School of Engineering
Institute of Materials
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Polymer Science 2025/26

Exercise 6 – Solution

1. From the following multiple-choice questions, only one answer is correct. In the exam, each such question will be worth 2 points.

Which statement is *true*?

a) *trans*-1,4-polyisoprene is a soft, amorphous material that crystallizes only under large deformation. ☐

b) For a polycondensation driven to high conversion, a dispersity of 2 and a Poisson-type distribution of the molecular weight are expected. ☐

c) In the free-radical polymerization of ethylene, an increase in initiator concentration increases the polymerization rate but decreases the average molecular weight. ■

d) Bisphenol-A polycarbonate (PC) cannot crystallize because of irregularities in its chemical structure. ☐

trans-1,4-polyisoprene is crystalline and rigid. The _cis_-1,4-isomer (natural rubber) is the soft, amorphous one that can undergo strain-induced crystallizes.

At high conversion, step-growth polymerizations follow a Flory-Schulz distribution with a dispersity of 2.

PC is amorphous but it can crystallize if given enough time.

Which polymerization conditions do you expect to result in a thermoset?

a) The polymerization of 2-aminoterephthalic acid (2-aminobenzene-1,4-dicarboxylate) at high temperature. ☐

b) Reaction between ethylene glycol (ethane-1,2-diol) and 1,6-hexandiamine in the presence of catalytic amounts of an acid. ☐

c) The reaction between phosgene and bisphenol A at high temperature. ☐

d) The reaction of benzene-1,3,5-triisocyanate and ethylene glycol (ethane-1,2-diol) in the absence of water. ■

The polymerization of an XY_2-type monomer (one amine, two carboxylic acids) gives hyperbranched polymers (see Exercise Sheet 1).

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Ethane-1,2-diol and 1,6-hexandiamine are both nucleophiles and do not react with each other. A condensation would require an electrophilic comonomer such as a diacid or a diacid chloride.

The reaction of phosgene and bisphenol A is the polycondensation route to PC. Both monomers are difunctional, so the product is a linear thermoplastic, not a thermoset.

A thermoset forms when a crosslinked network is created during polymerization. Benzene-1,3,5-triisocyanate is a tri-functional monomer whose reaction with the difunctional diol can produce a three-dimensional, infinite network, i.e. a thermoset.

Which is the best description of poly(tetrafluoroethylene)?

a) Petroleum-derived polymer that crystallizes preferably in an orthorhombic unit cell. ☐
b) Perfluorinated polymer that crystallizes preferably via a helical conformation. ■
c) Polymer with high chemical resistance and high melting temperature due to strong dipolar interactions between the polymer chains. ☐
d) Material with a very high friction coefficient that is industrially produced via the free radical polymerization of tetrafluoroethane. ☐

PTFE is a perfluorinated polymer. Because of the large fluorine atoms, the polymer backbone adopts a helical conformation to minimize steric repulsion. Crystallization from this conformation (which has a nearly perfectly cylindrical cross-section) results in a hexagonal unit cell, not an orthorhombic one.

PTFE is a nonpolar polymer. The high melting temperature does not result from dipolar interactions but is largely entropically determined, reflecting the low conformational entropy of its stiff, helical chains in the melt.

The monomer required for PTFE is tetrafluoroethylene, not tetrafluoroethane. Besides, PTFE has an exceptionally low friction coefficient, which is why it's used as a non-stick coating (Teflon®).

Which of the following statements about polymer chain conformations is *correct*?

a) The "freely rotating chain" model allows greater flexibility than the "freely jointed chain" model, resulting in a smaller root-mean-square end-to-end distance, R_n, for a given chain length n. ☐
b) Flory´s characteristic ratio C_∞ quantifies the deviation of a real polymer chain from the ideal chain model and is defined as the ratio of the actual bond length to the bond length of a fully extended, infinitely stiff polymer chain. ☐
c) The size of a polymer chain, represented by the root-mean-square end-to-end distance, R_n, depends on the bond length, l, and the number of bonds in the chain, n, and it scales as $n^{1/2}$. ■
d) For a freely jointed chain, the radius of gyration, R_g, is always larger than the root-mean-square end-to-end distance, R_n, regardless of chain length. ☐

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The freely rotating chain includes a fixed bond angle, which restricts the number of accessible conformations compared to the freely jointed chain. Therefore, its flexibility is reduced (not increased), and it predicts a larger (not smaller) root-mean-square end-to-end distance.

Flory's characteristic ratio does not compare bond lengths but quantifies the deviation of the real chain's mean-square end-to-end distance from the freely jointed chain model (see Slide 99).

For a freely jointed chain, the root-mean-square end-to-end distance is larger by a factor of $\sqrt{6}$ compared to the corresponding root-mean-square radius of gyration.

Which polymer is least suitable for microwave heating due to significant microwave absorption?

a) Polyethylene (PE) ☐
b) Poly(vinyl chloride) (PVC) ■
c) Poly(ethylene-*co*-tetrafluoroethylene) ☐
d) Polytetrafluoroethylene (PTFE). ☐

Only PVC has a significant net dipole moment due to the polar C–Cl bonds along the backbone, which enables the polymer to absorb microwave and heating.

In contrast, PE, PTFE, and the random copolymer are nonpolar or highly symmetric polymers with negligible dipole moments, making them transparent to microwaves.

Which polymer is most likely to undergo crystallization upon slow cooling from the melt?

a) Polycarbonate produced by polycondensation of bisphenol A and phosgene. ■
b) Polystyrene produced by living anionic polymerization of styrene. ☐
c) Polypropylene produced by free radical polymerization of propylene. ☐
d) Poly(lactic acid) obtained by ring-opening polymerization of stoichiometric amounts of L-lactide and D-lactide. ☐

PS and PP produced under the indicated conditions are atactic polymers with random side-group orientations. They are therefore amorphous and do not crystallize. PLA based on a random L/D-copolymer has an irregular backbone sequence, which likewise suppresses crystallization. Only polycarbonate can crystallize if given enough time during cooling from the melt, although it is normally used as an amorphous polymer under standard processing conditions.

2. The melting temperature of a crystalline lamella formed by a polymer is given by

$$T_m = T_{m0}\left(1 - \frac{2\sigma_e}{l\Delta H}\right)$$

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a) Explain the meaning of each term in this equation with reference to a schematic representation of a lamella, and discuss the physical origin of this relationship.

For a schematic representation, see Slide 181 of the class, which you should aim to reproduce. This expression relates the observed melting temperature T_m of a polymer lamella to its finite thickness l.

T_{m0}: the equilibrium (thermodynamic) melting temperature of an infinitely thick, perfect crystal in equilibrium with the amorphous phase.

ΔH: the melting enthalpy per unit volume (or per repeating unit) of the perfect crystal.

σ_e: the fold surface free energy, representing the energetic penalty associated with chain folding at the upper and lower surfaces of the lamellae.

l: the lamellar thickness, typically on the order of 10 nm.

In a lamellar crystal, the polymer chains are oriented approximately perpendicular to the lamellar surfaces. Because real polymer chains are much longer (often > 1000 nm), they must fold back and forth within the crystal. Chain folding is energetically unfavourable, especially for rigid chains, and contributes to a positive surface energy σ_e.

This surface energy effectively reduces the enthalpic gain of crystallization, leading to a melting-point depression for thinner lamellae. Therefore, T_m decreases with decreasing l.

b) In a semi-crystalline polymer, the lamellae are organized in the form of spherulites. What is a spherulite, and which mechanisms lead to the formation of spherulites from lamellar nuclei within a molten polymer when $T_g < T < T_{mo}$?

A spherulite is a roughly spherical, semi-crystalline superstructure formed from radially oriented lamellae separated by amorphous regions. In a typical semi-crystalline polymer, about 40–60% of the material is crystalline, depending on molecular structure and crystallization conditions.

For a schematic model, see Slide 197. Spherulite formation begins with nucleation of a lamella in the supercooled melt (i.e., for $T_g < T < T_{m0}$). The lamella grows laterally by chain deposition onto its fold surfaces, maintaining nearly a constant thickness. However, because the surrounding melt is entangled and viscoelastic, stresses can cause the lamella to tear or twist, generating screw dislocations that promote spiral or branching growth.

As new lamellar fragments grow and separate, they diverge due to the presence of amorphous chain segments connecting them. Repeated events of tearing, branching, and secondary nucleation lead to a radially symmetric, three-dimensional structure (the spherulite). In an exam, you should illustrate this process schematically as shown in the Slides.

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c) During injection molding, a highly stretched molten polymer comes into contact with the walls of a cold mold. What are the consequences for its morphology, assuming that the polymer can crystallize?

During injection molding, a molten polymer experiences strong flow and stretching near the cold mold walls. If the polymer is capable of crystallization, this flow-induced orientation greatly promotes crystallization, because the conformational entropy penalty is reduced: the chains are already partially extended and aligned.

As a result, lamellae stack preferentially along the flow direction, producing an oriented crystalline morphology near the surface. In highly stretched regions, shish-kebab structures can form: extended-chain crystals (shish) serve as nucleation centers for folded-chain lamellae (kebabs) that grow radially from them. Schematics are again useful to illustrate this flow-induced morphology.

3. a) What is the glass transition and how can it be measured? For a given polymer, do different measurement techniques give the same value for T_g? Explain briefly.

In the molten state, polymer chains constantly change their conformations on the picosecond timescale. Upon cooling, these conformational motions slow down progressively. The glass transition temperature (T_g) marks the temperature below which large-scale conformational rearrangements essentially cease, leaving only local motions (such as crankshaft motions, see later in the course).

Experimentally, T_g is not a sharp thermodynamic transition but a kinetic phenomenon that depends on how mobility is probed. It can be determined from changes in properties that reflect chain mobility, such as heat capacity (DSC), thermal expansion coefficient (dilatometry), or modulus (dynamic mechanical analysis). The measured T_g depends on the timescale (or frequency) of the experiment: faster measurements or higher cooling rates yield higher apparent T_g values.

b) Show schematically the shear modulus G as a function of temperature T for an amorphous polymer. Indicate the approximate orders of magnitude of G as well as the influence of molar mass M and measurement speed (or frequency). Add to the same graph the corresponding behavior of a semi-crystalline polymer and an elastomer.

The temperature-dependence of shear modulus G for an amorphous polymer follows four distinct regimes:

- **glassy region ($T < T_g$): $G \approx 10^9$–10^{10} Pa. The polymer behaves as a rigid glass with only vibrational motion.**
- **glass transition region ($T \approx T_g$): G drops rapidly by several orders of magnitude as segmental motions become active.**

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- **rubbery plateau ($T > T_g$): $G \approx 10^6$ Pa for high-molar-mass polymers where entanglements act as temporary crosslinks. The plateau is longer for higher molar masses.**
- **terminal flow region: ($T \gg T_g$): G decreases further as entanglements relax, and the polymer flows viscously.**

Measurement speed (or frequency) shifts the entire curve to higher temperatures for faster measurements. Semi-crystalline polymers show a secondary increase in G at the melting temperature due to the crystalline phase, while elastomers display a permanent rubbery plateau due to chemical crosslinks.

See, for example, Slides 167 and 211. Note: the Young's modulus is approximately three times G.

c) Briefly explain the principle of free volume theory. How does this theory account for the dependence of T_g on molar mass for linear chains? What is the effect of chain branching on T_g, and why?

The free volume theory describes the glass transition in terms of the available unoccupied space that enables segmental motion. Consider a dense packing of polymer segments represented as rigid spheres. Each segment occupies a volume v_0, including its own volume plus small interstitial voids. On heating, thermal vibrations increase this volume through the thermal expansion coefficient.

However, for a segment to move to a new position (i.e. to enable a conformational change), a void at least comparable to the size of a sphere must exist nearby. At a certain temperature, T_0, the fraction of volume available for such motion (the free volume, v_f) becomes sufficient for cooperative rearrangements. Above T_0, the system can continuously adjust its conformation and behaves a s a viscous liquid. Below T_0, the polymer remains trapped in a rigid glassy configuration.

Because T_g depends on dynamics, the observed T_g corresponds not to T_0 itself but to the temperature where v_f decreases to a critical value at which conformational motion effectively ceases on the timescale of the experiment.

Graphically, this is illustrated on a volume-temperature plot, where a change in slope marks the transition between the glassy and liquid-like regimes. The dependence of T_g on molar mass M arises, because the chain ends introduce additional free volume and increase segmental mobility. Therefore:

$$T_g = T_{g\infty} - \frac{K}{M} \quad .$$

Shorter chains (lower M) exhibit a lower T_g.

Branching also introduces more chain ends and hence more free volume, which tends to lower T_g. However, extensive branching or short, rigid side chains can restrict mobility and increase T_g, so the overall effect depends on the nature and density of the branches.

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