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

Polymer Science 2024

Exercise 4

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 $T = T_o$. 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_{fm}, as a function of θ and assuming that the glass transition takes place at v_{fmc}, the free volume for the hypothetical case of an infinitely long chain with no present end groups.

   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

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".

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:

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

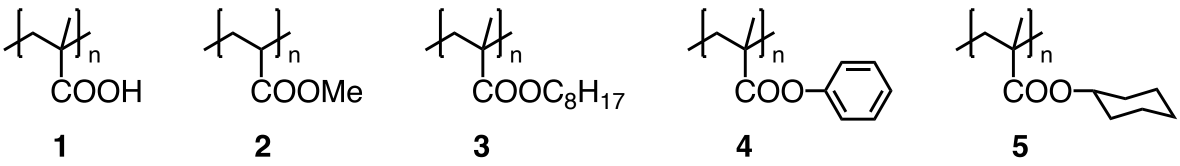
where M is the molar mass of each chemical group present in the repeating unit and Y_{gi} is the "molar function of the glass transition" for a group i (see the table at the end of this document). However, in the case of unbranched aliphatic polymers obtained by polycondensation:

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

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?

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



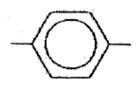
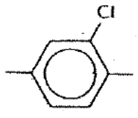
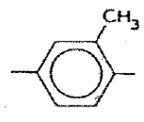
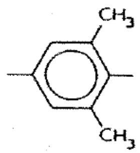
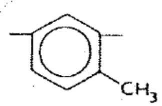
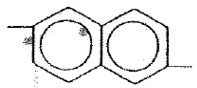
5. You receive two samples of polystyrene. The supplier informs you that sample #1 can crystallize while #2 can't. Does this seem possible to you? Explain your answer.

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	$-C(=O)-$	27,000	–
$-CH(C_2H_5)-$	10,500		35,000	$-C(=O)-O-$	8,000	12,000 I
$-CH(C_3H_7)-$	13,100		(55,000)	$-O-C(=O)-O-$	16,000	10,000 I
$-CH(C_6H_5)-$	35,000		28,000	$-C(=O)-O-C(=O)-$	(20,000)	?
$-CH(C_6H_4CH_3)-$	42,000		30,000	$-S-$	7,500	–
$-CH(OCH_3)-$	11,900		7,000	$-SO_2-$	(58,000)	?
$-CH(COOCH_3)-$	21,300		58,000	$-O-SO_2-O-$	(31,000)	?
$-C(CH_3)_2-$	8,400[1]	 (trans)	31,000	$-C(=O)-NH-$	12,000	1,800 I^{-1} + 2 × $10^6 \frac{n_\phi}{M}$
	15,000			$-O-C(=O)-NH-$	(25,000)	?
$-C(CH_3)(C_2H_5)-$	17,700			$-NH-C(=O)-NH-$	20,000	2,100 I^{-1}
$-C(CH_3)(C_6H_5)-$	(50,000)			$-Si(CH_3)_2-$	8,000	–
$-C(CH_3)(COOCH_3)-$	35,100					
$-CH(OH)-$	13,000					
$-CHF-$	11,000					
$-CHCl-$	20,000					
$-CF_2-$	13,000					
$-CCl_2-$	25,000					
$-CFCl-$	23,000					

[1] In polyisobutylene only!

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