

**Exercise 1.** Which feature distinguishes addition from condensation polymerization?

- a) Addition uses monomers with double bonds; condensation eliminates a small molecule.
- b) Addition eliminates water; condensation keeps all atoms of the monomer
- c) Addition forms only linear chains; condensation forms branched chains
- d) Addition occurs only with aliphatic monomers; condensation only with aromatic monomers

**Solution:**

a) Both parts of the statement are correct, while the other statements have one or both segments that are incorrect.

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**Exercise 2.** Which of the following statements about crystalline polymers is true?

- a) Crystalline polymers have irregular chain packing and low density.
- b) Crystalline polymers have ordered chain packing and higher density.
- c) Crystalline polymers always have lower melting points than non-crystalline polymers.
- d) Crystalline polymers cannot form strong intermolecular interactions.

**Solution:**

b) Crystalline packing is achieved via intermolecular interactions that result in ordered organization, yielding higher density, higher  $T_m$  and greater mechanical strength to the underlying polymer.

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**Exercise 3.** Which of the following statements about biological polymers is true?

- a) Unlike synthetic polymers, their sequences are always determined by a rigid template
- b) Unlike synthetic polymers, their assembly must occur under mild aqueous conditions.
- c) Unlike synthetic polymers, they can create amide and ester linkages.
- d) Unlike synthetic polymers, their three-dimensional structures are generally random.

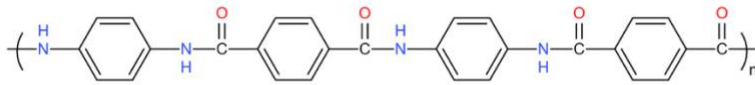
**Solution:**

b) Due to the fact that all biomolecules are made in cells, their assembly must take place under very mild aqueous conditions which is not the case with synthetic polymers. Other statements have incorrect elements.

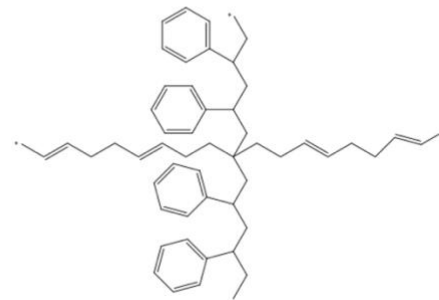
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**Exercise 4.** Identify what type of (co)polymer are below:

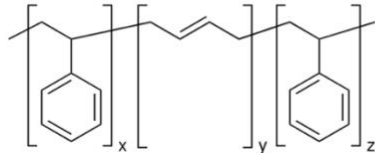
a) Kevlar



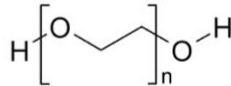
d) High impact polystyrene (HIPS)



b) Styrene-butadiene-styrene (SBS)



c) Polyethylene glycol (PEG)



**Solution:**

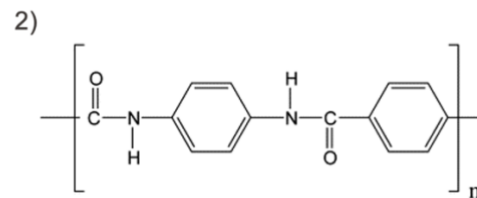
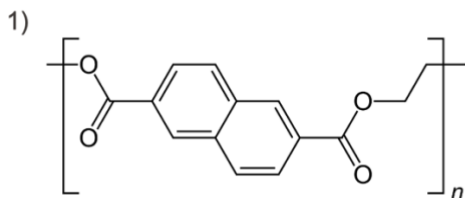
a) Alternating copolymer – 2 different species sequentially present in the chain

b) Block copolymer – Chemically distinct monomers are connected in separate blocks, each block containing x, y, or z repeated units;

c) Simple polymer – Only one chemical unit.

d) Graft copolymer – The polystyrene chain is locally modified with poly-butadiene chains (monomer: buta-1,3-diene), but the two groups are not in the same chain and are connected as “branches”.

**Exercise 5.** Consider the following condensation polymers.



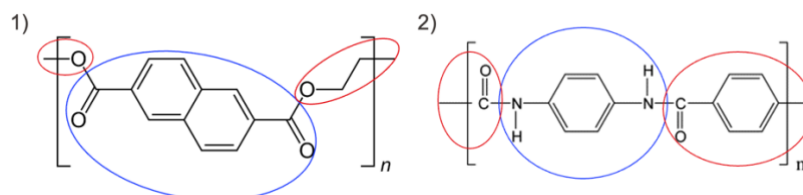
a) What subcategory of condensation polymers they belong to?

b) Label the two molecules comprising each repeating unit?

**Solution:**

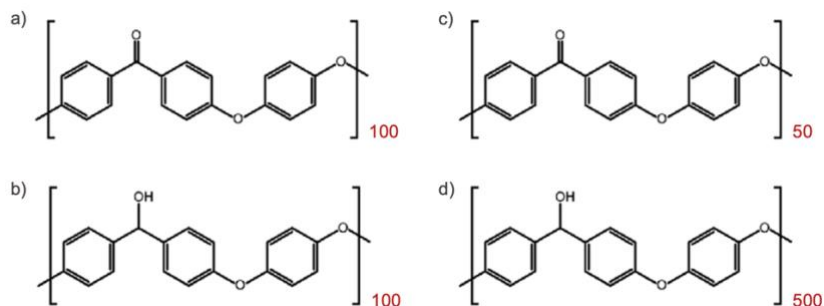
a) Polymer 1 is a polyester, while polymer 2 is a polyamide. This is established based on the functional groups in the backbone.

b) Different groups can be identified based on the fact that they are linked by ester (1) or amide (2) bond. See slides 18 and 22 for the details on how polyamide and polyester chains are formed, and which atoms are contributed by which group.



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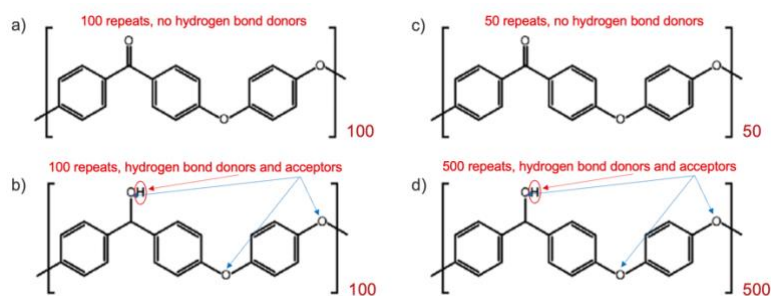
**Exercise 6.** Rank these polymers based on the expected melting point ( $T_m$ ) from highest to lowest:



**Solution:**

The two main parameters to take into consideration are the number of monomers (repeats) and capacity to make hydrogen bonds. The higher the number of monomers  $\rightarrow$  The higher the melting point. Greater capacity to form hydrogen bonds  $\rightarrow$  The higher the  $T_m$ .

For hydrogen bonds to form, there needs to be a donor (e.g., H bound to O or N) and an acceptor atom with free electron pair (e.g., O or N) in the molecule. Only molecules b) and d) have the hydrogen bond donor group (OH) which are suitable for this. Hence, they are the only polymers ones where we can have extra stabilizing effect from the intra- and inter-chain hydrogen bond interactions.



If we take into consideration the chain length and the hydrogen bond capacity the  $T_m$  values will be:

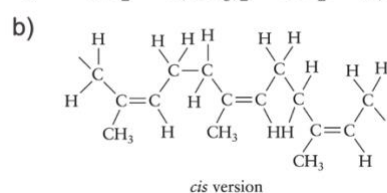
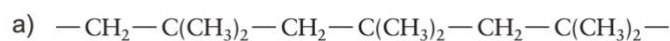
$$T_m \text{ (d)} > T_m \text{ (b)} > T_m \text{ (a)} > T_m \text{ (c)}$$

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**Exercise 7.** Sketch three repeating units of the addition polymer formed from:

- 2-Methylpropene
- 2-methyl-1,3-butadiene

**Solution:**



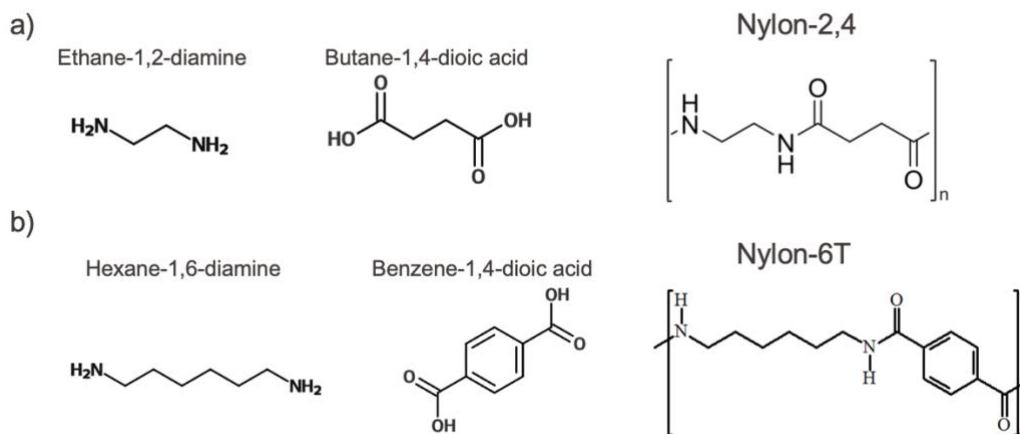
The first polymer is very similar to substituted ethene polymers, except the substituted group is a methyl group ( $-\text{CH}_3$ ), which in the context of monomer is considered to be part of the main chain; hence, 2-methylpropene for the name. But the linkage is such that the  $\text{CH}_3$  groups are to the side of the main chain. Similar to PVC, except replacing Cl with  $\text{CH}_3$ .

The second polymer is essentially isoprene used to make rubber. We just used the IUPAC name here instead of the common name. See slides on isoprene polymerization for extra clarifications.

**Exercise 8.** Draw the structural formula of the repeating unit of the polyamide formed by a condensation reaction between:

- Ethane-1,2-diamine and butane-1,4-dioic acid
- Hexane-1,6-diamine and benzene-1,4-dioic acid

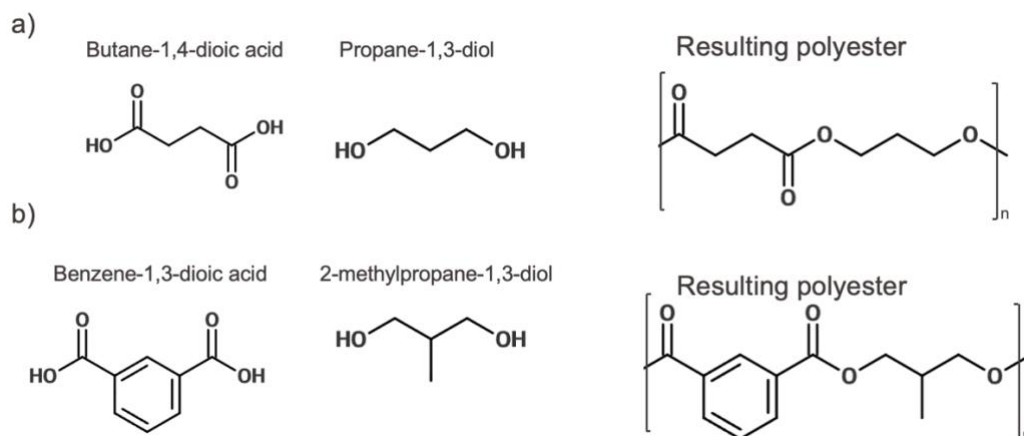
**Solution:**



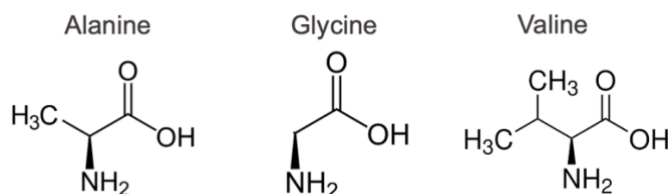
**Exercise 9.** Draw the structural formula of the repeating unit of the polyester formed by a condensation reaction between:

- Butane-1,4-dioic acid and propane-1,3-diol
- Benzene-1,3-dioic acid and 2-methylpropane-1,3-diol

**Solution:**

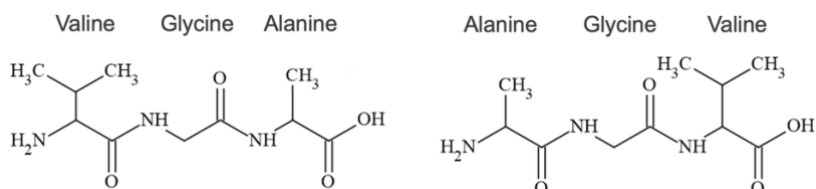


**Exercise 10.** Draw a structure of a short peptide (=mini-protein) assembled by sequentially connecting Valine, Glycine and Alanine (in that order) using peptide bonds.



*Hint:* There is more than one way to connect them.

**Solution:**



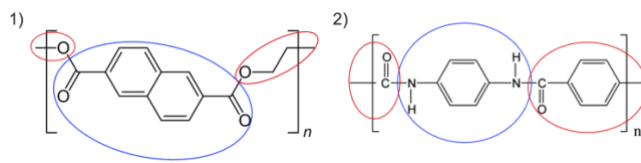
The connection is dependent on the orientation of amino acids (the relative orientation of  $\text{-NH}_2$  and  $\text{-COOH}$  groups). Therefore, this tri-peptide can be produced as:

- 1) Left molecule:  $\text{NH}_2 - \text{Valine} - \text{CO-NH} - \text{Glycine} - \text{CO-NH} - \text{Alanine} - \text{COOH}$
- 2) Right molecule:  $\text{COOH} - \text{Valine} - \text{NH-CO} - \text{Glycine} - \text{NH-CO} - \text{Alanine} - \text{NH}_2$

In nature proteins are always synthesized from the N-terminus to the C-terminus, therefore resembling the left molecule.

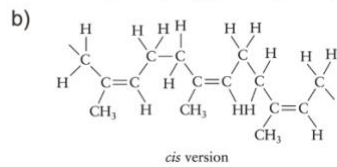
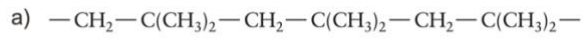
Quick Answers:

1. a)
2. b)
3. b)
4. a) alternating copolymer  
b) block copolymer  
c) simple polymer  
d) graft copolymer
5. a) Polymer 1 is a polyester, while polymer 2 is a polyamide.  
b)



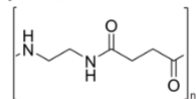
6.  $T_m(d) > T_m(b) > T_m(a) > T_m(c)$

7.

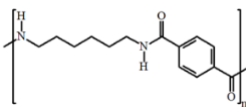


8.

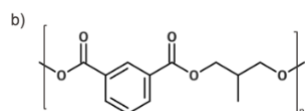
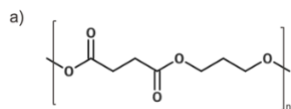
a) Nylon-2,4



b) Nylon-6T



9.



10.

