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Polymer Science 2025/26

Exercise 3

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.

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

3. Which of the following pairs has the highest melting point? Explain.
   a) pentane or octane?
   b) tetrahydrofuran (THF) or diethyl ether (Et_2O)?
   c) triethylamine or ethylamine?
   d) poly(ε-caprolactone) or nylon 6?

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

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

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_0, the equilibrium volume that minimizes U. Show that at this minimum the cohesive energy density defines the compression modulus:

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

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

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)?

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.

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.

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:

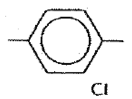
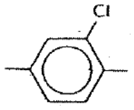
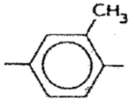
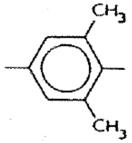
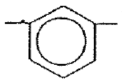
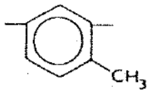
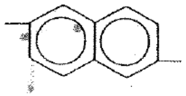
$$T_g = \frac{Y_g}{M} = \frac{\sum_i Y_{gi} + \sum_i Y_g(I_{xi})}{M} \quad , \tag{4}$$

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}	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		30,000	$-S-$	7,500	—
$-CH(OCH_3)-$	11,900		7,000	$-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-$	(58,000)	?
$-CH(COOCH_3)-$	21,300		58,000	$-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-O-$	(31,000)	?
$-C(CH_3)_2-$	8,400[1] 15,000	 (trans)	31,000	$-\overset{O}{\overset{\|}{C}}-NH-$	12,000	$1{,}800\,I^{-1} + 2 \times 10^6 \frac{n_\phi}{M}$
$-C(CH_3)(C_2H_5)-$	17,700			$-O-\overset{O}{\overset{\|}{C}}-NH-$	(25,000)	?
$-C(CH_3)(C_6H_5)-$	(50,000)			$-NH-\overset{O}{\overset{\|}{C}}-NH-$	20,000	$2{,}100\,I^{-1}$
$-C(CH_3)(COOCH_3)-$	35,100			$-\underset{\underset{CH_3}{\mid}}{\overset{CH_3}{\overset{\mid}{Si}}}-$	8,000	—
$-CH(OH)-$	13,000					
$-CHF-$	11,000					
$-CHCl-$	20,000					
$-CF_2-$	13,000					
$-CCl_2-$	25,000					
$-CFCl-$	23,000					

[1] In polyisobutylene only!