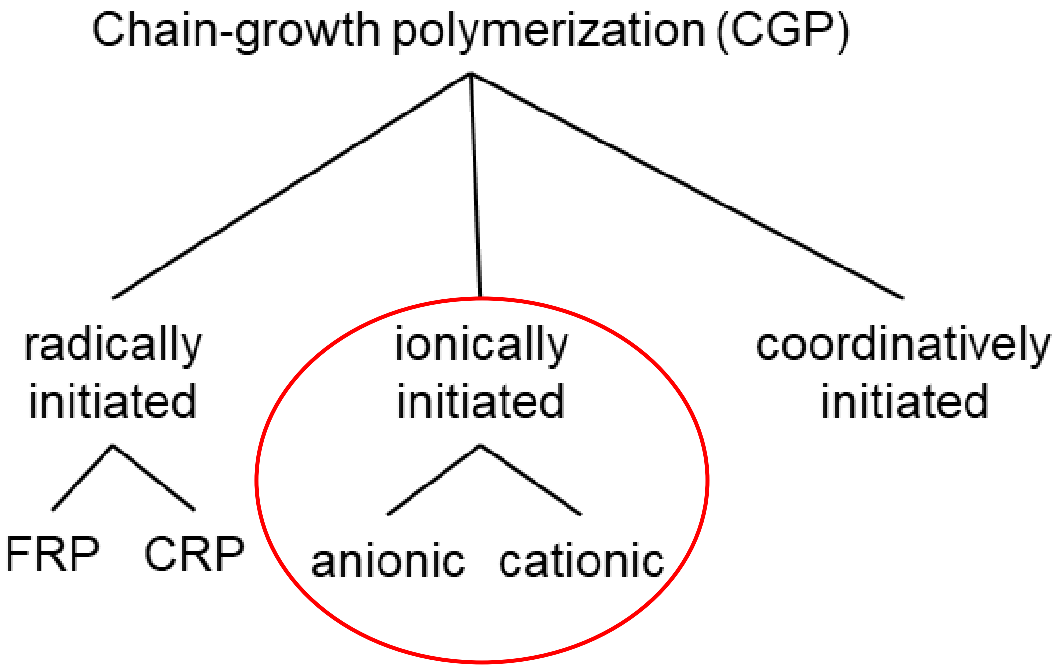
Polimerizzazioni a Catena
(chain-growth polymerizations)



Chain-growth polymerization (CGP)

radically initiated

FRP

CRP

ionically initiated

anionic

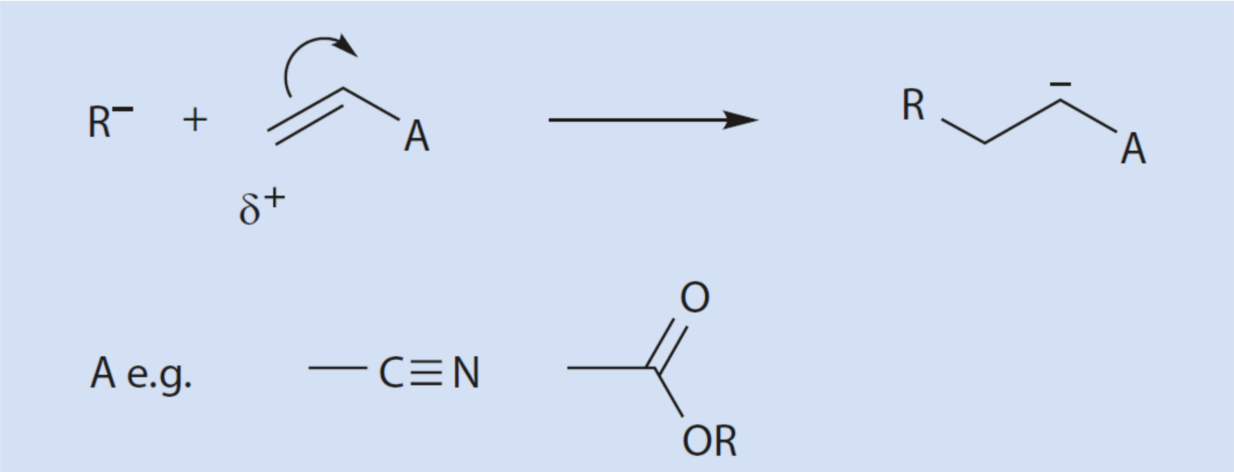
cationic

coordinatively initiated

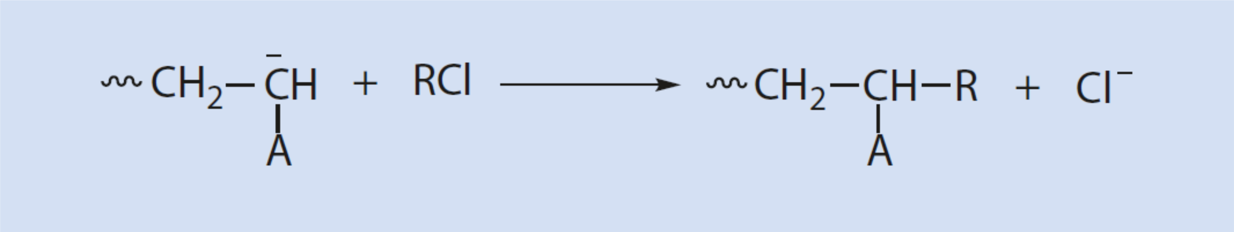
Ionic Polymerizations

Polimerizzazione Anionica

Alta selettività verso monomeri con gruppi elettron **attrattori** adiacenti al doppio legame vinilico

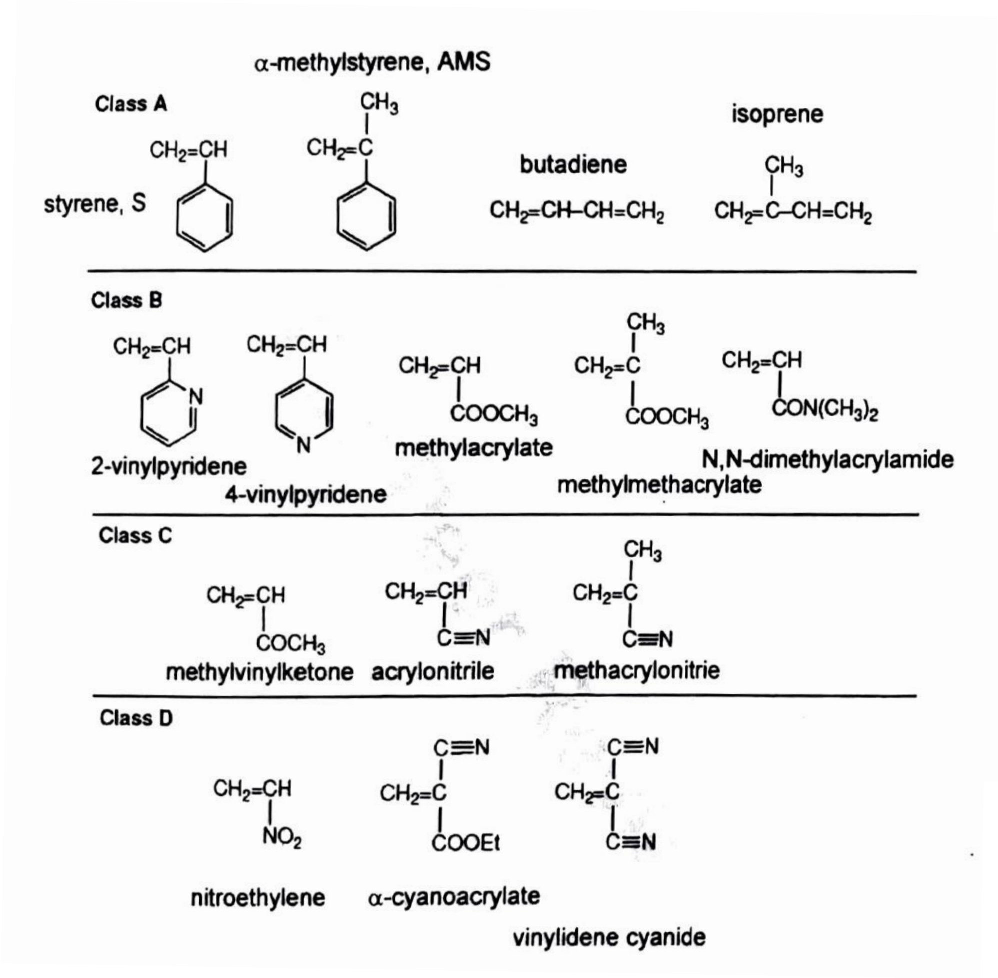


Reagenti e solventi devono essere purificati con grane cura: tracce di acqua o alcoli portano a deattivazione delle specie attive.
Solventi migliori sono THF, idrocarburi alifatici e aromatici. Anche la presenza di clorurati (CH_2Cl_2 e CH_3Cl) porta a reazioni di terminazione della catena



$$\sim CH_2-\underset{A}{\overset{-}{C}H} + RCl \longrightarrow \sim CH_2-\underset{A}{CH}-R + Cl^-$$

Monomers



Class A

styrene, S

$CH_2{=}CH$

α-methylstyrene, AMS

$CH_2{=}C(CH_3)$

butadiene

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

isoprene

$CH_2{=}C(CH_3){-}CH{=}CH_2$

Class B

2-vinylpyridene

4-vinylpyridene

methylacrylate

$CH_2{=}CH{-}COOCH_3$

methylmethacrylate

$CH_2{=}C(CH_3){-}COOCH_3$

N,N-dimethylacrylamide

$CH_2{=}CH{-}CON(CH_3)_2$

Class C

methylvinylketone

$CH_2{=}CH{-}COCH_3$

acrylonitrile

$CH_2{=}CH{-}C{\equiv}N$

methacrylonitrie

$CH_2{=}C(CH_3){-}C{\equiv}N$

Class D

nitroethylene

$CH_2{=}CH{-}NO_2$

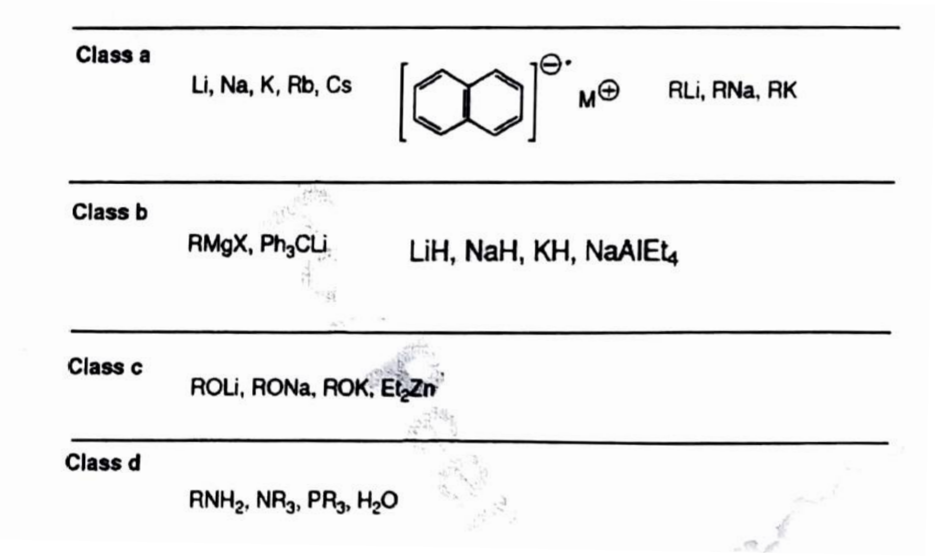
α-cyanoacrylate

$CH_2{=}C(C{\equiv}N){-}COOEt$

vinylidene cyanide

$CH_2{=}C(C{\equiv}N){-}C{\equiv}N$

Initiators



Class a

Li, Na, K, Rb, Cs

$M^{\oplus}$

RLi, RNa, RK

Class b

RMgX, Ph_3CLi

LiH, NaH, KH, $NaAlEt_4$

Class c

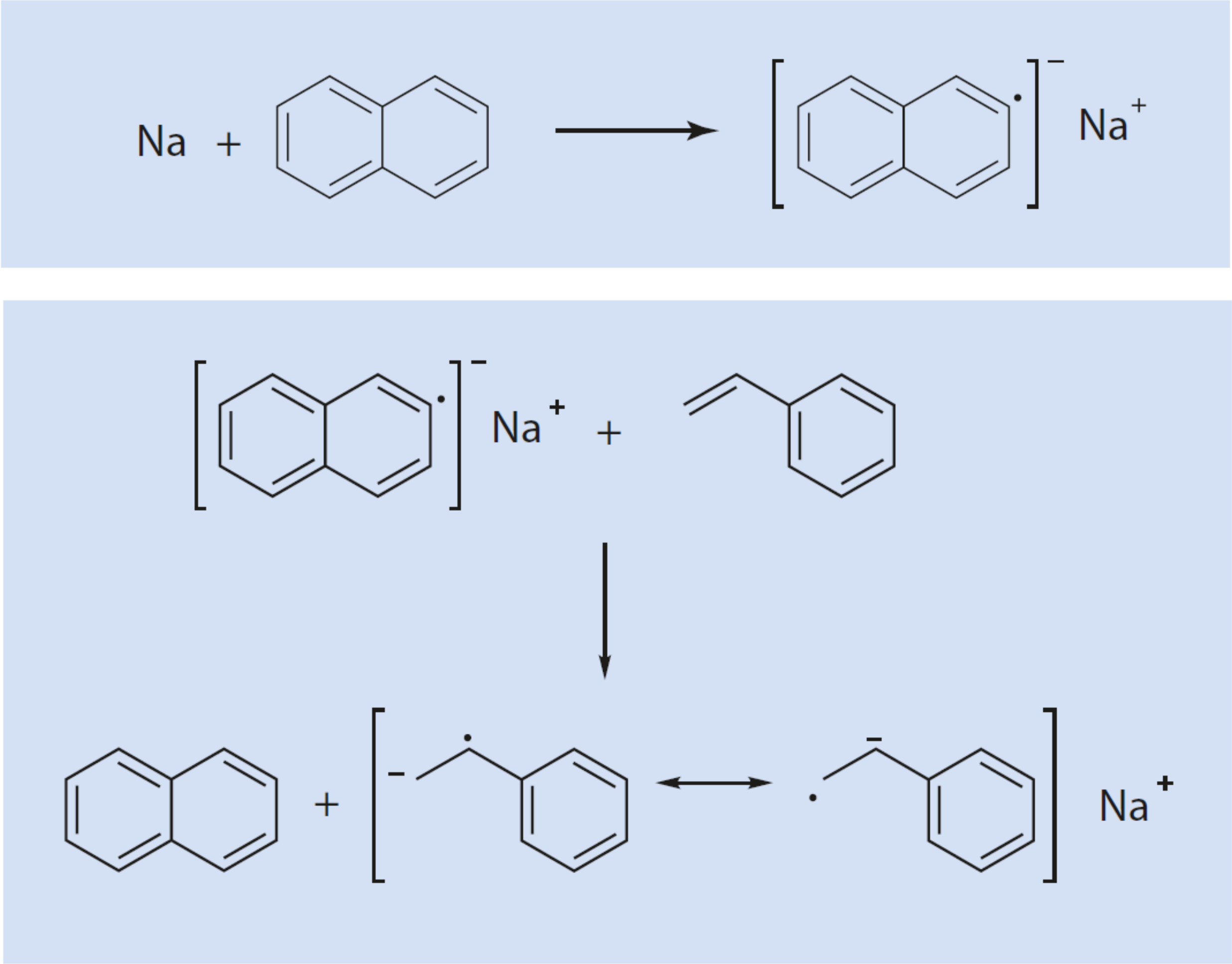
ROLi, RONa, ROK, Et_2Zn

Class d

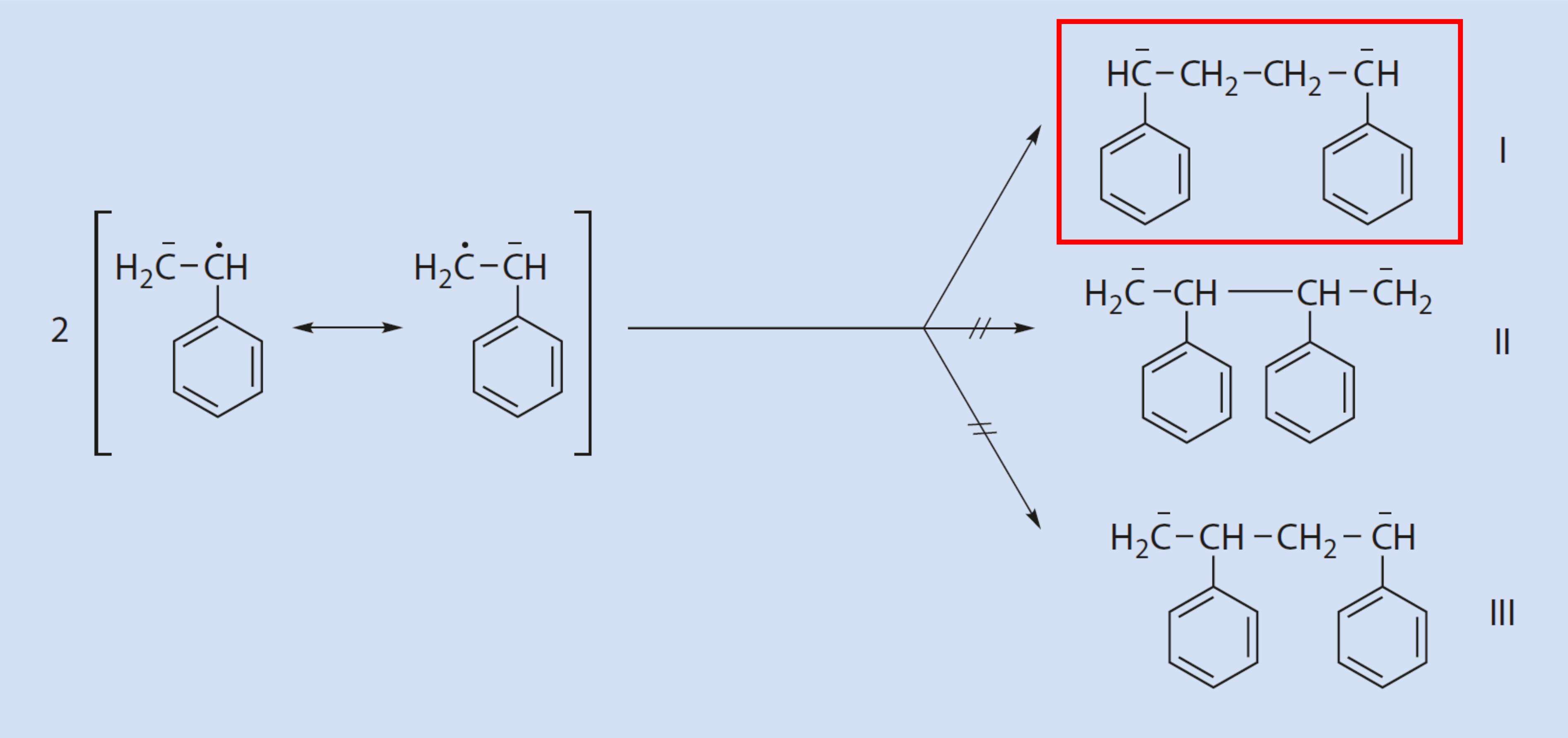
RNH_2, NR_3, PR_3, H_2O

Alternativamente, reazioni di inziazione possono avvenire attraverso **trasferimento elettronico**.

Ad esempio, dalla reazione tra **Na** e **naftalene** si forma un **radicale anione** che puo’ essere utilizzato per iniziare la **polimerizzazione anionica dello stirene**:



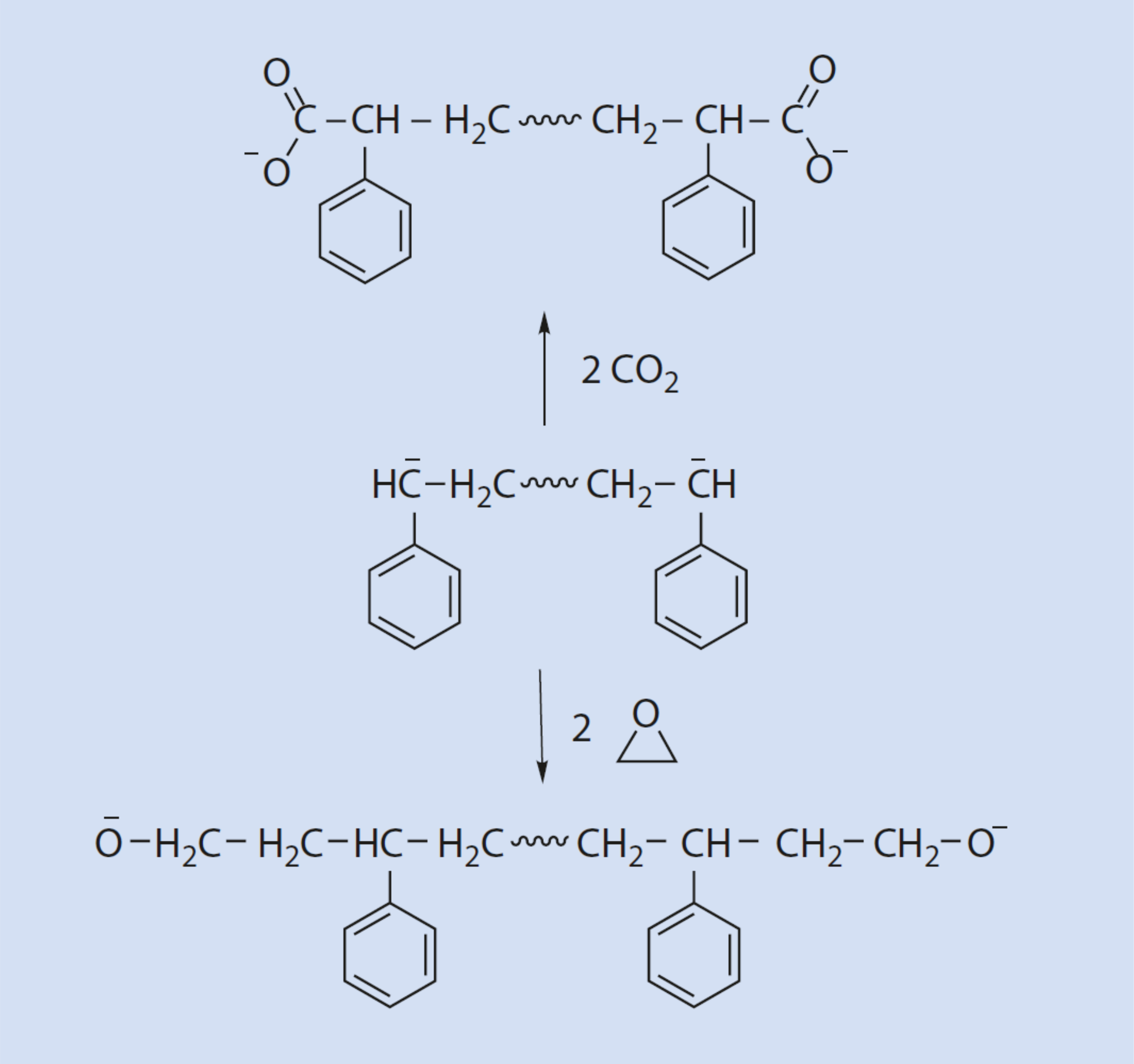
Il **radicale anionico dello stirene** dimerizza a formare un **di-anione**



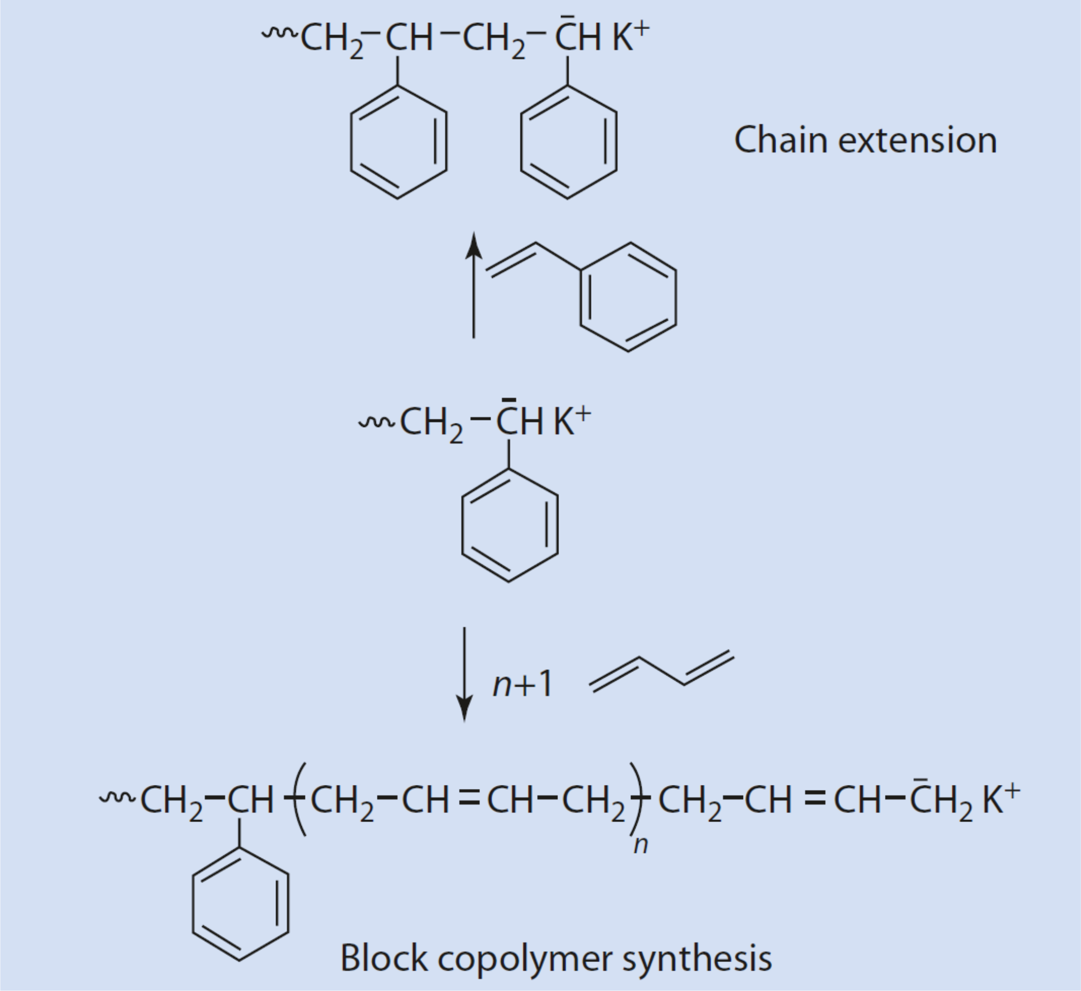
I) è il composto piu’ stabile e quello che in effetti si forma.

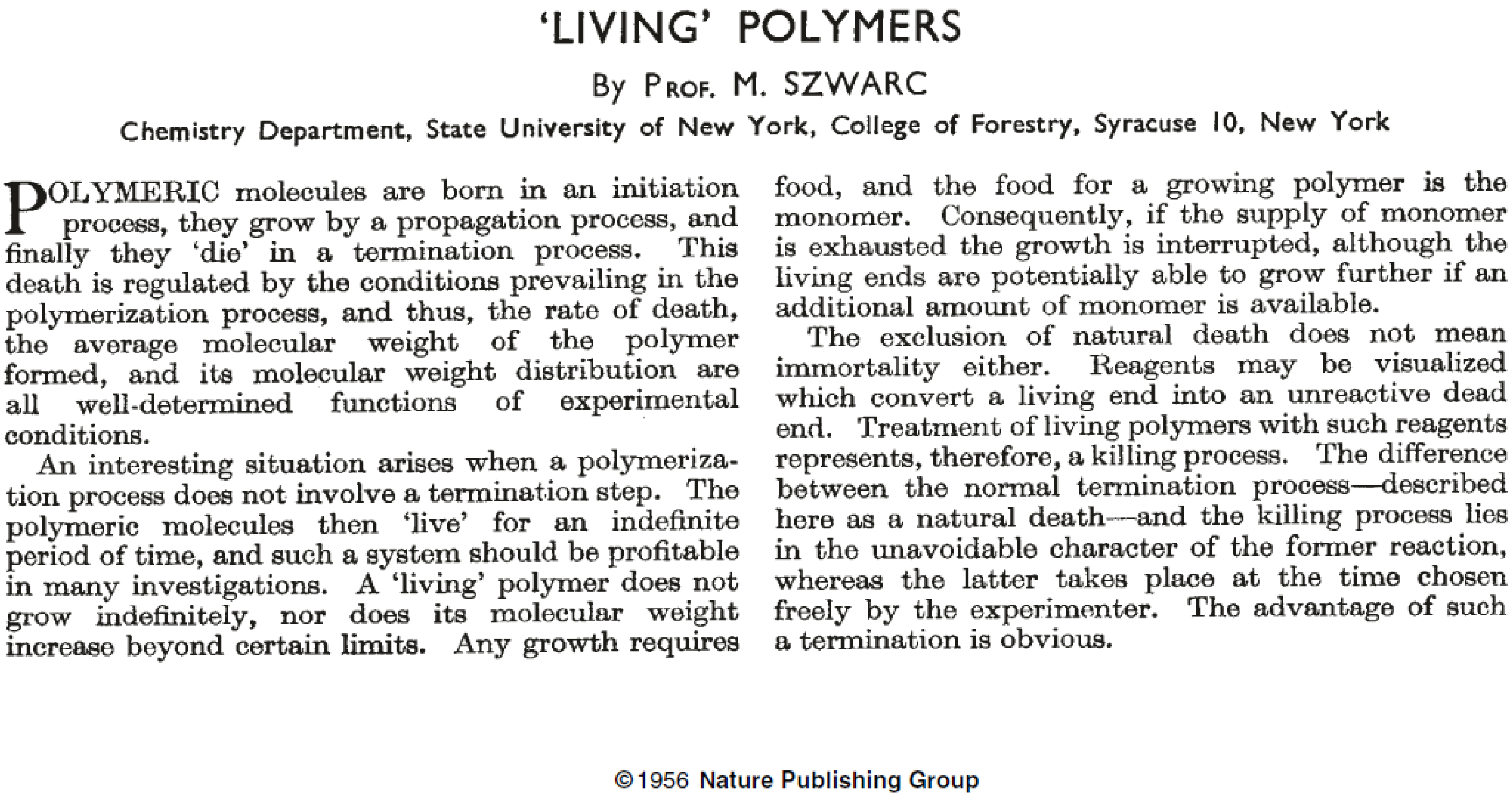
Il di-anione puo’ addizionare monomero e diventa un polimero che accresce da entrambi i lati (con una carica negativa da entrambe le parti).

Aggiungendo appropriati **agenti terminatori** possiamo sintetizzare polimeri **telechelici**.



Se manteniamo la soluzione di polimerizzazione anidra e senza contaminanti, **anioni polistirenici viventi** (*living polystyrene anions*) possono essere preservati per tempi relativamente lunghi. La polimerizzazione puo’ essere ripresa in piu’ stadi successivi, oppure possiamo facilmente sintetizzare **copolimeri a blocchi**, aggiungendo **un secondo monomero**.





'LIVING' POLYMERS

By Prof. M. SZWARC

Chemistry Department, State University of New York, College of Forestry, Syracuse 10, New York

POLYMERIC molecules are born in an initiation process, they grow by a propagation process, and finally they 'die' in a termination process. This death is regulated by the conditions prevailing in the polymerization process, and thus, the rate of death, the average molecular weight of the polymer formed, and its molecular weight distribution are all well-determined functions of experimental conditions.

An interesting situation arises when a polymerization process does not involve a termination step. The polymeric molecules then 'live' for an indefinite period of time, and such a system should be profitable in many investigations. A 'living' polymer does not grow indefinitely, nor does its molecular weight increase beyond certain limits. Any growth requires food, and the food for a growing polymer is the monomer. Consequently, if the supply of monomer is exhausted the growth is interrupted, although the living ends are potentially able to grow further if an additional amount of monomer is available.

The exclusion of natural death does not mean immortality either. Reagents may be visualized which convert a living end into an unreactive dead end. Treatment of living polymers with such reagents represents, therefore, a killing process. The difference between the normal termination process—described here as a natural death—and the killing process lies in the unavoidable character of the former reaction, whereas the latter takes place at the time chosen freely by the experimenter. The advantage of such a termination is obvious.

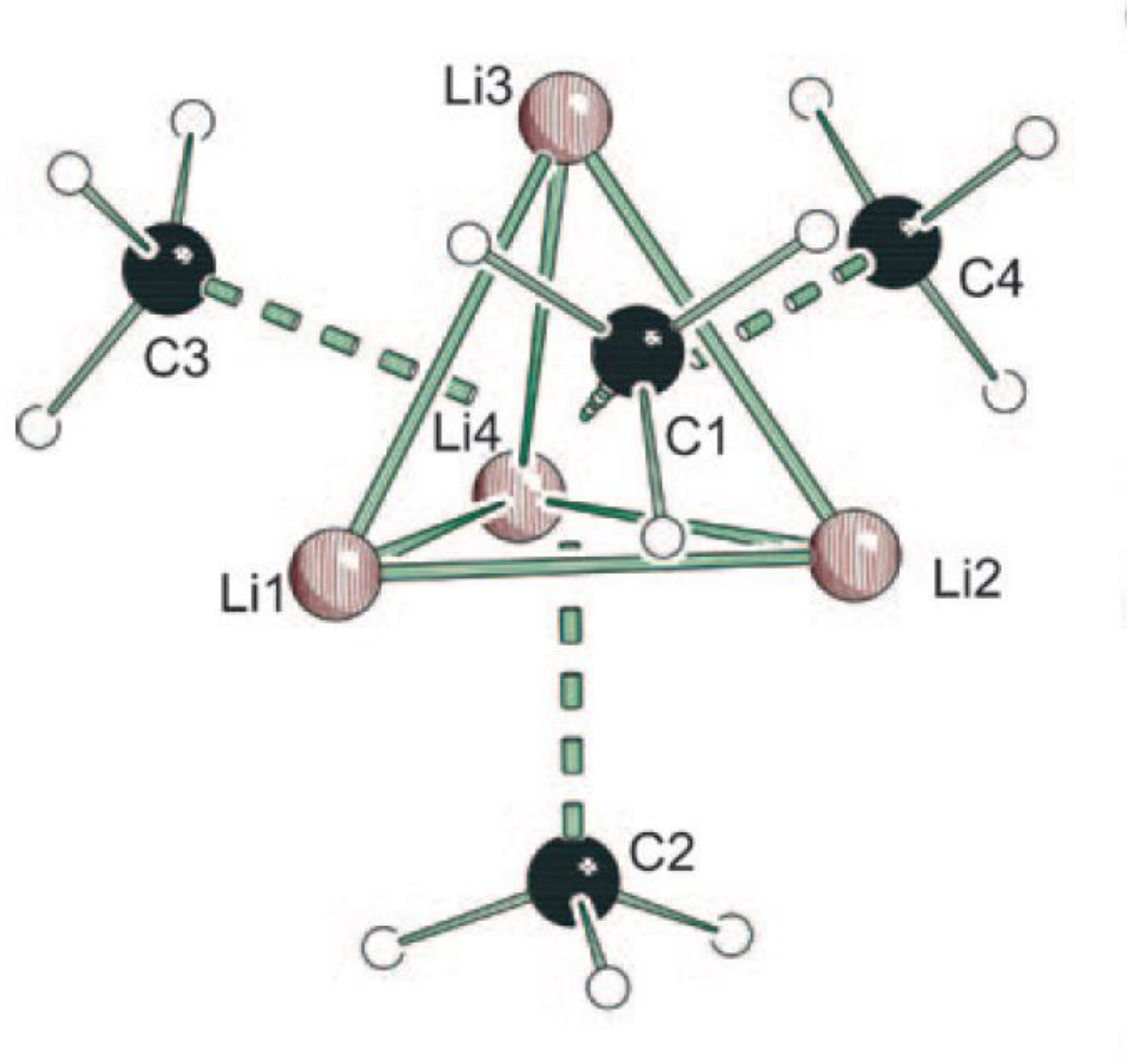
(1) *Styrene polymerization*:

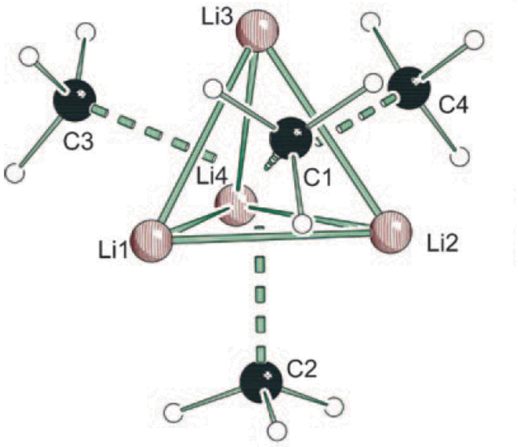
Menthyllithium [2] > s-C_4H_9Li [4] > i-C_3H_7Li [4–6] > i-C_4H_9Li > n-C_4H_9Li [6] > t-C_4H_9Li [4]

(2) *Diene polymerization*:

Menthyllithium [2] > s-C_4H_9Li [4] > i-C_3H_7Li [4–6] > t-C_4H_9Li [4] > i-C_4H_9Li > n-C_4H_9Li [6]

Typical aggregate of MeLi:





Organolithium compounds are often schematically depicted as monomeric species with one lithium atom and a carbanionic group, such as MeLi or *n*BuLi. However, the structures of these compounds are much more complicated, and the understanding of these principles is necessary for describing the reactivity. In general, the molecular structure of lithium organics in solution and in the solid state is affected by three factors: Electrostatic interactions between counter charges (localised as well as delocalised), the coordination sphere of the lithium atom (*e.g.*, solvent molecules, coordinating Lewis bases) and the steric demand of the more or less bulky substituents at the lithiated carbon centre and/or at the ligand. Without the addition of Lewis bases organo-lithium compounds tend to build oligomeric structures, above all tetramers and hexamers. An important building principle of these structures is the arrangement of the lithium atoms to Li_3 triangles, which join each other to form lithium polyhedra (Figure 1). These Li_3 faces are capped by the Cα atoms, so that the carbanionic centre possesses three contacts to the lithium atoms.

C. Strohmann *Chem. Eur. J.* **2009**, 15, 3320 – 3334

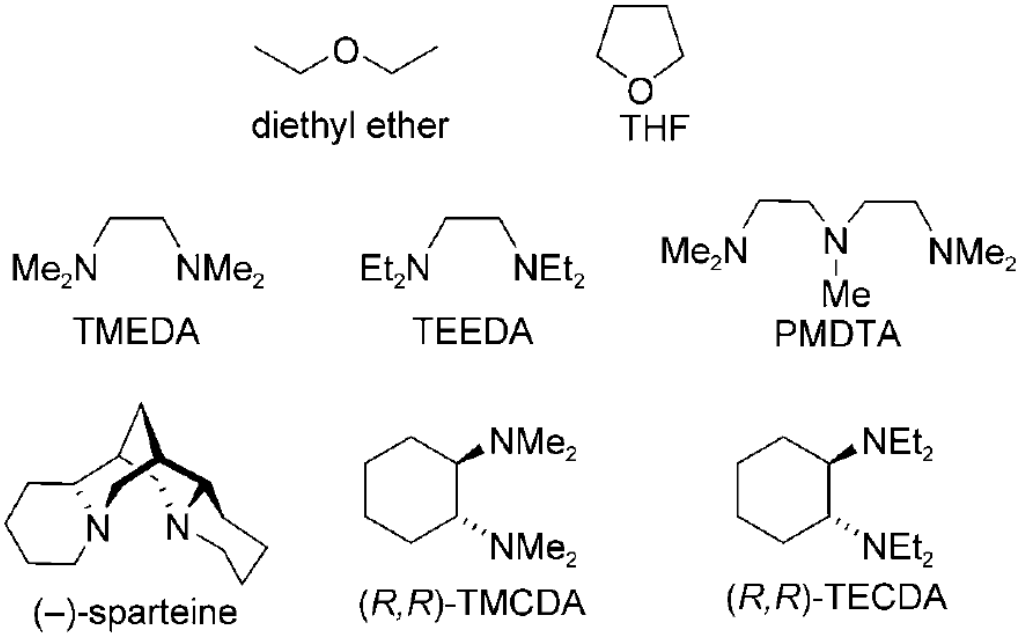


Figure 3. Often-used Lewis bases for the coordination of organolithium compounds.

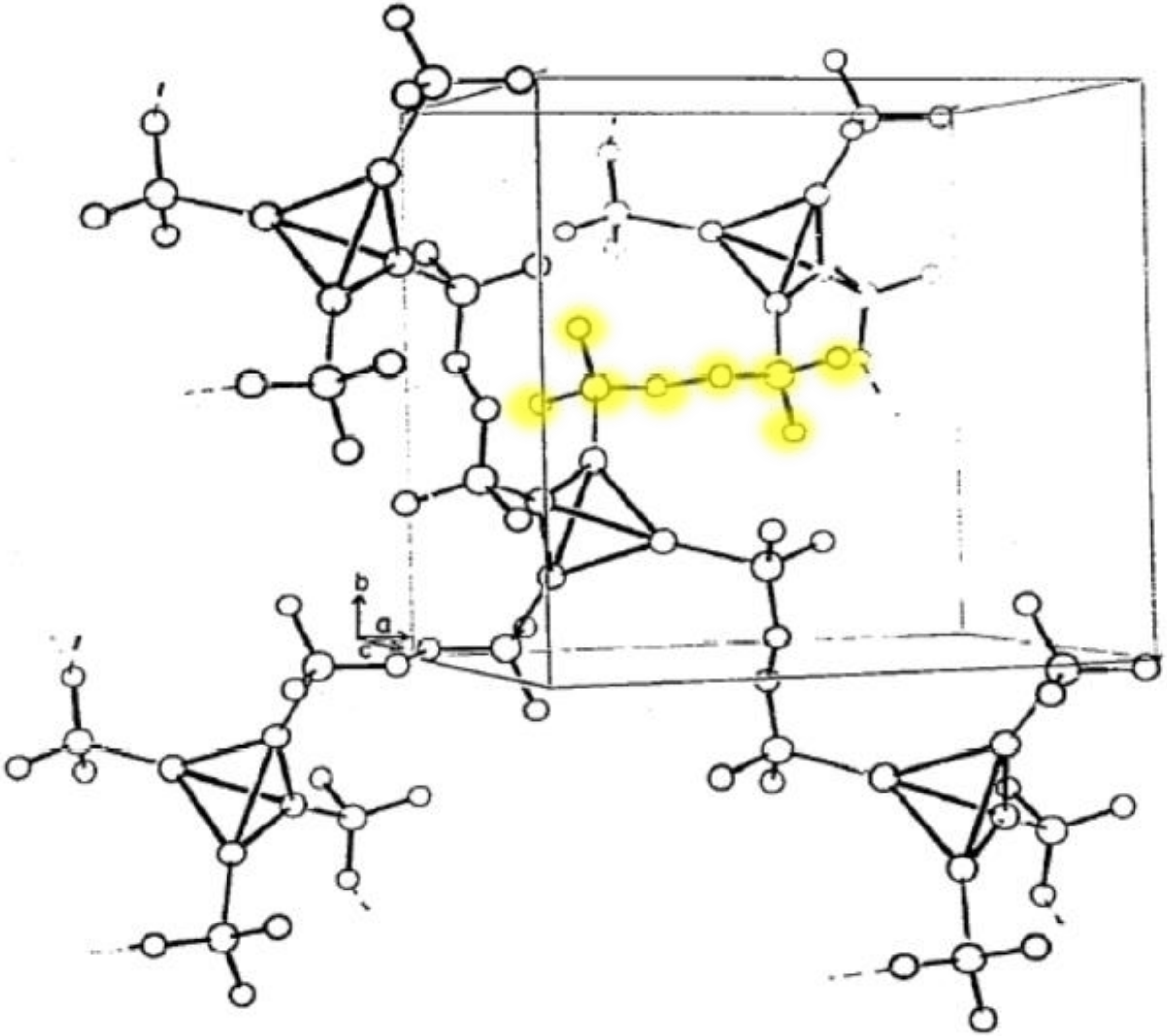
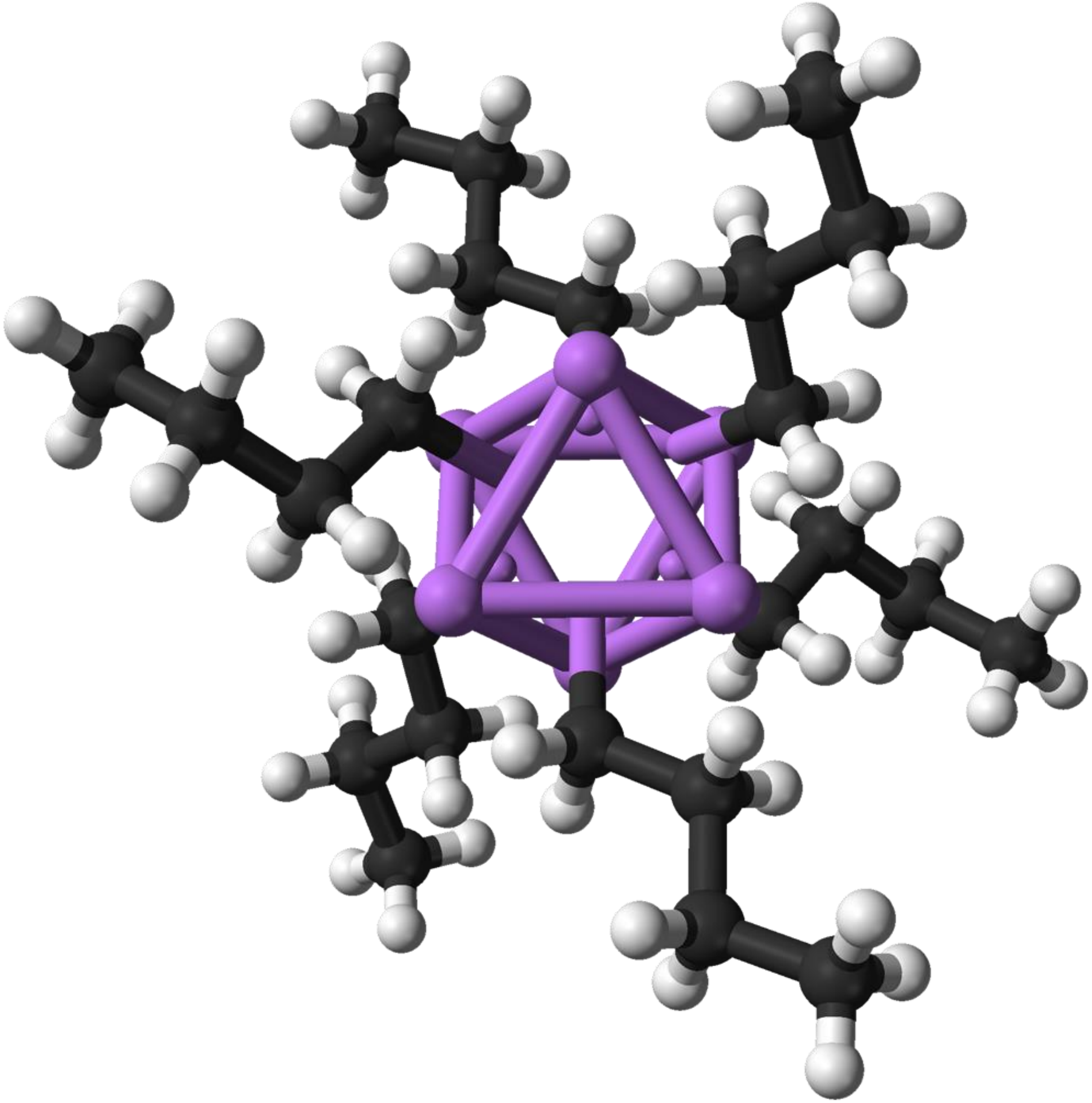


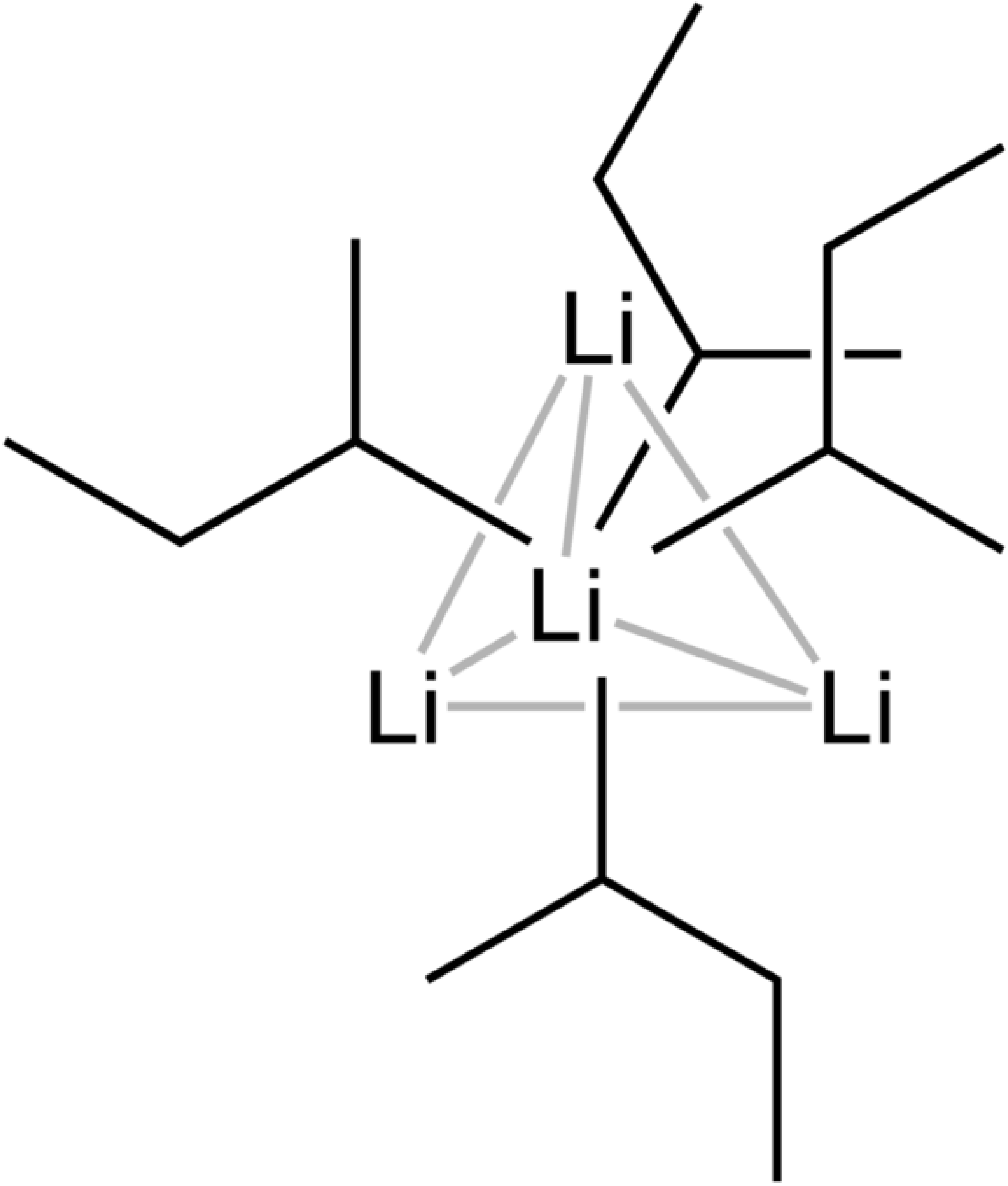
Fig. 2. Räumliche Verknüpfung der MeLi-Assoziate (Assoziat mit Zentrum auf 3/4 3/4 3/4 in der gezeichneten Zelle weggelassen. desgleichen alle Methylgruppen des MeLi).

E. Weiss et al. *J. Organometal. Chem.* **1978**, *160*, 1

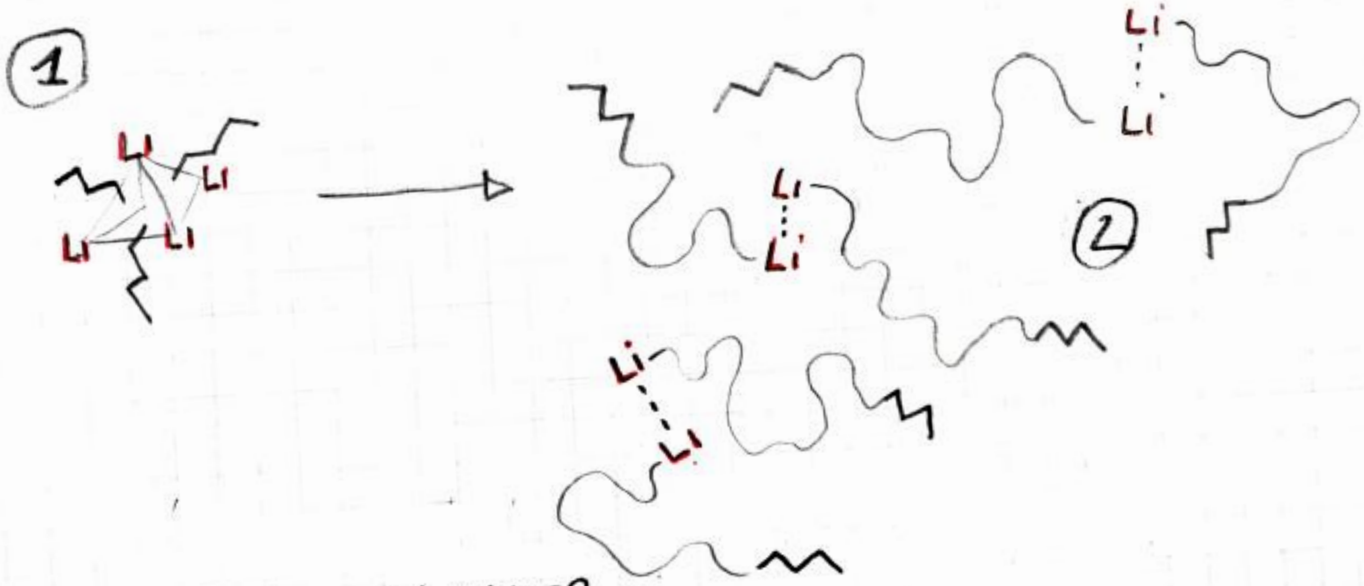
Typical aggregate of n-BuLi:



Typical aggregate of s-BuLi:



LARGER
AGGREGATES ARE
PREDOMINANT AT THE
BEGINNING OF THE POLYMERIZATION ①



WHILE THE POLYMER
GROWS ② AGGREGATE DISGREGATES

Effect of solvent:

Winstein spectrum of structures for a carbanionic chain end (R^-)

$$\begin{array}{ccccccccc} (RMt)_n & \rightleftharpoons & n\,RMt & \rightleftharpoons & R^-,Mt^+ & \rightleftharpoons & R^-//\,Mt^+ & \rightleftharpoons & R^- + Mt^+ \\ \mathbf{1} & & \mathbf{2} & & \mathbf{3} & & \mathbf{4} & & \mathbf{5} \end{array}$$

In addition to the aggregated (**1**) and unassociated (**2**) species, it is necessary to consider the intervention of free ions (**5**) and the contact (**3**) and solvent-separated (**4**) ion pairs; Mt^+ represents a metallic counterion such as an alkali metal cation.

Anionic Polymerization of Isoprene:

The stereochemistry of the anionic polymerization of isoprene using RLi as initiators depends mainly on monomer concentration and solvent.

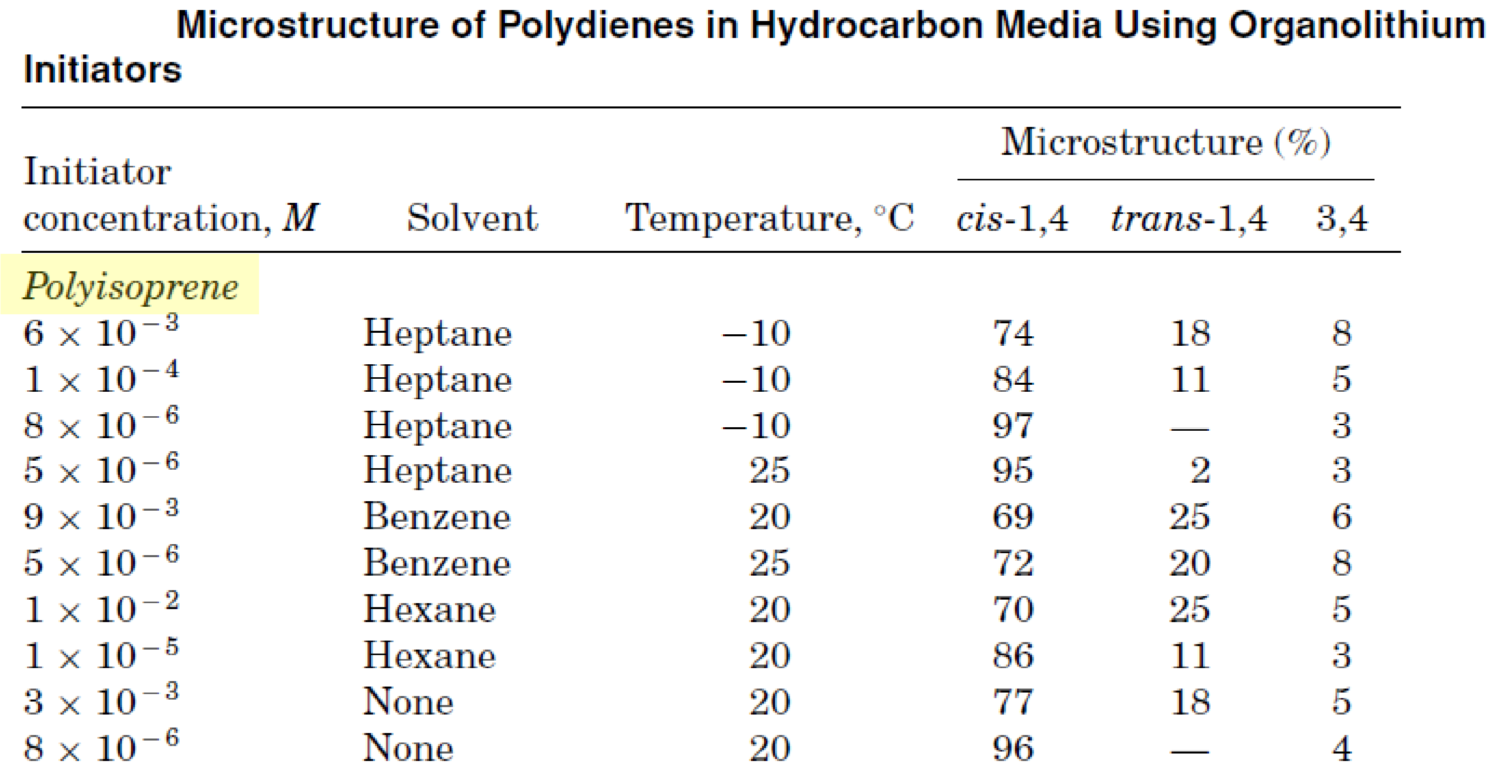
It was proposed that isomerization of the initially formed *cis* form of the active chain end occurs competitively with monomer addition at each step of the reaction. Thus, when the concentration of monomer is high relative to the chain-end concentration, isomerization of the *cis* form does not compete effectively with monomer addition. However, at low concentrations of monomer relative to chain ends, the isomerization does compete and significant amounts of the *trans* form will be in equilibrium with the *cis* form.

In polar media, the unique, high 1,4 stereospecificity that is observed in hydrocarbon media is lost and large amounts of 3,4-poly(isoprene) enchainments are obtained.

OTHER FACTORS TO BE CONSIDERED:

There are several important structural differences for polydienyl anions in polar media versus hydrocarbon solvents: (1) chain ends are generally not associated into higher aggregates in polar media compared to hydrocarbon; (2) the charge distribution of unsymmetrical allylic anions is a function of solvent, counterion, and temperature; (3) the kinetic and equilibrium distribution of chain-end configurations can vary with solvent and counterion; (4) the distribution of contact ion pairs, solvent-separated ion pairs, and free ions can vary with solvent, counterion, and temperature.

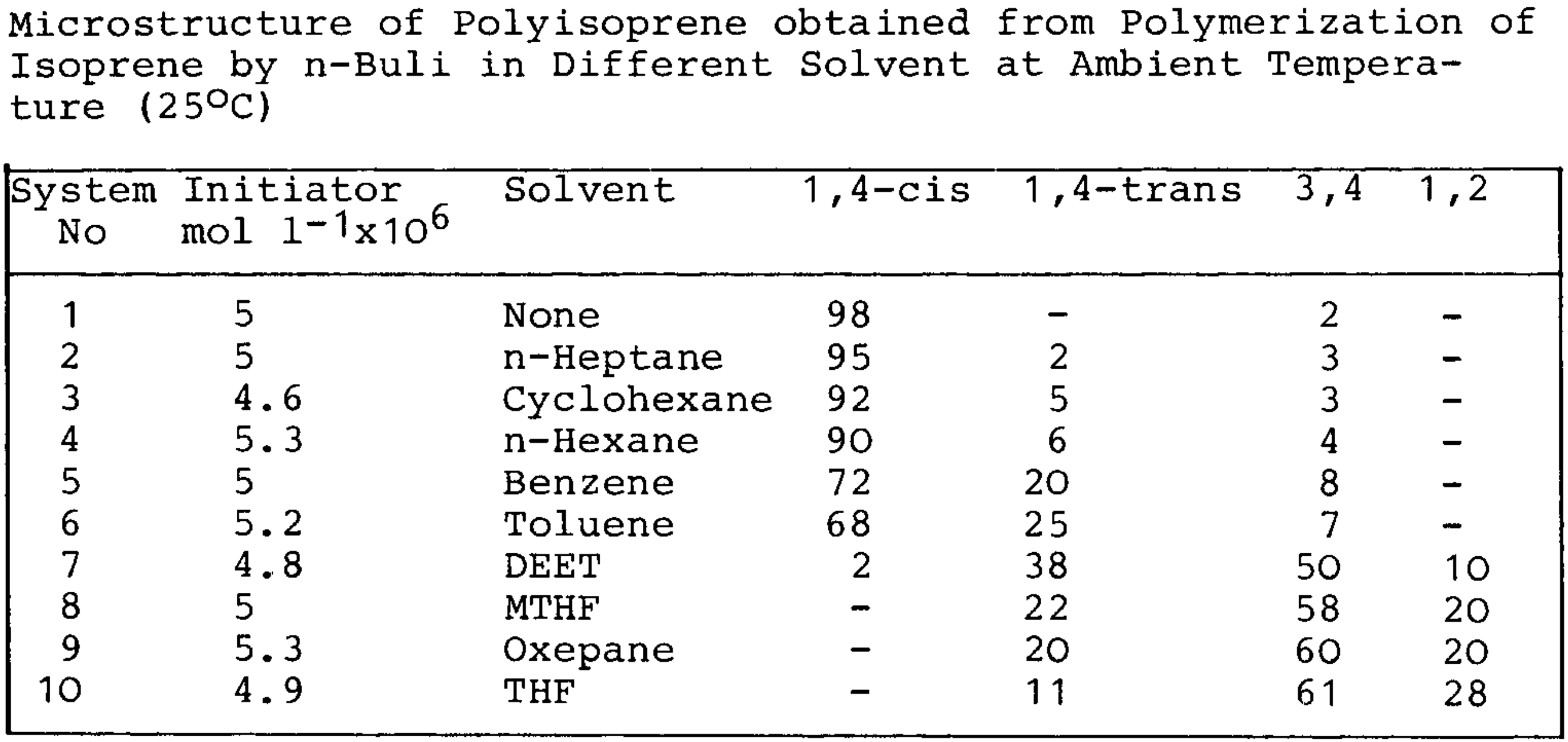
Anionic Polymerization of Isoprene:



Microstructure of Polydienes in Hydrocarbon Media Using Organolithium Initiators

Initiator concentration, *M*	Solvent	Temperature, °C	Microstructure (%)		
			cis-1,4	*trans*-1,4	3,4
Polyisoprene					
6×10^{-3}	Heptane	−10	74	18	8
1×10^{-4}	Heptane	−10	84	11	5
8×10^{-6}	Heptane	−10	97	—	3
5×10^{-6}	Heptane	25	95	2	3
9×10^{-3}	Benzene	20	69	25	6
5×10^{-6}	Benzene	25	72	20	8
1×10^{-2}	Hexane	20	70	25	5
1×10^{-5}	Hexane	20	86	11	3
3×10^{-3}	None	20	77	18	5
8×10^{-6}	None	20	96	—	4

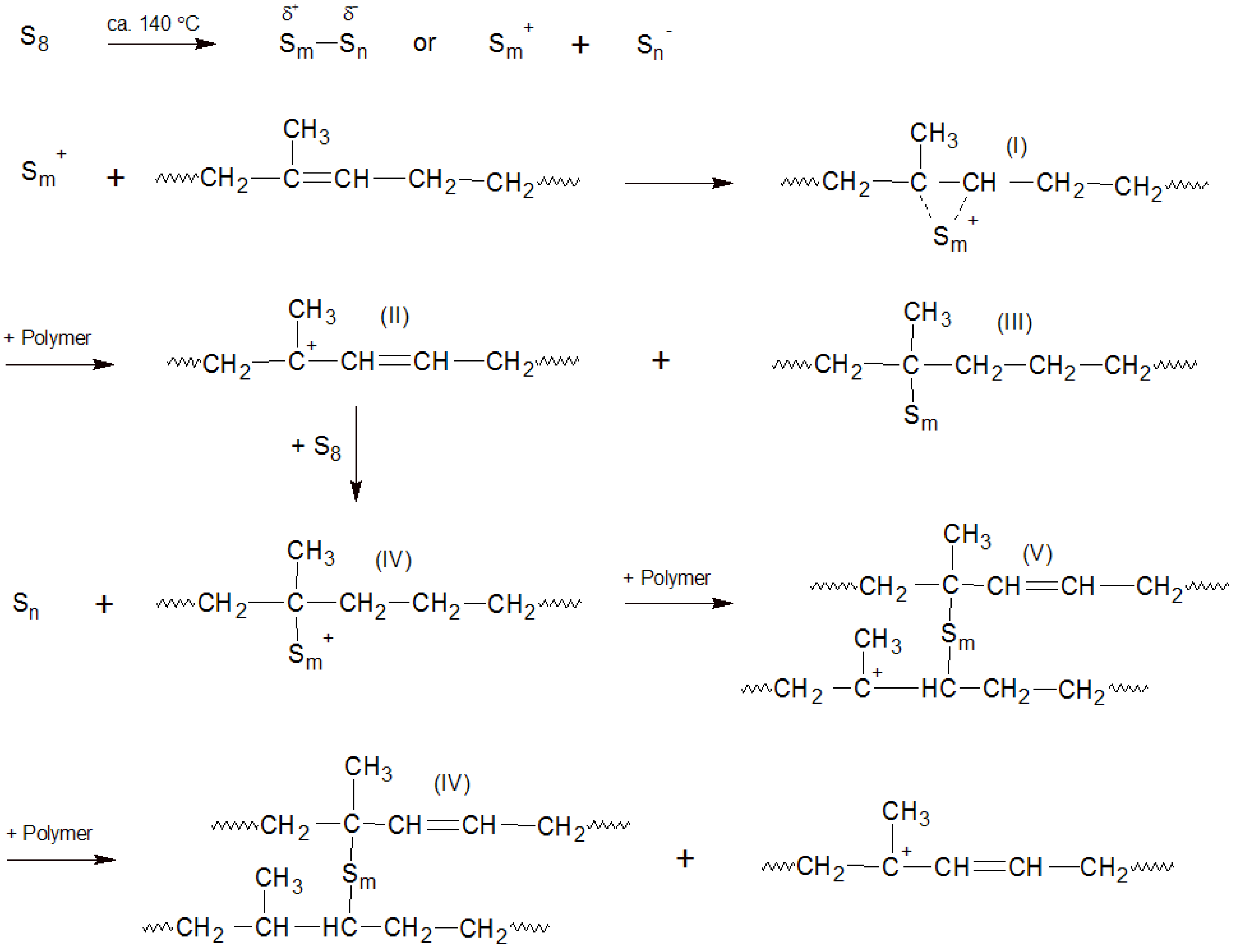
Anionic Polymerization of Isoprene:



Microstructure of Polyisoprene obtained from Polymerization of Isoprene by n-Buli in Different Solvent at Ambient Temperature (25°C)

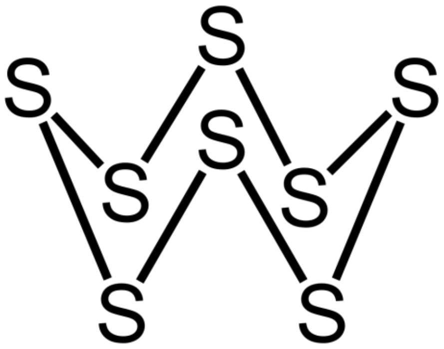
System No	Initiator mol l^{-1}x10^{6}	Solvent	1,4-cis	1,4-trans	3,4	1,2
1	5	None	98	-	2	-
2	5	n-Heptane	95	2	3	-
3	4.6	Cyclohexane	92	5	3	-
4	5.3	n-Hexane	90	6	4	-
5	5	Benzene	72	20	8	-
6	5.2	Toluene	68	25	7	-
7	4.8	DEET	2	38	50	10
8	5	MTHF	-	22	58	20
9	5.3	Oxepane	-	20	60	20
10	4.9	THF	-	11	61	28

Vulcanization of PI with S_8:



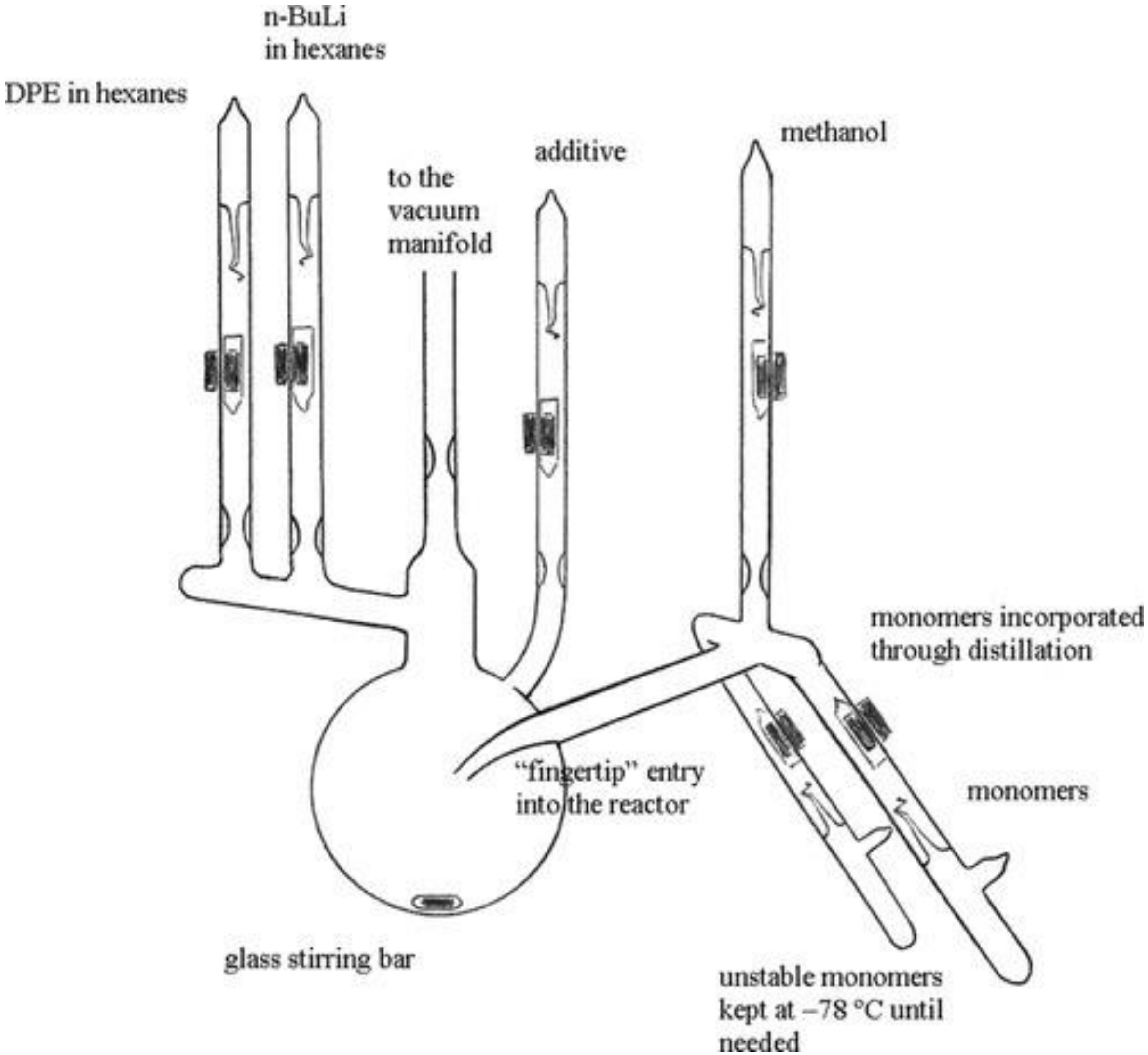
Vulcanization of PI with S_8:

The process starts with the formation of a persulfonium ion (I) by reaction of an isoprene unit with a polarized sulfur molecule or with a sulfur cation. The persulfonium ion reacts than with another isoprene unit by allylic hydrogen abstraction to produce a polymeric allylic carbocation (II). In a third step a sulfur molecule (cyclic S_8) combines with the allylic cation to produce another sulfonium ion (IV) which releases (monomeric) sulfur. The polymeric sulfonium ion then undergoes crosslinking by anionic addition to a polymeric double bond to create a new carbocation (V) which then either reacts with another sulfur molecule or it abstracts a hydrogen from another isoprene unit to create a new polymeric cation (II).



Sealed apparatus for a complex anionic polymerization

Courtesy: Profs. A. Hirao and T. Ishizone, TIT, Japan


n-BuLi
in hexanes
DPE in hexanes
to the
vacuum
manifold
additive
methanol
monomers incorporated
through distillation
"fingertip" entry
into the reactor
monomers
glass stirring bar
unstable monomers
kept at –78 °C until
needed

Anionic Polymerization of Acrylates and Methacrylates:

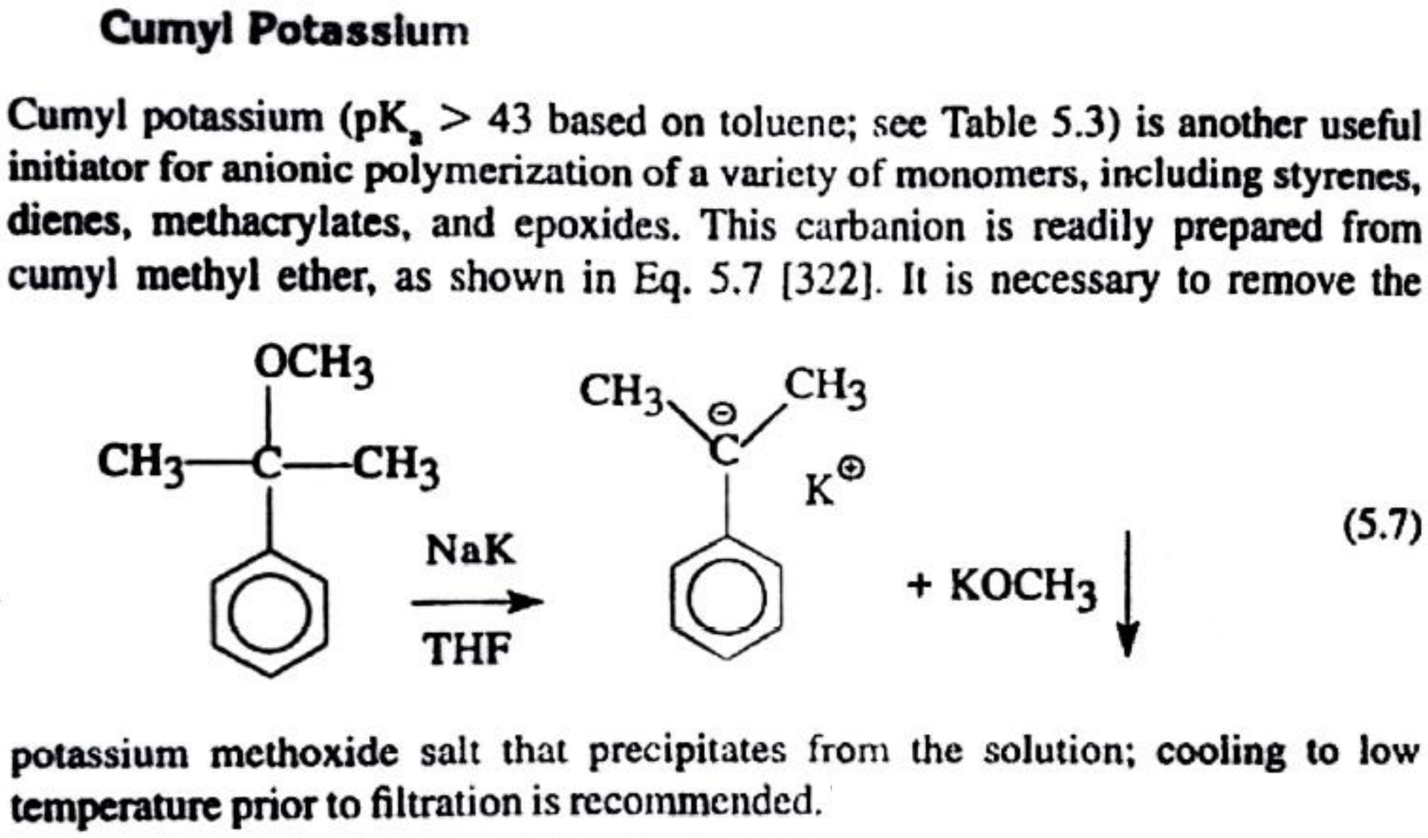
This might suffer from different problems related to the high reactivity of RLi compounds towards acrylates/methacrylates, which makes such side reactions are not negligible.

1) Site of addition of RLi on A/MA
2) Chemical nature of species that propagate
3) Side reactions

There are ways to solve these problems and provide a **living anionic polymerization** of **A** and **MA**.

A. Use of sterically hindered initiators
B. Addition of LiCl
C. Addition of methoxy-ethoxydes ($LiOCH_2CH_2OCH_3$)

A. Use of sterically hindered initiators for the anionic polymerization of Acrylates/Methacrylates:



Cumyl Potassium

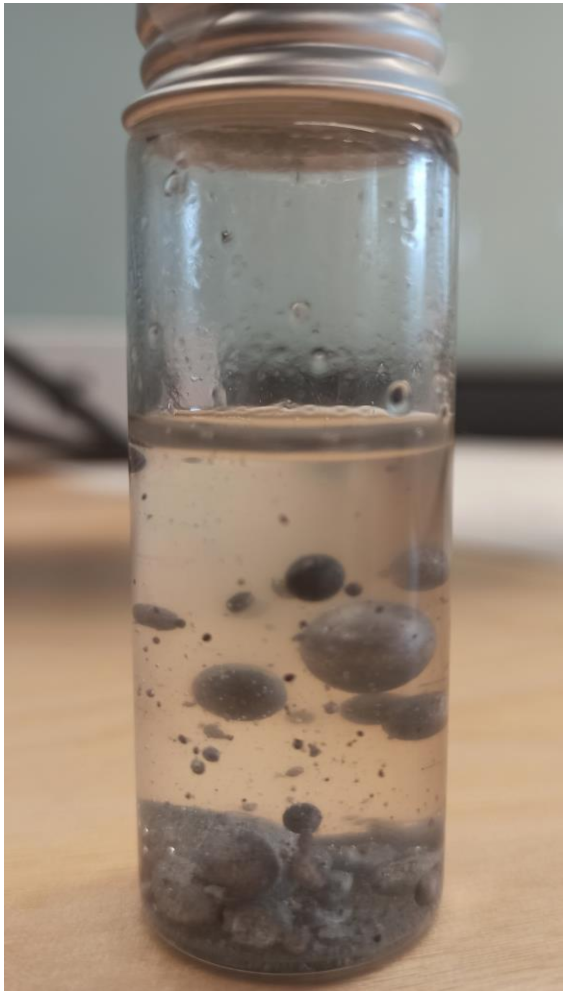
Cumyl potassium (pK_a > 43 based on toluene; see Table 5.3) is another useful initiator for anionic polymerization of a variety of monomers, including styrenes, dienes, methacrylates, and epoxides. This carbanion is readily prepared from cumyl methyl ether, as shown in Eq. 5.7 [322]. It is necessary to remove the

(5.7)

potassium methoxide salt that precipitates from the solution; cooling to low temperature prior to filtration is recommended.

A. Use of sterically hindered initiators for the anionic polymerization of Acrylates/Methacrylates:

NaK alloy (lega eutettica)



A. First success in anionic polymerization of MMA using CuK (1974)

The initiation is still faster than propagation but lower than with sterically less hindered initiators. Hence, it is easier to evenly distribute all components at the beginning of the polymerization reaction.

CuK cannot attach the ester groups under the applied conditions. However we have to consider that CuK is not so easy to prepare. KOMe precipitates out and needs to be filtered off.

B. Use of LiCl for the anionic polymerization of Acrylates/Methacrylates:

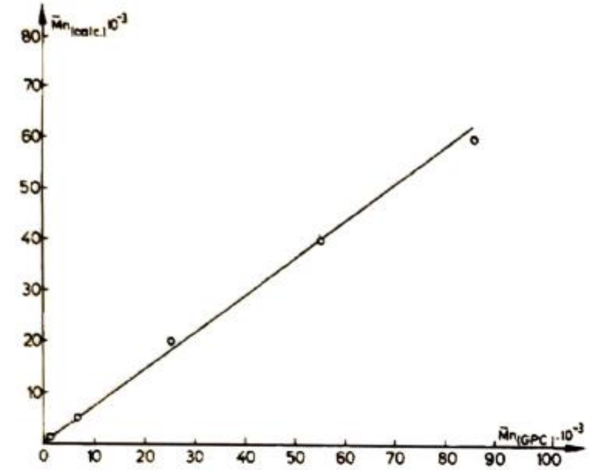
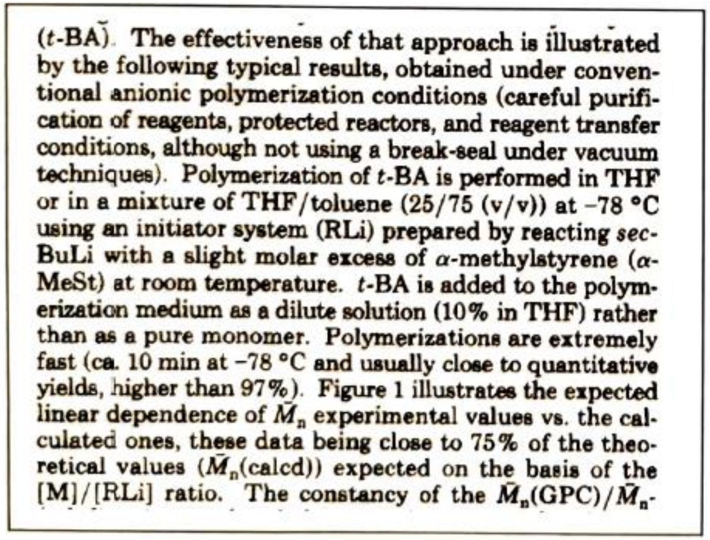


Figure 1. Plot of calculated $\bar{M}_n$ (i.e., grams of reacted *t*-BA per mole of RLi) vs. experimental values obtained from GPC (polystyrene calibration). [LiCl] = 12.66 × 10^{-3} mol L^{-1} and [RLi] = 6.6 × 10^{-3} mol L^{-1} in THF at −78 °C.



(*t*-BA). The effectiveness of that approach is illustrated by the following typical results, obtained under conventional anionic polymerization conditions (careful purification of reagents, protected reactors, and reagent transfer conditions, although not using a break-seal under vacuum techniques). Polymerization of *t*-BA is performed in THF or in a mixture of THF/toluene (25/75 (v/v)) at −78 °C using an initiator system (RLi) prepared by reacting *sec*-BuLi with a slight molar excess of α-methylstyrene (α-MeSt) at room temperature. *t*-BA is added to the polymerization medium as a dilute solution (10% in THF) rather than as a pure monomer. Polymerizations are extremely fast (ca. 10 min at −78 °C and usually close to quantitative yields, higher than 97%). Figure 1 illustrates the expected linear dependence of $\bar{M}_n$ experimental values vs. the calculated ones, these data being close to 75% of the theoretical values ($\bar{M}_n$(calcd)) expected on the basis of the [M]/[RLi] ratio. The constancy of the $\bar{M}_n$(GPC)/$\bar{M}_n$-

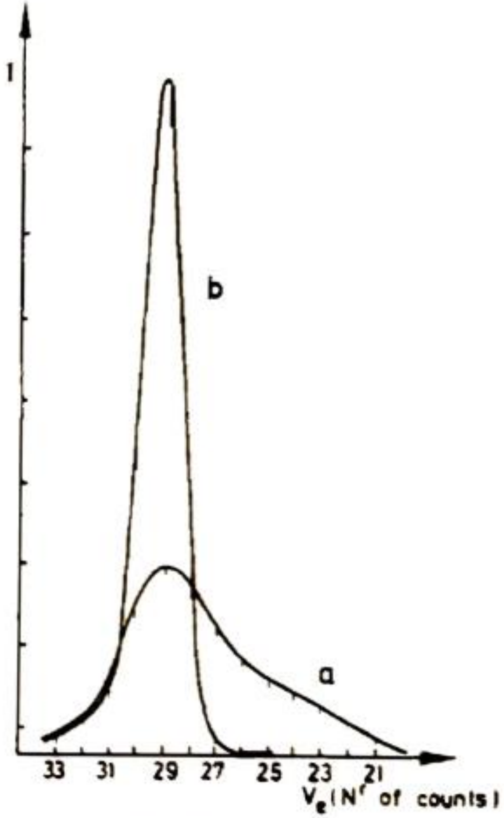


Figure 2. Influence of LiCl on the MW distribution as seen in gel permeation chromatograms: (a) no salt, $\bar{M}_w/\bar{M}_n$ = 3.61; (b) LiCl/RLi = 5.02, $\bar{M}_w/\bar{M}_n$ = 1.20. (Conditions: (a) [RLi] = 6.6 × 10^{-3} mol L^{-1}; (b) [RLi] = 6.6 × 10^{-3} mol L^{-1} and [LiCl] = 33.46 × 10^{-3} mol L^{-1} in THF at −78 °C.)

P. Theyssié et al. *Macromolecules* **1987**, *20*, 1442

B. Use of LiCl for the anionic polymerization of Acrylates/Methacrylates

Some Remarks

- The presence of few equivalents of LiCl results in the formation of higher (mixed) aggregates at the chain ends.

- Such aggregates have a reduced intrinsic reactivity and additionally reduce chain transfer and side reactions because of steric protection.

- When the use of LiCl is coupled to the use of bulky initiator, sterically hindered side chain (tBu group), and low temperature (-78°C) further control is gained.

C. Use of Li-methoxyethoxides for the anionic polymerization of Acrylates/Methacrylates:

KINETICS AND MECHANISMS OF ANIONIC POLYMERIZATION OF (METH)ACRYLATES IN THE PRESENCE OF LITHIUM 2-METHOXYETHOXIDE

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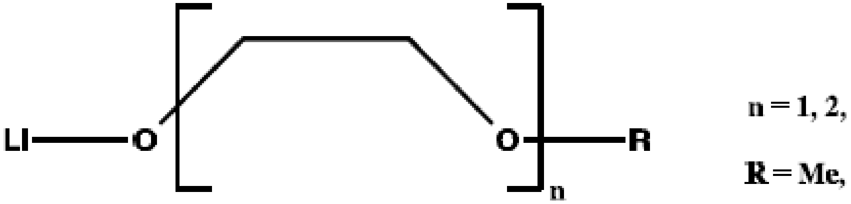
Bruno Vuillemin, Christophe Navarro

Elf-Atochem S.A., GRL, F-64170 Artix, France



C. **Use of Li-methoxyethoxides** for the anionic polymerization of Acrylates/Methacrylates:

The MWD is narrow ($M_w/M_n < 1.1$ at -40 °C ≤ T ≤ 0 °C) with a unimodal, symmetrical distribution for an almost quantitative monomer conversion.

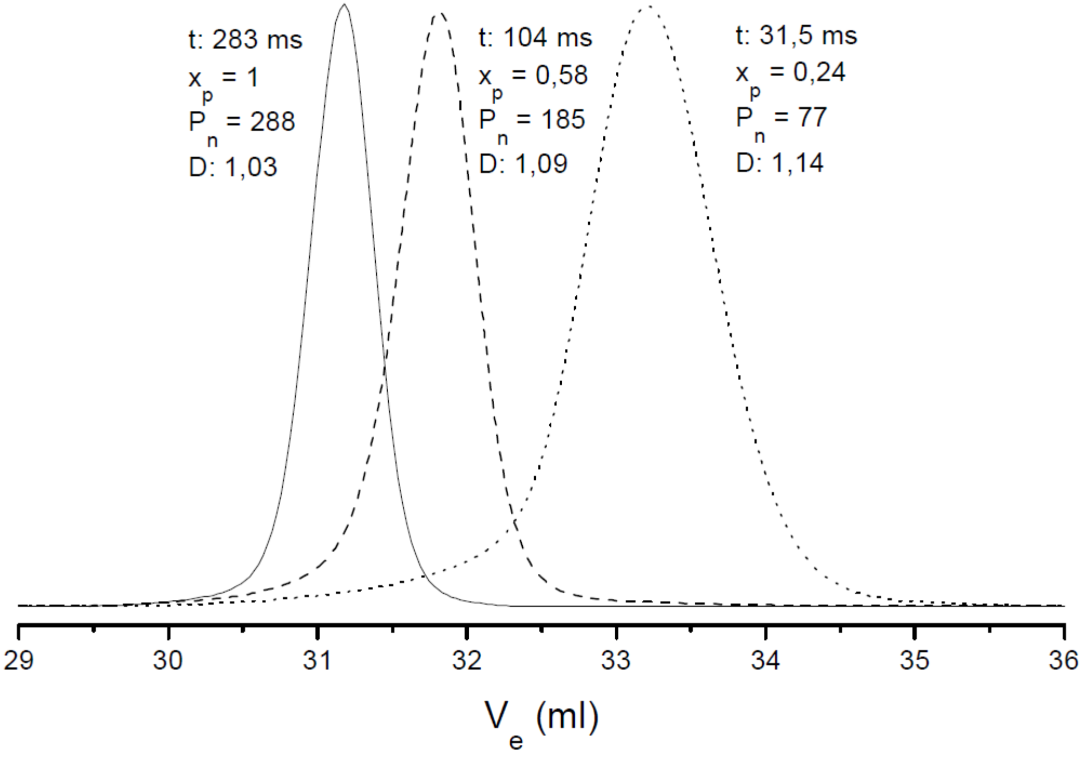


Fig.2: SEC of obtained polymer. Experimental conditions: T = -20 °C; $[I]_0 = 10^{-3}$ mol/l ; $[M]_0$ = 0,2 mol/l, $[LiOEM]/[I]_0$ = 5 in a 95/5 toluene/THF solution.

C. Use of Li-methoxyethoxides for the anionic polymerization of Acrylates/Methacrylates:

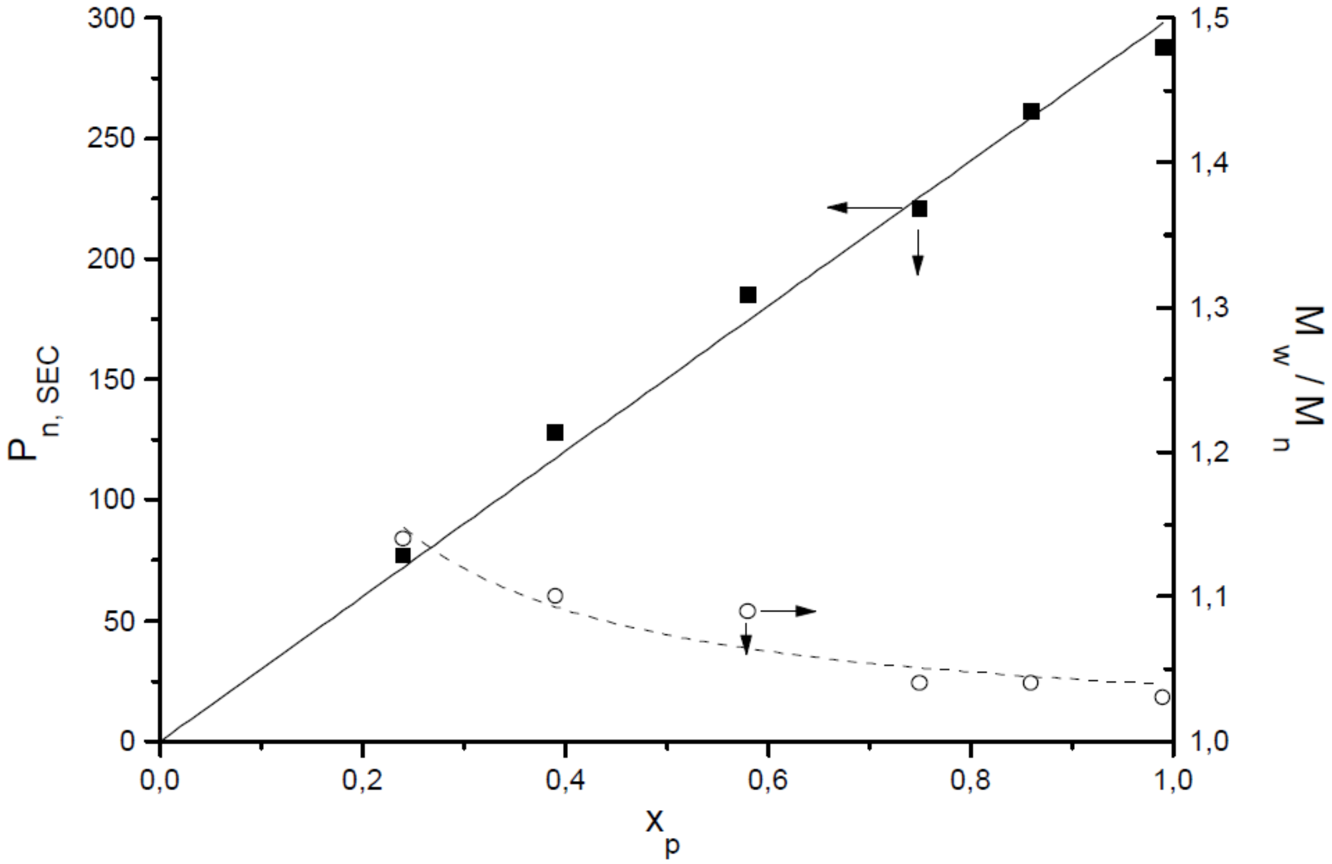


Fig.3: Degree of polymerization versus conversion for the anionic polymerization of MMA initiated by DPH-Li in the presence of $[LiOEM]/[I]_0 = 5$ in toluene/THF 95/5 mixture at -20 °C

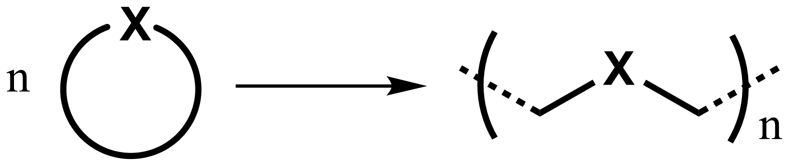
GENERAL REMARKS ON AGGREGATION OF ANIONIC CHAIN ENDS

In polymer chemistry the concentration of lithiated chain ends is much lower than in common organic reactions. This favours the formation of lower aggregates and renders their structure elucidation practically impossible. For high molar mass-chains it is unlikely that the active ends aggregate at all (due to concentration an shear effects).

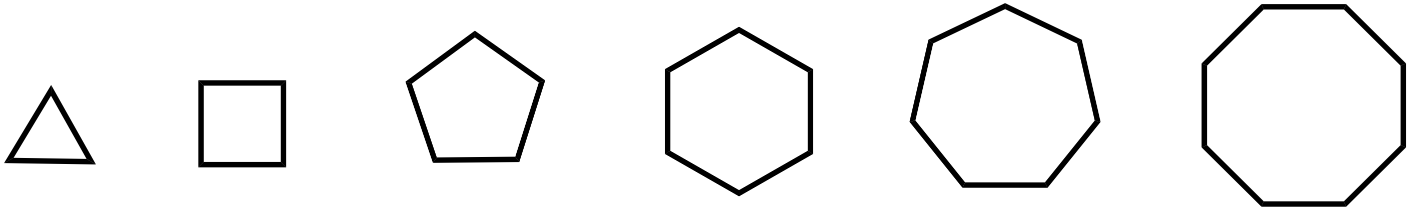
Addition of components like complexing agents (*e.g.* TMEDA) and salts (alkali halides and alkoxides) leads to their incorporation into the aggregates. This results in changing the equilibria and in altering the chain ends reactivity. Large aggregates can additionally shield the active chain end sterically and thus reduce the rate of *back-biting* and other side reactions.

In anionic polymerization the interaction between active chain ends and counter ion (aggregate) determines kinetics and side reactions (e.g. *back-biting*). Hence, counter ions can serve as a means to influence the outcome of the polymerization. This is not so in FRP, where no charge compensation is required and thus no handle is present. In other words: anionic polymerization is much more complex but also more adjustable and versatile.

Anionic “Living” Ring-Opening Polymerization (LROP)



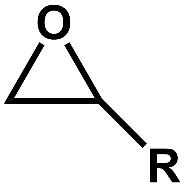
Thermodynamic stability of cyclic monomers is dependent on the strain in the ring structure:



strain energy *(kcal/mol)**	27.5	26.5	6.2	0.0	6.3	9.7

Thermodynamics alone does not guarantee polymerization, a site for nucleophilic attach by initiator is needed:

LROP of epoxides



R = H or CH_3

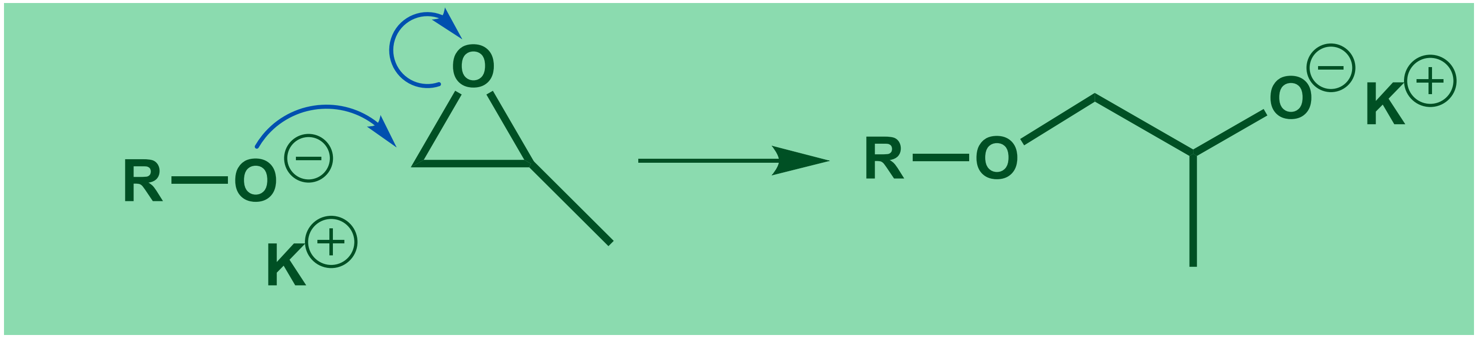
* K.B. Wilberg, Angew. Chem. 1986, 25, 312

Anionic “Living” Ring-Opening Polymerization (LROP)

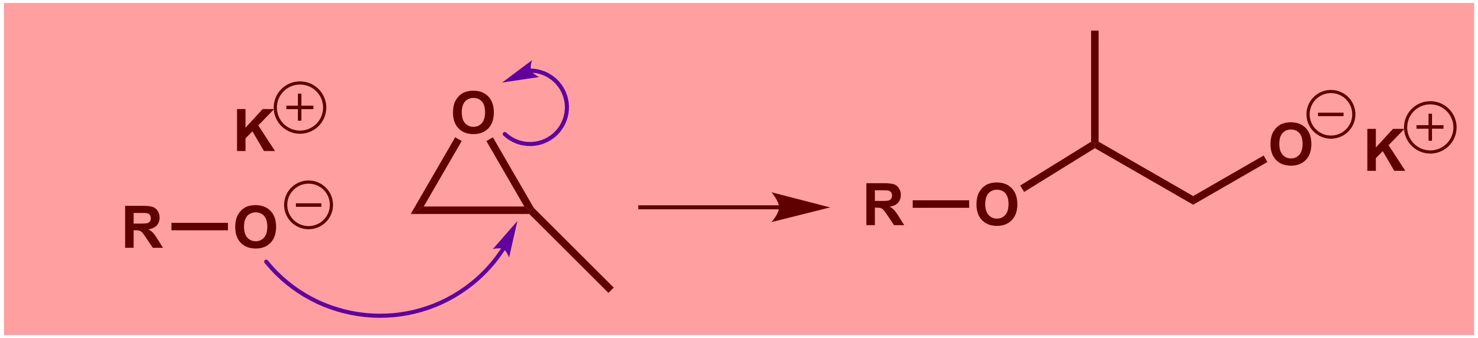
Proceeds in agreement with the S_N2 mechanism (*i.e.* nucleophilic bimolecular substitution at the carbon atom)

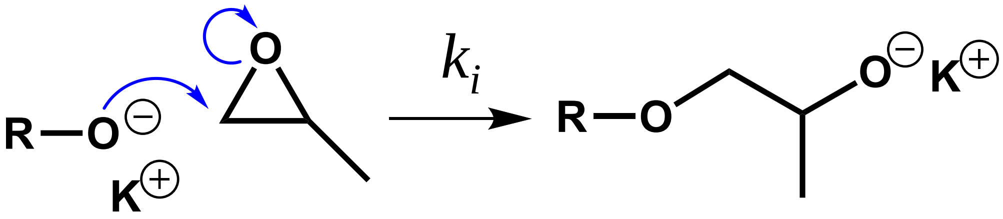
In the presence of KOH:

$$\mathrm{KOH + R\text{-}OH \longrightarrow R\text{-}O^{\ominus}\ K^{\oplus} + H_2O}$$

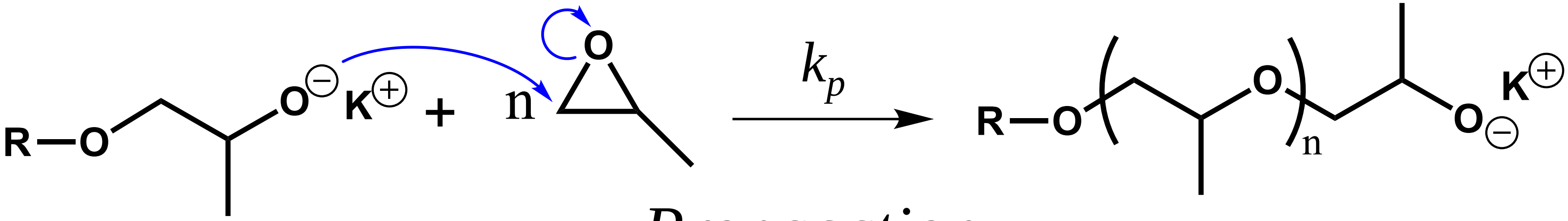


Initiation





Initiation

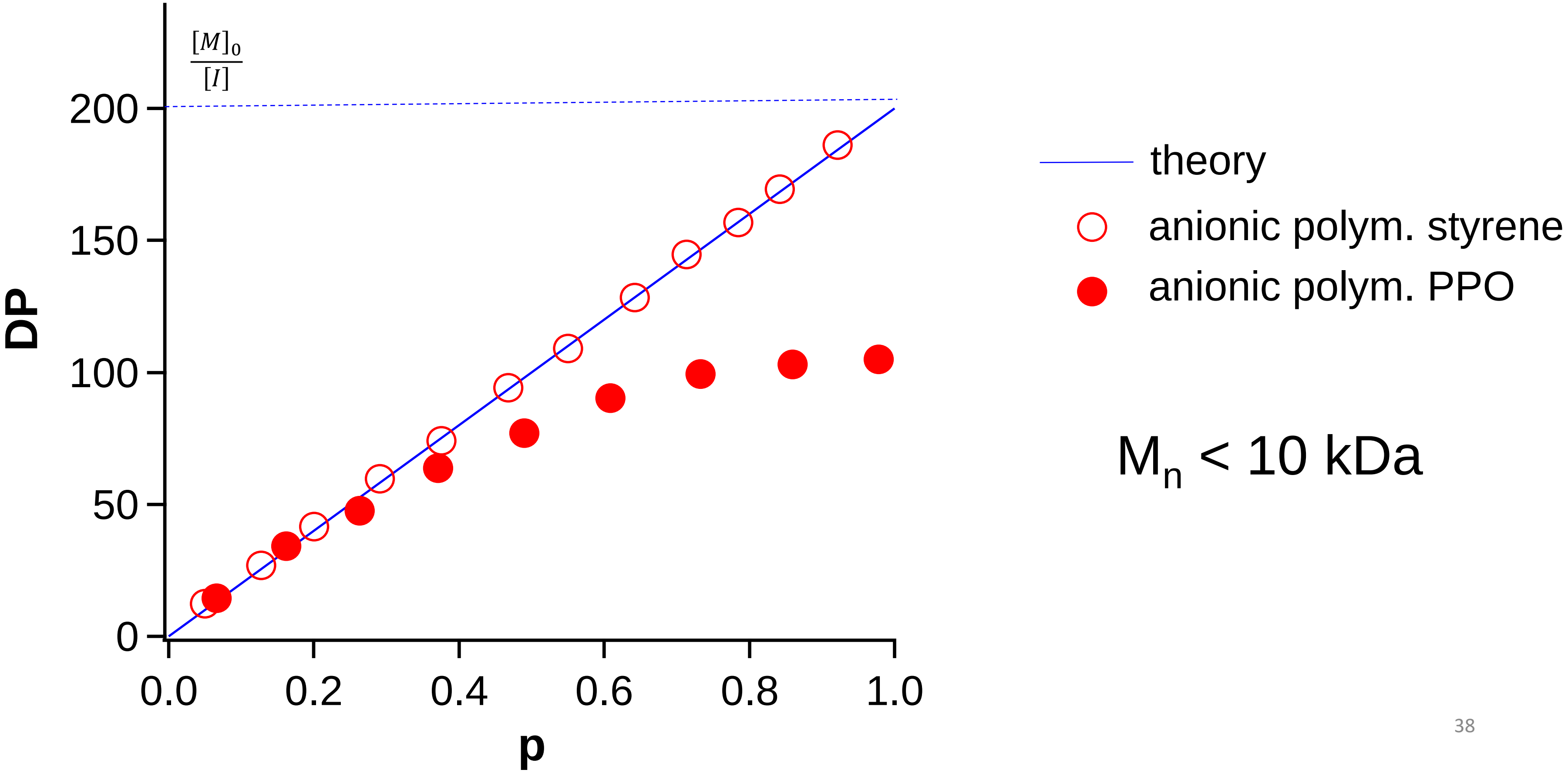


Propagation

(mainly head-to-tail structure)

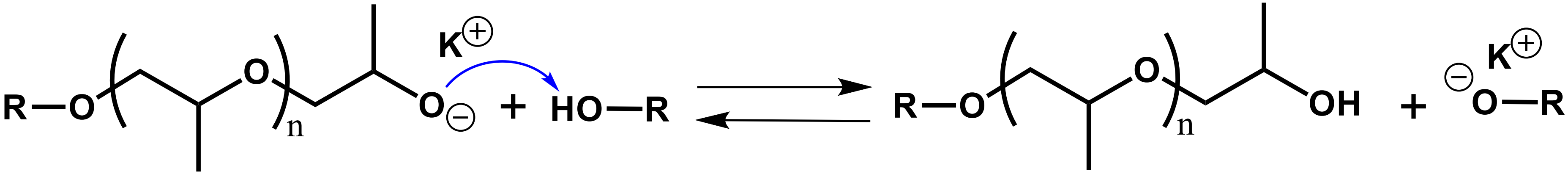
- In “living” polymerizations terminations and irreversible transfer reactions are absent. (IUPAC) *(polymer grows until all monomer is consumed)*
- “…living polymers should retain at least some ability to grow.” (Michael Szwarc)

$$\mathbf{DP} = \frac{[M]_0 - [M]}{[P^*]} = \frac{[M]_0 - [M]}{[I]} = \mathbf{p}\frac{[M]_0}{[I]}$$



M_n < 10 kDa

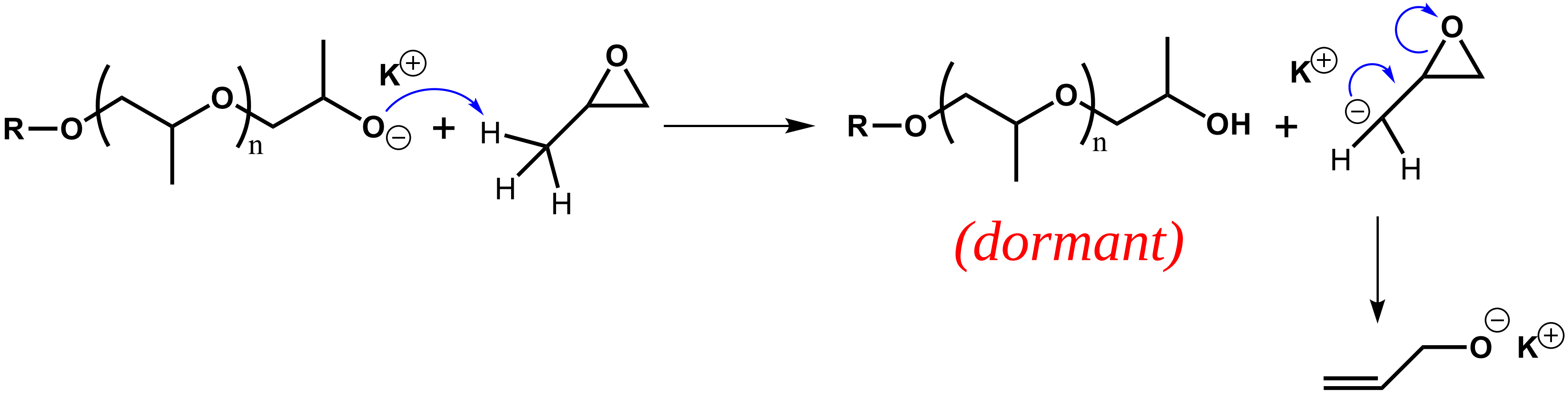
Exchange reaction



(dormant)

R can be another polymer (or you can have **H_2O** in the system)

Chain transfer to monomer

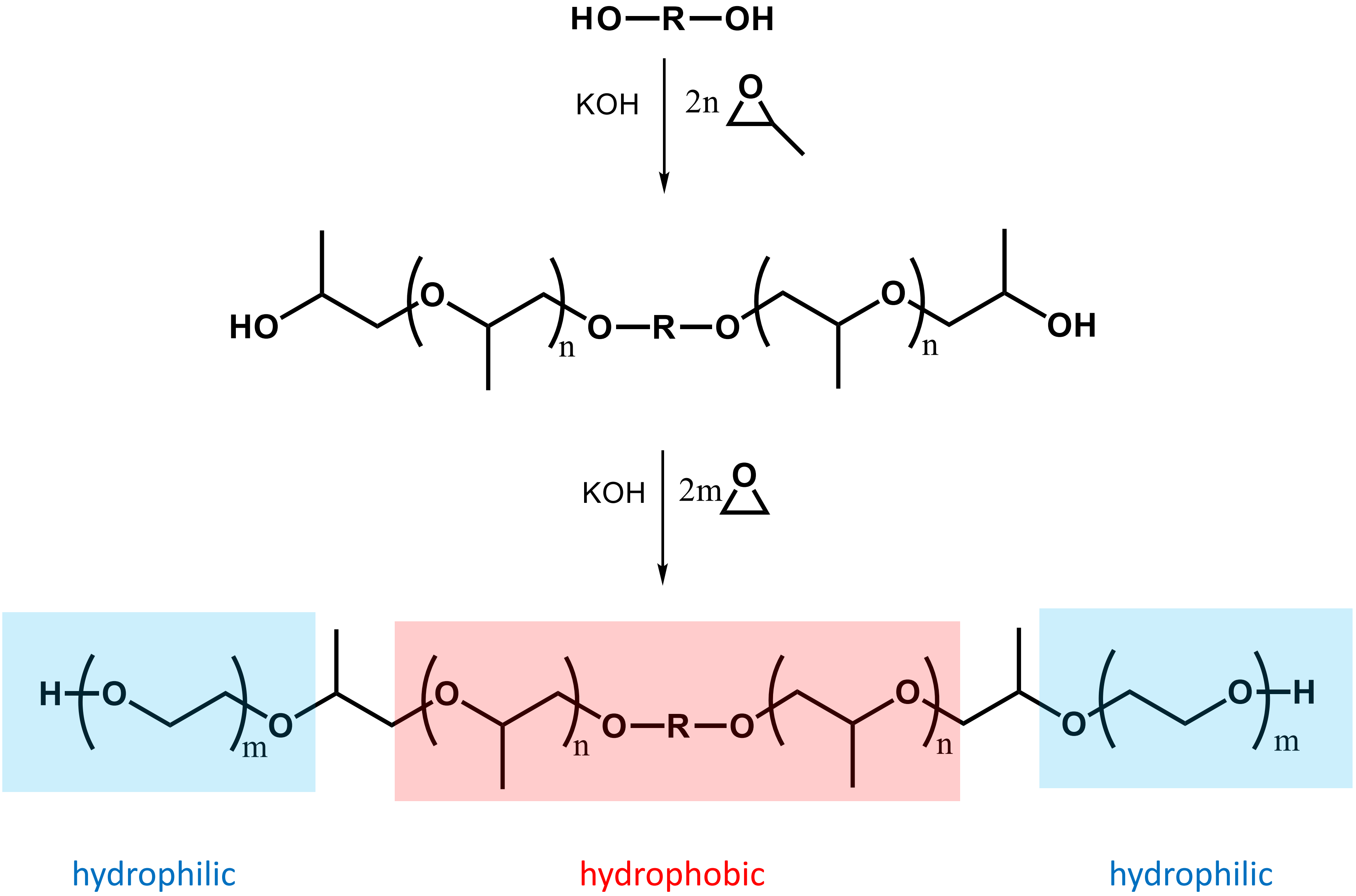


(dormant)

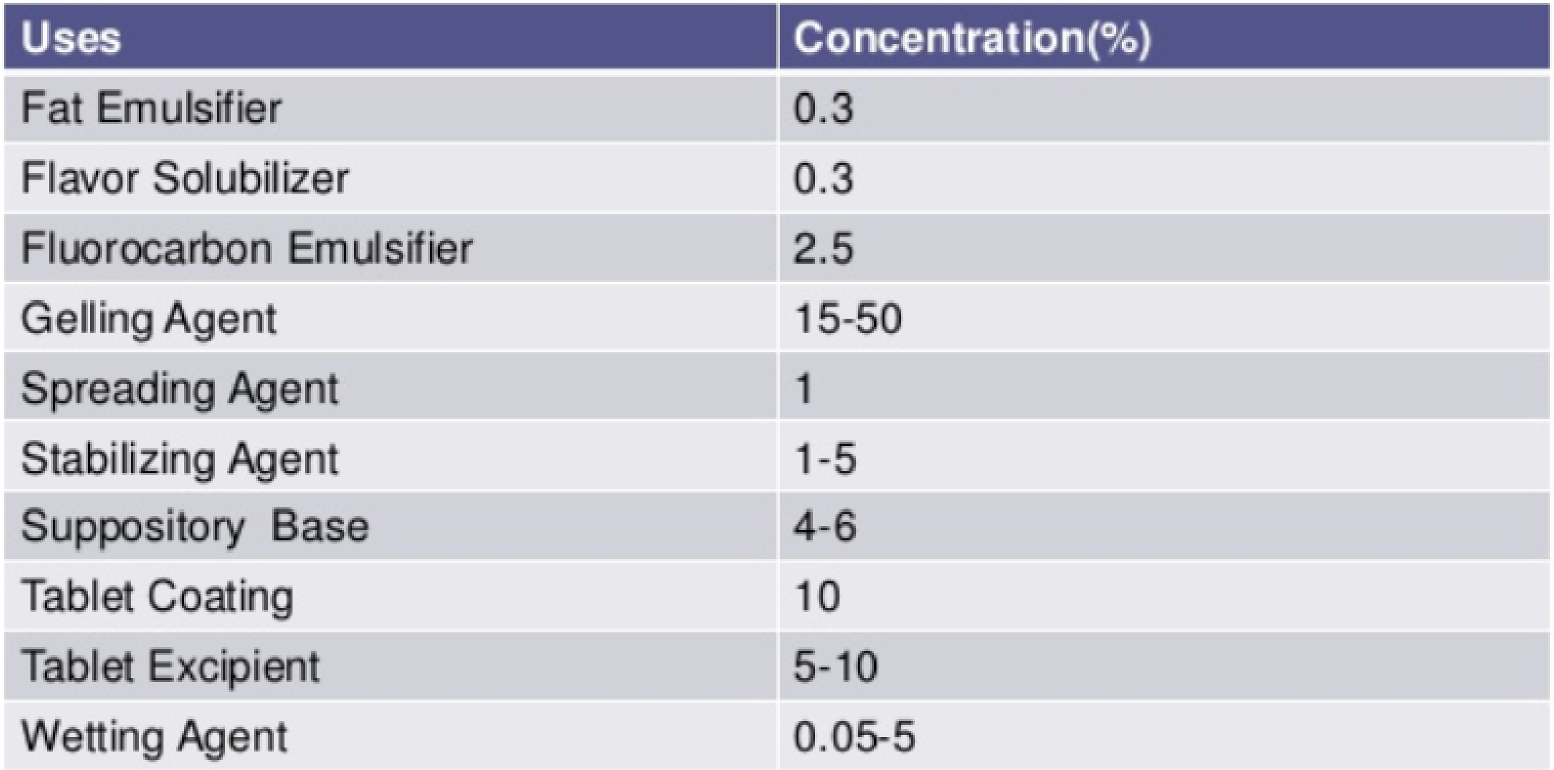
can initiate polymerization

Determination of unsaturated groups (NMR, IR…)

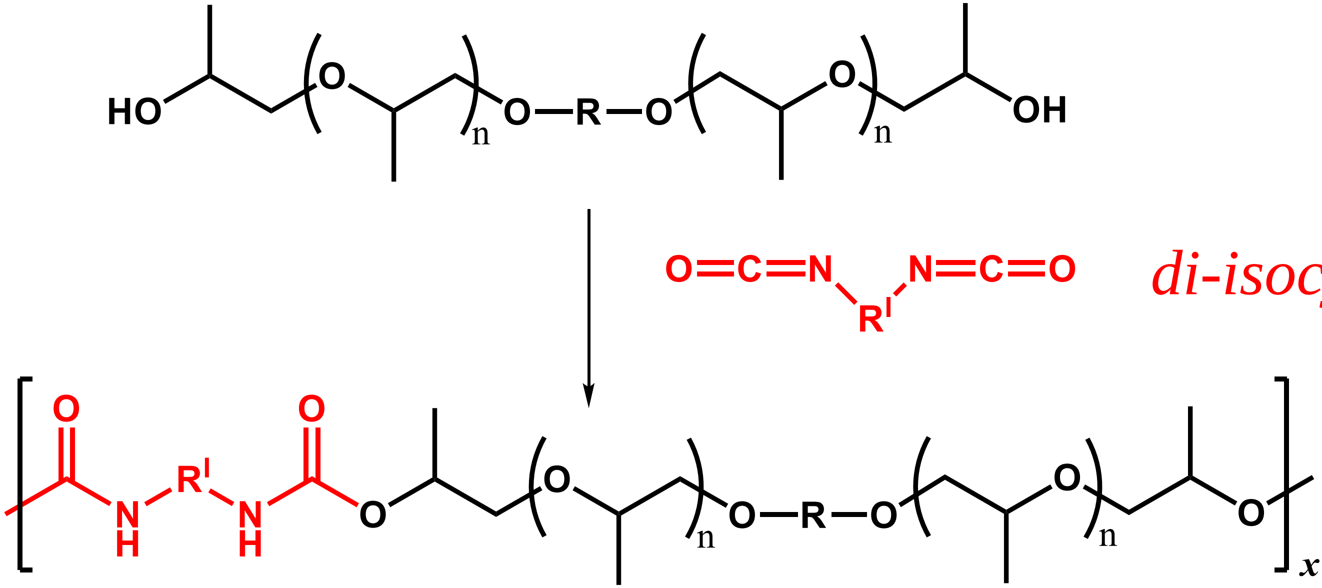
Block copolymers



poloxamer or pluronic



Uses	Concentration(%)
Fat Emulsifier	0.3
Flavor Solubilizer	0.3
Fluorocarbon Emulsifier	2.5
Gelling Agent	15-50
Spreading Agent	1
Stabilizing Agent	1-5
Suppository Base	4-6
Tablet Coating	10
Tablet Excipient	5-10
Wetting Agent	0.05-5



di-isocyanate

polyurethane