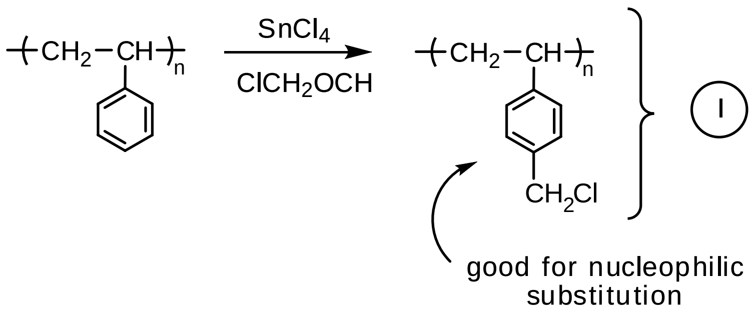
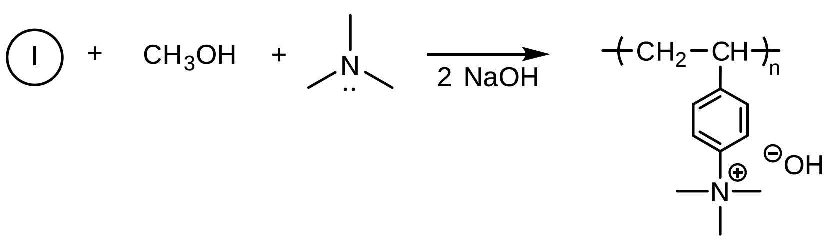
10.569 Synthesis of Polymers
Prof. Paula Hammond
Lecture 29: Functionalization Case Studies:
Biomaterials Systems, LC Polymers

Aromatic Substitutions

e.g. chloromethylation

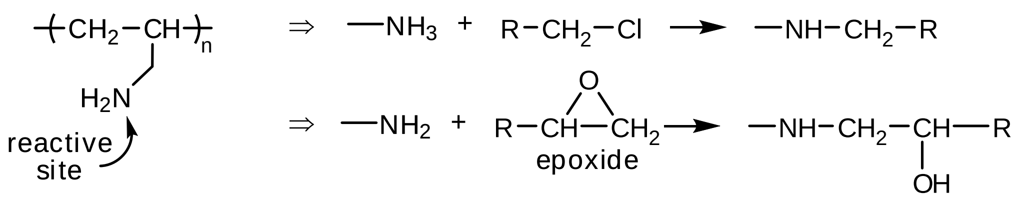




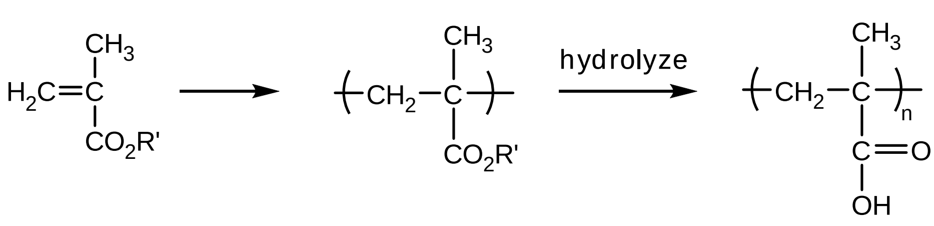
Other Useful Functionalizations

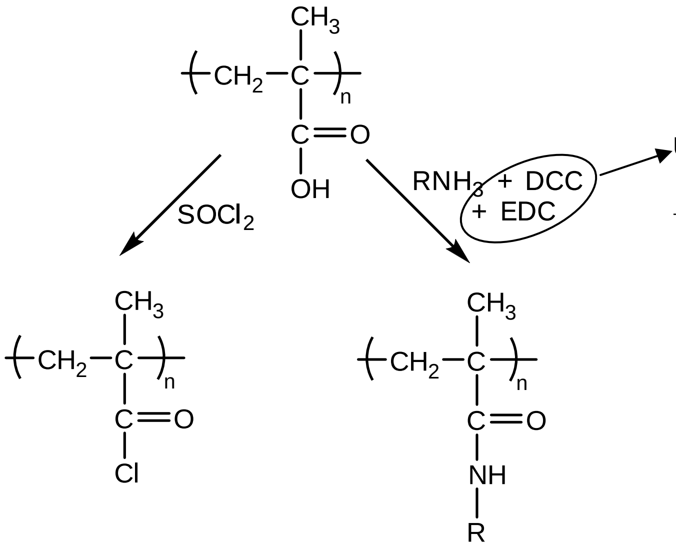
- can use reactive amines

e.g.



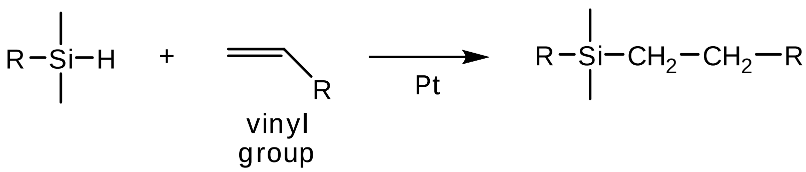
- methacrylate chemistry



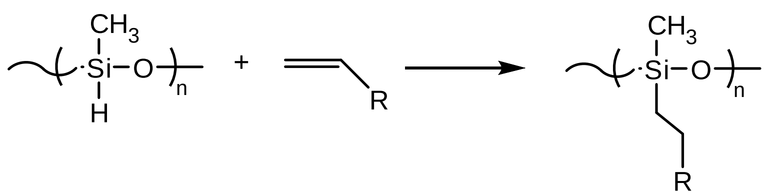


Used in Merrifield synthesis
(step growth)
→ activates carboxylic acid, which is attacked by amine

- hydrosilation
  - general reaction



on polymers



Handout

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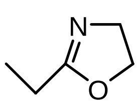
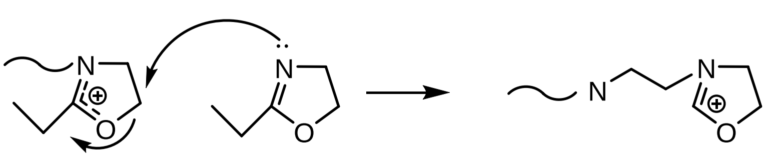
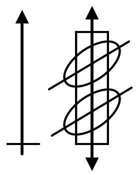


2-ethyl-2-oxazoline
cationic ring-opening polymerization

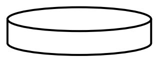


Backbone can be converted to polyethylene amine.

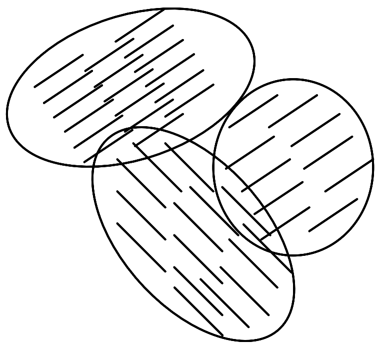
Liquid Crystals (LC's)



→ Board-shaped
"calamitic" can orient preferentially



→ disc-shaped
"discotic"



crystals orientation
domains of different orientation
guide light along domains

polydomains

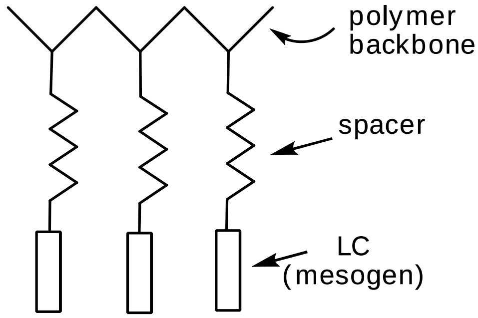
Align LC → using EM field
can allow light to pass through

Applications: displays – need mechanical stability
storage – freeze in orientation and read later
glassy polymer

→ How to attach LC to polymers

1. How to form polymer w/LC side group
2. Block copolymer: LC side chain block and glassy block

Design “Case Study” – LC Side Chain Polymers

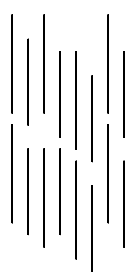


Requirements
-Backbone: determines T_g
- mechanical properties
- chemical stability
- can affect switching times/ response times

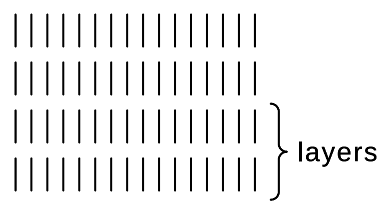
-Alkyl spacer group
- choose spacer group: alkyl and ethylene oxide (most common)

↑ shorter ⇓ leads to nematic phases

↑ more flexible b/c CH_2O bond



Unidirectional Ordered
⇒ nematic



Stacked: 2D order
⇒ smectic
more ordered system

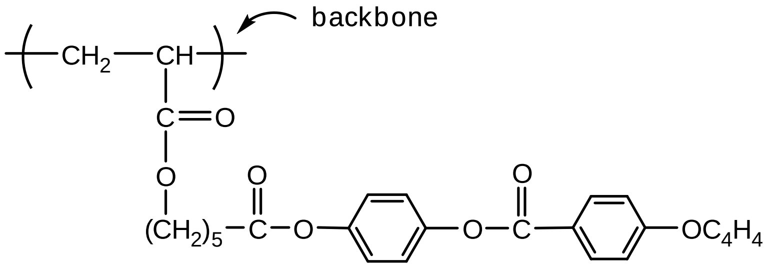
Longer spacers form smectic phases
alkyl group will order

-Mesogen
-LC properties
optoelectronic response
alignment
time
dipole

-Other factors

- does PDI matter?
  - For this application, it depends which phase you're going for
  - For LC polymers, can lose some less stable phases w/high PDI

Example:



PDI	Increasing T $\rightarrow$
a 1.2	$S_F \rightarrow RN \rightarrow S_A \rightarrow N \rightarrow I$
b 2.9	$S_F \rightarrow N \rightarrow I$

close for both PDI

S_F = smectic F
I = isotropic clearing point
N = nematic

- High MW/Low MW?
  - Oligometric $\rightarrow$ stable image
  - High MW $\rightarrow$ storage
- Selected polymer chem. (side group react w/backbone?)
  - need 100% substitution?