SS 2019

Vorlesung Polymermaterialien

Free and controlled radical polyerization

FRP and CRP

Polymerization methods: overview

- Free radical polymerization (PS, PMMA)
- Controlled radical polymerization
- Ionic polymerization (cationic, anionic)
- Ring opening polymerization (ROP: PLA, PCL, aliphatic PC)
- Transition metal-catalyzed polymerizations (polyolefines, polyinsertion, ROMP, ADMET, cross-coupling)
- Polyaddition (isocyanate chemistry, thiol-ene and azide-alkyne click chemistry)
- Polycondensation (PET, PA, PC)

chain growth

step growth

Elementary steps of free radical polymerization

1) Initiator dissociation

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

2) Initiation

$$R^* + M \xrightarrow{k_i} R\text{-}M^*$$

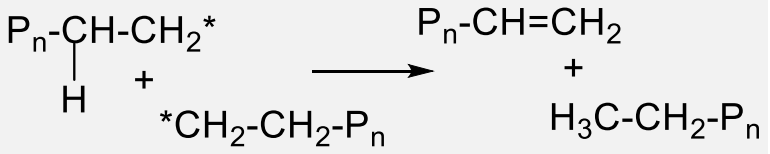
3) Propagation

$$R\text{-}M^* + nM \xrightarrow{k_p} R\text{-}M_n^*$$

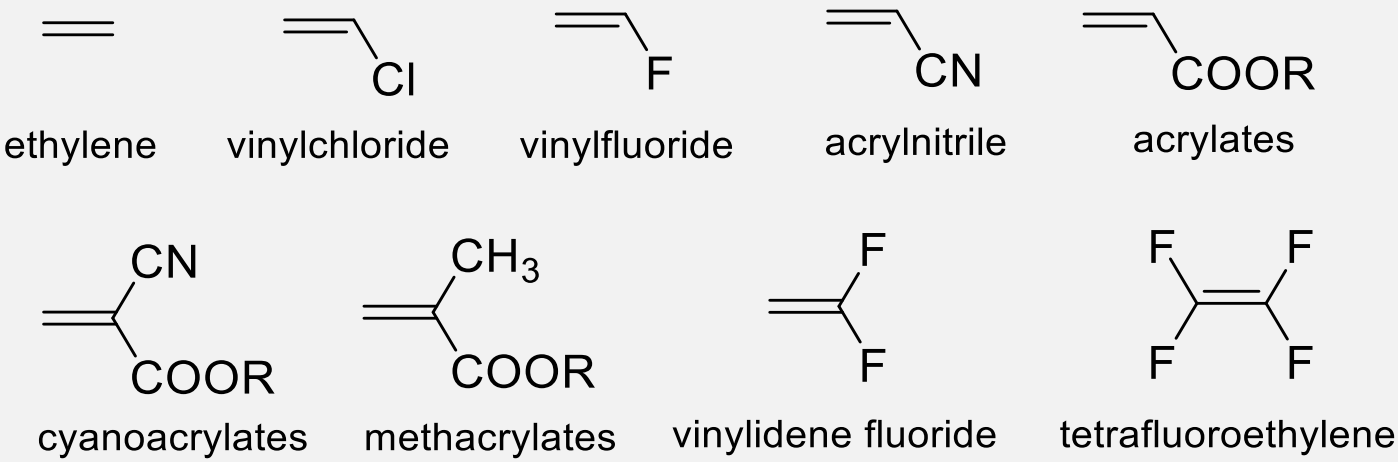
4) Termination

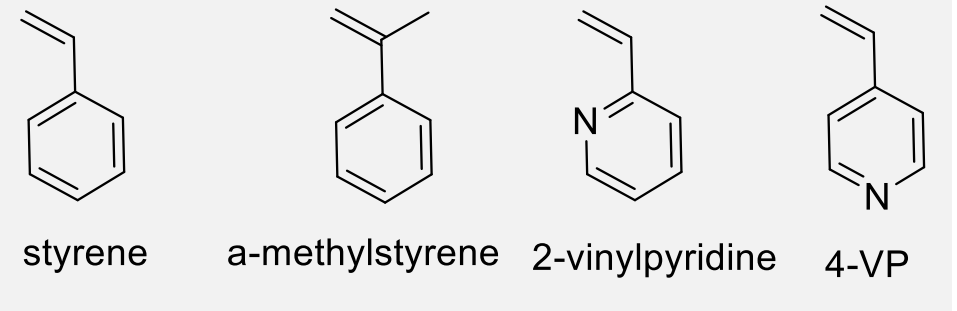
$$R\text{-}M_n^* + {}^*M_m\text{-}R \xrightarrow{k_t} R\text{-}M_{n+m}\text{-}R \qquad \textit{recombination}$$

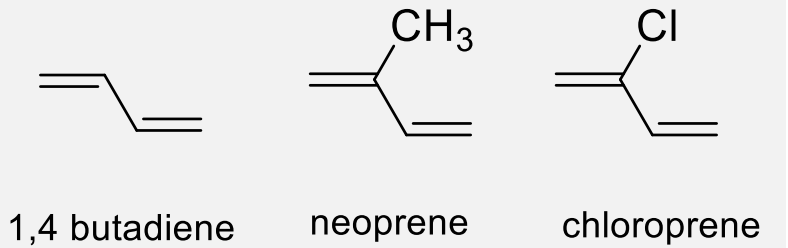
$$R\text{-}M_n^* + {}^*M_m\text{-}R \xrightarrow{k'_t} R\text{-}M_n^{H} + {}^{=}M_m\text{-}R \qquad \textit{disproportionation}$$



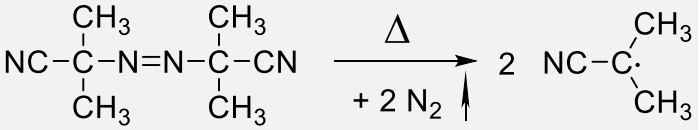
Monomers for free radical polymerization



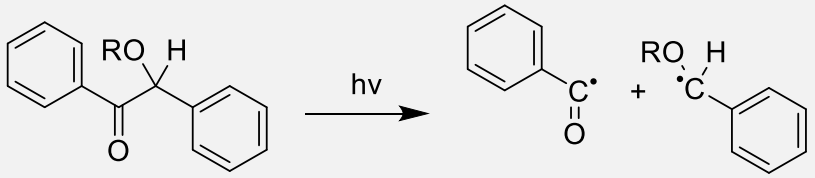




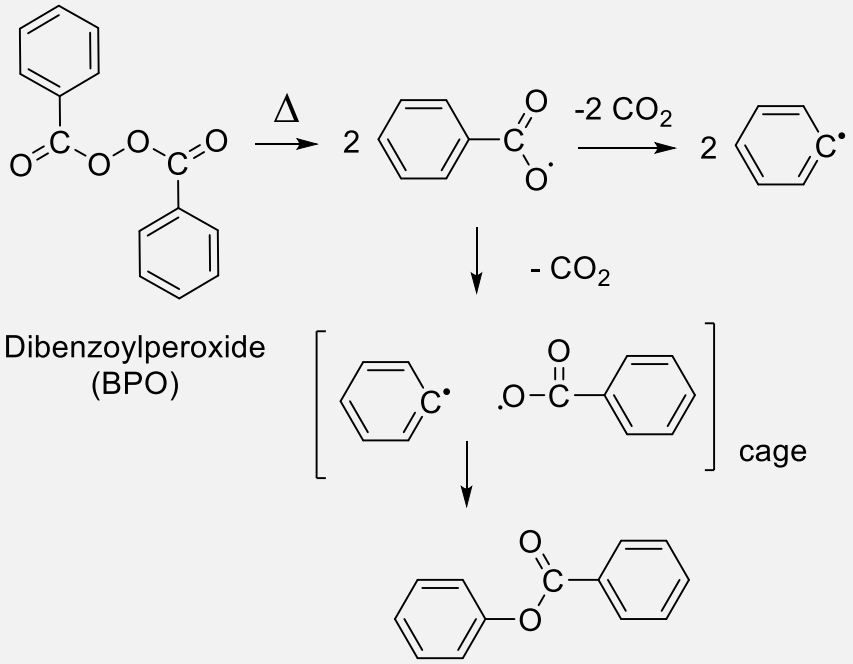
Initiators



Azobisisobutyronitril (AIBN)



Benzoinether



Dibenzoylperoxide (BPO)

$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH\cdot$

Fenton-Reagenz

$AB \xrightarrow{\gamma} AB^{+\cdot} \longrightarrow A^+ + B\cdot$ gamma-rays

$AB + e^- \longrightarrow AB^{-\cdot} \longrightarrow A\cdot + B^-$ beta-rays

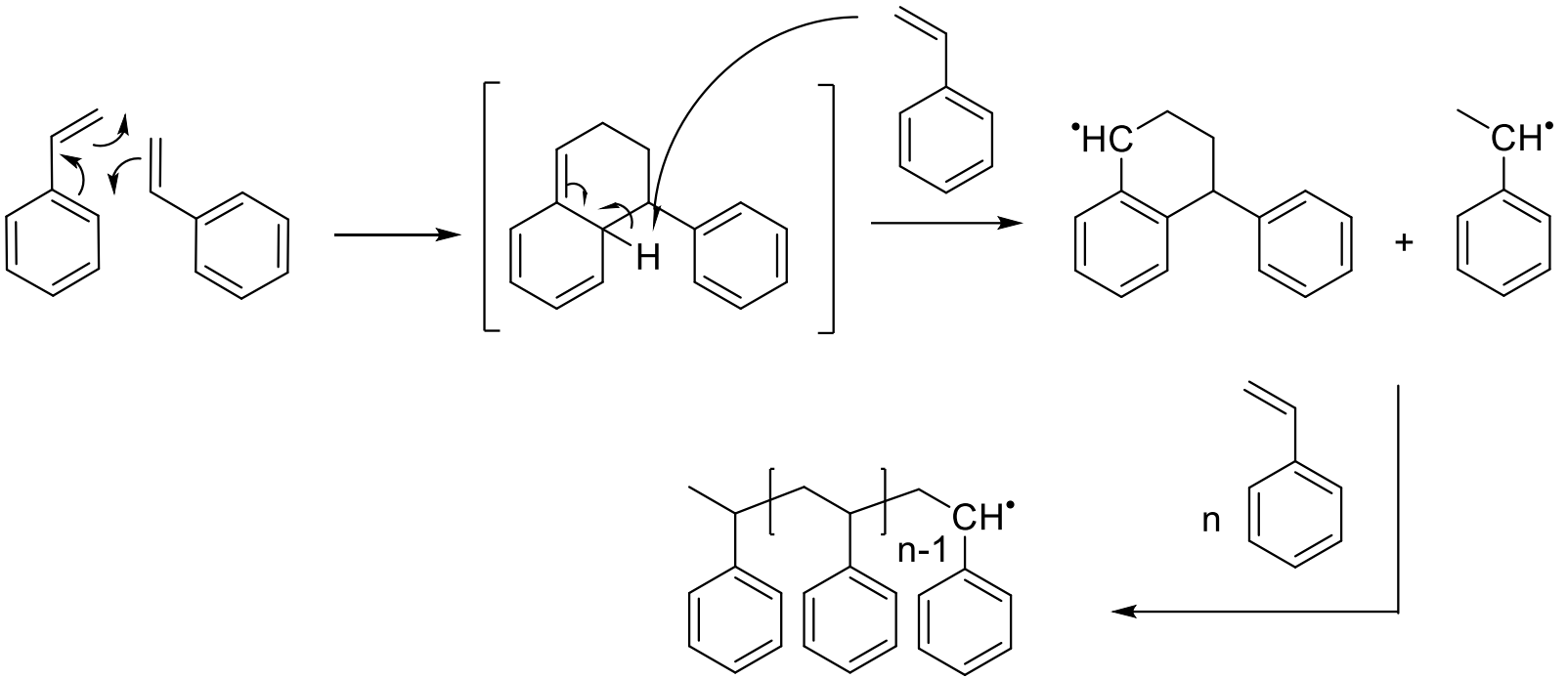
oxygen, peroxides, hydroperoxides, peracids, peroxodisulfates

<u>Kenngrössen von Initiatoren:</u>
Halbwertszeit, bei der die Häfte des Initiators zerfallen ist (gilt für eine T)

Auto-initiation of styrene

Thermally-initiated polymerizations: polymerization in the absence of initiators

- Impurities!
- Styrene and MMA show auto-initiation



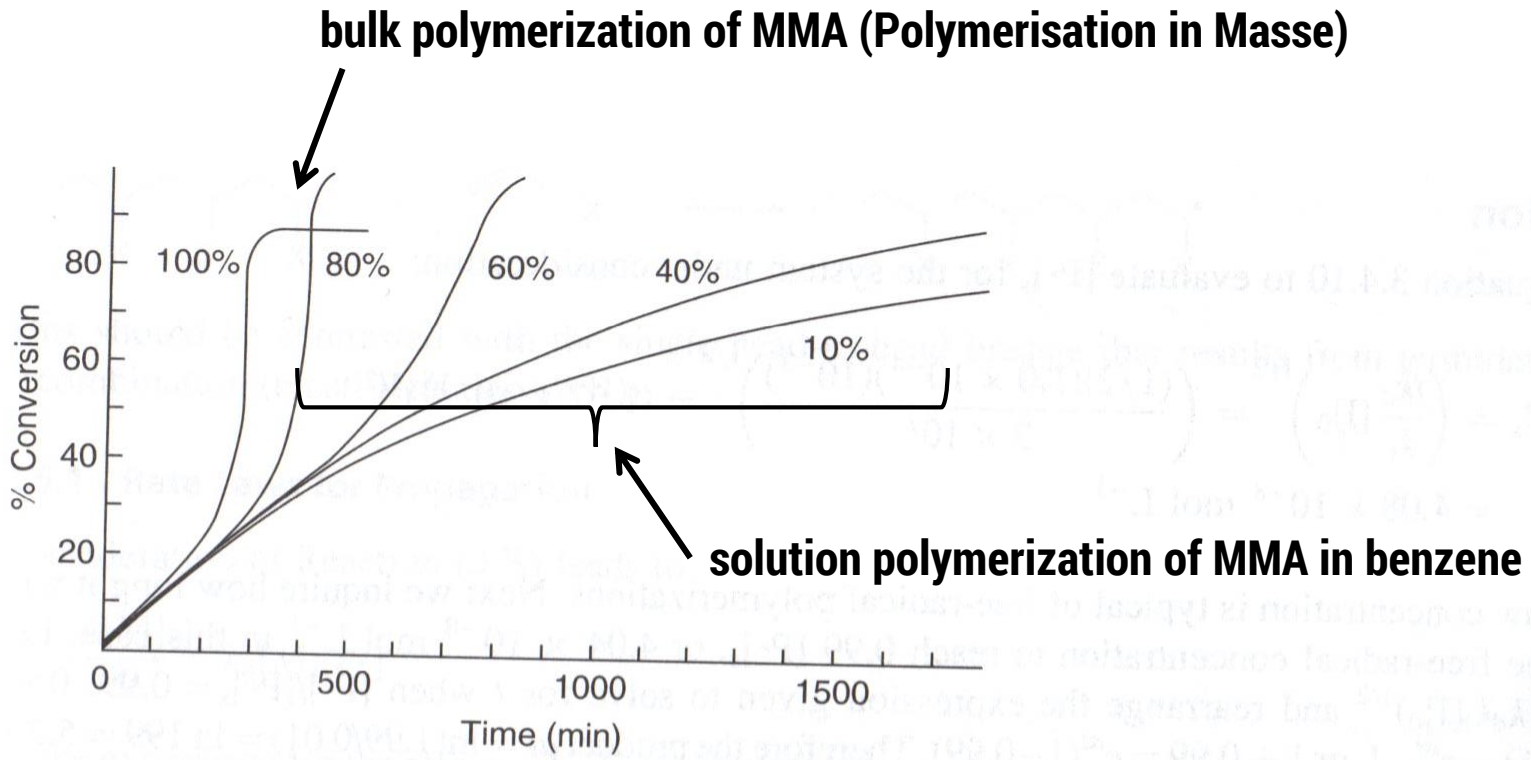


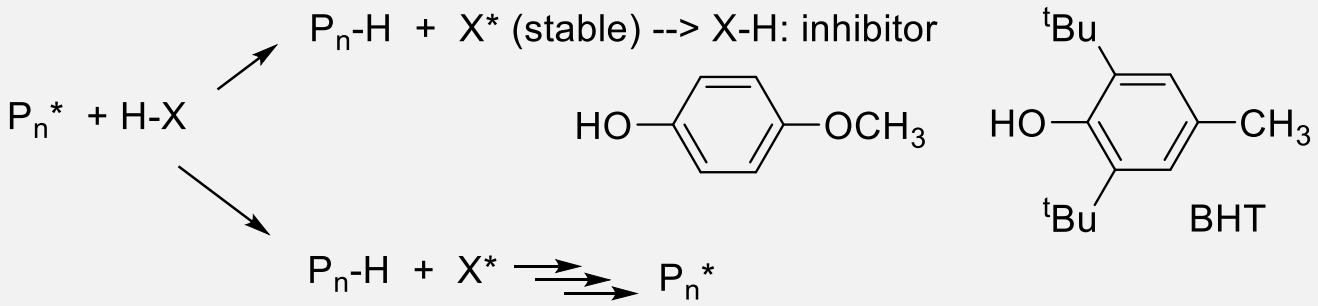
Figure 3.2 Acceleration of the polymerization rate for methyl methacrylate at the concentrations shown in benzene at 50°C. (Reprinted from Schulz, G.V. and Harborth, G., *Makromol. Chem.*, 1, 106, 1948. With permission.)

Hiemenz & Lodge, p. 89

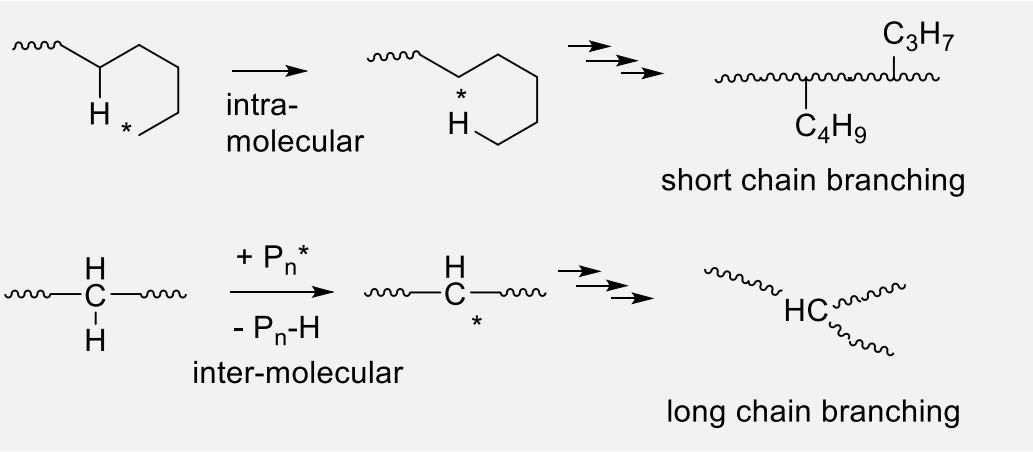
Chain transfer

Next to initiation, propagation and termination there is *chain transfer* of various kinds. Chain transfer= H abstraction and transfer of radical

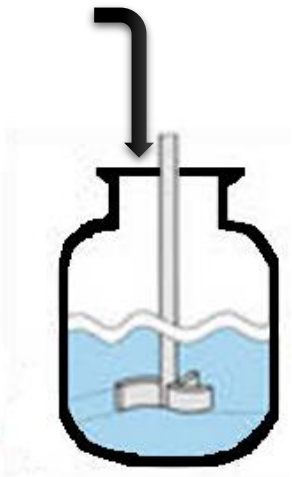
chain transfer with monomer, initiator, chain transfer agents (= modulator/ regler):



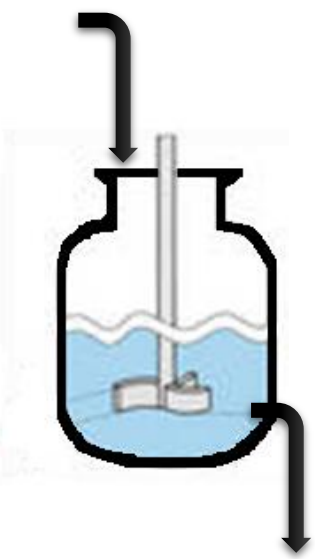
chain transfer (with polymer):



Technical processes



discontinuous
„batch“
(Chargenbetrieb)



continuous
c.f. flow
reactions

- bulk polymerization (Massepolymerisation)
- precipitation polymerization (Fällungspolymerisation)
- bead polymerization (Perlpolymerisation)
- emulsion polymerization (Emulsionspolymerisation)

Technical processes

❖ **Solution polymerisation**
Both monomer and polymer dissolved in solvent

❖ **Bulk polymerisation**
No solvent, monomer= solvent for polymer

❖ **Precipitation polymerisation**
Polymer not soluble, precipitates

❖ **Bulk solution polymerisation**
Polymer soluble in monomer

❖ **Bulk precipitation polymerisation**
Polymer not soluble in monomer

❖ **Dispersion polymerisation**
Dispersed polymer particles stabilized in organic media

❖ **Suspension polymerisation**
„bead" polymerisation
Stirred dispersion, mostly in water, 10µm-5mm size, stabilized particles polymerisation in droplets
Initiator monomer-soluble

❖ **Emulsion polymerisation**
Initiator water-soluble
Polymerisation in micelles, not in monomer droplets

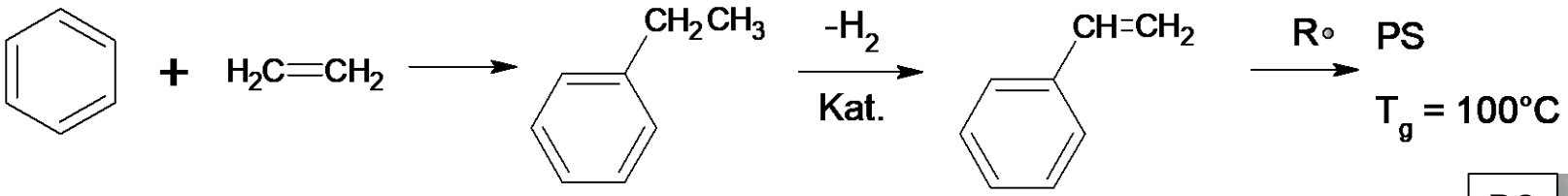
❖ **Miniemulsion**
Larger amount of tenside
Monomer droplets smaller, 50-500 nm, Polymerisation in monomer droplets

❖ **Microemulsion**
Thermodynamic stable Mixture of two immiscible Liquids
Larger amount of tenside
Small particle size 10-100 nm

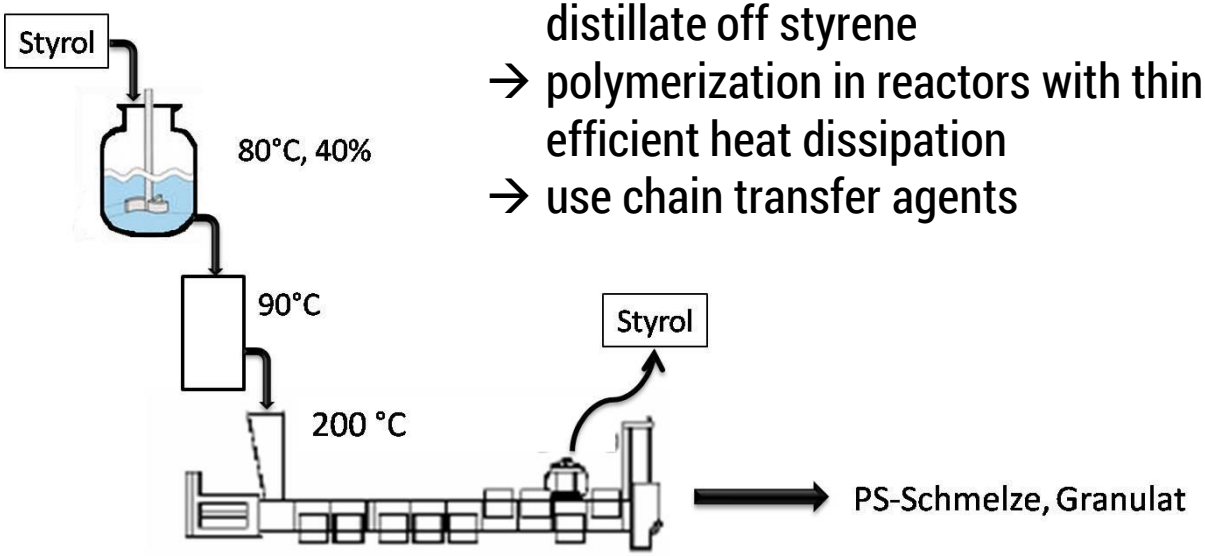
❖ **Gas phase polymerisation**
Technologically very important
Transition metal-initiated, PE, PP

❖ **Solid state polymerisation**
In solids or crystals, initiation via ionising radiation or UV

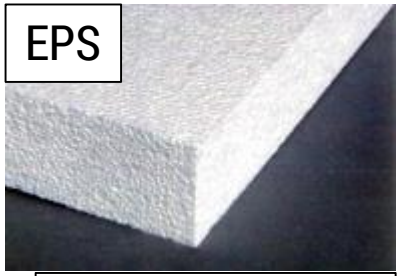
Industrial polymerization of styrene



remember the Trommsdorff-effect for bulk polymerizations!



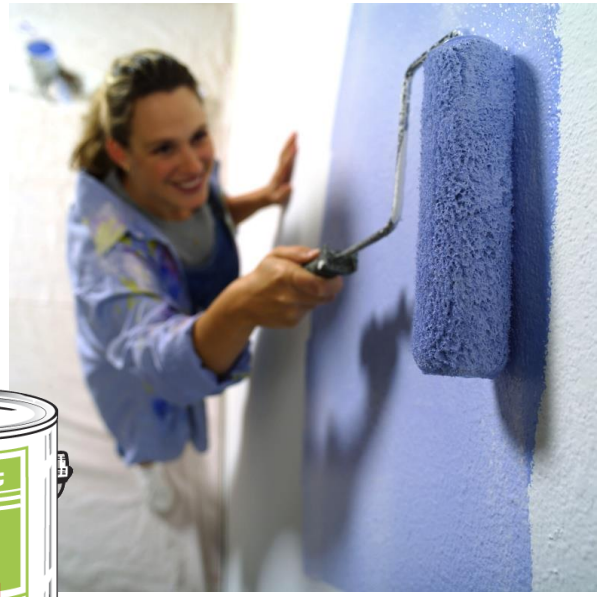
→ polymerize to low conversion ~40% and distillate off styrene
→ polymerization in reactors with thin layers for efficient heat dissipation
→ use chain transfer agents



Styropor: 200-fache Vergrößerung

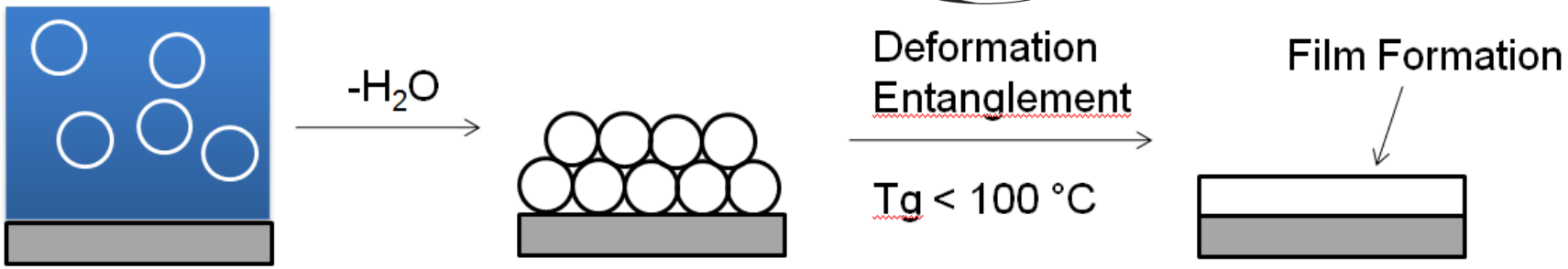
Emulsion polymerization

Emulsion polymerization: H20, monomer, tenside, initiator (water-soluble)
-polymerization in micelles
-efficient cooling



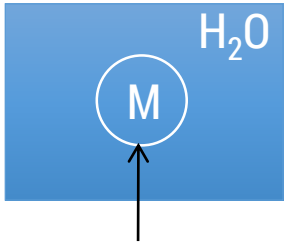
Systems:
- Styrene, butadiene
- VC, -acrylate-, vinylacetate-copolymers

Applications:
- Rubber, e.g. SBR
- Coatings
- Adhesives
- Paper coatings

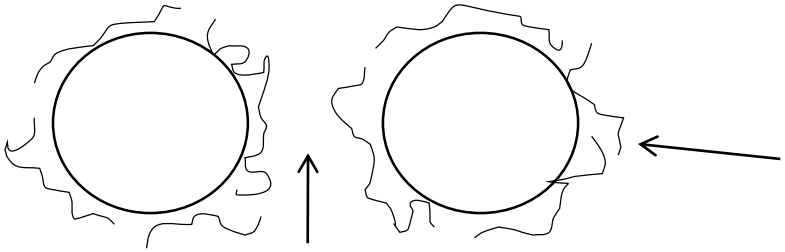


Bead polymerization („Perl-Polymerisation“)

Water, monomer, initiator (hydrophobic), sometimes stabilizing polymers



Monomer-soluble initiator



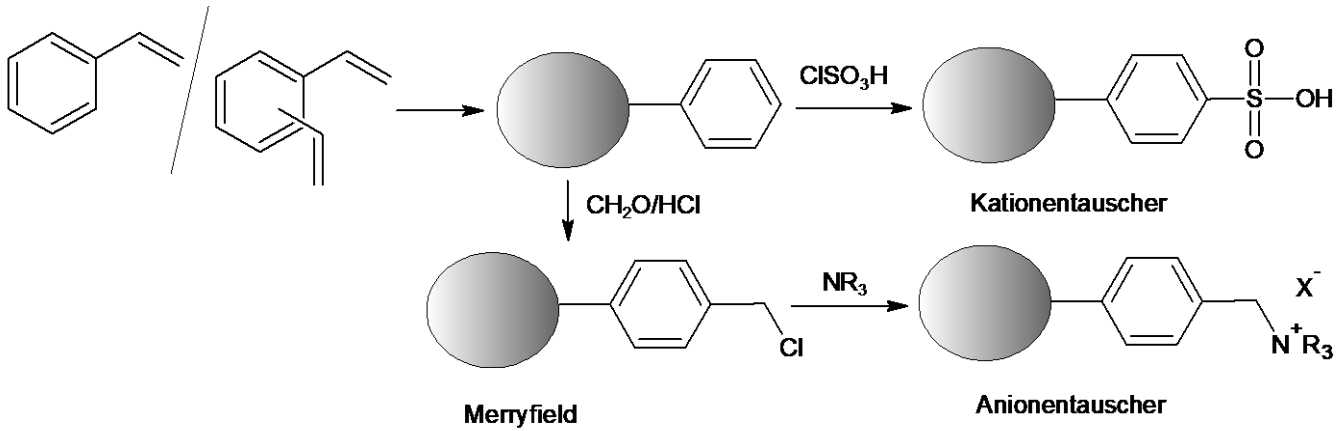
Schutzkolloid
(e. g. water-soluble
Polymers such as PVA)

Particle diameter adjusted by stirring speed (~100 µm – mm)

bead polymerization are bulk polymerizations with water as efficient cooling medium

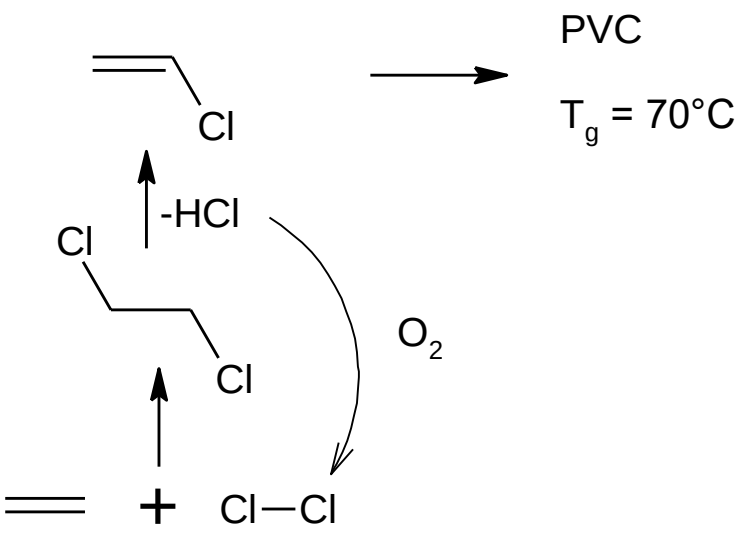
Applications:

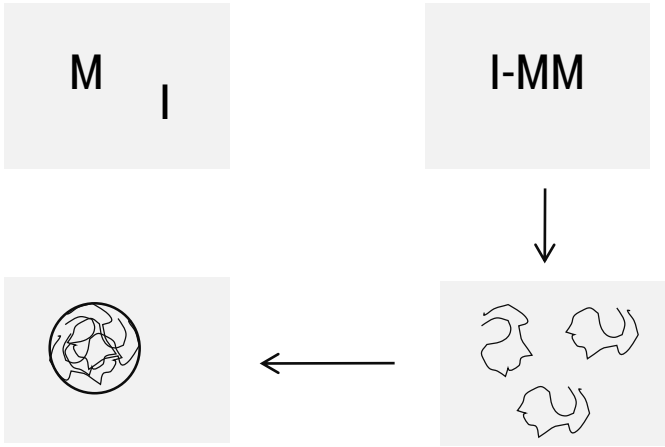
- Ion exchange resins
- Merryfield resins



Bulk precipitation polymerization: PVC

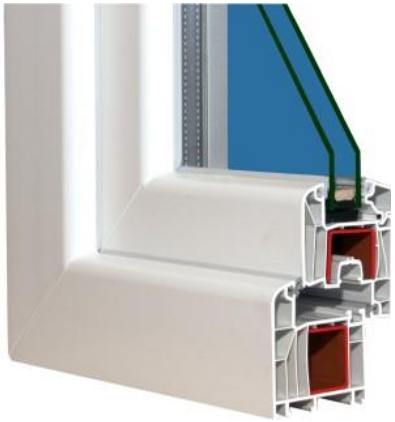
Polyvinylchlorid (PVC)

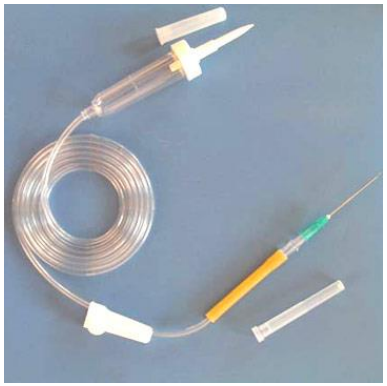




long chains are not soluble in monomer
→ precipitation

Hart-PVC:
- Fensterrahmen
- Rohre
- Fassadenelemente
- Rollläden





Weich-PVC:
- Kabelummantelungen
- Folien
- Fußbodenbelägen
- Schläuche (Medizin)
- Beschichtungen

Technical processes

preferred technical processes for polymer production

polymer	bulk	suspension	solution	precipi-tation	gas phase	emulsion	mechanism
HDPE		+	+	+	+		z, m
LDPE	+	+					r
PP	+	+	+		+		z,m
PS	+	+				+	r,m
PMMA	+	+	+			+	r
B-rubber				+			c
ABS			+			+	r
SBS				+			a
PAN				+			r

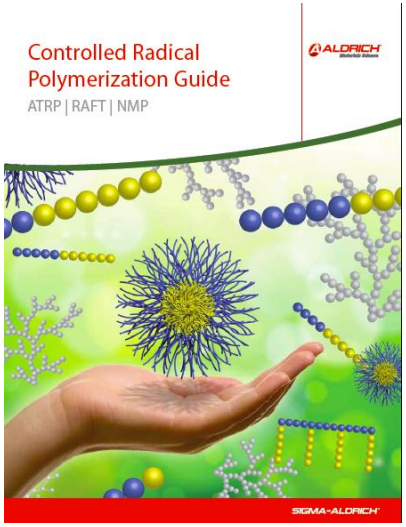
z: Ziegler-Natta, m: metallocene, r: radical, c: cationic, a: anionic

Controlled radical polyerization

CRP

Reviews:

1) Atom Transfer Radical Polymerization:
Chem. Rev., 2001, 101 (9), pp 2921–2990
2) Metal-catalyzed living radical polymerization
Chem. Rev., 2001, 101 (12), pp 3689–3746
3) Controlled/living radical polymerization: features, developments, perspectives
Prog. Polym. Sci. 2007, 32, 93
4) New polymer synthesis by nitroxide mediated polymerization *Chem. Rev.* 2001, *101,* 3661-3688



http://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/SAJ/Brochure/1/controlled-radical-polymerization-guide.pdf

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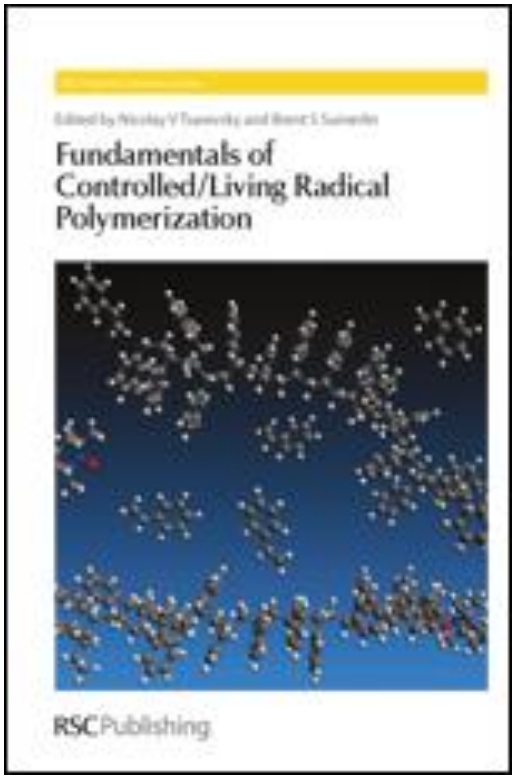
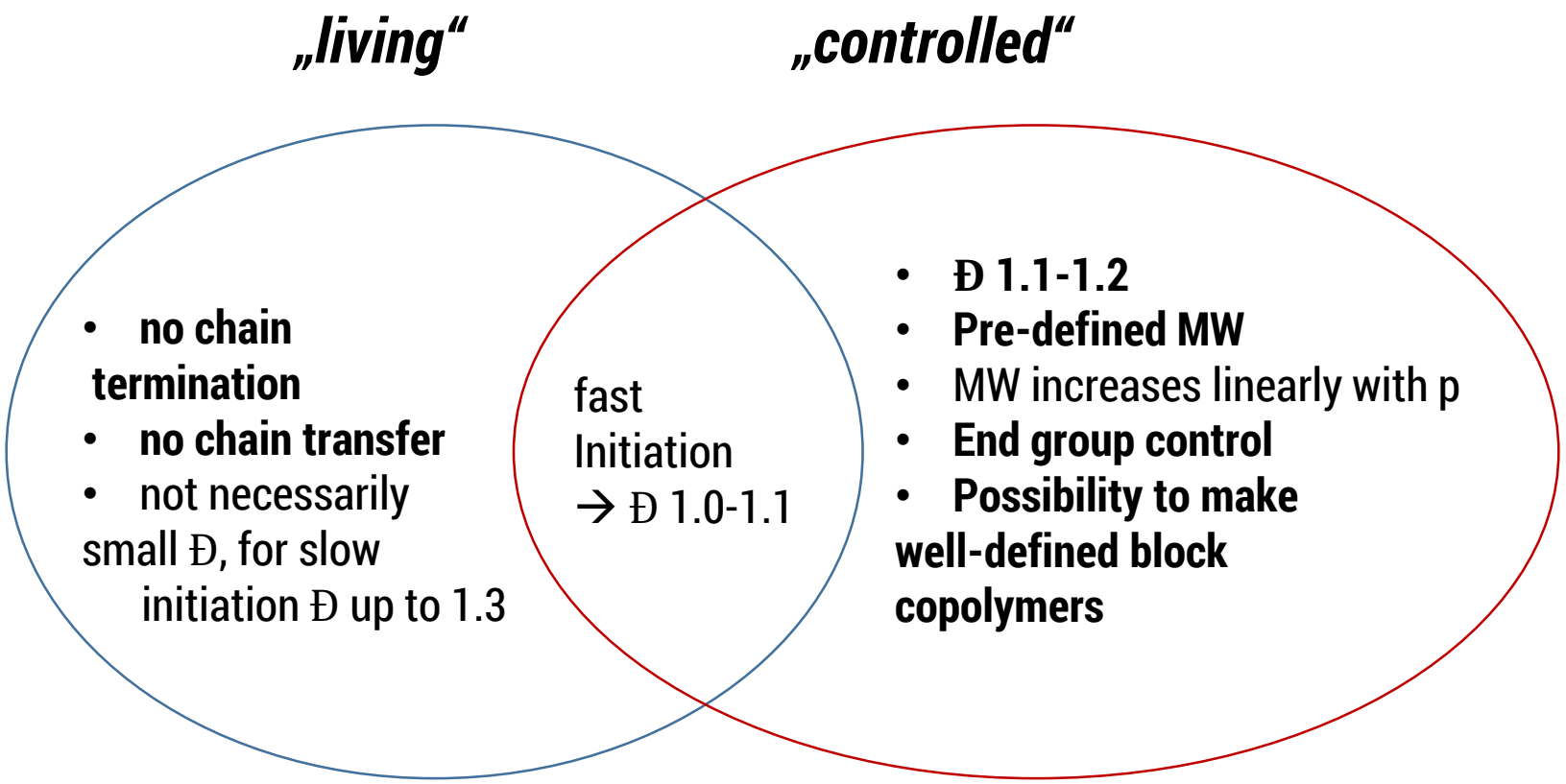


Terminology

Terms used throughout the literature:

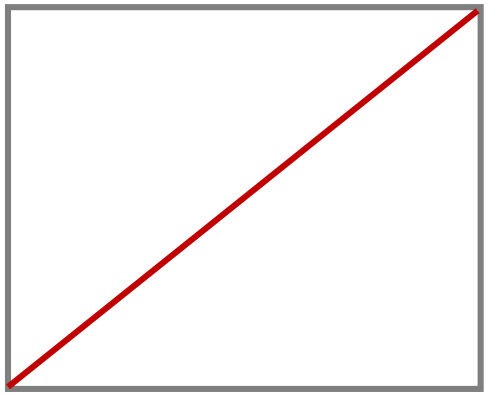
- ***„Living polymerization“***
- „Quasi-living polymerization“
- ***„Controlled radical polymerization“***
- „Living free polymerization“
- „Living free radical polymerization“



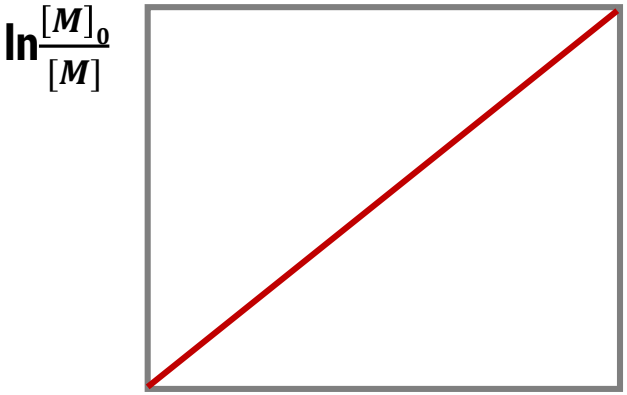
DP, conversion and time

linear increase of DP with p, pre-defined molecular weight

Linear behaviour of ln $[M_0]/[M]$ versus t (first order with respect to monomer conc.)



$DP = p[M]_0/[I]_0$



$\ln\frac{[M]_0}{[M]} = kt$

→ compare a plot of DP versus p for step growth and free radical polymerization!

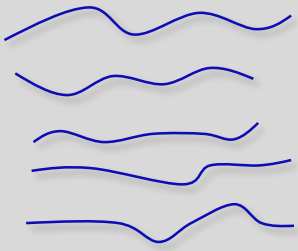
Advantages and possibilities of controlled radical polymerization

Structurally defined polymer architectures

- Pre-defined molecular weight and narrow distribution (D< 1.2)
- End-functional polymers
- Block, graft and star copolymers

narrow distribution

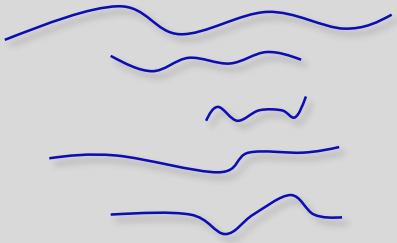
Đ ~1.1-1.2



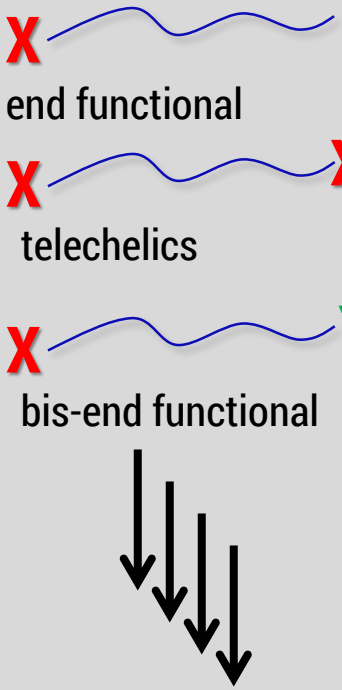
broad distribution

(step growth, free-radical)

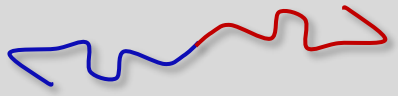
Đ 1.5-2



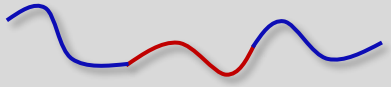
end functionalization



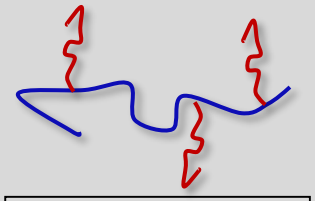
block copolymers



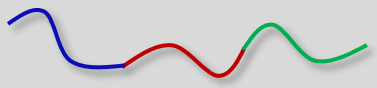
diblock copolymer



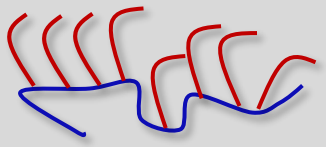
triblock copolymer



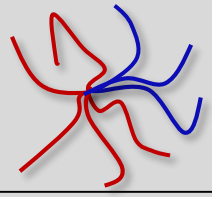
graft copolymer



triblock terpolymer



comb polymer

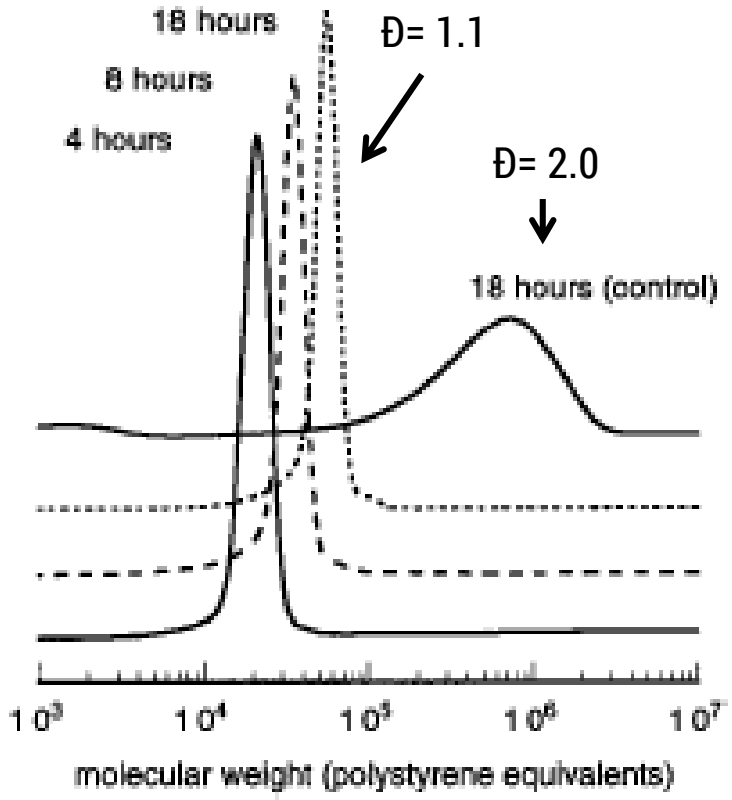


star block copolymer

Advantages and possibilities of controlled radical polymerization

Narrow molecular weight distribution (how narrow is“ narrow“ ?)

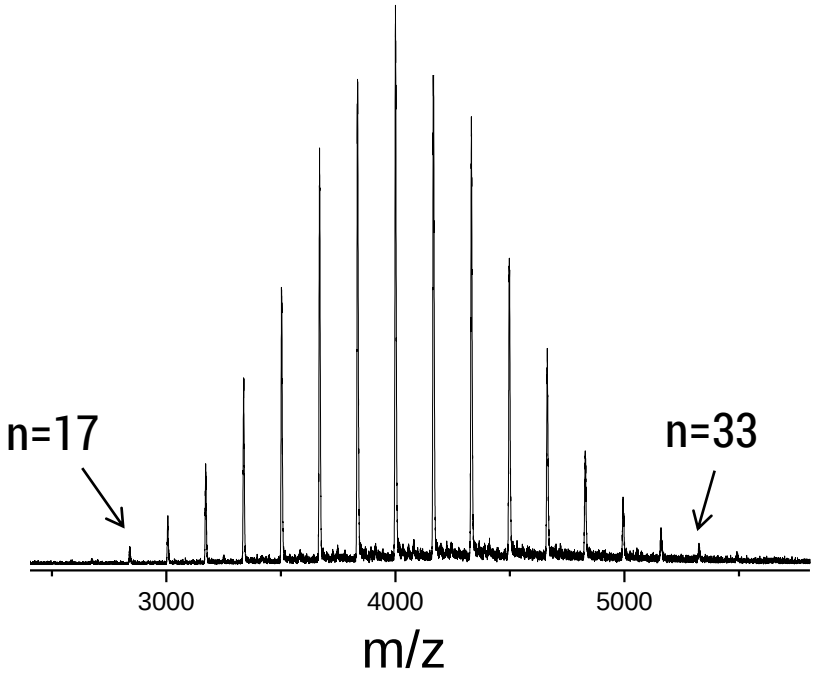
SEC (size exclusion chromatography) or
GPC Gelpermeationschromatographie



Chiefari et al., *Macromolecules*, **1998**, *31*, 5559

MALDI-ToF: matrix-assisted laser desorption ionisation time-of-flight

$M_{n,MALDI}$= 4036 g/mol
$Đ_{MALDI}$= 1.014
(→ $M_{n,GPC}$= 7900 g/mol)

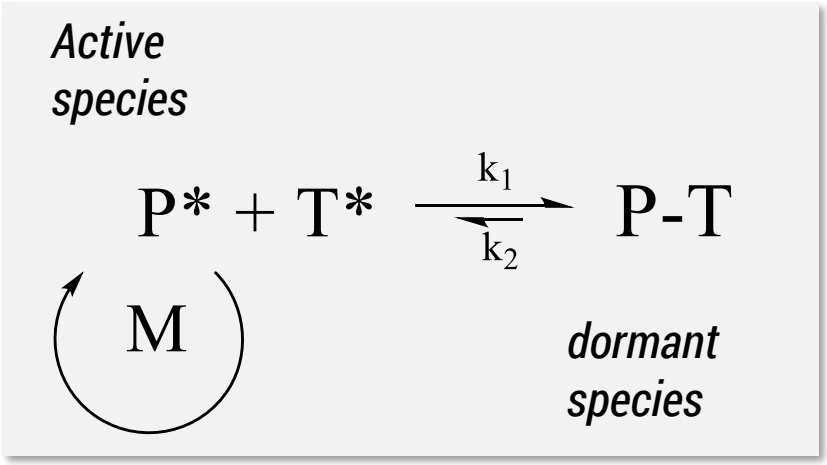


Kohn et al. *ACS Macro Lett* **2012**, *1*, 1170

Principle of controlled radical polymerization

CRP: reducing the concentration of radicals by reversible termination:

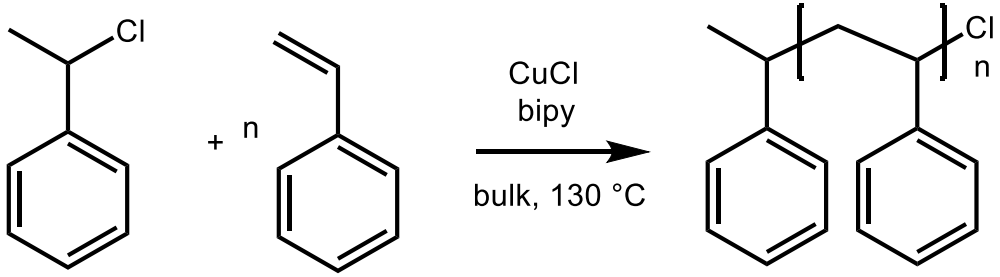
→ Probability for chain-chain recombination and disproportionation is drastically reduced
→ Probability for transfer is drastically reduced
→ Reduced radical concentration leads to slower kinetics (smaller k_p)
→ $K_p < k_i$: fast initiation compared to propagation leads to narrow distribution



P*: active species: polymer radical, can add monomer
T*: stable radical or species that only reacts with polymer radical but does not add monomer
P-T: dormant species, inactive

Applies to ATRP and NMP, RAFT is different!

ATRP: First examples



Initiation

$$R\text{-}Cl + Cu^{I}L_x \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} R^* + Cl\text{-}Cu^{II}L_x$$

$$R\text{-}Cl \xrightarrow{M} \text{(no reaction)} \qquad R\text{-}Cl \xrightarrow{k_i,\ M} R\text{-}M\text{-}Cl$$

$$R\text{-}M\text{-}Cl + Cu^{I}L_x \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} RM^* + Cl\text{-}Cu^{II}L_x$$

Propagation

$$P\text{-}Cl + Cu^{I}L_x \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P^* + Cl\text{-}Cu^{II}L_x$$

$$P^* \xrightarrow{M,\ k_p} \text{(chain growth)}$$

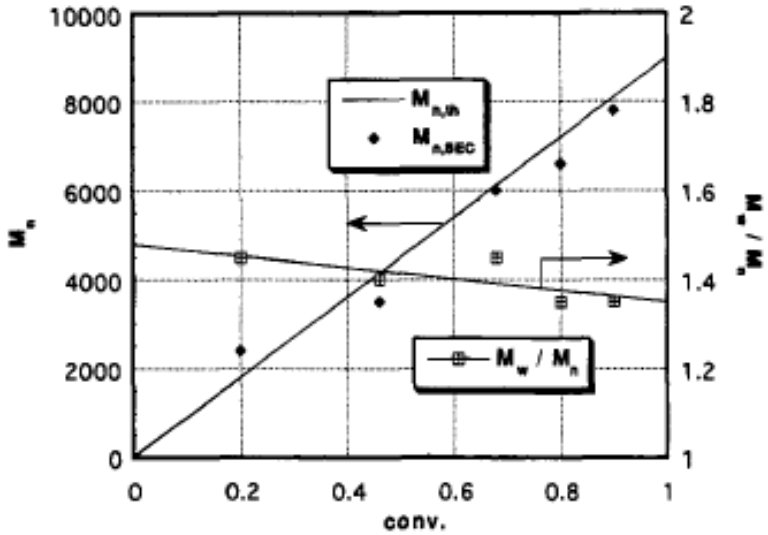
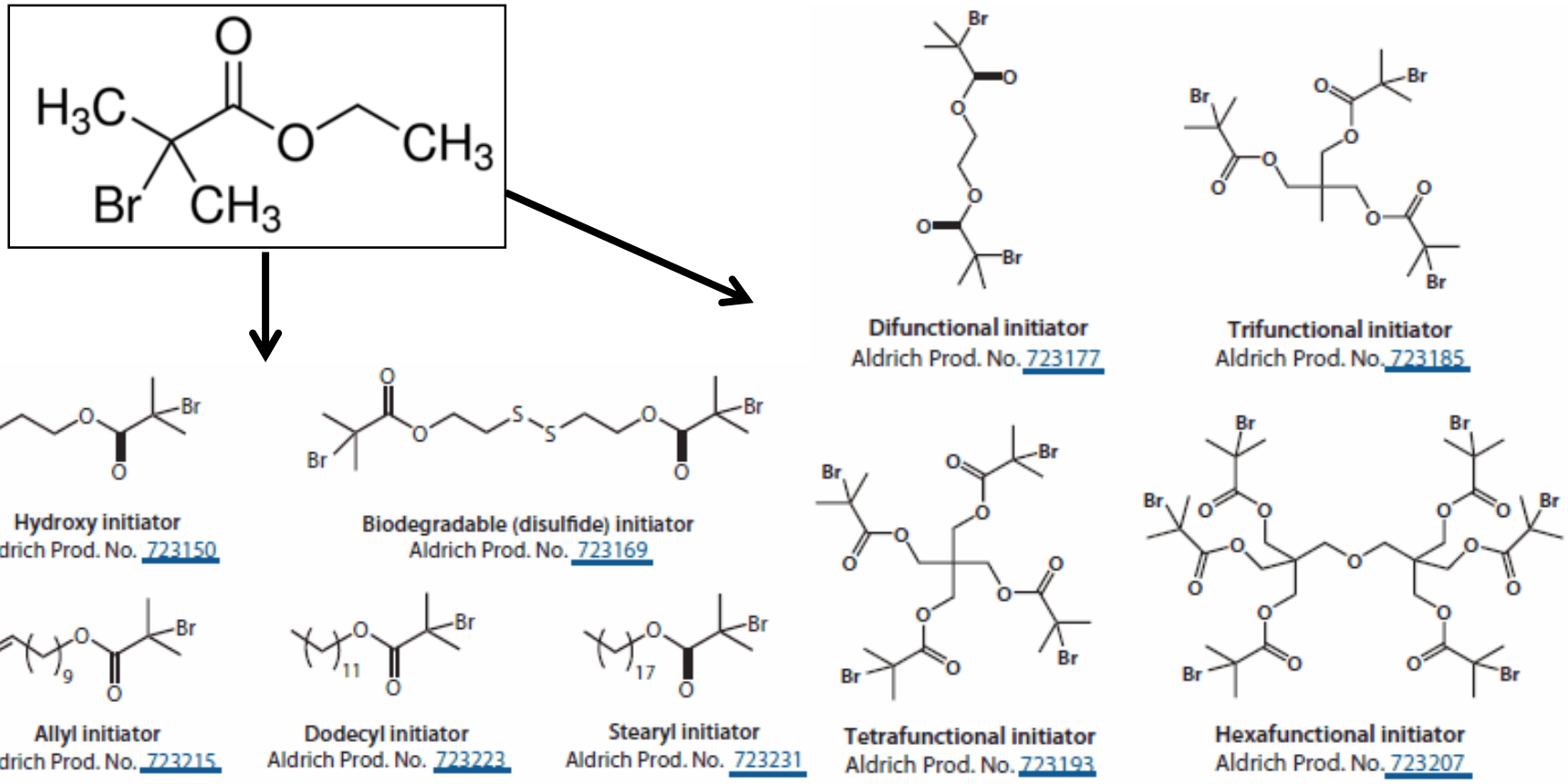


Figure 1. Dependence of molecular weights and polydispersities on conversion in bulk polymerization of styrene at 130 °C with $[1\text{-PECl}]_0 = 0.1$ mol/L, $[CuCl]_0 = 0.1$ mol/L, $[bpy]_0 = 0.3$ mol/L.

Matyjaszewsji, JACS 1995, 117, 5614

Commercial initiators based on EBiB

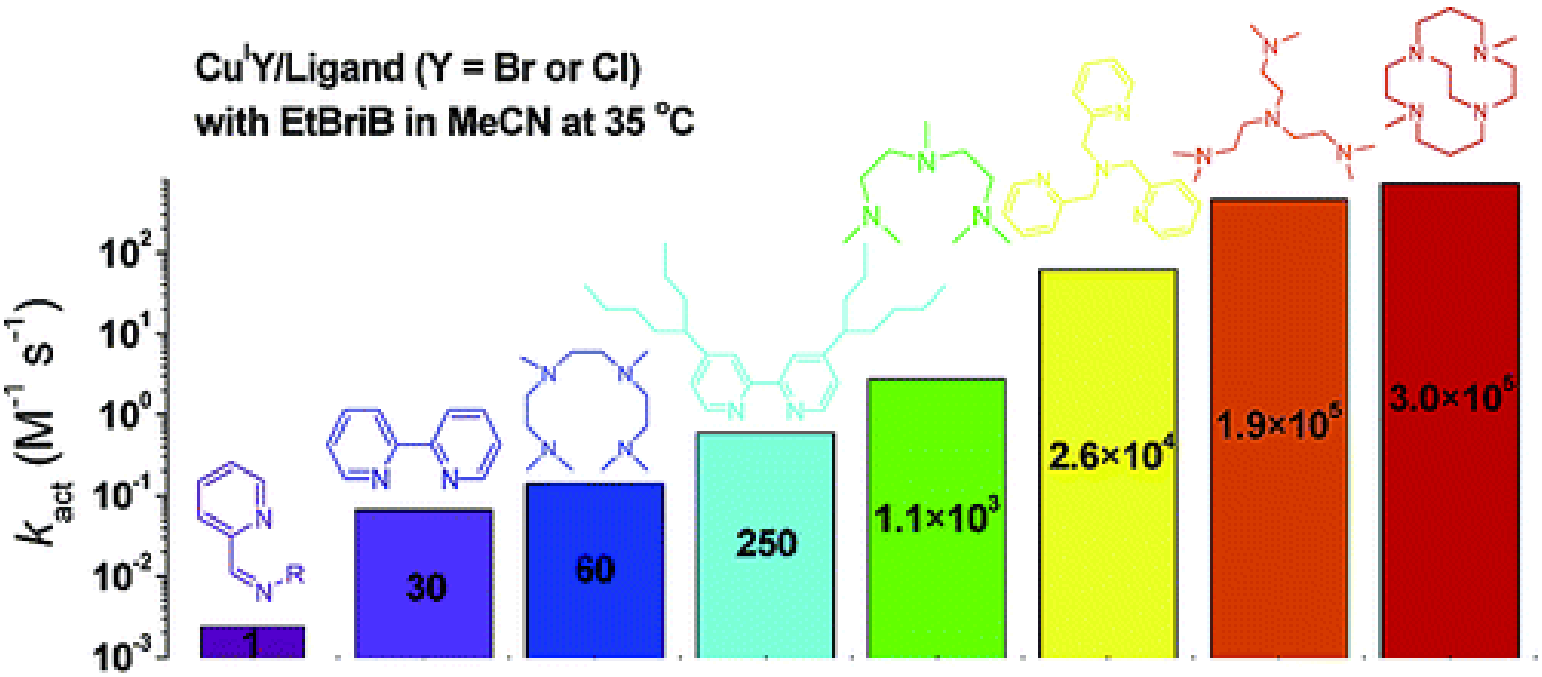
ATRP initiators based on Ethyl α-bromoisobutyrate (EBiB)



http://www.sigmaaldrich.com/materials-science/material-science-products.html?TablePage=111766260

Ligands for ATRP

The structure of ATRP ligands controls concentrations of active and dormant species

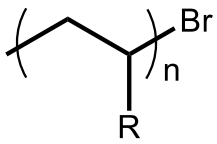


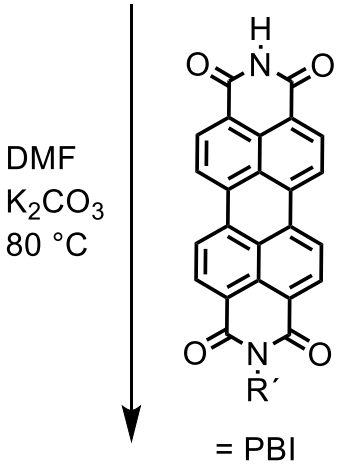
Tang, Matyjazewski, *Macromolecules*, 2006, 39 (15), pp 4953–4959

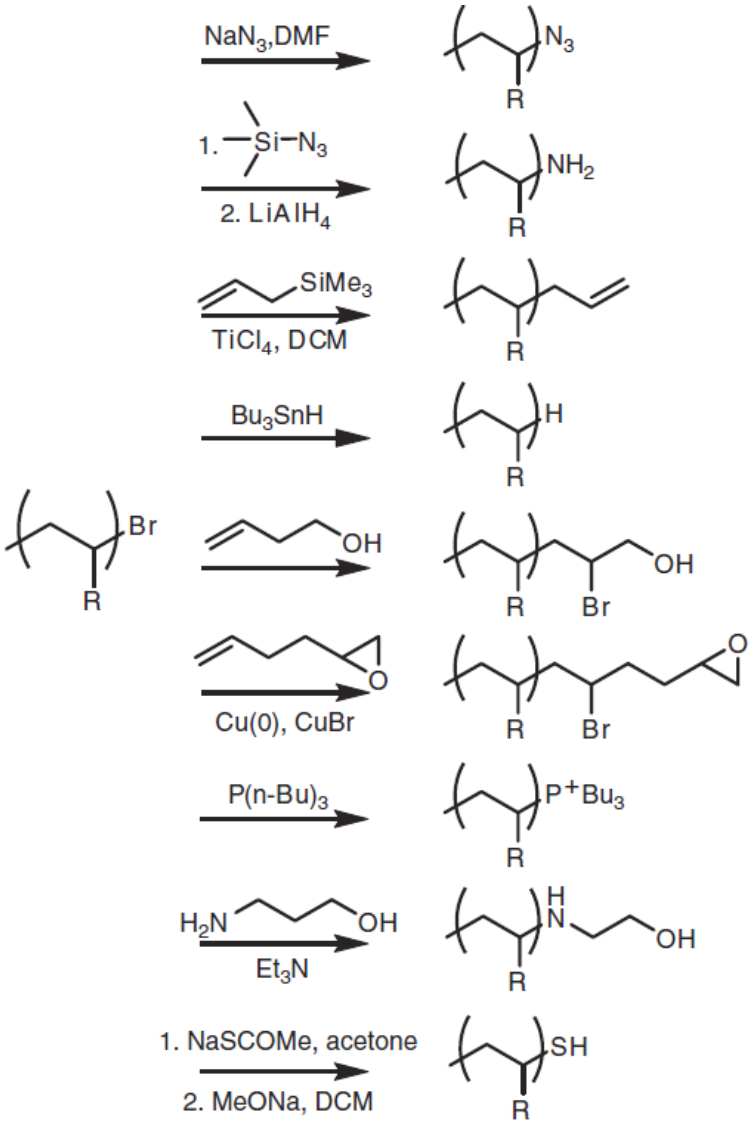
End group modification of ATRP polymers

End group functionalization of Bromide-terminated polymers made by ATRP

dye labelling



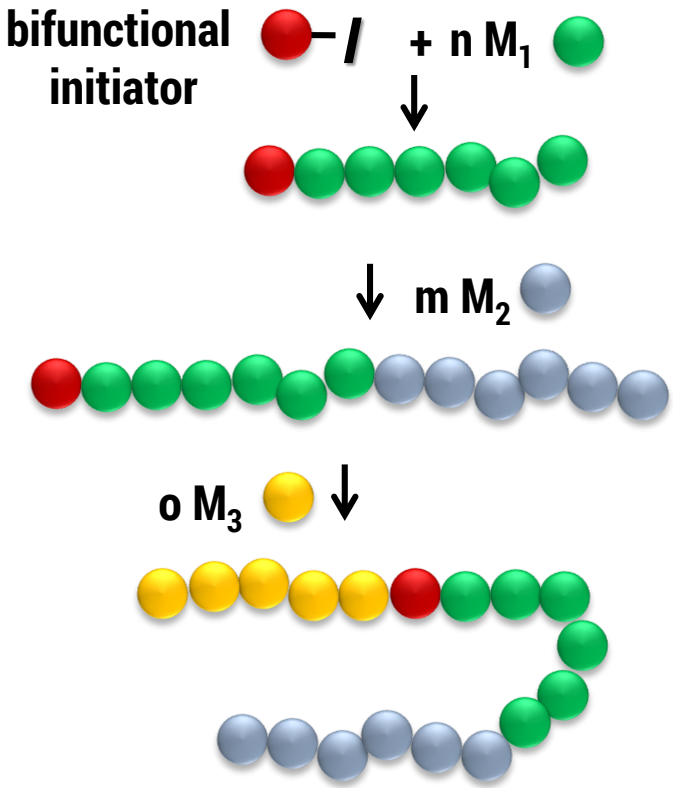


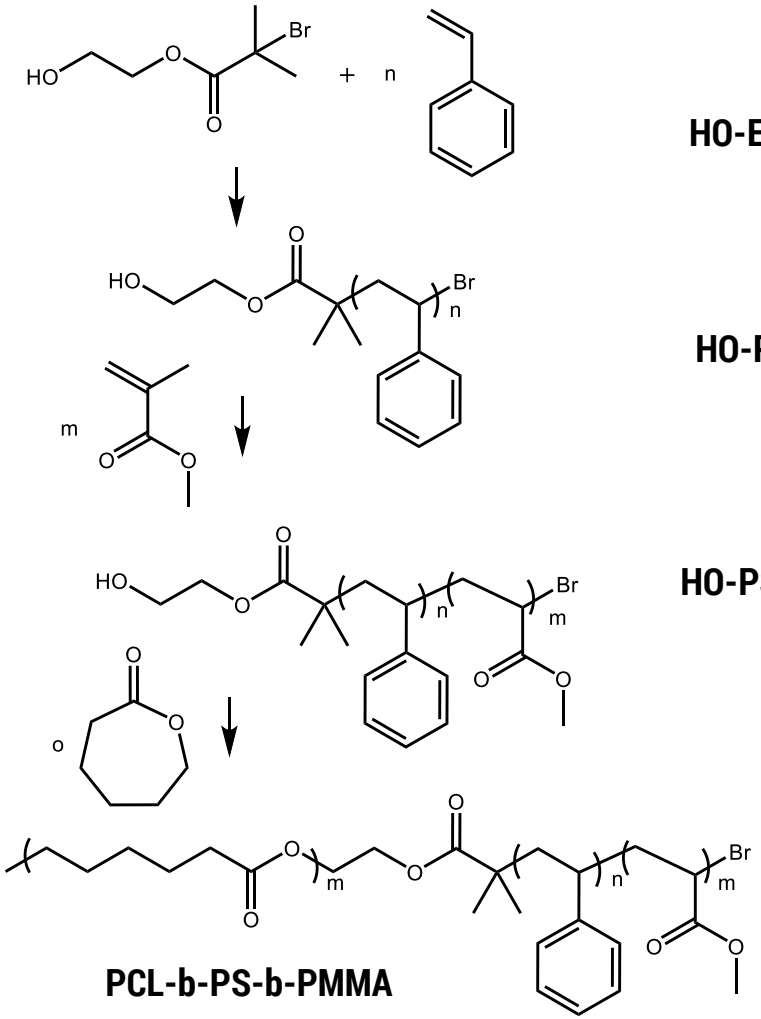


Polym Int 2014; **63**: 803–813

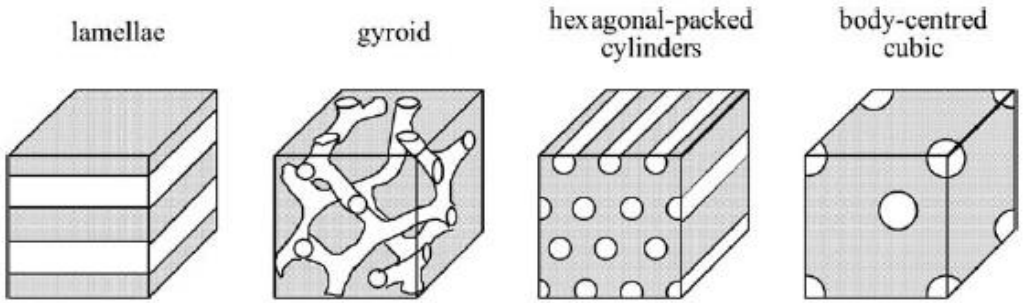
Advantages and possibilities of controlled radical polymerization

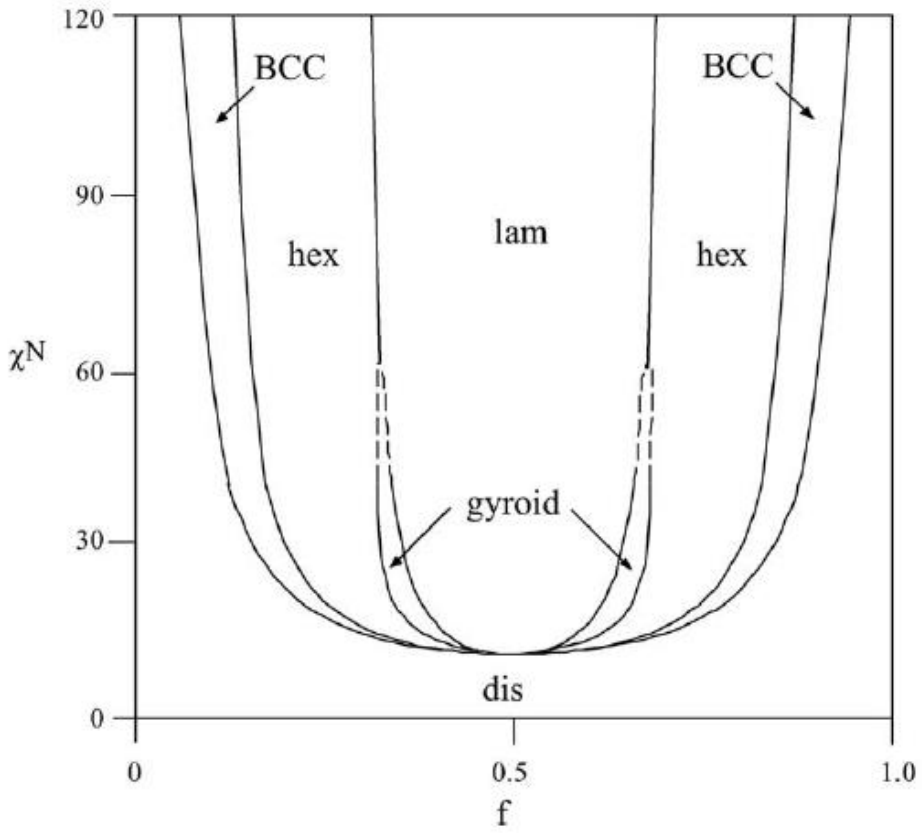
Quantitative end group functionalization enables block copolymer synthesis
Example: Triblock terpolymer synthesis using HO-EBiB and ATRP





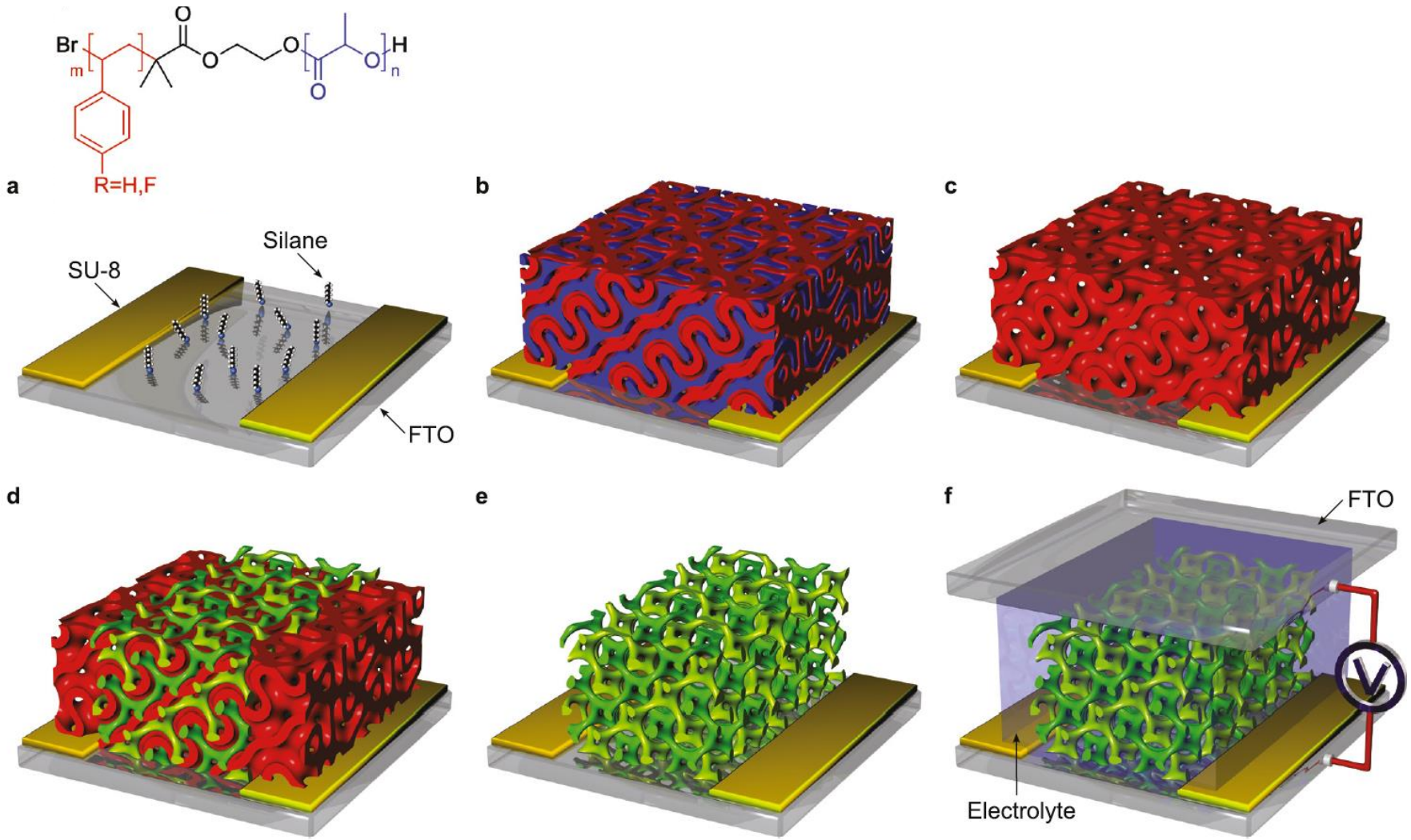
Microphase separation of block copolymers





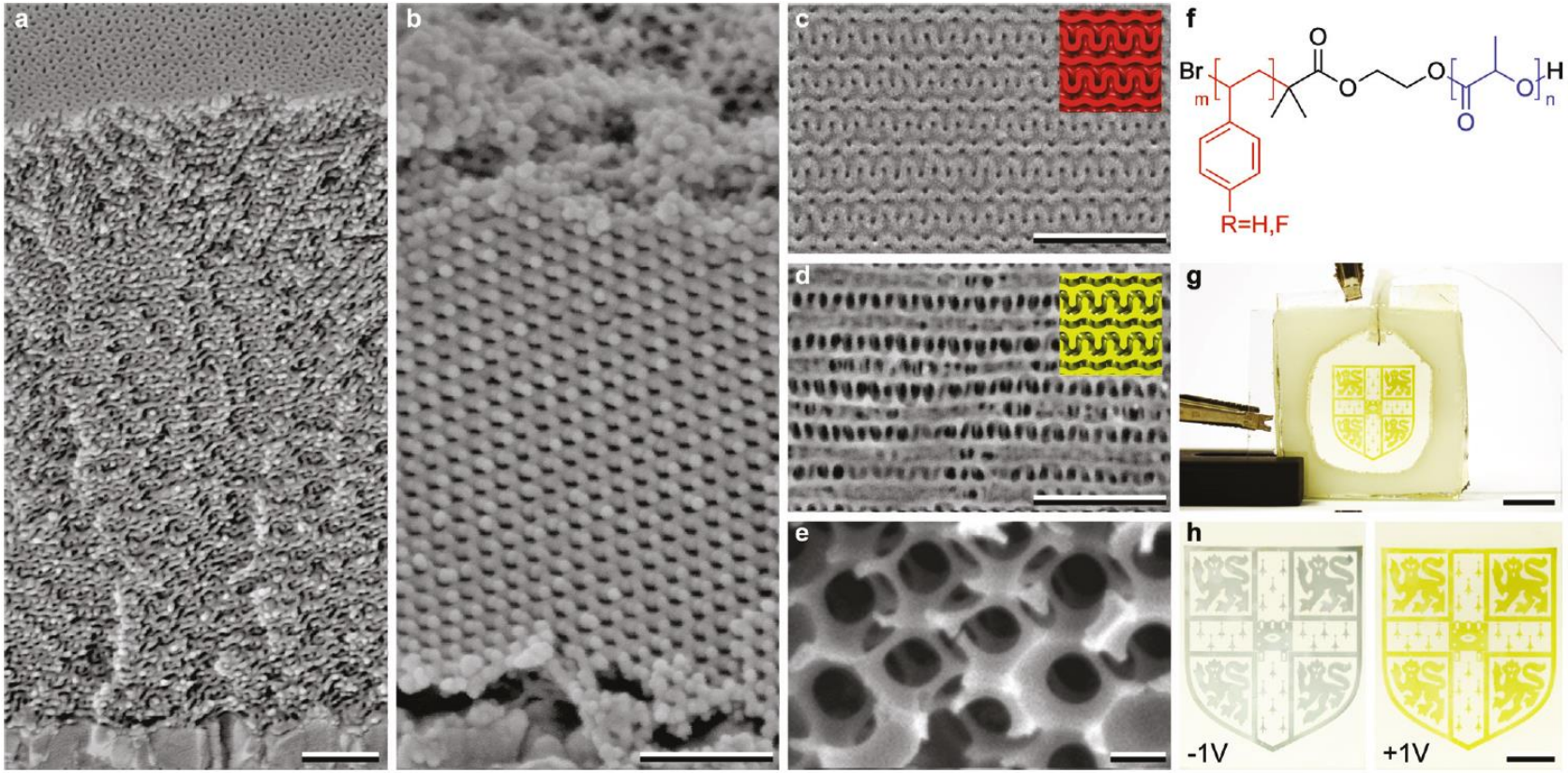
I.W. Hamley et al.
Curr. Op.
Solid State &
Mater. Sci.
8 (2004) 426–438

Sacrifical block copolymer templates based on gyroidal PFS-b-PLA



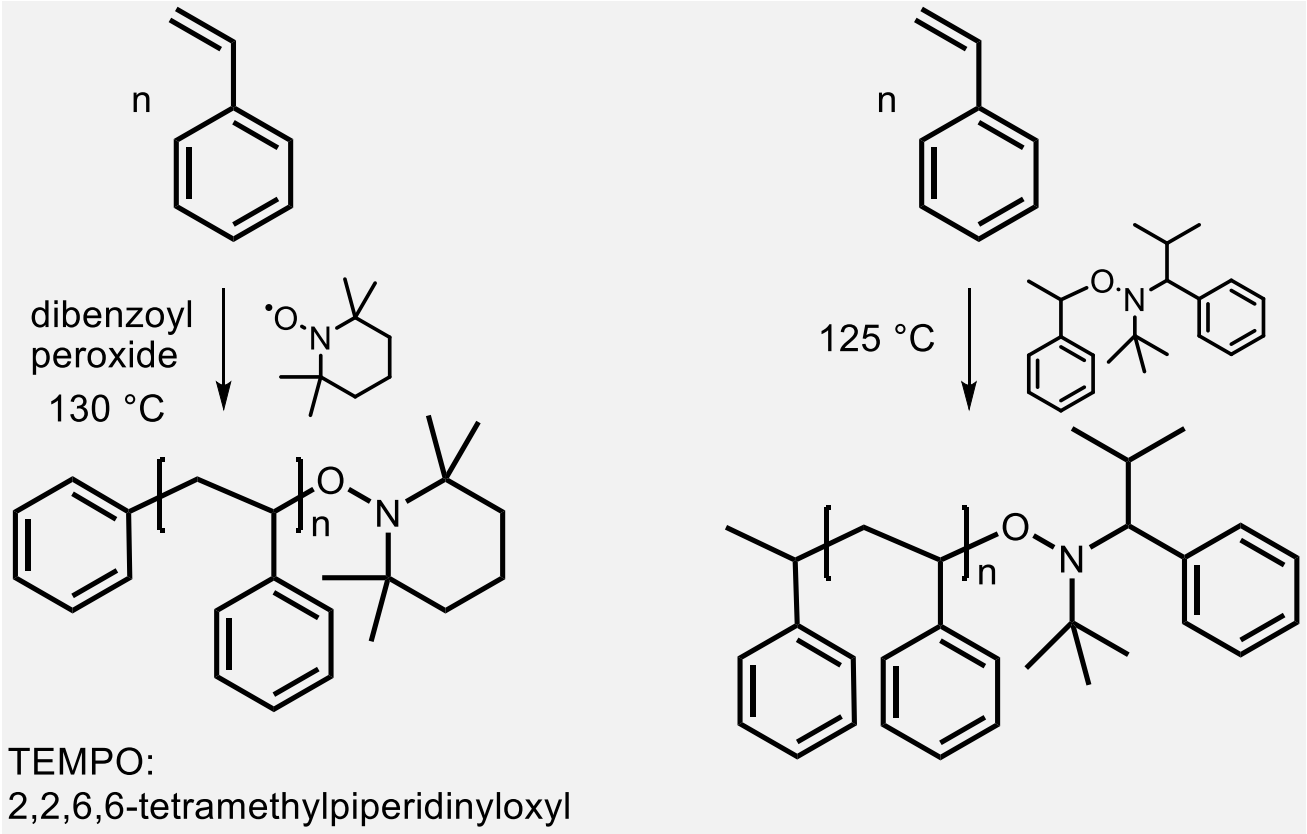
Scherer et al. Adv. Mater. 2012

Sacrifical block copolymer templates based on gyroidal PFS-b-PLA



Scherer et al. Adv. Mater. 2012

Nitroxide mediated polymerization NMP

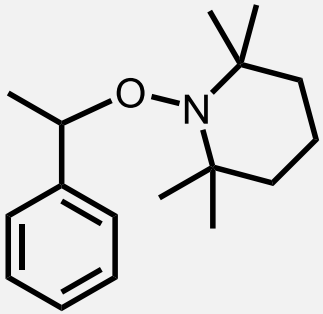


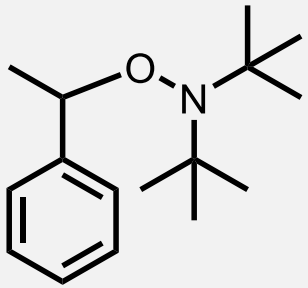
- C-O Bond thermally unstable → equilibrium between two radicals and covalently attached nitroxide
- Nitroxide stable enough to not initiate polymerization, but recombination with growing chain possible
- Two component initiator system (free radical initiator + nitroxide) or unimolecular alkoxyamines

Georges et al, *Macromolecules* 1993,26, 2987-2988

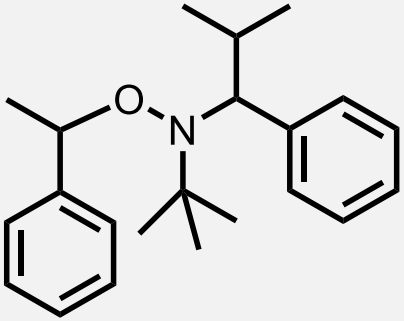
Alkoxamines as uniumolecular initiators

TEMPO-based



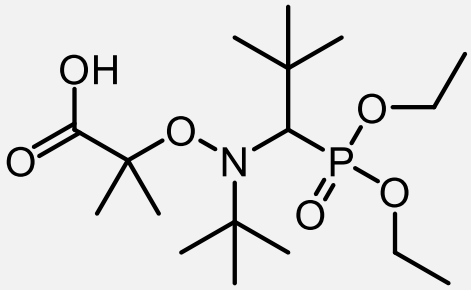


TIPNO-based



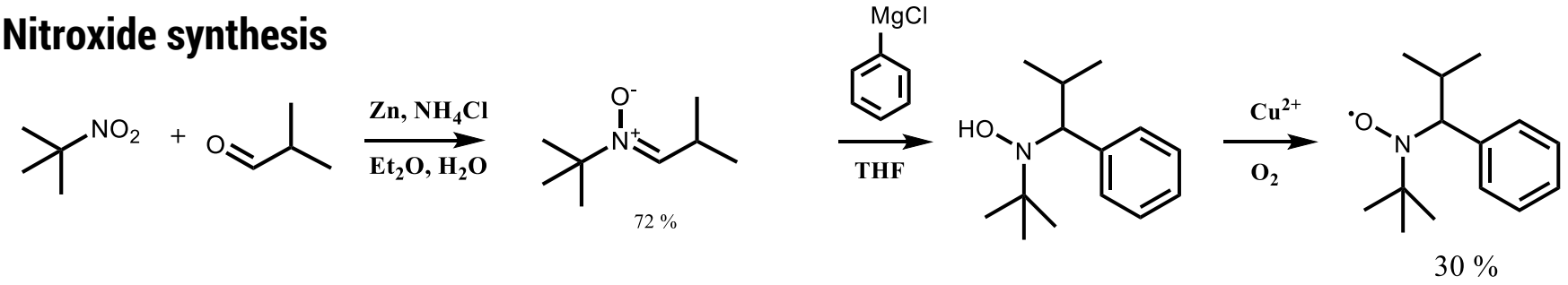
2,2,5-Trimethyl-4-phenyl-
3-azahexane-3-nitroxide

water soluble

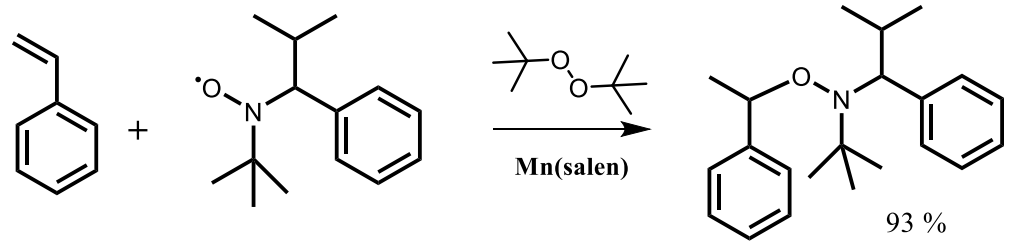


Alkoxamine synthesis

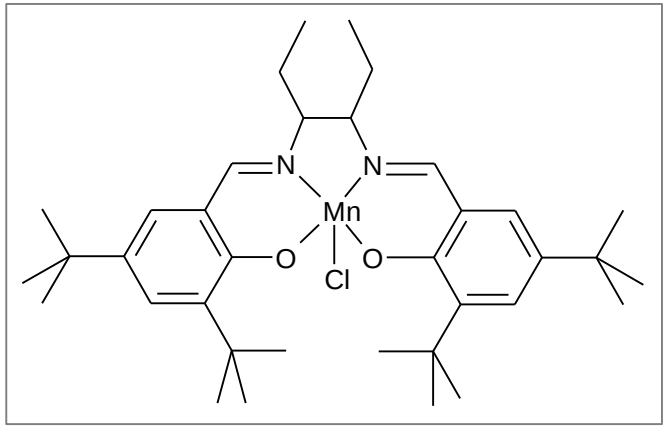
Nitroxide synthesis



Alkoxamine synthesis



2,2,5-Trimethyl-3-
(1-phenylethoxy)-
4-phenyl-3-azahexane



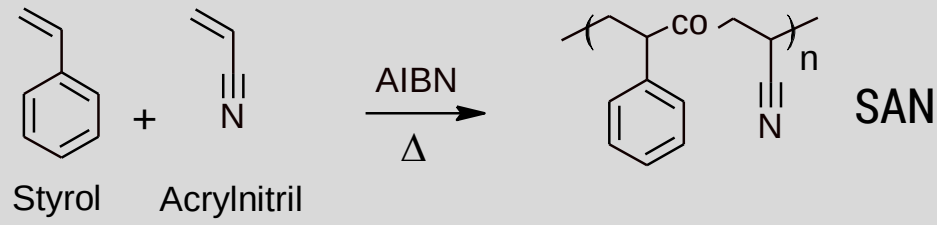
Mn(salen) „Jacobsen kat“

Hawker et al, *JACS* **1999,** *121,* 3904

RAFT: Reversible Addition-Fragmentation Chain Transfer Polymerization

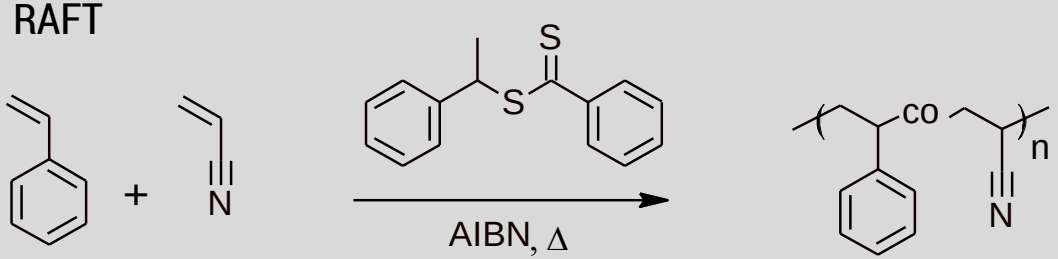
Aim: radical polymerisation with controlled character using RAFT
Idea: free radical polymerisation in the presence of dithioester

Free radical

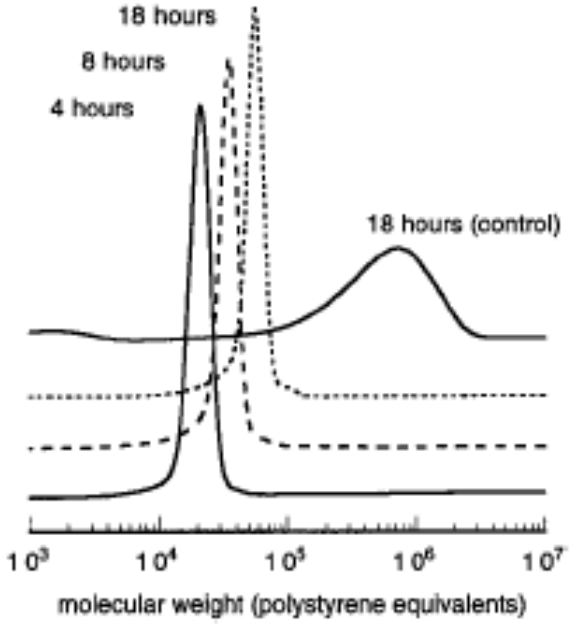


Styrol Acrylnitril

RAFT



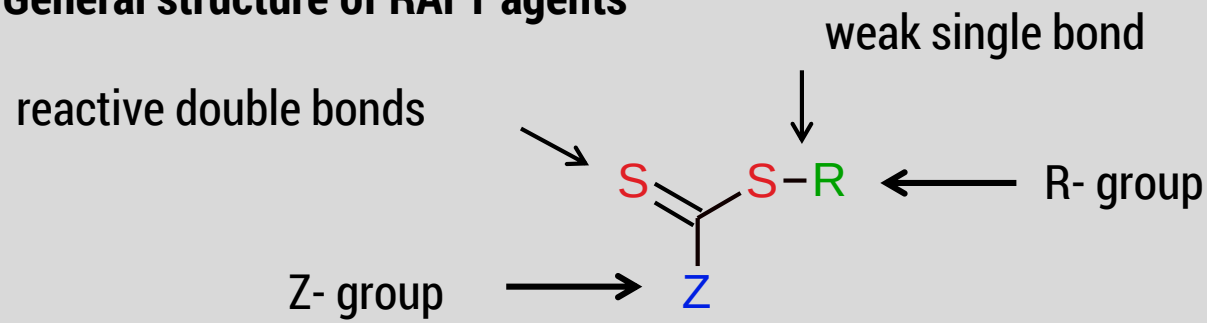
SEC

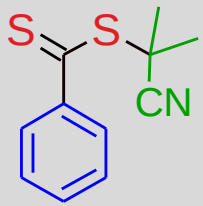


Chiefari et al., *Macromolecules*, **1998**, *31*, 5559

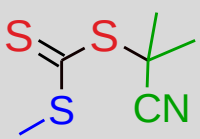
RAFT: Reversible Addition-Fragmentation Chain Transfer Polymerization

General structure of RAFT agents

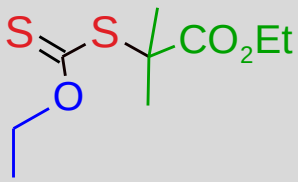




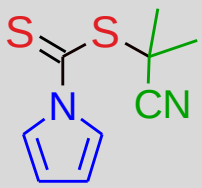
Dithioester



Trithiocarbonate



Xanthogenate

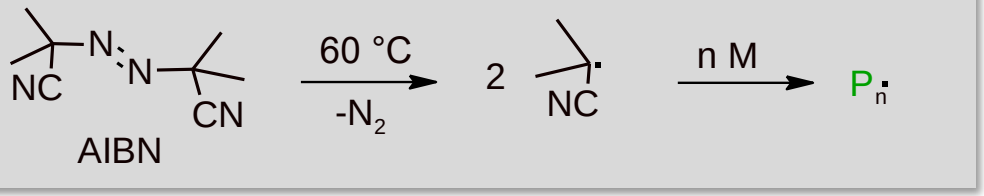


Dithiocarbamate

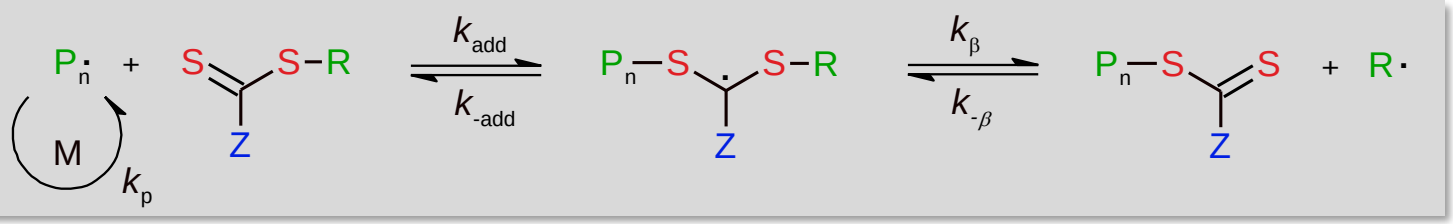
Barner-Kowollik, Perrier, J. Polym. Sci. Polym. Chem. 2008, 46, 5715

The RAFT mechanism

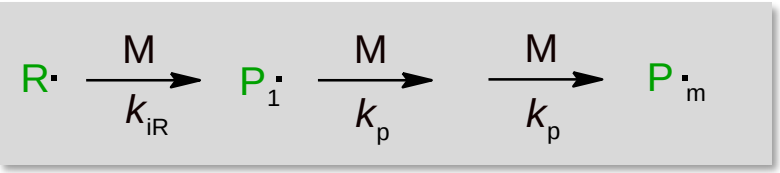
1. Initiator decomposition and initiation



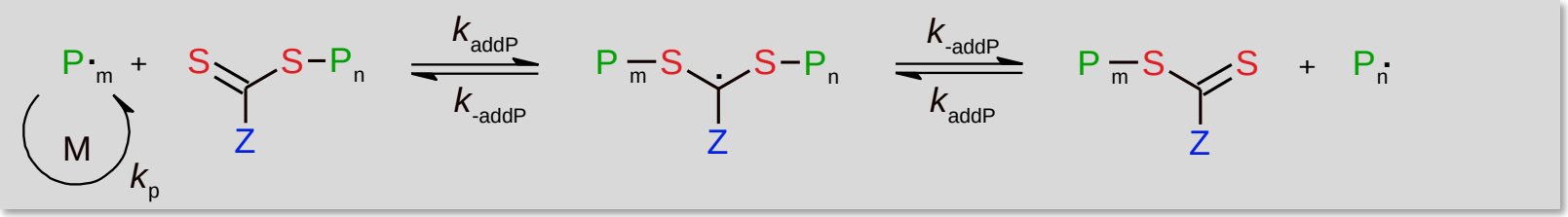
2. Pre-equilibrium



3. Re-Initiation

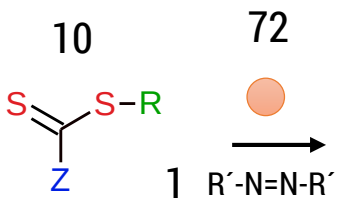


4. Main equilibrium



End group functionalization

End groups of Macro-RAFTs for [M]/[RAFT]/[I]=72/10/1



8 RAFT chains

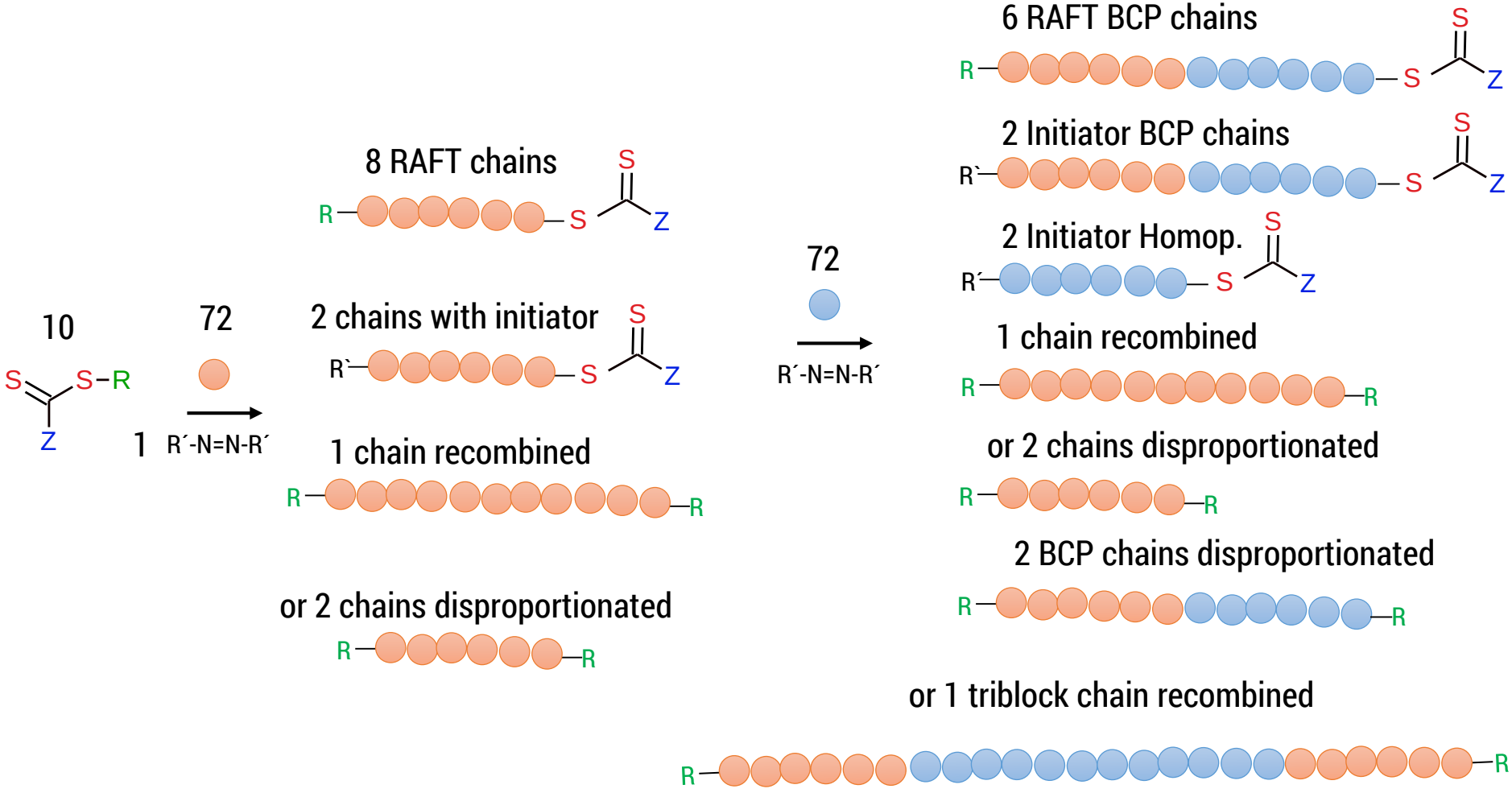
2 chains with initiator

1 chain recombined

or 2 chains disproportionated

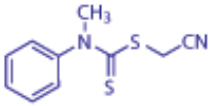
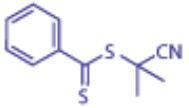
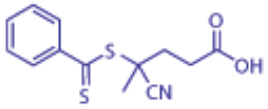
Keddie, *Chem. Soc. Rev.* **2014**, 43, 496

Block copolymer synthesis via RAFT



Keddie, *Chem. Soc. Rev.* **2014**, 43, 496

Optimal choice of RAFT reagent

	styrenes	acrylates	acrylamides	methacrylates	methacrylamides	vinyl esters	vinyl amides
	—	—	—	—	—	+++	+++
	+++	+++	+++	—	—	—	—
	++	+	—	+++	+++	—	—
	++	+	+	+++	+++	—	—
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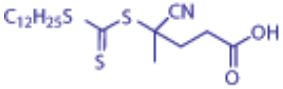
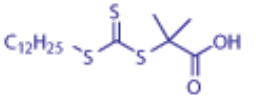
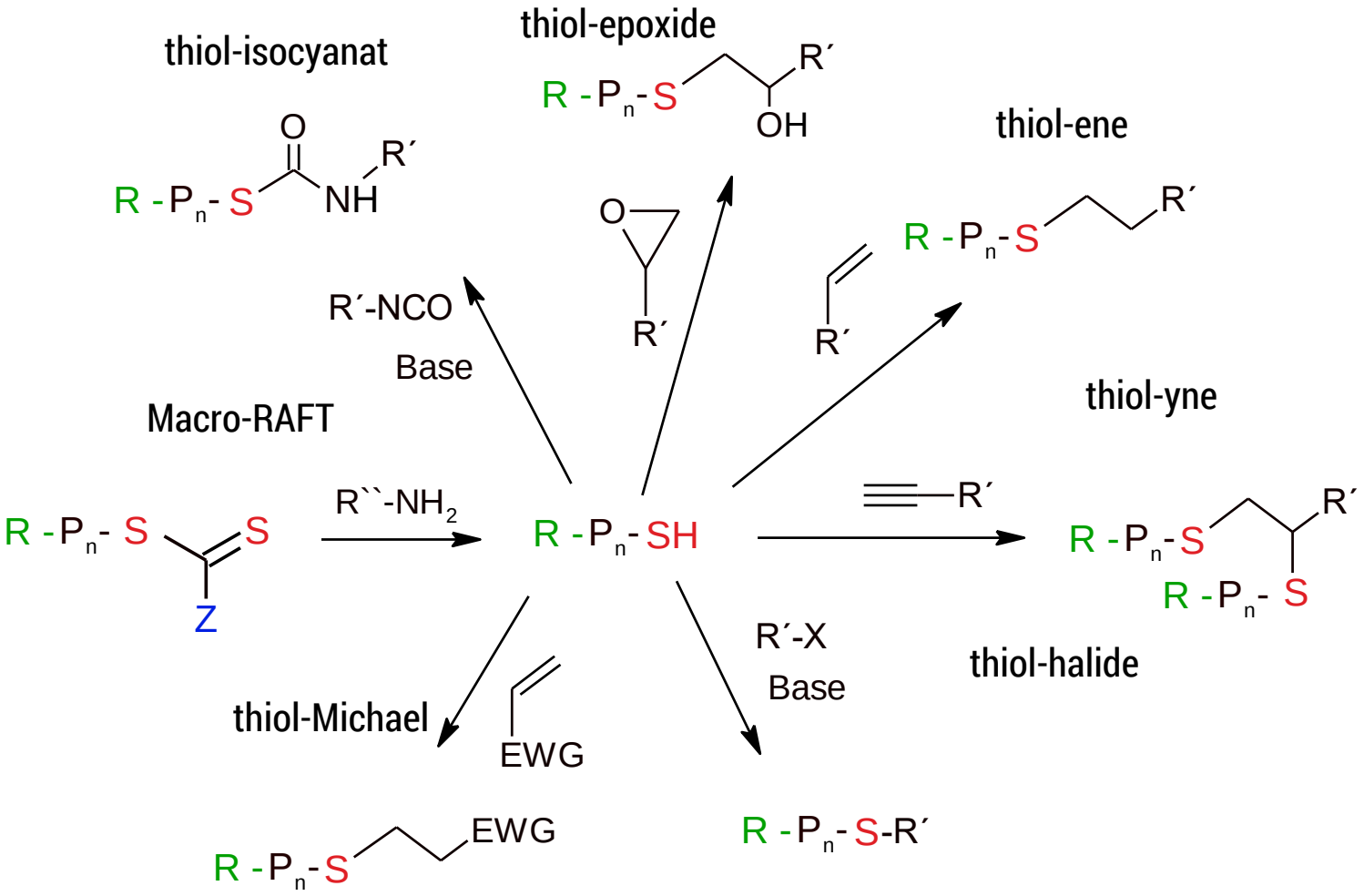
	+++	++	++	+++	+++	—	—
	+++	+++	+++	+	+	—	—

http://www.sigmaaldrich.com/materials-science/polymer-science/raft-polymerization.html

Post-functionalization and polymer analogous reactions



Comparison ATRP – NMP - RAFT

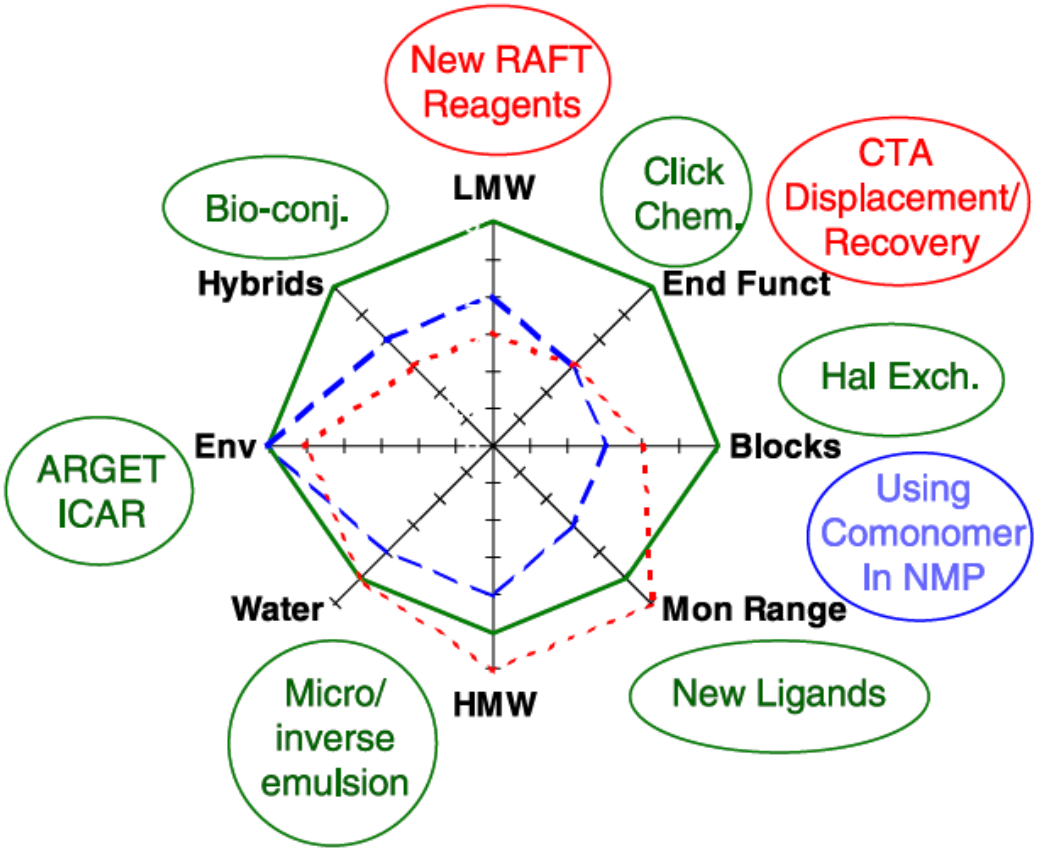
Vorteile RAFT:

- Keine Metalle
- Mildere Bedingungen
- Breite Monomerauswahl
- Hohe Molmassen

Nachteile RAFT:

- Farbige Polymere
- Licht- und wärme-empfindliche Polymere
- Geruchsintensive Nebenprodukte

Vergleich mit ATRP und NMP:



Braunecker et al., Progress Polym. Sci. **2007**, *32*, 93