Montogue

Quiz MST03
Reviewed Solutions to *Polymer Science and Technology*, 3rd Ed., by J.R. Fried
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PROBLEM DISTRIBUTION

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PROBLEMS

■ Chapter 1 – Introduction to Polymer Science

Problem 1.1

A polymer sample combines five different molecular-weight fractions of equal weight. The molecular weights of these fractions increase from 20,000 to 100,000 in increments of 20,000. Calculate the number-average molecular weight $\bar{M}_n$, the weight-average molecular weight $\bar{M}_w$, and the z-average molecular weight $\bar{M}_z$. Based upon these results, comment on whether this sample has a broad or narrow molecular-weight distribution compared to typical commercial polymer samples.

Problem 1.2

A 50-g polymer sample was fractioned into six samples of different weights given in the table below. The viscosity-average molecular weight, $\bar{M}_v$, of each was determined and is included in the table. Estimate the number-average and weight-average molecular weights of the original sample. For these calculations, assume that the molecular-weight distribution of each fraction is extremely narrow and can be considered to be *monodisperse*. Would you classify the molecular-weight distribution of the original sample as narrow or broad?

Fraction	Weight (g)	$\bar{M}_v$
1	1.0	1500
2	5.0	35,000
3	21.0	75,000
4	15.0	150,000
5	6.5	400,000
6	1.5	850,000

Problem 1.4

The following requested calculations refer to Examples 1.1, 1.2, and 1.3 in the text:

(a) Calculate the z-average molecular weight, $\bar{M}_z$, of the discrete molecular weight distribution described in Example 1.1.

(b) Calculate the z-average molecular weight, $\bar{M}_z$, of the continuous molecular weight distribution shown in Example 1.2.

(c) Obtain an expression for the z-average degree of polymerization, $\bar{X}_z$, for the Flory distribution described in Example 1.3.

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■ Chapter 2 – Polymer Synthesis

Problem 2.1

If the half-life time, $t_{1/2}$, of the initiator AIBN in an unknown solvent is 22.6 h at 60°C, calculate its dissociation rate constant, k_d, in units of reciprocal seconds.

Problem 2.2

Styrene is polymerized by free-radical mechanism in solution. The initial monomer and initiator concentrations are 1 M (molar) and 0.001 M, respectively. At the polymerization temperature of 60°C, the initiator efficiency is 0.30. The rate constants at the polymerization temperature are as follows:

Dissociation rate constant, k_d = 1.2×10^{-5} s^{-1}
Propagation rate constant, k_p = 176 M^{-1}s^{-1}
Termination rate constant, k_t = 7.2×10^7 M^{-1}s^{-1}

Given this information, determine the following:
(a) Rate of initiation at 1 min and at 16.6 h.
(b) Steady-state free-radical concentration at 1 min.
(c) Rate of polymerization at 1 min.
(d) Average free-radical lifetime, τ, at 1 min, where τ is defined as the radical concentration by the rate of termination.
(e) Number-average degree of polymerization at 1 min.

Problem 2.5

If the number-average degree of polymerization for polystyrene obtained by the bulk polymerization of styrene at 60°C is 1000, what would be the number-average degree of polymerization if the polymerization were conducted in a 10% solution in toluene (900 g of toluene per 100 g of styrene) under otherwise identical conditions? The molecular weights of styrene and toluene are 104.12 and 92.15, respectively. State any assumptions that are needed.

Problem 2.6

Assume that a polyesterification is conducted in the absence of solvent or catalyst and that the monomers are present in stoichiometric ratios. Calculate the time (min) required to obtain a number-average degree of polymerization of 50 given that the initial dicarboxylic acid concentration is 3 mol L^{-1} and that the polymerization rate constant is 10^{-2} L mol^{-1} s^{-1}.

Problem 2.9

Find the azeotropic composition for the free-radical copolymerization of styrene and acrylonitrile.

■ Chapter 3 – Conformation, Solutions, and Molecular Weight

Problem 3.3

(a) What is the osmotic pressure (units of atm) of a 0.5 wt% solution of poly(methylmethacrylate) ($\bar{M}$ = 100,000) in acetonitrile (density, 0.7857 g·cm^{-3}) at 45°C for which $[\eta]$ = 4.8×10^{-3} M$^{0.5}$?
(b) What is the osmotic head in units of cm?
(c) Estimate the Flory interaction parameter for polysulfone in methylene chloride.
(d) Based upon your answer above, would you expect methylene chloride to be a good or poor solvent for polysulfone?

Problem 3.5

The following viscosity data were obtained for solutions of polystyrene (PS) in toluene at 30°C.

c (g·dL^{-1})	t (s)
0	65.8
0.54	101.2
1.08	144.3
1.62	194.6
2.16	257.0

Using this information:
(a) Plot the reduced viscosity as a function of concentration.
(b) Determine the intrinsic viscosity and the value of the Huggins constant, k_H.
(c) Calculate the molecular weight of PS using Mark-Houwink parameters of a = 0.725 and K = 1.1×10^{-4} dL g^{-1}.

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Problem 3.7

The use of universal calibration curves in GPC is based upon the principle that the product $[\eta]M$, the hydrodynamic volume, is the same for all polymers at equal elution volumes. If the retention volume for a monodisperse polystyrene (PS) sample of 50,000 molecular weight is 100 mL in toluene at 25°C, what is the molecular weight of a fraction of poly(methyl methacrylate) (PMMA) at the same elution volume in toluene at 25°C? The Mark-Houwink parameters, K and a, for PS are given as 7.54×10^{-3} mL·g^{-1} and 0.783, respectively; the corresponding values for PMMA are 8.12×10^{-3} mL·g^{-1} and 0.71.

Problem 3.9

The (reduced or excess) Rayleigh ratio (R_θ) of cellulose acetate (CA) in dioxane was determined as a function of concentration by low-angle laser light-scattering measurements. Data are given in the following table. If the refractive index (n_o) of dioxane is 1.4199, the refractive-index increment (dn/dc) for CA in dioxane is 6.297×10^{-2} cm^{3}g^{-1}, and the wavelength λ of the light is 6328 Å, calculate the weight-average molecular weight of CA and the second virial coefficient (A_2).

$c \times 10^3$ (g·mL^{-1})	$R(\theta)$ (cm^{-1})
0.5034	0.239
1.0068	0.440
1.5102	0.606
2.0136	0.790
2.517	0.902

■ Chapter 4 – Solid-State Properties

Problem 4.2

A tensile strip of polystyrene that is 10 cm in length, 5 cm in width, and 2 cm in thickness is stretched to a length of 10.5 cm. Assuming that the sample is isotropic and deforms uniformly, calculate the resulting width and the percent volume change after deformation.

Problem 4.3

A polymer has a crystalline growth parameter (n) of 2 and a rate constant (k) of 10^{-2} s^{-2} at 100°C. The polymer is melted and then quenched to 100°C and allowed to crystallize isothermally. After 10 s, what is the percent crystallinity of the sample?

Problem 4.4

What is the % volume change that is expected at 100% elongation of natural rubber, assuming that no crystallization occurs during deformation?

Problem 4.7

Polytetrafluoroethylene has been reported to exhibit a negative Poisson ratio. Explain why this polymer exhibits this unusual behavior.

Problem 4.8

A sample of poly(ethylene terephthalate) is reported to be 20% crystalline.
(a) What is the expected density of this sample?
(b) What is the expected specific heat increment of this semicrystalline sample?
(c) What is the expected heat of fusion of this sample?

Problem 4.9

Twenty wt% of a styrene oligomer having a number-average degree of polymerization of 7 is mixed with a commercial polystyrene sample having a number-average molecular weight of 100,000.
(a) What is the T_g(K) of the styrene oligomer?
(b) What is the T_g(K) of the polystyrerene mixture?

Problem 4.10

The 1% secant modulus of a polystyrene sample is 3 GPa.
(a) What is the nominal stress (MPa) of this sample at a nominal strain of 0.01?
(b) What is the true stress (MPa) of this sample at a nominal strain of 0.01?
(c) What is the percent change in volume of this sample at the nominal strain of 0.01?

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■ Chapter 5 – Viscoelasticity and Rubber Elasticity

Problem 5.1

Show that $|E^*| = \sigma^o/\varepsilon^o$ and $|D^*| = 1/E^*$.

Problem 5.2

Show that the work per cycle per unit volume during dynamic tensile oscillation of a viscoelastic solid may be given as $\pi\sigma^o\varepsilon^o \sin \delta$ (eq. (5.30)).

Problem 5.8

If the maximum in the α-loss modulus of polystyrene at 1 Hz occurs at 373 K, at what temperature would the maximum occur at 110 Hz if the activation energy for this relaxation is 840 kJ·mol^{-1}?

Problem 5.9

(a) Calculate the relaxation modulus, in SI units of GPa, at 10 seconds after a stress has been applied to three Maxwell elements linked in parallel using the following model parameters:

$E_1 = 0.1$ GPa; $\tau_1 = 10$ s
$E_2 = 1.0$ GPa; $\tau_2 = 20$ s
$E_3 = 10$ GPa; $\tau_3 = 30$ s

(b) Does this model give a realistic representation of stress relaxation behavior of a real polymer? Explain.

Problem 5.10

An elastomeric cube, 2 cm on a side, is compressed to 95% of its original length by applying a mass of 5 kg. What force is required to stretch a strip of the same elastomer by 50%? The initial length of the strip is 2 cm and its original cross-sectional area is 1 cm^2.

Problem 5.11

If the stress at 23°C of an ideal rubber is 100 psi when stretched to twice its original length, what would be the stress at a 50% extension?

Problem 5.12

The length of an ideal rubber band is increased 100% to 12.0 cm at 23°C. Stress on this rubber band increases by 0.2 MPa when it is heated to 30°C at 100% elongation. What is its tensile modulus in MPa at 23°C when it is stretched 2%?

■ Chapter 11 – Polymer Processing and Rheology

Problem 11.1

Poly(vinyl acetate) (PVAc) is extruded at 180°C at constant temperature through capillary rheometer having a ram (reservoir) diameter of 0.375 in. and a capillary with an inside diameter of 0.041 in. and length of 0.622 in. The data provided give the efflux time to extrude 0.0737 in.^{3} at different ram loads. Using the following data:

Ram load (lb$_f$)	Efflux time (min)
97.5	5.32
145	1.58
217	0.31
250	0.17

(a) Determine the power-law parameters n and m for PVAc and state all assumptions used to obtain your results.
**(b)** Plot the apparent viscosity, η, in units of Pa·s versus the nominal shear rate at the wall, $\dot{\gamma}_w$ (s^{-1}), using logarithmic coordinates.

Problem 11.2

Plot the dimensionless velocity profile for polystyrene flowing in a capillary at 483 K.

Problem 11.3

As illustrated, two capillaries of identical length are connected to the same liquid reservoir in which a power-law fluid is held. The tubes differ in radii by a factor of 2. When a pressure is applied to the reservoir, the volumetric flow rates from the two tubes differ by a factor of 40. What is the value of exponent n? How different are the nominal shear rates in the two cases?

Reservoir

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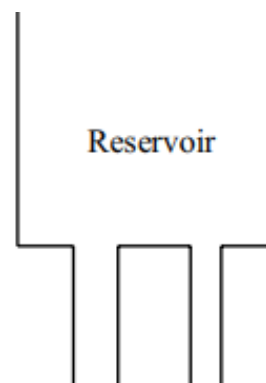
Problem 11.4

Molten polystyrene flows through a circular tube at 210°C under a pressure drop of 1000 psi. Given that the inside diameter of the tube is 0.25 in. and that the tube is 3 in. in length, calculate the following:

(a) The (nominal) shear stress at the wall in units of N m^{-2}.
(b) The (nominal) shear rate at the wall in s^{-1}.
(c) The volumetric flow rate in cm^3·s^{-1}.
Assume that flow is isothermal, steady, and fully developed.

Problem 11.5

(a) Given that tensile (Trouton's) viscosity is defined as

$$\eta_T = \frac{\sigma}{\dot{\varepsilon}}$$

where σ and ε are the *true* tensile stress and *true* strain, respectively, show that

$$\ln(L) = \left(\frac{1}{\eta_T}\right)\sigma t + \ln(L_0)$$

when viscosity is independent of $\dot{\varepsilon}$ and L_0 is the *initial* length of the sample.
(b) A strip of polyisobutylene (800,000 molecular weight) is subjected to a fixed tensile load at ambient conditions. Initially, the sample is 0.699 cm wide, 6.0 cm long, and 0.155 cm thick. The strip is hung vertically and a mass of 75 g is attached to the bottom of the strip. The sample length is then recorded as a function of time with the following measurements:

Time (min)	1	2	3	6	12	15	18	21	24
Length (cm)	6.90	7.00	7.10	7.25	7.48	7.60	7.69	7.79	7.90

Plot the data given in the form of $ln(L)$ versus σt and determine the value of tensile viscosity η_T in SI units. Comment on the probable phenomenological significance of the plot obtained by extrapolating the linear portion of the data.

SOLUTIONS

■ P1.1

The calculations are tabulated below.

Fraction No.	M_i	W_i	$N_i = W_i/M_i$
1	2.00E+04	1	5.000E-05
2	4.00E+04	1	2.500E-05
3	6.00E+04	1	1.667E-05
4	8.00E+04	1	1.250E-05
5	1.00E+05	1	1.000E-05
Total	3.00E+05	5	1.142E-04

To compute the number-average molecular weight, we write

$$\bar{M}_n = \frac{\sum\limits_{i=1}^{5} W_i}{\sum\limits_{i=1}^{5} N_i} = \frac{5}{1.142 \times 10^{-4}} = \boxed{43,800}$$

To compute the weight-average molecular weight, we write

$$\bar{M}_n = \frac{\sum\limits_{i=1}^{5} W_i M_i}{\sum\limits_{i=1}^{5} W_i} = \frac{300,000}{5} = \boxed{60,000}$$

To compute the *z*-average molecular weight, we write

$$\bar{M}_z = \frac{\sum\limits_{i=1}^{5} W_i M_i^2}{\sum\limits_{i=1}^{5} W_i M_i} = \frac{\left[\begin{array}{c} 1 \times 20,000^2 + 1 \times 40,000^2 + 1 \times 60,000^2 \\ +1 \times 80,000^2 + 1 \times 100,000^2 \end{array}\right]}{300,000} = \boxed{73,300}$$

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The polydispersity index is

$$PDI = \frac{\overline{M}_w}{\overline{M}_n} = \frac{60,000}{43,800} = 1.37$$

which indicates a fairly narrow distribution.

■ P1.2

The key here is to assume that $M_i \approx M_v$. The pertaining calculations are listed below.

Fraction	W_i (g)	$\overline{M}_i$	$N_i = W_i / \overline{M}_i$	$W_i \overline{M}_i$
1	1.0	1500	6.667E-04	1500
2	5	35000	1.429E-04	175000
3	21	75000	2.800E-04	1575000
4	15	150000	1.000E-04	2250000
5	6.5	400000	1.625E-05	2600000
6	1.5	850000	1.765E-06	1275000
Total	50.0		1.208E-03	7.877E+06

The number-average molecular weight is calculated as

$$\overline{M}_n = \frac{\displaystyle\sum_{i=1}^{6} W_i}{\displaystyle\sum_{i=1}^{6} N_i} = \frac{50}{1.208 \times 10^{-3}} = \boxed{41,400}$$

In turn, the weight-average molecular weight is

$$\overline{M}_w = \frac{\displaystyle\sum_{i=1}^{6} W_i M_i}{\displaystyle\sum_{i=1}^{6} W_i} = \frac{7.877 \times 10^6}{50} = \boxed{158,000}$$

The polydispersity index is

$$PDI = \frac{\overline{M}_w}{\overline{M}_n} = \frac{158,000}{41,400} = 3.82$$

Since the *PDI* is substantially greater than 1, we surmise that the polymer sample has a broad molecular weight distribution.

■ P1.4

Part (a): The polystyrene sample introduced in Example 1.1 had the following molecular weight distribution.
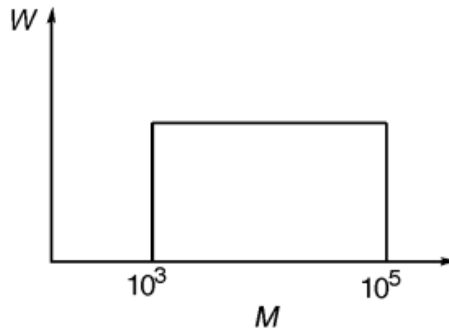
Mass	Molecular Wt.
1 g	10,000
2 g	50,000
2 g	100,000

The *z*-average molecular weight is given by equation (1.1) with $\alpha = 3$:

$$\overline{M}_z = \frac{\displaystyle\sum_{i=1}^{3} W_i M_i^2}{\displaystyle\sum_{i=1}^{3} W_i M_i}$$

$$\therefore \overline{M}_z = \frac{1 \times 10,000^2 + 2 \times 50,000^2 + 2 \times 100,000^2}{1 \times 10,000 + 2 \times 50,000 + 2 \times 100,000} = \boxed{81,000}$$

Part (b): The polymer sample introduced in Example 1.2 had the continuous molecular weight distribution illustrated on the next page.

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To find the *z*-average molecular weight, we evaluate the ratio of integrals

$$\bar{M}_z = \frac{\displaystyle\int_{10^3}^{10^5} M^2 dM}{\displaystyle\int_{10^3}^{10^5} M dM} = \frac{\left[M^3/3 \right]_{10^3}^{10^5}}{\left[M^2/2 \right]_{10^3}^{10^5}} = \frac{\frac{1}{3}\left[\left(10^5\right)^3 - \left(10^3\right)^3 \right]}{\frac{1}{2}\left[\left(10^5\right)^2 - \left(10^3\right)^2 \right]}$$

$$\therefore \boxed{\bar{M}_z = 66{,}670}$$

Part (c): The *z*-average degree of polymerization for a Flory-Schulz distribution is given by the following ratio, which is analogous to equation (1.1) for discrete molecular weight distributions,

$$\bar{X}_z = \frac{\displaystyle\sum_1^\infty X^2 W(X)}{\displaystyle\sum_1^\infty XW(X)} = \frac{\displaystyle\sum_{X=1}^\infty X^3 p^{X-1}}{\displaystyle\sum_{X=1}^\infty X^2 p^{X-1}} \quad (I)$$

Using Mathematica, it can be shown that the denominator is such that

In[533]:= **Sum$\left[X^2 * p^{X-1}, \{X, 1, \infty\} \right]$**

Out[533]= $-\dfrac{1 + p}{(-1 + p)^3}$

$$\therefore \sum_{X=1}^\infty X^2 p^{X-1} = -\frac{1+p}{\left(-1+p\right)^3} = \frac{1+p}{\left(1-p\right)^3}$$

Similarly, the numerator is

In[534]:= **Sum$\left[X^3 * p^{X-1}, \{X, 1, \infty\} \right]$**

Out[534]= $\dfrac{1 + 4p + p^2}{(-1 + p)^4}$

$$\therefore \sum_{X=1}^\infty X^3 p^{X-1} = \frac{1+4p+p^2}{\left(-1+p\right)^4} = \frac{1+4p+p^2}{\left(1-p\right)^4}$$

Substituting in (I) and simplifying,

$$\bar{X}_z = \frac{\displaystyle\sum_{X=1}^\infty X^3 p^{X-1}}{\displaystyle\sum_{X=1}^\infty X^2 p^{X-1}} = \frac{1+4p+p^2}{\left(1-p\right)^4} \times \frac{\left(1-p\right)^3}{1+p}$$

$$\therefore \bar{X}_z = \frac{1+4p+p^2}{\left(1-p\right)\left(1+p\right)}$$

$$\therefore \bar{X}_z = \frac{1+4p+p^2}{1^2 - p^2}$$

$$\therefore \boxed{\bar{X}_z = \frac{1+4p+p^2}{1-p^2}}$$

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■ P2.1

The concentration of AIBN varies according to the exponential law

$$[I] = [I]_0 \exp(-k_d t)$$

Setting $[I]/[I]_0$ and solving for dissociation constant k_d, we obtain

$$[I] = [I]_0 \exp(-k_d t) \;\rightarrow\; \frac{[I]}{[I]_0} = \exp(-k_d t)$$

$$\therefore \frac{1}{2} = \exp\left(-k_d t_{1/2}\right)$$

$$\therefore \ln\left(\frac{1}{2}\right) = -k_d t_{1/2}$$

$$\therefore -0.693 = -k_d t_{1/2}$$

$$\therefore 0.693 = k_d t_{1/2}$$

$$\therefore k_d = \frac{0.693}{t_{1/2}} = \frac{0.693}{22.6 \times 3600} = \boxed{8.52 \times 10^{-6} \; \text{s}^{-1}}$$

■ P2.2

Part (a): Firstly, we write the rate of initiation as given by equation (2.21),

$$R_i = 2 f k_d [I] = 2 \times 0.30 \times \left(1.2 \times 10^{-5}\right)[I] = 7.2 \times 10^{-6}[I] \quad (I)$$

At 1 min., the concentration of initiator is

$$[I] = [I_0] \exp(-k_d t) = 0.001 \times \exp\left[\left(-1.2 \times 10^{-5}\right) \times 60\right]$$

$$\therefore [I] = 0.00099928 \text{ M}$$

so that, substituting in (I),

$$R_i = \left(7.2 \times 10^{-6}\right) \times 0.00099928 = \boxed{7.195 \times 10^{-9} \; \text{M} \cdot \text{s}^{-1}}$$

Similarly, the concentration of initiator at $t = 16.6$ h is

$$[I] = [I_0] \exp(-k_d t) = 0.001 \times \exp\left[\left(-1.2 \times 10^{-5}\right) \times (16.6 \times 3600)\right]$$

$$\therefore [I] = 0.00048816 \text{ M}$$

so that, substituting in (I),

$$R_i = \left(7.2 \times 10^{-6}\right) \times 0.00048816 = \boxed{3.515 \times 10^{-9} \; \text{M} \cdot \text{s}^{-1}}$$

Part (b): The free-radical concentration in question is given by equation (2.24):

$$[\text{IM}_x] = \left(\frac{f k_d}{k_t}\right)^{\frac{1}{2}} [I]^{1/2} = \left[\frac{0.3 \times \left(1.2 \times 10^{-5}\right)}{\left(7.2 \times 10^7\right)}\right]^{\frac{1}{2}} \times 0.00099928^{\frac{1}{2}} = \boxed{7.069 \times 10^{-9} \; \text{M}}$$

Part (c): The rate of chain propagation is given by equation (2.18),

$$R_o = k_p [\text{IM}_x \cdot][\text{M}] \quad (II)$$

where the monomer concentration [M] after 1 min is determined as

$$[M] = [M]_0 \exp\left(-k_p [\text{IM}_x \cdot] t\right) = 1.0 \times \exp\left[-176 \times \left(7.069 \times 10^{-9}\right) \times 60\right]$$

$$\therefore [M] = 0.999925 \text{ M}$$

so that, substituting in (II),

$$R_o = 176 \times \left(7.069 \times 10^{-9}\right) \times 0.999925 = \boxed{1.244 \times 10^{-6} \; \text{M} \cdot \text{s}^{-1}}$$

Part (d): The rate of termination is given by (2.23). Therefore, the average free-radical lifetime τ may be written as

$$\tau = \frac{[\mathrm{IM}_x \cdot]}{R_t} = \frac{[\mathrm{IM}_x \cdot]}{2k_t [\mathrm{IM}_x \cdot]^2} = \frac{1}{2k_t [\mathrm{IM}_x \cdot]}$$

$$\therefore \tau = \frac{1}{2 \times (7.2 \times 10^7) \times (7.069 \times 10^{-9})} = 0.982 \text{ s} = \boxed{982 \text{ ms}}$$

Part (e): The N-A average degree of polymerization can be obtained by taking the ratio of the rate of polymerization, which we've calculated in part (c), and the rate of termination, which is given by equation (2.23):

$$\bar{X}_n = \frac{R_p}{R_t} = \frac{R_p}{2k_t [\mathrm{IM}_x \cdot]^2} = \frac{1.244 \times 10^{-6}}{2 \times (7.2 \times 10^7) \times (7.07 \times 10^{-9})^2} = \boxed{173}$$

■ P2.5
With reference to Table 2.4, we read a chain-transfer constant $C = 0.125 \times 10^{-4}$ for styrene monomer with toluene as the chain-transfer agent. Accordingly,

$$[\mathrm{M}] = \frac{100}{104.12} = 0.9604$$

The concentration of chain-transfer agent (toluene) is

$$[\mathrm{SH}] = \frac{900}{92.15} = 9.767$$

Further, the initial degree of polymerization is $(\bar{X}_n)_0 = 1000$. Using equation (2.30), we find that

$$\frac{1}{\bar{X}_n} = \frac{1}{(\bar{X}_n)_0} + C \frac{[\mathrm{SH}]}{[\mathrm{M}]}$$

$$\therefore \frac{1}{\bar{X}_n} = \frac{1}{1000} + (0.125 \times 10^{-4}) \times \frac{9.767}{0.9604} = 1.127 \times 10^{-3}$$

$$\therefore \bar{X}_n = (1.127 \times 10^{-3})^{-1} = \boxed{887.3}$$

■ P2.6
The kinetic equation to use in this case is (2.9), namely

$$\bar{X}_n = [A - A]_0 kt + 1$$

Solving for time,

$$\bar{X}_n = [A - A]_0 kt + 1 \quad \rightarrow \quad t = \frac{\bar{X}_n - 1}{[A - A]_0 k}$$

$$\therefore t = \frac{50 - 1}{3 \times 10^{-2}} = 1630 \text{ s} = \boxed{27.2 \text{ min}}$$

■ P2.9
Setting $f_1 = F_1$ and $f_2 = 1 - f_1$, we substitute in equation (2.48) to obtain

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

$$\therefore f_1 = \frac{r_1 f_1^2 + f_1 \times (1 - f_1)}{r_1 f_1^2 + 2 f_1 \times (1 - f_1) + r_2 \times (1 - f_1)^2}$$

Referring to Table 2.6, we see that the reactivity ratios for styrene/acetonitrile copolymerization are $r_1 = 0.29$ and $r_2 = 0.02$; therefore,

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$$f_1 = \frac{0.29 f_1^2 + f_1(1 - f_1)}{0.29 f_1^2 + 2 f_1(1 - f_1) + 0.02(1 - f_1)^2}$$

We can solve this equation for f_1 using MATLAB's *fsolve* command,

```
>> copol = @(f1) f1 - (0.29*f1^2 + f1*(1 - f1))/(0.29*f1^2 + 2*f1*(1
- f1) + 0.02*(1-f1)^2);
x0 = 0.1;
fsolve(copol,x0)

ans =
    0.5799
```

As shown, $F_1 = f_1 = 0.580$.

■ P3.3

Part (a): The form of the Mark-Houwink-Sakurata equation provided in the problem statement is such that $a = 0.5$ in equation (3.101). As noted on page 140, this indicates that the solvent at hand is a θ solvent and hence the second or greater virial coefficients in equation (3.85) all equal zero:

$$\Pi = RTc\left(\frac{1}{\bar{M}_n} + \cancel{A_2 c + A_3 c^2 + \ldots}\right)$$

$$\therefore \Pi = \frac{RTc}{\bar{M}_n}$$

Substituting the given data into this expression yields the osmotic pressure Π:

$$\Pi = \frac{82.06 \times 318 \times (0.5/100)}{100,000} = \boxed{1.305 \times 10^{-3} \text{ atm}}$$

Part (b): Here, all we have to do is solve hydrostatic equilibrium equation (3.88) for h,

$$\Pi = \rho g h \quad \rightarrow \quad h = \frac{\Pi}{\rho g}$$

$$\therefore h = \frac{(1.305 \times 10^{-3}) \times 1,013,250}{0.7857 \times 981} = \boxed{1.7155 \text{ cm}}$$

Note that we have used the conversion 1 atm = 1,013,250 dyn/cm^2.

Part (c): This is a simple exercise. Referring to Table 3.3, we read a solubility parameter $\delta = 9.92$ (cal·cm^{-3})$^{1/2}$ for polysulfone and $\delta = 9.92$ (cal·cm^{-3})$^{1/2}$ for methylene chloride. The Flory interaction parameter is proportional to the difference between solubility parameters of polymer and solvent; since these are equal in the case at hand, we conclude that $\chi_{12} = 0$.

Part (d): Since the solubility parameters are similar (identical, in fact), we surmise that methylene chloride is a good solvent for polysulfone.

■ P3.5

**Part (a):** The viscosity can be written on the basis of time data:

$$\eta_i = \frac{\eta - \eta_s}{\eta_s} \approx \frac{t - t_s}{t_s}$$

Using $t_s = 65.8$ s as the reference time (since this is the time for which $c = 0$), we have

$$\eta_i \approx \frac{t - 65.8}{65.8}$$

Then, we divide this expression by concentration c to obtain the reduced viscosity. The calculations are summarized to the side. The viscosity plot is also shown next.

c (g/dL)	t (s)	η_i	η_i/c
0	65.8	0.000	
0.54	101.2	0.538	0.996
1.08	144.3	1.193	1.105
1.62	194.6	1.957	1.208
2.16	257	2.906	1.345

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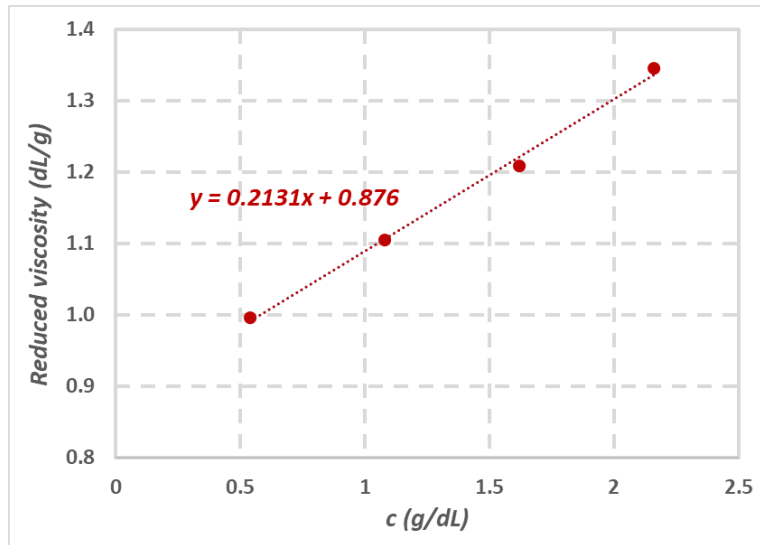
Part (b): The reduced viscosity η_i/c and the concentration c are related by

$$\frac{\eta_i}{c} = [\eta] + k_H [\eta]^2 c$$

Clearly, the line described by the equation above has vertical intercept equal to the intrinsic viscosity $[\eta]$; since the line obtained in the previous part has intercept equal to 0.876, it immediately follows that

$$\boxed{[\eta] = 0.876 \ \text{dL} \cdot \text{g}^{-1}}$$

In turn, the slope of the line equals $k_H[\eta]^2$, so that

$$k_H [\eta]^2 = 0.2131$$

$$\therefore k_H = \frac{0.2131}{[\eta]^2} = \frac{0.2131}{0.876^2} = \boxed{0.278}$$

Part (c): All we have to do is substitute the pertaining data into the MHS equation and solve for molecular weight $\bar{M}_v$:

$$[\eta] = K\bar{M}_v^a \quad \rightarrow \quad 0.876 = \left(1.1 \times 10^{-4}\right) \times \bar{M}_v^{0.725}$$

$$\therefore \bar{M}_v = \left(\frac{0.876}{1.1 \times 10^{-4}}\right)^{\frac{1}{0.725}} = \boxed{240,000}$$

■ **P3.7**

Evoking the MHS equation, the so-called hydrodynamic volume $[\eta] \times M$ can be restated as

$$[\eta]M_v = KM_v^a \times M_v = KM_v^{1+a}$$

If this product is to be conserved, we may write

$$\left(KM_v^{1+a}\right)_{\text{PS}} = \left(KM_v^{1+a}\right)_{\text{PMMA}}$$

$$\therefore \left(7.54 \times 10^{-3}\right) \times \left(5 \times 10^4\right)^{1+0.783} = \left(8.12 \times 10^{-3}\right) \times M_v^{1+0.71}$$

$$\therefore 1.80 \times 10^6 = \left(8.12 \times 10^{-3}\right) \times M_v^{1.71}$$

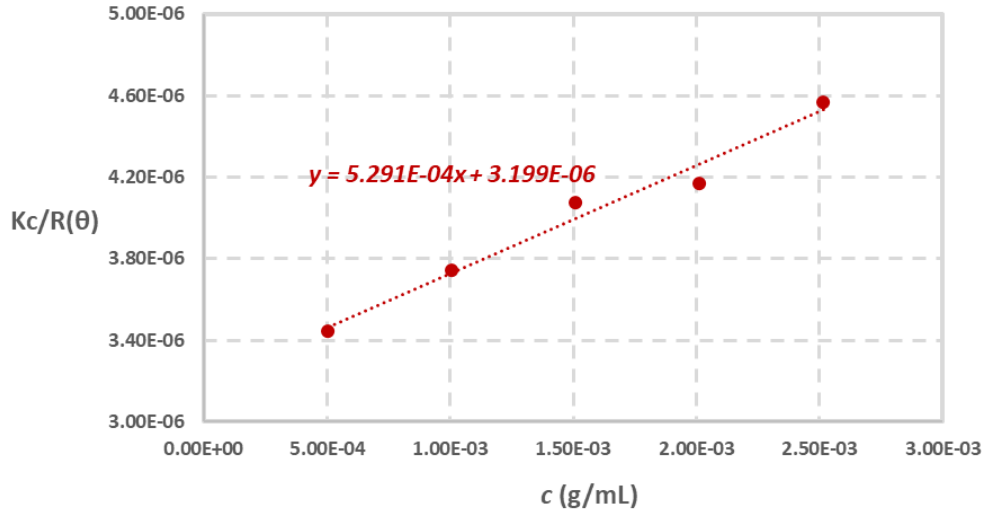$$\therefore M_v = \left(\frac{1.80 \times 10^6}{8.12 \times 10^{-3}}\right)^{\frac{1}{1.71}} = \boxed{76,000}$$

■ **P3.9**

The first step is to compute coefficient K, which is given by equation (3.92):

$$K = \frac{2\pi^2 n_0^2}{N_A \lambda^4} \left(\frac{dn}{dc}\right)^2$$

$$\therefore K = \frac{2\pi^2 \times 1.4199^2}{\left(6.02 \times 10^{23}\right) \times \left(6328 \times 10^{-8}\right)^4} \times \left(6.297 \times 10^{-2}\right)^2 = 1.635 \times 10^{-8}$$

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The data are processed and plotted below.

c (g/mL)	R(θ) (cm⁻¹)	Kc/R(θ)
5.03E-04	2.39E-06	3.44E-06
1.01E-03	4.40E-06	3.74E-06
1.51E-03	6.06E-06	4.07E-06
2.01E-03	7.90E-06	4.17E-06
2.52E-03	9.02E-06	4.56E-06

Referring to equation (3.100), we see that the molecular weight can be determined from the intercept of the linear fit, which is 3.199×10^{-6}, hence,

$$\frac{1}{\bar{M}_n} = 3.199 \times 10^{-6} \quad \rightarrow \quad \bar{M}_n = \frac{1}{3.199 \times 10^{-6}}$$

$$\therefore \boxed{\bar{M}_n = 313{,}000}$$

In turn, the second virial coefficient follows from the slope of the linear fit:

$$2A_2 = 5.291 \times 10^{-4} \quad \rightarrow \quad A_2 = \frac{5.291 \times 10^{-4}}{2}$$

$$\therefore \boxed{A_2 = 2.65 \times 10^{-4} \ \mathrm{mL \cdot mol \cdot g^{-2}}}$$

■ P4.2

The initial volume of the strip is $10 \times 5 \times 2 = 100 \ \mathrm{cm^3}$. The true strain in the longitudinal direction is

$$\varepsilon_L = \ln\left(\frac{L}{L_o}\right) = \ln\left(\frac{10.5}{10}\right) = 0.0488$$

Assuming that the material is isotropic and taking a Poisson ratio $v = 0.35$ from Table 4.13, we may write, for the transverse strain,

$$\varepsilon_T = \ln\left(\frac{W}{W_0}\right) = \ln\left(\frac{T}{T_0}\right) = -v\varepsilon_L = -0.35 \times 0.0488 = -0.0171$$

so that the final dimensions are

$$W = W_0 \times e^{-0.0171} = 5 \times e^{-0.0171} = \boxed{4.915 \ \mathrm{cm}}$$

$$T = T_0 \times e^{-0.0171} = 2 \times e^{-0.0171} = 1.966 \ \mathrm{cm}$$

and the final volume is

$$V = 10.5 \times 4.915 \times 1.966 = 101.46 \ \mathrm{cm^3}$$

This corresponds to a change in volume of 1.46%.

■ P4.3

Assuming that Avrami kinetics apply, the percent crystallinity after 10 s is calculated to be

$$\phi = 1 - \exp\left(-kt^n\right) = 1 - \exp\left(-0.01 \times 10^2\right) = 0.632 = \boxed{63.2\%}$$

■ P4.4

At 100% deformation, the longitudinal strain is

$$\varepsilon = \ln\left(L/L_0\right) = \ln\left(2L_0/L_0\right) = \ln\left(2\right) = 0.693$$

Taking a Poisson ratio $\nu = 0.49$ for natural rubber (Table 4.13), the volumetric strain may be obtained with equation (4.45),

$$\frac{\Delta V}{V_0} = \left(1 - 2\nu\right)\varepsilon = \left(1 - 2 \times 0.49\right) \times 0.693 = 0.0139 = \boxed{1.39\%}$$

■ P4.7

Teflon thickens upon elongation due to a rotation of crystals perpendicular to the draw direction.

■ P4.8

Part (a): Solving equation (4.6) for ρ and taking densities $\rho_a = 1.335$ g/cm³ and $\rho_c = 1.515$ g/cm³ from Table 4.5, we may write

$$\phi = \frac{\rho - \rho_a}{\rho_C - \rho_a} \quad \rightarrow \quad \rho = \phi\left(\rho_C - \rho_a\right) + \rho_a$$

$$\therefore \rho = 0.2 \times \left(1.515 - 1.335\right) + 1.335 = \boxed{1.371 \text{ g/cm}^3}$$

Part (b): The specific heat increment can be obtained by solving equation (4.26) for ΔC_p:

$$\phi = 1 - \frac{\Delta C_p}{\left(\Delta C_p\right)_{am}} \quad \rightarrow \quad \Delta C_p = \left(1 - \phi\right)\left(\Delta C_p\right)_{am} \quad \text{(I)}$$

But $\Delta C_p \times T_g = 115$ J·g⁻¹ (page 175) and $T_g = 69°C = 342$ K (Table 4.3), so that

$$\left(\Delta C_p\right)_{am} \times T_g = 115 \quad \rightarrow \quad \left(\Delta C_p\right)_{am} = \frac{115}{T_g}$$

$$\therefore \left(\Delta C_p\right)_{am} = \frac{115}{342} = 0.336 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$$

Substituting in (I) brings to

$$\Delta C_p = \left(1 - \phi\right)\left(\Delta C_p\right)_{am} = \left(1 - 0.2\right) \times 0.336 = 0.269 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$$

$$\therefore \Delta C_p = 0.269 \; \cancel{\text{J}} \cdot \text{g}^{-1} \cdot \text{K}^{-1} \times \frac{1}{4.18} \frac{\text{cal}}{\cancel{\text{J}}} = \boxed{0.0644 \text{ cal} \cdot \text{g}^{-1} \cdot \text{K}^{-1}}$$

Part (c): We can determine the heat of fusion ΔQ of a semicrystalline polymer using equation (4.25):

$$\phi = \frac{\Delta Q}{\Delta H_f} \quad \rightarrow \quad \Delta Q = \phi \times \Delta H_f \quad \text{(II)}$$

Referring to Table 4.4, the enthalpy of fusion for a repeating unit in poly(ethylene terephthalate) is 6.431 kcal·mol⁻¹. Substituting in (II) brings to

$$\Delta Q = 0.2 \times 6.431 = 1.286 \text{ kcal} \cdot \text{mol}^{-1}$$

$$\therefore \Delta Q = 1.286 \; \cancel{\text{kcal}} \cdot \text{mol}^{-1} \times 4.18 \frac{\text{kJ}}{\cancel{\text{kcal}}} = \boxed{5.375 \text{ kJ} \cdot \text{mol}^{-1}}$$

■ P4.9

Part (a): Noting that the degree of polymerization is 7 and a styrene oligomer has molar mass of 104, we may write

$$\bar{M}_n = 7 \times 104 = 728$$

The glass-transition temperature can be estimated with equation (4.27); parameters $T_g^\infty = 373$ K and $K = 1.2 \times 10^5$ are read from Table 4.11. Thus,

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$$T_{g,1} = T_g^{\infty} - \frac{K}{\overline{M}_n} = 373 - \frac{120{,}000}{728} = \boxed{208 \text{ K}}$$

Part (b): We first estimate the glass transition temperature of the polystyrene sample:

$$T_{g,2} = T_g^{\infty} - \frac{K}{\overline{M}_n} = 373 - \frac{120{,}000}{100{,}000} = 372 \text{ K}$$

Since $T_{g,1}$ and $T_{g,2}$ are spaced far apart, we can use equation (4.34) to estimate the glass-transition temperature of the polystyrene mixture:

$$\ln\left(\frac{T_g}{T_{g,1}}\right) = \frac{W_2 \ln\left(T_{g,2}/T_{g,1}\right)}{W_1\left(T_{g,2}/T_{g,1}\right) + W_2}$$

$$\therefore \ln\left(\frac{T_g}{208}\right) = \frac{0.8 \times \ln\left(372/208\right)}{0.2 \times \left(372/208\right) + 0.8} = 0.402$$

$$\therefore \frac{T_g}{208} = e^{0.402}$$

$$\therefore T_g = 208 \times e^{0.402} = \boxed{311 \text{ K}}$$

■ P4.10

Part (a): The nominal stress can be found with Hooke's law:

$$\sigma = E\varepsilon = \left(3 \times 10^9\right) \times 0.01 = 3 \times 10^7 \text{ Pa} = \boxed{30 \text{ MPa}}$$

Part (b): The true stress is

$$\sigma^T = \sigma\left(1 + \varepsilon\right) = 30 \times \left(1 + 0.01\right) = \boxed{30.3 \text{ MPa}}$$

Part (c): The change in volume can be determined with equation (4.45),

$$\Delta V = \left(1 - 2\nu\right)\varepsilon V_0 \quad \rightarrow \quad \frac{\Delta V}{V_0} = \left(1 - 2\nu\right)\varepsilon^T \quad (\text{I})$$

The true strain is

$$\varepsilon^T = \ln\left(\frac{1.01}{1.0}\right) = 0.00995$$

Also, the Poisson ratio for polystyrene may be taken as 0.35 (Table 4.13). Substituting in (I) brings to

$$\frac{\Delta V}{V_0} = \left(1 - 2 \times 0.35\right) \times 0.00995 = 0.00299 \approx \boxed{0.3\%}$$

■ P5.1

The absolute value of the complex modulus $E^{\star}$ is given by

$$\left|E^*\right| = \sqrt{\left(E'\right)^2 + \left(E''\right)^2}$$

Replacing the storage modulus with equation (5.14) and the loss modulus with equation (5.15), we obtain

$$\left|E^*\right| = \sqrt{\left[\left(\frac{\sigma^o}{\varepsilon^o}\right)\cos\delta\right]^2 + \left[\left(\frac{\sigma^o}{\varepsilon^o}\right)\sin\delta\right]^2}$$

$$\therefore \left|E^*\right| = \left(\frac{\sigma^o}{\varepsilon^o}\right) \times \underbrace{\sqrt{\cos^2\delta + \sin^2\delta}}_{=1}$$

$$\therefore \boxed{\left|E^*\right| = \left(\frac{\sigma^o}{\varepsilon^o}\right)}$$

Proceeding similarly with the dynamic tensile compliance, we may write

$$D^* \times \overline{D}^* = \left|D^*\right|^2$$

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where $D^* = D' - iD''$ and $\bar{D}^* = D' + iD''$, so that

$$\left| D^* \right|^2 = \left(D' - iD'' \right) \times \left(D' + D'' \right) = D'^2 - i^2 D''^2$$

$$\therefore \left| D^* \right|^2 = D'^2 + D''^2 \quad (I)$$

The storage compliance is given by equation (5.20),

$$D' = \left(\frac{\varepsilon^o}{\sigma^o} \right) \cos \delta$$

while the loss compliance is given by equation (5.21),

$$D'' = \left(\frac{\varepsilon^o}{\sigma^o} \right) \sin \delta$$

Substituting in (I) brings to

$$\left| D^* \right| = \sqrt{D'^2 + D''^2}$$

$$\therefore \left| D^* \right| = \sqrt{\left(\frac{\varepsilon^o}{\sigma^o} \right)^2 \underbrace{\left(\sin^2 \delta + \cos^2 \delta \right)}_{=1}} = \frac{\varepsilon^o}{\sigma^o}$$

$$\boxed{\therefore \left| D^* \right| = \frac{1}{\left| E^* \right|}}$$

■ P5.2

The work W may be obtained by integrating the dynamic stress σ^* over a full cycle (i.e., from 0 to 2π):

$$W = \int_0^{2\pi} \sigma^* d\varepsilon^*$$

But $\sigma^* = \sigma^o sin(\omega t + \delta)$ and $\varepsilon^* = \varepsilon^o sin(\omega t)$, giving $d\varepsilon^* = \varepsilon^o cos(\omega t)d(\omega t)$. Substituting above,

$$W = \sigma^o \varepsilon^o \int_0^{2\pi} \sin \left(\omega t + \delta \right) \cos \left(\omega t \right) d \left(\omega t \right)$$

Using the trigonometric identity

$$\sin \left(\omega t + \delta \right) \equiv \sin \left(\omega t \right) \cos \left(\delta \right) + \cos \left(\omega t \right) \sin \left(\delta \right)$$

we obtain

$$\frac{W}{\sigma^o \varepsilon^o} = \cos \left(\delta \right) \int_0^{2\pi} \sin \left(\omega t \right) \cos \left(\omega t \right) d \left(\omega t \right) + \sin \left(\delta \right) \int_0^{2\pi} \cos^2 \left(\omega t \right) d \left(\omega t \right) \quad (I)$$

Evaluating the first integral in (I),

$$\int_0^{2\pi} \sin \left(\omega t \right) \cos \left(\omega t \right) d \left(\omega t \right) = - \left. \frac{\cos^2 \left(2\omega t \right)}{2} \right|_{\omega t = 0}^{\omega t = 2\pi}$$

$$\int_0^{2\pi} \sin \left(\omega t \right) \cos \left(\omega t \right) d \left(\omega t \right) d \left(\omega t \right) = - \left[\frac{\cos^2 \left(4\pi \right)}{2} - \frac{\cos^2 \left(0 \right)}{2} \right] = 0$$

To evaluate the second integral in (I), note first that

$$\cos \left(2\theta \right) \equiv 2 \cos^2 \left(\theta \right) - 1$$

or

$$\cos^2 \left(\theta \right) = \frac{\cos \left(2\theta \right)}{2} + \frac{1}{2}$$

which leads to the tabulated integral

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$$\int \cos^2(\theta)d\theta = \frac{\sin(2\theta)}{4} + \frac{\theta}{2}$$

In the case at hand,

$$\int_0^{2\pi} \cos^2(\omega t)d(\omega t) = \left[\frac{\sin(2\omega t)}{4} + \frac{\omega t}{2}\right]_{\omega t=0}^{\omega t=2\pi}$$

$$\therefore \int_0^{2\pi} \cos^2(\omega t)d(\omega t) = \left[\frac{\sin(4\pi)}{4} + \frac{2\pi}{2}\right] - \left[\frac{\sin(0)}{4} + \frac{0}{2}\right] = \pi$$

Gleaning our results in (I),

$$\frac{W}{\sigma^o \varepsilon^o} = \cos(\delta) \times 0 + \sin(\delta) \times \pi$$

$$\therefore \boxed{W = \pi \sigma^o \varepsilon^o \sin(\delta)}$$

as we intended to show.

■ P5.8

This is a straightforward application of equation (5.37), which can be restated as

$$\ln\left(\frac{f_1}{f_2}\right) = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

so that

$$\therefore \ln\left(\frac{1}{110}\right) = -\left(\frac{840,000}{8.314}\right)\left(\frac{1}{373} - \frac{1}{T_2}\right)$$

$$\therefore -4.70 = -270.87 + \frac{101,034}{T_2}$$

$$\therefore T_2 = \frac{101,034}{270.87 - 4.70} = \boxed{379.6 \text{ K}}$$

■ P5.9

Part (a): The relaxation modulus is given by the summation

$$E(t) = \sum_{i=1}^{3} E_i \exp(-t/\tau_i)$$

$$\therefore E(t) = 0.1 \times \exp\left(-\frac{10}{10}\right) + 1.0 \times \exp\left(-\frac{10}{20}\right) + 10 \times \exp\left(-\frac{10}{30}\right)$$

$$\therefore \boxed{E(t) = 7.809 \text{ GPa}}$$

Part (b): The value is a bit high. In general, the Maxwell-Wichert model is a good representation of the behavior of stress relaxation modulus, particularly as the number of Maxwell elements increases.

■ P5.10

The first step is to estimate the bulk modulus K, namely

$$K = \frac{\Delta p}{\Delta V / V_0}$$

Here, the hydrostatic pressure is, in CGS units,

$$\Delta p = \frac{5000 \text{ g} \times 981 \frac{\text{cm}}{\text{s}^2}}{\left(6 \times 2^2\right) \text{cm}^2} = 204,000 \text{ dyn/cm}^2$$

(Note that a factor of 6 was included because the cube has 6 faces of 2^2 cm² area each.) The initial volume is $V_o = 2^3 = 8$ cm³ and the final volume as the cube is deformed to 95% of its length is $0.95^3 \times 2^3 = 6.86$ cm³. The variation in volume then becomes $\Delta V = 8 - 6.86 = 1.14$ cm² and the bulk modulus is determined as

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$$K = \frac{\Delta p}{\Delta V/V_0} = \frac{204{,}000}{(1.14/8.0)} = 1.43 \times 10^6 \text{ dyn/cm}^2$$

With reference to Table 4.13, the Poisson ratio for natural rubber may be taken as 0.49. Combining equations (4.54) and (4.56), we can relate the bulk and shear moduli:

$$\begin{cases} E = 2(1+v)G \\ K = \dfrac{E}{3(1-2v)} \end{cases} \rightarrow K = \frac{2(1+v)G}{3(1-2v)}$$

$$\therefore G = \frac{3(1-2v)K}{2(1+v)}$$

$$\therefore G = \frac{3 \times (1 - 2 \times 0.49) \times (1.43 \times 10^6)}{2 \times (1 + 0.49)} = 28{,}800 \text{ dyn/cm}^2$$

With an extension ratio $\lambda = 1.5$, the nominal stress is given by equation (5.157),

$$f^* = G_o\left(\lambda - \frac{1}{\lambda^2}\right) = 28{,}800 \times \left(1.5 - \frac{1}{1.5^2}\right) = 30{,}400 \text{ dyn/cm}^2$$

If the cross-sectional area of the elastomer equals 1 cm², the corresponding force is 30,400 × 1.0 = 30,400 dyn = 0.304 N.

■ P5.11

With $\lambda = 2$ (i.e., with the rubber specimen stretched to twice its original length), we can use equation (5.157) to estimate the shear modulus G_o,

$$f^* = G_o\left(\lambda - \frac{1}{\lambda^2}\right) \rightarrow G_o = \frac{f^*}{\lambda - 1/\lambda^2}$$

$$\therefore G_o = \frac{100}{2 - 1/2^2} = 57.1 \text{ psi}$$

Accordingly, with $\lambda = 1.5$ (i.e., with 50% extension), the corresponding stress is

$$f^* = 57.1 \times \left(1.5 - \frac{1}{1.5^2}\right) = \boxed{60.3 \text{ psi}}$$

■ P5.12

Let σ_1 denote the stress of the rubber band at 100% extension and 23°C; in turn, let σ_2 denote the stress of the rubber band at 100% extension and 30°C. From the problem statement, $\sigma_2 = \sigma_1 + 0.2$, so that

$$\sigma_1 = \left(\frac{296}{303}\right)\sigma_2 = \left(\frac{296}{303}\right) \times (\sigma_1 + 0.2)$$

$$\therefore \sigma_1 = 0.977\sigma_1 + 0.195$$

$$\therefore 0.023\sigma_1 = 0.195$$

$$\therefore \sigma_1 = \frac{0.195}{0.023} = 8.48 \text{ MPa}$$

We can substitute this stress value and the extension ratio $\lambda = 2$ into equation (5.157) and solve for the shear modulus:

$$f^* = G_o\left(\lambda - \frac{1}{\lambda^2}\right) \rightarrow G_o = \frac{f^*}{\lambda - 1/\lambda^2}$$

$$\therefore G_o = \frac{8.48}{2 - 1/2^2} = 4.85 \text{ MPa}$$

Therefore, for an extension of 2%, the stress σ_3 is

$$\sigma_3 = 4.85 \times \left(1.02 - \frac{1}{1.02^2}\right) = 0.285 \text{ MPa}$$

and the tensile modulus is estimated to be

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$$E = \frac{\sigma_3}{\varepsilon} = \frac{0.285}{0.02} = \boxed{14.3 \text{ MPa}}$$

■ P11.1

Part (a): Firstly, the ram area is $\pi \times 0.375^2/4 = 0.110$ in.^{2}. The pressure drop can be found by dividing the ram load P by the ram area,

$$\Delta p = \frac{P}{0.110}$$

The wall shear in the capillary is given by

$$\tau_w = \frac{R\Delta p}{2L} = \frac{(0.041/2) \times \Delta p}{2 \times 0.622} = 0.0165 \Delta p$$

The flow rate is obtained by dividing the extrusion volume (= 0.0737 in.^{3}) by the efflux time Δt,

$$Q = \frac{0.0737}{\text{Efflux time}} = \frac{0.0737}{\Delta t} \left[\text{in}^3/\text{min} \right]$$

We also need the apparent shear rate ϕ, namely

$$\phi = \frac{4Q}{\pi R^3} = \frac{4 \times Q}{\pi \times (0.041/2)^3} = 148{,}000 Q$$

A plot of $log(\tau_w)$ versus $log(\phi)$ will yield a straight line with n as the slope and $log(m')$ as the intercept, where

$$m = m' \left(\frac{4n}{3n+1} \right)^n \quad \text{(I)}$$

The data are processed and plotted below.

Ram load (lb)	Efflux time (min)	Δp (psi)	τ_w (psi)	$log(\tau_w)$	Q (in³ min⁻¹)	ϕ (min⁻¹)	$log(\phi)$
97.5	5.32	886.36	14.63	1.17	0.0139	2050.301	3.312
145	1.58	1318.18	21.75	1.34	0.0466	6903.544	3.839
217	0.31	1972.73	32.55	1.51	0.2377	35185.806	4.546
250	0.17	2272.73	37.50	1.57	0.4335	64162.353	4.807
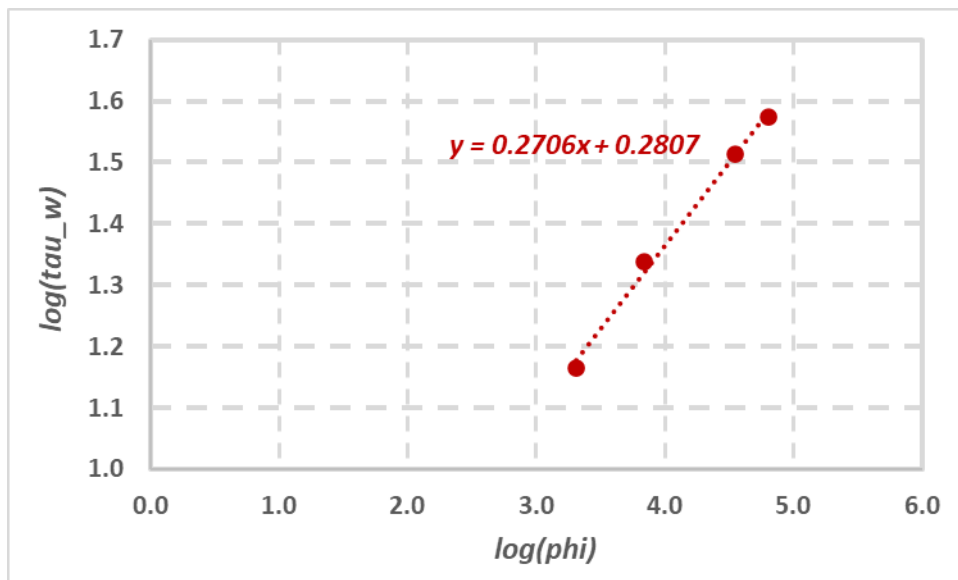
The slope of the linear fit is $n = 0.271$ and the intercept is $log_{10}\, m' = 0.281$, so that $m' = 10^{0.281} = 1.909$. Substituting in (I) brings to

$$m = 1.909 \times \left(\frac{4 \times 0.271}{3 \times 0.271 + 1} \right)^{0.271} = 1.661 \text{ psi-min}^{0.271}$$

$$\therefore m = 1.661 \text{ psi-min}^{0.271} \times \frac{1 \text{ MPa}}{145.038 \text{ psi}} \times \frac{60^{0.271} \text{ sec}^{0.271}}{1 \text{ min}^{0.271}} = \boxed{0.0347 \text{ MPa-s}^{0.271}}$$

The usual assumptions are fully-developed, isothermal, laminar, steady-state, and incompressible flow; negligible body forces, no slip at the wall, no viscous heating, and a running fluid with viscosity that is independent of pressure.

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Part (b): The shear rate at the wall, $\dot{\gamma}_w$, is related to the apparent shear rate, ϕ, by equation (11.40),
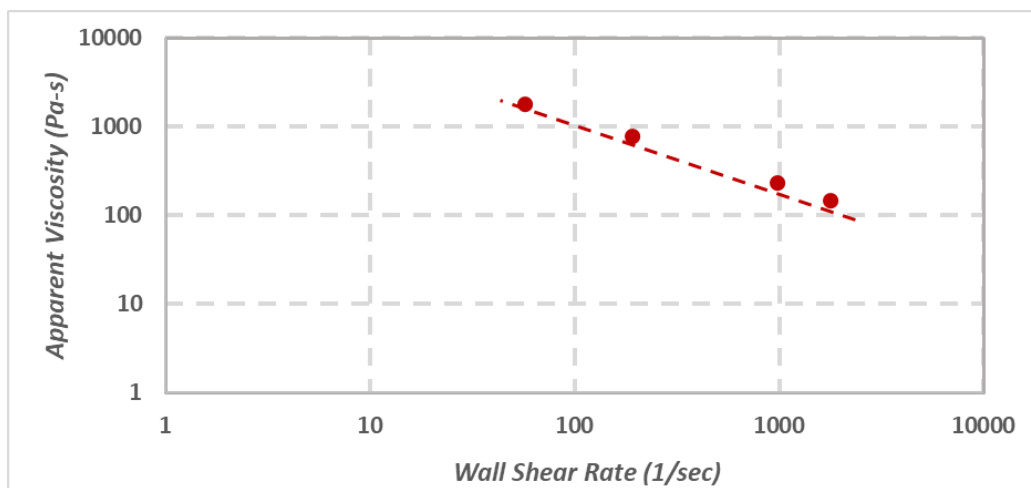
$$\dot{\gamma}_w = \frac{3n+1}{4n}\phi$$

Using $n = 0.271$ as determined in part (a), we obtain

$$\dot{\gamma}_w = \frac{3\times 0.271+1}{4\times 0.271}\phi = 1.673\phi$$

Then, the apparent viscosity η can be obtained by dividing the wall shear by the shear rate,

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} = \frac{\tau_w}{1.673\phi}$$

| $\dot{\gamma}_w$ (s⁻¹)	$log(\dot{\gamma}_w)$	τ_w (Pa)	η (Pa·s)	$log(\eta)$
57.17	1.76	100836	1763.8	3.25
192.49	2.28	149961	779.0	2.89
981.10	2.99	224424	228.7	2.36
1789.06	3.25	258554	144.5	2.16

With reference to equation (11.14), the apparent viscosity varies with shear rate according to

$$\eta = m\dot{\gamma}^{n-1} \quad \rightarrow \quad \log_{10}\eta = (n-1)\log_{10}\dot{\gamma} + \log_{10}m$$

This means that a plot of $\log_{10}\eta$ versus $\log_{10}\dot{\gamma}$ yields a straight line. The pertaining logarithms have been computed in the previous table; we proceed to plot these data, as shown below. The pertaining linear fit is found to be

$$\log_{10}\eta = -0.7294\log_{10}\dot{\gamma} + 4.5399$$

y = -0.7294x + 4.5399
R² = 0.9993
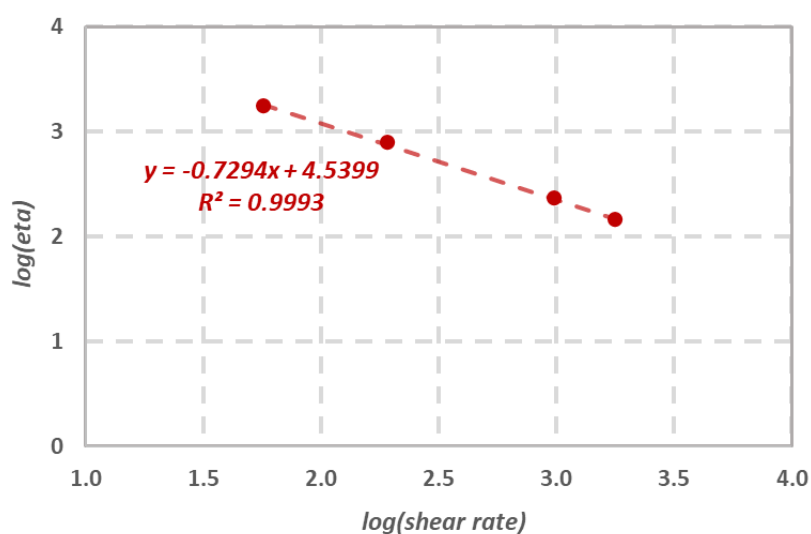
■ P11.2

The axial velocity profile for a non-Newtonian Poiseuille flow has the dimensionless form given in equation (11.27),
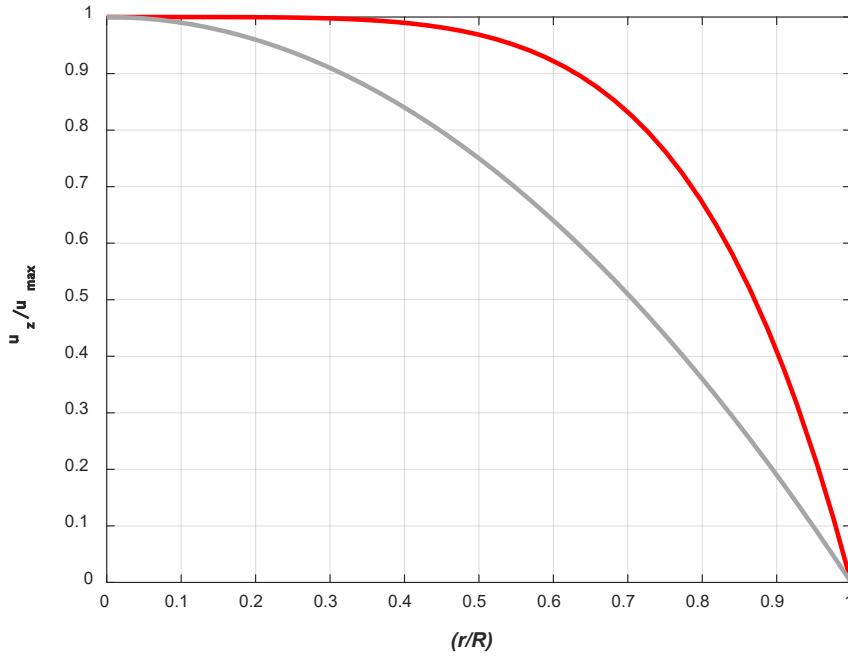
$$\frac{u_z}{u_z^{max}} = 1 - \left(\frac{r}{R}\right)^{(1+n)/n}$$

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For polystyrene at 210°C (= 483 K), an exponent $n = 0.25$ can be gleaned from Table 11.1, so that

$$\frac{u_z}{u_z^{\max}} = 1 - \left(\frac{r}{R}\right)^{(1+0.25)/0.25}$$

$$\therefore \frac{u_z}{u_z^{\max}} = 1 - \left(\frac{r}{R}\right)^{5.0}$$

This velocity profile is plotted for $r \in [0, 1]$ as the red curve below. The gray curve is the corresponding profile for a Hagen-Poiseuille (i.e., parabolic) flow.

■ P11.3

The volumetric flow rate Q for flow of a power-law fluid in a capillary is given by equation (11.28),

$$Q = \left(\frac{n\pi R^3}{1 + 3n}\right)\left(\frac{R\Delta p}{2mL}\right)^{1/n}$$

Assuming that radius is the only parameter that changes from one capillary to another, we may write the ratio

$$\frac{Q_2}{Q_1} = \frac{R_2^3 R_2^{1/n}}{R_1^3 R_1^{1/n}} = \left(\frac{R_2}{R_1}\right)^{3+\frac{1}{n}}$$

$$\therefore 40 = 2^{3+\frac{1}{n}}$$

Applying logarithms and solving for n,

$$\ln 40 = \ln 2^{3+\frac{1}{n}}$$

$$\therefore \ln 40 = \left(3 + \frac{1}{n}\right) \times \ln 2$$

$$\therefore 3 + \frac{1}{n} = \frac{\ln 40}{\ln 2}$$

$$\therefore \frac{1}{n} = \frac{\ln 40}{\ln 2} - 3$$

$$\therefore n = \left(\frac{\ln 40}{\ln 2} - 3\right)^{-1} = \boxed{0.431}$$

Now, the wall shear is given by equation (11.40),

$$\dot{\gamma}_w = \frac{3n+1}{4n}\phi = \frac{3n+1}{4n}\left(\frac{4Q}{\pi R^3}\right)$$

Hence, we have the ratio

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$$\frac{\dot{\gamma}_{w,1}}{\dot{\gamma}_{w,2}} = \frac{\cancel{\frac{3n+1}{4n}}\left(\frac{4Q_1}{\pi R_1^3}\right)}{\cancel{\frac{3n+1}{4n}}\left(\frac{4Q_2}{\pi R_2^3}\right)} = \left(\frac{R_2}{R_1}\right)^3\left(\frac{Q_1}{Q_2}\right)$$

$$\therefore \frac{\dot{\gamma}_{w,1}}{\dot{\gamma}_{w,2}} = (2)^3 \times \left(\frac{1}{40}\right) = 0.2$$

The larger capillary has wall shear 5 five times greater than the smaller one.

■ P11.4

Part (a): The first step is to convert the pressure drop from units of psi to pascals,

$$\Delta p = 1000 \; \cancel{psi} \times \frac{6894.76 \text{ Pa}}{\cancel{psi}} = 6.90 \times 10^6 \text{ Pa}$$

Then, the wall shear stress is given by equation (11.38),

$$\tau_w = \frac{R\Delta p}{2L} = \frac{(0.25/2) \times \left(6.90 \times 10^6\right)}{2 \times 3.0} = 144{,}000 \text{ Pa}$$

$$\therefore \boxed{\tau_w = 144{,}000 \text{ N} \cdot \text{m}^{-2}}$$

Part (b): For polystyrene at 210°C, we can refer to Table 11.1 and read parameters $m = 2.38 \times 10^4$ and $n = 0.25$. Then, solving the shear stress-shear rate relationship for $\dot{\gamma}_w$, we obtain

$$\tau_w = m\dot{\gamma}_w^n \quad \rightarrow \quad \dot{\gamma}_w = \left(\frac{\tau_w}{m}\right)^{\frac{1}{n}}$$

$$\therefore \dot{\gamma}_w = \left(\frac{144{,}000}{23{,}800}\right)^{\frac{1}{0.25}} = \boxed{1340 \text{ s}^{-1}}$$

Part (c): Noting that $R = 0.125$ in. $= 0.00318$ m and $L = 3$ in. $= 0.0762$ m, we appeal to equation (11.28) and write

$$Q = \frac{n\pi R^3}{1+3n}\left(\frac{R\Delta p}{2mL}\right)^{\frac{1}{n}} = \frac{0.25 \times \pi \times 0.00318^3}{1+3\times 0.25} \times \left[\frac{0.00318 \times \left(6.90 \times 10^6\right)}{2 \times 23{,}800 \times 0.0762}\right]^{\frac{1}{0.25}}$$

$$\therefore Q = 1.93 \times 10^{-5} \text{ m}^3/\text{s} = \boxed{19.3 \text{ cm}^3/\text{s}}$$

■ P11.5

Part (a): We can write the tensile stress-tensile strain rate for a Troutonian polymer as

$$\sigma = \eta_T \frac{d\varepsilon}{dt}$$

Separating variables and noting that true tensile strain $\varepsilon = ln(L/L_0)$,

$$\sigma = \eta_T \frac{d\varepsilon}{dt} \quad \rightarrow \quad \sigma dt = \eta_T d\varepsilon$$

$$\therefore \sigma dt = \eta_T d\left[\ln\left(L/L_0\right)\right]$$

Integrating,

$$\sigma t = \eta_T \ln\left(L/L_0\right)$$

Adjusting,

$$\frac{\sigma t}{\eta_T} = \ln\left(L/L_0\right)$$

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$$\therefore \frac{\sigma t}{\eta_T} = \ln(L) - \ln(L_0)$$

$$\therefore \ln(L) = \left(\frac{1}{\eta_T}\right)\sigma t + \ln(L_0)$$

as we intended to show.

Part (b): The tensile stress is given by the ratio $\sigma = F/A$, where weight $F = 75$ g × 981 cm/s² = 73,600 dyn. The cross-sectional area A can be obtained by noting that the initial volume $V = 6.0 \times 0.699 \times 0.155 = 0.650$ cm³, so that $A = 0.650/L$ at any point of the elongation process. The data are processed below.

Time (min)	Length (cm)	$\ln(L)$	A (cm²)	σ (dyn/cm²)	σt (g cm^{-1} s^{-1})
1	6.9	1.932	0.0942	7.813E+05	4.688E+07
2	7	1.946	0.0929	7.926E+05	9.511E+07
3	7.1	1.960	0.0915	8.039E+05	1.447E+08
6	7.25	**1.981**	0.0897	8.209E+05	**2.955E+08**
12	7.48	**2.012**	0.0869	8.470E+05	**6.098E+08**
15	7.6	**2.028**	0.0855	8.606E+05	**7.745E+08**
18	7.69	**2.040**	0.0845	8.707E+05	**9.404E+08**
21	7.79	**2.053**	0.0834	8.821E+05	**1.111E+09**
24	7.9	**2.067**	0.0823	8.945E+05	**1.288E+09**

A quick visualization of the $\ln(L)$ versus σt data reveals that a linear trend only holds for the five or six lowermost points, which are highlighted in bold in the foregoing table. Accordingly, we proceed to plot and fit the six lowermost points; the line thus obtained is shown next.
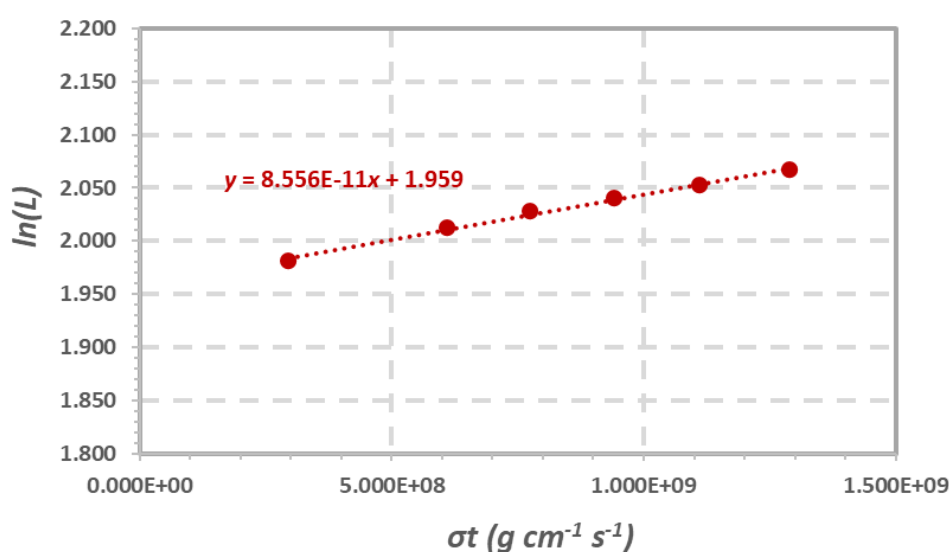
The line has slope equal to 8.556×10^{-11}, which, comparing to the linear equation derived in part (a), indicates that

$$\frac{1}{\eta_T} = 8.556 \times 10^{-11} \quad \rightarrow \quad \eta_T = \frac{1}{8.556 \times 10^{-11}}$$

$$\therefore \eta_T = 1.17 \times 10^{10} \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$$

But 1 g·cm^{-1}·s^{-1} = 1 poise = 0.1 Pa·s, so that

$$\eta_T = 1.17 \times 10^{10} \text{ P} = 1.17 \times 10^9 \text{ Pa} \cdot \text{s} = \boxed{1.17 \text{ GPa} \cdot \text{s}}$$

Note further that the intercept of the line is 1.959, which, comparing with the expression derived in part (a), indicates that

$$\ln(L_0) = 1.959 \quad \rightarrow \quad L_0 = e^{1.959}$$

$$\therefore L_0 = 7.092 \text{ cm}$$

This is substantially different from the actual L_0 of 6.0 cm. The difference is due to initial elastic deformation (stretching of coiled chains) prior to viscous flow (i.e., chain slippage).

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