

22 Macromolecules and aggregates

Solutions to exercises

Discussion questions

- E22.1(b)** (a) ΔS is the change in conformational entropy of a random coil of a polymer chain. It is the statistical entropy arising from the arrangement of bonds, when a coil containing N bonds of length l is stretched or compressed by nl , where n is a numerical factor giving the amount of stretching in units of l . The amount of stretching relative to the number of monomer units in the chain is $\nu = n/N$.
- (b) R_{rms} is one of several measures of the size of a random coil. For a polymer of N monomer units each of length l , the root mean square separation, R_{rms} , is a measure of the average separation of the ends of a random coil. It is the square root of the average value of R^2 , calculated by weighting each possible value of R^2 with the probability that R occurs.
- (c) R_g , the radius of gyration, is another measure of the size of a random coil. It is the radius of a thin hollow spherical shell of the same mass and moment of inertia as the polymer molecule.

All of these expressions are derived for the freely jointed random coil model of polymer chains which is the simplest possibility for the conformation of identical units not capable of forming hydrogen bonds or any other type of specific bond. In this model, any bond is free to make any angle with respect to the preceding one (Fig. 22.3 of the text). We assume that the residues occupy zero volume, so different parts of the chain can occupy the same region of space. We also assume in the derivation of the expression for the probability of the ends of the chain being a distance nl apart, that the chain is compact in the sense that $n \ll N$. This model is obviously an oversimplification because a bond is actually constrained to a cone of angles around a direction defined by its neighbour (Fig. 22.4). In a hypothetical one-dimensional freely jointed chain all the residues lie in a straight line, and the angle between neighbours is either 0° or 180° . The residues in a three-dimensional freely jointed chain are not restricted to lie in a line or a plane.

The random coil model ignores the role of the solvent: a poor solvent will tend to cause the coil to tighten; a good solvent does the opposite. Therefore, calculations based on this model are best regarded as lower bounds to the dimensions of a polymer in a good solvent and as an upper bound for a polymer in a poor solvent. The model is most reliable for a polymer in a bulk solid sample, where the coil is likely to have its natural dimensions.

- E22.2(b)** No solution.
- E22.3(b)** The formation of micelles is favored by the interaction between hydrocarbon tails and is opposed by charge repulsion of the polar groups which are placed close together at the micelle surface. As salt concentration is increased, the repulsion of head groups is reduced because their charges are partly shielded by the ions of the salt. This favors micelle formation causing the micelles to be larger and the critical micelle concentration to be smaller.
- E22.4(b)** A surfactant is a species that is active at the interface of two phases or substances, such as the interface between hydrophilic and hydrophobic phases. A surfactant accumulates at the interface and modifies the properties of the surface, in particular, decreasing its surface tension. A typical surfactant consists of a long hydrocarbon tail and other non-polar materials, and a hydrophilic head group, such as the carboxylate group, $-\text{CO}_2^-$, that dissolves in a polar solvent, typically water. In other words, a surfactant is an amphiphathic substance, meaning that it has both hydrophobic and hydrophilic regions.

How does the surfactant decrease the surface tension? Surface tension is a result of cohesive forces and the solute molecules must weaken the attractive forces between solvent molecules. Thus molecules

with bulky hydrophobic regions such as fatty acids can decrease the surface tension because they attract solvent molecules less strongly than solvent molecules attract each other. See Section 22.15(b) for an analysis of the thermodynamics involved in this process.

Numerical Exercises

E22.5(b) For a random coil, the r.m.s. separation is

$$R_{\text{rms}} = l(N)^{1/2} = (1.125 \text{ nm}) \times (1200)^{1/2} = \boxed{38.97 \text{ nm}}$$

E22.6(b) Polypropylene is $\text{---}(\text{CH}(\text{CH}_3)\text{CH}_2)\text{---}_n$, where n is given by

$$n = \frac{M_{\text{polymer}}}{M_{\text{monomer}}} = \frac{174 \text{ kg mol}^{-1}}{42.1 \times 10^{-3} \text{ kg mol}^{-1}} = 4.13 \times 10^3$$

The repeat length is the length of two C—C bonds. The contour length is

$$R_c = nl = (4.13 \times 10^3) \times (2 \times 1.53 \times 10^{-10} \text{ m}) = \boxed{1.26 \times 10^{-6} \text{ m}}$$

The r.m.s. separation is

$$R_{\text{rms}} = ln^{1/2} = (2 \times 1.53 \times 10^{-10} \text{ m}) \times (4.13 \times 10^3)^{1/2} = \boxed{1.97 \times 10^{-8} \text{ m}} = 19.7 \text{ nm}$$

E22.7(b) The number-average molar mass is

$$\bar{M}_n = \frac{1}{N} \sum_i N_i M_i = \frac{[3 \times (62) + 2 \times (78)] \text{ kg mol}^{-1}}{5} = \boxed{68 \text{ kg mol}^{-1}}$$

The mass-average molar mass is

$$\bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{3 \times (62)^2 + 2 \times (78)^2}{3 \times (62) + 2 \times (78)} \text{ kg mol}^{-1} = \boxed{69 \text{ kg mol}^{-1}}$$

E22.8(b) For a random coil, the radius of gyration is

$$R_g = l(N/6)^{1/2} \quad \text{so} \quad N = 6(R_g/l)^2 = 6 \times (18.9 \text{ nm}/0.450 \text{ nm})^2 = \boxed{1.06 \times 10^4}$$

E22.9(b) (a) Osmometry gives the number-average molar mass, so

$$\begin{aligned} \bar{M}_n &= \frac{N_1 M_1 + N_2 M_2}{N_1 + N_2} = \frac{\left(\frac{m_1}{M_1}\right) M_1 + \left(\frac{m_2}{M_2}\right) M_2}{\left(\frac{m_1}{M_1}\right) + \left(\frac{m_2}{M_2}\right)} = \frac{m_1 + m_2}{\left(\frac{m_1}{M_1}\right) + \left(\frac{m_2}{M_2}\right)} \\ &= \frac{100 \text{ g}}{\left(\frac{25 \text{ g}}{22 \text{ kg mol}^{-1}}\right) + \left(\frac{75 \text{ g}}{7.33 \text{ kg mol}^{-1}}\right)} [\text{assume } 100 \text{ g of solution}] = \boxed{8.8 \text{ kg mol}^{-1}} \end{aligned}$$

(b) Light-scattering gives the mass-average molar mass, so

$$\bar{M}_w = \frac{m_1 M_1 + m_2 M_2}{m_1 + m_2} = [(0.25) \times (22) + (0.75) \times (7.33)] \text{ kg mol}^{-1} = \boxed{11 \text{ kg mol}^{-1}}$$

E22.10(b) $\tau = \frac{4\pi a^3 \eta}{3kT}$ [see E22.10(a)]

$$\eta(\text{H}_2\text{O}, 20^\circ\text{C}) = 1.00 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1} \text{ [Handbook of Chemistry and Physics, 81st Edition]}$$

$$\begin{aligned} \tau &= \frac{4\pi \times (4.5 \times 10^{-9} \text{ m})^3 \times 1.00 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}}{3 \times 1.381 \times 10^{-23} \text{ J K}^{-1} \times 293 \text{ K}} \\ &= \boxed{9.4 \times 10^{-8} \text{ s}} \end{aligned}$$

E22.11(b) The rate of sedimentation is proportional to the sedimentation constant S

$$S = \frac{b\bar{M}_n}{fN_A}$$

The frictional coefficient f is proportional to the radius a of the sedimenting substance. The buoyancy b is the same for both of our substances because the density of the polymers, and therefore their specific volumes, are the same. The mass of a particle varies with its volume, and therefore with the cube of its radius. Thus

$$S \propto a^3/a = a^2 \quad \text{so} \quad \frac{\text{rate}_1}{\text{rate}_2} = \left(\frac{a_1}{a_2}\right)^2 = (8.4)^2 = \boxed{71}$$

with the larger particle sedimenting faster.

E22.12(b) The molar mass is related to the sedimentation constant

$$\bar{M}_n = \frac{SRT}{bD} = \frac{SRT}{(1 - \rho_{\text{water}}v_{\text{solute}})D}$$

where we have assumed the data refer to aqueous solution at 298 K.

$$\begin{aligned} \bar{M}_n &= \frac{(7.46 \times 10^{-13} \text{ s}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{[1 - (1000 \text{ kg m}^{-3}) \times (8.01 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1})] \times (7.72 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})} \\ &= \boxed{120 \text{ kg mol}^{-1}} \end{aligned}$$

E22.13(b) The drift speed is the speed s at which the frictional force fs precisely balances the gravitational force $m_{\text{eff}}g$

$$s = \frac{m_{\text{eff}}g}{f} = \frac{(1 - \rho_{\text{solution}}/\rho_{\text{solute}})mg}{6\pi a\eta_{\text{solv}}}$$

The mass of the particle is

$$\begin{aligned} m &= \rho_{\text{solute}}V = 4\pi\rho_{\text{solute}}a^3/3 = 4\pi \times (1250 \text{ kg m}^{-3}) \times (15.5 \times (10^{-6} \text{ m})^3)/3 \\ &= 1.95 \times 10^{-11} \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{So } s &= \frac{[1 - (1000 \text{ kg m}^{-3})/(1250 \text{ kg m}^{-3})] \times (1.95 \times 10^{-11} \text{ kg}) \times (9.81 \text{ m s}^{-2})}{6\pi \times (15.5 \times 10^{-6} \text{ m}) \times (8.9 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1})} \\ &= \boxed{1.47 \times 10^{-4} \text{ m s}^{-1}} \end{aligned}$$

E22.14(b) The molar mass is related to the sedimentation constant

$$\bar{M}_n = \frac{SRT}{bD} = \frac{SRT}{(1 - \rho_{\text{solution}}v_{\text{solute}})D}$$

where we have assumed the data refer to aqueous solution at 298 K.

$$\bar{M}_n = \frac{(5.1 \times 10^{-13} \text{ s}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})}{[1 - (0.997 \text{ g cm}^{-3}) \times (0.721 \text{ cm}^3 \text{ g}^{-1})] \times (7.9 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})} = \boxed{56 \text{ kg mol}^{-1}}$$

E22.15(b) In a sedimentation experiment, the mass-average molar mass is given by

$$\bar{M}_w = \frac{2RT}{(r_2^2 - r_1^2)b\omega^2} \ln \frac{c_2}{c_1} \quad \text{so} \quad \ln \frac{c_2}{c_1} = \frac{\bar{M}_w(r_2^2 - r_1^2)b\omega^2}{2RT}$$

This implies that

$$\ln c = \frac{\bar{M}_w r^2 b \omega^2}{2RT} + \text{constant}$$

so the plot of $\ln c$ versus r^2 has a slope m equal to

$$m = \frac{\bar{M}_w b \omega^2}{2RT} \quad \text{and} \quad \bar{M}_w = \frac{2RTm}{b\omega^2}$$

$$\begin{aligned} \bar{M}_w &= \frac{2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K}) \times (821 \text{ cm}^{-2}) \times (100 \text{ cm m}^{-1})^2}{[1 - (1000 \text{ kg m}^{-3}) \times (7.2 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1})] \times [(1080 \text{ s}^{-1}) \times (2\pi)]^2} \\ &= \boxed{3.1 \times 10^3 \text{ kg mol}^{-1}} \end{aligned}$$

E22.16(b) The centrifugal acceleration is

$$a = r\omega^2 \quad \text{so} \quad a/g = r\omega^2/g$$

$$a/g = \frac{(5.5 \text{ cm}) \times [2\pi \times (1.32 \times 10^3 \text{ s}^{-1})]^2}{(100 \text{ cm m}^{-1}) \times (9.8 \text{ m s}^{-2})} = \boxed{3.9 \times 10^5}$$

Solutions to problems

Solutions to numerical problems

P22.1 For a rigid rod, $R_g \propto l$ [Problem 22.15] $\propto M$, but for a random coil $R_g \propto N^{1/2}$ [22.7] $\propto M^{1/2}$. Therefore, poly (γ -benzyl-L-glutamate) is rod-like whereas polystyrene is a random coil (in butanol).

P22.3 $\ln \frac{c_1}{c_2} = \frac{mb\omega^2(r_1^2 - r_2^2)}{2kT}$ [22.42] $= \frac{2\pi^2 \bar{M}_w b v^2 (r_1^2 - r_2^2)}{RT}$ [$\omega = 2\pi v$]

and hence

$$\begin{aligned} v &= \left(\frac{RT \ln \left(\frac{c_1}{c_2} \right)}{2\pi^2 \bar{M}_w b (r_1^2 - r_2^2)} \right)^{1/2} \\ &= \left(\frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (\ln 5)}{2\pi^2 \times (1 \times 10^2 \text{ kg mol}^{-1}) \times (1 - 0.75) \times (7.0^2 - 5.0^2) \times 10^{-4} \text{ m}^2} \right)^{1/2} \\ &= 58 \text{ Hz, or } \boxed{3500 \text{ r.p.m.}} \end{aligned}$$

Question. What would the concentration gradient be in this system with a speed of operation of 70 000 r.p.m. in an ultracentrifuge?

P22.4

$$b = 1 - \rho v_s = 1 - (0.765 \text{ g cm}^{-3}) \times (0.93 \text{ cm}^3 \text{ g}^{-1}) = 0.289;$$

$$T = 308.15 \text{ K}$$

$$D/(\text{cm}^2 \text{ s}^{-1}) = (1.3 \times 10^{-4}) \times (M_w/\text{g mol}^{-1})^{-0.497}$$

$$\frac{bD}{SRT} = \frac{1}{M_w} (1 + 2B'c + 3gB'^2c^2 + \dots)$$

or

$$\frac{b}{SRT} = \frac{1}{M_w D} + \frac{2B'}{M_w D} c + \frac{3gB'^2}{M_w D} c^2 + \dots$$

$c/(\text{mg cm}^{-3})$	2.0	3.0	4.0	5.0	6.0	7.0
$S/(10^{-13} \text{ s})$	14.8	13.9	13.1	12.4	11.8	11.2
$(b/SRT)/(\text{g}^{-1} \text{ cm}^{-2} \text{ s mol})$	7.62	8.11	8.61	9.10	9.56	10.07

The regression fit of the form

$$\frac{(b/SRT)}{(\text{g}^{-1} \text{ cm}^{-2} \text{ s mol})} = A + Bc + Cc^2 \quad \text{yields}$$

$$A = 6.639, \quad \text{standard deviation} = 0.040$$

$$B = 0.494 \text{ mg}^{-1} \text{ cm}^3, \quad \text{standard deviation} = 0.019 \text{ mg}^{-1} \text{ cm}^3$$

$$C = -0.000 697 \text{ mg}^{-2} \text{ cm}^6, \quad \text{standard deviation} = 0.002 112 \text{ mg}^{-2} \text{ cm}^6$$

$$R = 0.999 940 \text{ (Note that the standard deviation of } C \text{ is greater than its value.)}$$

$$\frac{1}{\overline{M_w D}} = A(\text{g}^{-1} \text{ cm}^{-2} \text{ s mol})$$

$$\frac{1}{\left(\frac{\overline{M_w}}{\text{g/mol}}\right) \times (1.3 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}) \times \left(\frac{\overline{M_w}}{\text{g/mol}}\right)^{-0.497}} = 6.639 \text{ cm}^{-2} \text{ s}$$

$$\frac{1}{\left(\frac{\overline{M_w}}{\text{g/mol}}\right)^{0.503}} = 8.631 \times 10^{-4}$$

$$\boxed{\overline{M_w} = 1.23 \times 10^6 \text{ g mol}^{-1}}$$

$$\frac{2B'}{\overline{M_w D}} = B(\text{g}^{-1} \text{ cm}^{-2} \text{ s mol})$$

$$B' = \frac{B(\text{g}^{-1} \text{ cm}^{-2} \text{ s mol})}{2(1/\overline{M_w D})} = \frac{(0.494 \text{ mg}^{-1} \text{ cm}^3) \times (\text{g}^{-1} \text{ cm}^{-2} \text{ s mol})}{2 \times (6.639 \text{ g}^{-1} \text{ cm}^{-2} \text{ s mol})}$$

$$\boxed{B' = 3.72 \times 10^{-2} \text{ mg}^{-1} \text{ cm}^3}$$

We might test the significance of the form of the third term in the expression, namely

$$C = \frac{3gB'^2}{\overline{M_w D}}$$

by using the value of C obtained by the fitting process to calculate the value of g . But we must note again that the standard deviation of C is greater than C itself; hence the value of g obtained by this calculation could not be considered significant. g is about 1/4 for a good solvent, but cyclohexane is a theta solvent for polystyrene. There is no reason for them to agree; they are different samples; there is no fixed value of M for polystyrene.

P22.11
$$\frac{\Pi}{c} = \left(\frac{RT}{\overline{M}_n} \right) \times \left[1 + \left(\frac{B}{\overline{M}_n} \right) c \right] \text{ [Example 7.5]}$$

$\Pi = \rho gh$; so

$$\frac{h}{c} = \frac{RT}{\rho g \overline{M}_n} + \frac{BRT}{\rho g \overline{M}_n^2} \cdot c$$

and we should plot $\frac{h}{c}$ against c . Draw up the following table

$c/(\text{g}/100 \text{ cm}^3)$	0.200	0.400	0.600	0.800	1.00
h/cm	0.48	1.12	1.86	2.76	3.88
$\frac{h}{c}/(100 \text{ cm}^4 \text{ g}^{-1})$	2.4	2.80	3.10	3.45	3.88

The points are plotted in Fig. 22.1, and give a least-squares intercept at $2.04\bar{3}$ and a slope $1.80\bar{5}$

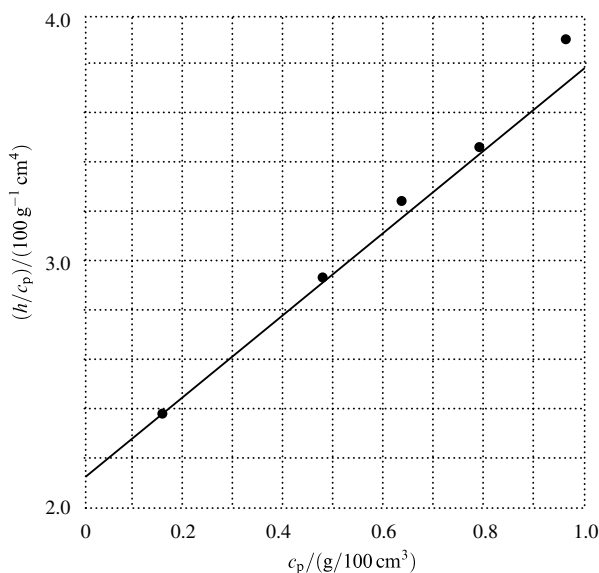


Figure 22.1

Therefore,
$$\frac{RT}{\rho g \overline{M}_n} = (2.04\bar{3}) \times (100 \text{ cm}^4 \text{ g}^{-1}) = 2.04\bar{3} \times 10^{-3} \text{ m}^4 \text{ kg}^{-1}$$

and hence

$$\overline{M}_n = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{(0.798 \times 10^3 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (2.04\bar{3} \times 10^{-3} \text{ m}^4 \text{ kg}^{-1})} = \boxed{155 \text{ kg mol}^{-1}}$$

From the slope

$$\frac{BRT}{\rho g \overline{M}_n^2} = (1.80\bar{5}) \times \left(\frac{100 \text{ cm}^4 \text{ g}^{-1}}{\text{g}/(100 \text{ cm}^3)} \right) = 1.80\bar{5} \times 10^4 \text{ cm}^7 \text{ g}^{-2} = 1.80\bar{5} \times 10^{-4} \text{ m}^7 \text{ kg}^{-2}$$

and hence

$$\begin{aligned} B &= \left(\frac{\rho g \bar{M}_n}{RT} \right) \times \bar{M}_n \times (1.805 \times 10^{-4} \text{ m}^7 \text{ kg}^{-2}) \\ &= \frac{(155 \text{ kg mol}^{-1}) \times (1.805 \times 10^{-4} \text{ m}^7 \text{ kg}^{-2})}{2.043 \times 10^{-3} \text{ m}^4 \text{ kg}^{-1}} \\ &= \boxed{13.7 \text{ m}^3 \text{ mol}^{-1}} \end{aligned}$$

Solutions to theoretical problems

P22.12 $dN \propto e^{-(M-\bar{M})^2/2\gamma} dM$

We write the constant of proportionality as K , and evaluate it by requiring that $\int dN = N$. Put

$$M - \bar{M} = (2\gamma)^{1/2}x, \quad \text{so} \quad dM = (2\gamma)^{1/2}dx$$

$$\begin{aligned} \text{and } N &= K(2\gamma)^{1/2} \int_a^\infty e^{-x^2} dx \quad \left[a = \frac{-\bar{M}}{(2\gamma)^{1/2}} \right] \\ &\approx K(2\gamma)^{1/2} \int_0^\infty e^{-x^2} dx [a \approx 0] = K(2\gamma)^{1/2} \frac{1}{2}\pi^{1/2} \end{aligned}$$

Hence, $K = \left(\frac{2}{\pi\gamma} \right)^{1/2} N$. It then follows that

$$\begin{aligned} \bar{M}_n &= \left(\frac{2}{\pi\gamma} \right)^{1/2} \int_0^\infty M e^{-(M-\bar{M})^2/2\gamma} dM \\ &= \left(\frac{2}{\pi\gamma} \right)^{1/2} (2\gamma) \int_0^\infty \left(x e^{-x^2} + \frac{\bar{M}}{(2\gamma)^{1/2}} e^{-x^2} \right) dx \\ &= \left(\frac{8\gamma}{\pi} \right)^{1/2} \times \left[\frac{1}{2} + \left(\frac{\pi}{8\gamma} \right)^{1/2} \bar{M} \right] = \boxed{\bar{M} + \left(\frac{2\gamma}{\pi} \right)^{1/2}} \end{aligned}$$

P22.14 A simple procedure is to generate numbers in the range 1 to 8, and to step north 1 or 2, east 3 or 4, south for 5 or 6, and west for 7 or 8 on a uniform grid. One such walk is shown in Fig. 22.2.

Roughly, they would appear to vary as $N^{1/2}$.

P22.15 We use the definition of the radius of gyration given in Footnote 4 and Problem 22.17, namely

$$R_g^2 = \frac{1}{N} \sum_j R_j^2$$

(a) For a sphere of uniform density, the centre of mass is at the centre of the sphere. We may visualize the sphere as a collection of a very large number, N , of small particles distributed with equal

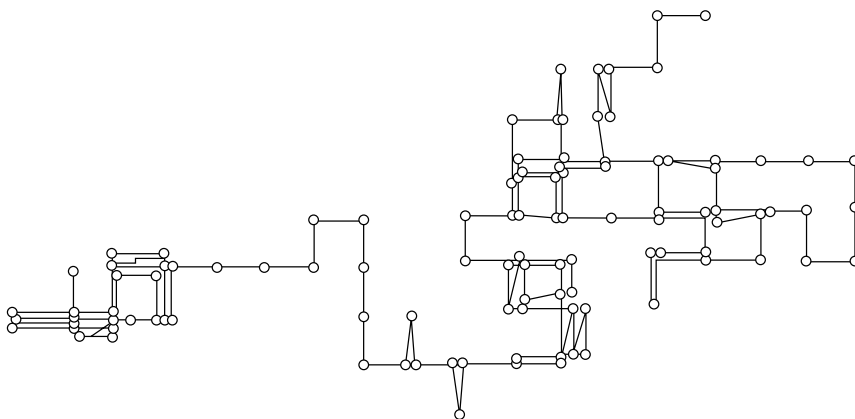


Figure 22.2

number density throughout the sphere. Then the summation above may be replaced with an integration.

$$R_g^2 = \frac{\frac{1}{N} \int_0^a N r^2 P(r) dr}{\int_0^a P(r) dr}$$

$P(r)$ is the probability per unit distance that a small particle will be found at distance r from the centre, that is, within a spherical shell of volume $4\pi r^2 dr$. Hence, $P(r) = 4\pi r^2 dr$. The denominator ensures normalization. Hence

$$R_g^2 = \frac{\int_0^a r^2 P(r) dr}{\int_0^a P(r) dr} = \frac{\int_0^a 4\pi r^4 dr}{\int_0^a 4\pi r^2 dr} = \frac{\frac{1}{5}a^5}{\frac{1}{3}a^3} = \frac{3}{5}a^2, \quad \boxed{R_g = \left(\frac{3}{5}\right)^{1/2} a}$$

- (b) For a long straight rod of uniform density the centre of mass is at the centre of the rod and $P(r)$ is constant for a rod of uniform radius; hence,

$$R_g^2 = \frac{2 \int_0^{(1/2)l} r^2 dr}{2 \int_0^{(1/2)l} dr} = \frac{\frac{1}{3} \left(\frac{1}{2}l\right)^3}{\frac{1}{2}l} = \frac{1}{12}l^2, \quad \boxed{R_g = \frac{l}{2\sqrt{3}}}$$

For a spherical macromolecule

$$a = \left(\frac{3V_m}{4\pi N_A}\right)^{1/3} = \left(\frac{3v_s M}{4\pi N_A}\right)^{1/3}$$

and so

$$\begin{aligned} R_g &= \left(\frac{3}{5}\right)^{1/2} \times \left(\frac{3v_s M}{4\pi N_A}\right)^{1/3} \\ &= \left(\frac{3}{5}\right)^{1/2} \times \left(\frac{(3v_s/\text{cm}^3 \text{g}^{-1}) \times \text{cm}^3 \text{g}^{-1} \times (M/\text{g mol}^{-1}) \times \text{g mol}^{-1}}{(4\pi) \times (6.022 \times 10^{23} \text{ mol}^{-1})}\right)^{1/3} \\ &= (5.690 \times 10^{-9}) \times (v_s/\text{cm}^3 \text{g}^{-1})^{1/3} \times (M/\text{g mol}^{-1})^{1/3} \text{ cm} \\ &= (5.690 \times 10^{-11} \text{ m}) \times \{(v_s/\text{cm}^3 \text{g}^{-1}) \times (M/\text{g mol}^{-1})\}^{1/3} \text{ cm} \end{aligned}$$

$$\text{That is, } R_g/\text{nm} = \boxed{0.05690 \times \{(v_s/\text{cm}^3 \text{g}^{-1}) \times (M/\text{g mol}^{-1})\}^{1/3}}$$

When $M = 100 \text{ kg mol}^{-1}$ and $v_s = 0.750 \text{ cm}^3 \text{ g}^{-1}$,

$$R_g/\text{nm} = (0.05690) \times \{0.750 \times 1.00 \times 10^5\}^{1/3} = \boxed{2.40}$$

For a rod, $v_{\text{mol}} = \pi a^2 l$, so

$$\begin{aligned} R_g &= \frac{v_{\text{mol}}}{2\pi a^2 \sqrt{3}} = \frac{v_s M}{N_A} \times \frac{1}{2\pi a^2 \sqrt{3}} \\ &= \frac{(0.750 \text{ cm}^3 \text{ g}^{-1}) \times (1.00 \times 10^5 \text{ g mol}^{-1})}{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (2\pi) \times (0.5 \times 10^{-7} \text{ cm})^2 \times \sqrt{3}} \\ &= 4.6 \times 10^{-6} \text{ cm} = \boxed{46 \text{ nm}} \end{aligned}$$

Comment. R_g may also be defined through the relation

$$R_g^2 = \frac{\sum_i m_i r_i^2}{\sum_i m_i}$$

Question. Does this definition lead to the same formulas for the radii of gyration of the sphere and the rod as those derived above?

P22.17 Refer to Fig. 22.3.

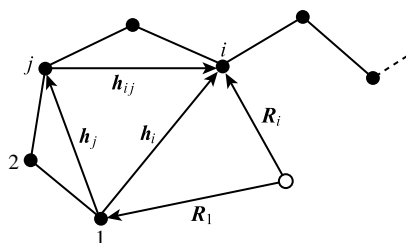


Figure 22.3

Since $\mathbf{R}_i = \mathbf{R}_1 + \mathbf{h}_i$ and $\sum_i \mathbf{R}_i = 0$,

$$N\mathbf{R}_1 + \sum_i \mathbf{h}_i = 0$$

and hence $\mathbf{R}_1 = -\frac{1}{N} \sum_i \mathbf{h}_i$

$$R_1^2 = \frac{1}{N^2} \sum_{ij} \mathbf{h}_i \cdot \mathbf{h}_j, \quad \mathbf{R}_1 \cdot \sum_i \mathbf{h}_i = -\frac{1}{N} \sum_{ij} \mathbf{h}_i \cdot \mathbf{h}_j$$

$$\begin{aligned} R_g^2 &= \frac{1}{N} \sum_i R_i^2 \text{ [new definition]} = \frac{1}{N} \sum_i \{(\mathbf{R}_1 + \mathbf{h}_i) \cdot (\mathbf{R}_1 + \mathbf{h}_i)\} \\ &= \frac{1}{N} \left(N R_1^2 + \sum_i h_i^2 + 2\mathbf{R}_1 \cdot \sum_i \mathbf{h}_i \right) = \frac{1}{N} \left(\sum_i h_i^2 - \frac{1}{N} \sum_{ij} \mathbf{h}_i \cdot \mathbf{h}_j \right) \end{aligned}$$

Since $\mathbf{h}_i \cdot \mathbf{h}_j = \frac{1}{2}(h_i^2 + h_j^2 - h_{ij}^2)$ [cosine rule]

$$R_g^2 = \frac{1}{N} \left(\sum_i h_i^2 + \frac{1}{2N} \sum_{ij} h_{ij}^2 - \frac{1}{2} \sum_i h_i^2 - \frac{1}{2} \sum_j h_j^2 \right)$$

$$= \boxed{\frac{1}{2N^2} \sum_{ij} h_{ij}^2} \text{ [the original definition]}$$

(In the last two terms, the summation over the second index contributes a factor N .)

- P22.21** (a) We seek an expression for a ratio of scattering intensities of a macromolecule in two different conformations, a rigid rod or a closed circle. The dependence on scattering angle θ is contained in the Rayleigh ratio R_θ . The definition of this quantity, in eqn 22.25, may be inverted to give an expression for the scattering intensity at scattering angle θ :

$$I_\theta = R_\theta I_0 \frac{\sin^2 \phi}{r^2},$$

where ϕ is an angle related to the polarization of the incident light and r the distance between sample and detector. Thus, for any given scattering angle, the ratio of scattered intensity of two conformations is the same as the ratio of their Rayleigh ratios:

$$\frac{I_{\text{rod}}}{I_{\text{cc}}} = \frac{P_{\text{rod}}}{R_{\text{cc}}} = \frac{P_{\text{rod}}}{P_{\text{cc}}}.$$

The last equality, stems from eqn 22.28, which related the Rayleigh ratios to a number of angle-independent factors that would be the same for both conformations and the structure factor (P_θ) that depends on both conformation and scattering angle. Finally, eqn 22.30 gives an approximate value of the structure factor as a function of the macromolecule's radius of gyration R_g , the wavelength of light, and the scattering angle:

$$P_\theta \approx 1 - \frac{16\pi^2 R_g^2 \sin^2(\frac{1}{2}\theta)}{3\lambda^2} = \frac{3\lambda^2 - 16\pi^2 R_g^2 \sin^2(\frac{1}{2}\theta)}{3\lambda^2}.$$

The radius of gyration of a rod of length l is

$$R_{\text{rod}} = l/[2(3)^{1/2}].$$

For a closed circle, the radius of gyration, which is the rms distance from the center of mass, is simply the radius of a circle whose circumference is l :

$$l = 2\pi R_{\text{cc}} \quad \text{so} \quad R_{\text{cc}} = \frac{l}{2\pi}.$$

The intensity ratio is:

$$\frac{I_{\text{rod}}}{I_{\text{cc}}} = \frac{3\lambda^2 - \frac{4}{3}\pi^2 l^2 \sin^2(\frac{1}{2}\theta)}{3\lambda^2 - 4l^2 \sin^2(\frac{1}{2}\theta)}.$$

Putting the numbers in yields:

$\theta/^\circ$	20	45	90
$I_{\text{rod}}/I_{\text{cc}}$	0.976	0.876	0.514

- (b) I would work at a detection angle at which the ratio is smallest, *i.e.*, most different from unity, provided I had sufficient intensity to make accurate measurements. Of the angles considered in part a, 90° is the best choice. With the help of a spreadsheet or symbolic mathematical program, the ratio can be computed for a large range of scattering angles and plotted:

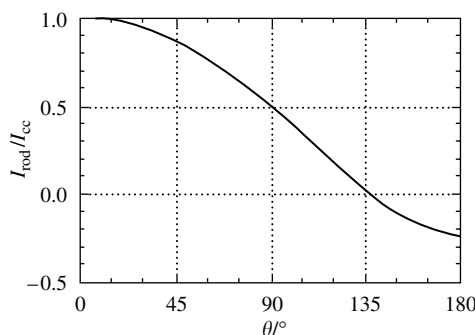


Figure 22.4

A look at the results of such a calculation shows that both the intensity ratio and the intensities themselves decrease with increasing scattering angle from 0° through 180° , that of the closed circle conformation changing much more slowly than that of the rod. Note: the approximation used above yields negative numbers for P_{rod} at large scattering angles; this is because the approximation, which depends on the molecule being much smaller than the wavelength, is shaky at best, particularly at large angles.

- P22.22** $\ln c = \text{const.} + \frac{\overline{M}_w b \omega^2 r^2}{2RT}$ [22.42, rearranged] and a plot of $\ln c$ against r^2 should be a straight line of slope $\frac{\overline{M}_w b}{RT}$. We draw up the following table

r/cm	5.0	5.1	5.2	5.3	5.4
$c/(\text{mg cm}^{-3})$	0.536	0.284	0.148	0.077	0.039
$r^2/(\text{cm}^2)$	25.0	26.0	27.0	28.1	29.2
$\ln(c/\text{mg cm}^{-3})$	-0.624	-1.259	-1.911	-2.564	-3.244

The points are plotted in Fig. 22.5. The least-squares slope is -0.623 . Therefore

$$\frac{\overline{M}_w(1 - \rho v_s)\omega^2}{2RT} = -0.623 \text{ cm}^{-2} = -0.623 \times 10^4 \text{ m}^{-2}$$

It follows that

$$\overline{M}_w = \frac{(-0.623 \times 10^4 \text{ m}^{-2}) \times (2) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})}{\{(1) - (1.001 \text{ g cm}^{-3}) \times (1.112 \text{ cm}^3 \text{ g}^{-1})\} \times [(2\pi) \times (322 \text{ s}^{-1})]^2} = \boxed{65.6 \text{ kg mol}^{-1}}$$

- P22.24** The sedimentation constant S must first be calculated from the experimental data.

$$S = \frac{s}{r\omega^2} [11] = \frac{1}{\omega^2} \frac{d \ln r}{dt} \text{ [Problem 22.2]}$$

Therefore, a plot of $\ln r$ against t will give S . We draw up the following table

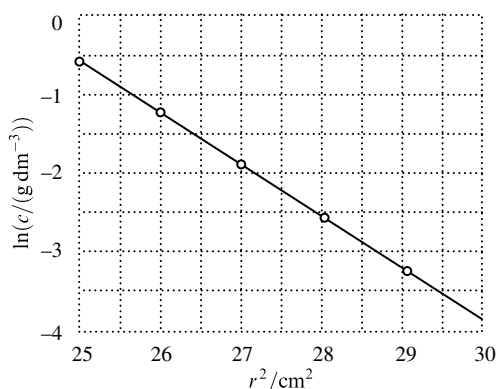


Figure 22.5

t/s	0	300	600	900	1200	1500	1800
r/cm	6.127	6.153	6.179	6.206	6.232	6.258	6.284
$\ln(r/\text{cm})$	1.813	1.817	1.821	1.826	1.830	1.834	1.838

The least-squares slope is $1.408 \times 10^{-5} \text{ s}^{-1}$, so

$$S = \frac{1.408 \times 10^{-5} \text{ s}^{-1}}{[(2\pi) \times (50 \times 10^3/60 \text{ s})]^2} = 5.14 \times 10^{-13} \text{ s} = \boxed{5.14 \text{ Sv}}$$

$$\text{Then } \bar{M}_n = \frac{SRT}{bD} [22.41] = \frac{(5.14 \times 10^{-13} \text{ s}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})}{(1 - 0.9981 \times 0.728) \times (7.62 \times 10^{-11} \text{ m}^2 \text{ s})^2} = \boxed{60.1 \text{ kg mol}^{-1}}$$

We need to determine the ratio of the actual frictional coefficient, f , of the macromolecule to that of the frictional coefficient, f_0 , of a sphere of the same volume, so that by interpolating in Table 23.1 we can obtain the dimensions of the molecular ellipsoid.

$$f = \frac{kT}{D} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (293 \text{ K})}{7.62 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}} = 5.31 \times 10^{-11} \text{ kg s}^{-1}$$

$$V_m = (0.728 \text{ cm}^3 \text{ g}^{-1}) \times (60.1 \times 10^3 \text{ g mol}^{-1}) = 43.8 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \\ = 4.38 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$$

$$\text{Then, } a = \left(\frac{3 V_m}{4\pi N_A} \right)^{1/3} = \left(\frac{(3) \times (4.38 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1})}{(4\pi) \times (6.022 \times 10^{23} \text{ mol}^{-1})} \right)^{1/3} = 2.59 \text{ nm}$$

$$f_0 = 6\pi a\eta = (6\pi) \times (2.59 \times 10^{-9} \text{ m}) \times (1.00 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) = 4.89 \times 10^{-11} \text{ kg s}^{-1}$$

$$\text{which gives } \frac{f}{f_0} = \frac{5.31}{4.89} = 1.09$$

Therefore, the molecule is either prolate or oblate, with an axial ratio of about 2.8 (Table 22.3).

P22.25

The peaks are separated by 104 g mol^{-1} , so this is the molar mass of the repeating unit of the polymer. This peak separation is consistent with the identification of the polymer as polystyrene, for the repeating group of $\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)$ (8 C atoms and 8 H atoms) has a molar mass of $8 \times (12 + 1) \text{ g mol}^{-1} = 104 \text{ g mol}^{-1}$. A consistent difference between peaks suggests a pure system

and against different numbers of subunits (of different molecular weight) being incorporated into the polymer molecules. The most intense peak has a molar mass equal to that of n repeating groups plus that of a silver cation plus that of terminal groups:

$$M(\text{peak}) = nM(\text{repeat}) + M(\text{Ag}^+) + M(\text{terminal}).$$

If the both ends of the polymer have terminal t -butyl groups, then

$$M(\text{terminal}) = 2M(t\text{-butyl}) = 2(4 \times 12 + 9) \text{ g mol}^{-1} = 114 \text{ g mol}^{-1},$$

$$\text{and } n = \frac{M(\text{peak}) - M(\text{Ag}^+) - M(\text{terminal})}{M(\text{repeat})} = \frac{25578 - 108 - 114}{104} = 243.8.$$

Obviously this is not an integer. Revisit the assumption of two t -butyl groups on the ends:

$$M(\text{terminal}) = M(\text{peak}) - nM(\text{repeat}) - M(\text{Ag}^+).$$

If $n = 243$, then

$$M(\text{terminal}) = (25578 - 243 \times 104 - 108) \text{ g mol}^{-1} = 198 \text{ g mol}^{-1},$$

which does not correspond to a whole number of t -butyl groups! Try again, supposing this time that there is a single t -butyl group at one end and a hydrogen atom at the other. Then:

$$n = \frac{M(\text{peak}) - M(\text{Ag}^+) - M(\text{terminal})}{M(\text{repeat})} = \frac{25578 - 108 - 58}{104} = 244.3.$$

This is not an integer either. If $n = 244$, then

$$M(\text{terminal}) = (25578 - 244 \times 104 - 108) \text{ g mol}^{-1} = 94 \text{ g mol}^{-1},$$

not a whole number of butyl or butane groups.

P22.26

$$(a) \quad \frac{\eta}{\eta^*} = 1 + [\eta]c + k'[\eta]^2c^2 = \frac{t}{t^*}$$

$$\text{or } F = \frac{t/t^* - 1}{c} = [\eta] + k'[\eta]^2c$$

A linear regression of F against c yields an intercept equal to $[\eta]$ and a slope equal to $k'[\eta]^2$.

(1) *In toluene*: Linear regression ($R = 0.99954$) yields

$$[\eta] = 0.08566 \text{ L g}^{-1} = \boxed{0.086 \text{ L g}^{-1}}; \quad \text{standard deviation} = 0.00020 \text{ L g}^{-1}$$

$$k'[\eta]^2 = 0.002688 \text{ L}^2 \text{ g}^{-2}; \quad \text{standard deviation} = 0.000057 \text{ L}^2 \text{ g}^{-2}$$

Then

$$k' = \frac{0.002688 \text{ L}^2 \text{ g}^{-2}}{(0.08566 \text{ L g}^{-1})^2} = \boxed{0.37}$$

(2) *In cyclohexane*: Linear regression ($R = 0.98198$) yields

$$[\eta] = 0.04150 \text{ L g}^{-1} = \boxed{0.042 \text{ L g}^{-1}}; \quad \text{standard deviation} = 0.00018 \text{ L g}^{-1}$$

$$k'[\eta]^2 = 0.0006001 \text{ L}^2 \text{ g}^{-2}; \quad \text{standard deviation} = 0.000116 \text{ L}^2 \text{ g}^{-2}$$

Then

$$k' = \frac{0.000\ 600\overline{1}\ \text{L}^2\ \text{g}^{-2}}{(0.041\ 50\ \text{L g}^{-1})^2} = \boxed{0.35}$$

(b) $[\eta] = K \overline{M}_v^a$ or $\overline{M}_v = \left(\frac{[\eta]}{K}\right)^{1/a}$

(1) *In toluene*

$$\overline{M}_v = \left(\frac{0.085\ 66\ \text{L g}^{-1}}{1.15 \times 10^{-5}\ \text{L g}^{-1}}\right)^{(1/0.72)}\ \text{g mol}^{-1} = \boxed{2.4 \times 10^5\ \text{g mol}^{-1}}$$

(2) *In cyclohexane*

$$\overline{M}_v = \left(\frac{0.041\ 50\ \text{L g}^{-1}}{8.2 \times 10^{-5}\ \text{L g}^{-1}}\right)^{(\frac{1}{1/2})}\ \text{g mol}^{-1} = \boxed{2.6 \times 10^5\ \text{g mol}^{-1}}$$

(c) $[\eta]/(\text{L g}^{-1}) = \Phi (r_{\text{rms}}/\text{m})^3/M$, $\Phi = 2.84 \times 10^{26}$

$$r_{\text{rms}} = \left(\frac{[\eta]M}{\Phi}\right)^{1/3}\ \text{m}, \quad \text{where } r_{\text{rms}} = \langle r^2 \rangle^{1/2}$$

(1) *In toluene:* $r_{\text{rms}} = \left(\frac{0.085\overline{66} \times 2.39 \times 10^5}{2.84 \times 10^{26}}\right)^{1/3}\ \text{m} = \boxed{42\ \text{nm}}$

(2) *In cyclohexane:* $r_{\text{rms}} = \left(\frac{0.041\overline{50} \times 2.56 \times 10^5}{2.84 \times 10^{26}}\right)^{1/3}\ \text{m} = \boxed{33\ \text{nm}}$

(d) $M(\text{styrene}) = 104\ \text{g mol}^{-1}$
average number of monomeric units, $\langle n \rangle$ is

$$\langle n \rangle = \frac{\overline{M}_v}{M(\text{styrene})}$$

(1) *In toluene*

$$\langle n \rangle = \frac{2.39 \times 10^5\ \text{g mol}^{-1}}{104\ \text{g mol}^{-1}} = \boxed{2.3 \times 10^3}$$

(2) *In cyclohexane*

$$\langle n \rangle = \frac{2.56 \times 10^5\ \text{g mol}^{-1}}{104\ \text{g mol}^{-1}} = \boxed{2.5 \times 10^3}$$

(e) Consider the geometry in Fig. 22.6.

For a polymer molecule consisting of $\langle n \rangle$ monomers, the maximum molecular length, L_{max} , is

$$\begin{aligned} L_{\text{max}} &= 2l \langle n \rangle \cos \theta \\ &= 2(0.154\ \text{nm}) \langle n \rangle \cos 35^\circ \\ &= (0.2507\ \text{nm}) \langle n \rangle \end{aligned}$$

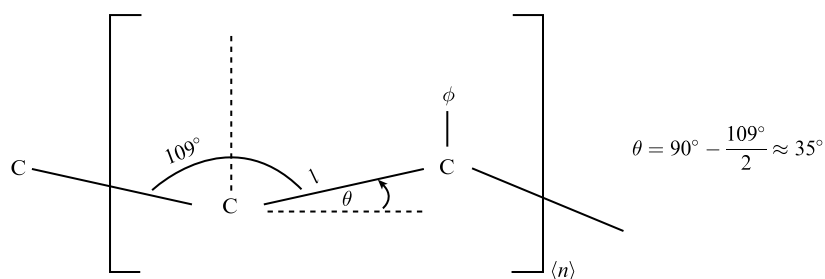


Figure 22.6

$$(1) \text{ In toluene: } L_{\max} = (0.2507 \text{ nm}) \times (2.30 \times 10^3) = \boxed{5.8 \times 10^2 \text{ nm}}$$

$$(2) \text{ In cyclohexane: } L_{\max} = (0.2507 \text{ nm}) \times (2.46 \times 10^3) = \boxed{6.2 \times 10^2 \text{ nm}}$$

$$(f) \quad R_g = \left(\frac{\langle n \rangle}{3}\right)^{1/2} l = (0.0889 \text{ nm}) \langle n \rangle^{1/2}$$

$$\text{Kirkwood-Riseman: } r_{\text{rms}}^{\text{KR}} = \left(\frac{[\eta]M}{\Phi}\right)^{1/3} = \left(\frac{[\eta]M}{2.84 \times 10^{26}}\right)^{1/3}$$

$$r_{\text{rms}} = (2\langle n \rangle)^{1/2} l [39] \quad \text{or} \quad \langle n \rangle^{1/2} l$$

Solvent	$\langle n \rangle$	R_g / nm	$r_{\text{rms}}^{\text{KR}} / \text{nm}$	$r_{\text{rms}} / \text{nm}$
Toluene	2.30×10^3	$\boxed{4.3}$	42	$\boxed{10.4 \text{ or } 7.4}$
Cyclohexane	2.46×10^3	$\boxed{4.4}$	33	$\boxed{10.8 \text{ or } 7.6}$

- (g) There is no reason for them to agree; they are different samples; there is no fixed value of M for polystyrene. The manufacturer's claim appears to be valid.