10.569 Synthesis of Polymers
Prof. Paula Hammond

Lecture 30: Surface Functionalization of Polymers, Graft Copolymerization, Approaches to Making Comb and Graft Architectures, Grafting onto Existing Polymer Surfaces, Surface Engineering Using Graft Copolymers

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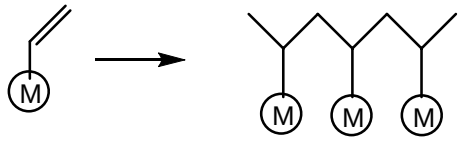
Papers by Zaschke et al, Adams + Gronski, Zentel, Finkelmann on Liquid Crystals

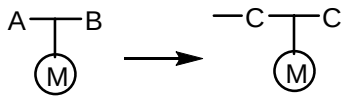
Potential Approaches to LC Polymers

A. Polymerization of an LC functionalized chain growth monomer

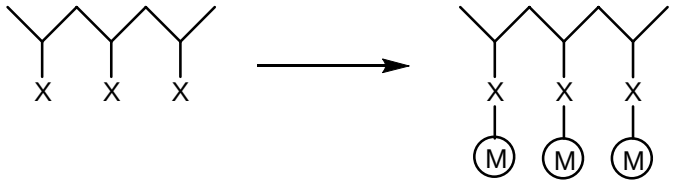


(could also be ring monomer)

B. Step growth approach using a monomer w/functional group



C. Functionalization of existing backbone



Pros and Cons

A. Direct polymerization of functional chain growth monomer

i) anionic

pros: - controlled MW, MWD (monodispers)
- can make block copolymers, α-ω functionalized polymers
- 100% substitution

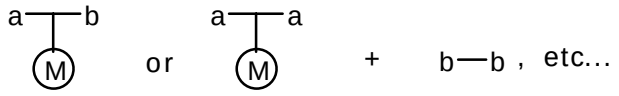
cons: ~C$^{\ominus}$ very reactive, could react with mesogen (M)
(bulky side groups can impede propagation)

ii) free radical

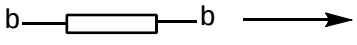
pros: - works with broad range of monomers
(more backbones accessible)
- can make random copolymers with non-functional monomer
(can go from 100% and approach 0% with
Bernoullian distribution – depends on reactivity ratios)

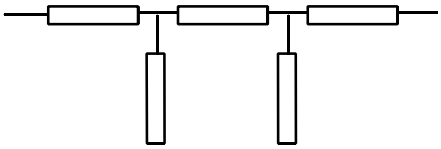
cons: - cannot have good control of MW
- inability to make blocks

B. Step growth



pros: - useful if we wish to combine with main chain group
- choose





electroactuators

main chain/side chain combination

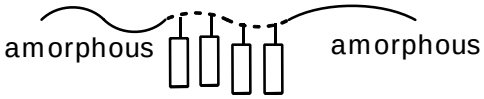
cons: - low MW (except at high π)
- slow reaction
- broad PDI

C. Functionalization of existing polymer
(polymer-analogous rxns)

pros: - can approach polymerization of "base" monomer independent of side group reactivity, solubility, bulk
- can choose well-defined approaches
$\Rightarrow$ control MW
$\Rightarrow$ control PDI
- can change yield $\Rightarrow$ change % substitution $\Rightarrow$ random copolymers!

cons: - not easy to obtain 100% substitution (possible but depends on solvent, etc…)
- challenges in isolating polymer, depending on system (purification)
- sometimes functionalization (modification chemistry) can attack/ affect backbone

Creating block copolymer with LC block/amorphous, etc



Stabilize LC, C*: fast switching speed but fragile display
$\rightarrow$ stabilize w/amorphous region

Polymer Surface Functionalization

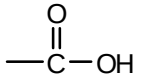
Motivation: - Improving adhesion
- Modify frictional properties
- Attach specific chemistries
- Modify barrier properties

Some Common Methods of Polymer (Plastic) Surfaces

- High energy surface treatments

  Flame treatments
  Corona treatments
  Plasma treatments (CO_2, air, ...)
  γ-irradiation, e-beam

  } in the presence of air

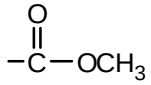
  
  —OH groups

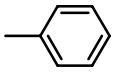
- works on most plastic and resin surfaces (PE, PP)

  e.g. w/ H_2SO_4/CrO_3
  or basic solutions —OH , 

  (PP, LDPE, HDPE, polycarbonates, etc...)

- Modify specific groups on polymer chain

  e.g.  of PMMA surfaces

  or  of PS surfaces

  etc...