10.569 Synthesis of Polymers
Prof. Paula Hammond
Lecture 10: Introduction to Radical Polymerization

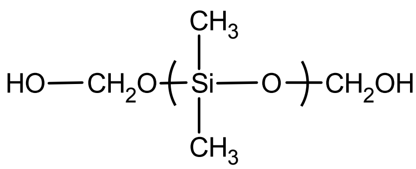
Segmented Copolymers

Segmented Polyurethanes (Prof. Hammond's thesis)

(1) "soft segment" → ends in –OH groups
- oligomer
- low T_g (liquid-like at 25°C)

HO OH
oligomeric diols

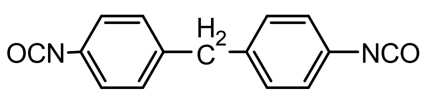
$HO-\!\left(-(CH_2)_4\cdot O-\right)\!-H$
simple polyether



MW:
~ 1000 – 10,000

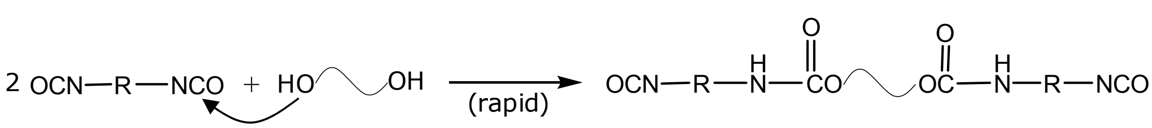
(2) Diisocyanate: (-N=C=O)

e.g.
OCN-R-NCO
$OCN-(CH_2)_6-NCO$



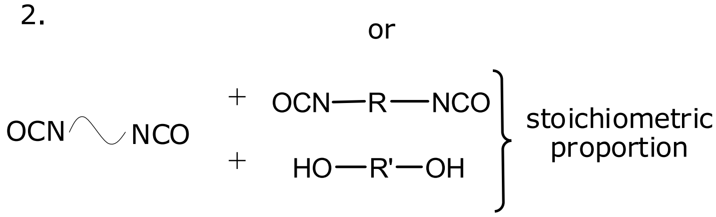
(3) Chain extender
- Connector between different units
- Almost always short diol
  - ex:
    $HO-(CH_2)_n-OH$

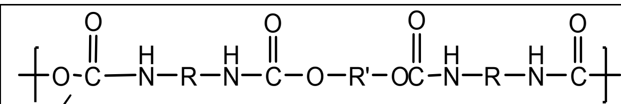
To get segmented polyurethane:
1. Endcap soft segment w/diisocyanate:

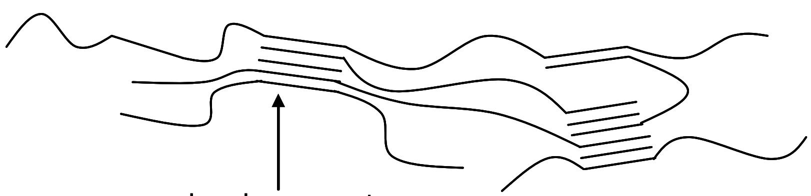


no byproduct

2.



soft	isocyanate	chain extender	
1	2	1	
1	3	2	Hard Segment
1	4	3	Can be made longer by adding diol and diisocyanate in equal proportions
-	-	-	[ ]$_3$
-	-	-	[ ]$_4$

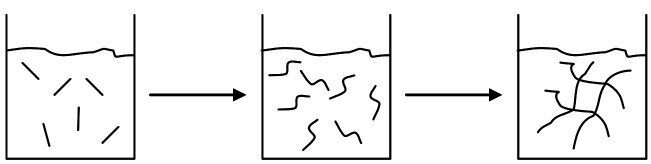


hard segment
→ hard domains

physical network
- held together by hydrogen bonds
- some deg of crystallinity
→ T_m (flow temp)

App:
→ Nike shoe soles
→ biodegradable scaffolds

Step Growth Polymerization



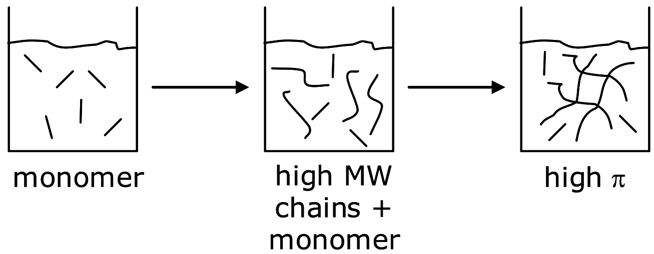
Polymers at high π

- 2^{nd} order kinetics
- MW↑ linearly with time ($\overline{p_n} = 1 + [a]_o kt$)
- MW $\propto \frac{1}{1-\pi}$
- All species in rxn bath are reactive
- Need high π for high MW

Chain Growth (Addition)

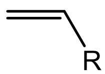
- monomer activation required for polymerization
- only activated monomer/polymer growing chains are active in rxn (v. small fraction at given time)
- growing chains get large rapidly then terminate, deactivates chain
- new monomer is activated

$R^* + M \rightarrow RM^*$
$RM^* + M \rightarrow RMM^*$
$\downarrow$
RMn^*

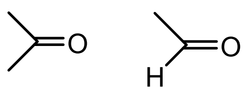


- have only monomer
  high MW polymer
  growing chains
- MW ≠ f(π)
  unless "living" system
  although it is $f[M]_o$

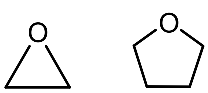
Addition monomers are:



vinyl groups (C=C)

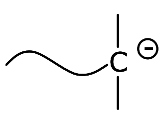


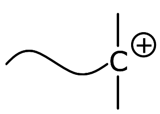
ketones (C=O)
aldehydes

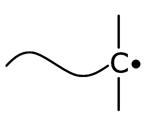


heterocyclic ring monomers
(strained)

Propagating (active) species:

anionic 

cationic 

free radical 

Processes in Addition Polymerization:

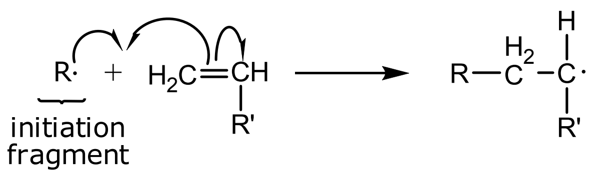
1. Initiation
2. Propagation
3. Termination
4. Transfer of charge or active species from one chain to another

(but not always present)

Free Radical Polymerization

Kinetics: $I \rightarrow 2R\bullet$

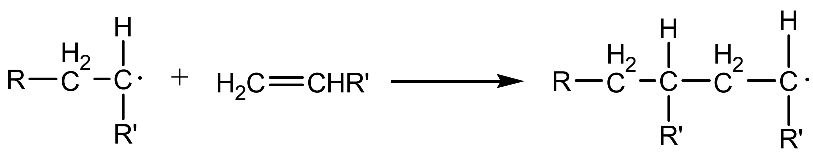
1. Initiation:



2. Propagation Step:

$$RM\cdot + M \longrightarrow RM_2\cdot$$

$$RM_n\cdot + M \longrightarrow RM_{n+1}\cdot$$



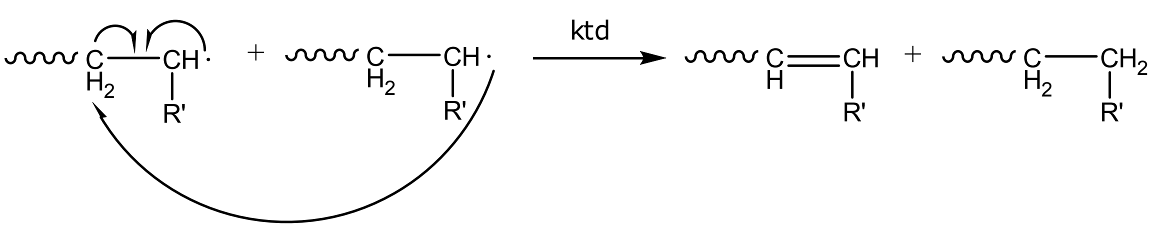
3. Termination:

   Happens one of 2 ways:

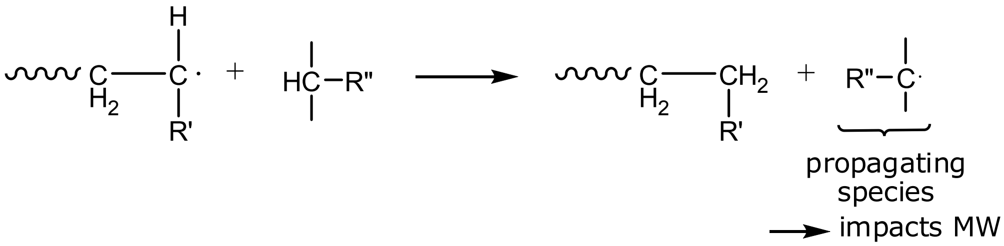
   a. coupling

$$RM_n\cdot + RM_p\cdot \longrightarrow RM_{n+p}—R$$ doubling size of polymer

   b. disproportionation



4. Chain Transfer:



Kinetic Rate Expression

Initiation:

$$I \xrightarrow{k_d} 2\,R\cdot \quad \text{dissociation (rate determining)}$$

$$R\cdot + M \longrightarrow RM\cdot$$

$$\frac{d[RM\cdot]}{dt} = f\,\frac{d[R\cdot]}{dt}$$

(f ↑ efficiency factor)

$$-\frac{d[I]}{dt} = k_d[I] = \frac{1}{2}\frac{d[R\cdot]}{dt}$$

($\frac{1}{2}$ ↑ create 2 fragments)

$$\frac{d[RM\cdot]}{dt} = f\,\frac{d[R\cdot]}{dt} = 2fk_d[I] \quad k_d \sim 10^{-4} - 10^{-6}\ \frac{l}{mol\cdot\sec}$$

Propagation

$$RM_n\cdot + M \longrightarrow RM_{n+1}\cdot$$

$$R_p = -\frac{d[M]}{dt} = k_p\underbrace{[M\cdot]}[M]$$

$[M\cdot] \equiv [Mn\cdot]$ any active monomer

(assume equal reactivity for all M· species)

$$k_p \sim 10^2 - 10^4\ \frac{l}{mol\cdot\sec}$$

Termination

$$M_i\cdot + M_j\cdot \longrightarrow M_{i+j}$$

$$R_t = -\frac{d[M\cdot]}{dt} = 2k[M\cdot]^2$$

assume same disproportionation:

let $k_t = k_{tc} + k_{td}$

k_t ~ 10^6 – 10^8 $\frac{l}{mol \cdot \sec}$

How fast are you creating polymer?

Polymerization rate

$$-\frac{d[M\cdot]}{dt} = R_p = k_p[M\cdot][M]$$

Assume steady state free radical concentration [M·]

$\Rightarrow R_i = R_t$

$$2k_t[M\cdot]^2 = 2k_d f[I]$$

Solve for [M·]:

$$[M\cdot] = \left(\frac{k_d f[I]}{k_t}\right)^{\frac{1}{2}}$$ plug into R_p expression

$$R_p = k_p\left(\frac{k_d f[I]}{k_t}\right)^{\frac{1}{2}}[M]$$

Generic Form:

$$R_p = \left(\frac{k_p^2}{2k_t}R_i\right)^{\frac{1}{2}}[M]$$