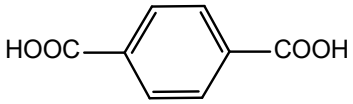
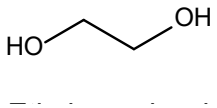
Exercises 5: Semicrystalline Polymers

5.1: Polyethylene terephthalate (PET) is an important polymer for the production of synthetic fibers, foils and liquid containers (*e.g.* lemonade-bottles). It is produced by condensation of terephthalic acid with ethylene glycol (Fig. below). The raw material has a degree of crystallinity of up to 60%.



Terephthalic acid

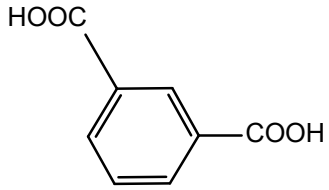


ethylene glycol

Depending how it is processed and thermally treated, it may exist both as an amorphous transparent or as a semi-crystalline material. The semi crystalline material might appear transparent or opaque and white depending on its crystal structure and crystal spherulite size.

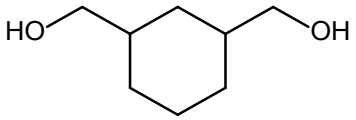
a.) Draw the structure of the polymer.

b.) You use 5% of isophthalic acid (Fig. a below) in the synthesis of your polymer. How does this influence the degree of crystallinity and the melting temperature of your polymer, compared to the unmodified polymer ? What happens if you use 5 % of cyclohexane-dimethanol (Fig. b below) instead of ethylene glykol in your synthesis?



Isophthalic acid

(a)



Cyclohexane dimethanol

(b)

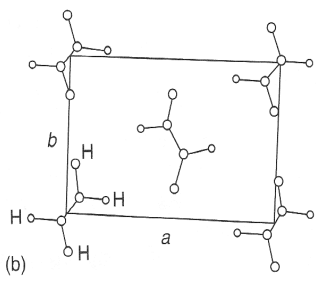
c.) How would you process the homopolymer (from part a) in order to obtain a transparent product ?

d.) Calculate the density of the polymer, if its degree of crystallinity by weight is exactly 50%. Calculate the degree of crystallinity by volume.

Density amorphous ρ_a: 1370 kg/m^3
Density 100% crystalline ρ_c: 1455 kg/m^3

e.) What methods do you know to measure the degree of crystallinity of a polymer?

5.2: Use the crystallographic data of the unit cell to determine the crystal density of polyethylene (a = 7.4Å, b = 4.9Å, c = 2.5Å, α = β = γ = 90°)



(b)

5.3: Chemical evidence for chain folding in polyethylene crystals is obtained by etching polymer crystals with fuming nitric acid, which cleaves the chain at the folded surface. The resulting chain fragments are separated chromatographically and their molecular weights determined by osmometry. The folded chain is pictured as crossing through the crystal, emerging and folding back, then reentering and recrossing the crystal, and so on. According to this picture, the shortest chain showing up in the chromatograms should equal the crystal thickness in length. The second shortest chain exceeds twice this value by same amount, which measures the length of the loop made by the chain outside the crystal. Molecular weights for the two shortest chain observed in an experiment of this sort were 1260 and 2530. Since the cleaved chains end in nitro and carboxyl groups, 60 should be subtracted from each of these molecular weights to give the polyethylene chain weight. Calculate the degree of polymerization of each molecule and the chain length (use the length of the unit cell along the chain axis, 2,53Å, as the distance per repeat unit). Compare the latter with the crystal thickness determined by x-ray diffraction, 105Å. What does the ratio of chain lengths for the first and second peaks suggest about the tightness of folding?

5.4: The melting points of a series of poly(α-olefin) crystals were studied.
All of the polymers were isotactic and had chain substituents of different bulkiness.
Discuss the trends in these data.

Table 13.4 Values of T_m for Poly(α-olefin) Crystals in Which the Polymer Has the Indicated Substituent

Substituent	T_m (°C)
$-CH_3$	165
$-CH_2CH_3$	125
$-CH_2CH_2CH_3$	75
$-CH_2CH_2CH_2CH_3$	−55
$-CH_2CH(CH_3)CH_2CH_3$	196
$-CH_2C(CH_3)_2CH_2CH_3$	350

Source: From Billmeyer, F.W., in *Textbook of Polymer Science*, 2nd ed., Wiley-Interscience, New York, 1971.

5.5: Poly(ethylene terephthalate) was crystallized at 110°C and the densities listed below were measured after the indicated time of crystallization. Determine the Avrami exponent m and calculate the value of K. What does the value of m indicate?

t [min]	ρ [g.cm^3]	t [min]	ρ [g.cm^3]
0	1.3395	35	1.3578
5	1.3400	40	1.3608
10	1.3428	45	1.3625
15	1.3438	50	1.3655
20	1.3443	60	1.3675
25	1.3489	70	1.3685
30	1.3548	80	1.3693

ρ_c = 1.3695 [g.cm^3]