School of Engineering
Institute of Materials
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Polymer Science 2024

Exercise 3

1. Suppose that the potential inter-chain interaction energy is $U = -Ar^{-6} + Br^{-12}$ per mole of repeating unit of a polymer, and that the molar volume of a repeating unit is $V \sim r^3$.

   a) Express U as a function of V, and find V_o, the value of V which corresponds to E_{coh}, i.e. a minimum of U. Show that the compression modulus is

   $$K = -V_0 \left.\frac{\partial^2 U}{\partial V^2}\right|_0 = \frac{8E_{coh}}{V_0}$$

   b) Estimate the compression modulus of a polymer with $\delta = 18$ $(J/cm^3)^{1/2}$

2. Why is the glass transition not a "second-order thermodynamic transition"?

3. It is well known that polyvinylchloride (PVC) is not miscible with its own monomer (VC). This gives the polymer a characteristic particle structure that remains even after melt processing, which is often detrimental for its mechanical properties. The solubility parameters (in $(Mpa)^{1/2}$) of PVC are $\delta_D = 18.2$, $\delta_P = 7.5$, $\delta_H = 8.3$, $R_{A0} = 3.5$, where R_{A0} is the radius of its *solubility sphere* in the '$2\delta_D$-δ_P-δ_H space' (the necessity of doubling the δ_D axis is based on experimental observations). The solubility parameter values of VC are: $\delta_D = 15.4$, $\delta_P = 8.1$, $\delta_H = 2.4$. Confirm that PVC is immiscible with VC on the basis of these data.

4. Let's try to better understand the theory of "free volume"! As we have seen, at a temperature of absolute 0, each segment of a glassy amorphous polymer will occupy a volume v_o. When the temperature is increased, the molecules start to vibrate and the volume increases. The thermal expansion coefficient of the glass is α_{glass} such that $V = \alpha_{glass} v_o T$. According to the free volume theory, above a certain temperature T_o, holes begin to appear that are large enough to allow the displacement of chain segments. Thus, conformational changes become possible. We then enter the liquid state (or rubbery state in the case of a polymer, see Exercise 3!), with a thermal expansion coefficient of α_{liquid}. However, because the glassy state is an out-of-equilibrium state, an average "free volume", v_{fm}, is trapped in the glassy state. v_{fm} is the excess volume compared to a hypothetically "equilibrated" glassy state.

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a) Show that $v_{fm} = v_o(T - T_o)(\alpha_{liquid} - \alpha_{glass})$.

We assume that the probability of finding a hole of size v_o appearing within a certain time interval is proportional to $\exp(-v_o/v_{fm})$. In other words, the *relaxation time* for these conformational changes is $\tau = \tau_o \exp(v_o/v_{fm})$ and therefore the viscosity $\eta = \eta_o \exp(v_o/v_{fm})$.

b) Express η in terms of T, T_o and the thermal expansion coefficients. What happens to the viscosity of the liquid when T tends towards T_o?

c) If we cool at a given speed, we will effectively stop the conformational changes at a temperature, $T > T_o$ (when the viscosity becomes too high to allow conformational changes over the timescale of the experiment). This temperature will be the experimental glass transition temperature, T_g. Draw the evolution of the volume as a function of T for different constant cooling rates, indicate T_g for each rate.

d) In DSC measurements, often a characteristic enthalpy peak is observed at around the glass transition temperature during heating if a faster heating rate is applied compared to the cooling rate of the previous cooling scan (see Slide 209). This enthalpy peak is, however, also observed upon "aging", which is a densification in the glassy state of the material upon resting. Explain this behavior with the help of a schematic illustration of the evolution of the volume (or enthalpy) as a function of the temperature.

e) You cool an amorphous polymer relatively quickly from the rubbery state to a temperature well below the T_g, and you heat it up much more slowly. Schematically show the evolution of the volume as a function of the temperature.

Reading suggestions:

- Lecture Notes of Chapters 3.1 and 3.2.

(You can download these documents from the Moodle-folder 'Reading Recommendation'.)

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