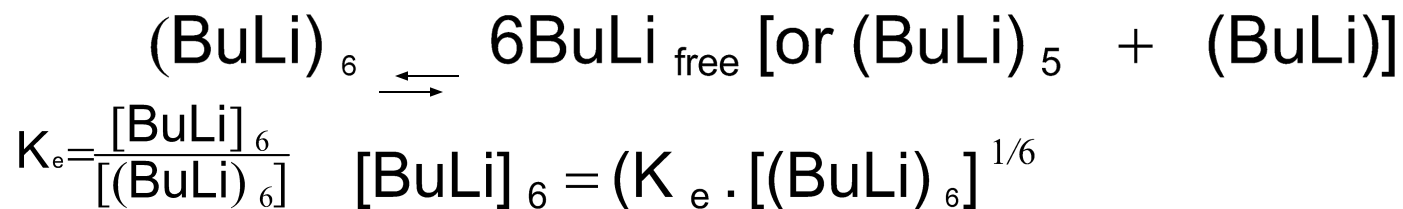
Kinetics of Anionic Polymerization in Non-polar Solvents

Remark : Aggregates are in equilibrium with ion pairs

Aggregates usually do not participate in chain growth, but rates of aggregation and disaggregation are extremely fast

All sites do contribute to the polymerization and the two criteria of livingness apply

- 1) **Initiation** Initiator molecules = inverses micelles (structure controversial)
 Influence of the initiation process Specific case of BuLi (aggregate involves 6 molecules)



If free BuLi is able to initiate the polymerization

Initiation process is given by following rate reaction $R_i = k_i K_e^{1/6} [M][\text{BuLi}]^{1/6}$

2) Propagation $R_p = \frac{-d[M]}{dt} = k_p K_e [M][M^-]^{1/2}$

$$\ln \frac{[M]_0}{[M]} = k_p K_e [M^-]^{1/2}$$

Various Attempts to Prepare Efficient Bifunctional Initiators

Aim is to obtain a difunctional initiator exhibiting

carbon-lithium bonds and yet soluble in non polar media

- An ultrafine Lithium dispersion can be used to initiated the polymerization

but no precise control of molar mass

not possible for low molar masses

- Addition of BuLi to stilbene : soluble, efficient ?

- Addition compounds of BuLi onto divinylbenzenes

and derivates. but rather broad molar mass distribution

not stable and polar additives are required

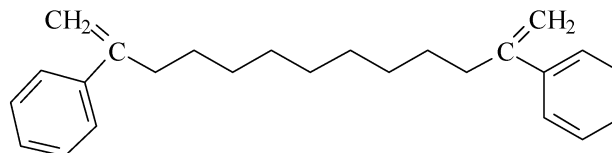
- Use of 1,1,4,4,- tetraphenyl-1,4,-dilithiobutane obtained from a Li dispersion and 1,1-diphenylethylene

but polar additives to increase the yield

Other Attempts

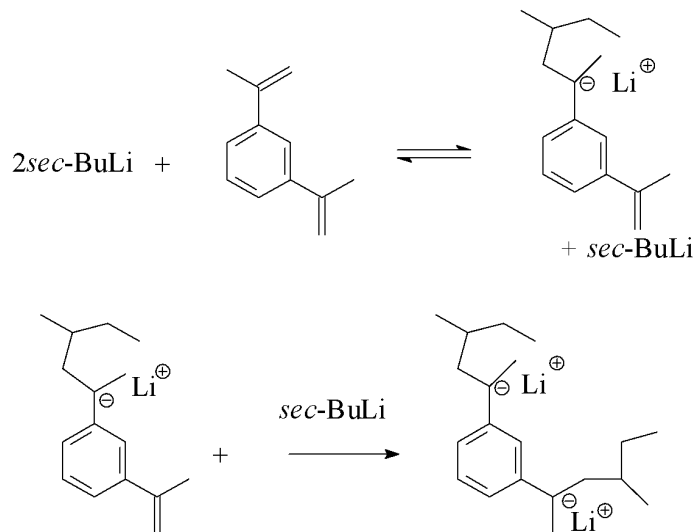
**BASED ON ADDITION OF BULI ONTO DIFUNCTIONAL MONOMERS EXHIBITING :
LOW CEILING TEMPERATURE, (i.e. high equilibrium monomer concentration)**

1) α,ω -bis(phenylvinylidenyl)alkanes



or α,ω -diisopropenyldiphenylalkanes

2) Diisopropenylbenzenes



Initiator System :
***sec*-BuLi/*m*-DIB**



Case of DIB in Benzene, cyclohexane, heptane, or Ethylbenzene**Diadduct formation**

sec-BuLi is added at 40° C to DIB (1DIB / 2BuLi) under efficient stirring, at high dilution

The reaction mixture is kept at 45°C during at least 1/2 h until complete addition of BuLi

(followed by u.v. spectroscopy ,NMR)

Polymerization

Then is cooled rapidly to 10°C and monomer (styrene, isoprene is added, 15 minutes are allowed for the initiation to proceed.

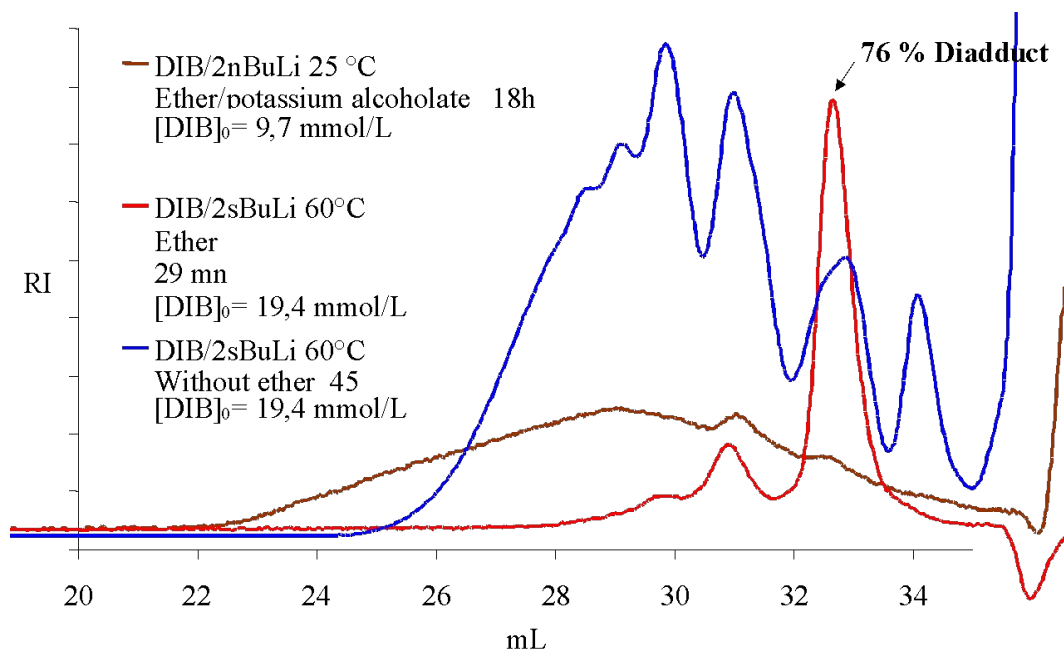
Thus the temperature is risen to 25°C to 40°C

(50-60°c for dienes) to allow propagation to set in. The viscosity of the reaction medium increases with chain growth

Killing with MeOH or any other proton donating substance.

SEC Diagrams of the reaction products of 1,3-DIB with 2 BuLi

Influence of the DIB Concentration



in Cyclohexane or in Hexane, with **Ether** (after 30 mn)

[DIB]₀ = 19,2 mmol/L Diadduct : 75%

[DIB]₀ = 1,2 mmol/L Diadduct : 55%

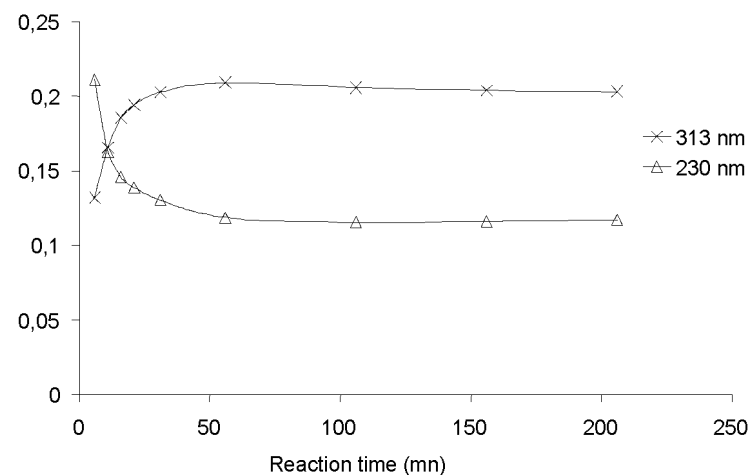
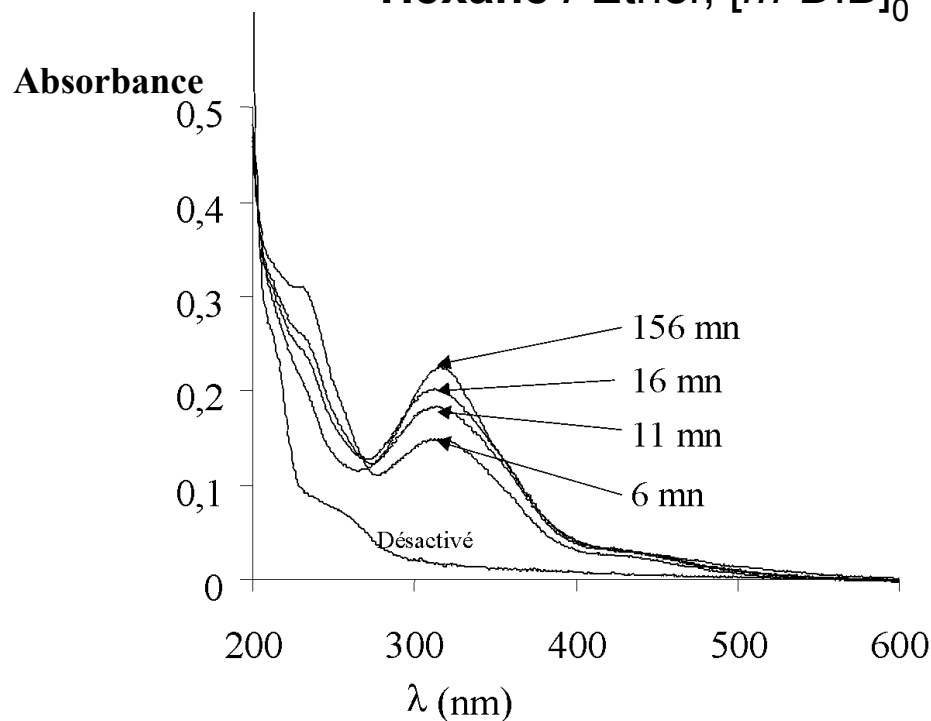
in Cyclohexane or in Hexane, with **Ether** or with **Ether/Pot. Alcoholate** (after 8 mn)

[DIB]₀ = 19,2 mmol/L Diadduct : 65%

[DIB]₀ = 1,2 mmol/L Diadduct : 45%

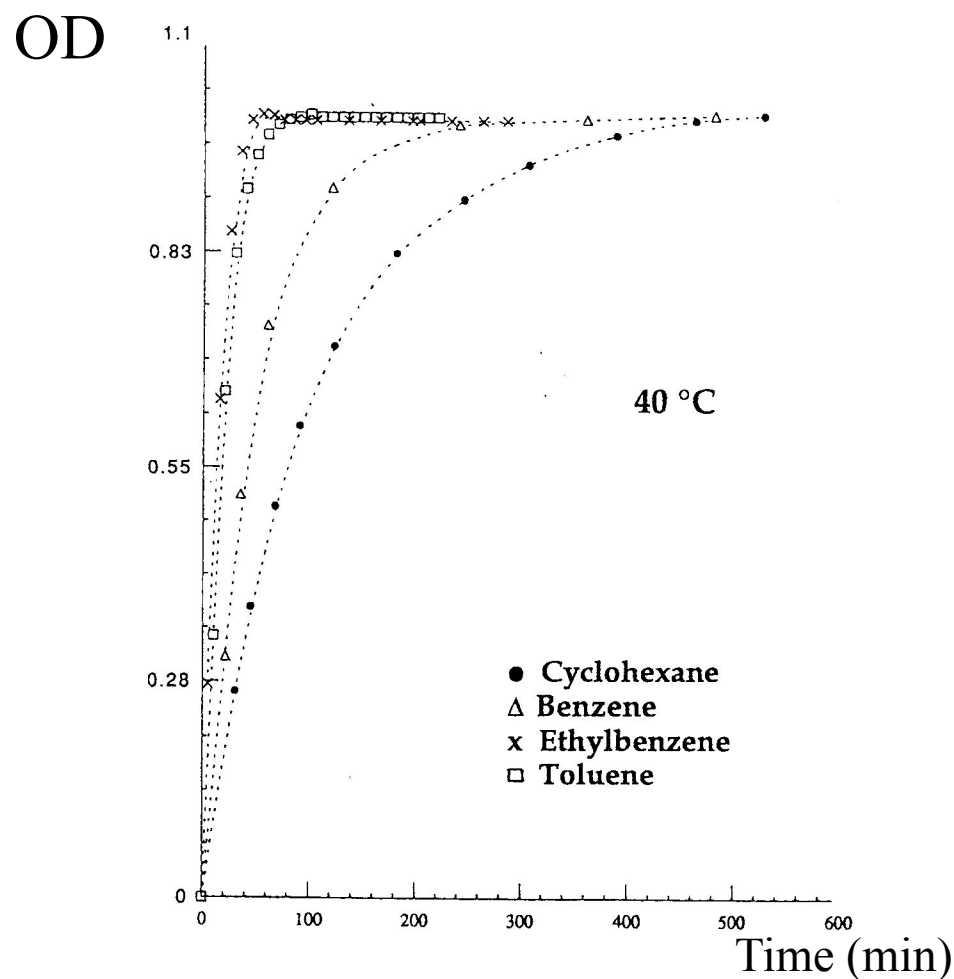
Evolution of the optical density versus reaction time Reaction DIB / 2 BuLi

Hexane / Ether, $[m\text{-DIB}]_0 = 1,168 \text{ mmol/L}$



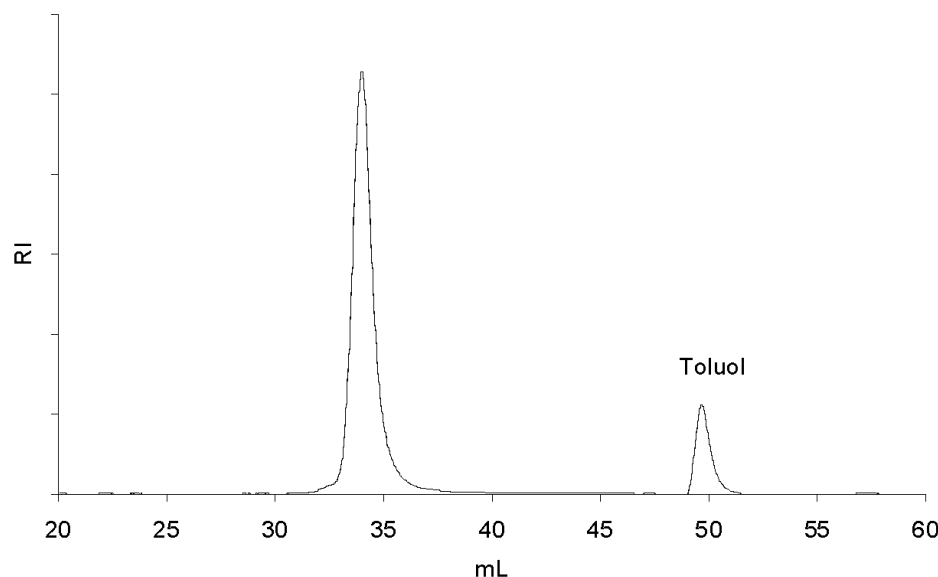
- Carbanionic species are stable
- 8% remaining double bonds (*m*-DIB), UV and NMR

Evolution of the optical density versus time for the reaction DIB / BuLi



Characterization of polymers made with DIB /2 BuLi

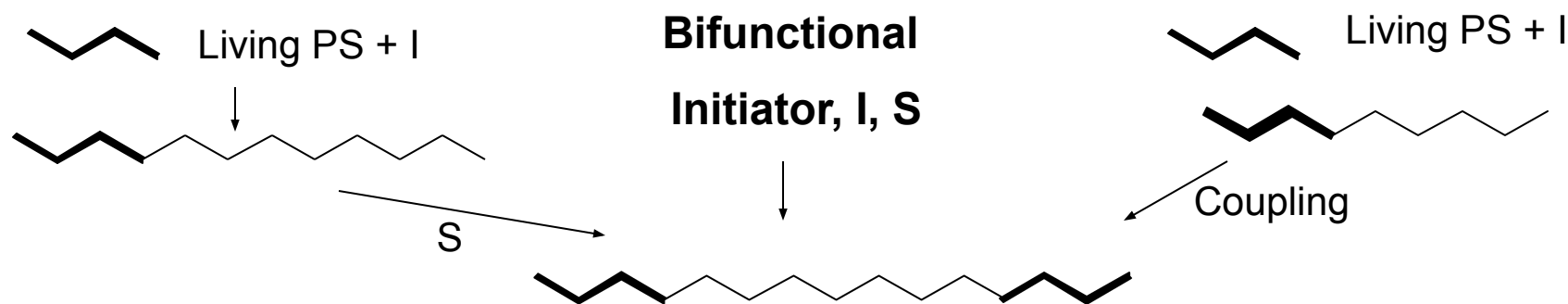
- DP $n_{exp} = DP_{th}$ (calculated under the assumption of 2 sites per polymer molecule)
- Sharp molar mass distribution :
 $M_w/M_n < 1.1$ and $M_{WLS} = MWSEC$
it means no ramifications
- Difunctionality also results from :
Polycondensation : M_n increases by a factor of at least 10
The radii of gyration are compatible with those of linear polymers.
Synthesis and studies of thermoplastic elastomers.
Most interesting point : crosslinking occurs after addition of an appropriate linking agent

**SEC Diagram****HO-SBR-OH** **$M_w = 44\,000$** **g/mole** **$M_w / M_n = 1,1$**

- Chain end titration
(Naph Isocyanates)
- Chain extension
- Crosslinking

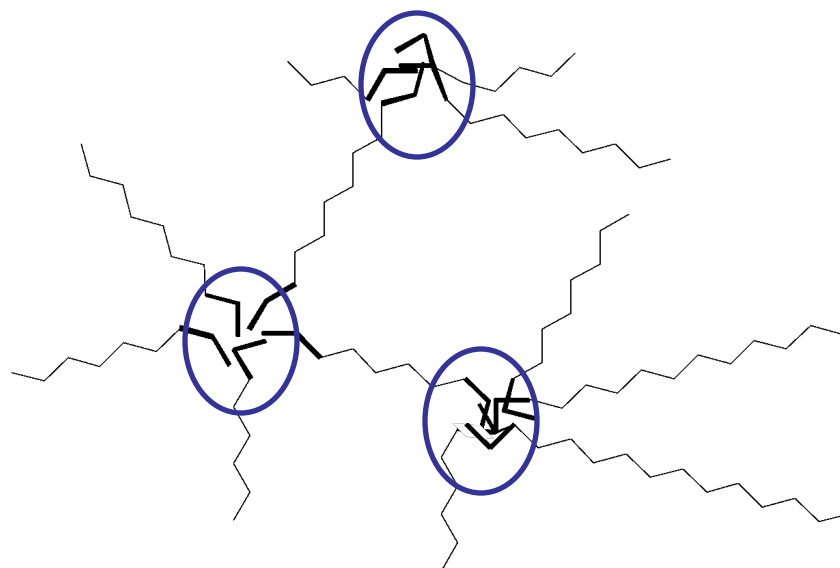
THERMOPLASTIC ELASTOMERS FROM TRIBLOCK COPOLYMERS

Triblock synthesis via anionic polymerization



T_g PS 100°C

T_g PI -60°C

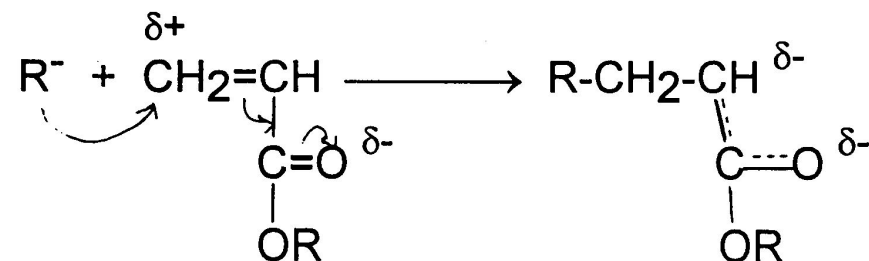


Conclusions NON POLAR SOLVENTS

- The MWD distribution is narrow Poisson Type
 - Most of ion-pairs are aggregated, only a small fraction of non-aggregated ion-pairs adds monomers
 - Bifunctional initiators complex !
 - Solvating agents increase rate of polymerization but stability, microstructure
 - The stereochemistry in the polymerization of dienes is determined by the nature of solvent and counterion
- Li⁺ in non polar solvents cis-1,4 structures are formed
- Large counterions or in polar solvents trans-1,4 and 1,2 (3,4) microstructure is obtained

General Structure of the Monomers

Vinyl or isopropeny group with electron-withdrawing side group

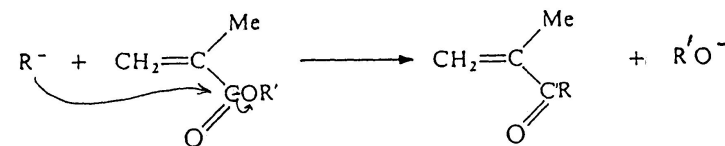


The polar side group makes the monomers highly reactive and stabilizes the anionic end-group

- Styrene related Monomers o-methoxystyrene
 ester or keto-substituted styrenes
 vinyl pyridine
 isopropenyl pyridine
- Acrylic Monomers (ordered to increasing reactivity)
 alkylmethacrylates, alkylacrylates
 viny ketones, isopropenyl ketones
 acrolein, methacrolein
 (meth) acrylonitrile,
 dialyl methylene malonates
 alkyl α - fluoro or cyanoacrylates
- Non-Vinyl Monomers isocyanides, isocynates

Potential problems due to polar side groups

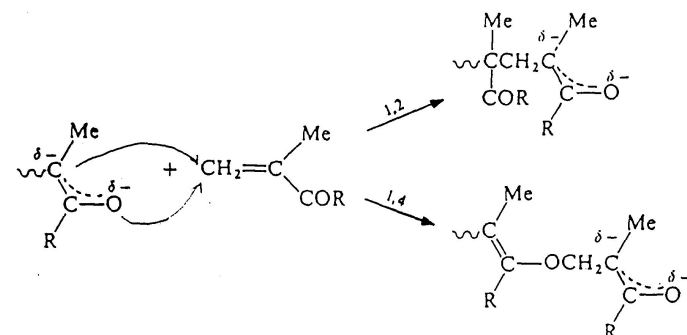
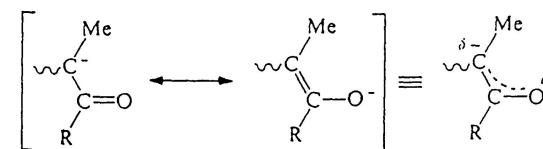
- Attack of the initiator or living end at the carbonyl group of the monomer may lead to termination



- Activation of the protons in the α position to the carbonyl group may lead to transfer

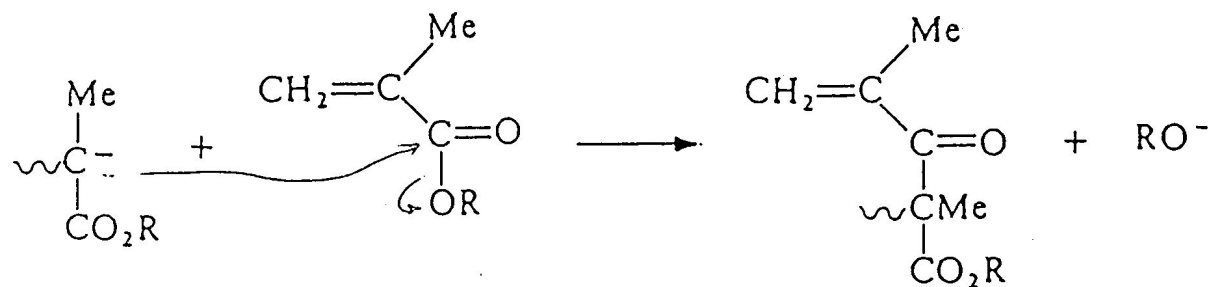


- Due to the bidentate character of the active centres, they may attack the monomer not only by the carbanion (1,2-addition) but also by the enolate oxygen (1,4-addition)

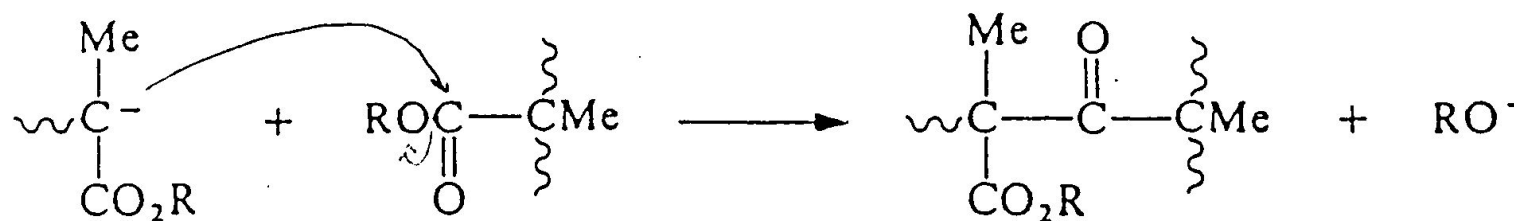


Possible Termination Reactions

• Attack of Monomer Carbonyl Group

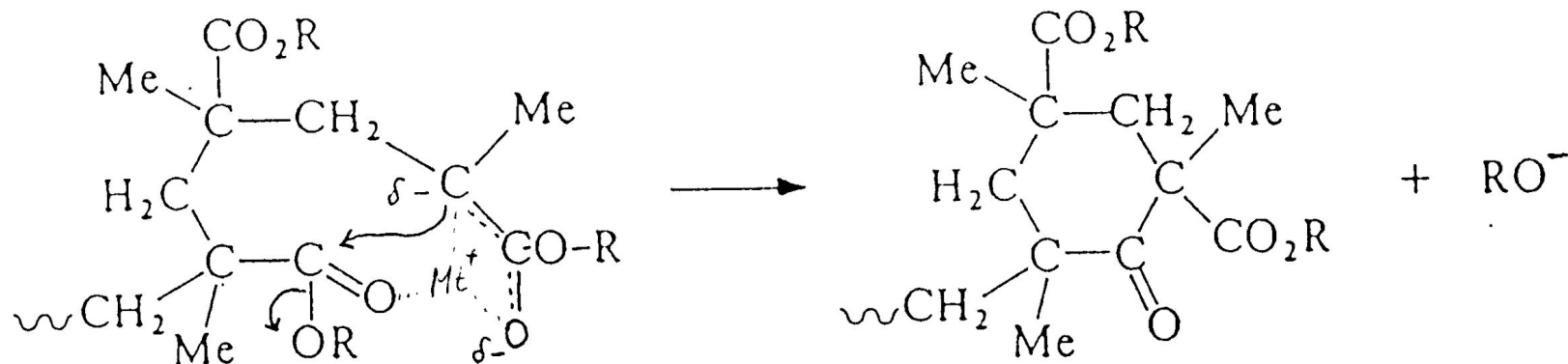


I • Intermolecular Attack of Carbonyl Group



Possible Termination Reactions

- Termination by backbiting

cyclic β -Ketoester

The efficiency of backbiting is given by the ratio k_t/k_p . It depends on the size of the Counteranion, the polarity of the solvent, as on monomer structure



Systems investigated

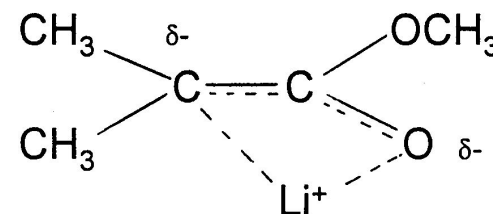
Monomers: **Methacrylates:** MMA, tBuMA
 acrylates: tBuA, nBA
 (vinyl ketones: tBuVK)

Initiators **ester enolates, lithiated alkyl isobutyrate (MIB-Li)**
 hydrocarbons: DPM-Li (Na, K) Cumyl-Cs

Additives **LiB Φ_4 CsB Φ_3 CN**
 Cryptand 2,22
 LiCl, TBuOLi, AlR₃

Solvents **THF, Toluene**

Temperature **-100°C + 20°C**

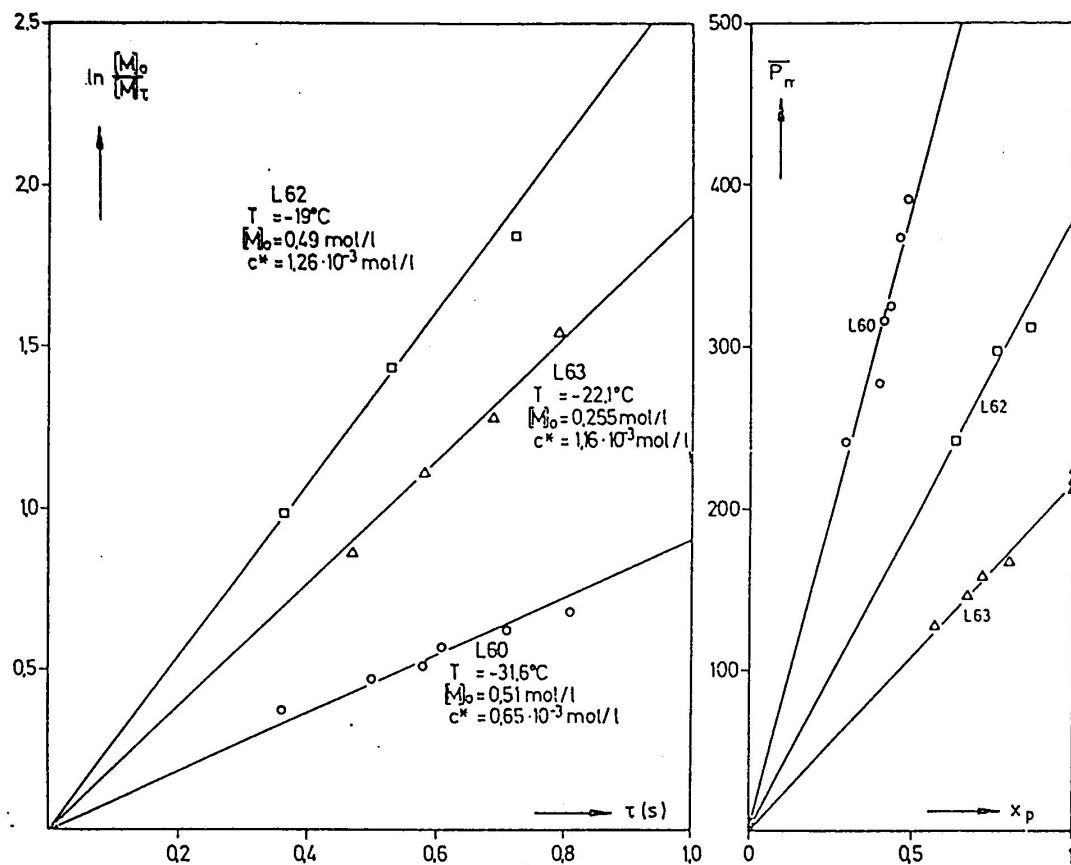


MIB-Li

Kinetic reactors

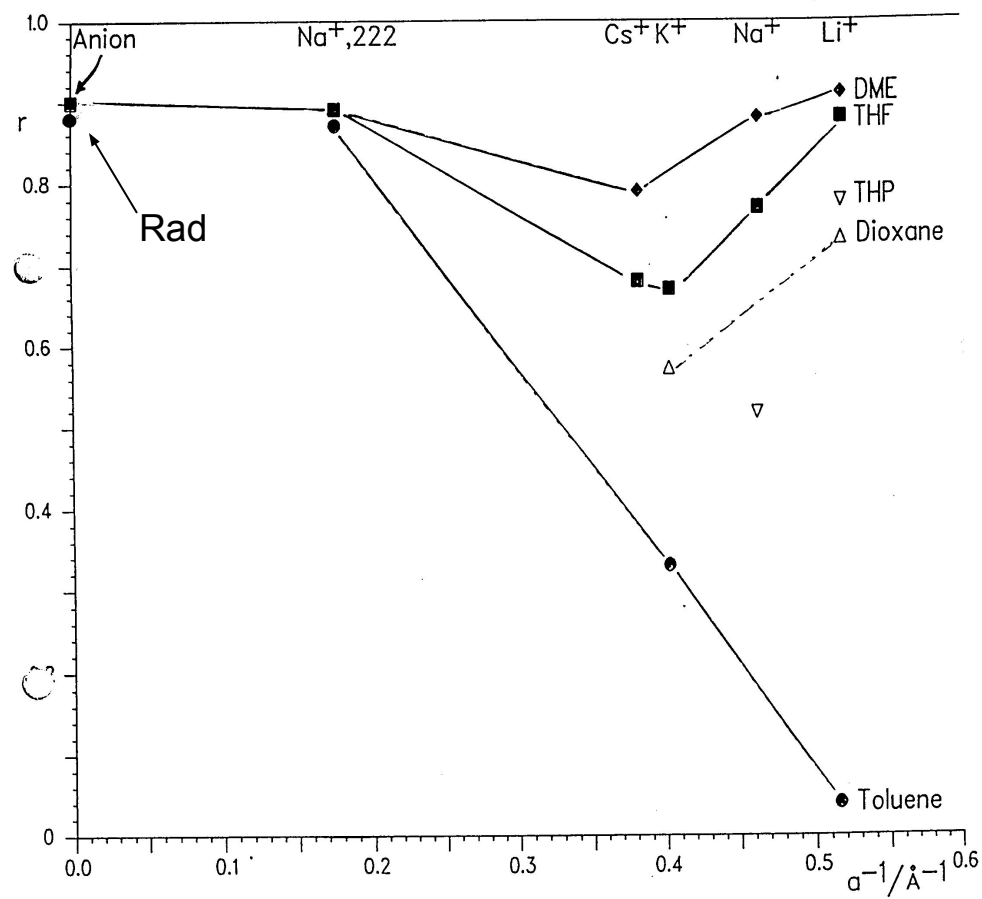
- **Stirred tank reactors ($t_{1/2} \geq 2s$)**
- **Flow tube reactor ($0.02s \leq t_{1/2} \leq 2s$)**

Polymerization of MMA in THF

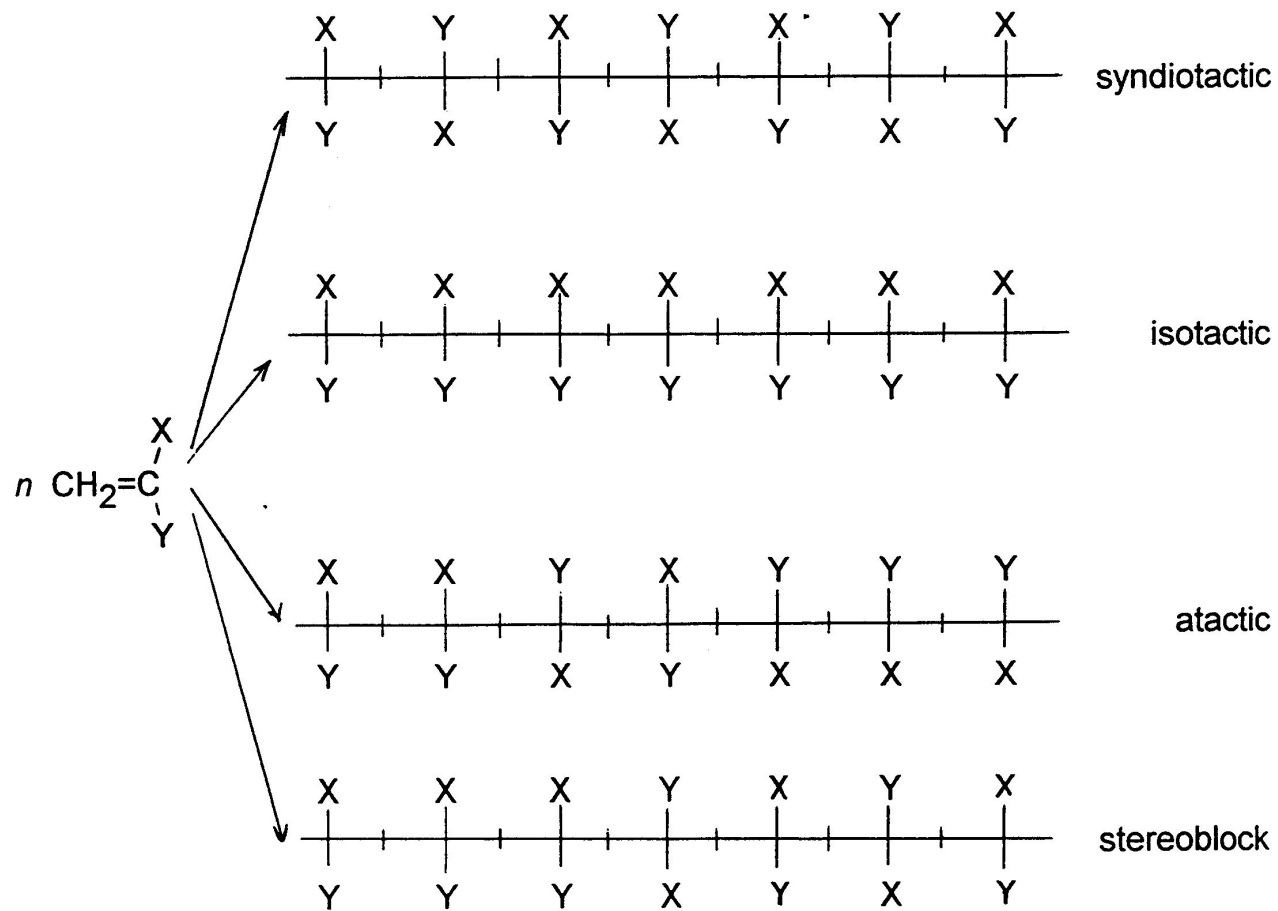


The first order time-conversion plots of $\overline{P}_n$ vs conversion indicate a **living polymerization** of MMA in THF with Cs^+ counterion up to -20°C

Tacticity of PMMA: dependence on Solvent and counterion (around -50°C)



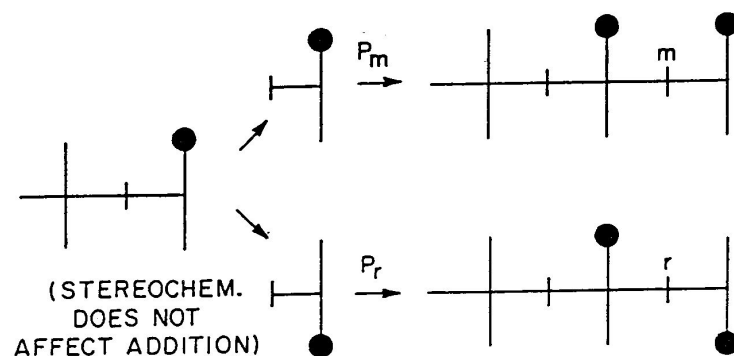
r = fraction of racemic (syndiotactic dyads)



Statistics of Tactic Placements

Bernoullian statistics

Placement depends only one parameter, $P_n = 1 - P_r$



Dyads:

$$m = P_m$$

$$r = 1 - P_m$$

Triads:

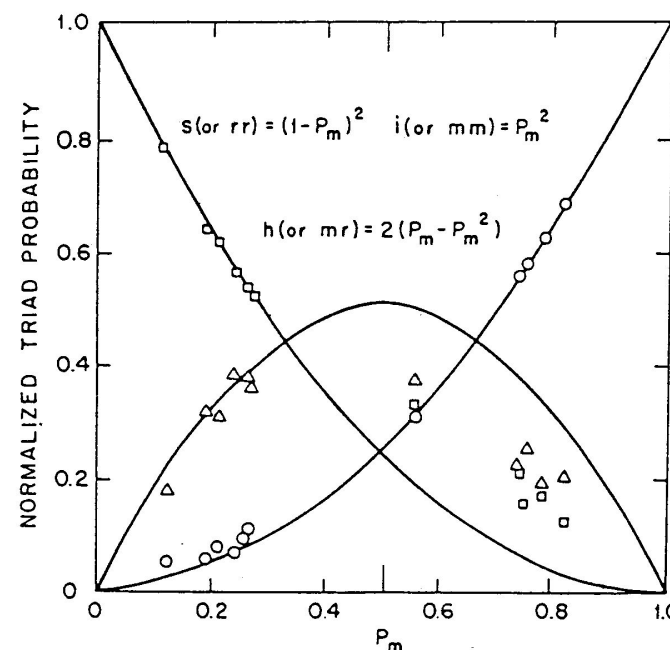
$$I = mm = P_m^2$$

$$H = mr + rm = 2 P_m(1 - P_m)$$

$$S = rr = (1 - P_m)^2$$

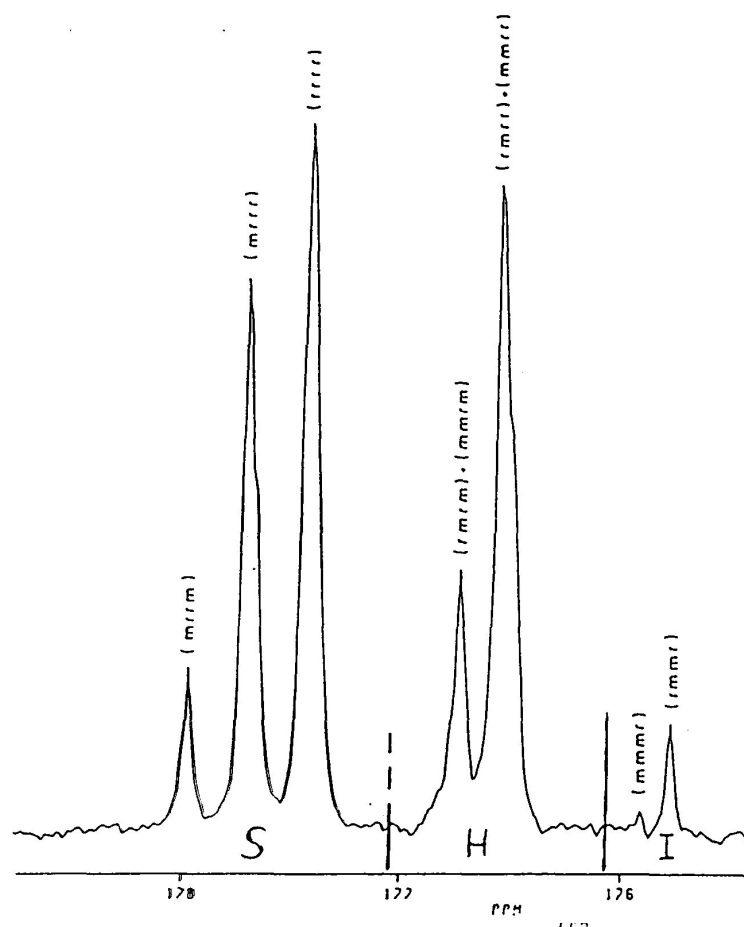
Persistence ratio:

$$\rho = 2m \cdot r / (H) = 1$$



Bovey Diagram

Determination of Tacticity by ^{13}C NMR (Triads, Pentads)



Carbonyl region of the 100-MHz ^{13}C NMR spectrum of PMMA prepared by anionic polymerization in THF in the presence of Na^+ counterion. Solvent: CDCl_3 .

$$m = mm + mr/2$$

$$r = rr + mr/2$$

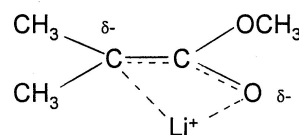
α Substituent			
	Designation	Projection	Bernoullian probability
Triad	Isotactic, <i>mm</i> (<i>i</i>)		P_m^2
	Heterotactic, <i>mr</i> (<i>h</i>)		$2P_m(1 - P_m)$
	Syndiotactic, <i>rr</i> (<i>s</i>)		$(1 - P_m)^2$
Pentad	<i>mmmm</i> (isotactic)		P_m^4
	<i>I</i> <i>mmmr</i>		$2P_m^3(1 - P_m)$
	<i>rmmr</i>		$P_m^2(1 - P_m)^2$
	<i>mmrm</i>		$2P_m^3(1 - P_m)$
	<i>H</i> <i>mmrr</i>		$2P_m^2(1 - P_m)^2$
	<i>rmrm</i> (heterotactic)		$2P_m^2(1 - P_m)^2$
	<i>rmrr</i>		$2P_m(1 - P_m)^3$
	<i>mrrm</i>		$P_m^2(1 - P_m)^2$
	<i>S</i> <i>rrrm</i>		$2P_m(1 - P_m)^3$
	<i>rrrr</i> (syndiotactic)		$(1 - P_m)^4$

SEC MIB / THF -65°C

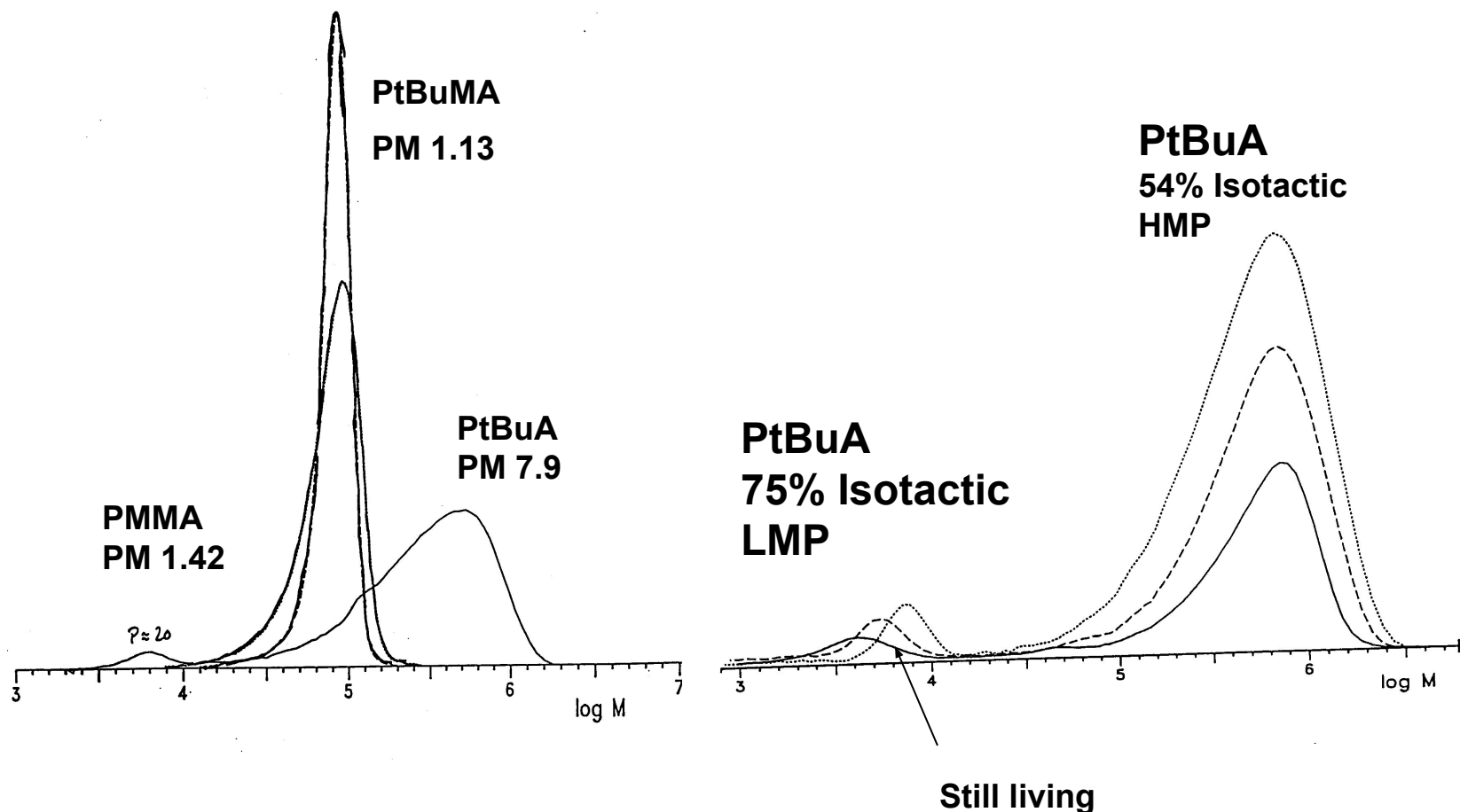
P_n around 500

lithiated alkyl isobutyrate (MIB-Li)

Monomer conversion 80-100%

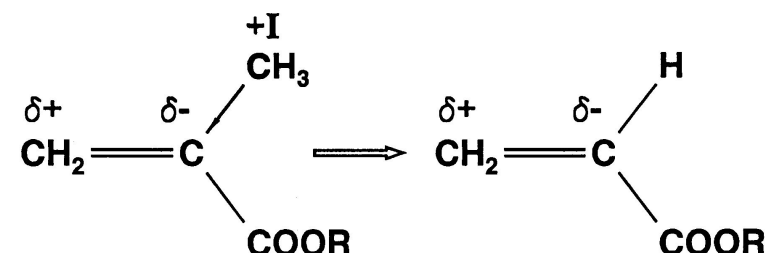


MIB-Li



Differences between Acrylates and Methacrylates

Reactivity of the monomer increases
 Reactivity of active center (anion) decreases
 Steric requirements decreases



Anionic polymerization of:

tBuMA ***
 MMA **

tBuA *
 nBuA ?

Problems with primary acrylates

- Very fast difficult to control
- Termination (incomplete monomer conversion)
- Broad Molecular Weight Distribution

Propagation is faster than aggregation broadening of MWD

Termination by backbiting is faster than for methacrylates

Acid H / carbonyl group Transfer to Polymer



Modification of active centers by additives

Use of New initiating systems, Other Polym. Process ARTP

Additives in Anionic Polymerization of Meth(acrylates)

- Common-Ion Salts: suppress dissociation

$\text{LiB}\emptyset_4$, $\text{NaB}\emptyset_4$, $\text{CsB}\emptyset_3\text{CN}$

- σ -Ligands: complexation of counterion

Peripheral solvation:

Glymes, Crown ethers

TDMA, Spartein

« ligand separation »

Cryptands

- μ -Ligands: coordination with ion pair

(formation of a new kind of active species)

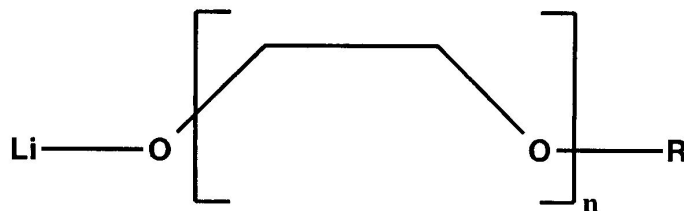
Alkoxides ($\text{tBuOLi}\dots$)

Alkali Halides (LiCl)

Al Alkyls (AlR_3 , AlR_2OR) in toluene

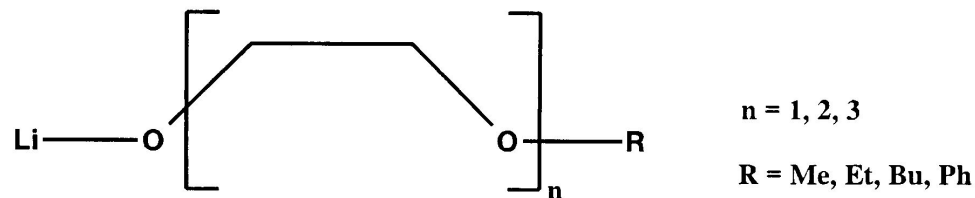
- σ , μ -Ligands:

Alkoxy Alkoxides (in toluene)



$n = 1, 2, 3$

$R = \text{Me, Et, Bu, Ph}$

Additives in Anionic Polymerization of Meth(acrylates)Alkoxy Alkoxides as additives

- very inexpensive
- very fast polymerization even in non polar solvents
- no increase of termination reactions
- highly syndiotactic PMM even at 0°C (75-80% rr)
- Well-controlled polymerization of primary acrylates
- Controlled block copolymerization of MMA with primary acrylates (2-ethyl acrylates, n-butyl-acrylates)

Additives in Anionic Polymerization of Meth(acrylates)**Effect of Additives: case of LiCl
(Teyssie)**

- Drastic decrease of polymolecularity, especially in the case of *tert*-butyl acrylate
- Rate constants of propagation decrease to 10-50%

LiCl breaks the aggregates by forming the 1:1 and 2:1 adducts with ion pair

- The rate constant of propagation of the 1:1 adducts is comparable to that of the ion pair, the rate constant of the 2:1 adduct is low
- The rate of termination is not significantly influenced by LiCl
- The rate of the complexation equilibrium with LiCl is higher than that of the association. This accounts for the narrower MWD
- There is no significant effect of LiCl on the tacticity of the polymers formed

Additives in Anionic Polymerization of Meth(acrylates)

Effect of Additives: Aluminium Alkyls (Tsvetanov, Hatada, Ballard, Haddelton)

Non-polar solvents (toluene ...)

Low polymerization rates

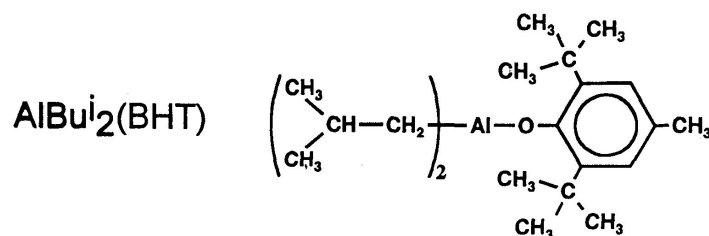
In situ purification of monomer and solvent

Low cost

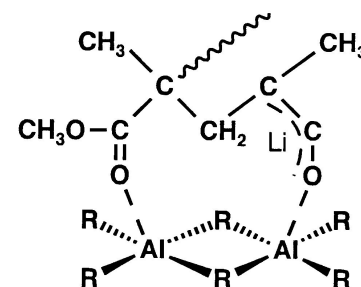
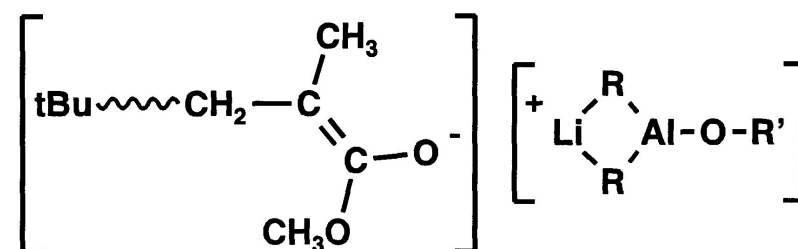
PMMA-Li forms ate complexes with Al alkyl

Coordination of Al with penultimate ester group

Living polymerization



Tentative mechanism:



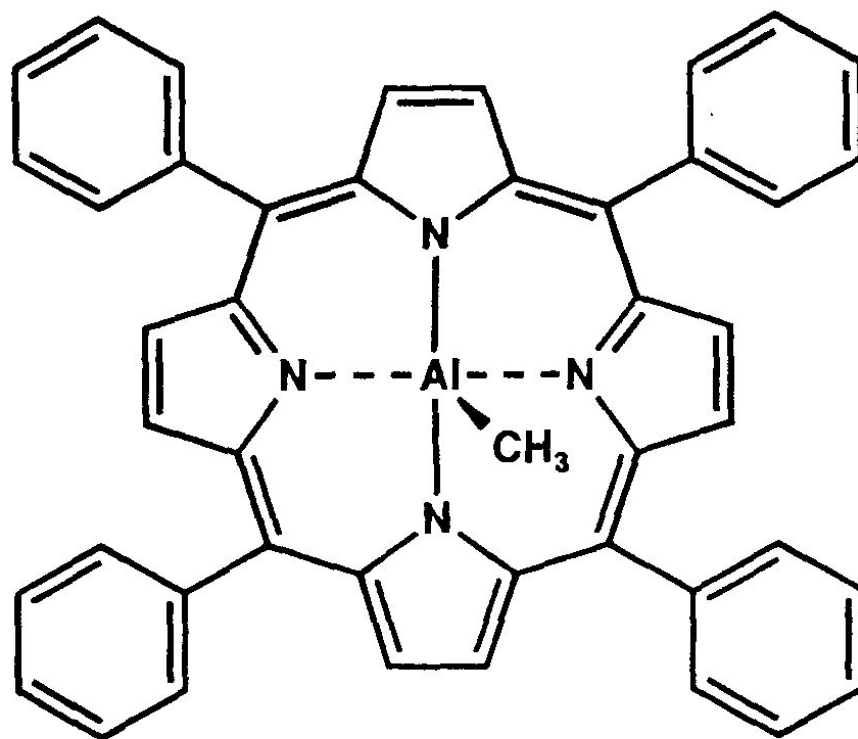
dimeric structure of Al alkyl

⇒ "penultimate effect"

⇒ rr-triads

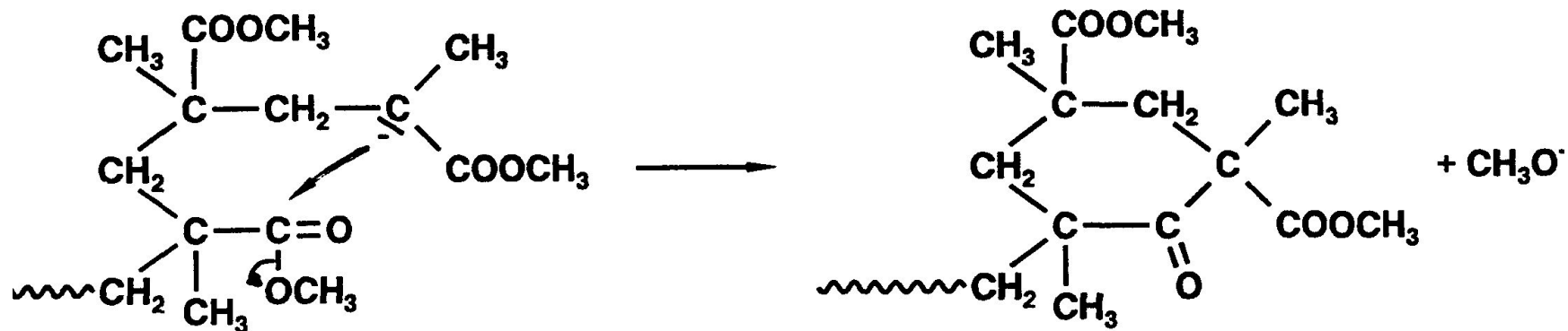
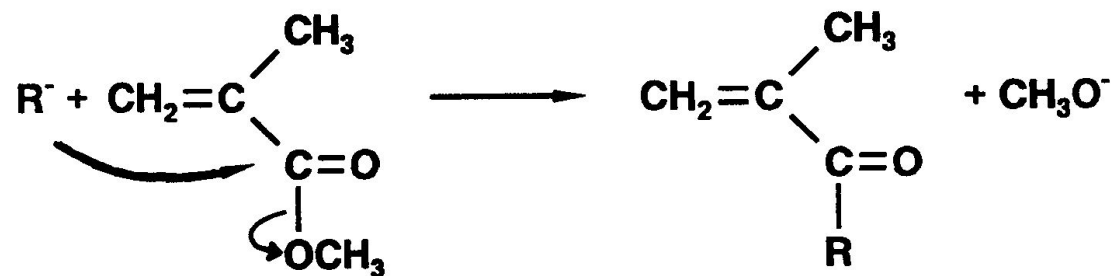
Al-Porphyrin / AlBuⁱ(BHT)₂ / CH₂Cl₂ / 35°C

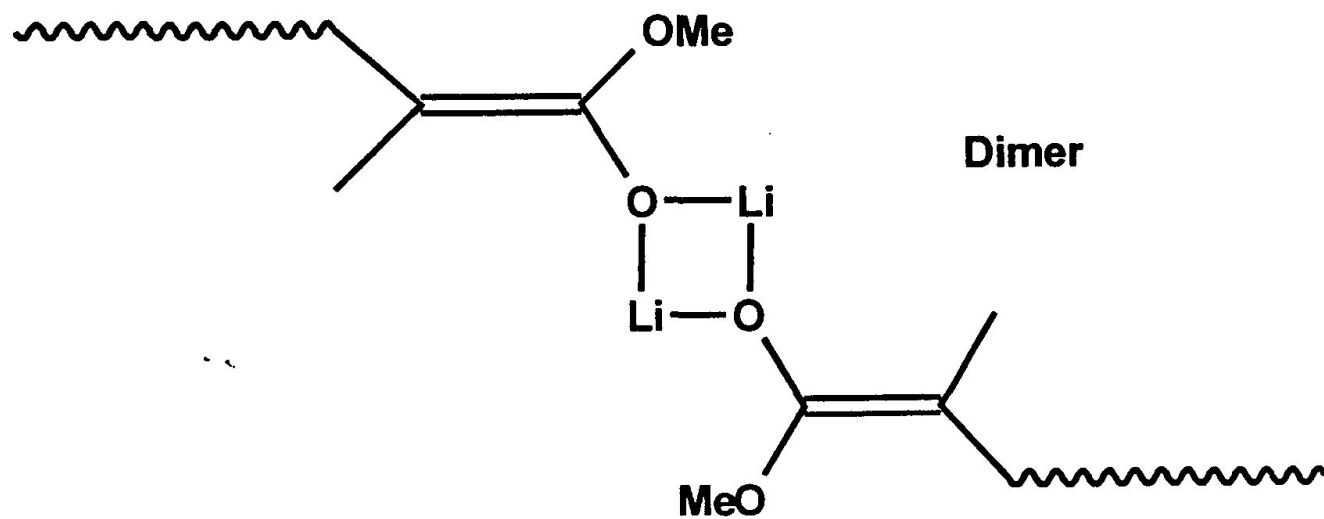
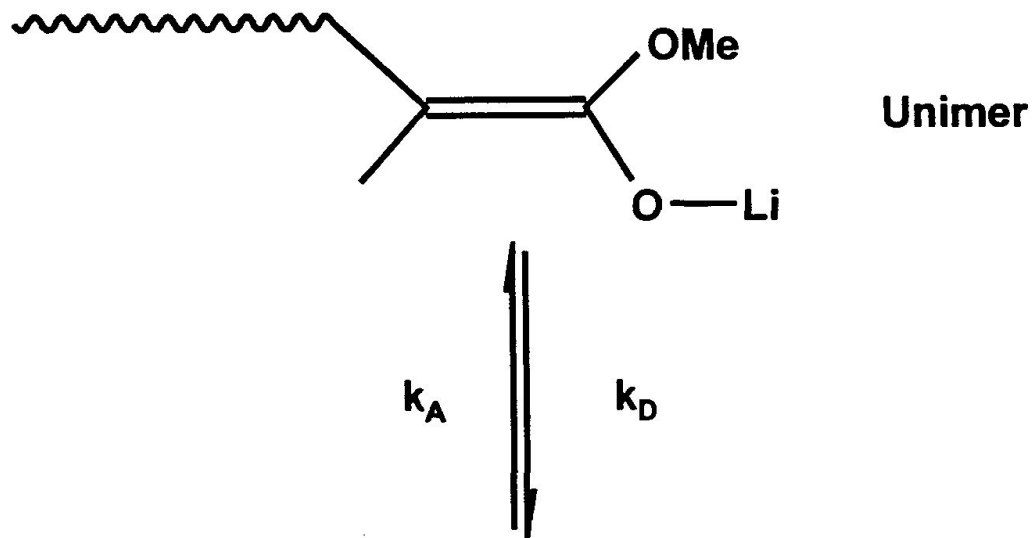
Al-TPP



Conclusion

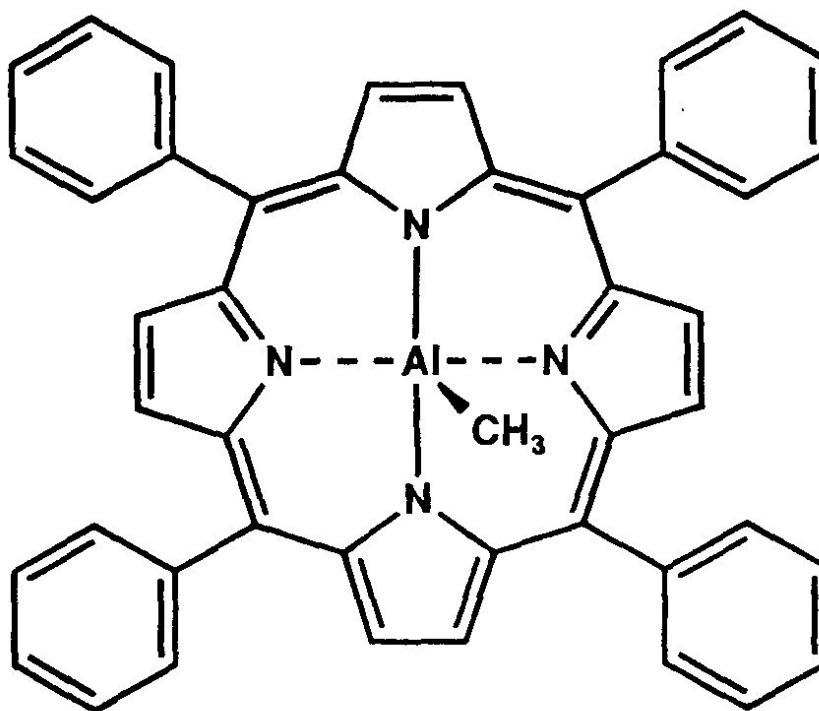
- Living poly(methacrylates) and poly(acrylates) can exist as free anions, periphelary solvated contact ions-pairs, and aggregates in polar solvents, such as THF
- The rate of polymerization is determined by the position of the dissociation and aggregation equilibria
- The reactivity of the associated ion pairs is much lower than that of the non-associated ones
- The MWD of the polymers formed is determined by the dynamics of the aggregation equilibrium

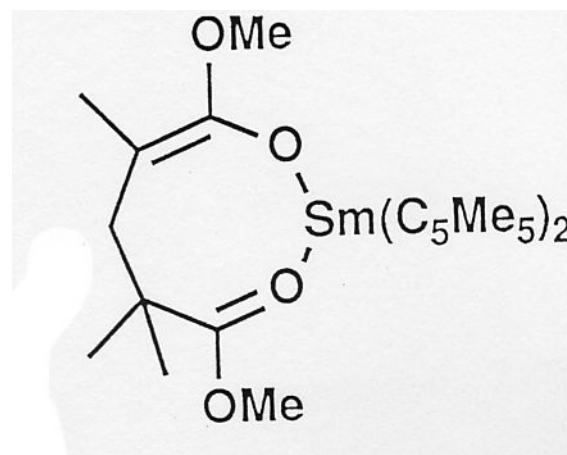
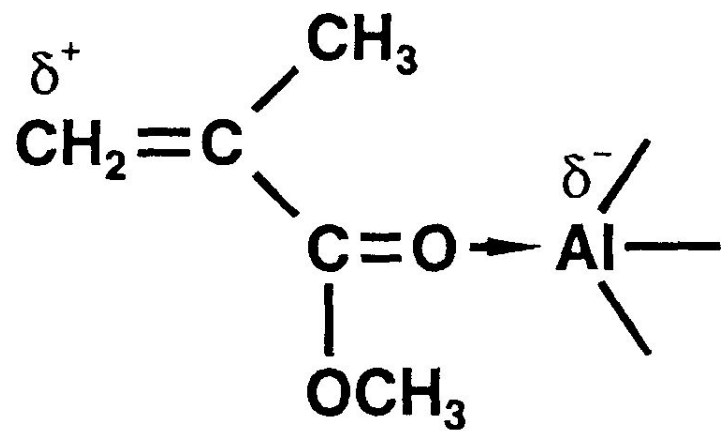


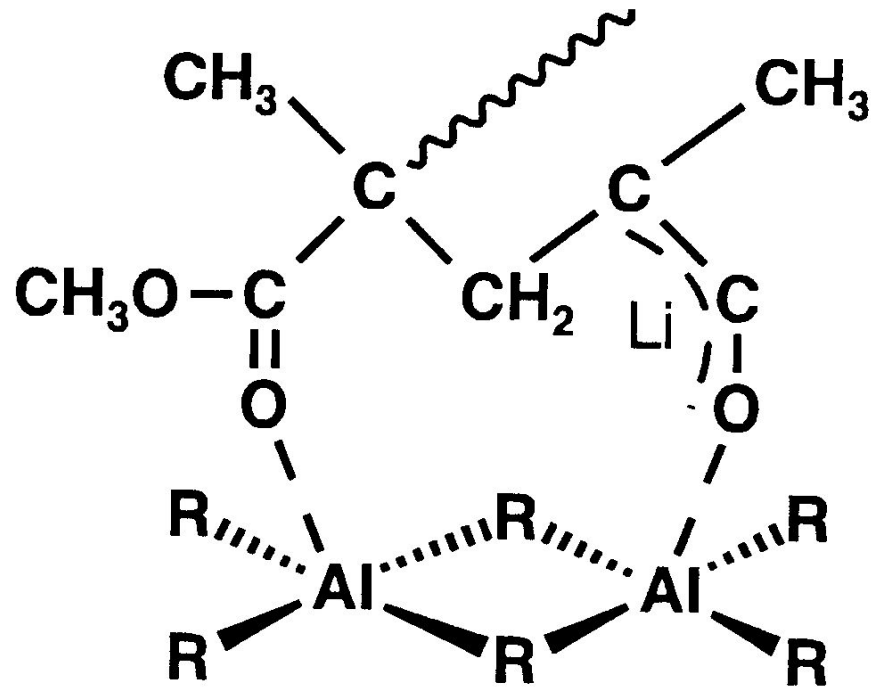


Al-Porphyrin / AlBuⁱ(BHT)₂ / CH₂Cl₂ / 35°C

Al-TPP







dimeric structure of Al alkyl
 $\Rightarrow$ "penultimate effect"
 $\Rightarrow$ rr-triads

