

Chapter 2

Chain Dimensions, Structures, and Transitional Phenomena

Exercises

E2.1 (a) Calculate the root mean square end-to-end distance and the radius of gyration for a molecule in molten polypropylene of molecular weight 10^5 . [Data: carbon-carbon bond length = 1.54×10^{-8} cm; tetrahedral bond angle = 109.5° ; steric parameter, $\sigma = 1.6$ at 140°C .] (b) How extensible is the molecule? (*Hint*: Calculate the ratio of the extended chain length to the average chain end separation.)

Answer:

(a) Molar mass of repeat unit of polypropylene = 42 g mol^{-1}

Degree of polymerization = $(10^5 \text{ g mol}^{-1}) / (42 \text{ g mol}^{-1}) = 2381$

Number of C–C bonds in the main chain = $2 \times 2381 = 4762$

From Eq. 2.8 (polymer text):

$$\begin{aligned}\langle r^2 \rangle_0 &= \sigma^2 n l^2 \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right) \\ &= (1.6)^2 (4762) (1.54 \times 10^{-8} \text{ cm})^2 \frac{(1 + 1/3)}{1 - 1/3} \\ &= 5.78 \times 10^{-12} \text{ cm}^2\end{aligned}$$

RMS end-to-end distance, $\langle r^2 \rangle_0^{1/2} = 2.4 \times 10^{-6} \text{ cm} = 240 \text{ \AA}$

From Eq. 2.4 (polymer text):

$$\begin{aligned}\text{Radius of gyration, } \langle S^2 \rangle^{1/2} &= \langle r^2 \rangle_0^{1/2} \sqrt{6} \\ &= 2.4 \times 10^{-6} \text{ cm} / \sqrt{6} \\ &= 9.8 \times 10^{-7} \text{ cm} (= 98 \text{ \AA})\end{aligned}$$

(b) The most highly extended form involves the all-*trans* conformation of the polymer backbone:



The projection of the bond length on the chain length direction is

$$(1.54 \times 10^{-8}) \cos 35.25^\circ = 1.26 \times 10^{-8} \text{ cm.}$$

For $n = 4762$, the end-to-end distance of a fully extended chain $= 4762 \times 1.26 \times 10^{-8}$ or 60×10^{-6} cm.

$$\text{Therefore, extensibility} = \frac{(60 - 2.4) \times 10^{-6} \text{ cm}}{2.4 \times 10^{-6} \text{ cm}} = 24 \text{ times}$$

E2.2 Assuming that the RMS end-to-end distance is an approximate measure of the diameter of the spherical, coiled polymer molecule in dilute solution, compare the volume occupied by one molecule of polyisobutylene of molecular weight 10^6 :

(a) In a solid at 30°C (density $= 0.92 \text{ g/cm}^3$).

(b) In a *theta*-solvent.

Take the value of the steric parameter σ for the polymer as 2.0 and the carbon-carbon bond length as 1.54×10^{-8} cm.

Answer:

$$\begin{aligned} \text{(a) Volume} &= \frac{(10^6 \text{ g mol}^{-1})}{(6.02 \times 10^{23} \text{ molecules mol}^{-1})(0.92 \text{ g cm}^{-3})} \\ &= 1.81 \times 10^{-8} \text{ cm}^3 (= 1.81 \times 10^6 \text{ \AA}^3) \end{aligned}$$

$$\text{(b) Molar mass of repeating unit (C}_4\text{H}_8) = 56 \text{ g mol}^{-1}$$

$$\text{Degree of polymerization} = (10^6 \text{ g mol}^{-1}) / (56 \text{ g mol}^{-1}) = 17857$$

$$\begin{aligned} \text{Number of backbone chain bonds,} \\ n &= 2 \times 17857 = 35714 \end{aligned}$$

In a *theta* solvent, polymer chains have unperturbed dimensions.

Therefore, from Eq. 2.8 (polymer text):

$$\begin{aligned} \langle r^2 \rangle_0 &= \sigma^2 n l^2 \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right), \text{ where } \theta = 109.5^\circ, \cos \theta \approx -1/3 \\ &= (2.0)^2 (35714) (1.54 \times 10^{-8} \text{ cm})^2 (2) \\ &= 6.78 \times 10^{-11} \text{ cm}^2 \end{aligned}$$

$$\begin{aligned} \text{Volume} &= (\pi/6) (\langle r^2 \rangle_0^{3/2}) \\ &= 2.92 \times 10^{-16} \text{ cm}^3 (= 2.92 \times 10^8 \text{ \AA}^3) \end{aligned}$$

E2.3 The RMS end-to-end distance is $2.01 \sqrt{n} \text{ \AA}$ for *cis*-polyisoprene and $2.90 \sqrt{n} \text{ \AA}$ for *trans*-polyisoprene, n being the total number of bonds in each real chain. Compare the chain stiffness of the two polymers.

Answer:

An idea of chain stiffness can be gained from the ratio $\langle r^2 \rangle_0^{1/2} / \langle r^2 \rangle_f^{1/2}$. Since for *cis*- and *trans*-polyisoprene of the same molecular weight (i.e., same n), $\langle r^2 \rangle_f^{1/2}$ values are the same, the ratio of $\langle r^2 \rangle_0^{1/2}$ values is a measure of the ratio of chain stiffnesses of the two polymers. Thus, *trans*-

polyisoprene is 2.90/2.01 or 1.4 times stiffer than *cis*-polyisoprene.

E2.4 From the data given above calculate the values of σ and C_∞ for *cis*- and *trans*-polyisoprene, given that the length of an isoprene repeating unit is 4.60×10^{-10} m.

Answer:

Since there are 4 bonds per isoprene repeating unit, average length of each bond, $l = (4.60 \times 10^{-10} \text{ m})/4 = 1.15 \times 10^{-10} \text{ m}$.

From Eq. 2.8 (polymer text), noting that $\theta = 109.5^\circ$,

$$\sigma = \langle r^2 \rangle_0^{1/2} / \sqrt{2nl}$$

$$\text{Also, } C_\infty = \langle r^2 \rangle_0 / nl^2$$

For *cis*-polyisoprene,

$$\sigma = \frac{(2.01\sqrt{n})10^{-10} \text{ m}}{\sqrt{2n}(1.15 \times 10^{-10} \text{ m})} = 1.2$$

$$C_\infty = \frac{(2.01\sqrt{n} \times 10^{-10} \text{ m})^2}{n(1.15 \times 10^{-10} \text{ m})^2} = 3.1$$

For *trans*-polyisoprene,

$$\sigma = \frac{(2.90\sqrt{n})10^{-10} \text{ m}}{\sqrt{2n}(1.15 \times 10^{-10} \text{ m})} = 1.8$$

$$C_\infty = \frac{(2.90\sqrt{n} \times 10^{-10} \text{ m})^2}{n(1.15 \times 10^{-10} \text{ m})^2} = 6.4$$

E2.5 Given that the RMS end-to-end distance $\langle r^2 \rangle_0^{1/2}$ is $(2.90\sqrt{n})10^{-8}$ cm for *trans*-polyisoprene, where n is the total number of bonds in the real chain, and the length of an isoprene repeating unit is 4.60×10^{-8} cm, calculate the number of monomer units a *trans*-polyisoprene molecule has per equivalent random (freely-jointed) chain link.

Answer:

Let the degree of polymerization, i.e., the number of repeating units in the polymer chain be x . Since there are 4 bonds per isoprene unit, the number of bonds (n) in a chain is $n = 4x$.

It is given that

$$\langle r^2 \rangle_0^{1/2} = (2.90\sqrt{n})10^{-8} \text{ cm}$$

$$\text{So, } \langle r^2 \rangle_0 = (2.90 \times 10^{-8})^2(4x) \text{ cm}^2$$

$$= 33.64 \times 10^{-16}x \text{ cm}^2$$

Since the length of an isoprene repeating unit is given as 4.60×10^{-8} cm, the contour length (nl) of the chain is

$$nl = 4.6 \times 10^{-8}x \text{ cm}$$

From Eq. P2.5.4 (polymer text), number of links (N) in an equivalent freely-jointed chain is

$$N = \frac{(4.6 \times 10^{-8}x \text{ cm})^2}{(33.64 \times 10^{-16}x \text{ cm}^2)} = 0.63x$$

Therefore,

$$\frac{n}{N} = \frac{4x}{0.63x} = 6.35$$

So the number of isoprene units per equivalent freely-jointed chain link $= 6.35/4 = 1.59$.

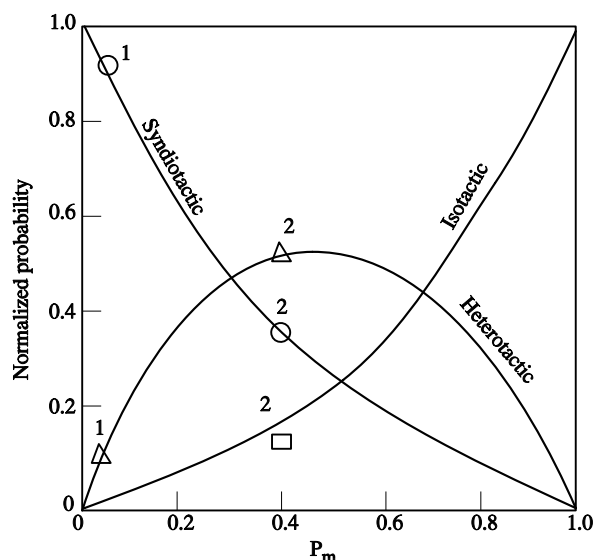


Figure E2.6 Test of Bernoullian model with data for polymer 1 and polymer 2 of Exercise E2.6.

E2.6 The α -methyl resonance in poly(α -methyl styrene) is found to be split into three peaks which are assigned to isotactic, heterotactic, and syndiotactic triads. Fractions of the polymers in the three configurations determined by the area of these peaks are given below for poly(α -methyl styrene) prepared with two different catalysts [Brownstein, S., Bywater, S., and Worsfold, D. J., *Makromol. Chem.*, **48**, 127 (1961)]:

Polymer	Catalyst	Fraction of polymer		
		Iso	Hetero	Syndio
1	BF ₃	—	0.11	0.89
2	Na-Naphthenide	0.13	0.48	0.39

Determine the probability P_m and test for consistency with Bernoullian statistics. What do the values of P_m obtained in the two cases signify ?

Answer:

Test for Bernoullian fitting may be done by placing the data for fractional areas representing polymer fractions in *iso*, *syndio*, and *hetero* configurations on the probability curves for the different triad sequences. This is done in Fig. E2.6 by placing, for polymer 1, the syndio point (0.89) on the theoretical probability curve for syndiotactic triad to obtain the P_m value and then letting the other points fall where they may on the vertical line at this P_m . This gives $P_m = 0.06$.

For polymer 2, the data are fitted similarly in Fig. E2.6 by placing the hetero point on the theoretical curve to obtain P_m and then letting the other points on the vertical line at the same P_m . This gives $P_m = 0.4$.

It is seen that the fractions fall near the theoretical curves, showing both types of catalysis have single P_m values for poly(α -methyl styrene). That the P_m value in both cases is less than 0.5, it suggests that the steric strain is greatest if two consecutive units have the same configuration.

E2.7 The density of crystalline polyethylene is 0.996 g/cm^3 , while the density of amorphous polyethylene is 0.866 g/cm^3 . Calculate the percentage of crystallinity in a sample of linear polyethylene of density 0.970 g/cm^3 and in a sample of branched polyethylene of density 0.917 . Why do the two samples have considerably different crystallinities ?

Answer:

Crystalline PE, $\rho_c = 0.996 \text{ g cm}^{-3}$

Amorphous PE, $\rho_a = 0.866 \text{ g cm}^{-3}$

Branched PE, $\rho = 0.917 \text{ g cm}^{-3}$.

Using Eq. P2.14.6 (polymer text), mass fraction of crystalline component is

$$x_c = \frac{(0.996 \text{ g cm}^{-3}) \left[(0.917 - 0.866) \text{ g cm}^{-3} \right]}{(0.917 \text{ g cm}^{-3}) \left[(0.996 - 0.866) \text{ g cm}^{-3} \right]} = 0.426$$

So the polymer is 42.6% crystalline.

For linear PE, $\rho = 0.970 \text{ g cm}^{-3}$. Therefore, mass fraction of crystalline component is

$$x_c = \frac{(0.996 \text{ g cm}^{-3}) \left[(0.970 - 0.866) \text{ g cm}^{-3} \right]}{(0.970 \text{ g cm}^{-3}) \left[(0.996 - 0.866) \text{ g cm}^{-3} \right]} = 0.821$$

So the polymer is 82.1% crystalline.

The samples have completely different crystallinities since branched molecules do not crystallize as easily as linear ones.

E2.8 Chemically both wax and polyethylene can be described as polymethylene and represented by $-(\text{CH}_2)_n-$, but while the former is a brittle solid the latter is a tough plastic. What are the reasons for this difference in mechanical behavior?

Answer:

There are three main reasons for the difference.:

(a) Polyethylene chains are long enough to connect individual systems together within a lamellar crystallite by chain folding and the chains also wander between lamellae, connecting several of them together [see Fig. 2.17 (polymer text)]. These effects add strong covalent bond connections both within the lamellae and between them. On the other hand, only weak van der Waals forces hold chains together in wax.

(b) Certain portions of polyethylene are amorphous. The chains in these portions are rubbery, imparting flexibility to the entire material. Wax is 100% crystalline, by contrast.

(c) The long chain in polyethylene allows for molecular entanglement which helps hold the material together under stress. (In the melt, chain entanglements also cause the viscosity to be raised very significantly.)

E2.9 Draw a $\log E$ versus temperature plot for a linear, amorphous polymer and indicate the position and name the five regions of viscoelastic behavior. How is the curve changed if (a) the polymer is semicrystalline, (b) the polymer is crosslinked, and (c) the experiment is run faster ?

Answer:

See Section 2.6 in polymer text.

E2.10 To be a useful plastic, an amorphous polymer must be below its T_g at the ambient tempera-

ture, while crystalline polymers may be either above or below their T_g 's. Why ?

Answer:

Amorphous polymers have the highest modulus below T_g and the modulus drops sharply above T_g [see Fig. 2.21 (polymer text)]. Crystalline polymers, however, have high values of modulus even beyond T_g and up to T_m .

E2.11 Explain the following

- By dipping into liquid nitrogen, an adhesive tape loses its stickiness.
- A hollow rubber ball when cooled in liquid nitrogen and thrown hard against the wall breaks into pieces.
- A dinner bell coated with latex paint and kept in a freezer makes louder noise than the one coated and kept at room temperature.
- Molding or extrusion of plastics too close to T_g can result in a stiffening of the material.
- The T_g of a semicrystalline polymer is often higher than the same polymer in a completely amorphous state.
- In emulsion polymerization of styrene, often carried out at 80°C, the reaction does not proceed quite to 100% conversion.
- When nylon shirts are washed and hung up to drip-dry, creases straighten out by themselves.
- The postage stamp, which is coated with linear poly(vinyl alcohol) adhesive, needs to be moistened with water (or saliva) before applying.

Answer:

- An adhesive must be able to flow on a molecular scale to “grip” surfaces. Below T_g it is a glassy solid and has so no adhesive property.
- Below T_g the hollow rubber ball becomes glassy and brittle. On impact against a hard wall it, therefore, breaks just like glass.

- When cyclical or repetitive motions of stress and strain are involved, it is more convenient to talk about dynamic mechanical moduli. The complex Young's modulus E^* has the formal definition

$$E^* = E' + iE''$$

where E' is the *storage modulus* (a measure of the energy stored elastically during deformation) and E'' is the *loss modulus* (a measure of energy converted to heat); the quantity i represents the square root of minus one; the quantity E''/E' is $\tan \delta$, called the *loss tangent*.

At the glass-to-rubber transition (T_g), there occurs a maximum in $\tan \delta$ or the loss modulus and the polymers are thus capable of damping out noise and vibrations. At temperatures below T_g the polymer behaves elastically, and there occurs little or no flow to convert the applied energy into internal work in the material.

To explain more explicitly, let h be the energy dissipated as heat per unit volume of material per unit time because of flow in shear deformation. Then

$$h = \sigma(d\gamma/dt) = \eta(d\gamma/dt)^2$$

Thus the work dissipated is proportional to the viscosity (η) of the material at fixed straining rate $d\gamma/dt$. At low temperatures, η is very high but γ and $d\gamma/dt$ are vanishingly small and h is negligible. As the structure is loosened in the transition region, η decreases but $d\gamma/dt$ becomes much more significant so that h (and hence the loss modulus and $\tan \delta$) increases. Thus, a dinner bell coated with latex paint and kept in a freezer (below T_g) makes louder noise than the one coated and kept at

room temperature (above T_g).

(d) Since an increased pressure causes a decrease in the total volume, an increase in T_g is expected based on the prediction of decreased free volume. An increase of pressure can thus bring about *vitrification* (transition to glassy state). In molding or extrusion operations which require application of pressure, T_g may be raised sufficiently to cause stiffening of the material.

(e) Semicrystalline polymers exhibit glass transitions, though only in the amorphous portions of these polymers. The T_g may be increased due to crystallites restricting molecular motion.

(f) Polystyrene has a T_g of 100°C. At the reaction temperature of about 80°C, the reaction will not proceed quite to 100% conversion because the remaining monomer no longer depresses the polymer glass transition below the reaction temperature and the mixture becomes glassy with a concomitant fall in the reaction rate.

(g) Water acts as a plasticizer to depress T_g below the ambient temperature. This helps creases to straighten out when nylon clothes are hung up to drip-dry.

(h) Linear poly(vinyl alcohol) is plasticized by water (or saliva) and is softened due to lowering of its T_g . On migration of the water away from the adhesive surface, it “sticks”.

E2.12 When polyethylene is chlorinated, chlorine replaces hydrogen at random. The softening point of this chlorinated product depends on the chlorine content. It is found that small amounts of chlorine (10 to 50 wt% Cl) lowers the softening point while large amounts (~ 70%) raise the softening point. Rationalize this observation on the basis of intermolecular forces.

Answer:

Polyethylene has a high degree of crystallinity because of its highly symmetrical structure. Small amounts of chlorine destroy the regularity of the structure and lower the softening point in the direction of T_g (ca -120°C). Large amounts of chlorine hinder rotation about single bonds, raising T_g . The polarity and intermolecular interactions also increase, leading to increase of T_m .

E2.13 Account for the fact that the coefficient of volume expansion below T_g is smaller than that above T_g . Why is it said that in the glassy state the polymer is not in a true thermodynamic equilibrium?

Answer:

It is pertinent to address the second part of question first. The Gibbs free energy, G , is dependent on the sample volume V through two variables, namely, the average internuclear separation between segments of the neighboring chains in close packed regions and the number and size of holes present. While the former is a function of the thermal vibrations and rotations of the bonds and groups and is related to the heat content, the latter is primarily related to the entropy. At temperatures above T_g both these variables adjust themselves continuously with changing temperature, provided the changes are made sufficiently slowly to allow time for segmental diffusion. In this way, the actual volume of the sample always represents a minimum corresponding to thermodynamic equilibrium and the polymer is thus in a state of thermodynamic equilibrium.

At temperatures below T_g the segmental motions become frozen and the holes become immobilized. Though the internuclear separation between segments of neighboring chains can still adjust itself below T_g as the thermal vibrations of the atoms become reduced, the free volume of the sample cannot decrease because the holes are no longer able to diffuse out of the structure. Thus the volume of the sample below T_g does not represent a minimum corresponding to thermodynamic equilibrium and the polymer is not in a true thermodynamic equilibrium. Since at all temperatures below T_g the

volume of the sample is larger than the equilibrium volume of a true liquid at that temperature, the coefficient of expansion below T_g will be smaller than that above T_g .

E2.14 A newly prepared thermoplastic polymer has a T_g of 110°C and a melt viscosity of 1.2×10^6 poises at 140°C . The polymer, however, degrades above 160°C . Can this polymer be processed with an extruder which performs best when the melt viscosity is about 2×10^3 poises? If not, what can be done to make the polymer processable?

Answer:

Substituting $\eta = 1.2 \times 10^6$ poise, $T = 140^\circ\text{C}$, and $T_g = 110^\circ\text{C}$ in the WLF equation [Eq. 2.32 (polymer text)],

$$\log\left(\frac{\eta}{\eta_g}\right) = \frac{-17.44 \times (140 - 110)}{51.6 + (140 - 110)}$$

So, $\eta_g = 3.1 \times 10^{12}$ poise.

Now substituting $\eta_g = 3.1 \times 10^{12}$ poise, $T_g = 110^\circ\text{C}$, and $T = 160^\circ\text{C}$ in the WLF equation yields $\eta_{160^\circ\text{C}} = 8.1 \times 10^3$ poise.

Since $\eta_{160^\circ\text{C}}$ is greater than η of processability, the polymer cannot be used with the extruder. A plasticizer may be added to bring down the viscosity of the polymer to a usable level.

E2.15 The following data were obtained [L. Mandelkern, G. M. Martin, and F. A. Quinn, *J. Res. Natl. Bur. Stand.*, **58**, 137 (1957)] for the glass transition temperature T_g of the copolymers of vinylidene fluoride and chlorotrifluoroethylene, as a function of the weight fraction w_1 of the first comonomer.

w_1	0	0.14	0.35	0.40	0.54	1.0
T_g ($^\circ\text{C}$)	46	19	-3	-8	-15	-38

What would be the T_g of a copolymer with $w_1 = 0.75$?

Answer:

The T_g of the copolymer is plotted against the weight fraction w_1 in Fig. E2.15. The curves for the linear equation [Eq. 2.44 (polymer text)], the Fox equation [Eq. 2.46 (polymer text)], and the Wood equation [Eq. 2.47 (polymer text)] are drawn on the same graph. The best fit is seen to be given by the Wood equation with $k = 0.385$.

From Eq. 2.47 (polymer text):

$$T_g = \frac{w_1 T_{g,1} + k w_2 T_{g,2}}{w_1 + k w_2}$$

With $w_1 = 0.75$, $w_2 = 0.25$, $T_{g,1} = -38 + 273$ or 235°K , $T_{g,2} = 46 + 273$, or 319°K , and $k = 0.389$, this equation gives

$$T_g = \frac{0.75 \times (235^\circ\text{K}) + 0.385 \times 0.25 \times (319^\circ\text{K})}{0.75 + 0.385 \times 0.25} = 245^\circ\text{K} (= -28^\circ\text{C})$$

E2.16 Two polystyrene standards (monodisperse) of molecular weights 1.8×10^6 and 1.6×10^5 have T_g values of 105.9°C and 104.7°C , respectively. Calculate the T_g value of a highly polydisperse

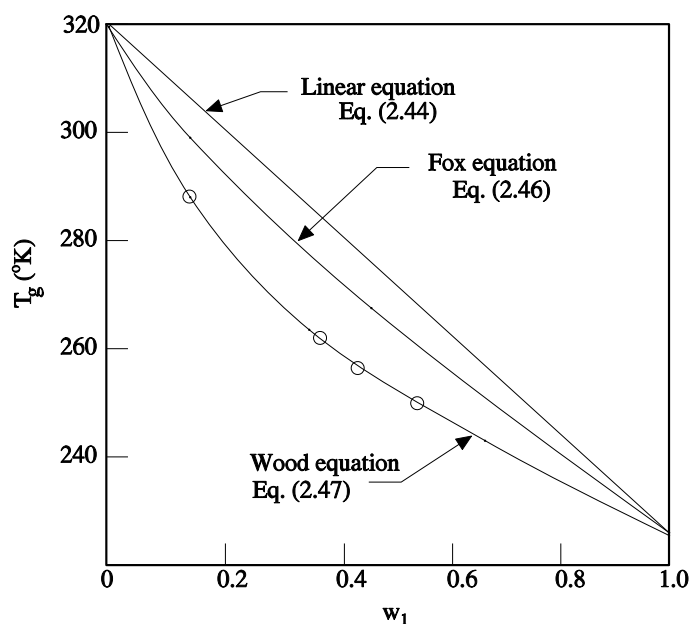


Figure E2.15 Plot of T_g against composition for copolymers of vinylidene fluoride and chlorotri-fluoroethylene according to (a) the linear equation, (b) the Fox equation, and (c) the Wood equation. Circles represent experimental points (data of Exercise E2.15).

polystyrene made up of four low polydisperse components as shown below:

Component	Wt. fraction (w)	\overline{M}_n
1	0.05	1.5×10^6
2	0.41	4.8×10^5
3	0.39	1.2×10^5
4	0.15	3.7×10^4

Answer:

Assuming that Eq. 2.35 (polymer text) is applicable,

$$(273 + 105.9)^\circ\text{K} = T_{g,\infty} - K/1.8 \times 10^6$$

$$(273 + 104.7)^\circ\text{K} = T_{g,\infty} - K/1.6 \times 10^5$$

Solving, $T_{g,\infty} = 379^\circ\text{K}$ and $K = 2.1 \times 10^5^\circ\text{K g mol}^{-1}$.

Using the definition of number average molecular weight [cf. Eq. 4.6 (polymer text)],

$$\frac{1}{\overline{M}_n} = \frac{w_1}{M_1} + \frac{w_2}{M_2} + \frac{w_3}{M_3} + \frac{w_4}{M_4}$$

$$\frac{(T_{g,\infty} - T_g)}{K} = \left[\frac{0.05}{1.5 \times 10^6} + \frac{0.41}{4.8 \times 10^5} + \frac{0.39}{1.2 \times 10^5} + \frac{0.15}{3.7 \times 10^4} \right] \text{mol g}^{-1}$$

$$\frac{(379 - T_g)^\circ\text{K}}{(2.1 \times 10^5^\circ\text{K g mol}^{-1})} = 0.82 \times 10^{-5} \text{mol g}^{-1}$$

Solving, $T_g = 377.3^\circ\text{K}$ ($\equiv 104.3^\circ\text{C}$)

E2.17 A new polymer with a weight average degree of polymerization of 1400 and five atoms in

the repeating unit has a melt viscosity of 1500 poises at 190°C. What will be the viscosity at the same temperature if its molecular weight is doubled?

Answer:

Weight average number of chain atoms (see page 80 of polymer text) in new polymer, $\mathcal{Z}_1 = 5 \times 1400 = 7000$. If \overline{M}_w is doubled, $\mathcal{Z}_2 = 14000$.

Using Eq. 2.49 (polymer text), $\eta_2/\eta_1 = (\mathcal{Z}_2/\mathcal{Z}_1)^{3.4} = 2^{3.4}$

Hence, $\eta_2 = (1500 \text{ poise})(2^{3.4}) = 15834 \text{ poise}$.

E2.18 A vinyl polymer with a \mathcal{Z} value of 200 has a melt viscosity of 100 poises. What would the viscosity of this polymer be if $\mathcal{Z} = 800$?

Answer:

Let $\mathcal{Z}_c = 600$

From Eq. 2.48 (polymer text),

$$\frac{\eta_1}{\eta_2} = \frac{K_L(200)}{K_L(600)} = 1/3$$

$$\eta_2 = 3\eta_1 = 300 \text{ poise}$$

From Eq. 2.49 (polymer text),

$$\frac{\eta_2}{\eta_3} = \frac{K_H(600)^{3.4}}{K_H(800)^{3.4}}$$

$$\eta_3 = (300 \text{ poise})(800/600)^{3.4} = 798 \text{ poise}$$

E2.19 A polymer with a T_g of 105°C and a \mathcal{Z} value of 400 is found to have a melt viscosity of 500 poises at 170°C. What will be the melt viscosity at 150°C if $\mathcal{Z} = 800$? Assume $\mathcal{Z}_c = 600$. (Hint: Combine the DP dependence with the WLF equation.)

Answer:

At 170°C, for $\mathcal{Z} = 400$, one obtains from Eq. 2.48 (polymer text):

$$K_L = \frac{5000 \text{ poise}}{400} = 12.5 \text{ poise}$$

At 170°C, for $\mathcal{Z} = 600$,

$$\text{Eq. 2.48 (polymer text): } \eta = (12.5 \text{ poise})(600) = 7500 \text{ poise}$$

$$\text{Eq. 2.49 (polymer text): } K_H = (7500 \text{ poise})/(600)^{3.4} = 2.69 \times 10^{-6} \text{ poise}$$

At 170°C, for $\mathcal{Z} = 800$,

$$\text{Eq. (2.49): } \eta = (2.69 \times 10^{-6} \text{ poise})(800)^{3.4} = 19964 \text{ poise}$$

From WLF equation [cf. Eq. 2.32 (polymer text)]:

$$\text{At } 170^\circ\text{C, } \eta_T = 19964 \text{ poise, } T - T_g = 170 - 105 = 65^\circ\text{C,}$$

$$\log \eta_g = \log(19964) + \frac{17.44 \times 65}{51.6 + 65} = 14.0$$

At 150°C, $T - T_g = 150 - 105 = 45^\circ\text{C,}$

$$\log \eta_T = 14.0 - \frac{17.4 \times 45}{5.6 + 45} = 5.87$$

which gives $\eta_T = 7.5 \times 10^5$ poise.

E2.20 Account for the fact that if a strip of rubber is brought into contact with the temperature-sensitive lips and stretched rapidly, an instantaneous warming of the strip can be easily perceived.

Answer:

Stretching a strip of rubber rapidly produces an adiabatic extension and involves the phenomenon known as *strain-induced crystallization*. Thus, when unvulcanized natural rubber is stretched, sections of coiled rubber molecules in it are aligned (in the direction of strain) and crystallized, thereby releasing heat and warming up the rubber strip, as can be perceived by temperature-sensitive lips. Conversely, on releasing the strain, the molecules return to the original coiled (more probable) state, absorbing heat in the process, and so the rubber strip cools.

E2.21 A polyisoprene rubber has 2.5% of its repeating units crosslinked by sulfur vulcanization. Estimate the modulus of the sample at low extensions. (Density of vulcanizate = 0.94 g/cm^3 at 25°C .)

Answer:

Molar mass of isoprene repeat unit (C_5H_8) = 68 g mol^{-1} .

Fraction of isoprene units crosslinked = $2.5/100 = 0.025$.

Molar mass of chain lengths between crosslinks

$$\begin{aligned} &\approx (68 \text{ g mol}^{-1})/0.025 \\ &= 2720 \text{ g mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Young's modulus, } E &= \frac{3(0.94 \text{ g cm}^{-3})(8.7 \times 10^7 \text{ erg mol}^{-1} \text{ }^\circ\text{K}^{-1})(298 \text{ }^\circ\text{K})}{(2720 \text{ g mol}^{-1})} \\ &= 2.7 \times 10^7 \text{ dyne cm}^{-2} \\ &= 2.7 \text{ MN/m}^2 \end{aligned}$$

$$[1 \text{ dyne cm}^{-2} = 0.1 \text{ N m}^{-2}]$$

E2.22 A synthetic rubber containing 60% butadiene and 40% isoprene by weight was vulcanized with 5% (w/w) sulfur. Stress-strain measurements on this vulcanizate at low extensions yielded a value of $2.8 \times 10^7 \text{ dyne/cm}^2$ for Young's modulus. (a) Calculate the molecular weight of the chain lengths between crosslinks. (b) Assuming that all sulfur is used in crosslinking, determine how many sulfur atoms on average are used in each crosslink. (Density of vulcanizate = 0.93 g/cm^3 at 25°C .)

Answer:

Molar mass of butadiene (C_4H_6) = 54 g mol^{-1} .

Molar mass of isoprene (C_5H_8) = 68 g mol^{-1} .

Molar mass of average repeat unit

$$= \frac{(100 \text{ g})}{(60 \text{ g})/(54 \text{ g mol}^{-1}) + (40 \text{ g})/(68 \text{ g mol}^{-1})}$$

$$= 58.8 \text{ g mol}^{-1}$$

From Eq. 2.79 (polymer text),

$$\begin{aligned} M_c &= 3\rho RT/E \\ &= \frac{3(0.93 \text{ g cm}^{-3})(8.3 \times 10^7 \text{ erg mol}^{-1} \text{ }^\circ\text{K}^{-1})(298^\circ\text{K})}{(2.8 \times 10^7 \text{ dyne cm}^{-2})} \\ &= 2464 \text{ g mol}^{-1} \end{aligned}$$

$$\text{Fraction of repeat units crosslinked} = \frac{(58.8 \text{ g mol}^{-1})}{(2464 \text{ g mol}^{-1})} = 0.024$$

Let x = average number of sulfur atoms used in each crosslink.

Number of crosslinks in 100 g rubber = $5/32x$ mol.

According to Fig. 1.8 (polymer text), there is one crosslink per repeat unit.

Hence, fraction of repeat units crosslinked

$$= \frac{(5/32x \text{ mol})}{(100 \text{ g})/(58.8 \text{ g mol}^{-1})} = 0.092/x$$

Therefore, $x = 0.092/0.024 = 3.8$.

E2.23 The synthetic rubber in the above problem was vulcanized such that 1.2% of the monomer units in the polymer were crosslinked. (a) Calculate the stress at 25% elongation of the vulcanizate. (b) What would be the corresponding stress if 2.4% of the units are crosslinked? Assume random distribution of both monomers in the chain. (Density of vulcanizate = 0.93 g/cm^3 at 25°C .)

Answer:

Molar mass of butadiene (C_4H_6) = 54 g mol^{-1} .

Molar mass of isoprene (C_5H_8) = 68 g mol^{-1} .

Average molar mass of mer = 58.8 g mol^{-1} (see Exercise E2.22).

Average molar mass of chain length between crosslinks,

$$\begin{aligned} M_c &= \frac{(100 - 1.2)(58.8 \text{ g mol}^{-1})}{(1.2)} \\ &= 4841 \text{ g mol}^{-1} \end{aligned}$$

[According to Fig. 1.8 (polymer text), there is one such chain length for every monomer unit crosslinked.]

From Eq. 2.72 (polymer text), $\lambda = 1.25$ for 25% elongation.

(a) From Eq. 2.77 (polymer text):

$$\begin{aligned} \sigma &= \frac{(0.93 \text{ g cm}^{-3})(8.37 \times 10^7 \text{ ergs mol}^{-1} \text{ }^\circ\text{K}^{-1})(298^\circ\text{K})}{(4841 \text{ g mol}^{-1})} \\ &\quad \times \left[1.25 - \frac{1}{(1.25)^2} \right] \\ &= 2.9 \times 10^6 \text{ dyne cm}^{-2} \\ &= 0.29 \times 10^6 \text{ N m}^{-2} \quad (\equiv 0.29 \text{ MPa}) \end{aligned}$$

(b) Average molar mass of chain length between crosslinks,

$$\begin{aligned}
 M_c &= \frac{(100 - 2.4)(58.8 \text{ g mol}^{-1})}{(2.4)} = 2391 \text{ g mol}^{-1} \\
 \sigma &= \frac{(0.93 \text{ g cm}^{-3})(8.37 \times 10^7 \text{ erg mol}^{-1} \text{ }^\circ\text{K}^{-1})(298^\circ\text{K})}{(2391 \text{ g mol}^{-1})} \\
 &\quad \times \left[1.25 - \frac{1}{(1.25)^2} \right] \\
 &= 5.9 \times 10^6 \text{ dyne cm}^{-2} \\
 &= 0.59 \times 10^6 \text{ N m}^{-2} (\equiv 0.59 \text{ MPa})
 \end{aligned}$$

E2.24 An interesting experiment was described [G. V. Henderson, D. O. Cambell, V. Kuzmich, and L. H. Sperling, *J. Chem. Ed.*, **62**, 269 (1985)] to determine the extent of hydrogen bonding in gelled gelatin by observing the depth of indentation of a sphere into the surface of the gel. In a typical experiment 22 g gelatin was dissolved in 600 ml water and allowed to set in refrigerator at 5°C . A steel ball 4 cm in diameter and weighing 262 g made an indentation 1.20 cm deep when placed on the gelled gelatin. Assuming a molecular weight of 30,000 for the gelatin, calculate the number of hydrogen bonds per molecule.

Young's modulus (E) may be determined from indentation by using the equation

$$E = \frac{3(1 - \nu^2)F}{4h^{3/2}r^{1/2}}$$

where F represents the force of sphere against the gelatin surface ($= mg$ dynes), h represents the depth of indentation of sphere (cm), r is the radius of sphere (cm), g is the gravity constant, and ν is poisson's ratio (may be assumed to be 0.5).

Answer:

Force exerted by the steel ball,

$$\begin{aligned}
 F &= mg \\
 &= (262 \text{ g})(980 \text{ cm s}^{-2}) = 2.57 \times 10^5 \text{ dynes}
 \end{aligned}$$

Using the Hertz equation [L. H. Sperling, "Interpenetrating Polymer Networks and Related Materials", Plenum Press, New York, 1981, p. 177],

$$\begin{aligned}
 E &= \frac{3(1 - 0.5^2)(2.57 \times 10^5 \text{ dynes})}{4(1.2 \text{ cm})^{3/2}(2.0 \text{ cm})^{1/2}} \\
 &= 0.78 \times 10^5 \text{ dynes cm}^{-2} (\equiv 0.78 \times 10^4 \text{ Pa})
 \end{aligned}$$

[By comparison, a rubber band has a Young's modulus of about 10^6 Pa.]

According to the rubber elasticity theory (see Section 2.12 of polymer text), Young's modulus E is related to the crosslink density by [cf. Eq. 2.79 (polymer text)]:

$$E = 3\rho RT/M_c = 3nRT/N_{\text{Av}}$$

where n represents the number of active chain segments per unit volume and N_{Av} is Avogadro's number.

Assuming a tetrafunctional crosslinking mode (i.e., four chain segments emanating from the locus of the hydrogen bond) [*see* Sperling, L. H., "Introduction to Physical Polymer Science", Wiley Interscience, New York, 1986],

$$E = 6C_hRT$$

where C_h is the crosslink density (moles of hydrogen bonds per unit volume). Therefore,

$$\begin{aligned} C_h &= E/6RT \\ &= \frac{(0.78 \times 10^5 \text{ dynes cm}^{-2})}{6(8.31 \times 10^7 \text{ erg mol}^{-1} \text{ }^\circ\text{K}^{-1})(278 \text{ }^\circ\text{K})} \\ &= 5.6 \times 10^{-7} \text{ mol cm}^{-3} \end{aligned}$$

$$\begin{aligned} \text{Concentration of gelatin} &= \frac{(22 \text{ g})}{(3 \times 10^4 \text{ g mol}^{-1})(600 \text{ cm}^3)} \\ &= 1.22 \times 10^{-6} \text{ mol cm}^{-3} \end{aligned}$$

Number of hydrogen bonds per gelatin molecule

$$\begin{aligned} &= \frac{(5.6 \times 10^{-7} \text{ mol cm}^{-3})}{(1.22 \times 10^{-6} \text{ mol cm}^{-3})} \\ &= 0.46 \end{aligned}$$

E2.25 A 6.0 cm long rubber band is stretched to 15.0 cm. It is found that to keep the rubber band at this length when the temperature is raised from 27°C to 32°C, an additional stress of 1.5×10^5 Pa is to be applied. Calculate the modulus of this rubber at 1% elongation at 27°C. (Neglect any changes in volume with temperature.)

Answer:

From Eq. 2.72 (polymer text), $\lambda = 15.0/6.0 \text{ cm} = 2.5$. So, $\lambda - 1/\lambda^2 = 2.34$.

From Eq. 2.75 (polymer text),

$$\begin{aligned} \sigma_{32} - \sigma_{27} &= \left(\frac{nR}{N_{Av}} \right) (32 - 27)(2.34) \\ &= 1.5 \times 10^5 \text{ Pa} \frac{nR}{N_{Av}} \\ &= 1.28 \times 10^4 \end{aligned}$$

At 1% elongation, $\lambda = 1.01$, $\lambda - 1/\lambda^2 = 0.0297$.

$$\begin{aligned} \sigma &= \left(\frac{nR}{N_{Av}} \right) (T) \left(\lambda - \frac{1}{\lambda^2} \right) \\ &= (1.28 \times 10^4)(273 + 27)(0.0297) \\ &= 1.14 \times 10^5 \text{ Pa} \end{aligned}$$

$$\begin{aligned} E &= \sigma/\epsilon \\ &= \sigma/(\lambda - 1) \text{ [cf. Eq. (2.72)]} \\ &= \frac{(1.14 \times 10^5 \text{ Pa})}{(1.01 - 1)} \\ &= 1.14 \times 10^7 \text{ Pa } (\equiv 11.4 \text{ MPa}) \end{aligned}$$

E2.26 Two identical rubber bands, A and B, each 10 cm long, are tied together at their ends and stretched to a total length of 30 cm. The rubber bands A and B are at 25 °C and 140°C, respectively. Calculate the distance of the knot from the untied end of A.

Answer:

Before answering the question it would be pertinent to explain the phenomenon that a stretched rubber band with a fixed weight hanging from it becomes shorter when temperature is raised and longer when the temperature is lowered, showing that it has greater elastic modulus at higher temperatures, which is the opposite of that observed for most other materials.

In simple mechanistic terms, the elastic modulus of an elastomer is simply a measure of the resistance to the uncoiling of randomly oriented chains under stress. An applied stress tends to untangle the chains and align them in the direction of the stress, but an increase in temperature will increase the thermal motion of the chains and make chain orientation more difficult to induce. This will lead to a higher elastic modulus. Under a constant force some chain orientation will take place, but an increase in temperature will stimulate a reversion to a randomly coiled conformation and the elastomer will contract. The effect of lowering the temperature of an elastomer under stress can be similarly explained. (While this is satisfactory qualitative explanation of the above phenomenon, more rigorous thermodynamic explanation can be given.)

Qualitatively, it can now be predicted that the knot in the tied rubber band (A+B) will be nearer to the B end because a stretched elastomer shrinks when heated.

For a quantitative description let us denote the length of the tied rubber band by h with subscripts o and f for initial and final states. Using Eq. 2.75 (polymer text) one can write for the band A,

$$\sigma_A = \left(\frac{nRT_A}{N_{Av}} \right) \left(\frac{l_{Af}}{l_{Ao}} - \frac{l_{Ao}^2}{l_{Af}^2} \right) \quad (\text{E2.26.1})$$

Similarly, for the band B,

$$\sigma_B = \left(\frac{nRT_B}{N_{Av}} \right) \left(\frac{l_{Bf}}{l_{Bo}} - \frac{l_{Bo}^2}{l_{Bf}^2} \right) \quad (\text{E2.26.2})$$

If the system is to be in equilibrium, the stresses must be balanced, and therefore equal, i.e., $\sigma_A = \sigma_B$, or

$$\left(\frac{nRT_A}{N_{Av}} \right) \left(\frac{l_{Af}}{l_{Ao}} - \frac{l_{Ao}^2}{l_{Af}^2} \right) = \left(\frac{nRT_B}{N_{Av}} \right) \left(\frac{l_{Bf}}{l_{Bo}} - \frac{l_{Bo}^2}{l_{Bf}^2} \right)$$

Data:

$$T_A = 25^\circ\text{C} \equiv 298^\circ\text{K}, \quad l_{Ao} = 10 \text{ cm}$$

$$T_B = 140^\circ\text{C} \equiv 413^\circ\text{K}, \quad l_{Bo} = 10 \text{ cm}$$

$$l_{Af} + l_{Bf} = 30 \text{ cm}$$

Making necessary substitutions and rearrangements, a trial and error solution yields: $l_{Af} = 16.6$ cm, $l_{Bf} = 13.4$ cm.