10.569 Synthesis of Polymers
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Lecture 6: Other Polymers of Interest obtained by Step-Growth, Polyaramids, Polyimides, Segmented and Block Copolymers from Step Condensation Methods

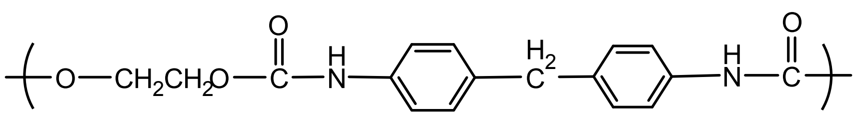
Far from equilibrium polymerizations:

Processing: Bulk reactions much less desirable
- extremely reactive, exotherms huge
high concentrations further increase R_p

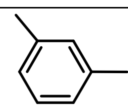
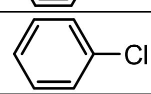
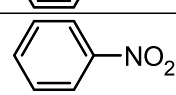
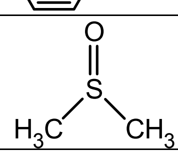
Better to use solution polymerization:
- can control heat removal, viscosity
- controlled by solvent choice (high capacity or low capacity solvent)

Must consider solvent effects:
- solubility of both monomers
- solubility of high MW polymer
$\rightarrow$ wrong (poor) solvent can lead to low MW product

e.g. polyisocyanate



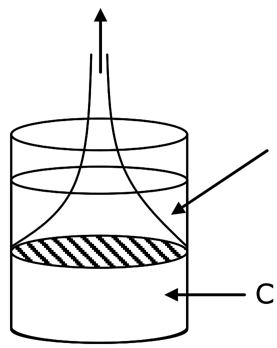
Inherent viscosity [dl/g, deciliter/gram]

		Solvent		Polarity	η_{inh} (relative to MW)
hazardous		Xylene		$\downarrow$	0.06
		Chlorobenzene			0.17
		Nitrobenzene			0.36
	DMSO (used in many biological systems)				0.69

For specific case of fast polymerization:
- low temps are often desired
-40oC ~ 80oC
large $\Delta H_{exo} \Rightarrow T \uparrow$ can lower $\pi \downarrow$
- at good conditions, it is very easy to get 100% π
- lower concentrations
- slow addition of monomer(s) $\rightarrow$ control exotherm, prevent clumping

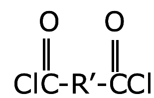
Alternatives to Solution Polymerization

Two Phase Polymerization



H_2O (aqueous phase) $H_2N\text{-}R\text{-}NH_2$ + Base

CH_2Cl (organic phase)



Draw polymer from interface

Interfacial Polymerization:

1. Reactants diffuse to interface
2. Immediate reaction $\rightarrow$ perfect stoichiometry at interface
   Form high MW polymer
3. Remove polymer $\rightarrow$ fresh interface

Polymerization continues until monomer is depleted in organic and/or H_2O phases.

Key Differences

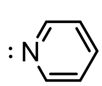
- Diffusion controlled (not kinetically)
- Bulk stoichiometry is irrelevant
- Treat 2 phases as reservoirs
- Higher concentrations in phases $\rightarrow$ higher mass transfer driving forces
- % conversion is not a factor in final MW

Details:

- addition of the base, HCl is generated

$$\underbrace{H_2\ddot{N}-R-\ddot{N}H_2}_{\text{unprotected amine is very reactive}} \xrightarrow{HCl} \underbrace{H_3\overset{\oplus}{N}-R-\overset{\oplus}{N}H_3}_{\text{non-reactive}}$$

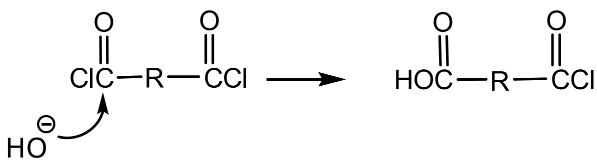
Nonreactive bases:



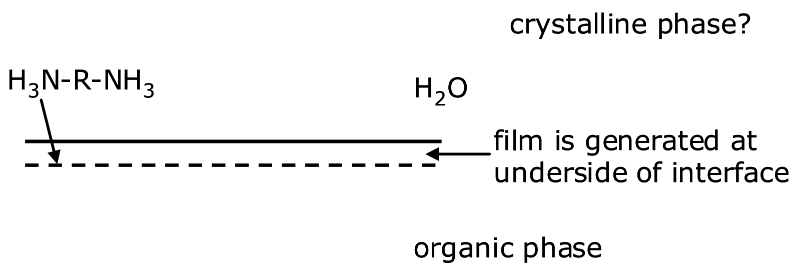
Pyridine

Na_2CO_3 } weak base

Avoid bases with HO^- (e.g. NaOH)
Because they can react with acid Cl groups:



-generally true that diamine has higher diffusion rate in organic phase than diacid chloride in H_2O phase

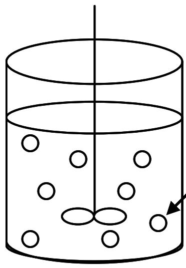


→ organic solvent ⇒ precipitant
must precipitate only high MW polymer

Advantages:
- No need for heavy refrigeration or cooling
  (have very little T-increase, phases absorb exotherm)
- Get high MW without perfect conversions or stoichiometry
  rate of withdrawal affects MW
  when rate ~ formation of chain formation
- Rates of withdrawal, organic solvent choice
- No high-η medium
- Polymer is readily separated from solvent and unreacted monomers

Products made this way:
- aliphatic polyamides
- aromatic polyamides
- polycarbonates
- polysulfides

Stirred Interfacial

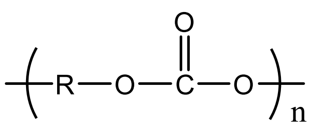


Organic phase (minority)
dispersed in aqueous phase

drops
~ μm to 1 mm in size

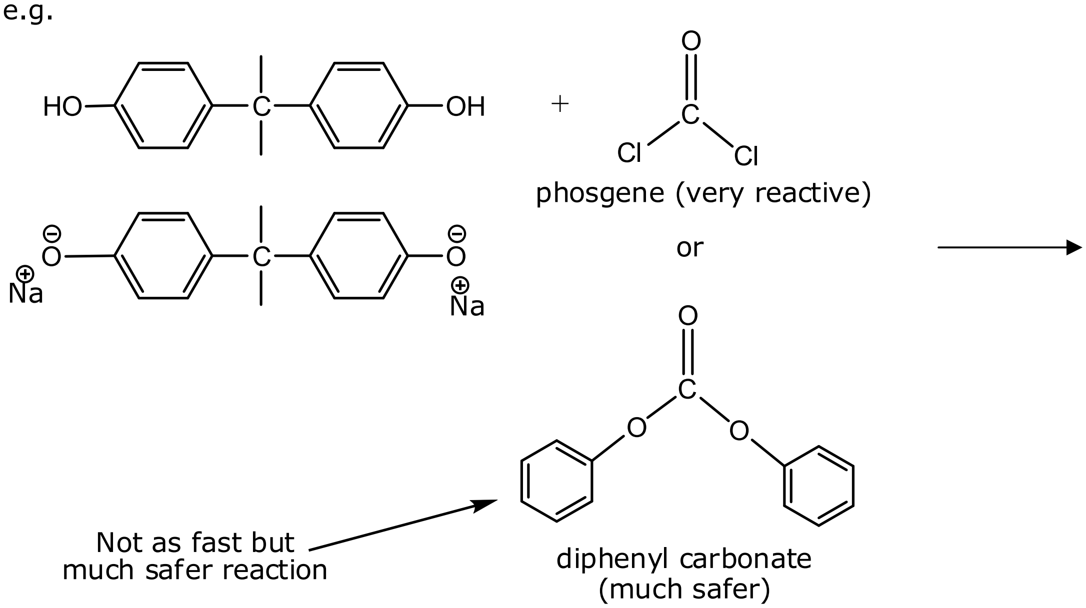
slow stir rate → generate bubble encapsulating products
fast stir rate → continuous removal of polymer from droplet
(shear) → fine particles of polymer
shear can remove polymer film
→ fresh interface
ex. Carbon-less carbon epoxy

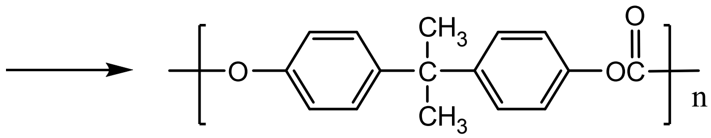
Polycarbonates:



formed from diol + carbonic acid

e.g.





formed via stirred interfacial process
- high $T_g \sim 150^oC$
- non-crystalline (bulky CH_3 groups to prevent crystalline phase the aromatic groups would try to form)
  $\Rightarrow$ fully amorphous $\rightarrow$ optical clarity
- tough material
- application: CDs, optical lenses, glasses, windshields