11:10 AM - 12:25 PM CHEM 2104

Lecture by Dr. Yannick Borguet

CHEM 466: TUE 18/03/2014:

# Radical polymerization

General facts:

Ⓐ - in 2009, ~230 (280 in 2012) million tons of polymer were produced worldwide
- 40-45% of those were produced via radical polymerization!

$\boxed{\text{\#1 technique in polymer industry}}$

Ⓑ Why: - tolerant to protic solvents/impurities
- " " $O_2$ & monomer stabilizer (consume radicals before starting polym)
- Large number of low priced monomers available

Ⓒ It is a chain growth polymerization ≠ step growth (polycondensat° for example)
⇒ composed of 3 distinct key mechanistic steps:

1. Initiation
2. propagation
3. termination

# (F) Radical Polym.

- 3 key mechanistic steps: initiation, propagation, termination

Initiation

$$i-X \rightleftharpoons i^{\bullet} + {}^{\bullet}X \overset{M}{\rightleftharpoons} i-R^{\bullet} + {}^{\bullet}X \rightleftharpoons i-R-X$$

(x = i for a symmetrical initiator)

Rev. Term

the key step in controlled radical polym.

Propagation n M

$$i-(R)_n R-\text{term} \xleftarrow{\text{terminator}} i-(R)_n R^{\bullet} + {}^{\bullet}X$$

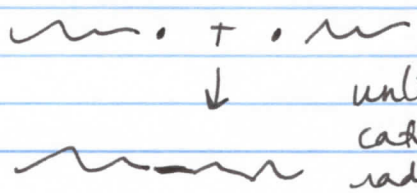
Irreversible Term.

Rev. Term.

$$i-(R)_n R-X$$

- irreversible termination gives a dead poly
- can occur at any $DP_n$, n value
- can give a new radical (CT rxns)

- reversible termination gives a controlled polym
- w/appropriate $^{\bullet}X$, rev. term. occurs throughout the polym
  - mediates chain end reactivity at all stages
  - reduces the concentration of active radical species
  - reduces chain-chain coupling probability



unlike anionic or cationic polym, radicals can combine to irreversibly terminate + give $\sim 2 \times DP_n$

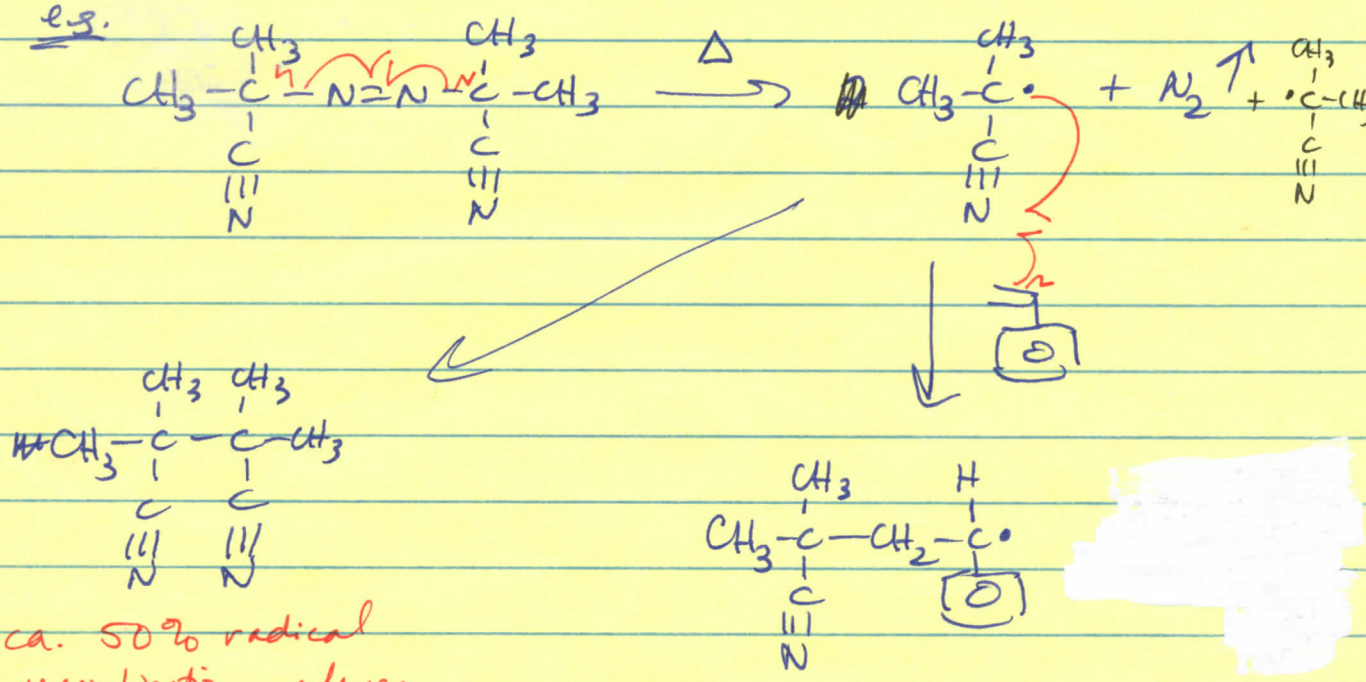
see other initiators, e.g. peroxide in text Table 3.1

## (1) Initiation

$$i\text{-}X \underset{}{\overset{k_{diss}}{\rightleftharpoons}} i^{\bullet} + X^{\bullet} \quad \text{rds for initiation}$$

$$i^{\bullet} + M \rightleftharpoons i\text{-}R^{\bullet}$$

e.g.



ca. 50% radical recombination reduces initiator efficiency

- initiator efficiency, $f$ = fraction of radicals from the initiator that successfully initiate polym

  typically $0.3 < f < 0.8$

- when a high conc. of radicals is present, much is destroyed $\Rightarrow$ lower $f$
  (by recombination + other side rxns)

∴ radicals are present typically @ low conc. ($\sim 10^{-8}$ M) + must be well mixed in the polym. mixture, i.e. radical solubility in monomer or monomer + solvent is important

- New Radicals are formed throughout the polym. time, b/c $t_{1/2}$ of initiators is typically minutes to hours
  (important to adjust polym T to achieve desired $t_{1/2}$ of initiator)

NOTE:

for example: AIBN:

$t_{1/2}$ = 0.1 h @ 101°C
= 1.0 h @ 82°C
= 10.0 h @ 64°C

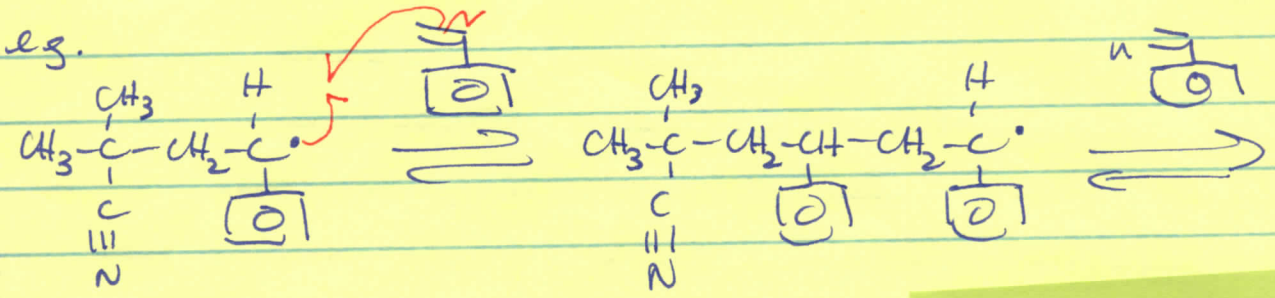
in chlorobenzene

[$k_{diss} \propto A e^{-E_a/RT}$]

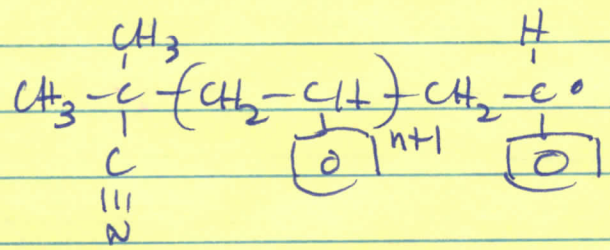
## (2) Propagation

$$i\text{-}R^{\bullet} + m \xrightarrow{k_{prop}} i\text{-}R\text{-}R^{\bullet}$$

e.g.

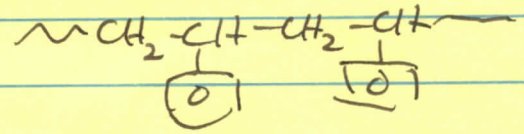


typically, in frp:
- 1 monomer is added every ~~ms~~ one millisecond
- ~~Rated~~ Chain grows for ~1 sec

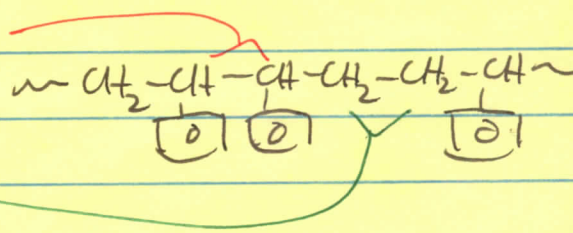


- regiochemistry is det'd. by steric + electronic (resonance + inductive) effects

~ 98% head-to-tail



~ 2% head-to-head or tail-to-tail



# (F) Radical Polym (cont'd)

(1) Initiation

(2) Propagation

(3) Termination

3 primary mechanisms:

termination in pairs of radicals
2 radicals → 0 radicals

- (a) radical coupling (combination or recombination)
- (b) disproportionation (H• (or other atom e.g. Cl•) abstraction)

1 radical + 1 non-radical → 1 non-radical (terminated chain) + 1 new radical

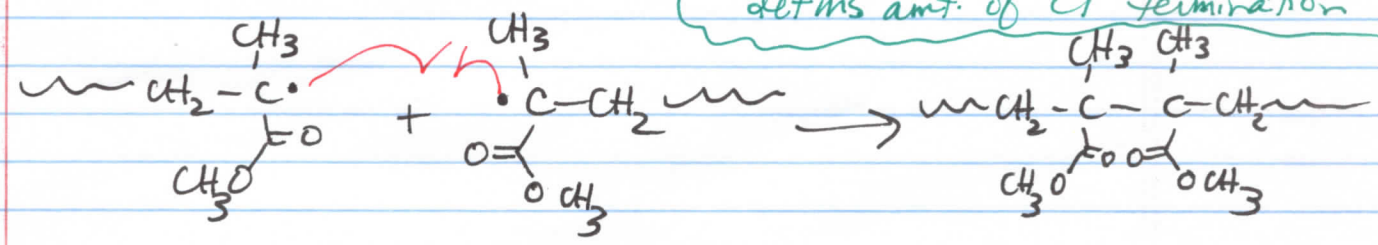
- (c) chain transfer (CT) reactions

The importance of these termination processes depends on the rxn conditions + the monomers:

- large amt. initiator → large # radicals + growing chains → large amt. termination
- ease of H• abstraction det'ns amt. of disproportionation
- CT constants for all components det'ms amt. of CT termination

## (a) radical coupling

e.g. irreversible termination



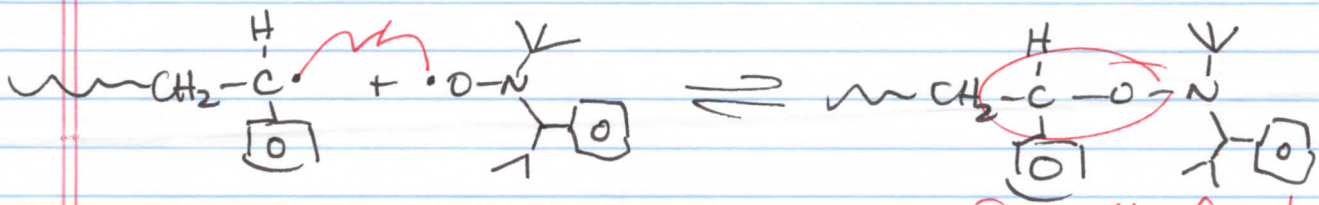
2 radicals → 0 radicals

head-to-head

(depending on regiochem of radical, could be tail-to-tail or head-to-tail, but statistically mainly head-to-head regiochem in radical coupling rxn)

Double the MW
$DP_n + DP_m \rightarrow DP_{m+n}$

e.g. reversible termination, which gives controlled polym

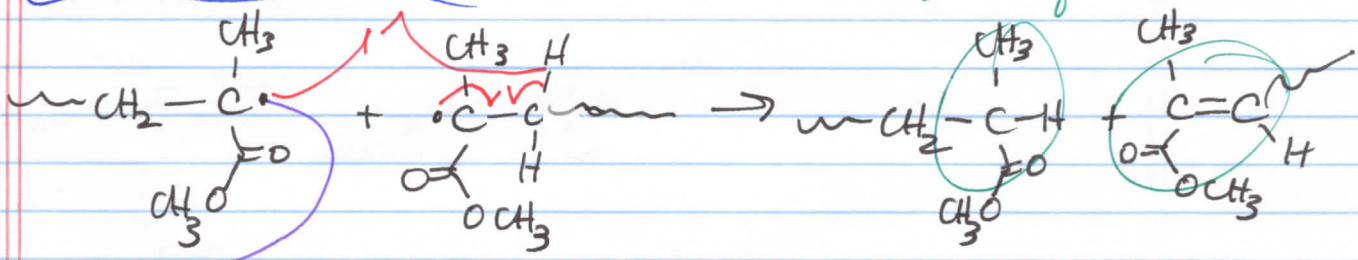


2 radicals

0 radicals, but thermally labile bond cleaves homolytically to give reversibility

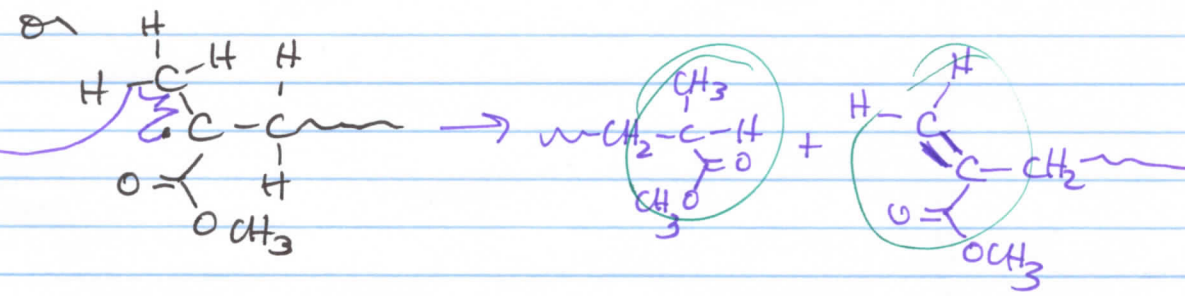
## (b) disproportionation

2 unique chain ends

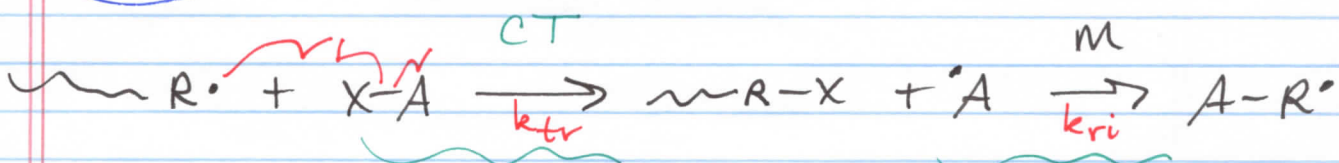


2 radicals

0 radicals



## (c) chain transfer — many rxns




(if A• can initiate polym)

- if $k_{tr}$ is large relative to $k_{prop}$ ⇒ low MW poly
- if $k_{tr}$ is large + rxn is reversible ⇒ controlled polym. (RAFT)

X–A can be:
① CT agent ② solvent ③ initiator ④ monomer ⑤ poly ⑥ impurity

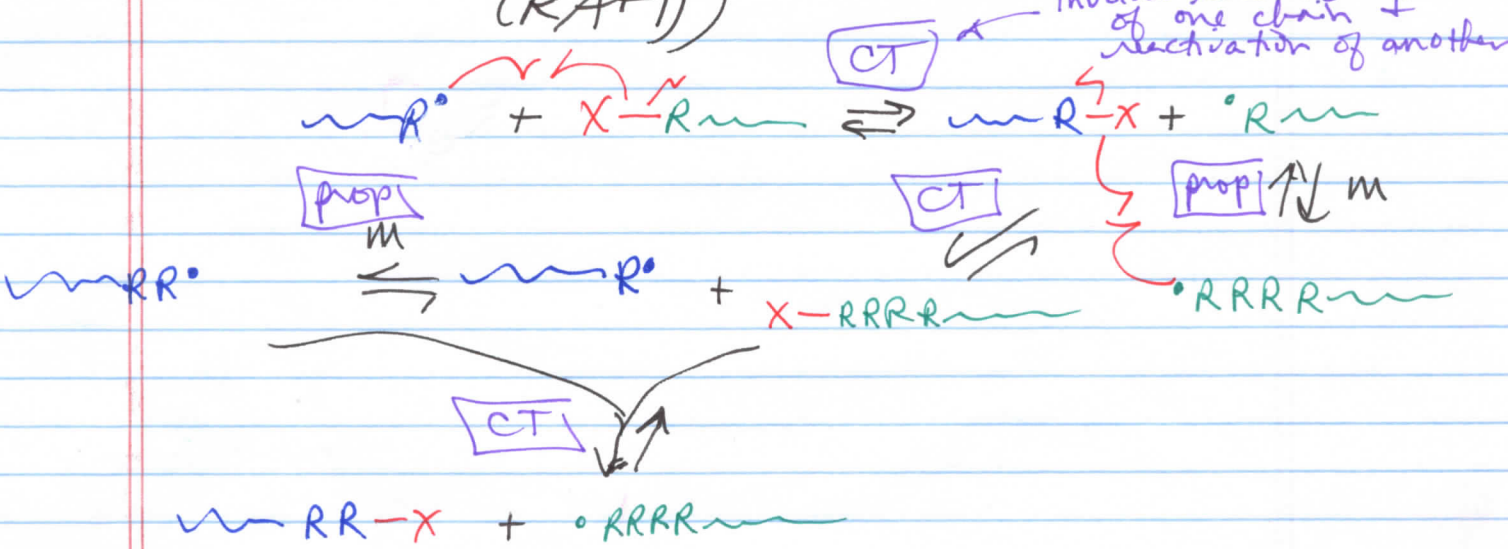
desirable

undesirable (usually)

desirable for prep of LDPE

$$CT_{constant} = \frac{k_{tr}}{k_{prop}}$$

- in uncontrolled polym, X–A can be added as a CT agent to limit DP + MW
- in controlled polym, the CT agent is attached to the poly chain end
  ⟹ chain end swapping to control poly growth (reversible addition–fragmentation chain transfer polym (RAFT))



① CT to CT agent (RAFT to be covered later)

• as CT constant ↑, DP ↓

② CT to solvent

• THF + other ethers have high CT constants, c.f. hydrocarbons due to α H• abstraction

(rxn of radicals gives α H• abstraction followed by rxn w/ $O_2$ gives formation of peroxides in ethers)

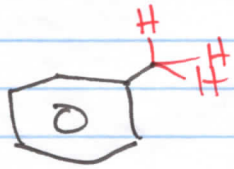
LAB SAFETY SIDE NOTE

it is a chain rxn.

eg. styrene polym

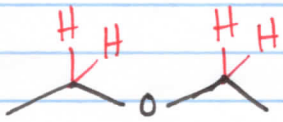
CT constants for styrene polym

$2.3 \times 10^{-6}$



$1.3 \times 10^{-5}$

low, good solvents



$5.6 \times 10^{-4}$ high

$CCl_4$ (Cl• abstraction) $1.1 \times 10^{-2}$ very high

$CBr_4$ (Br• abstraction) 2.2

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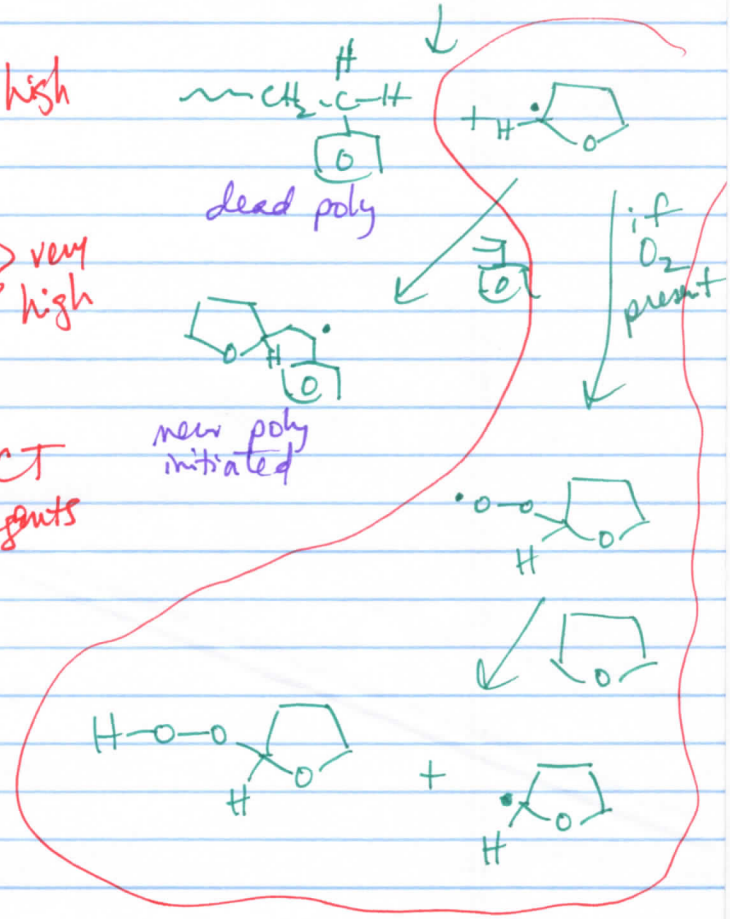
CT agents




DO NOT DISTILL ETHERS TO DRYNESS & CHECK FOR PRESENCE OF PEROXIDES FIRST!! highly unstable →

- for traditional radical polym, cannot control poly chain length by % conversion (as can be done for step-growth or living chain polyms)

∴ CT agents can be added to limit the $DP_n$ for polyms that produce too high MW poly