IONIC POLYMERIZATIONS

They are used to study the mechanism of polymerization reactions.

Some of the products may have intensive colour.

Such polymer products are not commercial.

Long lasting polimerizations, termination occurs only after complete disappearance of monomer, terminations are rare.

„Living polymerizations”

1. ANIONIC POLYMERIZATION

2. CATIONIC POLYMERIZATION

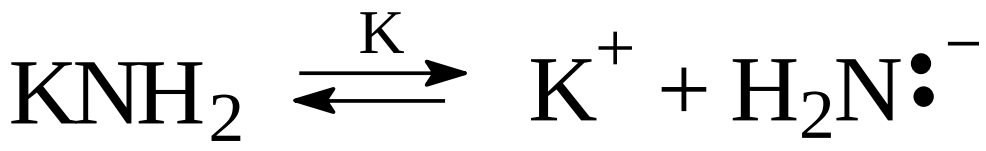
1. ANIONIC POLYMERIZATION

Initiation:

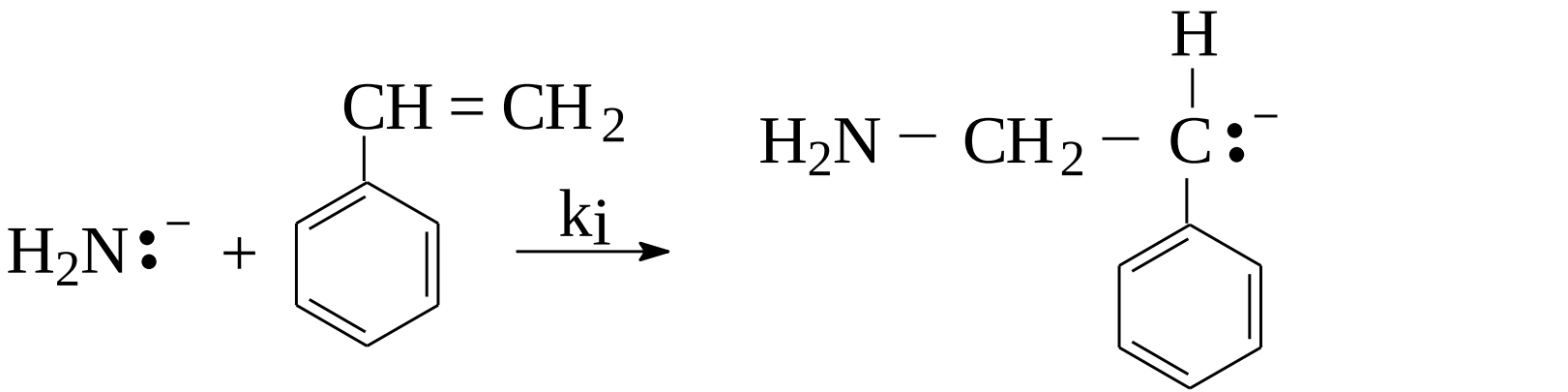
a) by metal amides
b) by electron transfer
c) by metal alkyls

a) by metal amides:

Polymerization of styrene with potassium amide in liquid ammonia at -33°C.



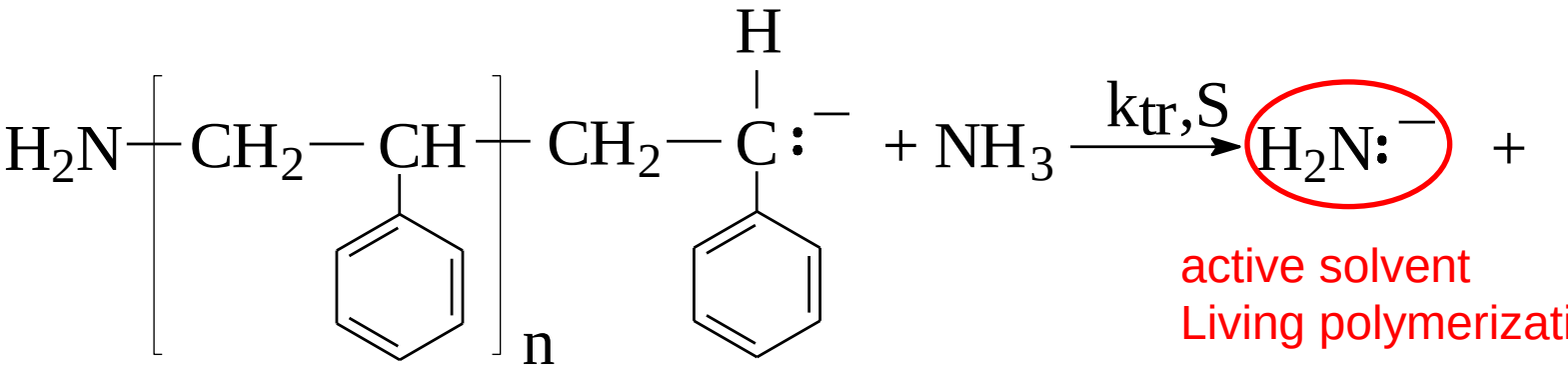
amide ion



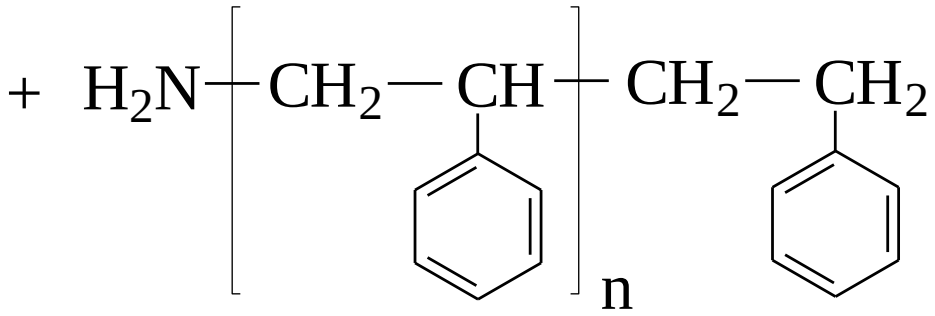
propagating anionic center

$$R_i = k_i \left[H_2N:^- \right] [M]$$

Chain-growth transfer termination to solvent:



active solvent
Living polymerization!



The final polymer product

2. CATIONIC POLYMERIZATION

b) Lewis acids and Friedel-Crafts catalyzators
($AlBr_3$, BF_3, $SnCl_4$, $ZnCl_2$, $TiBr_4$)

Example: cationic polymerization of isobutylene

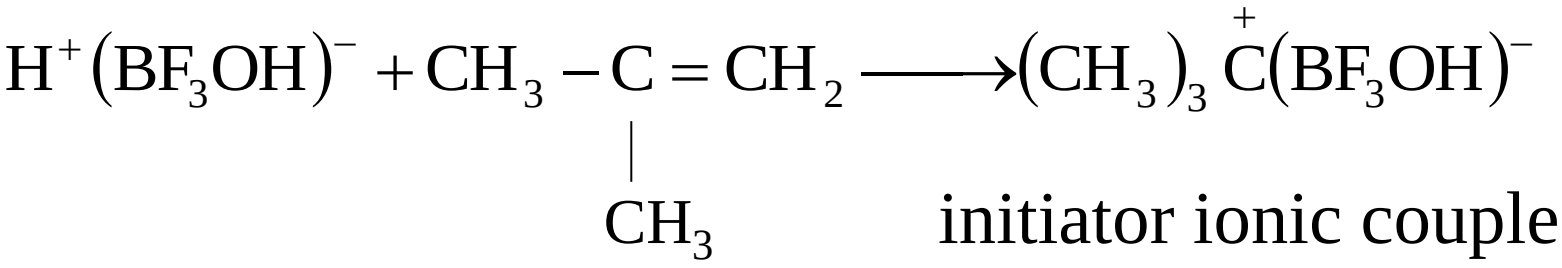
Isobutylene polymerizes with boron trifluoride (BF_3) and H_2O (at -100 °C)

BF_3 is catalyst, and H_2O is co-catalyst

$$BF_3 + H_2O \Leftrightarrow H^+(BF_3OH)^-$$

co-catalyst- catalyst

Example: cationic polymerization of isobutylene

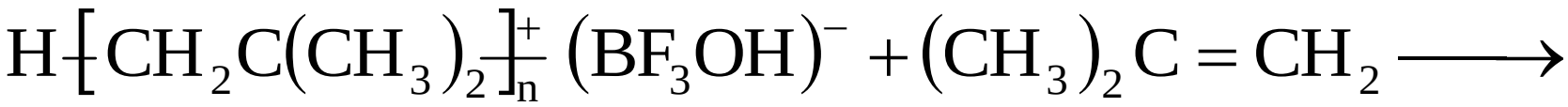


Shematic view: $C + RH \Leftrightarrow H^+(CR)^-$

$H^+(CR)^- + M \xrightarrow{k_i} HM^+(CR)^-$

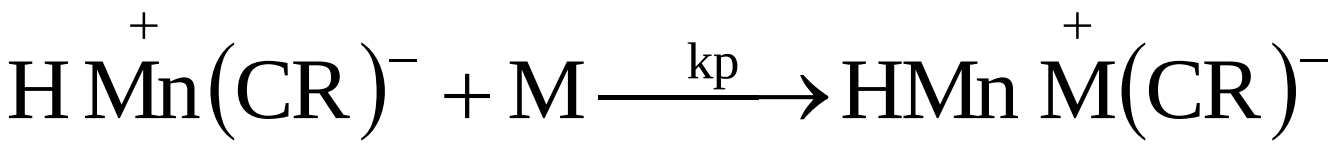
C = catalyst
RH = co-catalyst
M = monomer

PROPAGATION - ionic pair reacts with a monomer



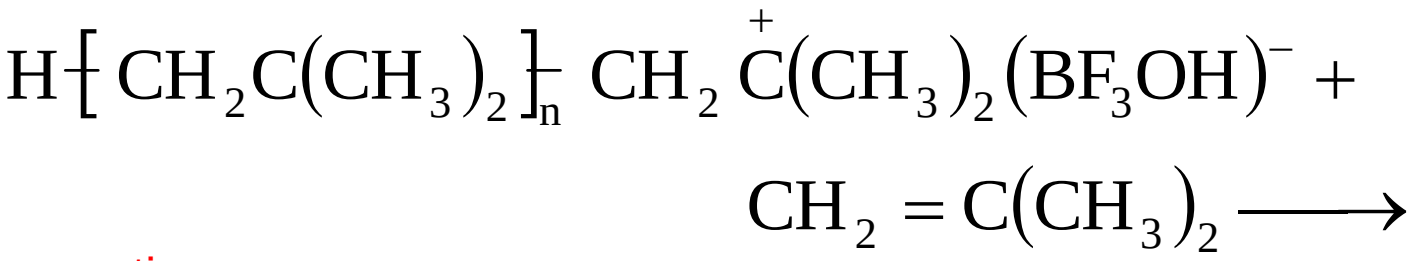


or schematically

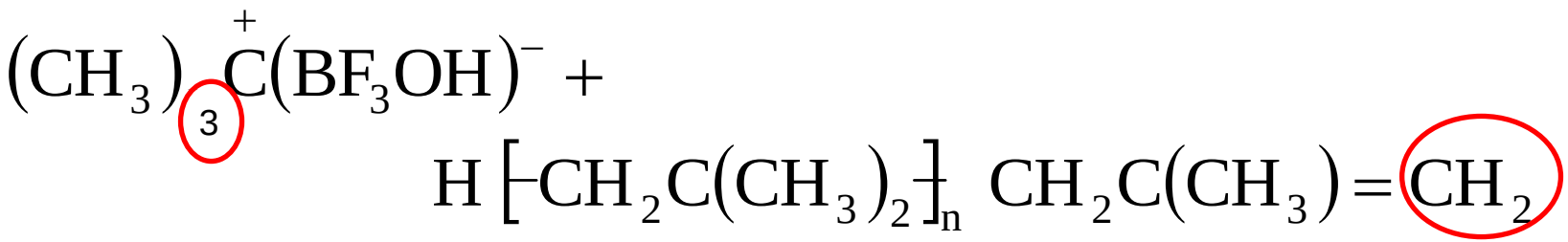


TERMINATION

a) most common reactions are chain-growth transfer to monomer with formation of unsaturated polymer molecule

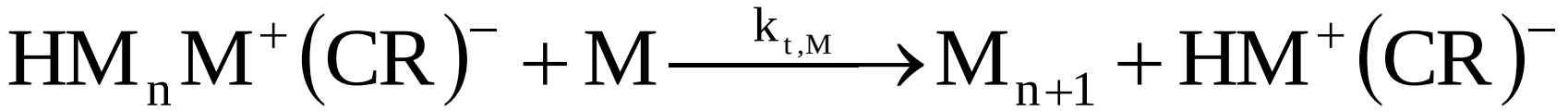


active monomer

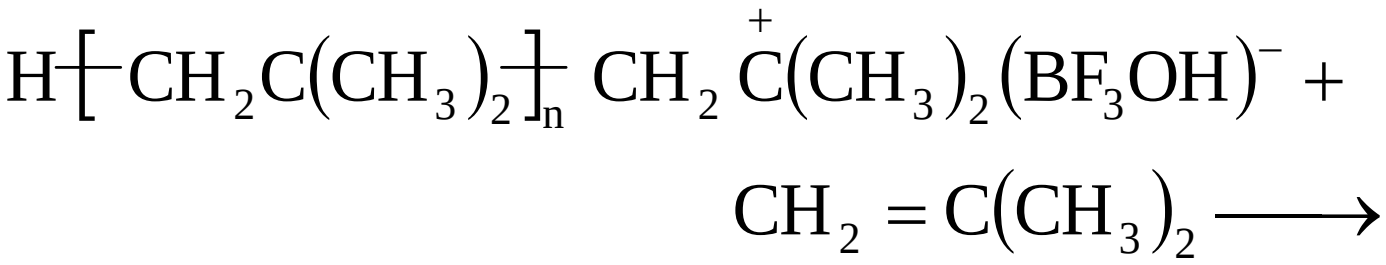


unsaturated polymer molecule

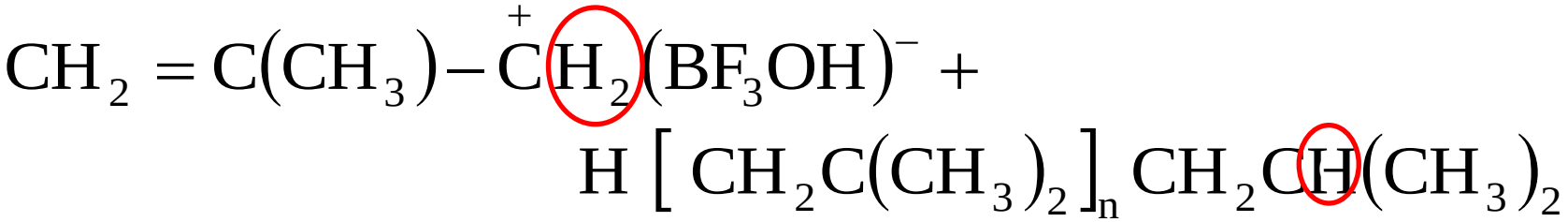
or



b) reaction of a chain-growth transfer to monomer with elimination of hydrogen from monomer



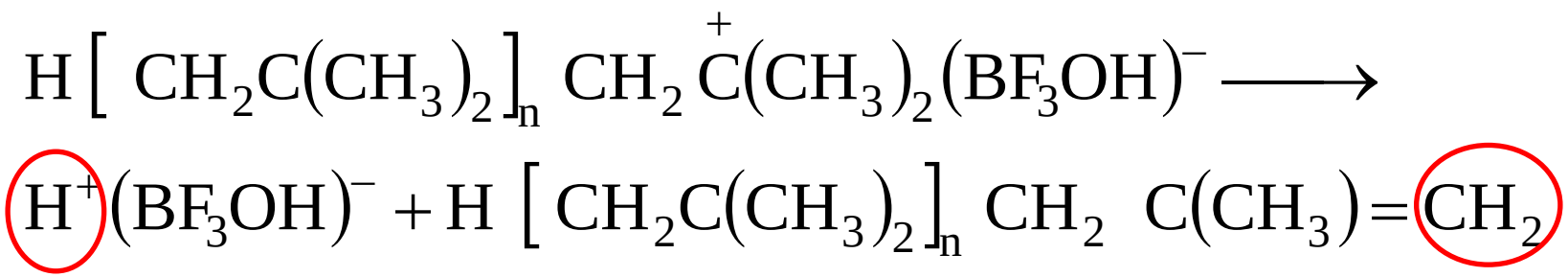
active monomer



polymer

c) rearrangement of a propagating ion pair

⇨ **Spontaneous termination:**



Active again!
Living polymerization!

or

