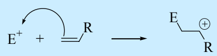
Cationic Polymerization

Concepts

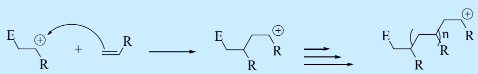
General Mechanism

Initiation

$$I_n \longrightarrow E^+$$



Propagation

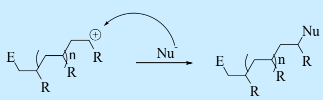


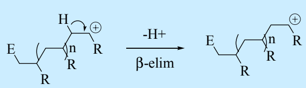
Cationic Polymerization

Concepts

General Mechanism

Termination





Cationic Polymerization

Chemistry

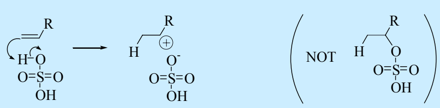
Initiators

1. Proton Acids

   e.g.

   CF_3SO_3H H_2SO_4 H_3PO_4

   (want a counterion that's not nucleophilic)



Cationic Polymerization

Chemistry

Initiators

2. Lewis Acids

e.g.

$AlCl_3$ BF_3 $SbCl_5$ $TiCl_4$ $ZnCl_2$ $RAlCl_2$

With Lewis acid initiators, you most often need a co-initiator

e.g. a "protogen"

$$BF_3 + H_2O \longrightarrow H^+[BF_3OH]^-$$

or a "cationogen"

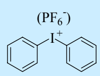
$$AlCl_3 + (CH_3)_3CCl \longrightarrow (CH_3)_3C^+ + (AlCl_4)^-$$

Cationic Polymerization

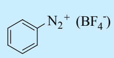
Chemistry

Initiators

3. Photoinitiators (activated by UV)



1



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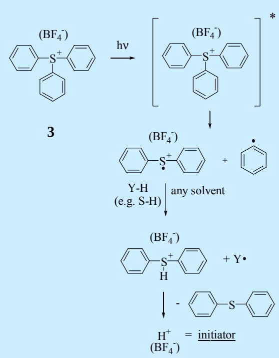
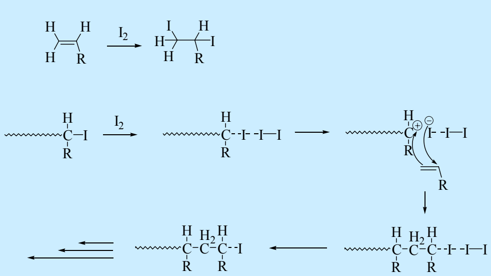


Cationic Polymerization

Chemistry

Initiators

3. Iodine



Cationic Polymerization

Kinetics: Initiation

1. Single Cation Initiatior

$$Y^+Z^- + M \xrightarrow{k_i} YM^+Z^-$$

$$R_i = k_i [M] [Y^+Z^-]$$

2. Cation Initiator Complex

$$I + ZY = Y^+ (IZ)^-$$

$$Ri = ki [M] [complex]$$

$$BF_3 + H_2O \rightarrow H^+BF_3OH^-$$

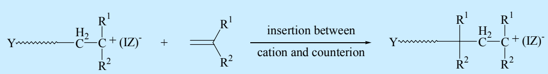
K = [H+BF3OH-]/[BF3] [H2O]

therefore: complex = [H+BF3OH-] = K [BF3] [H2O]

$$R_i = k_i [M] \{K [BF3] [H2O]\}$$

Cationic Polymerization

Propagation



$$YM_n^+(IZ)^- + M \xrightarrow{k_p} YM_nM^+(IZ)^-$$

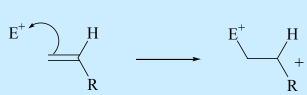
$$R_p = k_p [M] [M^+]$$

Cationic Polymerization

Propagation

Regiochemistry

Markowninkov addition – form the most stable carbocation



e^- donating R groups stabilize a cation thus increasing reactivity, and affect regiochemistry by directing the cation α to the donating group:

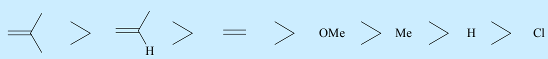
R = alkyl
aryl
halide
OR

Cationic Polymerization

Propagation

Factors affecting rate:

1. R groups: rate of propagation (and rate of initiation) fastest with monomer that yields most stable carbocation



Note: most stable carbocation reacts fastest

2. Counterion: larger and less tightly bound counterions give larger k_p

$ClO_4^- > TiClOH^- > I_3^-$

Cationic Polymerization

Examples

Solvent	ε	catalyst	k_p ($dm^3 mol^{-1} sec^{-1}$)
CH_2Cl_2	9.72	$HClO_4$	17.0
CH_2Cl_2	9.72	$TiCl_4/H_2O$	6.0
CH_2Cl_2	9.72	I_2	0.003

Cationic Polymerization

Propagation

3. Solvent Effects

Species

covalent

intimate ion pair

solvent separated ion pair

free ions

Cationic Polymerization

Propagation

Solvent	ε	catalyst	k_p ($dm^3 mol^{-1} sec^{-1}$)
CCl_4	2.3	$HClO_4$	.0012
40/60 : CCl_4/CH_2Cl_2	5.16	$HClO_4$	0.44
40/60 : CCl_4/CH_2Cl_2	7.0	$HClO_4$	3.20
CH_2Cl_2	9.72	$HClO_4$	17.0
CH_2Cl_2	9.72	$TiCl_4/H_2O$	6.0
CH_2Cl_2	9.72	I_2	0.003

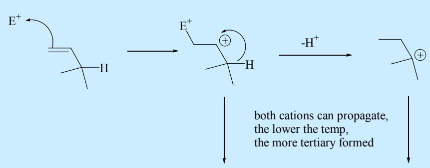
4. Temperature: E_a only 2-3 kcal/mole; that's low therefore reaction is fast and side reactions have higher E_a → use low temps for polym

Cationic Polymerization

Propagation

Rearrangements: aka Isomerization Polymerization

Not so bad: high DP when a regular pattern can be formed via simple rearrangement routes involving stable cations:

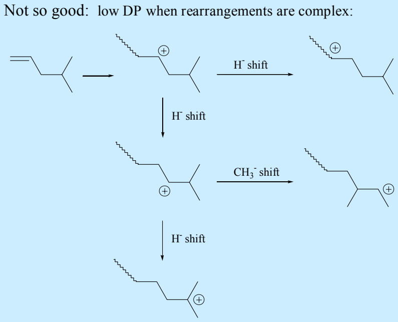


Cationic Polymerization

Propagation

Rearrangements: aka Isomerization Polymerization

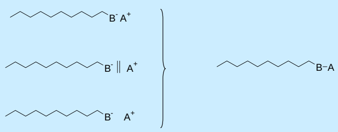
Not so good: low DP when rearrangements are complex:



Cationic Polymerization

Termination

Recombination of Ion Pairs – can control with solvent polarity



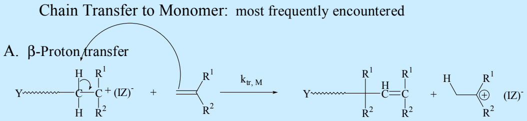
$$YM_n^+(IZ)^- \xrightarrow{k_t} YM_n\text{-}(IZ)$$

$$R_t = k_t [M^+]$$

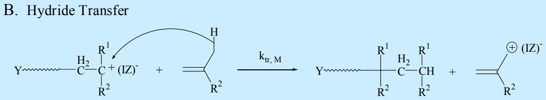
Chain Transfer Cationic Polymerization

Chain Transfer to Monomer: most frequently encountered

A. β-Proton transfer



B. Hydride Transfer



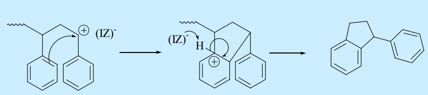
$$HM_nM^+(IZ)^- + M \xrightarrow{k_{tr,\,M}} M_{n+1} + HM^+(IZ)^-$$

$$R_{tr,\,M} = k_{tr,\,M} [M] [M^+]$$

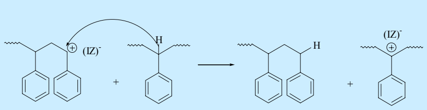
Chain Transfer Cationic Polymerization

Chain Transfer to Polymer: EAS or hydride transfer

1. Electrophilic Aromatic Substitution: "backbiting"



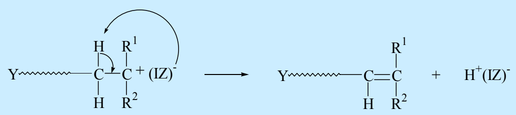
2. Hydride Transfer



Cationic Polymerization

Chain Transfer

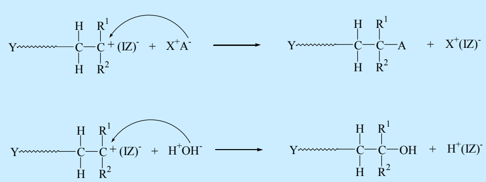
Spontaneous: aka: Chain Transfer to Counterion; this is actually termination



Cationic Polymerization

Chain Transfer

Transfer Agents, impurities, Solvent (S) (e.g. H_2O)



$$HM_nM^+(IZ)^+ + XA \xrightarrow{k_{tr,S}} HM_nMA + X^+(IZ)^-$$

Cationic Polymerization

Kinetics

Overall (first considering unimolecular termination)

$$R_i = Kk_i [I] [ZY] [M]$$

$$R_p = k_p [YM^+(IZ)^-] [M]$$

$$R_t = k_t [YM+(IZ)^-]$$

Apply steady state: $R_i = R_t$

$$[YM^+(IZ)^-] = \frac{K\, k_i\, [ZY]\, [M]}{k_t}$$

DP

$$DP = \frac{R_p}{R_t} = \frac{k_p[M]}{k_t}$$

Note: Increase in I, no change to DP

Cationic Polymerization

Kinetics

Overall with Chain Transfer

$R_{ts} = k_{ts} [YM^+(IZ)^-]$

$R_p = k_{tr,M} [YM^+(IZ)^-] [M]$

$R_{tr,S} = k_{tr,S} [YM^+(IZ)^-] [S]$

DP

$$DP = \frac{R_p}{R_t + R_{ts} + R_{tr,m} + R_{tr,S}}$$

$$= \frac{k_p [M]}{k_t + k_{ts} + k_{tr,m}[M] + k_{tr,S} [S]}$$

Cationic Polymerization

Energetics

Composite activation energy for rate of polymerization:

$E_R = E_i + E_p - E_t$

And for DP (= kinetic chain length)

$E_{DP} = E_p - E_t$

Often:

$E_p << E_i , E_t$ or E_{tr}

Therefore,

$E_R =$ negative

When this is the case, there is an increase in rate with a decrease in temp. Because, $R = Ae^{-Ea/RT}$ becomes $R = Ae^{Ea/RT}$

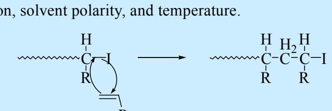
Cationic Polymerization

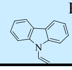
Living Polymerization

Polymerizations in which propagating centers do not undergo termination or transfer; i.e. propagating center has low reactivity such that termination and transfer reactions are effectively suppressed.

1. If you add more monomer, polymer keeps growing
2. Propagating center should persist throughout polymerization.

For Cationic, need to balance the stability of the carbocation with counterion, solvent polarity, and temperature.



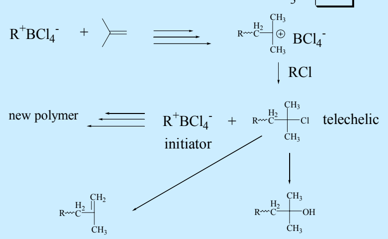
For  optimum conditions = HI, toluene, -40◦C

Cationic Polymerization

Telechelic Polymers via Cationic Polymerization

Telechelic Polymers: have relatively low mass ($M_n \leq 20{,}000$) with functional end groups. These can be used for further reaction to form block or network polymers.

How do you make these? With cationic polymerization, a good technique is by the "Inifer" method. Inifer is short for initiation-chain transfer. $BCl_3 + RCl \rightleftharpoons R^+BCl_4^-$



Cationic Polymerization

Types of Polymers Produced via Cationic Polymerization

Polymer	Application
Polyisobutylene Polybutenes	Adhesives, Sealants, Insulating oils, Lubricating oil, Moisture barriers
Isobutylene-Isoprene Copolymer (Butyl Rubber)	Inner tubes, Engine mounts, Chemical tank liners, Hoses, Gaskets
Isobutylene-Cyclopentadiene Copolymer	Ozone resistant rubber
Polyterpene Resins (Natural Product Based)	Inks, Varnishes, Paints, Adhesives
Coumarone-Indene Resins (Coal Based)	Flooring, Coatings, Adhesives
Poly(vinyl ethers)	Polymer modifiers, Tackifiers, Adhesives

Cationic Polymerization

Examples

Cationic Polymerization

Examples