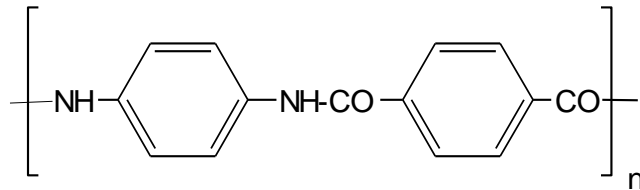**Review Exercises I**

1. Identify all the possible structural and stereoisomers that can result from the polymerization of 1,3-butadiene.

2. Calculate M_n and M_w and dispersity (Đ) for a hypothetical polymer sample that contains equimolar amounts of 3 uniform polymers having molecular weights 30 000, 60 000 and 90 000 g/mol.

3. Both aromatic polyamide Kevlar

and extended-chain linear polyethylene fiber contain a high degree of extended-chain crystallinity, however, the former is somewhat stronger than the latter. Why?

4. Nylon 66 – poly(iminoadipoyliminohexan-1,6-diyl) is opaque when pure. However, if adipic acid is substituted by isophtalic acid, the resulting polymer is transparent. Explain.

5. A paint is to be prepared from a poly(vinyl acetate) (PVAc) emulsion. PVAc has a T_g of about 28 °C and at ambient temperature the dried paint is very brittle and cracks easily. Suggest methods to overcome this problem.

6. Consider a family of polyesters with the general structure:
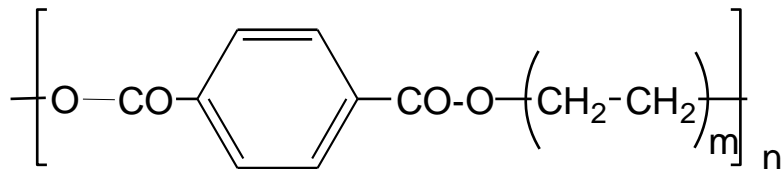
How would you expect the glass transition and crystalline melting temperatures to vary with the values of *m* and *n*? Give reasons for your answer.

7. Describe the differences in the properties and use of flexible plastics, rigid plastics, fibers and elastomers. What types of chemical structures are typical of each?

8. How would you experimentally determine whether the polymerization of an unknown monomer X was proceeding by a step-growth or chain mechanism?

Review Exercises II

1. Write concise definitions for the following terms
   a) cage effect
   b) chain transfer
   c) inhibitor
   d) termination by recombination ad disproportionation

2. Write the kinetic equation for rate of free-radical polymerization and define all the used symbols.

3. What effect would have increasing the initiator concentration on the degree of polymerization in the bulk free radical polymerization of styrene?

4. Ethylene does not polymerize at ordinary pressures under conventional free radical processes. Why is it so?

5. Polymerization of propylene can be performed with complex coordination catalysts. Provide an explanation why polymers with high molecular weights cannot be achieved with radical initiation.

6. Calculate the concentration of *terc*-butyl hydroperoxide which is necessary for achieving the initial polymerization rate of vinyl chloride $v_p=1.8 \times 10^{-5}$ mol l^{-1} s^{-1} if the initiator efficiency under the given polymerization conditions is f=0.68 , the rate constant of initiator decomposition is $k_d=3.0 \times 10^{-5}$ s^{-1}, monomer concentration 1.35 mol l^{-1} and $k_d/k_t^{0.5}=0{,}008$ $l^{0.5}$ $mol^{-0.5}s^{-0.5}$.

7. How would be the initial polymerization rate of styrene effected by dilution of the reaction system with an inert solvent if the volume of the reaction mixture increases twice.

Review Exercises III

1. Draw the curve (copolymerization diagram) of polymer composition versus monomer composition in the reaction feed for copolymerization of buta-1,3-diene (M_1) with styrene (M_2) if r_1=1.39 and r_2=0.78.

2. Consider copolymerization parameters:
   a) r_1=0.1 ; r_2=0.2
   b) r_1=0.1 ; r_2=10
   c) r_1=0; r_2=0
   d) r_1=1; r_2=15

   What will be the copolymer composition at the stage of low monomer conversion (max. 5%) ? Monomers M_1 and M_2 are in equimolar ratio in the reaction feed.

3. Derive the formula of copolymerization equation for the copolymerization under azeotropic conditions. Calculate the reaction feed composition (in wt.%) for azeotropic copolymerization of tetrafluroethylene (M_1) and ethylene (M_2) if r_1=0.85 and r_2=0.15.

4. The product of copolymerization of monomers M_1 and M_2 contains 72.6 mol% m_1 structural units if the reaction feed contains 33.3 mol% M_1 monomer. Under given copolymerization conditions monomer M_2 does not homopolymerize. Calculate the copolymerization parameters r_1; r_2.

5. How does the change of emulsifying agent concentration influence the number average polymerization degree P_n of a polymer synthesized by radical emulsion polymerization under given conditions (T, initiator and monomer concentration).

6. Explain the role of stabilizers in suspension polymerization.

7. What type of free radical polymerization technique would you choose for styrene polymerization if you ask for a transparent polymer. Explain.