10.569 Synthesis of Polymers
Prof. Paula Hammond
Lecture 28: Introduction to Polymer Functionalization: Motivations, Yield, Crystallinity, Solubility Issues, Common Functionalization Approaches

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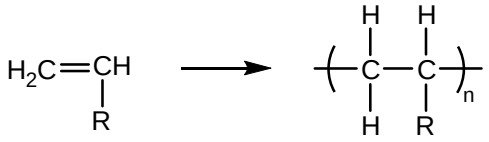
Polymer Functionalization

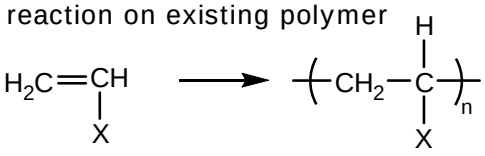
Can make a polymer with desired side group R via

- direct route

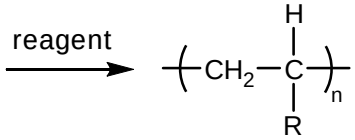


- or perform reaction on existing polymer

a)



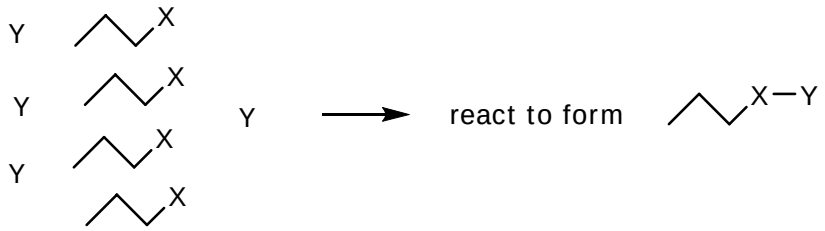
b)



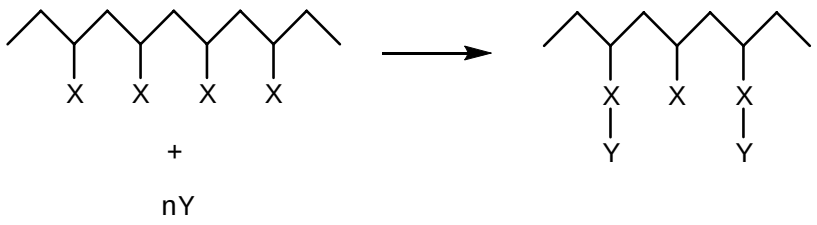
Issues with reactions on polymers

Reactions on Polymers vs Reactions on Small Molecules

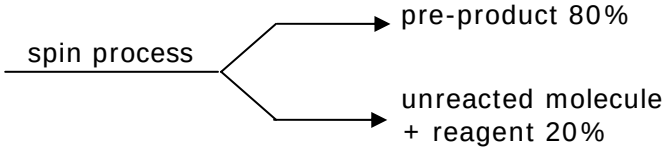
Small Molecule

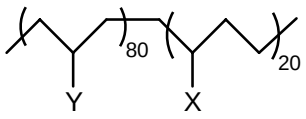


Polymer Chain



1. Yield has different meaning
   Small molecules: 80% yield



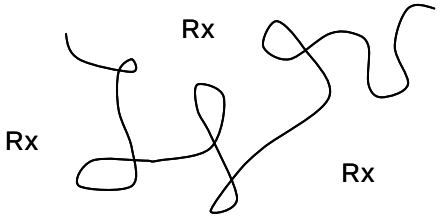
Polymer chain: 80% yield → 

no separation to "pure" component

form copolymer with 80% functionalized groups

2. Localized concentration effects

(e.g. high MW polymer in intermediate solvents)

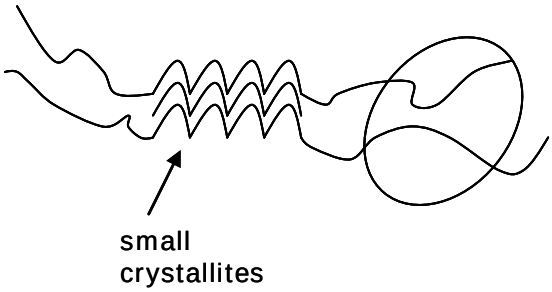


polymer chains may "hide" access of reagent

very large solvent effects

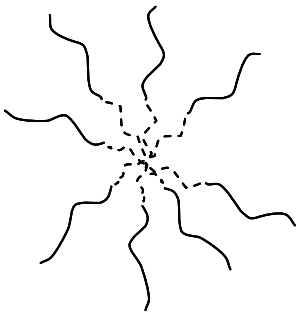
3. Polymer morphology

(e.g. semicrystalline polymers)



→ can be relatively impermeable to solvent + reagent

Block copolymers in selective solvent

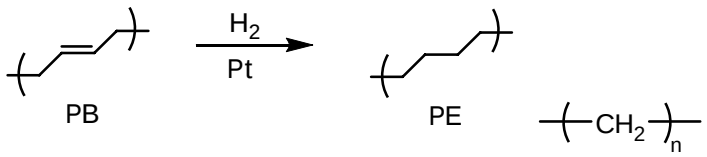


solvophobic block is less accessible to reaction

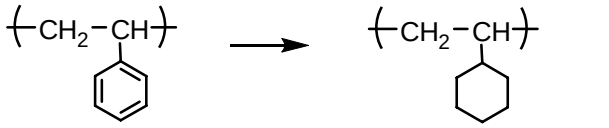
} can be advantageous for selective modification of blocks

Selective Hydrogenation

e.g.

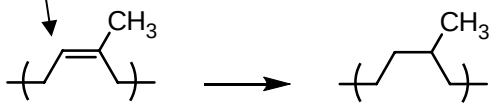


rubber waxy crystalline solid



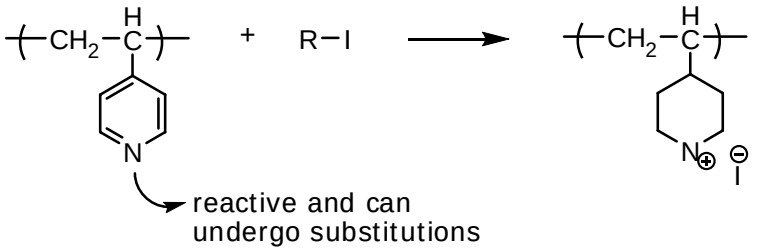
polyV-cyclohexane

poly 1,4 cis polyisoprene
(rubbery low T_g)



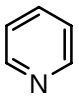
limit crystallinity

4. Sterics are amplified
Steric hindrance can reduce reactivity of neighboring units



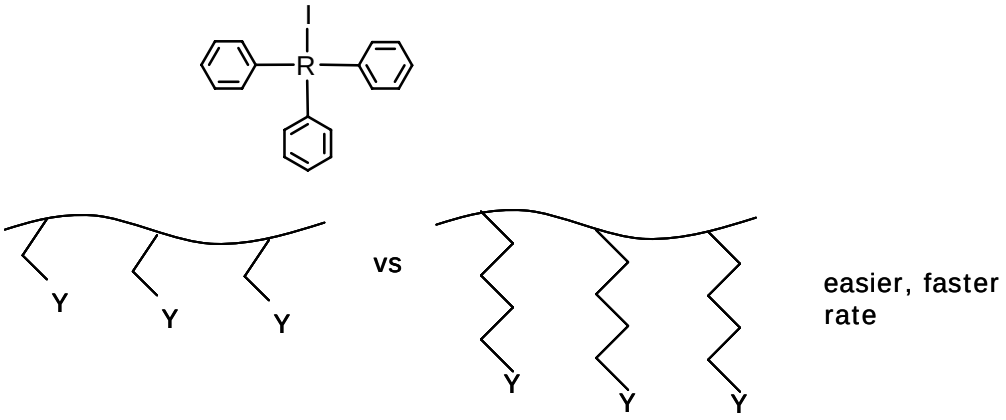
polyvinyl pyridine
PVP

R = C_4H_9 is 4x faster reaction rate than
R = $C_{18}H_{37}$

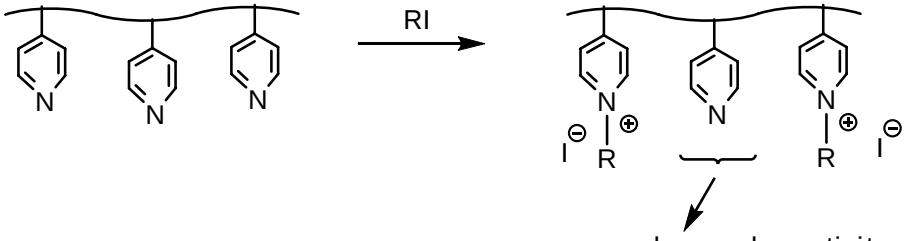
But rates are the same for  + R−I

Note: sterics can often be alleviated with alkyl or ethylene oxide

e.g.



5. Electrostatics can play a role in reaction rate



lowered reactivity
by factor of 3
due to charge repulsion

- unfavorable to make a new N^+ group here b/c of neighboring $^+$s
- by saturating with salt (e.g. NaCl) helps reduce distance between $^+$ and $^-$ charge

Debye length

$\therefore$ more able to react  s close to each other

Consider Kinetics

AAA<u>A</u>AAAA
$\downarrow k_o$
AAAB<u>A</u>AAAA
$\downarrow k_1$

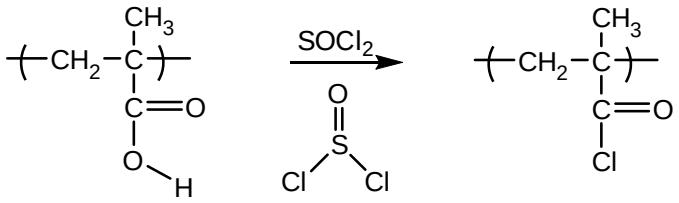
different reactivity than previous with 2A partners

vs.

AAAB<u>A</u>BAAA
$\downarrow k_2$

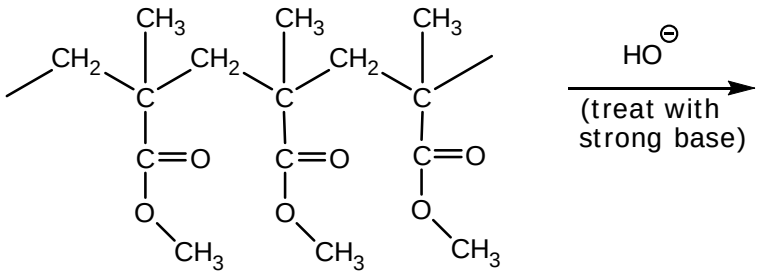
if $k_o = k_1 = k_2$
Bernoullian distribution of functionalization

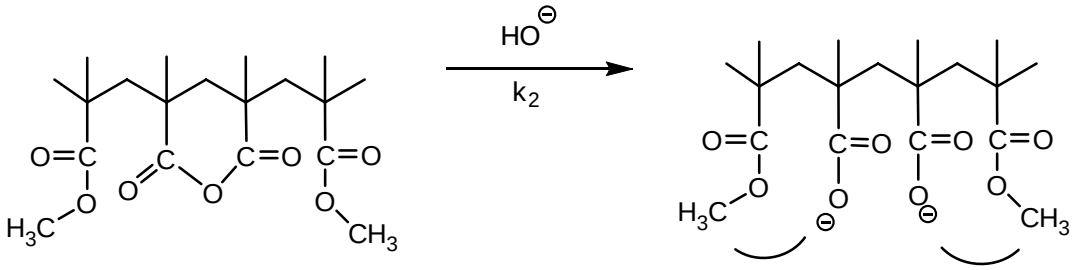
e.g. for highly reactive systems



auto-acceleration (a.k.a. autocatalytic effects)

e.g. hydrolysis of PMMA



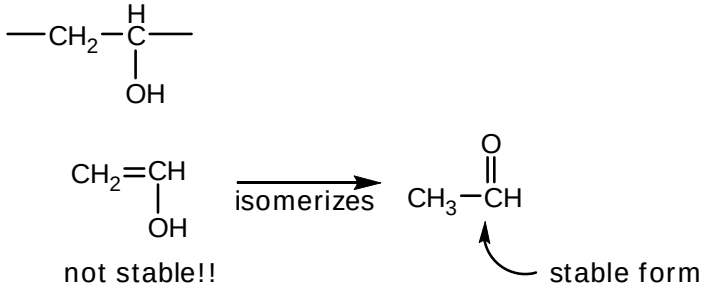


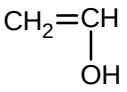
$k_2 > k_1 \Rightarrow$ autocatalysis

Common Polymer Functionalization

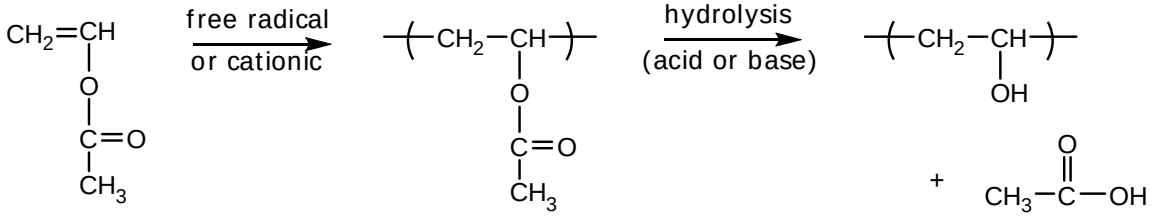
Make polymers that are otherwise inaccessible

1. Polyvinyl alcohol (PVA)

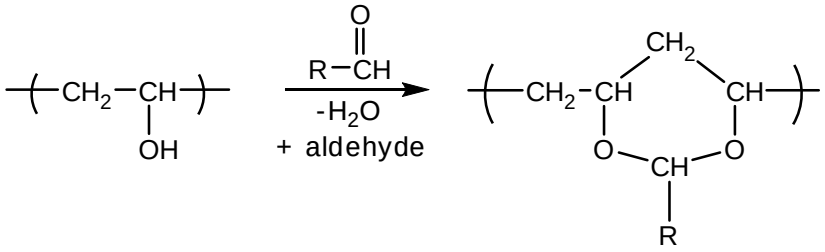


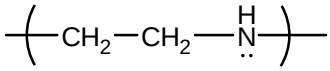
∴ cannot polymerize 

Polyvinyl Acetate

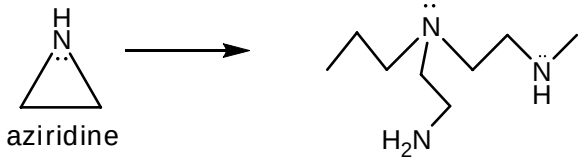


Polyvinyl acetyls are made from PVOH



Also 

Linear polyethylene imine



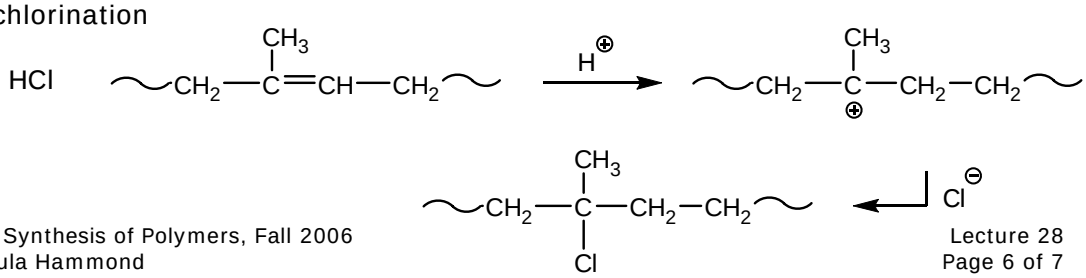
aziridine

Instead use 2-ethyl-2-oxazoline
(EOX)

2. Halogentation of vinyl polymers
   - improves water resistance
   - improves fire/flame stability (chlorination and some case 1 bromination)

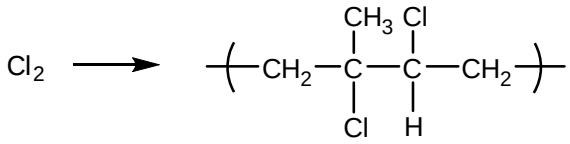
chlorination of natural rubber

Hydrochlorination



Plain chlorination

Gives more Cl



Can add more Cl by free radical
→ aromatic substitutions next time