Polymer Science 2024

Exercise 4 – Solution

1. If you could follow Question 4 of the last Exercise Sheet, you are able to appreciate that the glassy state is "out-of-equilibrium" - you will never cool slowly enough that v_{fm} disappears at $T = T_{\mathrm{o}}$. Therefore, free volume will be trapped in the glassy state. According to the free volume theory, polymer chain ends can provide an additional free volume θ. Explain thus, within the framework of this theory, how T_{g} varies with M_{n} for a given cooling rate.

   In your answer, justify the empirical Fory-Fox law on Slide 143 (right side), by expressing the total free volume, $v_{f\mathrm{m}}$, as a function of θ and assuming that the glass transition takes place at $v_{f\mathrm{mc}}$, the free volume for the hypothetical case of an infinitely long chain with no present end groups.

   See Slide 143. Each chain end provides an additional free volume. Since there are $2\rho N_A/M_n$ chain ends per unit volume, where ρ is the density and N_A is the Avogadro number, the value of $v_{f\mathrm{m}}$ is given by:

$$v_{fm}(M_n, T_{g\infty}) = v_{fmc} + v_o \frac{2\theta\rho N_A}{M_n} = (\alpha_{liquid} - \alpha_{glass}) v_o (T_{g\infty} - T_o) + v_o \frac{2\theta\rho N_A}{M_n}$$

   where v_{o} is the volume that the system would occupy at equilibrium in the absence of thermal energy. Let us now assume that the glass transition always takes place at $v_{f\mathrm{mc}}$ (the free volume for the hypothetical case of no present end groups), so that:

$$v_{fmc}(T_{g\infty}) = v_{fm}(M_n, T_g)$$

$$(\alpha_{liquid} - \alpha_{glass}) v_o (T_{g\infty} - T_o) = (\alpha_{liquid} - \alpha_{glass}) v_o (T_g - T_o) + v_o \frac{2\theta\rho N_A}{M_n}$$

$$T_g = T_{g\infty} - \frac{2\theta\rho N_A}{(\alpha_{liquid} - \alpha_{glass}) M_n}$$

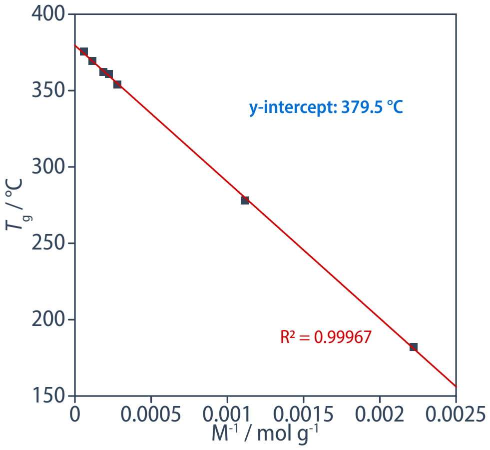
   In other words, for a given critical free volume, the apparent T_{g} will be the smaller the lower the molar mass.

Calculate the T_g of the polymer of infinite molar mass from the following data:

T_g (K)	182	278	354	361	362	369.5	375.5
M (Da)	500	1000	4000	5000	6000	10,000	20,000

Use the empirical Flory-Fox equation (Slide 143). Convert the molar masses into the reciprocal values and perform a linear regression. The intercept with the y-axis is the T_g of the polymer of infinite molar mass.

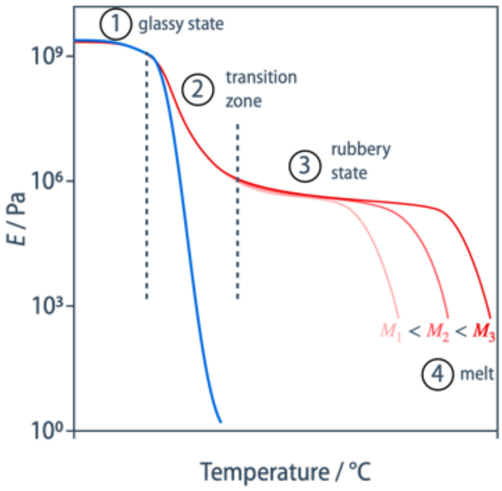
M g/mol	M^{-1} mol/g	T_g °C
500	0.002	182
1000	0.001	278
4000	2.5E-4	354
5000	2E-4	361
6000	1.66667E-4	362
10000	1E-4	369.5
20000	5E-5	375.5



2. Show the shape of the elastic modulus $E(T)$ of an amorphous polymer as a function of temperature by indicating the orders of magnitude of the modulus in the different characteristic regimes and describe the influence of the strain rate. Draw $E(T)$ for a "small molecule".

   Take the diagram from slide 132 (do not forget to put the correct orders of magnitude for the different regimes). The transition zone labelled as 2 is strongly influenced by the measurement condition, and the transition will take place at higher temperature for faster strain rates.

   The behavior of a small molecule corresponds to the limit where M is very small. In other words, this is the limit where the rubbery plateau disappears, and the glass transition marks a transition from the glassy state directly into the liquid state, where, by definition the modulus is zero (as long as the small molecule does not crystallize once it is above T_g).



3. Although it is difficult, if not impossible, to calculate the T_g of a given polymer *ab initio*, some authors have established correlations between the chemical structure of polymers and T_g. They consider in fact that in a polymer, each molecular group contributes in its own way to the value of T_g (law of additivity). For example, Van Krevelen and Hoftyzer have shown that in some cases:

$$T_g = \frac{Y_g}{M} = \frac{\sum_i Y_{gi}}{M}$$

where M is the molar mass of each chemical group present in the repeating unit and Y_{gi} is the "molar function of the glass transition" for a group i (see the table at the end of this document). However, in the case of unbranched aliphatic polymers obtained by polycondensation:

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

where $Y_g(I_{xi})$ is a correction term which takes polar groups into account. This term is associated with an interaction factor I_x. Considering this information, calculate the T_g of poly(ethylene terephthalate) (interaction factor $I = 0.5$). Note that this type of approach also applies to many other physical properties. Use the table at the end of this document.

Is your result reasonable?

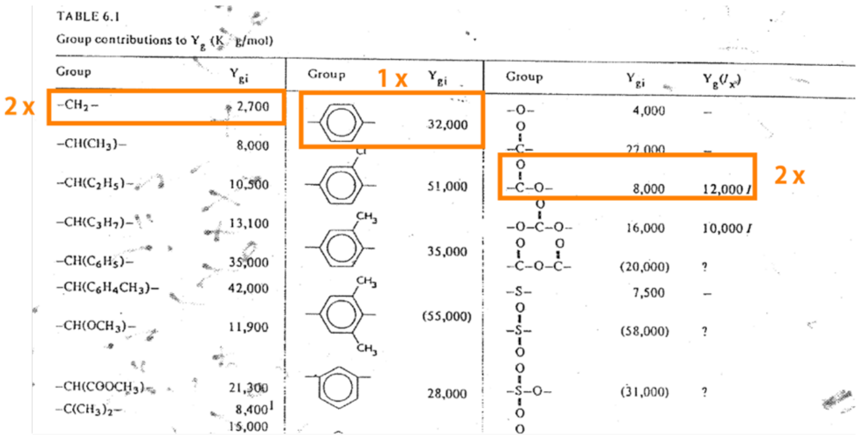


TABLE 6.1

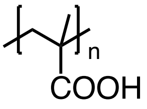
Group contributions to Y_g (K g/mol)

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	$-\overset{\overset{O}{\|}}{C}-$	27,000	–
$-CH(C_2H_5)-$	10,500		35,000	$-\overset{\overset{O}{\|}}{C}-O-$	8,000	12,000 I
$-CH(C_3H_7)-$	13,100		(55,000)	$-O-\overset{\overset{O}{\|}}{C}-O-$	16,000	10,000 I
$-CH(C_6H_5)-$	35,000		28,000	$-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-$	(20,000)	?
$-CH(C_6H_4CH_3)-$	42,000			$-S-$	7,500	–
$-CH(OCH_3)-$	11,900			$-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-$	(58,000)	?
$-CH(COOCH_3)-$	21,300			$-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-$	(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.

4. Name the following polymer and order them according to their glass transition temperature. Explain your answer.



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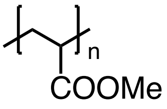

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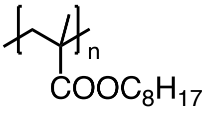

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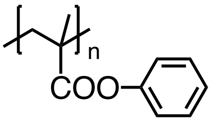

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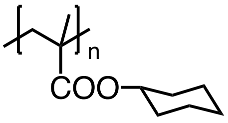

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In reference to 2, all other polymers are disubstituted at the main chain carbon, which generally leads to a rigidification of the polymer chain. In brackets are additional factors that further reduce chain mobility and increase T_g (exception is polymer 3, where the flexible substituent overcompensates the effect of the disubstitution, leading to an overall reduced T_g).

1: poly(methacrylic acid): $T_g \approx 228$ °C (hydrogen-bonding)

2: poly(methyl acrylate): $T_g \approx 10$ °C

3: poly(*n*-octyl methacrylate): $T_g \approx -20$ °C (flexible substituent)

4: poly(phenyl methacrylate): $T_g \approx 54$ °C (bulky substituent)

5: poly(cyclohexyl methacrylate): $T_g \approx 104$ °C (most bulky substituent)

5. You receive two samples of polystyrene. The supplier informs you that sample #1 can crystallize while #2 can't. Does this seem possible to you? Explain your answer.

   The PS is a vinyl polymer and can exist in an atactic, isotactic, or syndiotactic form. Commercial products are normally atactic, not capable to crystallize – therefore, atactic PS is amorphous and transparent. Isotactic and syndiotactic PS crystallize via a helical chain conformation. The presence of crystalline lamellae in a material typically causes significant scattering of visible light (due to the difference in refractive index between the crystalline phase and the amorphous phase). Such a material would therefore be opaque.

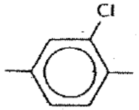
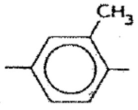
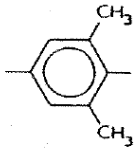
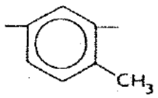
   To confirm our quick judgement of the samples #1 and #2, we can run a DSC experiment (which is not much time-consuming): for #2, only the glass transition at around 100 °C is expected to be observed, while #1 should additionally show a melting peak at a higher temperature (~ 270 °C).

Reading suggestions:

- Lecture Notes of Chapters 3.2.

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					

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[1] In polyisobutylene only!