UNESCO/IUPAC Postgraduate Course in Polymer Science

Lecture:

Controlled polymerization of vinyl monomers; anionic and free-radical methods

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TAILOR-MADE POLYMERS; EXAMPLES

A. HOMOPOLYMERS

with predetermined microstructure
(*polydienes, polyolefines*)

polymers with narrow MWD
(*calibration standards for SEC*)

functionalized polymers

(*reactive polymers, macromonomers, cross-linkers*)

- monofunctionalized (monochelic) **A-A-A-A-A-A-A-A-A-A-A -X**

- telechelic **X-A-A-A-A-A-A-A-A-A-A-A-X**

- polyfunctionalized

```
A-A-A-A-A-A-A-A-A-A-A
    |        |        |
    X        X        X
```

B. COPOLYMERS

(thermoplastic elastomers, blend compatibilizers, amphiphilic and ampholytic copolymers,etc

Random (statistic)

A-A-A-A-B-A-A-A-B-A-A-B-A

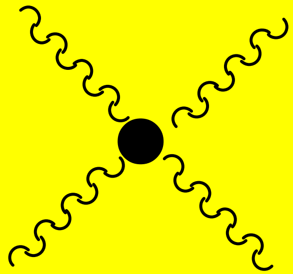
Block copolymers

A-A-A-A-A-A-B-B-B-B-B-B-B

Graft copolymers

```
A-A-A-A-A-A-A-A-A-A-A
    |         |
    B         B
    |         |
    B         B
    |         |
    B         B
    |         |
    B         B
```

Star polymers and copolymers



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WAYS TO TAILOR-MADE POLYMERS

1. Ionic controlled processes, "living" polymerization

A. Anionic

Initiators: organometallic nucleophiles (BuLi, ester enolates, *tert*-alkoxides), tetraalkylammonium salts, metaloporphyrines, lanthanocenes

Monomers: vinylic or heterocyclic (styrene, dienes, methacrylates, lactones, lactams)

B. Cationic

Initiators: Alkylhalides, water, in a combination with Lewis acids (H_2O + BF_3; RCl + $AlCl_3$)

Monomers: vinylic or heterocyclic (styrene, isobutene, vinyl ethers, dienes, THF)

C. Ziegler-Natta complex polymerization

Initiators: complexes of transition metal salts (Ti, V, W, Co) with aluminum alkyls or alkyl halides

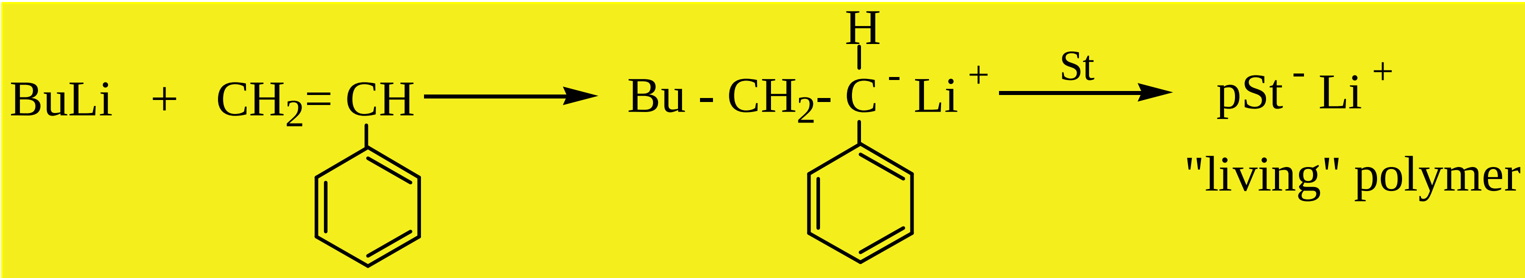
Monomers: vinylic (α-olefins, dienes, styrene, methacrylate)

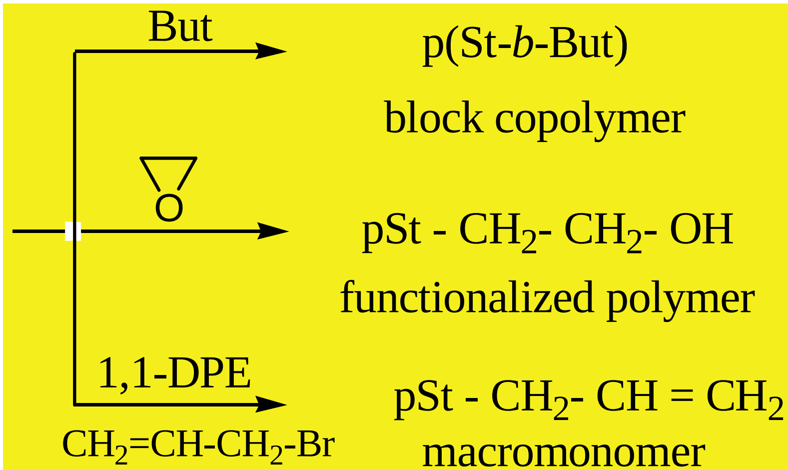
ANIONIC POLYMERIZATION

Non-polar vinyl monomers (styrene, dienes)

(very low extent of side reactions, long lifetime of active chains)

Scheme





Quirk: Anionic Polymerization.
M. Dekker, NY, 1996

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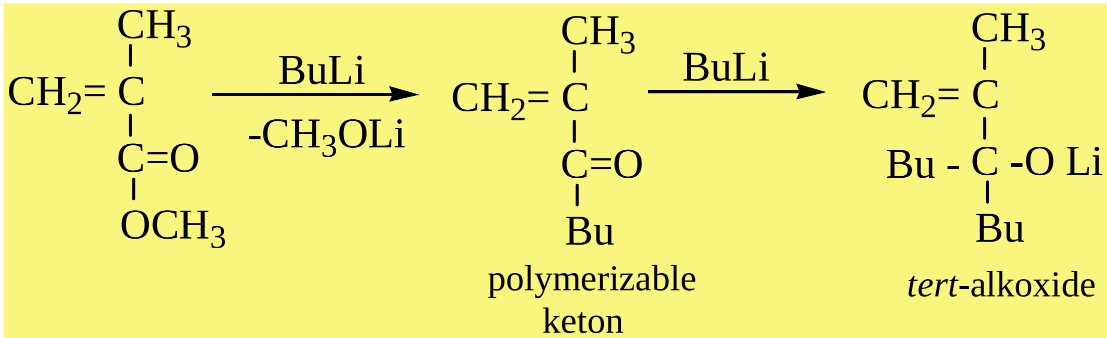
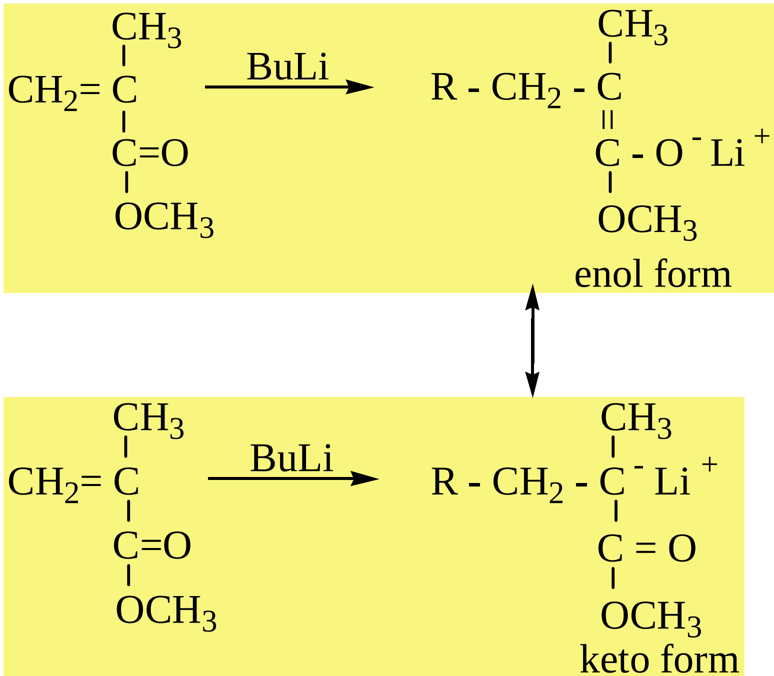
Reactions of R-Li+ initiator with methacrylate monomer

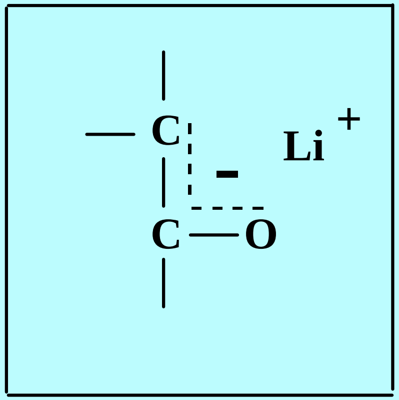
1,2-addition
(decomposition of initiator)



1,4-addition

3,4-addition





enolate-type active center

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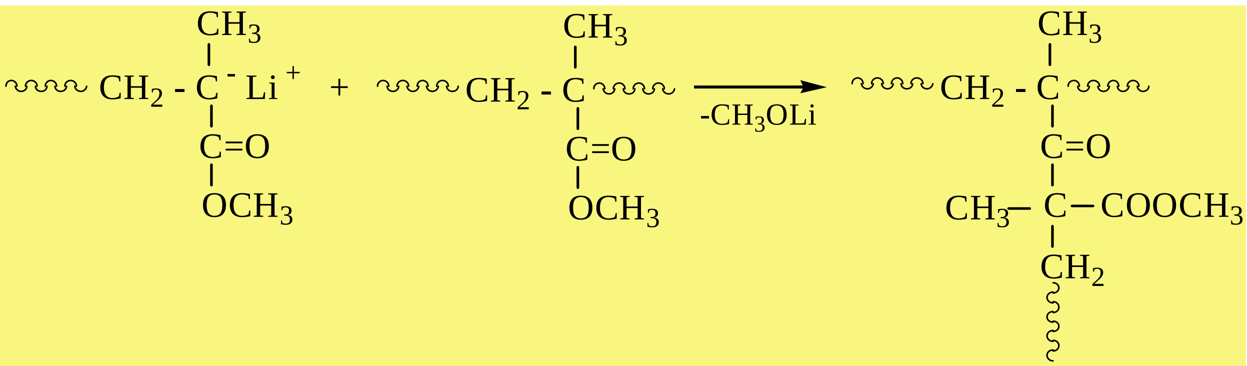
Side reactions of “living” PMMA chain

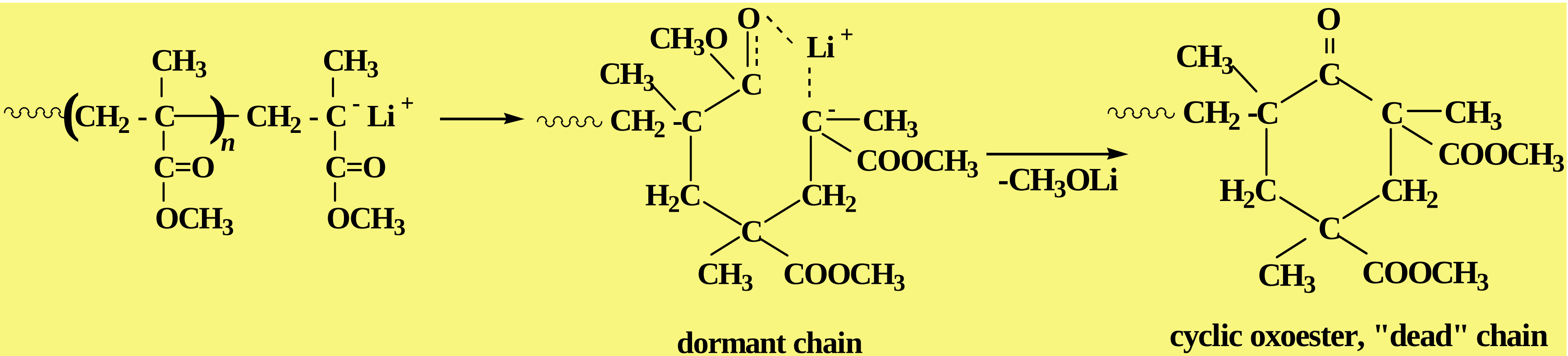
Branching



Self-termination by “back-biting” raction

Baskaran: Prog. Polym. Sci. 28, 521 (2003)

Vlcek: Prog. Polym. Sci. 24, 793 (1999)



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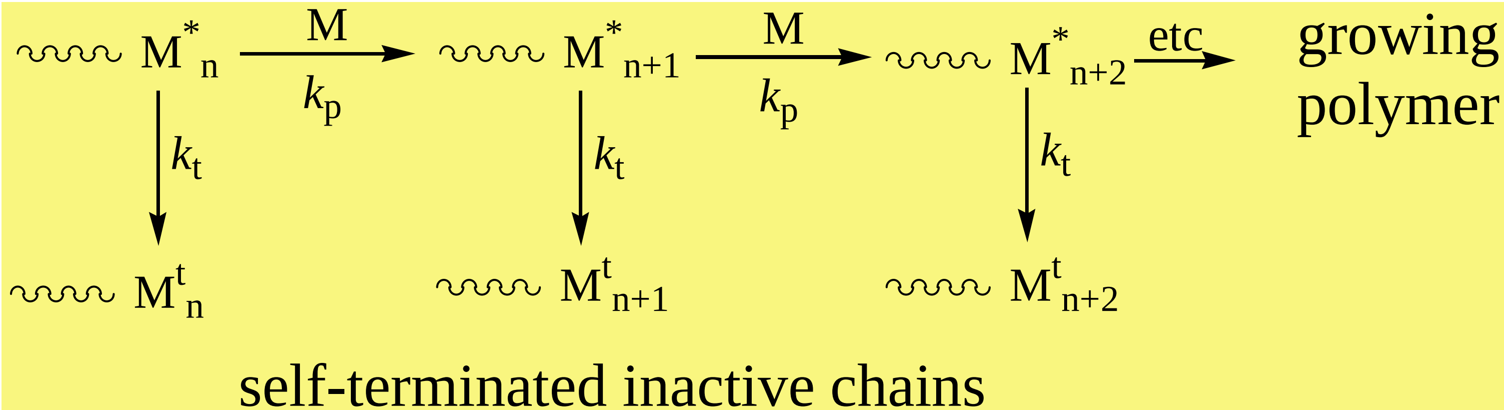
The reactions competing in MMA polymerization

Chain propagation *versus* self-termination



For "livingness" of polymerization, a ratio of rates of propagation and self-termination is important given by a ratio of the corresponding rate constants

$$k_p / k_t$$

Acrylic monomers exhibit distinctly higher tendency to all the mentioned side reactions than methacrylates

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METHODS OF ANIONIC CONTROLLED POLYMERIZATION OF POLAR VINYL MONOMERS

- **Group transfer polymerization** (GTP) initiated with silylketene acetal
  (*Webster, Hertler, Sogah, Bandermann*)
- **Metal-free anionic polymerization** (MFP) initiated with tetraalkyl ammonium salts
  (*Reetz, Sivaram, Bandermann*)
- **Polymerization initiated with metalloporphyrine initiators**
  (*Inoue, Aida*)
- **Polymerization by rare earth metal complexes**, initiated with lanthanocenes
  (*Yasuda, Okamoto, Novak*)
- **Ligated anionic polymerization** (LAP) initiated with complex alkali metal initiators
  (*Lochmann, Vlcek, Teyssié, Müller, Ballard, Sivaram*)

GROUP TRANSFER POLYMERIZATION (GTP)

Initiator: 1-methoxy-1-trimethylsilyloxy-2-methylpropene (MTS)

Catalysts: nucleophilic (for methacrylate polymerization) $(C_2H_5)_4\ N^+\ CN^-$;
$(C_4H_9)_4\ N^+\ F^-$; $[(CH_3)_2N]_3\ S^+\ HF_2^-$;carboxylate;
(0.1% mol/initiator)
electrophilic (for acrylate polymerization), Lewis acids, zinc halides,
alkylaluminium halides, HgI (10% mol/initiator)

Polymerization temperature: mostly from -30 to 30^{o}C

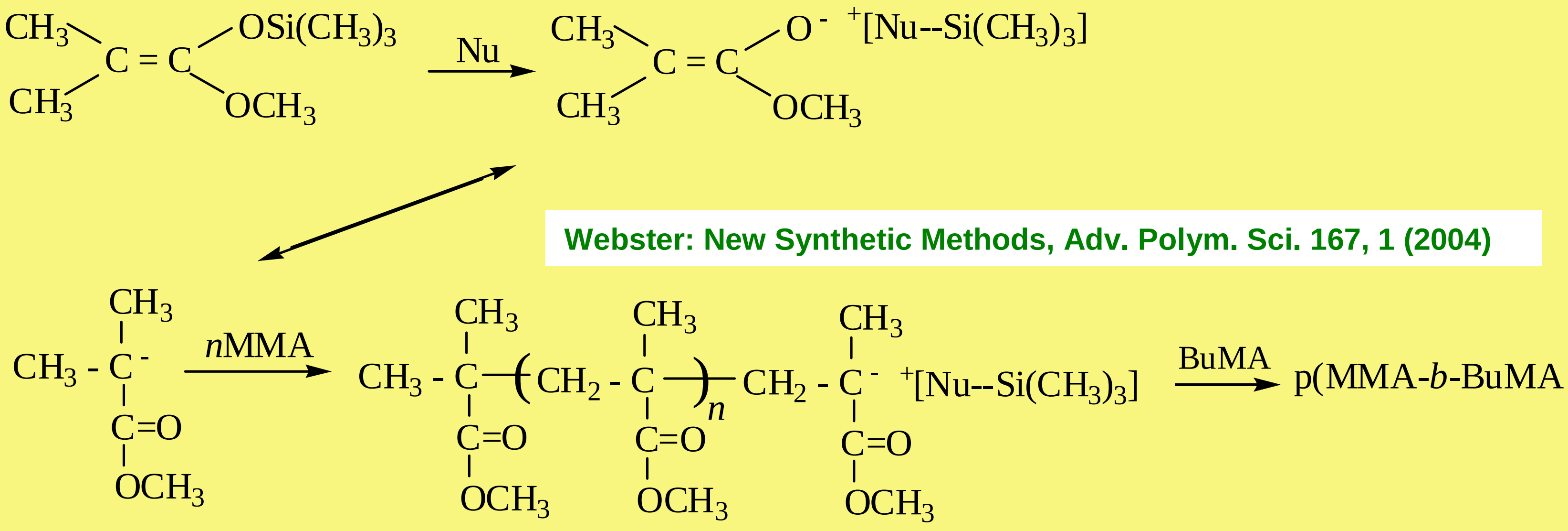
Solvents: THF, toluene, 1,2-dimethoxyethane, acetonitrile, DMF
(for nucleophilic catalysis)
dichloromethane, 1,2-dichloroethane (for electrophilic (catalysis)

Monomers: (meth)acrylic esters, N,N-dialkylmethacrylamides,
methacrylonitrile, epithiopropane

Block copolymerization: methacrylate – methacrylate
methacrylate – methacrylonitrile
epithiopropane – methacrylate
methacrylate – acrylate (different catalysts!!!!)

GTP – general scheme

- **Catalyst cleaves Si-O bond in an initiator forming enol-form of active center**
- **It is believed that the catalyst quickly migrates among initiator molecules or “living” growing chains**
- **Polymer chains remain active for a relatively long time and can thus initiate polymerization of another methacrylate, giving block copolymer**
- **GTP is accompanied with self-termination “back-biting” reaction as well as for typical anionic polymerization**



Webster: New Synthetic Methods, Adv. Polym. Sci. 167, 1 (2004)

METAL-FREE ANIONIC POLYMERIZATION (MFP)

Initiators - tetraalkylammonium salts (acrylate polymerization)

1. Alkyl or aryl thiolates, $BuS^{-}\ {}^{+}NBu_4$, room temperature

a) unstable initiators → thioethers

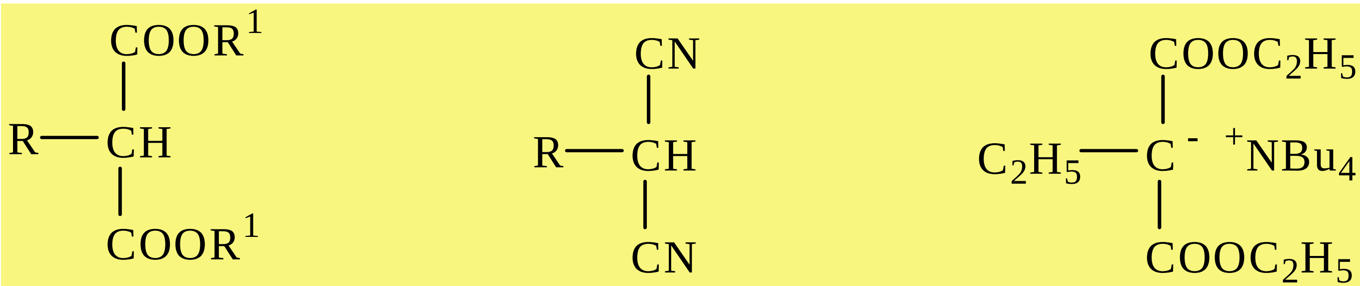
b) low-molecular-weight products (10^3), broad MWDs

2. Carbanionic salts (derivatives of alkylmalonic acid), room temperature

Bandermann: Macromol. Chem. Phys. 196, 2335 (1995)

a) more stable initiators

b) higher molecular weights (10^4)



diester

dinitrile

diethylester of ethylmalonic acid

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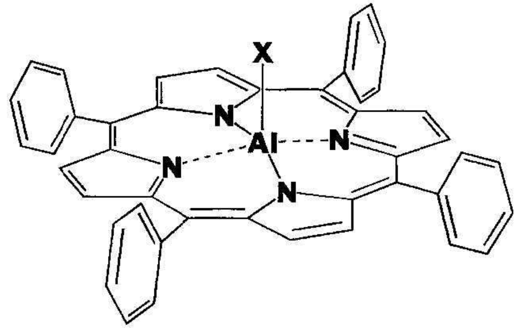
POLYMERIZATION BY METALOPORPHYRINS

Initiators: Metaloporhyrin derivatives
M = Al, Zn, Mn
X = Cl, alkyl, alkoxide, carboxylate, thiolate



Monomers: 1. heterocyclic; epoxides, lactones, lactides (M = Al, Zn, Mn; X = halide, alkoxide
2. vinylic; (meth)acrylates, methacrylonitrile (M = Al; X = alkyl, enolate, thiolate)

Conditions: CH_2Cl_2, toluene, bulk at 0-35°C; activation with visible light!!!!

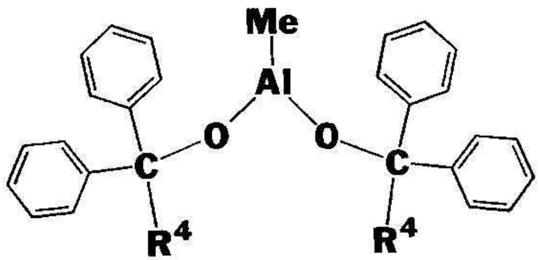
MMA polymerization by (TPP)Al-Me[a]

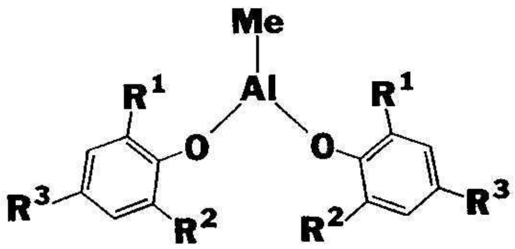
Temp. °C	Conv. %	$10^{-3}.\ M_n$ (calc)	$10^{-3}.\ M_n$ (SEC)	M_w/M_n
30	100	20.0	19.9	1.19
15	100	10.0	9.1	1.10

[a] room temp., visible light, > 12 hours

Aida: Prog. Polym. Sci. 19, 496 (1994)

Acceleration of the process by organoaluminium compounds





2a: R^4 = Ph
2b: R^4 = H

1b: R^1 = R^3 = *t*-Bu; R^2 = H
1c: R^1 = R^2= *t*-Bu; R^3 = Me
1d: R^1 = R^2= *t*-Bu; R^3 = H
1e: R^1 = R^2 = H; R^3 = *t*-Bu
1f: R^1 = R^2 = H; R^3 = OMe
1g: R^1 = *t*-Bu; R^2 = H; R^3 = OMe

MMA polymerization in CH_2Cl_2 at 35°C

Without additive, conversion 6% only after 2.5 h

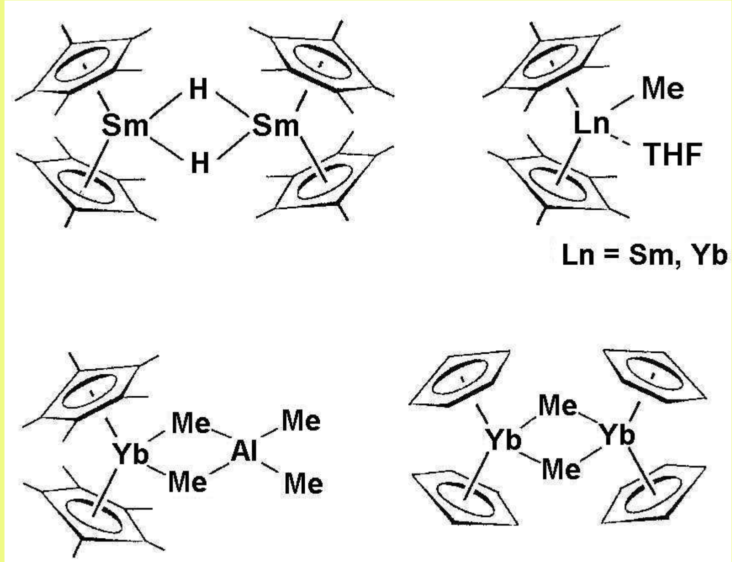
In the presence of **1a-d or 2a** complete conversion within minute!!

Addition of **1e-g or 2b** – no acceleration

Simple aluminium alkyls (Me_3Al) terminate polymerization at room temp.

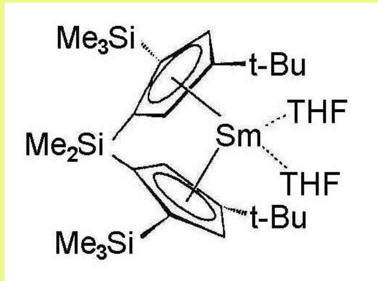
POLYMERIZATION INITIATED WITH LANTHANOCENES

Initiators: bis(pentamethylcyclopentadienyl) compounds of lanthanides



oxidation state III, $LaR(C_5Me_5)_2$

oxidation state II, $La(C_5Me_5)_2$



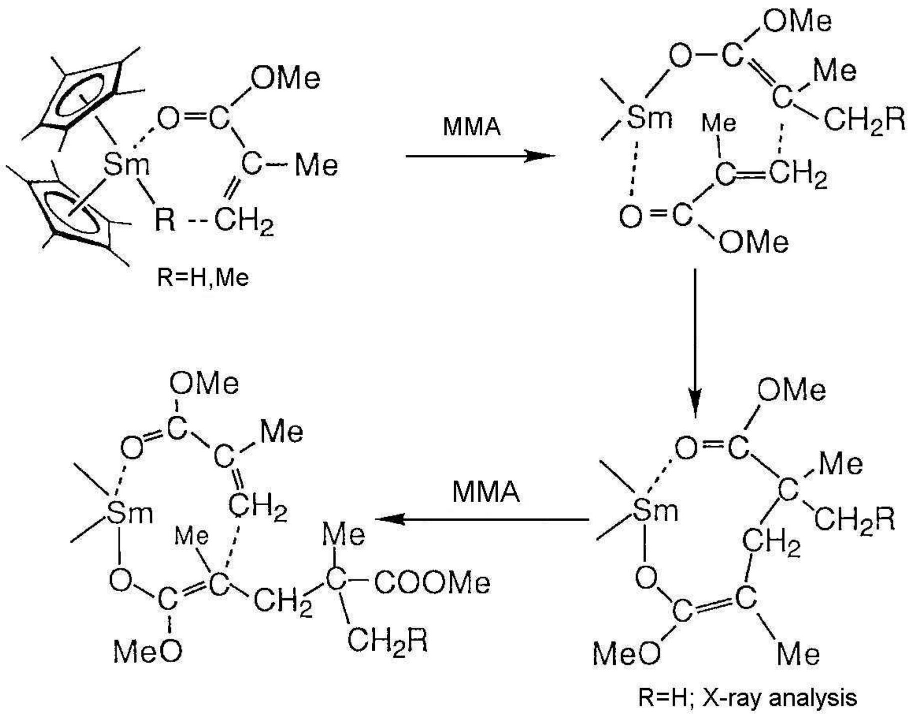
Yasuda: Macromolecules 28, 7886 (1995)

Monomers: 1. vinylic; (meth)acrylates, ethylene
2. heterocyclic; caprolactone, valerolactone

Conditions: toluene, THF, temperature from -90 to 60^{o}C

Mechanism of the lanthanocene initiated polymerization

Enolate-controlled process proceeding via 8-membered ring enolate intermediate



Monomer reactivity ratios

monomers	r_1	r_2
MMA/MeA	0.015	19.9
MMA/EtA	0.008	15.9
MMA/BuA	0.024	21.3

Synthesis of ABA triblock copolymer

Ln-R $\xrightarrow{\text{MMA}}$ **Ln-(PMMA)- R** $\xrightarrow{\text{MMA + BuA}}$ **poly(MMA-*b*-BuA-*b*-MMA)**

living PMMA — ABA triblock

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LIGATED ANIONIC POLYMERIZATION

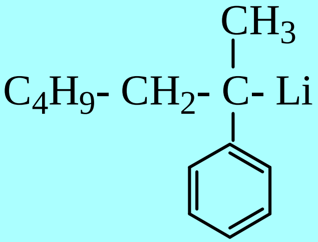
Principle: **Initiating complexes are composed of an intiator and additive (ligand) which tailor the environment of growing chain-end lowering thus its nucleophilicity and forming sterical hindrance**

Main types of the ligands

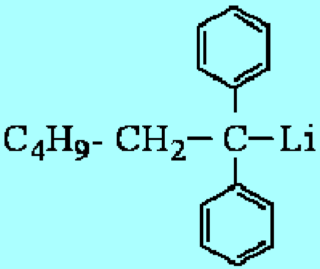
1. Alkali metal halides	Initiators: bulky organometallics, DPHLi Additives: almost exclusively LiCl Temp.: from -78 to 0^{o}C
2. Bidentate alkoxides	Initiators: bulky organometallics, DPHLi Additives: $CH_3O(CH_2$- $CH_2O)_2Li$, Temp.: $\leq$ -78^{o}C
3. Aluminum alkyls	Initiators: *t*-BuLi, ester-enolates Additives: triethyl, triisobutyl, biphenoxyalkylaluminums Temp.: from -78 to 20^{o}C
4. Alkali metal *tert*-alkoxides	Initiators: alkali metal ester-enolates Additives: mostly Li *tert*-butoxide Temp.: from -78 to 20^{o}C
5. Miscellaneous	(Li silanolates, Li perchlorate, TMEDA, etc)

Effect of LiCl on (meth)acrylate anionic polymerization

Initiators:
Bulky organolithiums



α-MeStLi



DPHLi

Effect of LiCl on polymerization of t-BuA initiated with αMeStLi

Solvent	LiCl/init m/m	Temp °C	M_w/M_n	Φ
THF	0	-78	3.61	-
THF	2	-78	1.30	0.80
THF	5	-78	1.20	0.77
75/25[a]	1.3	-78	1.20	0.72
75/25	1.2	-30	1.30	0.71
75/25	1.2	0	1.63	0.61

[a] toluene/THF (v/v)

Baskaran: Prog. Polym. Sci. 28, 521 (2003)

Effect of various Li salts on MMA polymerization in THF at -78°C

initiator	salt	Conv. %	SEC $10^{-3}.M_n$	SEC M_w/M_n	Φ
αMeStLi	-	99	41.0	1.20	0.67
-"-	**LiCl**	**99.5**	**32.5**	**1.09**	**0.85**
-"	LiF	99	46.5	1.17	9.58
-"-	LiBr	96	38.0	1.16	0.69
-"-	$LiBPh_4$	68	25.5	1.24	0.74
DPHLi	-	100	16.0	1.13	0.94
DPHLi	$LiBPh_4$	100	18.0	1.12	0.86
DPMPLi	**LiCl**	**93**	**22.0**	**1.09**	**0.93**

Bidentate lithium alkoxides

Ligands

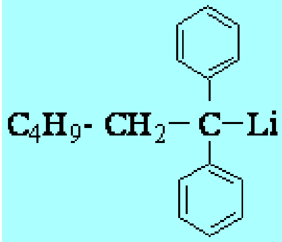
$CH_3O-(CH_2-CH_2O)_2-Li$
MEEOLi

$CH_3O-CH_2-CH_2O-Li$
MEOLi

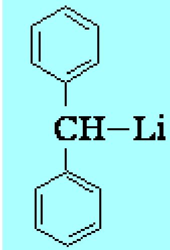
$(CH_3)_2N-(CH_2-CH_2O)_2-Li$
NEEOLi

$CH_3O-(CH_2-CH(CH_3)O)_2-Li$
MPPOLi

Initiators
(sterically hindered organolithiums)



DPHLi



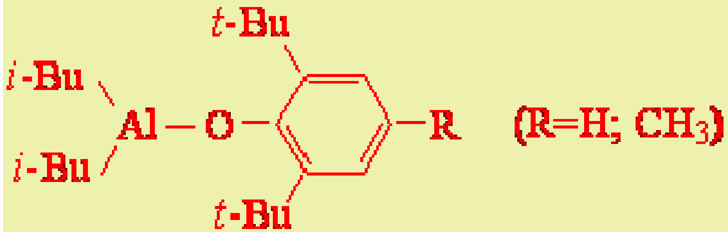
DPMLi

Alkyl	Ligand	Conv. %	M_n (theor) . 10^{-3}	SEC M_n .10^{-3}	SEC M_w/M_n
Bu	NEEOLi	46	8.6	23.0	1.65[b]
Bu	MPPOLi	25	4.3	13.0	2.00[b]
Bu	MEOLi	80	7.0	22.0	3.3
Bu	MEEOLi	100	24.7	34.0	1.30
Nonyl	MEEOLi	98	-	14.0	1.20
Et	MEEOLi	100	12.5	19.0	1.30
Me	MEEOLi	100	10.9	13.0	1.50

ALUMINIUM ALKYLS – MMA POLYMERIZATION

Initiators: *t*-BuLi; Li ester-enolates

Ligands: Et_3Al; (*i*-Bu)$_3$Al; toluene



Effect of Al/Li ratio on MMA polymerization

Al/Li m/m	Conv. %	M_n $.10^{-3}$	M_w/M_n
0.4	46	17.1	1.28
0.7	75	19.9	1.12
1.2	99	32.4	1.09
2.0	100	44.1	1.11
3.0	99	28.4	1.09

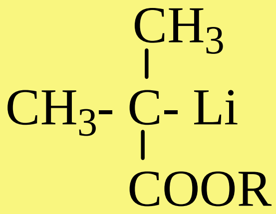
Lifetime of MMA growing chains – 4-doses experiment

Time min	∑ MMA mol/l	MMA/*t*-BuLi m/m	M_n $.10^{-3}$	Increment $M_n.10^{-3}$	M_w/M_n
65	1.06	75	11.7	11.7	1.09
130	2.12	150	23.2	11.5	1.10
195	3.18	225	33.9	10.7	1.1
260	4.24	300	44.1	10.2	11.1

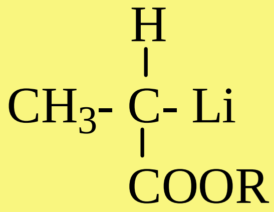
tert-Alkoxide-stabilized polymerization

Initiators:

Esters of 2-lithioisobutyric or 2-lithiopropionic acids, at -78 – 0^{o}C



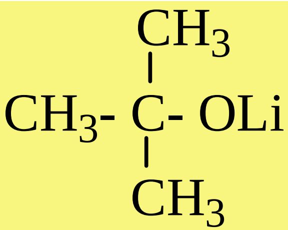
2-lithioisobutyrate



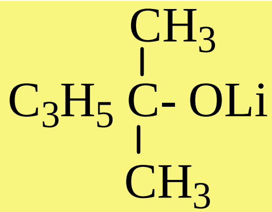
2-lithiopropionate

Additives:

Alkali metal *tert*-alkoxides, in THF, toluene/THF mixtures



Li *tert*-butoxide



Li *tert*-hexoxide

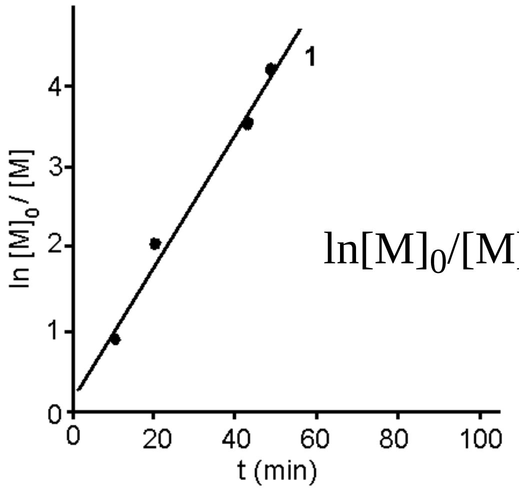
Vlcek: Prog. Polym. Sci. 24, 793 (1999)

Lifetime of PMMA living chains

Initiator: 1:10 MIB-Li/*t*-BuOLi system; THF; -60°C

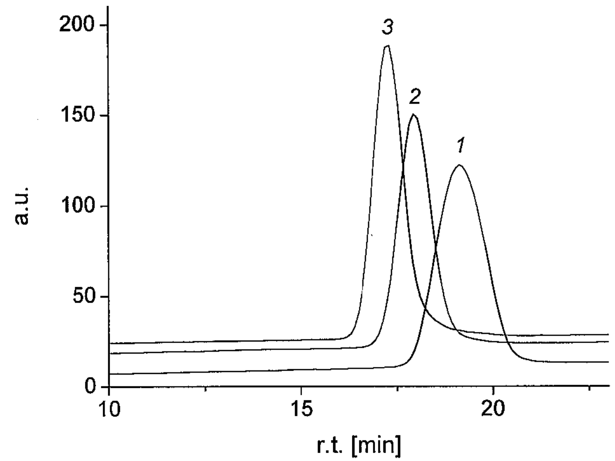
Dose	Δt^{b} min	t^{c} min	SEC $10^{-3} M_n$	M_w/M_n
1	0	60	7.8	1.20
2	60	150	19.0	1.11
3	150	250	30.1	1.12

[a] $[MMA]_0$ = 0.486 mol/l, mole ratio $[MMA]_0$:$[MIB\text{-}Li]_0$:$[t\text{-}BuOLi]_0$ = 50/1/10 in the first step, THF, T = -60 °C; [b] time period after the addition of the first dose; [c] total reaction time



$$\ln[M]_0/[M] = k_p [C^*]\, t$$

First order time-conversion plot, first dose



SEC eluograms, the numbers correspond to the doses

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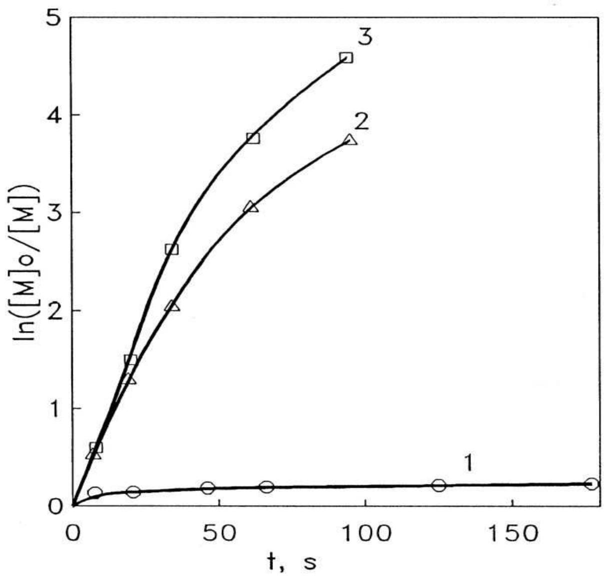
Polymerization of BuA initiated with tBIB-Li/*t*-BuOLi

Initiation: tBIB-Li in toluene/THF (9/1); -70°C

Run	*t*-BuOLi (exc)	Time (s)	Conv. (%)	10^{-3} M_n	M_w/M_n
1	0	8	12.7	2.9	7.8
		600	22.7	3.3	18.8
2	3	8	41.1	6.1	1.17
		600	99	14.0	1.31
3	10	8	45.1	5.8	1.15
		185	100	11.7	1.21

$$\ln[M]_0/[M] = k_p\,[C^*]\,t$$



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CONTROLLED RADICAL POLYMERIZATION
BASIC APPROACH

Simplified scheme of conventional FRP

Initiation:(diazocompounds, etc)

$$R-R \longrightarrow 2R^{\bullet} \xrightarrow[k_i]{2M} 2R-M^{\bullet}$$

Propagation:

$$R-M^{\bullet} \xrightarrow[k_p]{nM} R-M_n-M^{\bullet}$$

Spontaneous termination:(recombination, disproportiation)

$$2R-M_n-M^{\bullet} \xrightarrow[k_t]{} \text{non-active chains}$$

Rates of propagation and termination

$$R_p = k_p\,[R-M_n-M^{\bullet}] \times [M] \qquad R_t = k_t\,[R-M_n-M^{\bullet}]^2$$

Principle: Lowering the concentration of "living" macroradicals by reversible process perceptibly lowers the rate of termination

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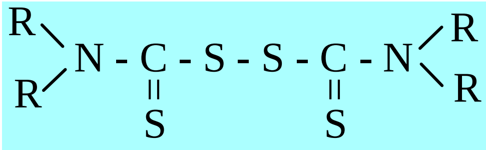
METHODS OF CONTROLLED RADICAL POLYMERIZATION

- **Iniferter Technique (*ini*tiation, trans*fer*, *ter*mination)**
- ***D*egenerative *T*ransfer (DT)**
- ***R*eversible *A*ddition-*F*ragmentation Chain *T*ransfer (RAFT)**
- **Stable Counter-Radicals (nitroxide-mediated, NMP or TEMPO)**
- ***A*tom-*T*ransfer *R*adical *P*olymerization (ATRP)**

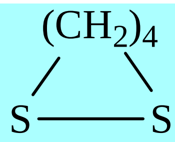
INIFERTERS

Initiators: Diazocompounds, peroxides

Iniferters: Radical end-capping particles forming dormant macroradicals with weak C-S bond

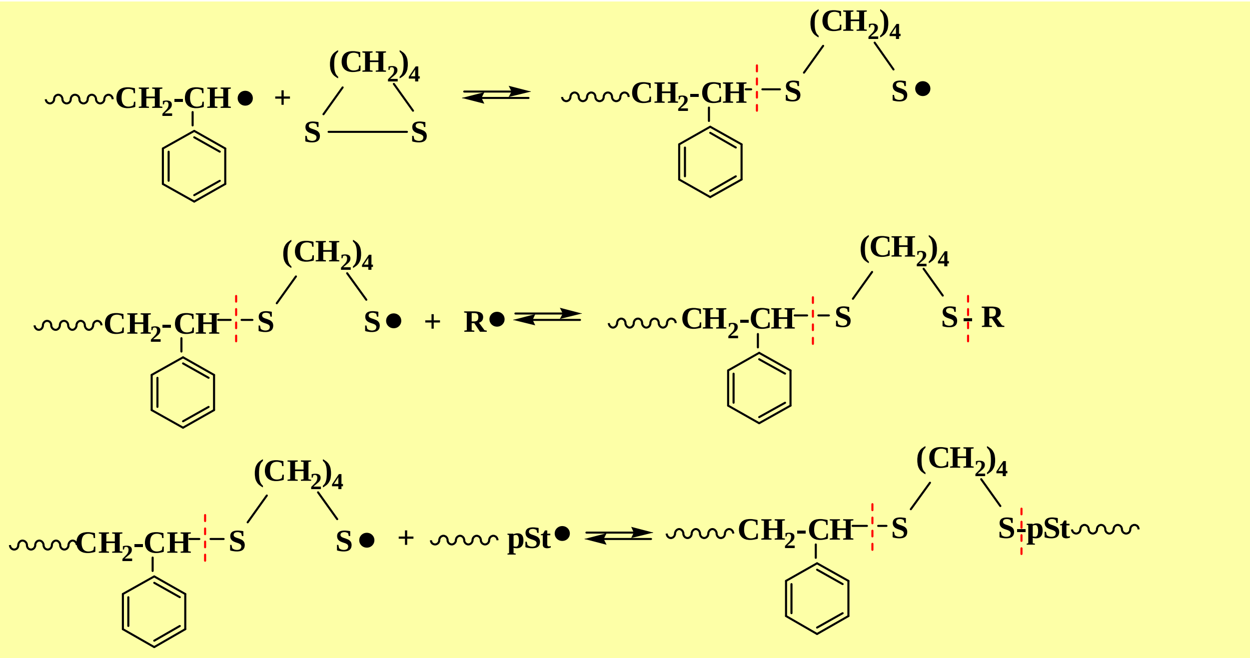


tetraalkylthiuram disulfide



tetramethylene disulfide

Probable mechanism



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DEGENERATIVE TRANSFER

Initiators: **diazocompounds, peroxides (AIBN, Bz_2O_2)**

Transfer agents: iodoform, alkyliodides (CH_3I, R-I)

Monomers: styrene, (meth)acrylates, acrylamide

Prevailingly applied to a tailoring of oligomers with predetermined DP

1) Transfer reaction to RX

$$A\bullet + M \xrightarrow{k_i} AM\bullet$$

$$AM\bullet + (i-1)\,M \xrightarrow{k_p} AM_i\bullet$$

$$AM_i\bullet + R\text{-}X \xrightarrow{k_{tr1}} AM_i - X + R\bullet$$

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

$$R - M\bullet + (i-1)\,M \xrightarrow{k_p} RM_i - X$$

$$RM_i\bullet + R\text{-}X \xrightarrow{k_{tr1}} RM_i - X + R\bullet$$

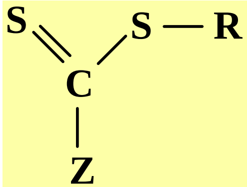
2) Transfer reaction to chain

$$RM_i - X + RM_j\bullet \underset{k_{tr2}}{\overset{k_{tr2}}{\rightleftharpoons}} RM_i\bullet + RM_j - X$$

RAFT – basic scheme

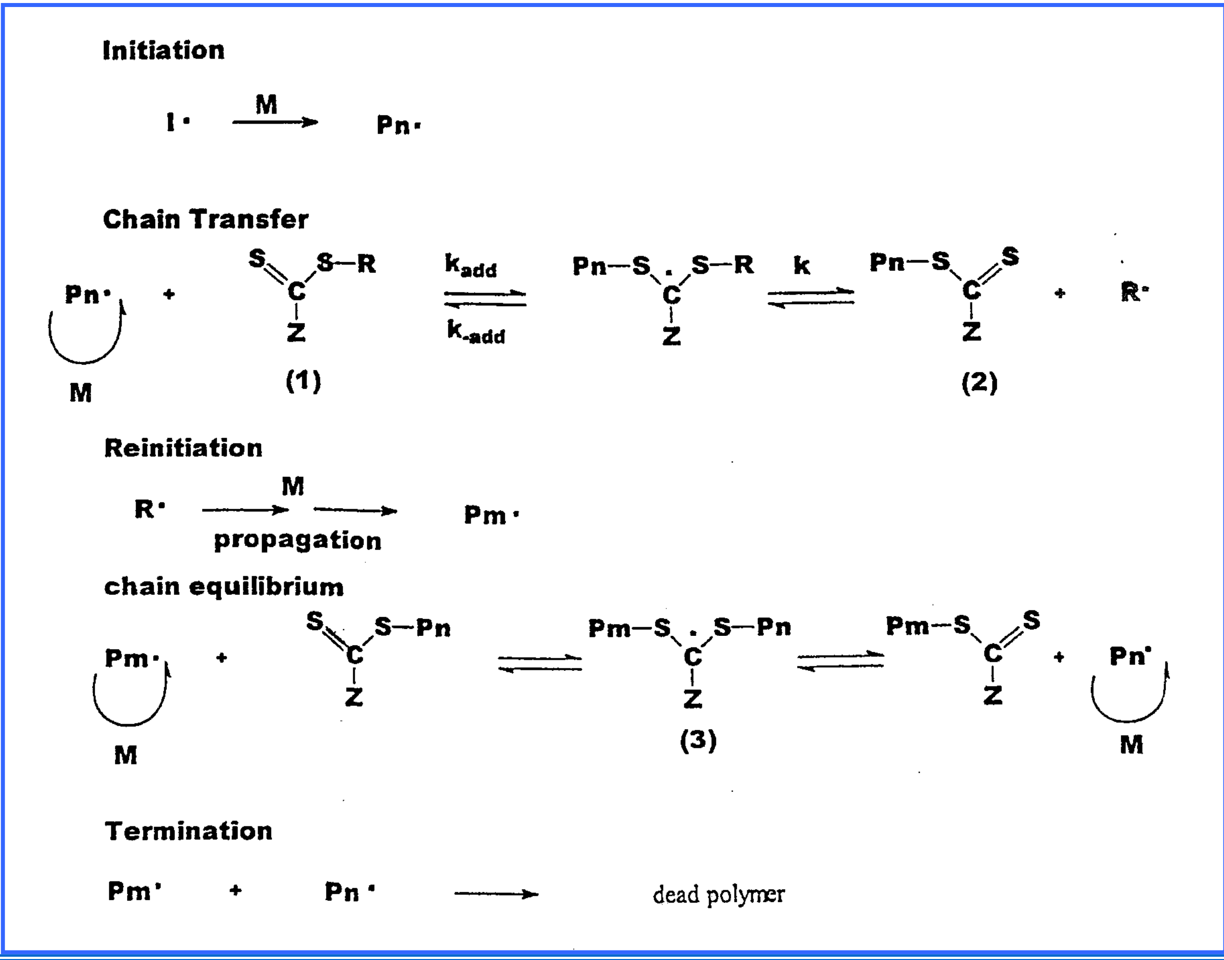
Initiators: diazocompounds, peroxides

RAFT agents: thiocarbonyl thiocompounds



R = $-C(CH_3)_2Ph$; $-CH_2Ph$

Z = alkyl



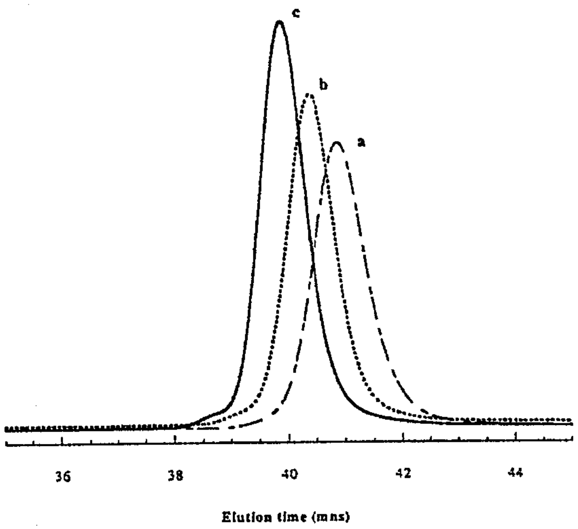
Lowe: Prog. Polym. Sci. 32, 283 (2007)

Effect of RAFT agent on polymerization

Raft agents: dithiocarbamates with various R and Z substituents

Monomer	Time (h)	Conv. (%)	M_n (theor)	M_n (exp)	M_w/M_n
EtA[a,c]	3	99		69000	2.83
EtA	4	87	7350	7750	1.2
St[b,c]	24	98		376000	2.26
St	24	94	8170	7730	1.22
MMA[a,c]	4	52		70800	2.28
MMA	7	98	8150	10740	1.74

[a] 50% in toluene, 80°C, AIBN; [b] in bulk, 110°C, thermal initiat.; [c] no RAFT agent



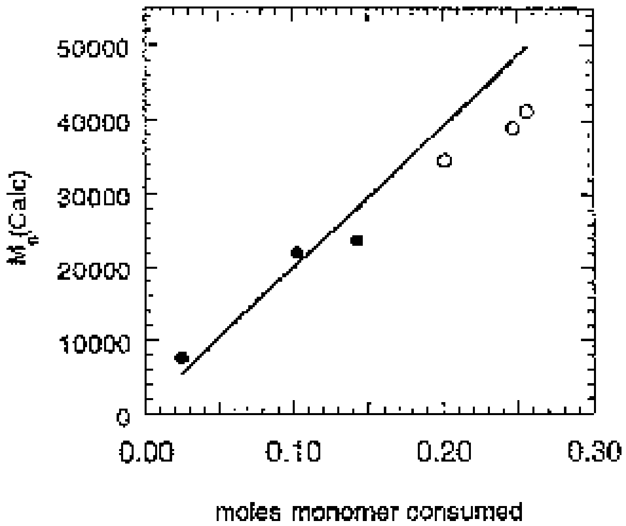
GPC traces of pSt prepared in the presence of dithiocarbamate

a) 36%; M_n= 14700; PDI=1.16
b) 63%; M_n= 26200; PDI=1.12
c) 86%; M_n= 33500; PDI=1.10

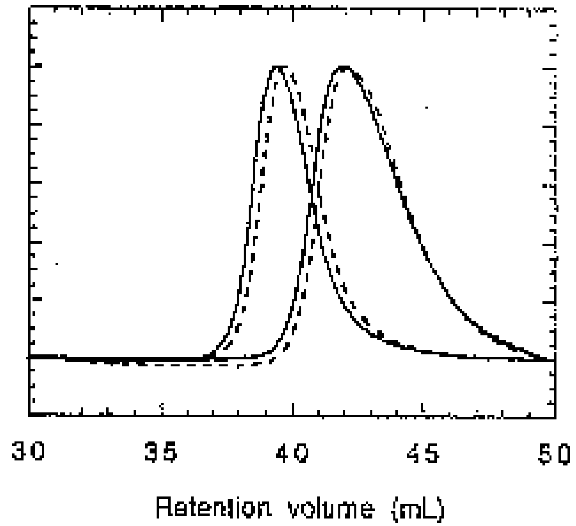
Synthesis of poly(St-*b*-MMA) by RAFT polymerization in emulsion

Initiator: 4,4'-azobis(4-cyanopentanoic acid)
RAFT agent: benzyl dithioacetate

Temp. °C	Time min	Monomer added (ml) St	MMA	Conv. %	M_n	M_w/M_n
80	30	6	0	43	7700	1.37
	75	15	0	99	23700	1.35
90	100	15	7.5	84	39000	1.56
	190	15	15	92	41300	1.57



M_n evolution vs. monomer consumption



SEC traces of p(St-*b*-MMA) and pSt;
dashed line – UV det, solid line – RI det

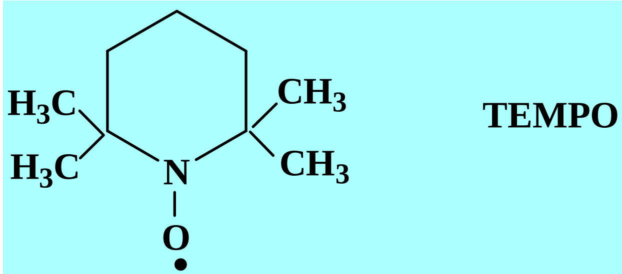
STABLE COUNTER-RADICALS

Initiators: Diazocompounds, peroxides

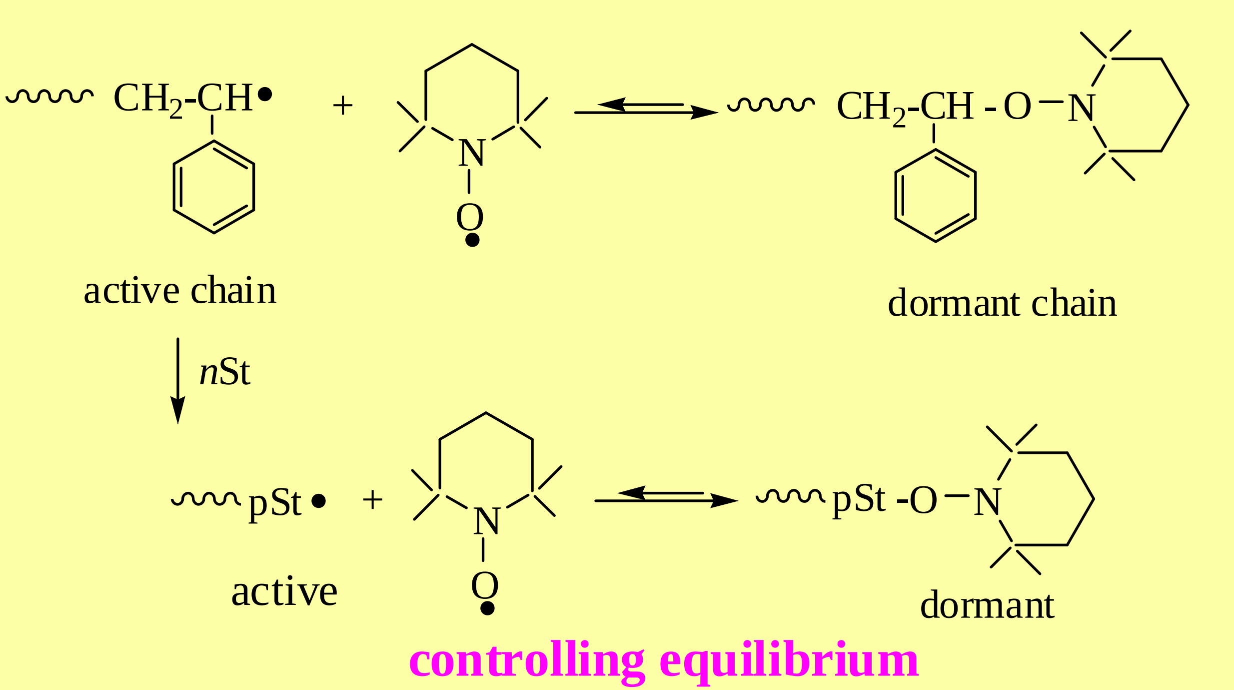
Nitroxide radicals;

2,2,6,6-tetramethyl-1-piperidinyloxy radical

Georges: Macromolecules 26, 5316 (1993)



Probable mechanism



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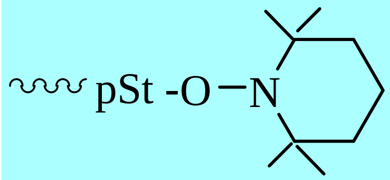
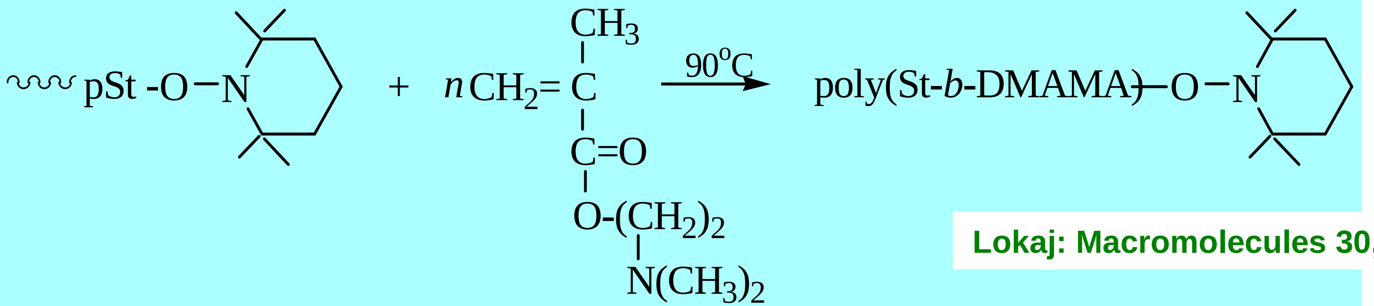
TEMPO-mediated synthesis of poly(styrene-*b*-2-dimethylaminoethyl methacrylate) copolymer

<u>1st step:</u> Synthesis of pSt macroinitiator by controlled radical polymerization in bulk in the presence of TEMPO



<u>2nd step:</u> Bulk polymerization of DMAMA by pSt-TEMPO macroinitiator => p(St-*b*-DMAMA) with TEMPO termini



Lokaj: Macromolecules 30, 7644 (1997)

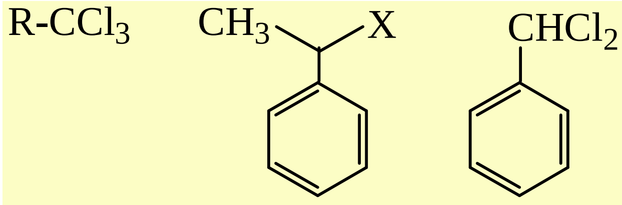
pSt M_n .10^{-3}	Time h	DMAMA %	M_n .10^{-3} SEC	M_n .10^{-3} NMR	M_w/M_n
53.4	2	40	67.1	107.1	1.25
(1.13)[a]	8	39	67.0	105.0	1.29
28.1	2	26	34.0	43.0	1.28
(1.10)[a]	8	29	36.3	45.4	1.30

[a] polydispersity indexes

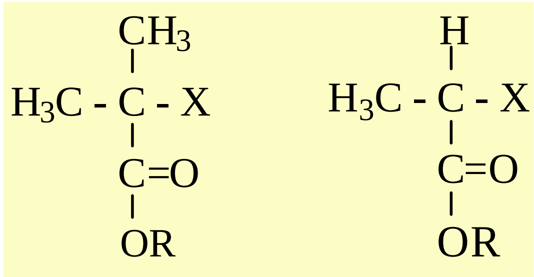
ATRP - three-component initiating system

1. Initiator – organic halides

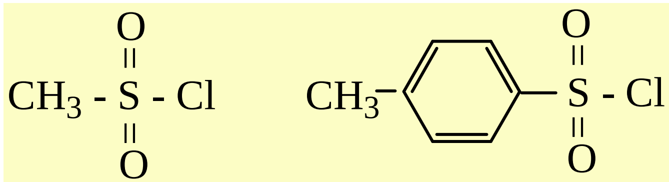
Alkyl halides



Esters of 2-haloacids



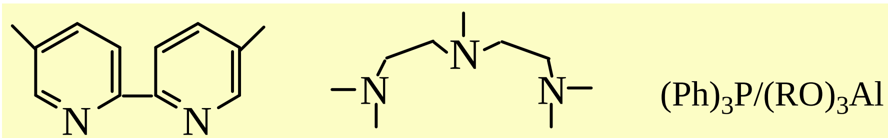
Sulfonyl halides



2. Catalyst – transition metal salts in the lower oxidation state

CuCl, CuBr, $FeCl_2$, $RuCl_2$

3. Complexing ligand – aminocompounds, phosphorus compounds



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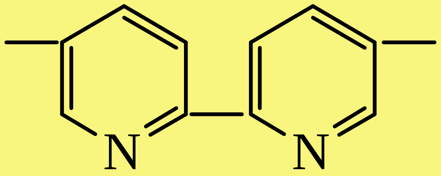
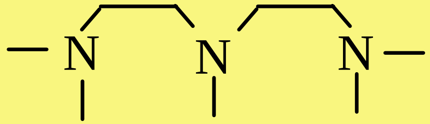
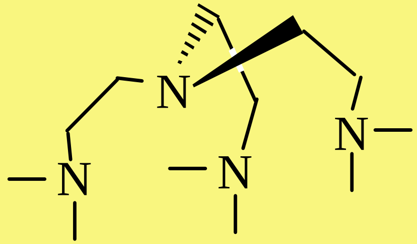
Amine-type ligands



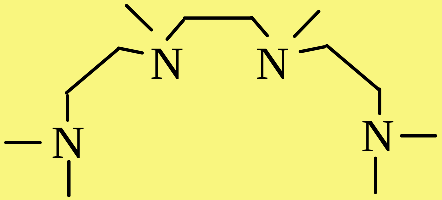
2,2'-bipyridyl (bPy)
5,5'-disubstituted



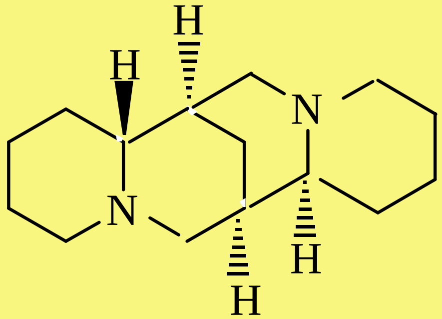
N,N,N',N'',N''-pentamethyl diethylene triamine (PMDETA)



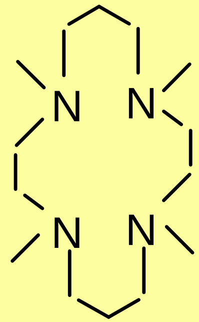
tris[2-(dimethylamino)ethyl] amine (Me_6TREN)



1,1,4,7,10,10-hexamethyltriethylene tetramine (HMTETA)



sparteine



1,4,8,11-tetramethyl-1,4,8,11-tetraaza-cyclotetradecane (Me_4cyclam)

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ATRP – basic scheme

Initiation

$$R{-}X + CuX \xrightarrow{Lig} R\bullet + [CuX_2 \cdots Lig] \xrightarrow{M} R{-}M\bullet + [CuX_2 \cdots Lig]$$

Propagation

$$R{-}M\bullet + [CuX_2 \cdots Lig] \xrightarrow{nM} R{-}M_n{-}M\bullet + [CuX_2 \cdots Lig]$$

Determining equilibrium

$$P_n{-}X + Mt^nX / Lig \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P_n^\bullet + Mt^{n+1}X_2 / Lig$$

$$P_n^\bullet \; (+ M, \; k_p)$$

dormant **active**

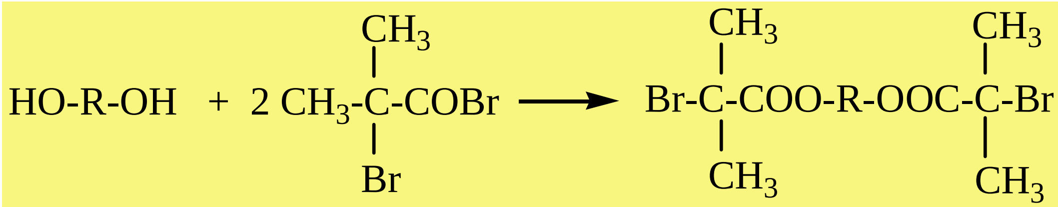
Matyjaszewski: Chem. Rev. 101, 2921 (2001)

Sawamoto: Chem. Rev. 101, 3669 (2001)

Multifunctional ATRP initiators

Bifunctional

diesters of 2-haloacids

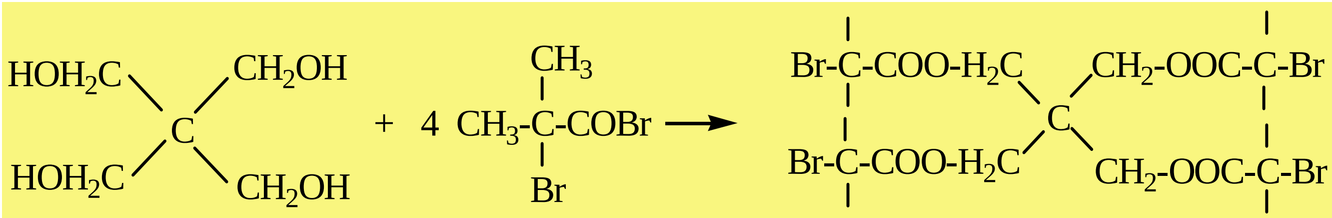


substituted urethanes or ureas

$$OCN\text{-}R\text{-}NCO + 2\,HO\text{-}CH_2\text{-}CCl_3 \longrightarrow Cl_3C\text{-}CH_2O\text{-}CONH\text{-}R\text{-}NHCO\text{-}OCH_2\text{-}CCl_3$$

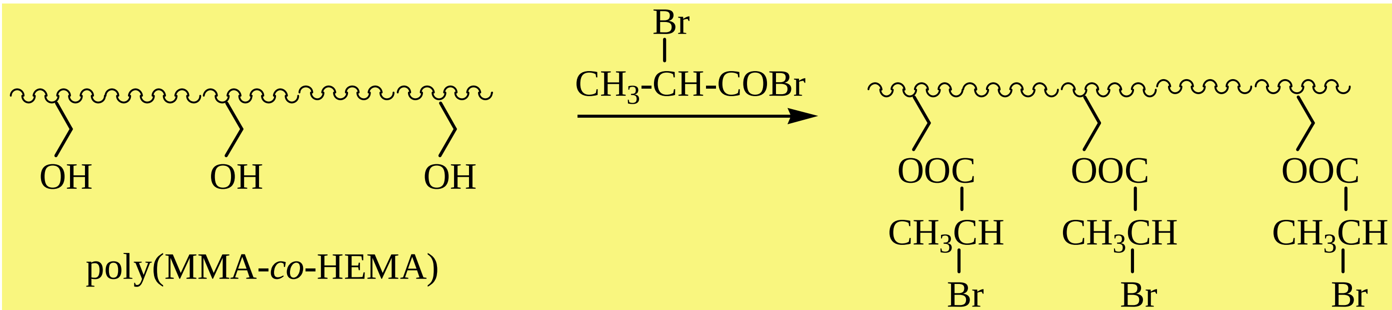
Tetrafunctional

tetraesters (pentaerythritol)



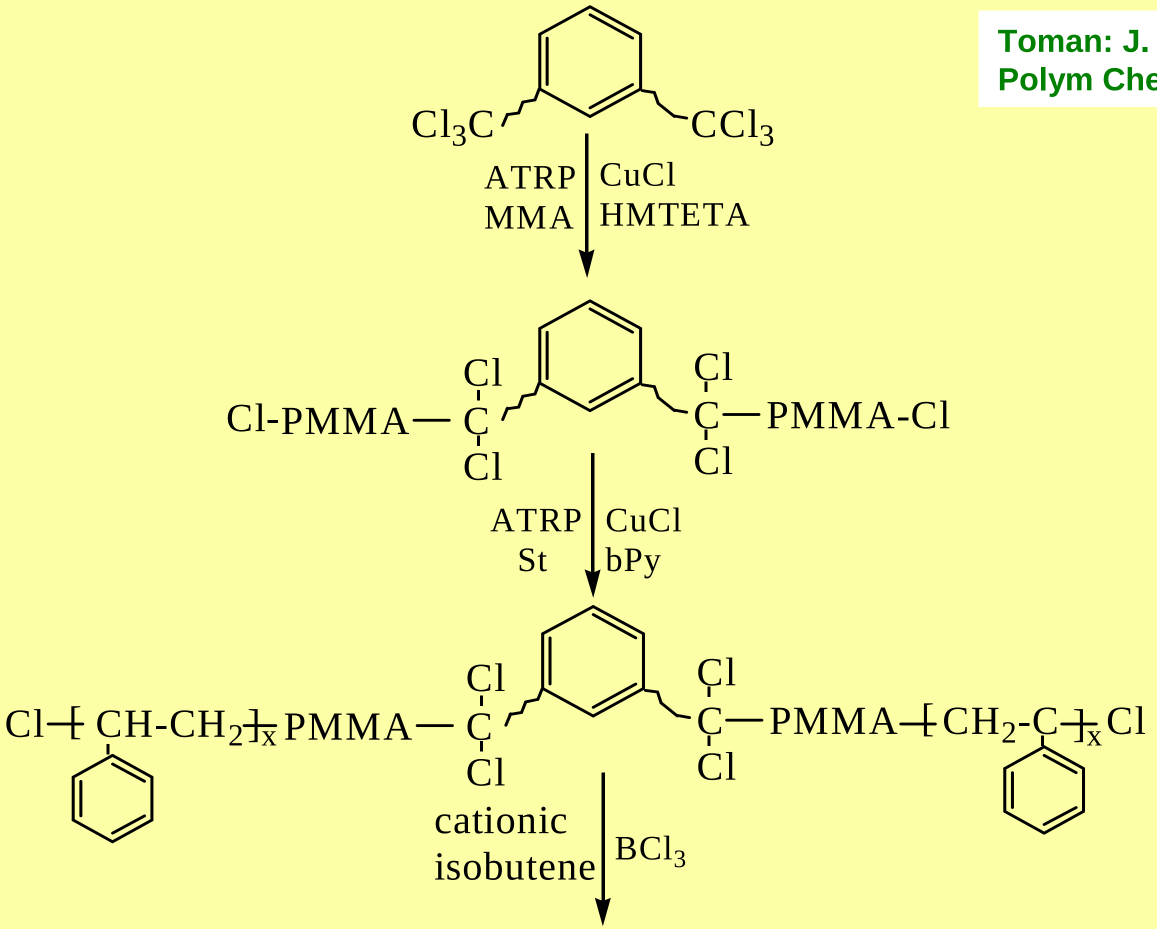
Polyfunctional

polymeranalogous reactions



Multiblock copolymer by a combination of ATRP and cationic polymerization

Toman: J. Polym. Sci. Part A-Polym Chem. 43, 3823 (2995)



poly(isobutene-*b*-styrene-*b*-MMA-*b*-styrene-*b*-isobutene)

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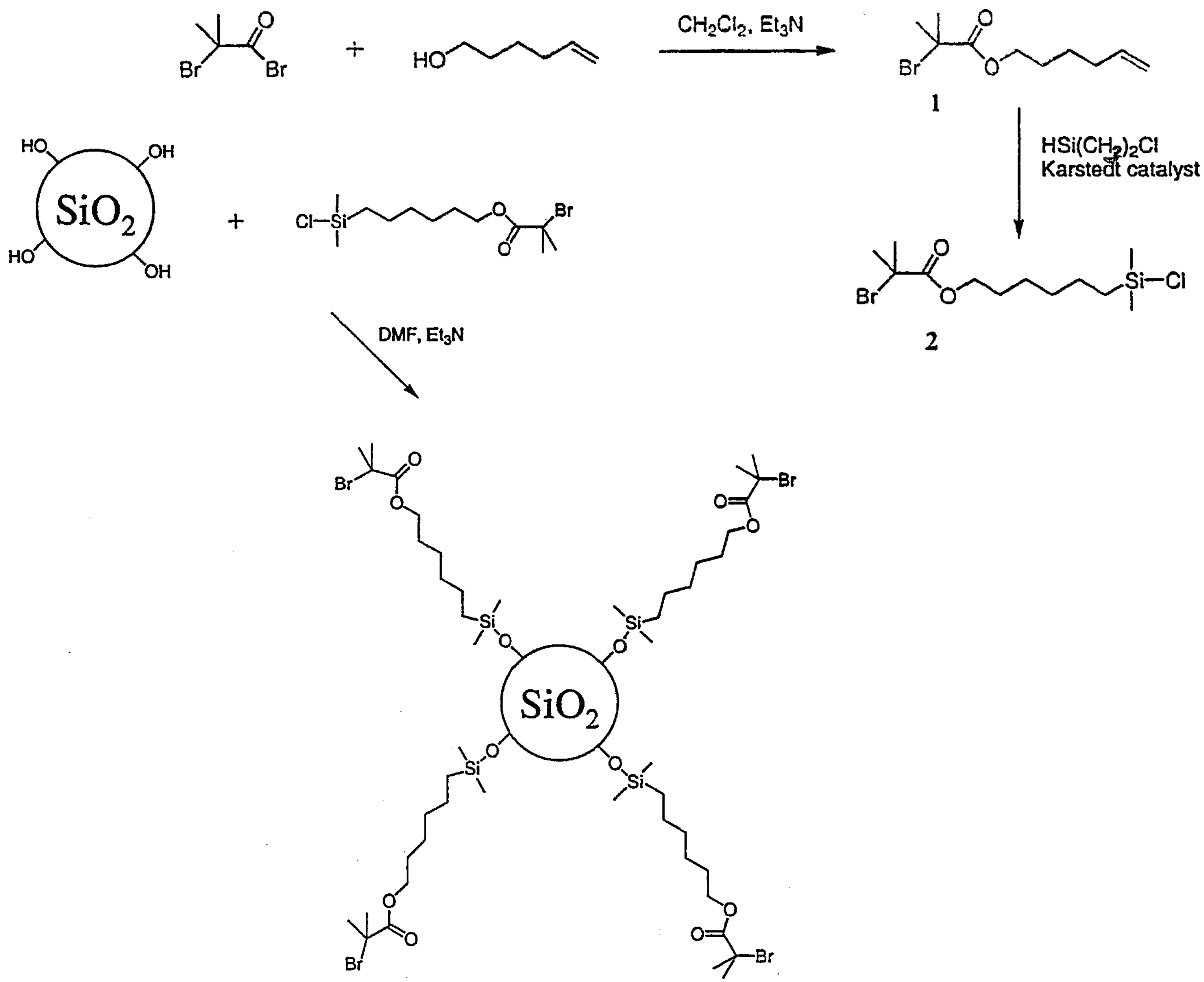
ATRP grafting of silica surface with BuA

Synthesis of functionalized ATRP initiator

Anchoring of the initiator onto silica particles



Reverse ATRP (RATRP)

Principle: Reversible deactivation of growing macroradical with a salt of transition metal in the higher oxidation state

Initiators: Commonly used radical initiators, mostly diazocompounds

General scheme

Initiating system: diazocompound, $CuCl_2$, ligand (subst. bPy)

Initiation

$$R-R \longrightarrow 2\,R\bullet$$

$$R\bullet + M + [CuCl_2 \cdots Lig] \longrightarrow R-M\bullet + [CuCl_2 \cdots Lig]$$

Propagation

$$R-M\bullet + [CuCl_2 \cdots Lig] \xrightarrow{nM} R\text{-}M_n\text{-}M\bullet + [CuCl_2 \cdots Lig]$$

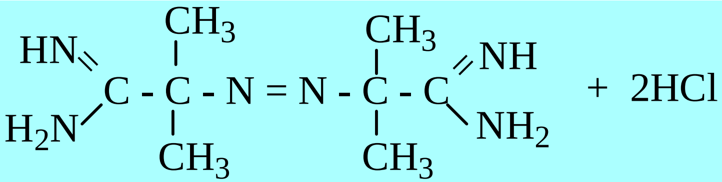
Determining equilibrium between active and dormant chains

$$\mathbf{R\text{-}M_n\text{-}M\bullet + [CuCl_2 \cdots Lig] \rightleftharpoons R\text{-}M_{n+1}\text{-}Cl + CuCl}$$

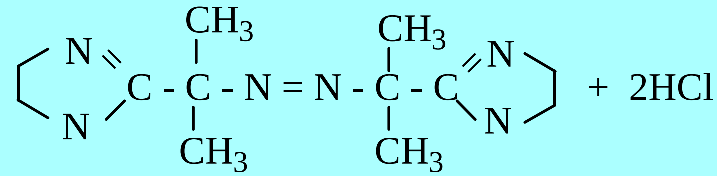
active chain *dormant chain*

RATRP of BuMA in emulsion

Water-soluble initiators: $K_2S_2O_8$; soluble azoinitiators



2,2'-azobis(2-methylpropionamidine) dihydrochloride, **V-50**



2,2'-azobis[2-(2-diimidazolin-2-yl)propane dihydrochloride, **VA-044**

Catalyst: 2,2'-bipyridine, $CuBr_2$; non-ionic surfactant

Run[a]	Init	T °C	$CuBr_2$ m/m[b]	Time min	Conv. %	10^{-3} M_n	M_w/ M_n	Φ[c]
1	V-50	90	0	15	98	255.5	3.56	<0.1
2	V-50	90	1	300	92	69.2	1.26	0.4
3	V-50	90	2	350	60	76.2	1.19	0.2
4	VA-044	80	1.5	240	37	15.3	1.43	0.7
5	VA-044	70	1.5	540	84	47.3	1.28	0.5

[a] $[I]_0/[BuMA]_0$ = 1/400; $[CuBr_2]_0$/[l\bPy]$_0$ =1/2; [b] $[CuBr_2]_0/[I]_0$ mole ratio; [c] initiator efficiency

Single electron transfer-living radical polymerization – SET-LRP

Three-component initiating system:

- Initiator: alkyl halides, sulfonyl halides, haloforms
- Catalyst: zerovalent metallic copper Cu(0), fine powder or tin wire
- Ligand: nitrogen compounds, Me_6TREN, PMDETA
- Solvents: aprotic polar solvent (DMSO), protic solvents (water, alcohols)

Possible SET activation mechanism

$$\text{P-X} \xrightarrow[\text{L, solvent}]{\text{Cu(0)}} \{\text{P-X}^{\bullet -} : \text{Cu(I)/L}^{+}\} \longrightarrow \{\text{P}^{\delta +\bullet}\text{X}^{-} : \text{Cu(I)/L}^{+}\} \longrightarrow \text{P}^{\bullet} + \text{Cu(I)X/L}$$

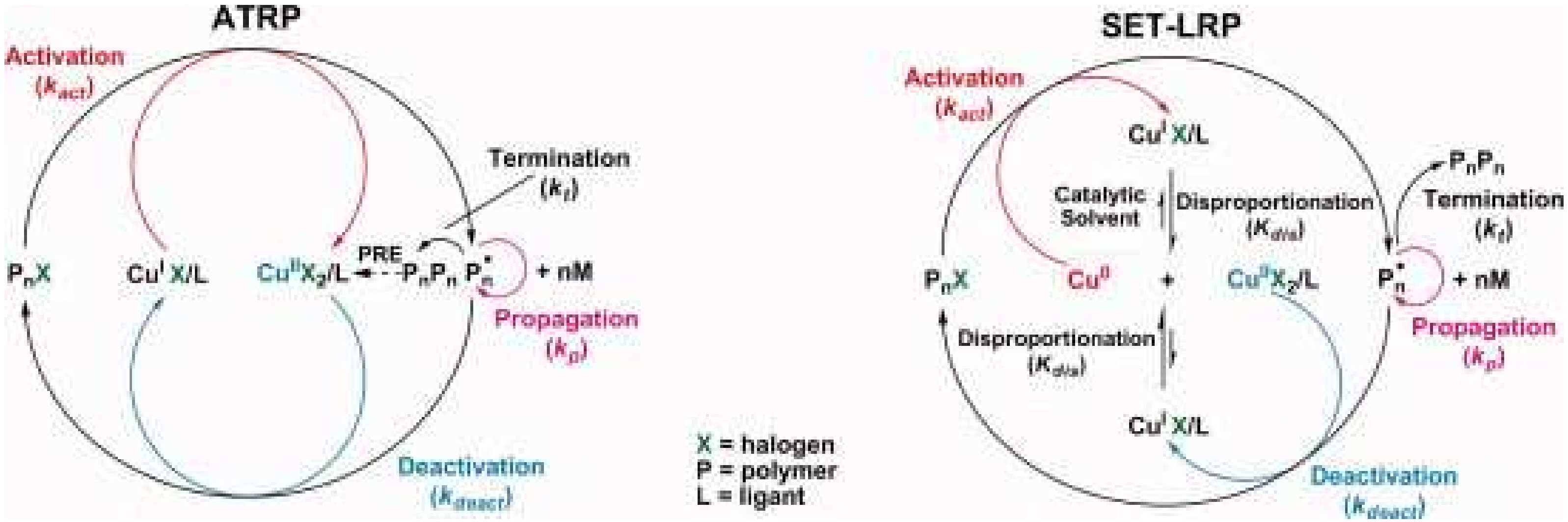
$$\text{P-X} \xrightarrow[\text{L, solvent}]{\text{Cu(0)}} \{\text{P}^{\delta +\bullet}\text{X}^{-} : \text{Cu(I)/L}^{+}\} \longrightarrow \text{P}^{\bullet} + \text{Cu(I)X/L}$$

$$2\ \text{Cu(I)X/L} \rightleftharpoons \text{Cu(0)} + \text{Cu(II)X}_2\text{/L}$$

Monomers: Acrylates, methacrylates, styrene (?), vinylchloride

Percec: Chem. Rev. 109, 5069 (2009)

SET-LRP vs. ATRP, scheme



M	Initiator	Ligand	Ratio[a] m/m	Time min	Convers. %	SEC	
						$M_n.10^{-3}$	M_w/M_n
MA	MBrP	Me_6TREN	220/1/1/1	50	100	20	1.3
MA	$CHBr_3$	Me_6TREN	220/1/0.1/0.1	70	90	18	1.6
MMA	DCAP	PMDETA	200/1/1/1	300	90	20	1.3
VC	$CHBr_3$	TREN	350/1/1/1	200	85	32	1.6

[a] monomer/initiator/Cu(0)/ligand

LAP and ATRP - comparison

	LAP	ATRP
Advantages	Better control over the process	Synthesis of macroinitiators, easy preparation of block copolymers
	Very narrow MWDs (<1.1)	Less time- and labor-consuming
	Controlling the microstructure	Non-sensitive to protic impurities, water-resistant
	Easy functionalization of chains	Elevated temparatures, low costs
Drawbacks	Very sensitive to protic impurities	Broader MWDs (1.3 or more)
	High purity requested, low temperature; i.e. high costs	Lower control over the process
	Side reactions (polar vinyl monomers)	Hardly controllable microstructure
	No monomers with OH, COOH, NH_2 groups	No dienes

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