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

Polymer Science 2025/26

Exercise 3 – Solution

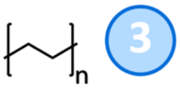
1. Classify the following polymers according to their rigidity (1 = most rigid, 4 = least rigid): polyethylene, poly(ether ether ketone), poly(ethylene terephthalate), polypropylene. Explain your choice.

   Some simple structural rules help estimate chain rigidity:

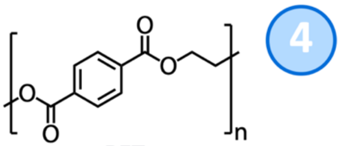
   - **benzene rings in the main chain greatly increase rigidity**
   - **bulky side groups hinder rotation around single bonds and therefore increase rigidity**
   - **electronic delocalization and planarization of conjugated units can restrict rotation and increase rigidity.**

   Applying these rules:

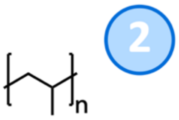
   - **PEEK: aromatic rings in the backbone and polar ether/ketone linkages make it the most rigid**
   - **PP: the CH_3 side group introduces some steric hindrance compared to PE (though not very strong, see Slide 97)**
   - **PE: no side groups and aromatic rings, fully aliphatic, very flexible.**
   - **PET: surprisingly low characteristic ratio ($C_\infty = 4.7$), likely due to flexible C–O bonds and the way catenary bonds are defined (see Q3, Ex. 2). Despite the aromatic rings, it is the least rigid in this set.**



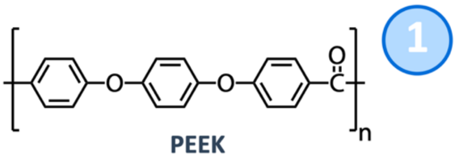
PE



PET



PP



PEEK

2. Place the following molecules into order of increasing boiling point: CH_4, CH_2O, CH_3OH. Explain your answer!

CH_4	**only London dispersion forces → lowest boiling point (≈ -161 °C)**
CH_2O	**London dispersion + permanent dipole-dipole interactions → intermediate boiling point (≈ -19 °C)**
CH_3OH	**London dispersion + dipole-dipole + hydrogen bonding → highest boiling point (≈ 65 °C)**

3. Which of the following pairs has the highest melting point? Explain.

   a) pentane or octane? **–130 °C vs. –57 °C, larger molar mass, stronger London dispersion forces and better cohesive energy for octane.**

   b) tetrahydrofuran (THF) or diethyl ether (Et_2O)? **–108 vs. –116 °C, permanent dipole only for THF.**

   c) triethylamine or ethylamine? **–115 °C vs. –80 °C. Hydrogen bond formation only possible for ethylamine (a primary amine), while triethylamine (tertiary amine) cannot donate H-bonds.**

   d) poly(ε-caprolactone) or nylon 6? **+ 60 °C vs. + 260 °C. Hydrogen bonding only possible for nylon 6.**

4. Suppose the potential energy of interaction between two polymer repeat units is approximated by a Lennard-Jones-type form:

$$U = -\mathrm{A}r^{-6} + \mathrm{B}r^{-12} \quad , \tag{1}$$

per mole of repeat units, with the molar volume of a repeat unit scaling as $V \sim r^3$.

   a) Express U as a function of V. Determine V_o, the equilibrium volume that minimizes U. Show that at this minimum the cohesive energy density defines the compression modulus:

$$K = -V_0 \left.\frac{\partial^U}{\partial V^2}\right|_{V_0} = \frac{8E_{\mathrm{coh}}}{V_0} \quad . \tag{2}$$

   b) Estimate K for a polymer with solubility parameter δ = 18 $(\mathrm{J/cm^3})^{1/2}$

$$U = -Ar^{-6} + Br^{-12} = -AV^{-2} + BV^{-4} \qquad \frac{\partial U}{\partial V} = 2AV^{-3} - 4BV^{-5} \qquad \frac{\partial^2 U}{\partial V^2} = -6AV^{-4} + 20BV^{-6}$$

$$\frac{\partial U}{\partial V} = 0 \rightarrow 2AV^{-3} = 4BV^{-5} \rightarrow V_0^2 = \frac{2B}{A} \qquad U_0 = -A\frac{A}{2B} + B\frac{A^2}{4B^2} = -\frac{A^2}{4B}$$

$$\left.\frac{\partial^2 U}{\partial V^2}\right|_0 = -6A\frac{A^2}{4B^2} + 20B\frac{A^3}{8B^3} = \frac{A^3}{B^2} \qquad -V_0\left.\frac{\partial^2 U}{\partial V^2}\right|_0 = -\frac{V_0^2}{V_0}\frac{A^3}{B^2} = -\frac{1}{V_0}\frac{2B}{A}\frac{A^3}{B^2} = \frac{8U_0}{V_0}$$

$$\delta = \sqrt{\frac{E_{coh}}{V_0}}$$

$$K = 8\frac{E_{coh}}{V_0} = 8\delta^2 = 8 \cdot 18^2 J/cm^3 = 2600\ J/cm^3 \equiv 2.6\ GPa$$

5. The polarity of molecules arises from electronegativity differences between atoms (e.g., O vs. H in water). Why is polyethylene (PE) a non-polar polymer with no net dipole moment, even though C and H differ in electronegativity (2.5 vs. 2.1)? How does this compare to poly(vinyl chloride) (PVC)?

   In molecules like methane, each C–H bond has a small dipole, but the tetrahedral symmetry makes the vector sum zero. There is no net dipole. Similarly, in polyethylene, each CH_2 unit has small dipoles perpendicular to the chain. Adjacent units cancel each other, so the chain has no overall dipole. PE is non-polar.

   In water, by contrast, bond dipoles do not cancel because of the bent geometry, giving a strong net dipole. In PVC, the C–Cl bond has a much stronger dipole moment, and the repeating units lack perfect symmetry. The cancellation no longer occurs and PVC is polar.

6. Which statement is wrong?

   a) Polymers of high molar mass cannot be evaporated by simple heating without chemical degradation.
   b) The cohesive energy is the energy required to separate molecules in a liquid or solid.
   c) The compression modulus of a polymer depends little on temperature.
   d) The intramolecular bonds of polymers are associated with energies on the order of 10 kJ/mol per repeating unit.

   d)! Do not confuse intramolecular bonds with intermolecular bonds! ("intra" = "within".)

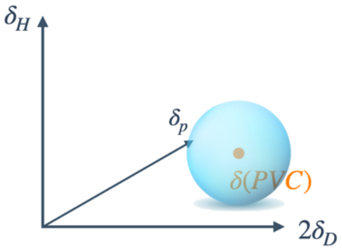
7. It is well known that poly(vinyl chloride) (PVC) is not miscible with its own monomer, vinyl chloride (VC). This immiscibility leads to a characteristic morphology that persists even after melt processing and can be detrimental to mechanical properties.

   The Hansen solubility parameters (in (Mpa)$^{1/2}$) of PVC are $\delta_D = 18.2$, $\delta_P = 7.5$, $\delta_H = 8.3$, with a solubility sphere radius $R_{A0} = 3.5$. For VC, $\delta_D = 15.4$, $\delta_P = 8.1$, $\delta_H = 2.4$. Note: In Hansen space, the dipolar axis δ_D must be doubled based on experimental convention. Using these data, verify quantitatively that PVC and VC are immiscible.

   Let the spere's center coordinates be (x, y, z) and its radius be r. A point (a, b, c) will be in the sphere, if

   $$(x-a)^2 + (y-b)^2 + (z-c)^2 < r^2$$

   In our case, we need to respect the doubling of the δ_D axis. Therefore



$$R^2_{(PVC-VC)}$$
$$= (2\delta_D(PVC) - 2\delta_D(VC))^2 + (\delta_H(PVC) - \delta_H(VC))^2 + (\delta_p(PVC) - \delta_p(VC))^2$$
$$= 5.6^2 + 5.9^2 + (-0.6)^2 > R^2_{A0}$$

   The monomer (VC) lies outside the PVC solubility sphere. → immiscible.

8. It is generally difficult (if not impossible) to predict the glass transition temperature T_g of a polymer *ab initio*. However, empirical group contribution methods provide correlations between chemical structure and T_g.
   One approach (according to Van Krevelen and Hoftyzer) assumes that each structural group contributes additively to T_g.

$$T_g = \frac{Y_g}{M} = \frac{\sum_i Y_{gi}}{M} \quad , \tag{3}$$

   where M is the molar mass of the repeating unit and Y_{gi} is the "molar function of the glass transition" for a group i (values are given in the table at the end of this document). For unbranched aliphatic polymers obtained by polycondensation, a correction must be added for interactions of polar groups:

$$T_g = \frac{Y_g}{M} = \frac{\sum_i Y_{gi} + \sum_i Y_g(I_{xi})}{M} \quad , \tag{4}$$

where $Y_g(I_{xi})$ is a correction term depending on the interaction factor I_x. Using the data provided, calculate the glass transition temperature of poly(ethylene terephthalate) (PET), assuming an interaction factor $I = 0.5$. Compare your result to the experimental T_g .

Note that this type of approach also applies to many other physical properties.

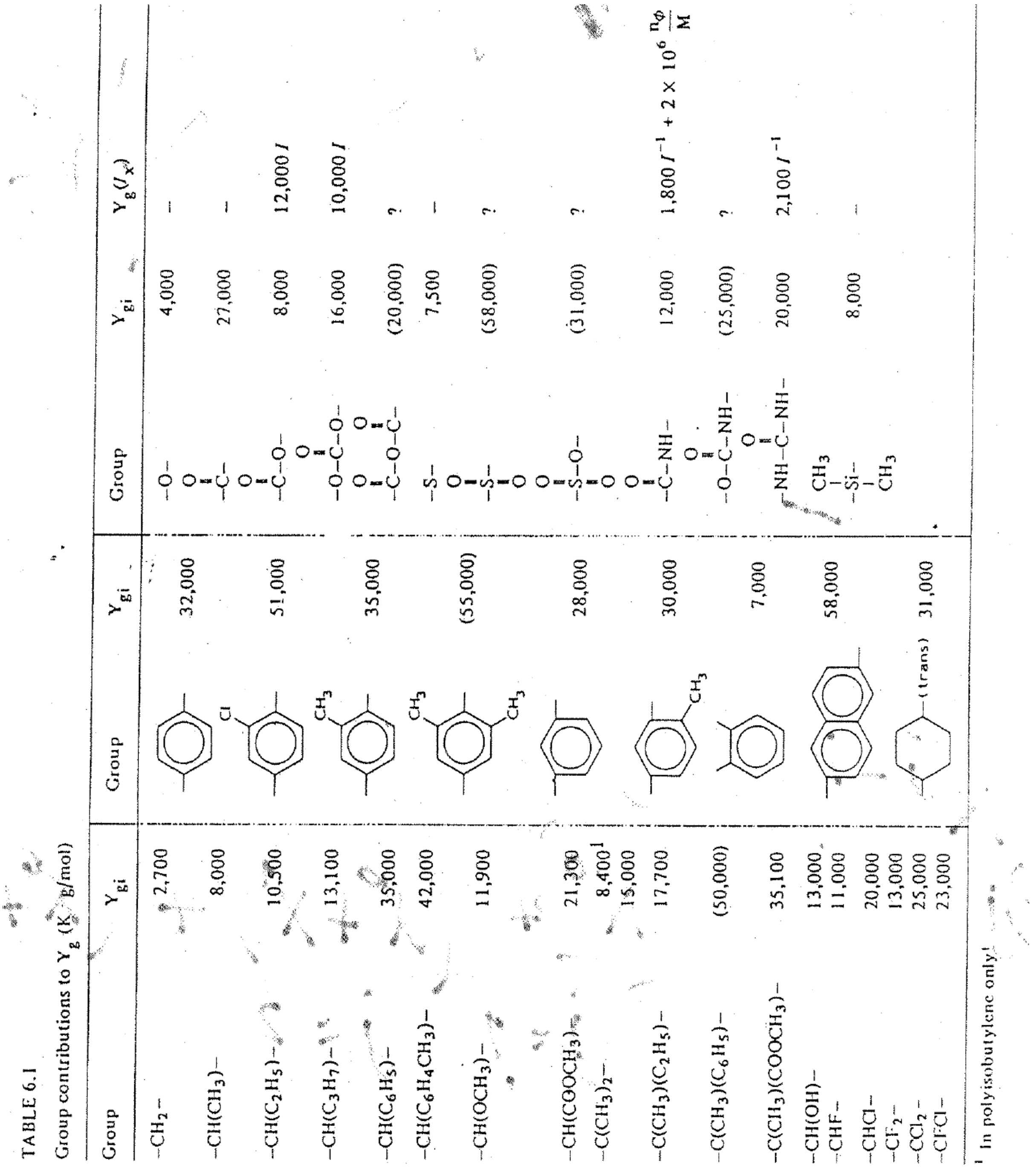


TABLE 6.1
Group contributions to Y_g (K · g/mol)

Group	Y_{gi}
$-CH_2-$	2,700
$-CH(CH_3)-$	8,000
$-CH(C_2H_5)-$	10,500
$-CH(C_3H_7)-$	13,100
$-CH(C_6H_5)-$	35,000
$-CH(C_6H_4CH_3)-$	42,000
$-CH(OCH_3)-$	11,900
$-CH(COOCH_3)-$	21,300
$-C(CH_3)_2-$	8,400[1] 15,000
$-C(CH_3)(C_2H_5)-$	17,700
$-C(CH_3)(C_6H_5)-$	(50,000)
$-C(CH_3)(COOCH_3)-$	35,100
$-CH(OH)-$	13,000
$-CHF-$	11,000
$-CHCl-$	20,000
$-CF_2-$	13,000
$-CCl_2-$	25,000
$-CFCl-$	23,000

Group	Y_{gi}
	32,000
Cl	51,000
CH_3	35,000
CH_3 CH_3	(55,000)
	28,000
CH_3	30,000
	7,000
	58,000
(trans)	31,000

Group	Y_{gi}	$Y_g(I_x)$
$-O-$	4,000	—
$-\overset{\overset{O}{\|}}{C}-$	27,000	—
$-\overset{\overset{O}{\|}}{C}-O-$	8,000	12,000 I
$-O-\overset{\overset{O}{\|}}{C}-O-$	16,000	10,000 I
$-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-$	(20,000)	?
$-S-$	7,500	—
$-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-$	(58,000)	?
$-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-$	(31,000)	?
$-\overset{\overset{O}{\|}}{C}-NH-$	12,000	$1{,}800\,I^{-1} + 2 \times 10^6 \frac{n_\phi}{M}$
$-O-\overset{\overset{O}{\|}}{C}-NH-$	(25,000)	?
$-NH-\overset{\overset{O}{\|}}{C}-NH-$	20,000	$2{,}100\,I^{-1}$
$-\overset{\overset{CH_3}{\|}}{\underset{\underset{CH_3}{\|}}{Si}}-$	8,000	—

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[1] In polyisobutylene only!

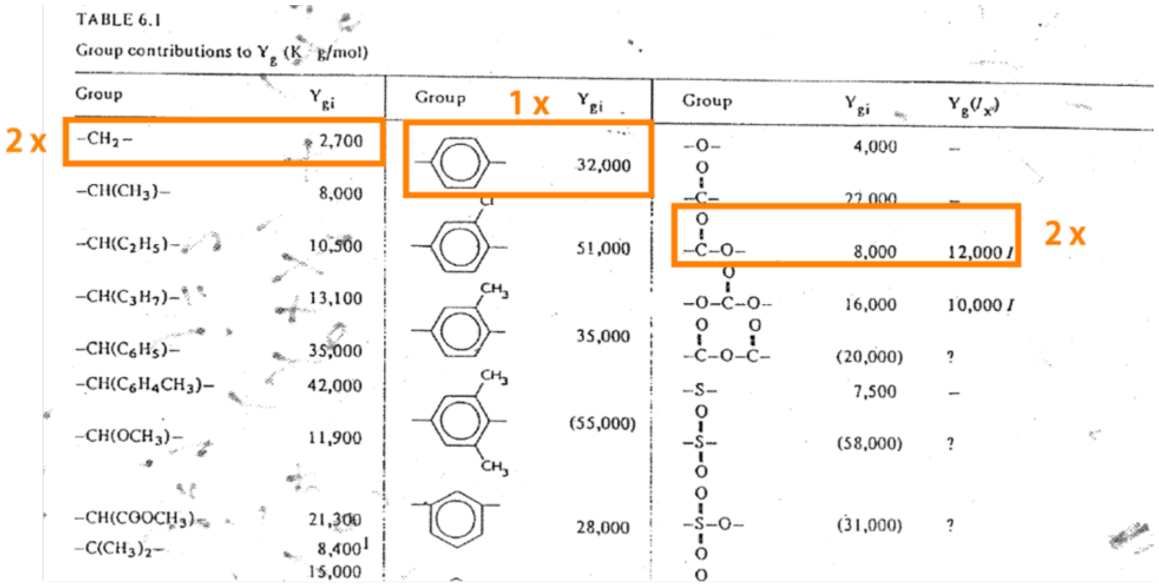

TABLE 6.1

Group contributions to Y_g (K g/mol)

Group	Y_{gi}	Group	Y_{gi}	Group	Y_{gi}	$Y_g(I_x)$
$-CH_2-$	2,700		32,000	$-O-$	4,000	–
$-CH(CH_3)-$	8,000		51,000	$-\overset{O}{\overset{\|}{C}}-$	27,000	–
$-CH(C_2H_5)-$	10,500		35,000	$-\overset{O}{\overset{\|}{C}}-O-$	8,000	12,000 I
$-CH(C_3H_7)-$	13,100		(55,000)	$-O-\overset{O}{\overset{\|}{C}}-O-$	16,000	10,000 I
$-CH(C_6H_5)-$	35,000		28,000	$-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$	(20,000)	?
$-CH(C_6H_4CH_3)-$	42,000			$-S-$	7,500	–
$-CH(OCH_3)-$	11,900			$-\underset{O}{\overset{O}{S}}-$	(58,000)	?
$-CH(COOCH_3)-$	21,300			$-\underset{O}{\overset{O}{S}}-O-$	(31,000)	?
$-C(CH_3)_2-$	8,400[1] 15,000					

$$T_g = \frac{5400 + 28000 + 32000}{192} K = 340.6K \equiv 68^{\circ}C$$

The glass transition temperature of PET ranges from 67 – 81 °C (depending on the conditions). So, this approach gives a fairly good estimate in this case.