Chem 466

Lecture # 2

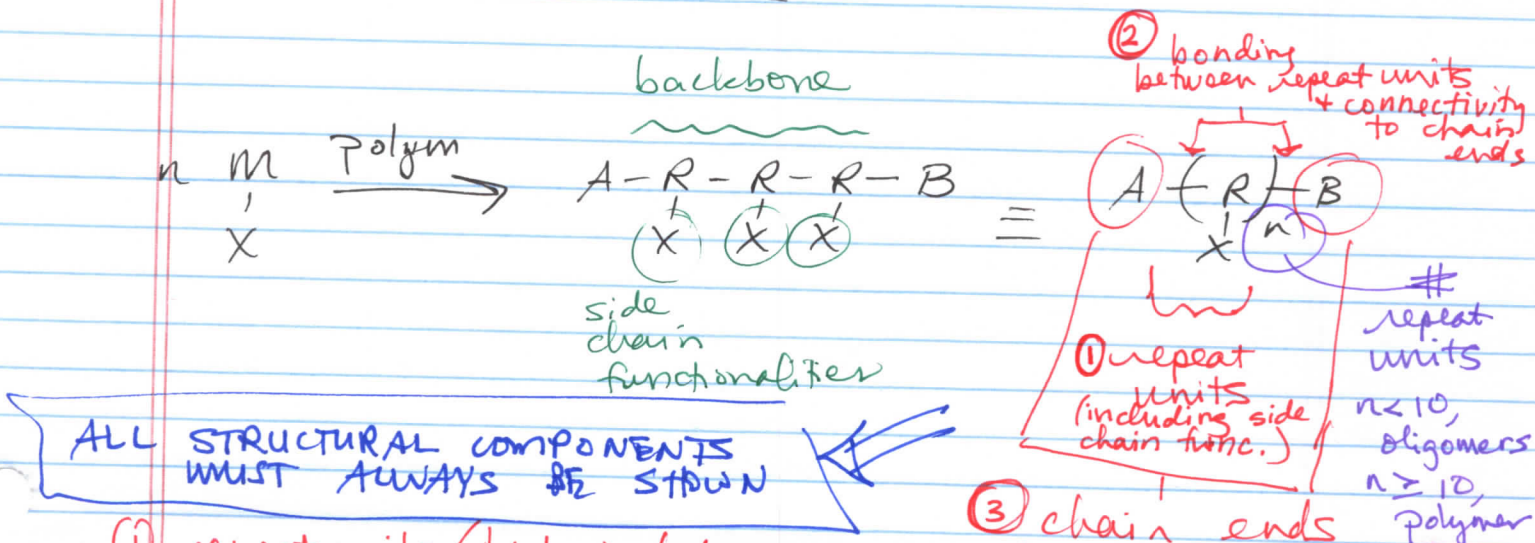
01/16/2014

- Quiz #1 $\bar{X} = 9.6$
  S.D. = 1.7

- Monday, January 20 is MLK holiday
  → no office hours

I. General Introduction to Polymers

(A) Structural features



ALL STRUCTURAL COMPONENTS MUST ALWAYS BE SHOWN

① repeat units (which include side chain functionality)

⊛ depend upon:
- composition of monomer
- polym. chem.
- post-polym. chemical modification rxns

⊛ can be same along backbone (homopolymer) or different (copolymers — statistical (random), alternating, block, gradient, etc.)
- the sequence is important, + is controlled during polym. and/or via post-polym. chem. transformations

⊛ # repeat units, $n = DP$, degree of polym. $= N$ (text)
- poly for $n \geq 10$
- since mol. wt. of monomer is typically ~ 100 Da poly mol. wt. typically ~ ≥ 1000 Da (text p.7)

② bonding between repeat units + connectivity to chain ends

- depends upon:
  - polym. chem.
  - monomer structure
  - initiator + ~~term~~ terminator structures (if employed for polym.)
  - post-polym. chem. transformations
- repeat units can be connected through 2 sites (linear poly) or more (branched or x-linked poly, eg)

③ chain ends

- depend upon chem. used for polym.
  - monomer structure
  - step-growth, condensation polym. vs. chain-growth, addition polym. mechanisms
  - initiator } chain-growth polyms.
  - terminator }
- can influence the poly properties
- must always be drawn

(B) Properties

⊛ for polys, as for small molecules, the properties (physical, chemical, mechanical, optical, etc.) depend upon:

will discuss throughout the semester

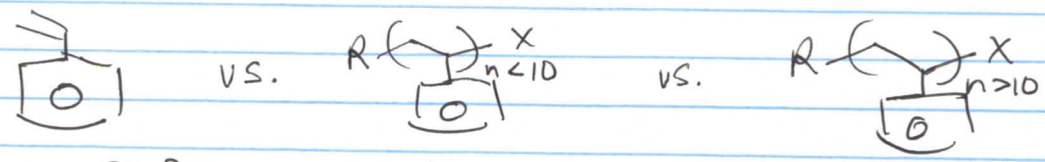
- composition
- stereochemistry
- topology / bonding sequence (architecture, regiochemistry, structural isomerism)
- chain length (degree of polym + mol. wt.)

⊛ general trends as degree of polym ↑, solubility ↓, viscosity ↑, thermal transition temperatures ↑

monomer → oligomer → polymer

monomer	oligomer	polymer
$n = 1$	$n < 10$	$n \gtrsim 10$
MW $\lesssim$ 500 Da (otherwise macromonomer)	MW $\lesssim$ 1000 Da	MW $\gtrsim$ 1000 Da

e.g., as seen for PS standards (slide #7 of Lecture #1)



$T_m = -31\,°C$	loss of xtallinity	$T_g \sim 100\,°C$
b.p. = 145–146 °C	as n↑, bp↑, T_g↑	no T_m
		no b.p. (before Δ decomp.)

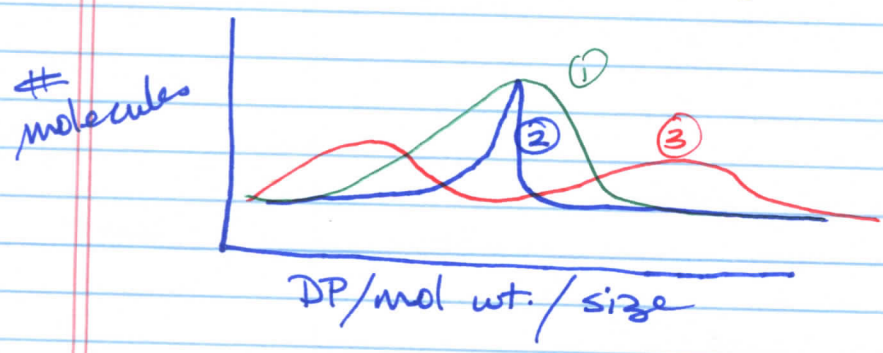
(C) Chain length (DP), mol. wt., mol. wt. distribution

- for synthetic polys, sizes are <u>not</u> homogeneous
  - distributions of degrees of polym.
  - distributions of mol. wt.

  ⟹ average values are det'd.

- polydispersity
  - a measure of the breadth of the mol. wt. distribution
  - polydispersity index = PDI ≥ 1

- mol. wt. distributions can be determined experimentally by separation + analysis of polys having diff. DP/MW/size



MW_{ave} 1 = 2 = 3

PDI 2 < 1 < 3

- mol. wt. distribution is controlled synthetically (to some extent) and also can be altered by fractionation or degradation

(∴ experimentally, important to report % conversion of monomer during polym. and yield of isolated poly, to indicate whether fractionation occurred during work-up of rxn + purification)

(*) $PDI = \frac{\bar{M}_w}{\bar{M}_n} = \frac{\text{wt. ave. MW}}{\text{\# ave. MW}}$

- where, $\bar{M}_w = \sum w_x M_x = \frac{\sum N_x M_x^2}{\sum N_x M_x}$

wt. fraction of poly chains having MW = M_x

\# moles of poly chains having MW = M_x

$$\left[\underset{\left((\text{mol})\left(\frac{g}{\text{mol}}\right)\right)}{w = N_x M_x} \Rightarrow w_x = \frac{N_x M_x}{\sum N_x M_x} \right]$$

- experimentally, $\bar{M}_w$ is determined from light scattering in solution — scattering intensity is greater for larger molecules $\Rightarrow$ biased by large molecules

- and, $\bar{M}_n = \frac{\text{total wt. of molecules}}{\text{total \# moles}} = \frac{\sum N_x M_x}{\sum N_x}$

  - experimentally, $\bar{M}_n$ is det'd. from methods that count # molecules (colligative properties), e.g., osmometry, freezing pt. depression, etc., and also by end group analysis, e.g. titration, NMR spectroscopy, etc.

(*) the full distribution of # molecules vs. mol. wt./size is observed by size exclusion chromatography or MALDI-tof mass spectrometry experimentally

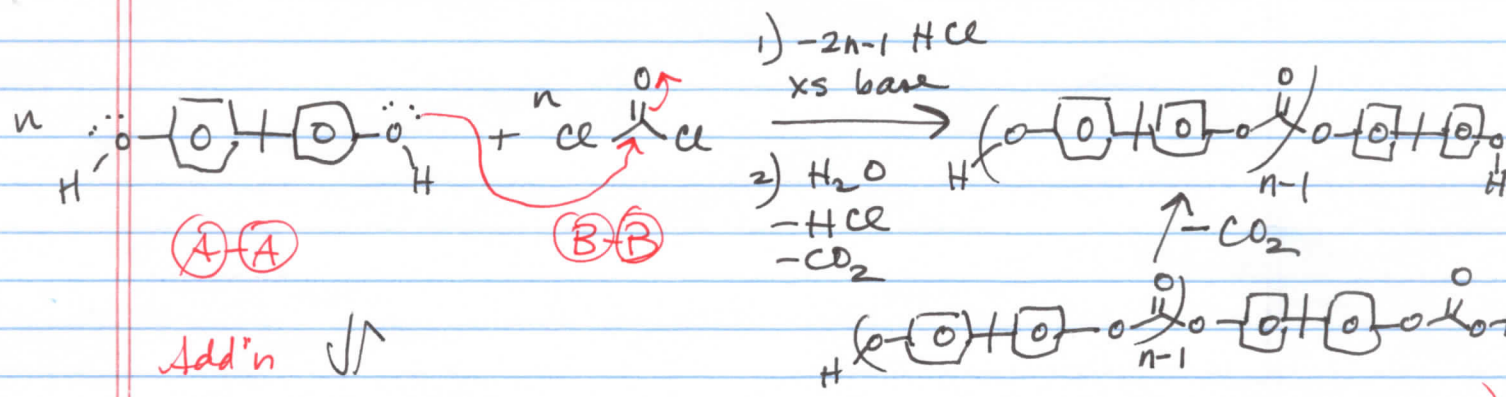
I. General Introduction to Polymers (cont'd)

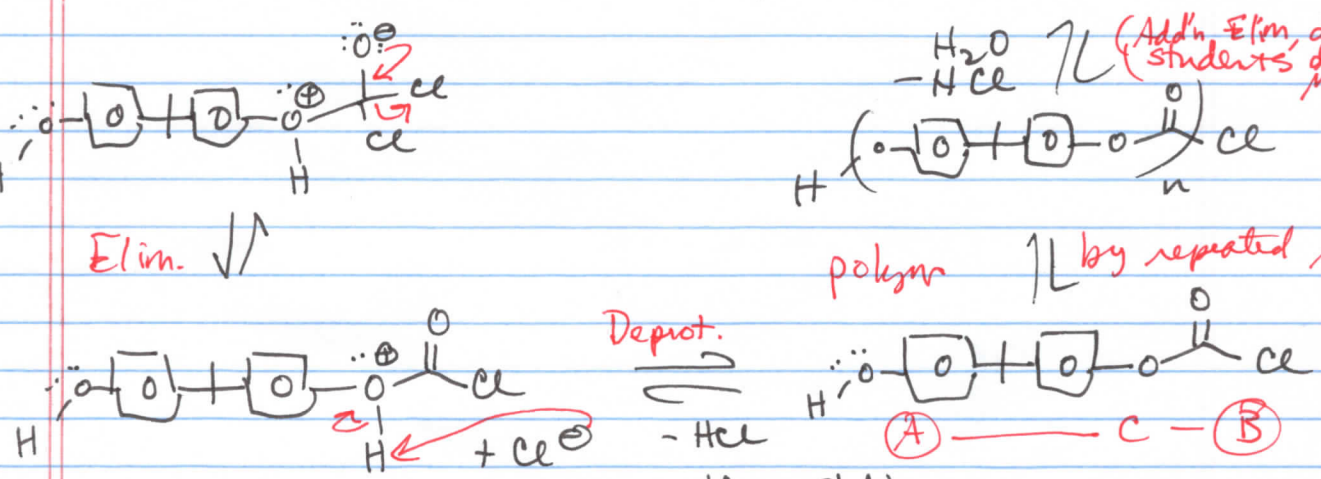
(D) Overview of Polym. Mechanisms

Condensation, step-growth vs. addition, chain-growth polymerizations

① Condensation vs. Addition Polyms – slide

Example chemistry: Poly(bisphenol A carbonate) via an AA + BB condensation polym of bisphenol A + phosgene





Base: e.g. Et_3N or

Base H ⊕ Cl ⊖ e.g. $Et_3\overset{\oplus}{N}HCl^{\ominus}$ or

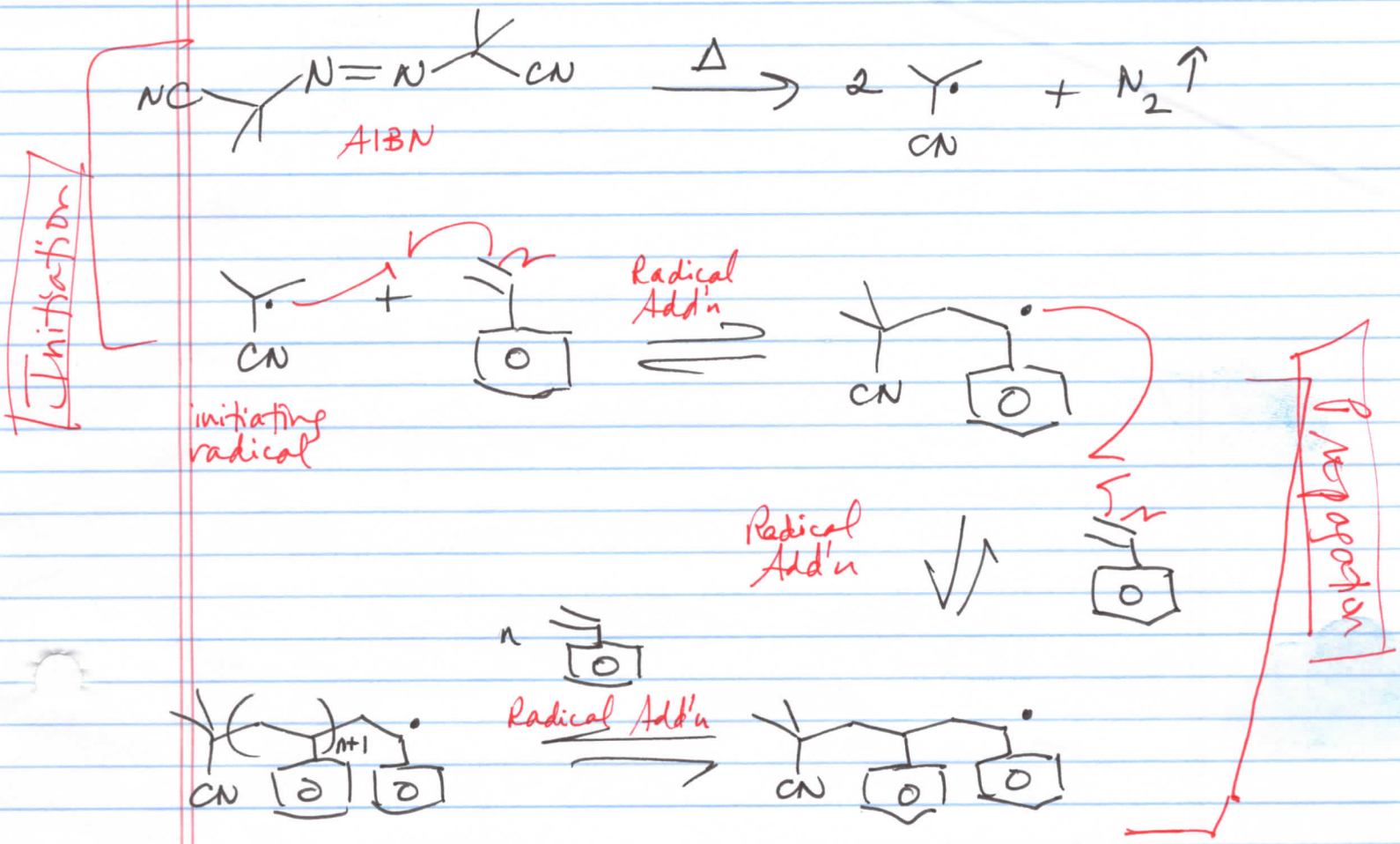
- Condensation, step-growth polyms are recognized by the functional groups along the polymer backbone that can be produced by coupling of functionalities, e.g. condensation rxns
  - however there are many exceptions, especially w/ possibilities for ring-opening, chain-growth polyms as alternatives
    (a poly may appear to originate from step-growth polym but may actually be from chain-growth polym)

② Condensation vs. Addition Polyms — slide

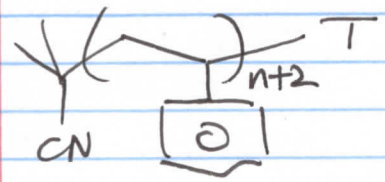
Example chemistry: Polystyrene via a traditional, non-controlled radical chain, addition polym. using AIBN (azobisisobutyronitrile) as the initiator

Three mechanistic steps are involved:

1) Initiation (places initiator @ α-chain end)
2) Propagation
3) Termination (places terminator @ ω-chain end)



Termination (highly reactive radicals can undergo several types of termination rxns — irreversible or reversible (basis of controlled radical polym)) [TBD later]



- same composition as monomer (no condensate)
- Δ bonding (due to addition rxn)

- Addition, chain-growth polymers are recognized, typically, by C–C bonds along the backbone — however, there are many exceptions, e.g. w/ possibilities for polym through other types of multiple bonds or polym by ring-opening rxns