

Lecture 31: "Living" Free Radical Approaches: Stable Free Radical Polymerization, Atom Transfer Radical Polymerization

Modification of Solid Polymer Surface

e.g. the $\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-OCH}_3$ of PMMA slab

the  of PS surface

Surface reactivity

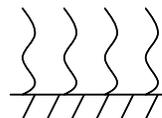
- must have access to functional groups
 - interfacial energy may impact presentation of functional groups to surface
 - surfaces are dynamic \rightarrow small rearrangement can occur
 - also have to consider surface impurities that might prevent or occlude access to functional groups
- \Rightarrow issues around solvent choice and surface properties

Solvent compatibility

- Need to have reaction solvent that wets surface but does not dissolve the solid
- \Rightarrow By altering solvents, get differing degrees of penetration into surface (varying from hundreds of nm to Å's)
 - \Rightarrow Solvent impacts % yield and kinetics
 - \Rightarrow availability of surface groups and solubility of reagent

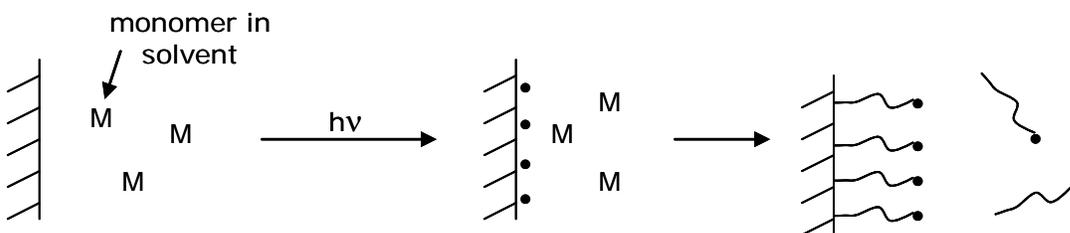
Remember surfaces are heterogeneous
Have morphology (e.g. crystallinity)
Have potential for plasticization w/solvent

Functionalization of Surfaces with Polymers

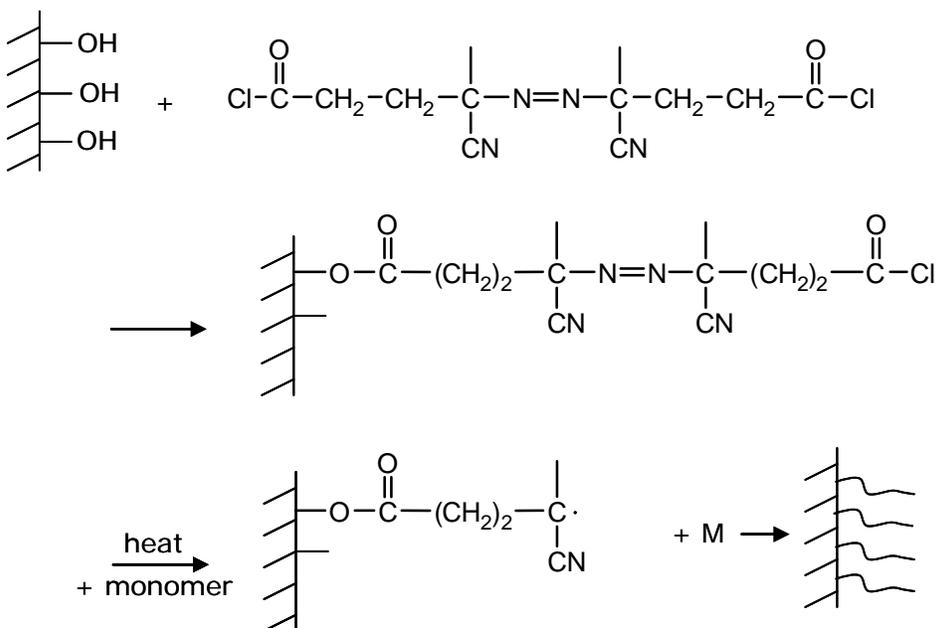


"Grafting From" Approaches

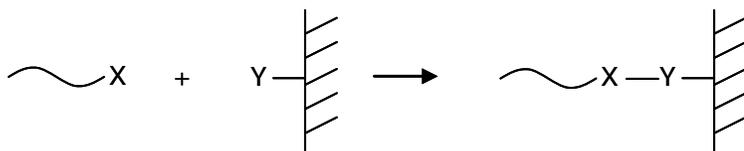
1. Surface irradiation w/high energy + monomer



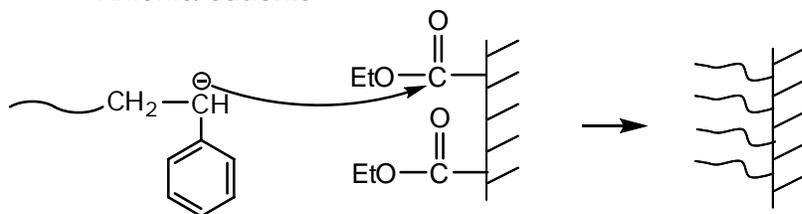
2. Covalent attachment of initiating species



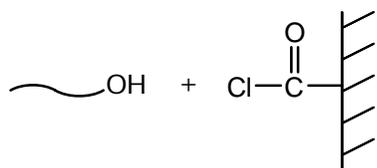
“Grafting To”



Anionic/Cationic



Step Growth



e.g. polyester

Issues for grafting to

Lower yields

Steric constraints to full coverage

Examples (Handout)

Free Radical

- Accounts for ~50% of all mass production of polymers
 - Emulsion
 - Suspension
 - Bulk solution

Most robust method of chain growth

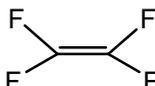
Insensitivity to solvent

Insensitivity to impurities (NH₃, H₂O)

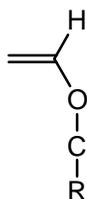
Insensitivity to atmospheric conditions

Open to widest variety of chain growth monomers

- vinyl halogens

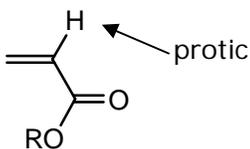


- vinyl esters



limited in ionic polymerization
easy in free radical polymerization

- acrylates



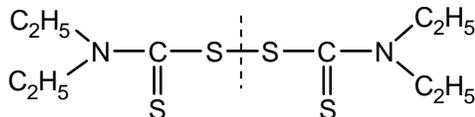
NOT vinyl ethers



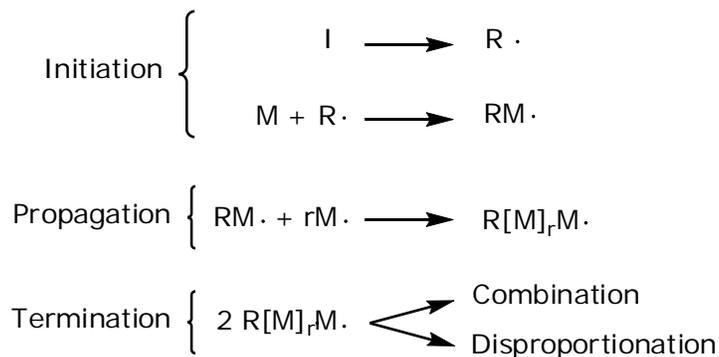
First Attempts at Living Free Radical Polymerization

(Otsa et al, 1982)

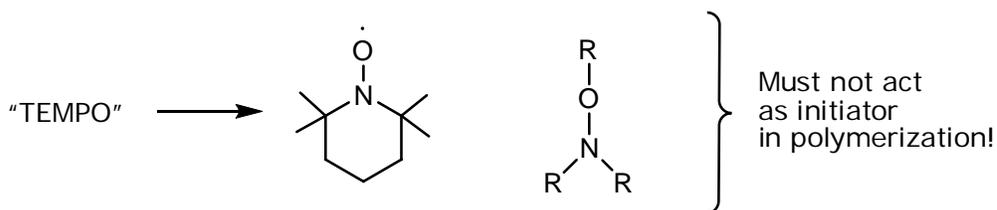
Initiators: $\left\{ \begin{array}{l} \text{initiator} \\ \text{transfer} \\ \text{termination} \end{array} \right.$ Plays all three roles



Original Free Radical Mechanism



Nitroxide Stable Free Radical



Stable Free Radical Mechanism

