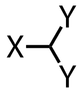
School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

Polymer Science 2024/25

Exercise 12 – Solution

1. Explain the principle and characteristics of a polycondensation and how it differs from polyaddition. Polycondensation of a mixture of X-X and Y-Y type monomers, where Y can react with X, leads to a linear polymer, but so do Y-X type monomers. What is the advantage of a Y-X monomer? Why do we nevertheless prefer the first approach in practice? What types of architecture would result from the polycondensation of monomers of types indicated below?

i)



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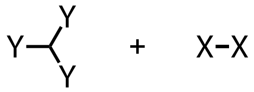
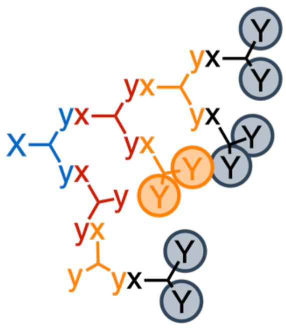


See Slides of Chapter 6.1. Polycondensation of a mixture of monomers of type X-X and Y-Y, where Y can react with X, leads to a linear polymer, but so do Y-X type monomers. Y-X type monomers bear the great advantage of an already perfect stoichiometry of the functional groups (see the general Carothers equation). In practice, however, we prefer the use of symmetric X-X and Y-Y monomers, because it is difficult to store a Y-X type monomer. The functions Y and X will tend to react together during storage! X-X and Y-Y monomers can be separated from each other, avoiding any premature reaction.

In the first case, we will get a "hyperbranched" polymer: imagine that the X of the monomer reacts first with the Ys, so that there will only be Ys on the surface of the growing polymer (highlighted in the circles below; ignore the X of the initial monomer, which will anyways be quickly lost by formation of a ring during the polymerization) - since the Ys of macromolecules cannot react together, each macromolecule will grow independently by reaction with monomers, but it will not react with a neighboring macromolecule. In the second case, the reaction of Y with X-X converts the former into X. Imagine that, as soon as there are only X groups on the surface of the macromolecules, they can react with the Y groups of a tri-functional monomer, but also with the Y groups of neighboring macromolecules. So, a strongly crosslinked polymer is very quickly obtained.

i)



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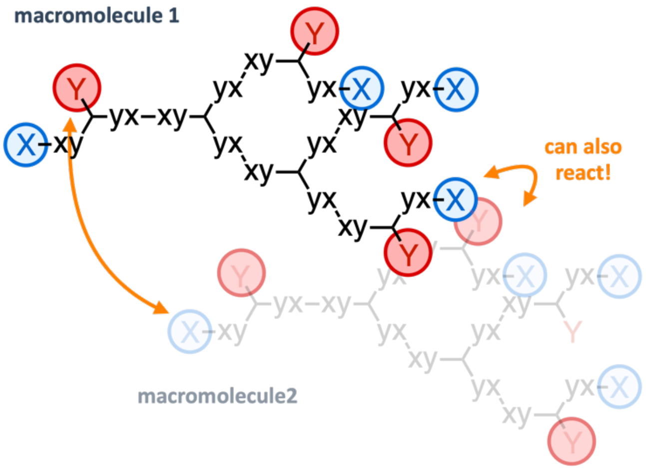
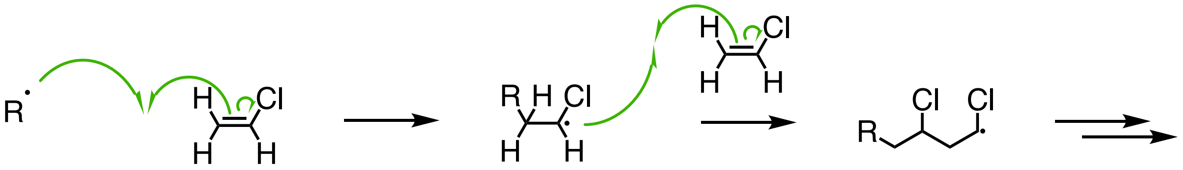


2. The radical polymerization of vinyl chloride can lead to different positional isomers. Explain why. Given that the free radical rather likes to position itself on the carbon attached to the chlorine (due to its electronegativity) which chain form dominates? Draw a detailed reaction mechanism.

   See Slide 41. This is a head-to-tail sequence according to the following reaction scheme:



3. The least expensive semicrystalline polymers (iPP, HDPE, LDPE) are relatively ductile, but other more expensive semicrystalline polymers (e.g. PET, PPS, or PEEK) are often preferred for engineering applications that require a sufficient rigidity. What is the fundamental difference between these two groups of polymers? Can you imagine, why a polymer like polyoxymethylene (POM) is considered as an engineering polymer in that regard (draw its chemical structure and judge its crystallization behavior)?

   The fundamental difference between these two groups is that the T_g of iPP, HDPE and LDPE is well below 0 °C. The amorphous part of these polymers is therefore in the rubbery state and contributes only little to the rigidity, which is therefore often too low for many technical applications.

   In contrast, the T_g of PET, PPS, and PEEK is relatively high. Their amorphous parts are glassy and the rigidity is comparable to that of the crystalline phase.

POM (also called polyacetal) has a very high crystallization rate (therefore high degree of crystallinity and high rigidity), which you may deduce from its chemical structure (linear, highly regular). It is therefore classified among the technical polymers despite its T_g << 0 °C.

4. Polycarbonate (PC) is an engineering polymer that can crystallize but I would not include it in a list of semicrystalline engineering polymers. Why? Why is it considered as an engineering polymer (contrary to the inexpensive amorphous polymers such as PS and PMMA)?

   PC can crystallize but it crystallizes too slowly under usual processing conditions (extrusion, injection, thermoforming, etc.). It is therefore almost exclusively used in its amorphous form. It differs from other glassy, amorphous polymers such as PS and PMMA by its excellent ductility and good impact resistance (see our course on crazing).

   In general, most high T_g semicrystalline engineering polymers crystallize slowly due to their rigid molecular structure (but not Nylons, which can be considered more flexible in that regard).