10.569 Synthesis of Polymers
Prof. Paula Hammond

Lecture 20: Intro to Anionic Polymerization, Monomers Applicable to Anionic Methods, Kinetics of "Nonliving" Anionic Polymerization

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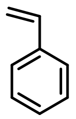
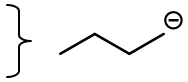
Choosing Initiators (for anionic polymerization)

(must be strong enough to initiate monomer)
→ should not attack any monomer side groups

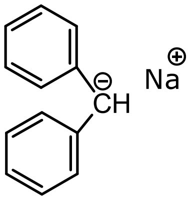
e.g. styrene:



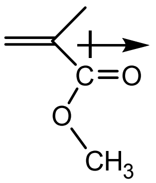
Readily initiated by any alkyl lithiums
(e.g. n-butyl Li, sec-butyl Li)
Cations: (Na) (Na)



CANNOT initiate with diphenyl methyl Na

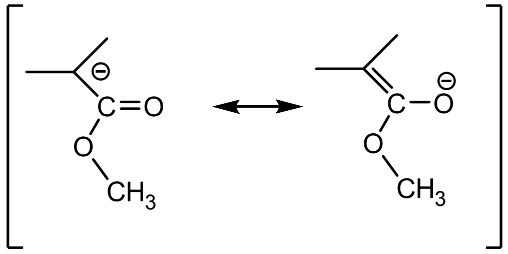


Compare with:



MMA

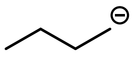
e- withdrawing effect
large due to inductance



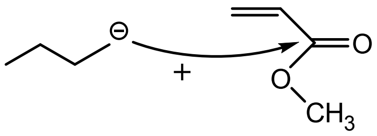
resonance

→ easy to initiate
→ fluorenyl Na^+, diphenyl methyl Na

But NOT:



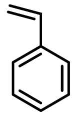
→ side rxns with ester



Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.

Kinetics of anionic polymerization

In protic media:



$$+ \quad \underbrace{NaNH_2}_{\text{initiator}} \text{ in } \underbrace{H_2O/NH_3^+}_{\text{solvent}}$$

Termination in ionic polymerization
⇒ only by transfer or side rxn
⇒ no coupling/disproportionation

IF transfer leads to anion that is reactive enough to initiate monomer ⇒ transfer
IF transfer leads to anion that won't initiate monomer ⇒ termination

$$NaNH_2 \overset{K}{\rightleftharpoons} \overset{\oplus}{Na} + \underset{\substack{\uparrow \\ \text{initiating species}}}{\overset{\ominus}{NH_2}}$$

$$\left[NH_2^-\right] = \frac{K\left[NaNH_2\right]}{\left[Na^+\right]}$$

1. Initiation:

$$NH_2^{\ominus} + M \xrightarrow{k_i} NH_2M^{\ominus}$$

2. Propagation:

$$NH_2M_i^{\ominus} + M \xrightarrow{k_p} NH_2M_{i+1}^{\ominus}$$

3. Transfer to solvent:

$$NH_2M_i^{\ominus} + \underset{\substack{\uparrow \\ \text{solvent}}}{NH_3} \xrightarrow{k_{tr,NH3}} NH_2M_iH + NH_2^{\ominus}$$

initiates more monomers
kinetic chain lives BUT
chain length shortens

4. Transfer to water: (termination event)

$$NH_2M_i^{\ominus} + H_2O \xrightarrow{k_{tr,H2O}} NH_2M_iH + HO^{\ominus}$$

relatively stable,
will not initiate
styrene

(only thing HO^- will initiate is epoxides)

$$R_i = k_i\left[NH_2^-\right]\left[M\right] = \frac{k_i K\left[M\right]\left[NaNH_2\right]}{\left[Na^+\right]}$$

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$$R_p = k_p[M^-][M]$$
$$R_{tr,NH_3} = k_{tr,NH_3}[M^-][NH_3]$$
$$R_{tr,H_2O} = k_{tr,H_2O}[M^-][H_2O]$$ termination

Steady state assumption: $[M^-]$ = constant

$R_i = R_{tr,H2O}$

$$\frac{k_i K[M][NaNH_2]}{[Na^+]} = k_{tr,H_2O}[M^-][H_2O]$$

rearrange to get expression for $[M^-]$

$$[M^-] = \frac{k_i K[M][NaNH_2]}{k_{tr,H2O}[H_2O][Na^+]}$$

$$\left. R_p = \frac{Kk_i k_p [M]^2[NaNH_2]}{k_{tr,H2O}[Na^+][H_2O]} \right\}$$ 2^{nd} order in [M]

$R_p \propto [M]^2$

(b/c: $[M^-] \propto [M]$)

$$\frac{1}{\overline{p_n}} = \underbrace{\frac{C_{NH3}[NH_3]}{[M]}}_{\text{transfer to solvent}} + \underbrace{\frac{C_{H2O}[H_2O]}{[M]}}_{\text{transfer to } H_2O}$$

Living Polymerizations

1. No transfer
   No termination events due to other side rxns that might occur due to impurities
   ⇒ need solvent with no protic groups (aprotic)
   ⇒ eliminate H_2O to get dry solvent
   O_2
   CO_2
   Other reactive species like NH_2, anything that can snatch H off
   "lifetime" of propagating anion can be very long
   (~ hours)

2. Need system with very rapid $R_i >> R_p$
   fast initiation
   start polymerization at same time to get highly controlled MW + polydispersity
   All chains start at the same time and finish the monomer off
   ~ monodisperse MW distribution

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Kinetics of Living Polymerizations

1. initiation: $R_i = k_i[I^-][M]$

$$\left.\begin{array}{ll}\text{2. propagation:} & R_p = k_p[M^-][M] \\ & \\ \text{Rapid initiation:} & [I]_o \cong [M^-]\end{array}\right\} \quad R_p = k_p[M][I]_o$$

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