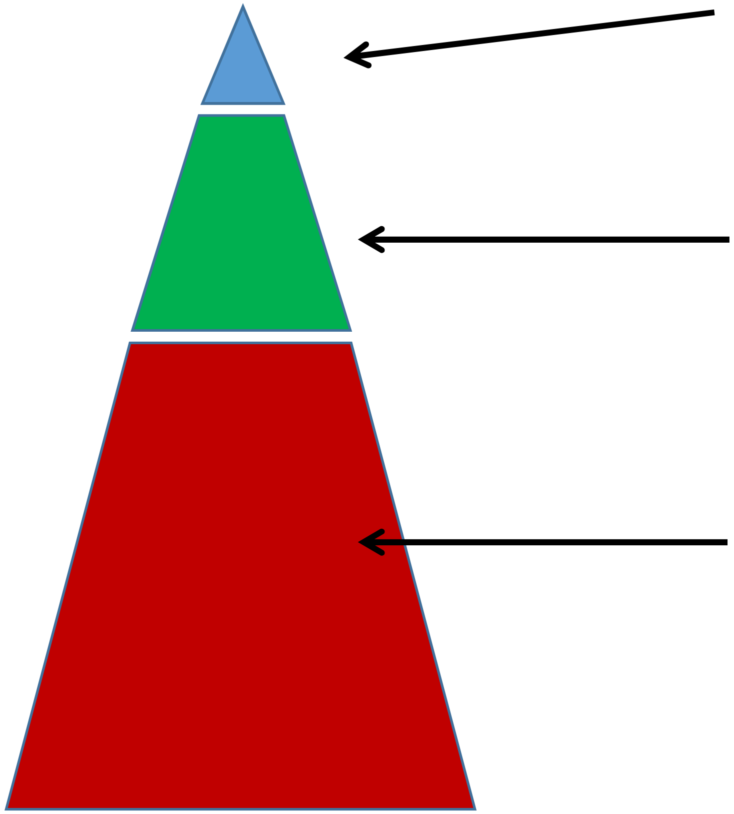
Synthetic methods in chemistry

Polymers made by radical polymerisation

Content

- Relevance and typical examples of polymers made by free radical polymerization (FRP)
- General aspects
- Elementary steps
- Monomer range
- Norrish-Trommsdorff-effect (gel effect)
- Technical processes
- Controlled radical polymerization (CRP)

Relevance of free radical polymerization (FRP)

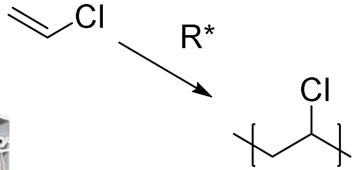


< 1% Hochleistungs-Kunststoffe
„High Performance Polymers“
PEEK, **F-Polymere**, LCP, PPS, PEI, PES

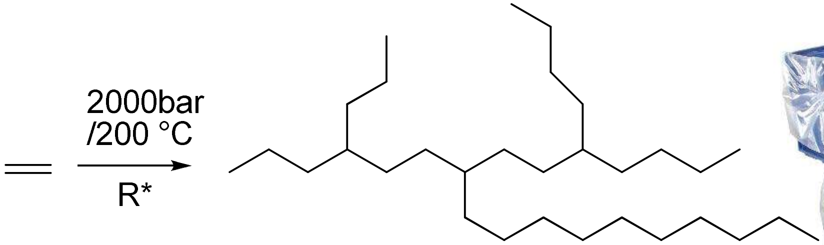
ca. 16% Technische Kunststoffe
„Engineering Plastics“
PC, **ABS**, **SAN**, **HIPS**, PP, **PMMA**, PA, PBT

84 % Standardkunststoffe
„Commodities“
Polyethylen PE (HDPE, **LDPE**, LLDPE)
Polypropylen PP
Polystyrol PS
Polyvinylchlroid PVC
Polyethylenterephthalat PET

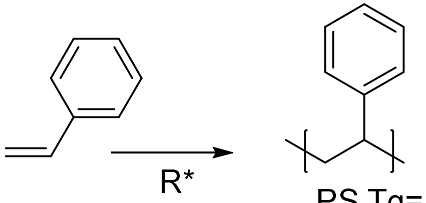
Industrial polymers made by FRP



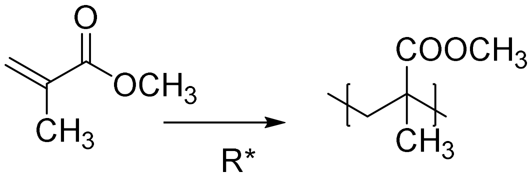
PVC
Tg=78°C



LDPE
(Low Density Polyethylene)
120°C < Tm < 80°C

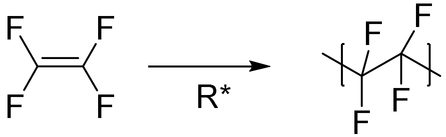


PS Tg=100°C

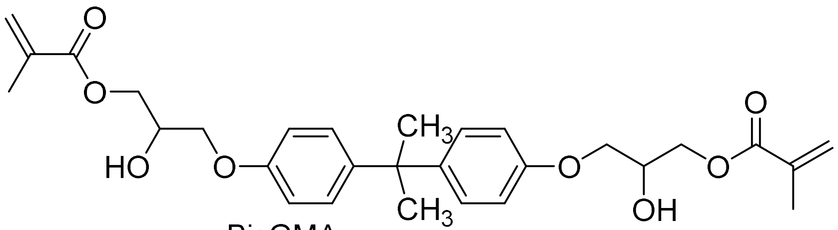


PMMA
Plexiglas
Röhm

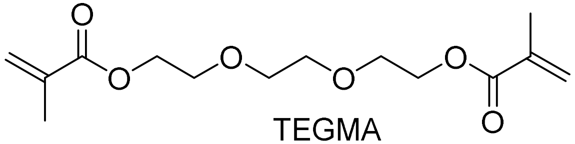
Tg=108



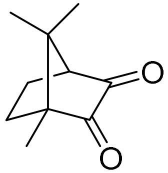
PTFE

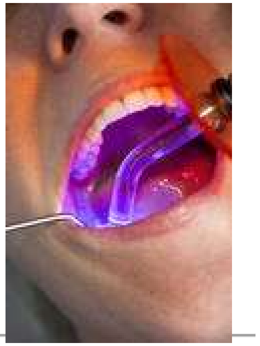


BisGMA



TEGMA



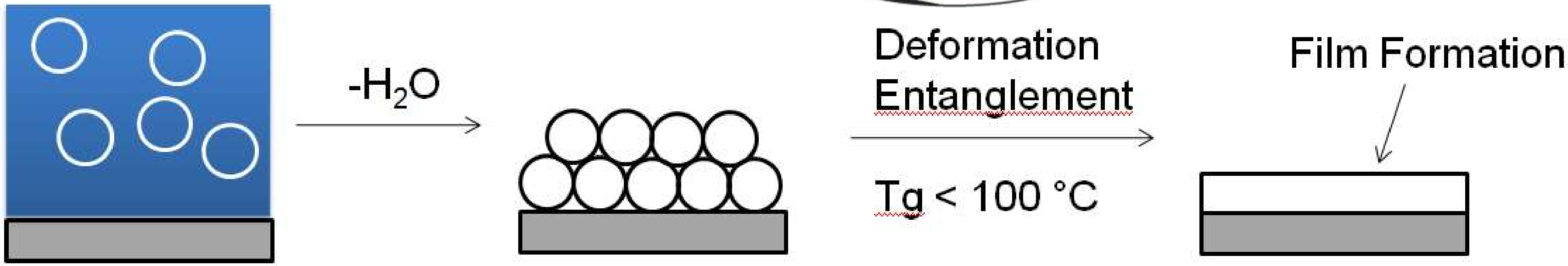


Emulsions and water-borne coatings

Emulsion Polymers

- **Systems:**
  - styrene, butadiene
  - VC-, acrylate-, vinylacetate-Copolymers

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



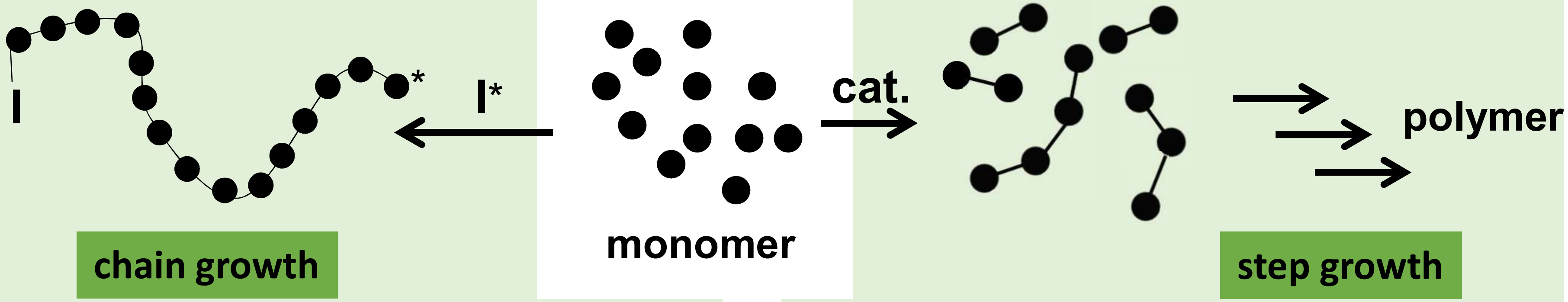
$-H_2O$

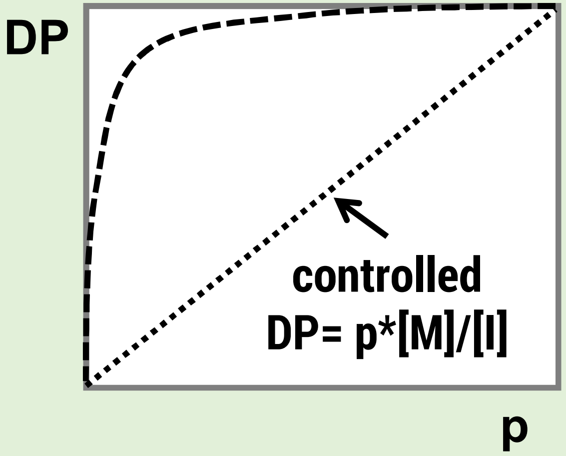
Deformation
Entanglement

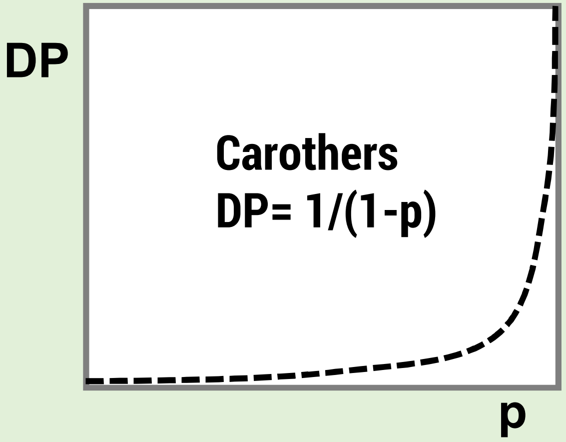
Tg < 100 °C

Film Formation

FRP is a chain growth process







- High molar mass for low conversion
- Kinetics: d[M]/dt, dilatometry, gravimetry
- Variants: **radical**, ionic, catalytic

- High molar mass only for high p
- Kinetics: end group titration, NMR
- Polycondensation, polyaddition

Elementary steps of FRP

1) Initiator dissociation

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

2) Initiation

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

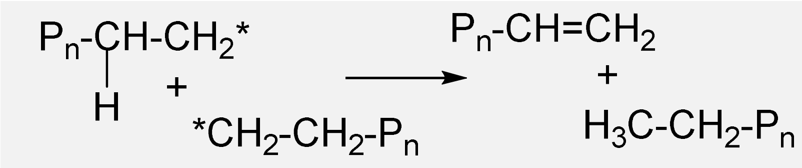
3) Propagation

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

4) Termination

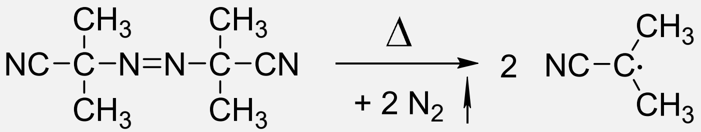
$$R\text{-}M_n^* + {}^*M_m\text{-}R \xrightarrow{k_t} R\text{-}M_{n+m}\text{-}R$$ *recombination*

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

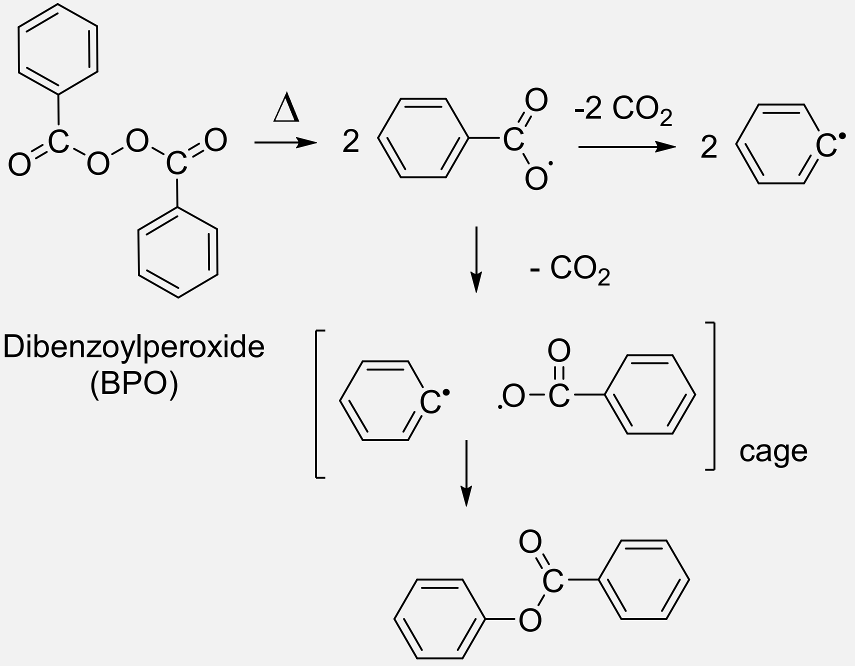


$$P_n\text{-}\underset{\substack{|\\H}}{C}H\text{-}CH_2^* + {}^*CH_2\text{-}CH_2\text{-}P_n \longrightarrow P_n\text{-}CH{=}CH_2 + H_3C\text{-}CH_2\text{-}P_n$$

Initiators



Azobisisobutyronitril (AIBN)



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

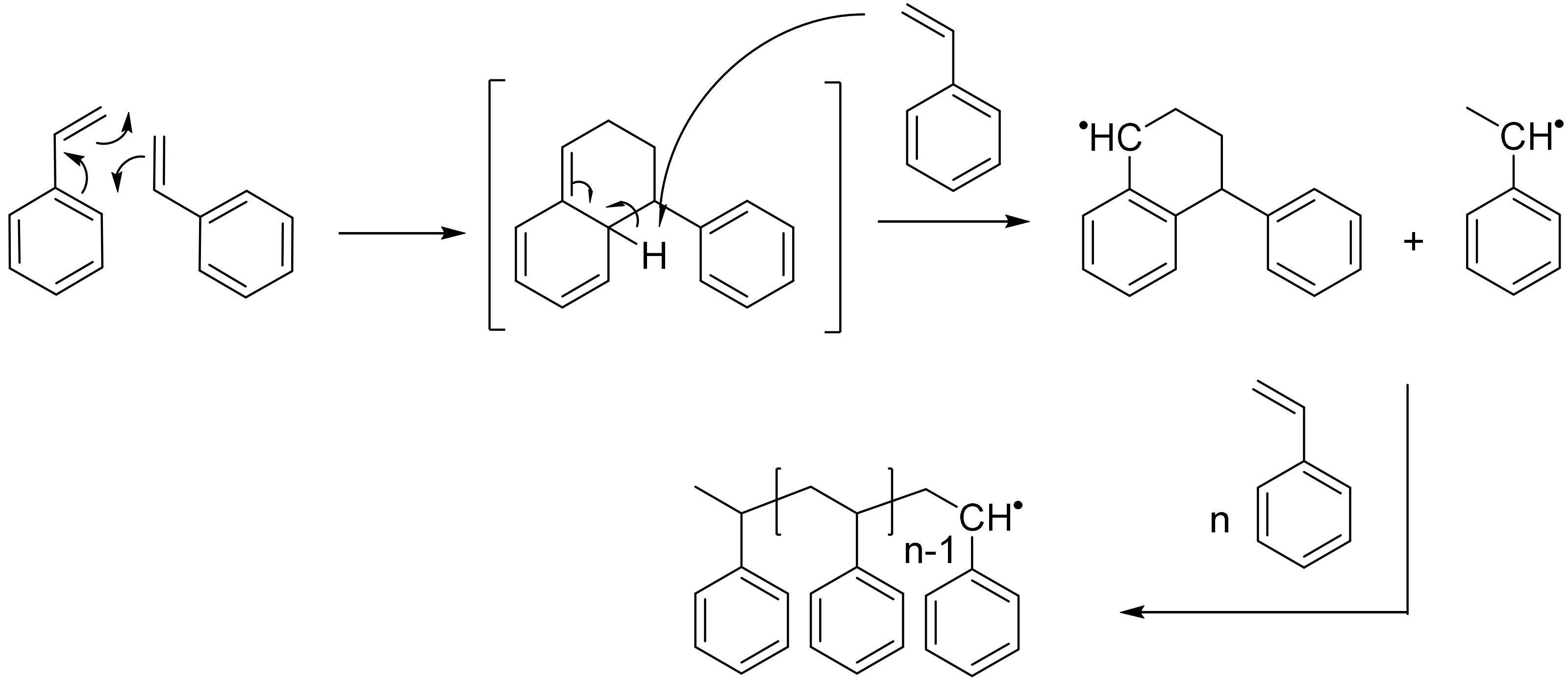
oxygen, peroxides, hydroperoxides, peracids, peroxodisulfates

Important parameters:

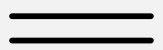
- Half-life (for one T)
- Radical efficiency **f** = 0 < f < 1
- (not all radicals start polymerization → cage effect!)

Auto-initiation of styrene

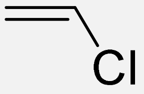
Thermally-initiated polymerizations: polymerization in the absence of initiators
- Impurities!
- Styrene and MMA show auto-initiation



Monomer range

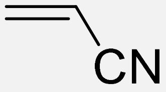


ethylene

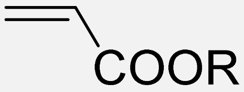


vinylchloride

vinylfluoride

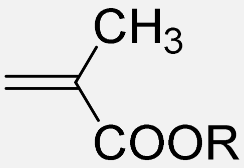


acrylnitrile

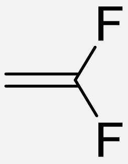


acrylates

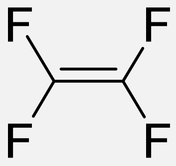
vinyl acetate



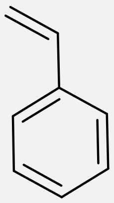
methacrylates



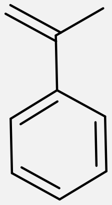
vinylidene fluoride



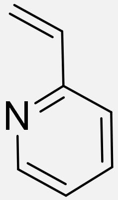
tetrafluoroethylene



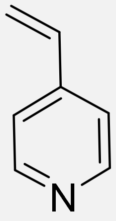
styrene



a-methylstyrene

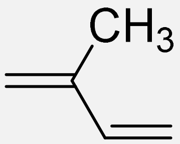


2-vinylpyridine

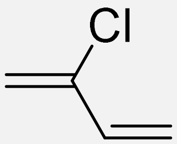


4-VP

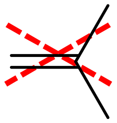
1,4 butadiene



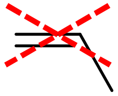
isoprene



chloroprene

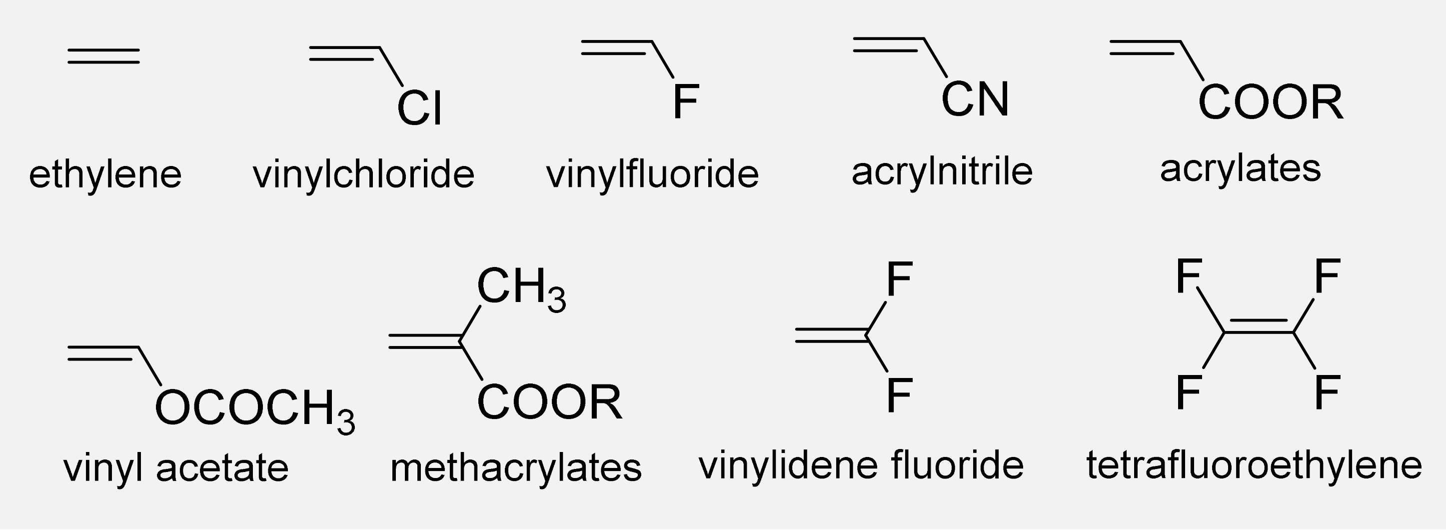


isobutylene



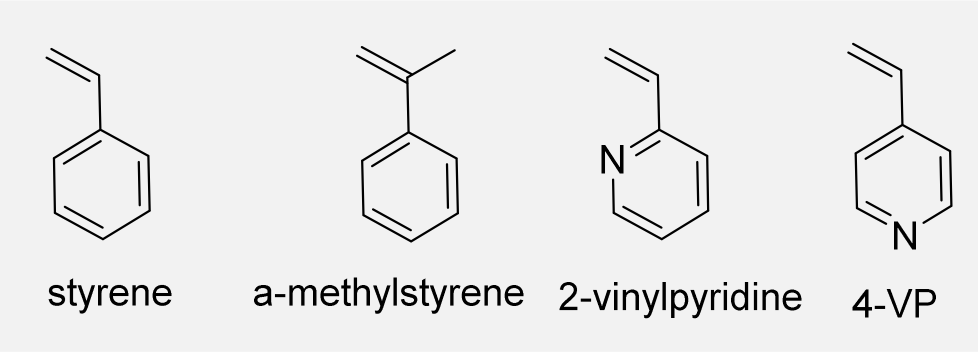
propene

Monomer range

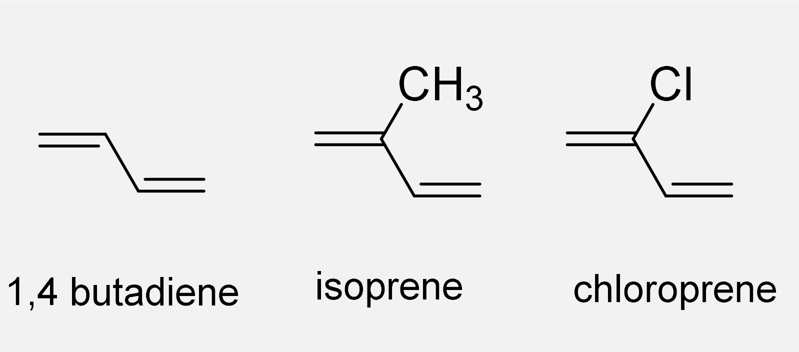


ethylene, vinylchloride, vinylfluoride, acrylnitrile, acrylates

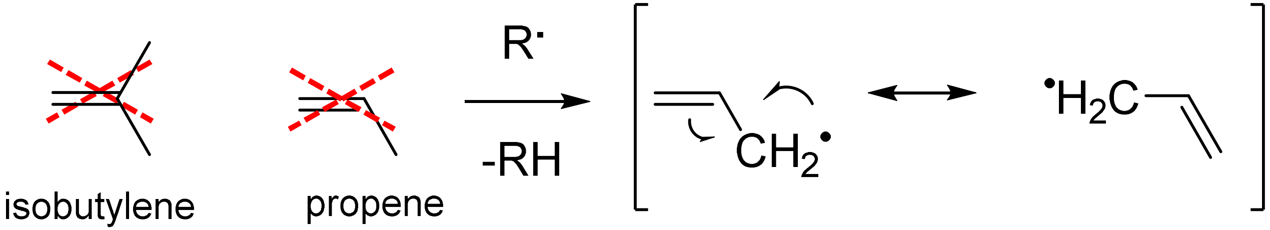
vinyl acetate, methacrylates, vinylidene fluoride, tetrafluoroethylene



styrene, a-methylstyrene, 2-vinylpyridine, 4-VP



1,4 butadiene, isoprene, chloroprene

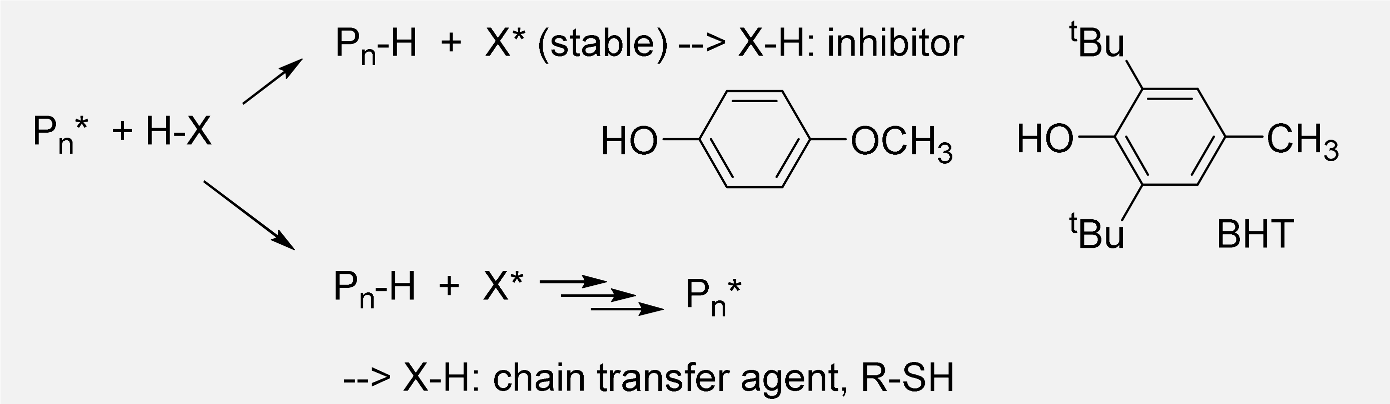


H radical abstraction leads to stable allyl radical

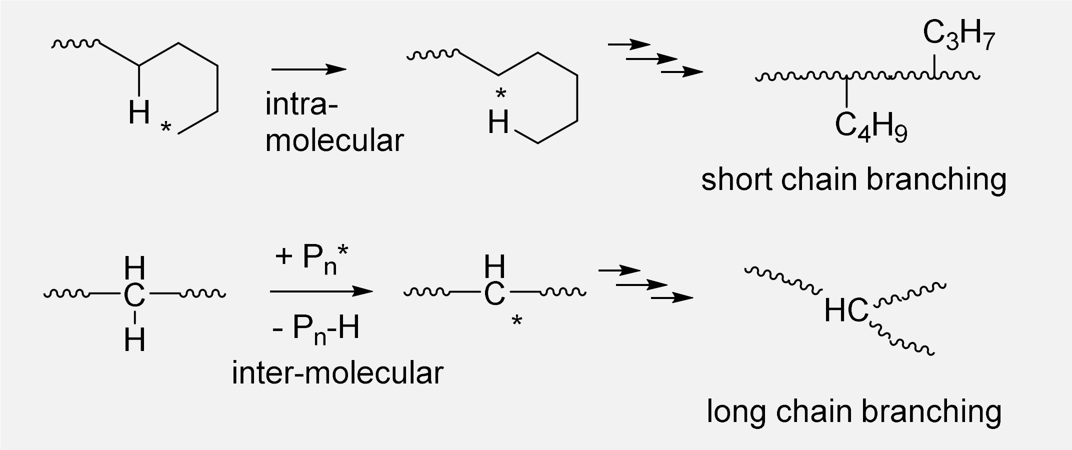
Chain transfer

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):



Trommsdorff-effect (gel effect)

bulk polymerization of MMA (Polymerisation in Masse)

solution polymerization of MMA in benzene

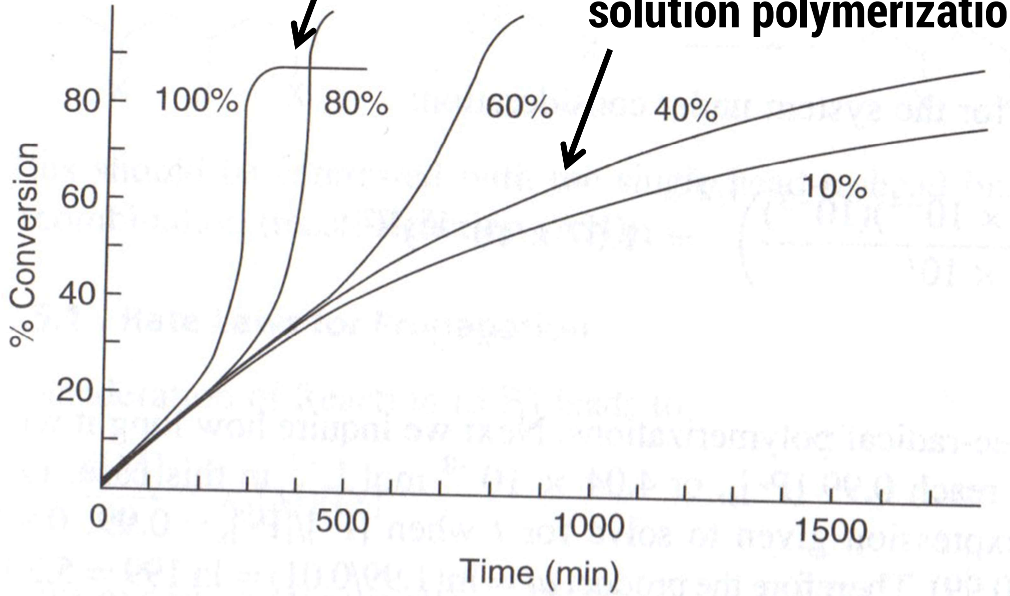
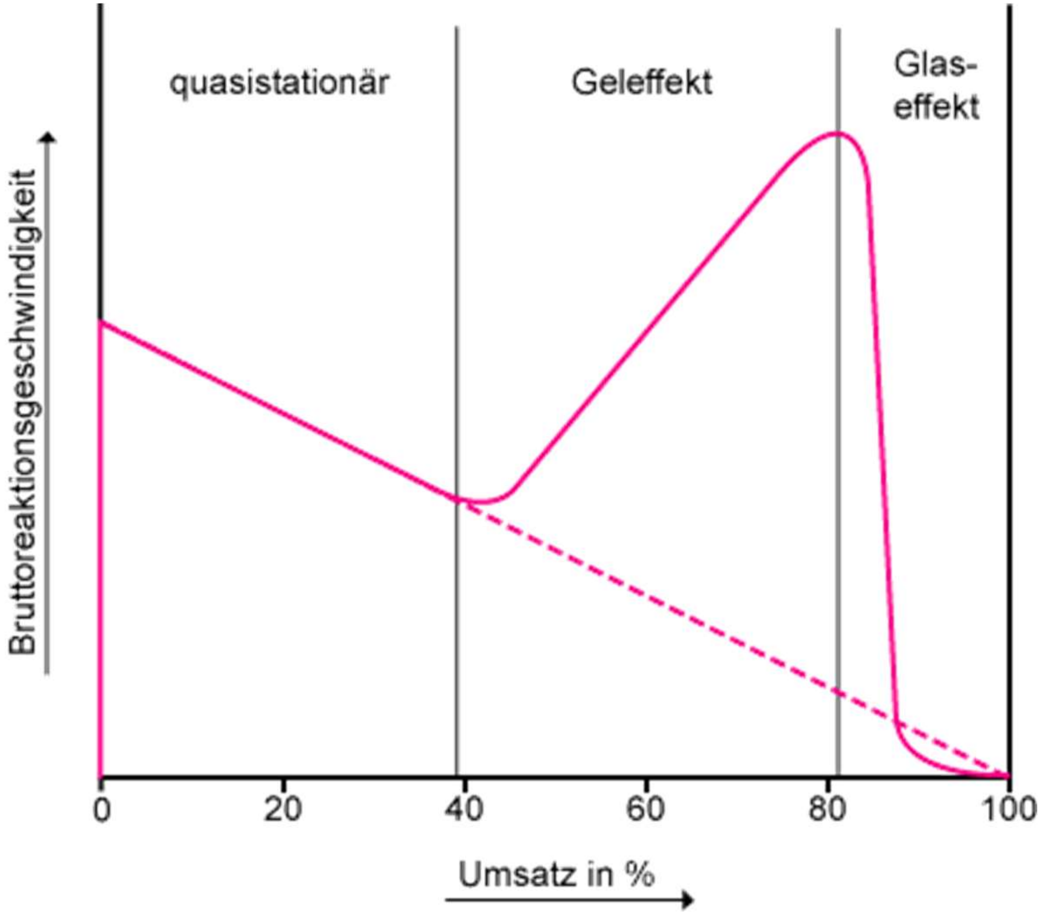


Figure 3.2 Acceleration of the polymerization rate for methyl methacrylate at the concentrations shown in benzene at 50°C. (Reprinted from Schulz, G.V. and Harborth, G., *Makromol. Chem.*, 1, 106, 1948. With permission.)

Lodge, p. 89

Trommsdorff-effect (gel effect, glas effect)



- quasi-stationary (Bodenstein) → $v_i = v_t$
- gel-effect (Trommsdorff): auto-acceleration due to reduced termination (diffusion of chains slows down) → $v_i > v_t$

  CAUTION: danger of explosion

→ Heat dissipation is a problem!

- glas effect: diffusion is further reduced until the reaction stops at p~80-90%

Reaction engineering

❖ **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

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

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

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

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

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

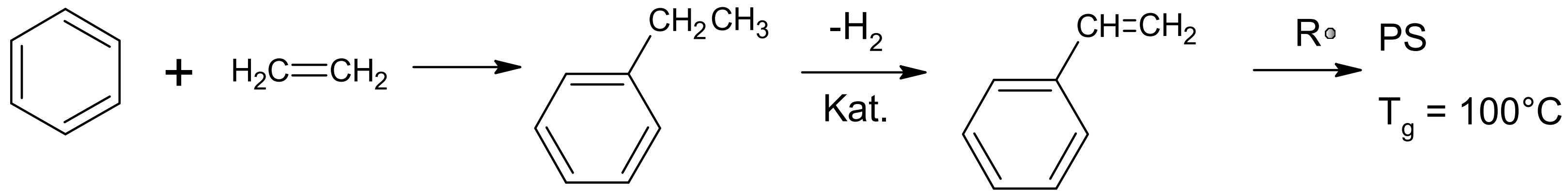
Technical processes of important polymers

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

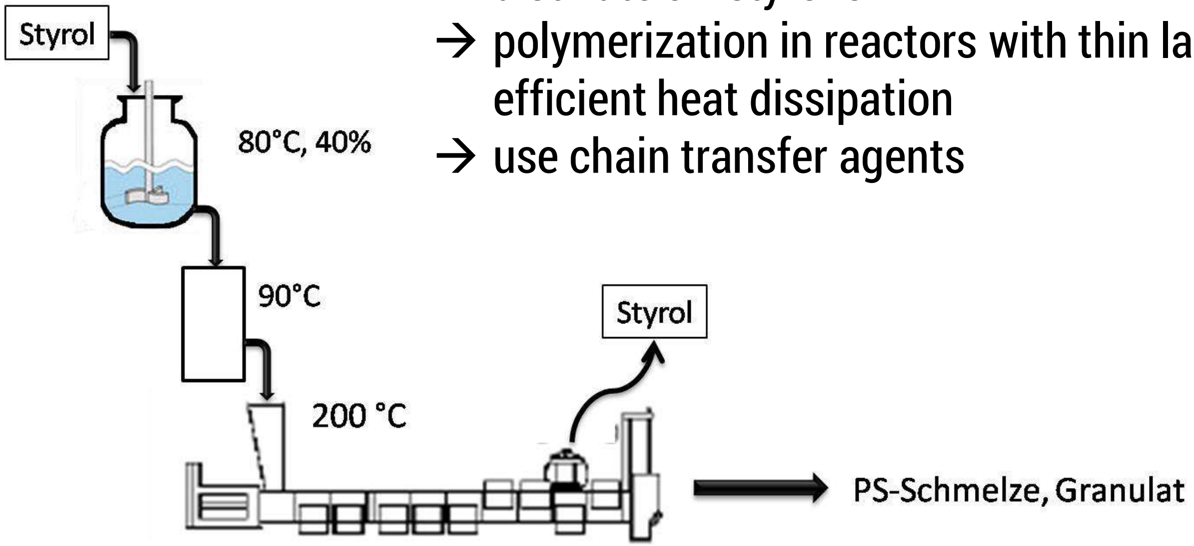
z: Ziegler-Natta, m: metallocene, r: radical, c: cationic, a: anionic

Industrial production of PS

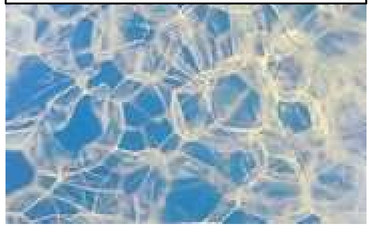


remember the Trommsdorff-effect for bulk polymerizations!

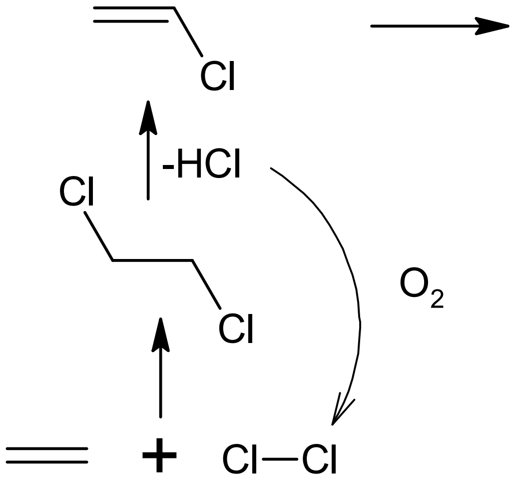
→ polymerize to low conversion ~40% and distillate off styrene
→ polymerization in reactors with thin layers for efficient heat dissipation
→ use chain transfer agents



Styropor: 200-fold magnification

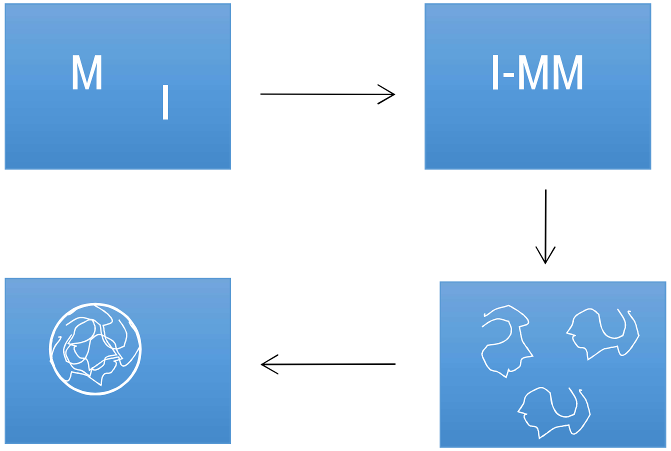


Industrial production of polyvinylchloride (PVC)



PVC

T_g = 70°C



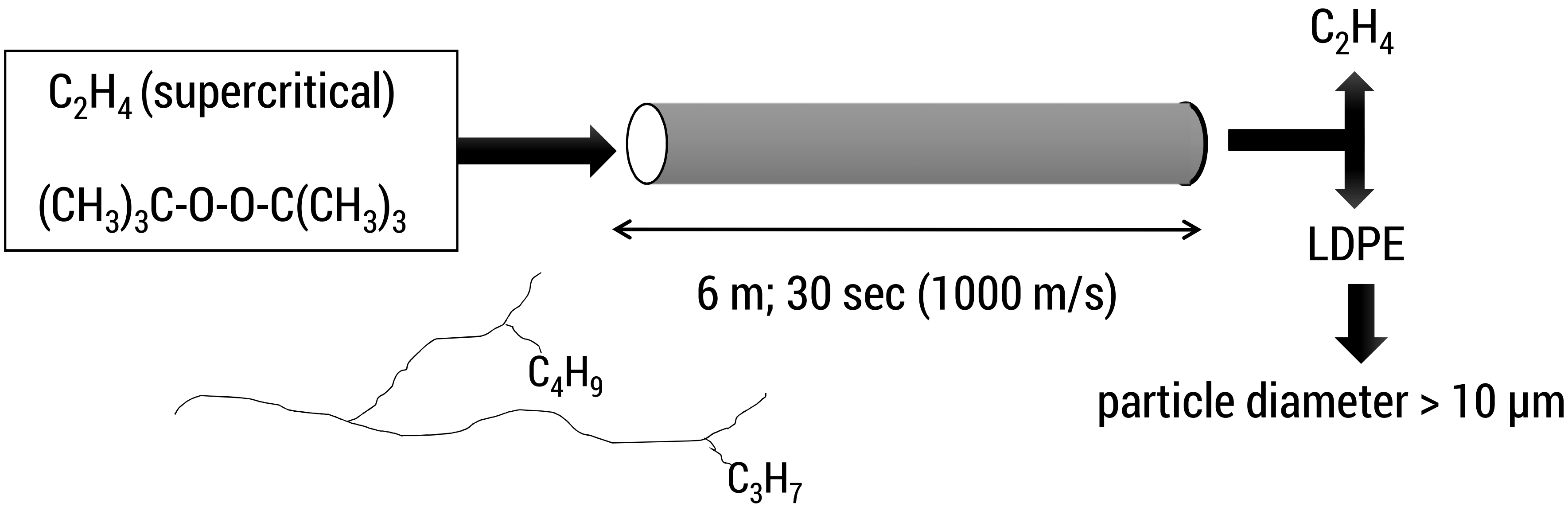
long chains are not soluble in monomer
→ precipitation

PVC (hard):
- window frames
- pipes
- Face elements
- roller blinds

PVC (soft):
- cabel insulation
- foils
- floor coverings
- tubings (medicine)
- laminates

Radical polymerization of ethylen: ICI process

ICI: 1936 (high pressure PE: 2000 bar, 200 °C) → low density PE (LDPE) ≙ short chain branching


C_2H_4 (supercritical)

$(CH_3)_3C\text{-}O\text{-}O\text{-}C(CH_3)_3$

6 m; 30 sec (1000 m/s)

C_2H_4

LDPE

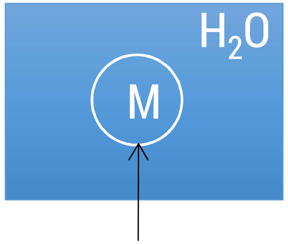
particle diameter > 10 µm

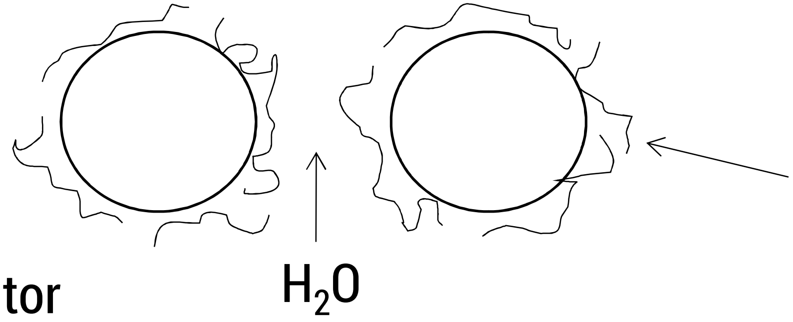
p (bar)	1	2500	2500
T (°C)	130	130	200
k_p/k_{abb}	0,05	0,7	3,0

Short chain branching: 10-20 C/1000 C
Long chain branching: 0,1-1 C/1000 C

Bead polymerization („Perlpolymerisation“)

two phase system, polymerization in monomer droplets, initiator is hydrophobic





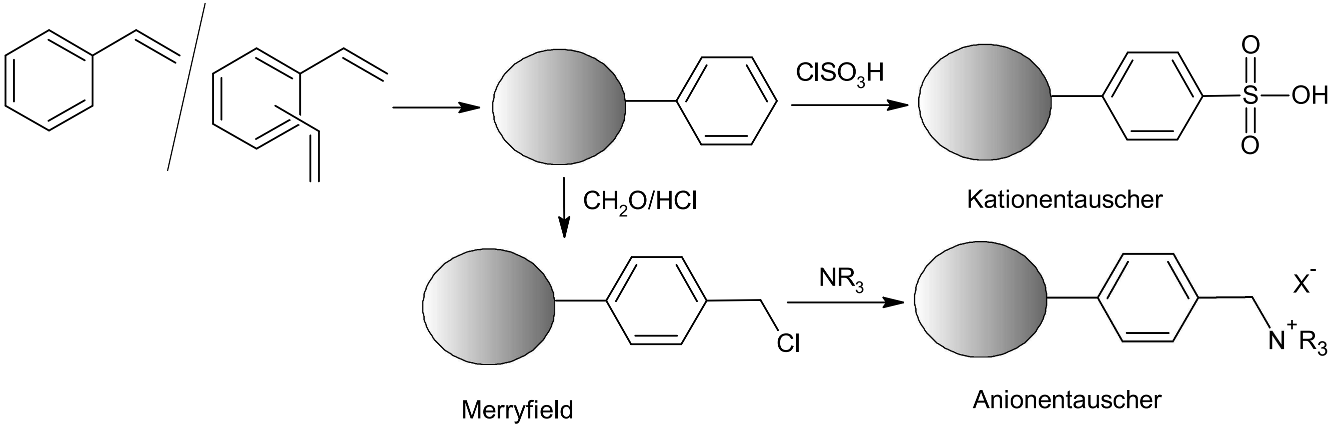
protective colloid
(e. g. water-soluble
polymers such as PVA)

monomer-soluble initiator
particle diameter ~ stirring speed

bead polymerization are bulk polymerizations in principle with water as efficient cooling medium

<u>Applications:</u>

Ion exchange resin



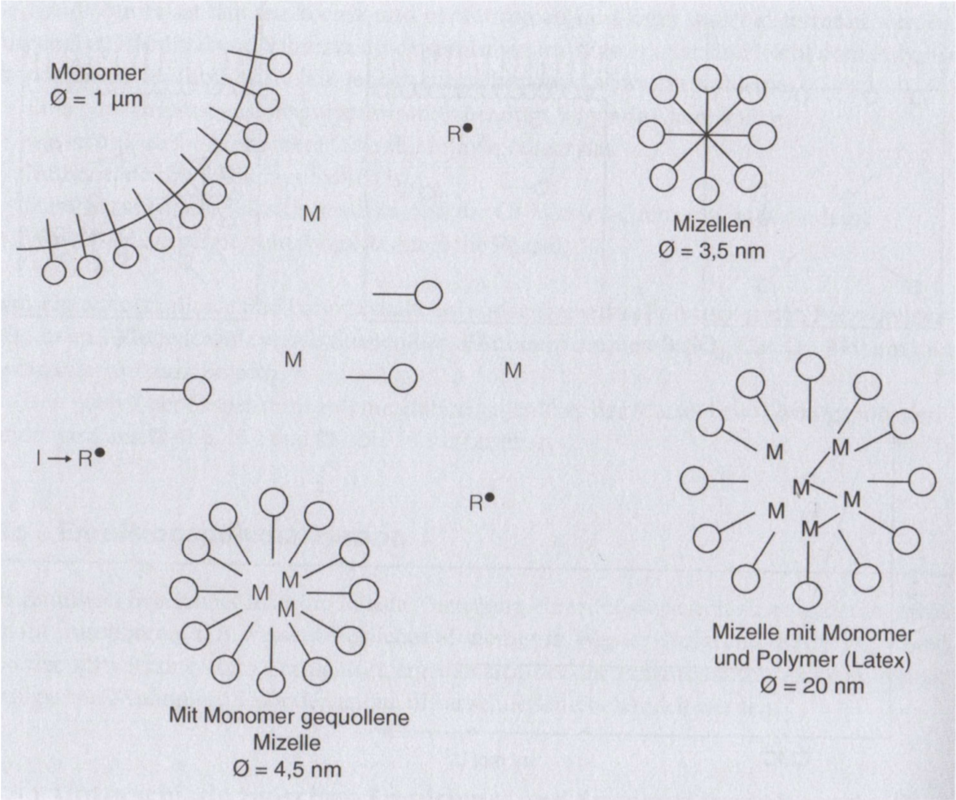
Emulsion polymerization

Typical components:
-water insoluble monomer
-water-soluble initiator
-emulsifier (soap)
-buffer
-water

Quantitative theory of Smith and Ewart

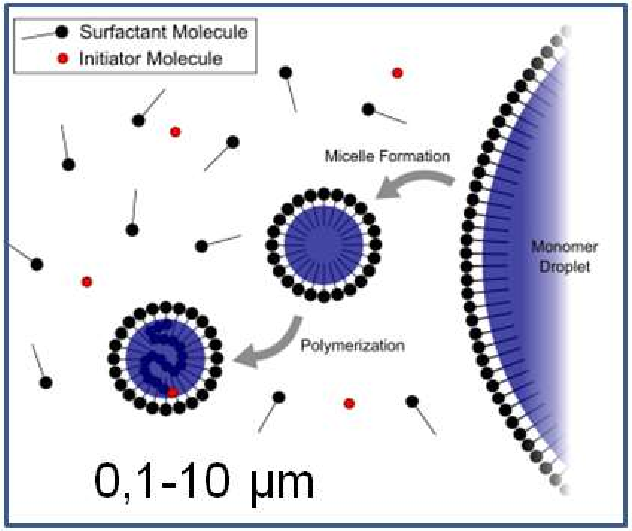
- every second micelle is loaded with one polymer chain
- No recombination! → higher MW

Difference compared to suspension polym.:
Polymerization takes place in micelles and not in Monomer droplets (initiator solubility!)
→ why? # micelles >> # monomer droplets



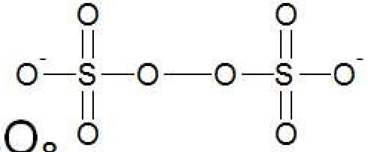
Emulsion polymerization

Emulsion Polymerisation



Monomer (water insoluble)

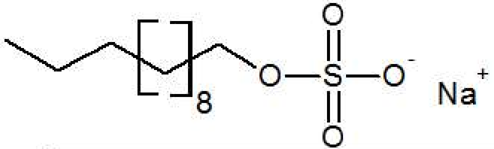
Initiator (water soluble!!) → $K_2S_2O_8$



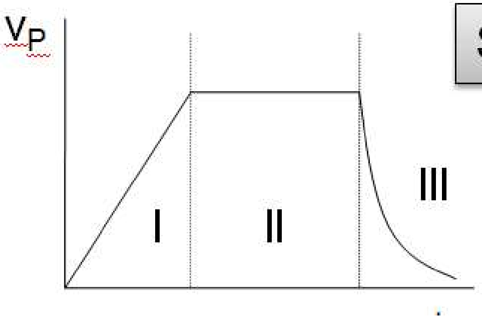
→ H_2O_2, H_2O_2 /Fe^{2+}

Emulsifier = Surfactant

e.g. Sodiumdodecylsulfat = SDS)



Per Latex: 1 Radikal
Chain termination and
Initiation with I·



Smith/Ewart

Phase I: $v_p \sim v_I$

Phase II: v_I = const

Phase III: no monomer droplet

Emulsion polymerization

Typical polymers made by emulsion polymerisation:

- PVC
- PS
- Polyacrylate
- Polyvinylacetate

Advantages:

- water as medium
- Efficient cooling (no NTE)
- Direct use of emulsion for e.g. paint production
- Facile stirring

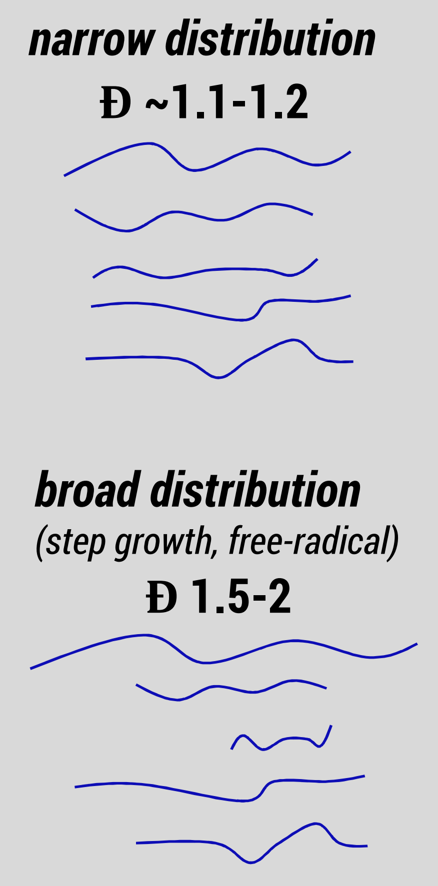
Disadvantages:

- Contaminantes (emulsifier etc)

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



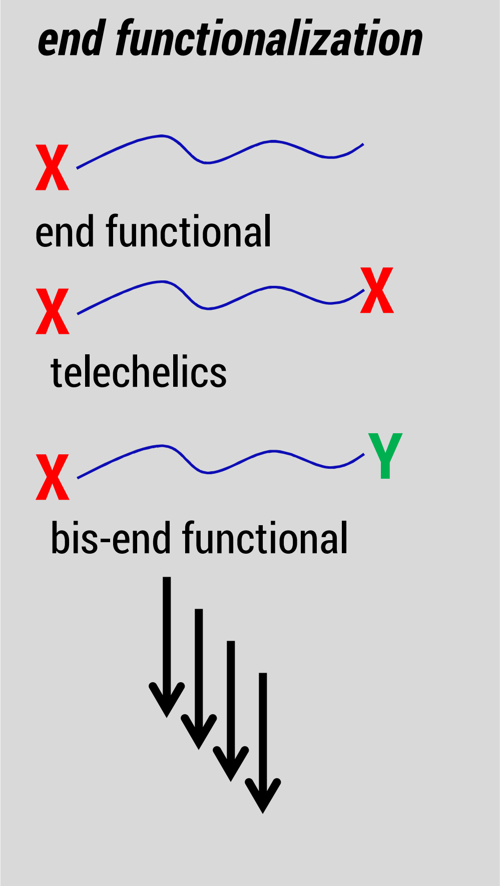
narrow distribution

Đ ~1.1-1.2

broad distribution

(step growth, free-radical)

Đ 1.5-2

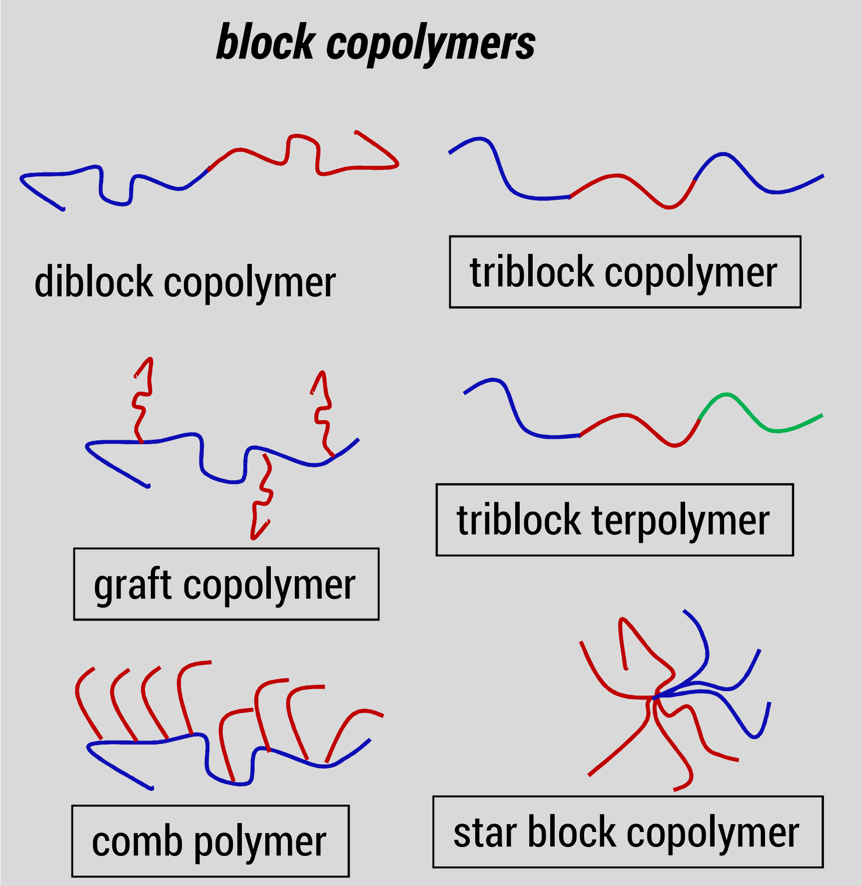


end functionalization

end functional

telechelics

bis-end functional



block copolymers

diblock copolymer

triblock copolymer

graft copolymer

triblock terpolymer

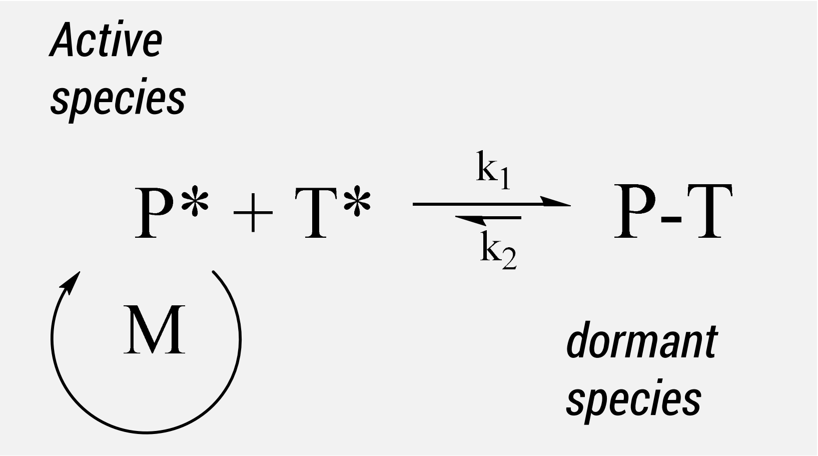
comb polymer

star block copolymer

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



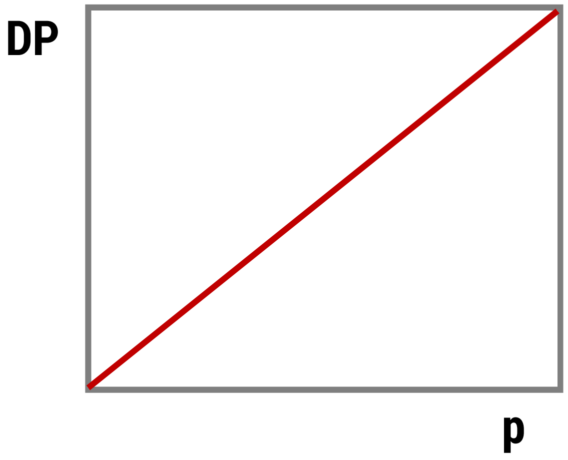
$$P^* + T^* \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P\text{-}T$$

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!

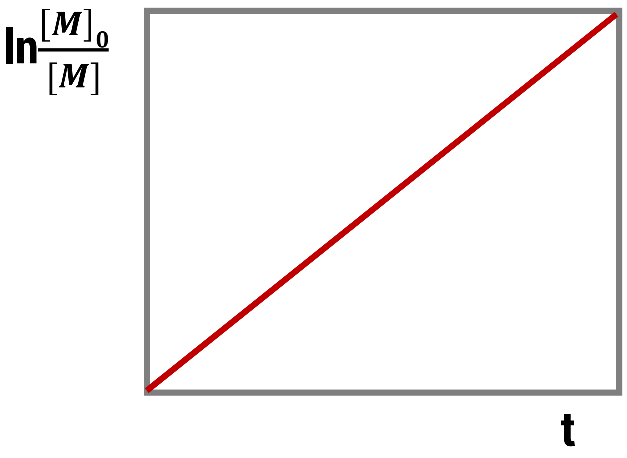
Chain length, conversion and time for CRP

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



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

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

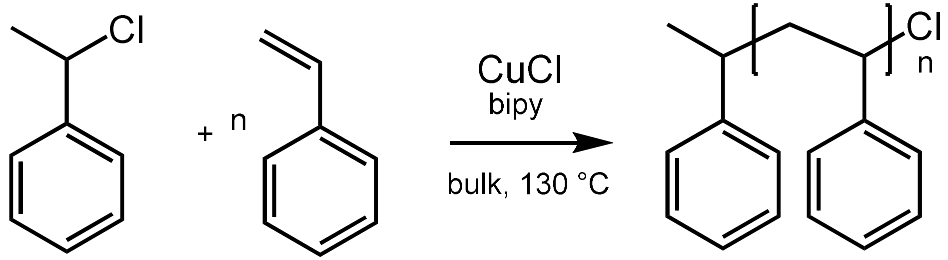


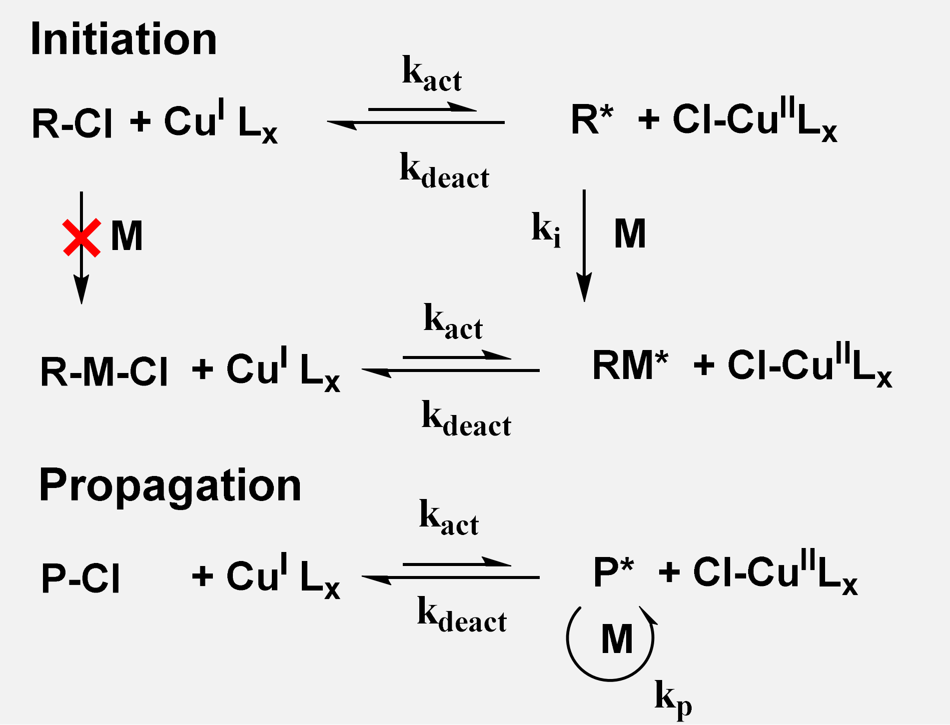
$\ln\frac{[M]_0}{[M]} = kt$

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

ATRP: First examples

First ATRP initiator: secondary chloride





Initiation

$$\begin{tikzcd}
R\text{-}Cl + Cu^{I}L_x \arrow[r, harpoon, shift left, "k_{act}"] \arrow[d, "\times\, M"] & R^* + Cl\text{-}Cu^{II}L_x \arrow[l, harpoon, shift left, "k_{deact}"] \arrow[d, "k_i"', "M"] \\
R\text{-}M\text{-}Cl + Cu^{I}L_x \arrow[r, harpoon, shift left, "k_{act}"] & RM^* + Cl\text{-}Cu^{II}L_x \arrow[l, harpoon, shift left, "k_{deact}"]
\end{tikzcd}$$

Propagation

$$\begin{tikzcd}
P\text{-}Cl + Cu^{I}L_x \arrow[r, harpoon, shift left, "k_{act}"] & P^* + Cl\text{-}Cu^{II}L_x \arrow[l, harpoon, shift left, "k_{deact}"] \arrow[loop below, "M", "k_p"']
\end{tikzcd}$$

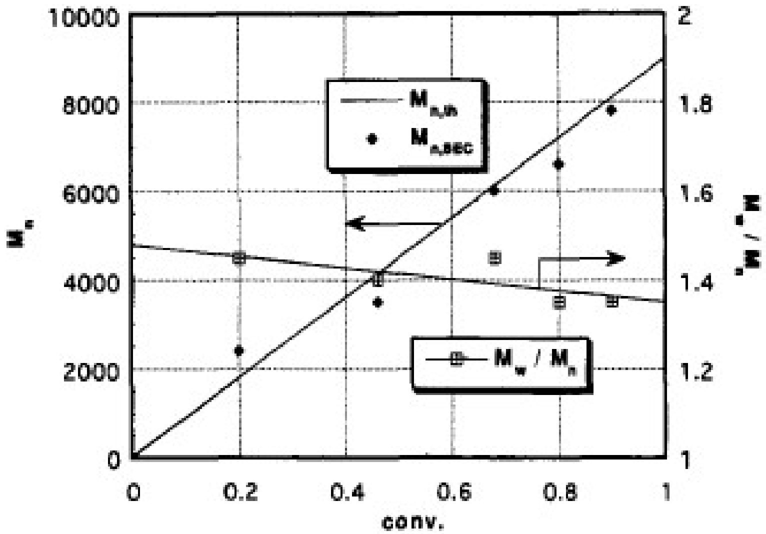
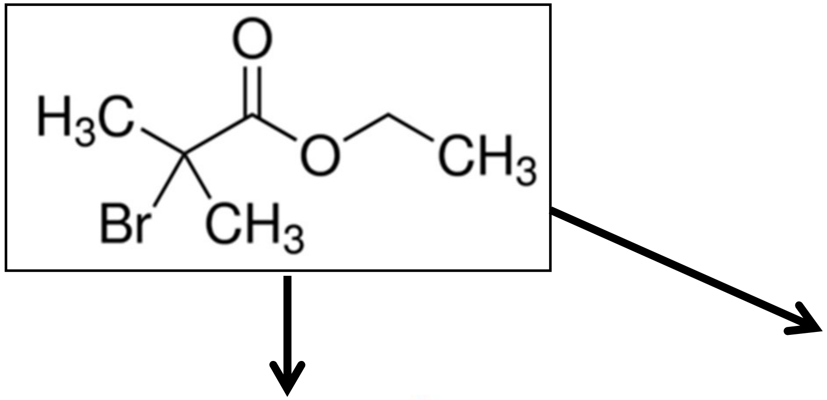


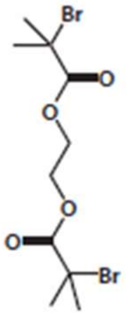
Figure 1. Dependence of molecular weights and polydispersities on conversion in bulk polymerization of styrene at 130 °C with $[1\text{-PECl}]_0 = 0.1$ mol/L, $[CuCl]_0 = 0.1$ mol/L, $[bpy]_0 = 0.3$ mol/L.

Matyjaszewsji, JACS 1995, 117, 5614

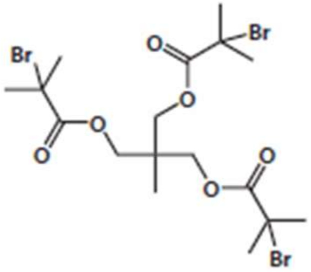
Commercial initiators based on EBiB

ATRP initiators based on Ethyl α-bromoisobutyrate (EBiB), a tertiary bromide

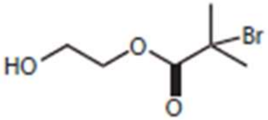




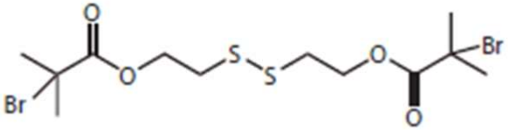
Difunctional initiator
Aldrich Prod. No. 723177



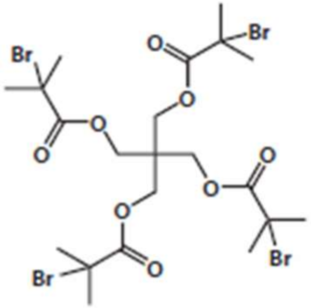
Trifunctional initiator
Aldrich Prod. No. 723185



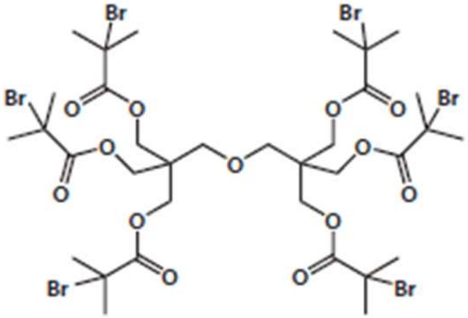
Hydroxy initiator
Aldrich Prod. No. 723150



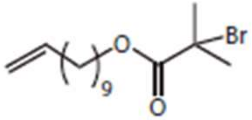
Biodegradable (disulfide) initiator
Aldrich Prod. No. 723169



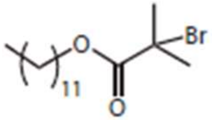
Tetrafunctional initiator
Aldrich Prod. No. 723193



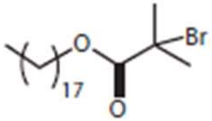
Hexafunctional initiator
Aldrich Prod. No. 723207



Allyl initiator
Aldrich Prod. No. 723215



Dodecyl initiator
Aldrich Prod. No. 723223

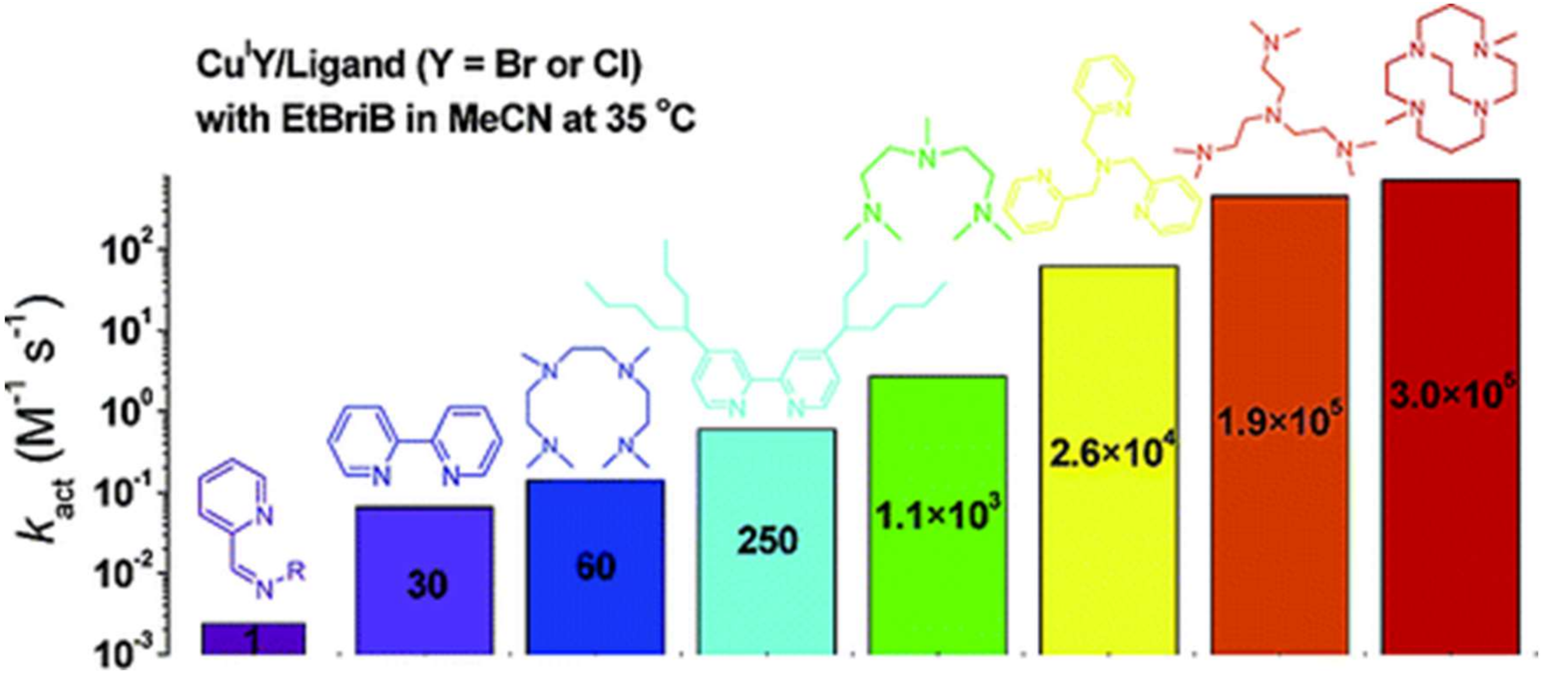


Stearyl initiator
Aldrich Prod. No. 723231

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

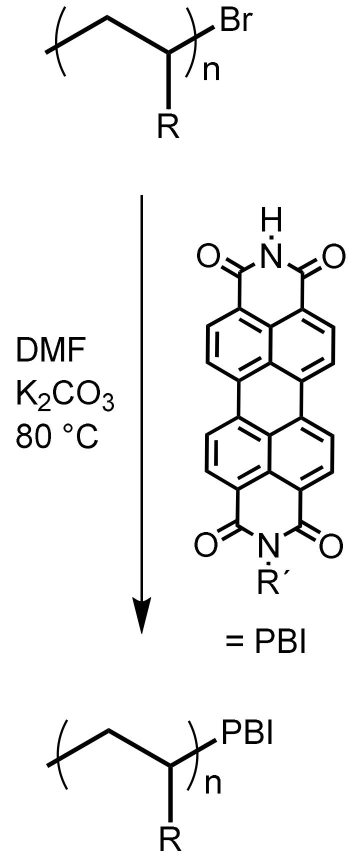


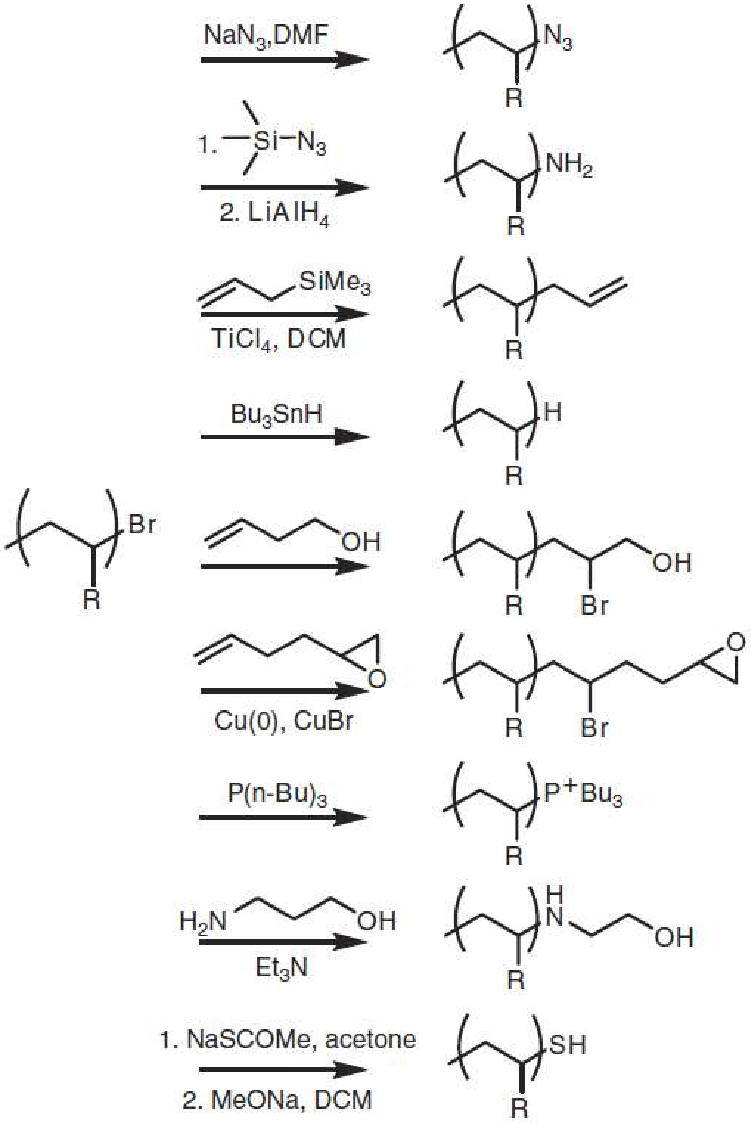
Tang, Matyjazewski, *Macromolecules*, 2006, 39 (15), pp 4953–4959

End group modification of ATRP polymers

End group functionalization of Bromide-terminated polymers made by ATRP

dye labelling

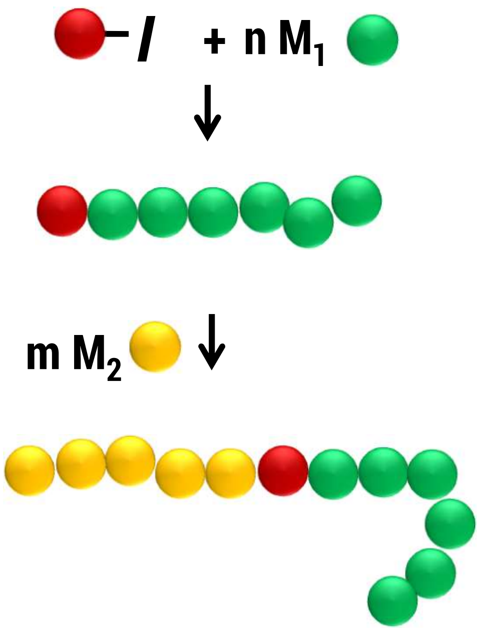




Polym Int 2014; **63**: 803–813

Advantages and possibilities of controlled radical polymerization

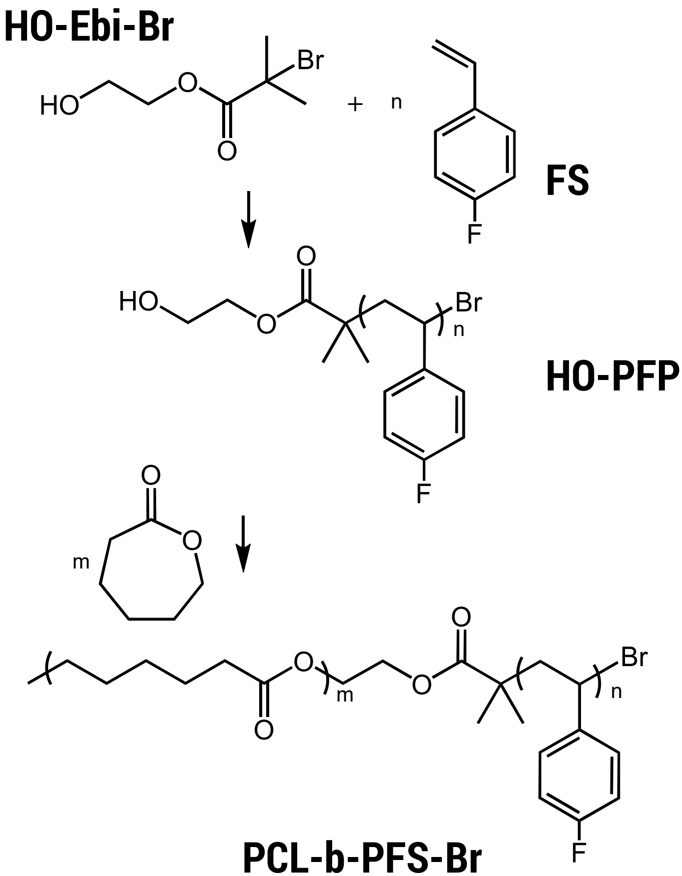
Quantitative end group functionalization enables block copolymer synthesis
Example: Triblock terpolymer synthesis using HO-EBiB and ATRP



bifunctional initiator

bifunctional macroinitiator

diblock copolymer



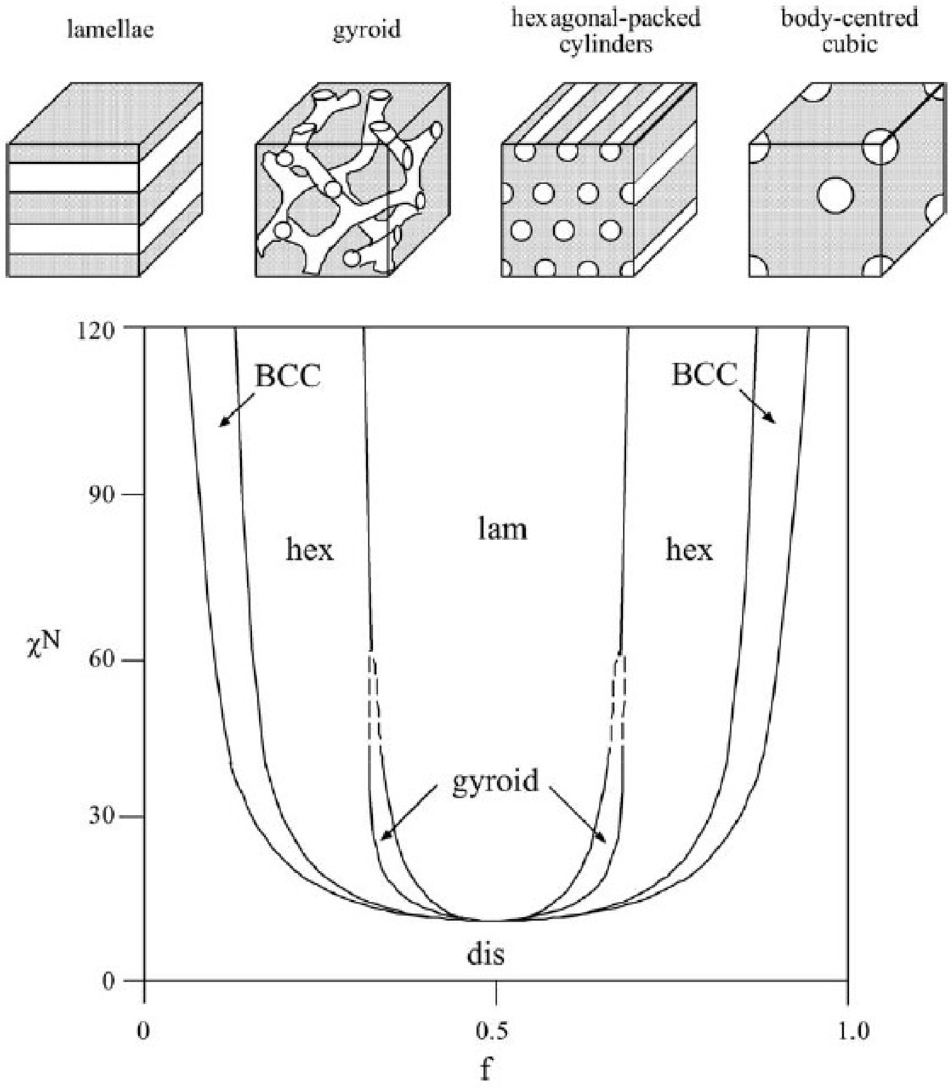
HO-Ebi-Br

FS

HO-PFPS-Br

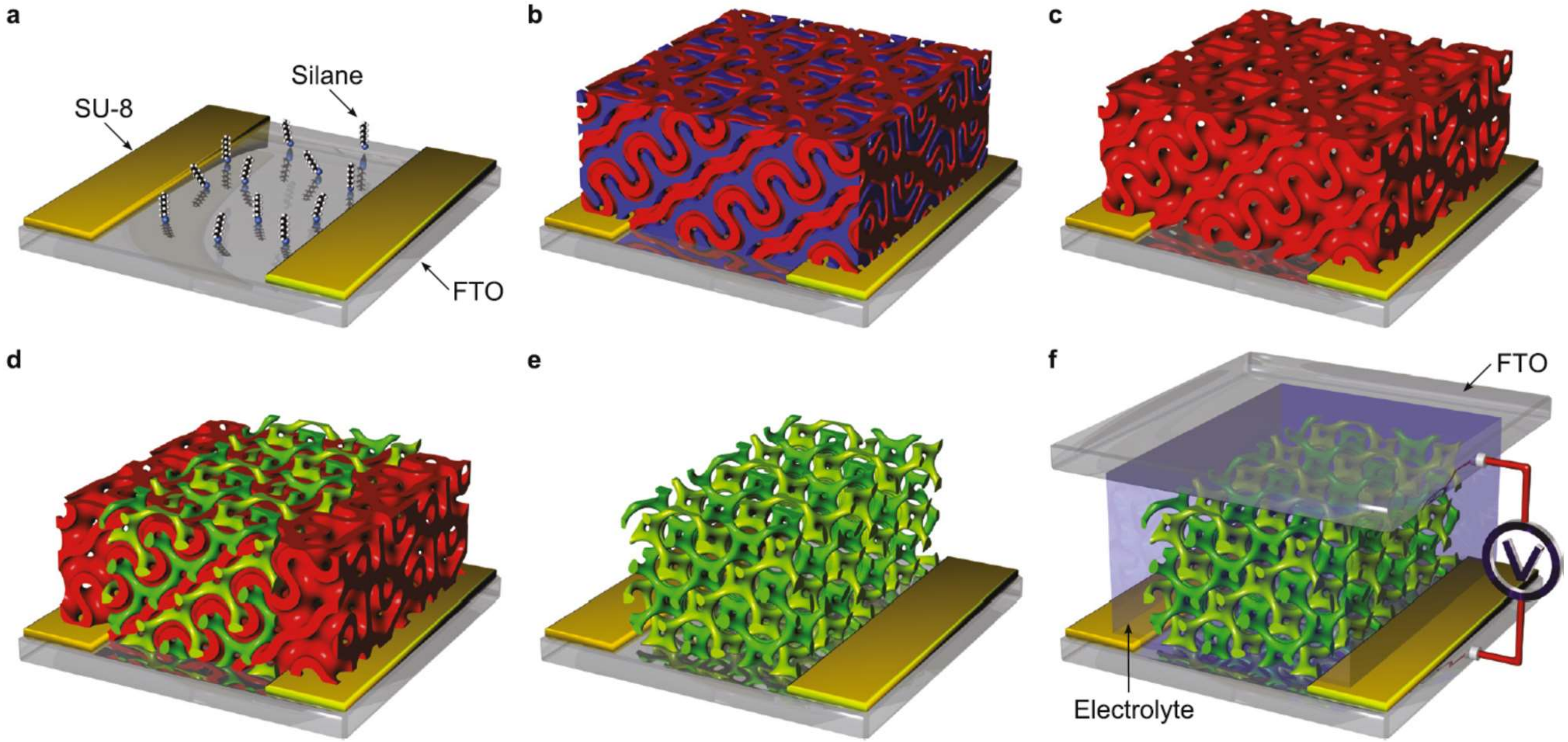
PCL-b-PFS-Br

Microphase separation of block copolymers



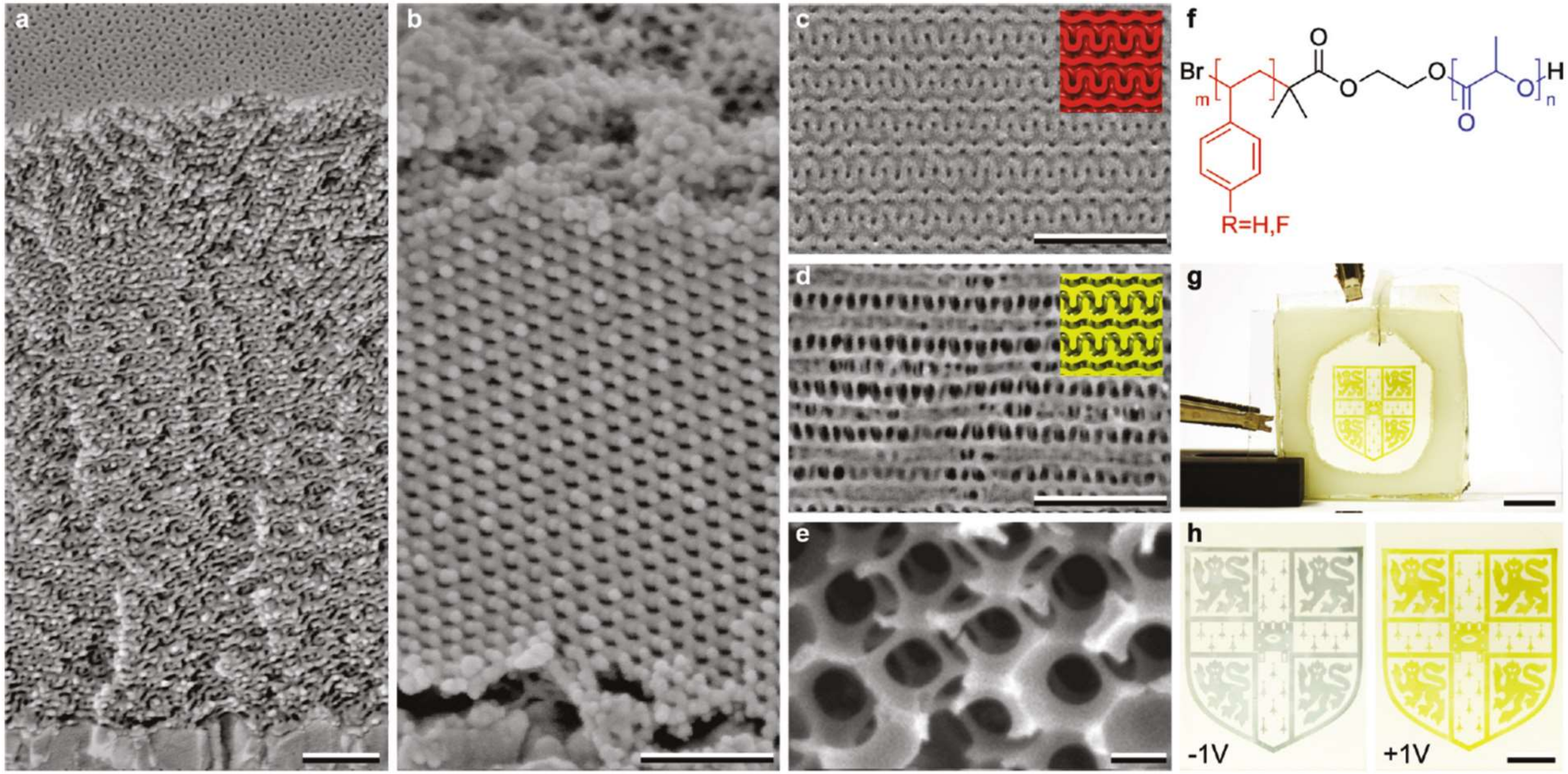
I.W. Hamley et al.
Curr. Op.
Solid State &
Mater. Sci.
8 (2004) 426–438

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