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

Polymer Science 2024/25

Exercise 8

1. The shear storage compliance (J_1) vs log (ω) curves of polyoctyl methacrylate at different T are superimposable. For a reference temperature T_0 = 100 °C, the horizontal displacements, α_T, necessary to carry out such a superposition are given in Table 1.

   Show that this data can be described by the empirical WLF-equation. What are the values of C_1 and C_2?

   Table 1: *Shift factors* for question 1.

T **(°C)**	**log(*α*(*T*))**	***T*** **(°C)**	**log(*α*(*T*))**
129.5	-0.87	44.4	2.46
120.3	-0.62	38.8	2.80
109.4	-0.30	34.2	3.10
100	0.00	30	3.38
89.4	0.37	25.3	3.72
80.2	0.73	19.8	4.14
70.9	1.12	15.1	4.53
65.8	1.35	9.9	4.99
59.8	1.63	4.4	5.56
54.5	1.90	-0.1	5.98
50.2	2.13	-5	6.52

2. The WLF equation can be used to calculate the melt viscosity changes with temperature. Suppose a polymer has a glass transition temperature of 0 °C. At 40 °C, it has a melt viscosity $\eta = 2.5 \cdot 10^4$ Pa s. What will its viscosity be at 50 °C?

3. In a relaxation test, a constant strain is applied and we look at the evolution of the stress as a function of time. In shear and for an applied strain, γ_0, for example, we can write

$$\sigma = G(t)\gamma_0$$

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where $G(t)$ is the relaxation modulus. According to the phenomenological models (springs and dashpot) generalized for a linear viscoelastic material

$$G(t) = G_\infty + \sum_1^n G_i e^{-t/\tau_i} \qquad (1)$$

where the parameters G_∞ and G_i are adjustable (within the limit of an infinite number of elements, the G_i can be replaced by a continuous function, the relaxation time spectrum, and the sum by an integral).

In Rouse's model for a dilute solution of N_m chains per unit volume, each containing n bonds, the expression for $G(t)$ becomes

$$G(t) = N_m kT \sum_{p=1}^{m} e^{-t/\tau_p} \qquad \tau_p \approx \frac{\xi m^2 r_s^2}{6\pi^2 p^2 kT} = C\frac{n^2}{p^2}, \qquad p = 1,2,\ldots$$

and C is a constant, provided that $m >> p$, and $m >> 1$.

i) What do m, p, ξ and r_s^2 mean? Why is the effective value of G_∞ equal to 0 in this case?

ii) If the monomeric friction coefficient $\xi_o = n\xi/m$, show that

$$\tau_p \approx \frac{\xi_o n^2 l^2}{6\pi^2 p^2 kT}, \qquad for \quad m \gg 1, p$$

and therefore, that the maximum relaxation time, the "Rouse relaxation time", is proportional to M^2.

iii) Draw schematically the evolution of $\sigma/N_m kT$ as a function of t/τ_1 for the component of $G(t)$ which corresponds to $p = 1$ (this is the slowest mode of relaxation). Add the contributions that correspond to $p = 2$ and 3 to the same diagram. In general, what can we say about the contribution to the stress of fast relaxation modes, when $t \geq \tau_1$?

iv) These expressions are valid for relatively long times (if we ignore the hydrodynamic effects related to the solvent), but one meets problems with very short times, where one must take the contributions of modes corresponding to high p into account. Indeed, the choice of m, which defines the maximum value of p, is arbitrary, but does the model remain reasonable when m approaches n?

v) Suppose that $\tau_1 = \infty$ and that $\tau_0 = 0$ for $p > 1$. Write the resulting expression for $G(t)$. What do you notice? Interpret this result.

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