Montogue

QUIZ MS302

Polymer Engineering

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PROBLEMS

Problem 1

The following data were obtained in the determination of the average molar mass of a polymer. True or false?

Molar mass	Mass (g)
75,000	1.2
56,000	2.0
40,000	3.6
25,000	5.0

1.( ) The number-average molar mass is greater than 32,000 g/mol.
2.( ) The number of molecules in 1 gram of polymer is greater than 1.85×10^{19}.
3.( ) The mass-average molar mass is greater than 38,000 g/mol.
4.( ) The polydispersity ratio of the polymer is greater than 1.25.

Problem 2 (Rudin, 1982, w/ permission)

Consider the three following polymer compound measurements, along with three techniques that could be used to carry out such measurements. Which of the following is the correct association?

X. Number-average molar mass of a soluble polymer obtained from reaction of glycol, phtalic anhydride, and acetic acid, with an approximate molar mass believed to be around 45,000.
Y. Weight-average molar mass of a polystyrene with molecular weight of about 500,000.
Z. Number-average molar mass of high molecular weight styrene-methyl methacrylate with uncertain styrene content.

1. Light scattering
2. Membrane osmometry
3. Vapor phase osmometry

A) X-1, Y-3, Z-2
B) X-3, Y-2, Z-1
C) X-3, Y-1, Z-2
D) X-2, Y-1, Z-3

Problem 3 (Chanda, 2013)

A solution containing 0.75 g of a protein polymer per 100 g of water is found to have an osmotic pressure of 12.0 torr at 25°C. Estimate the molar mass of the protein. Use R = 82.1 $\text{cm}^3\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

A) M = 11,600 g/mol
B) M = 23,200 g/mol
C) M = 34,100 g/mol
D) M = 40,900 g/mol

Problem 4

A polymer with number-average molar mass $\bar{M}_n$ = 430,000 and mass-average molar mass $\bar{M}_w$ = 1,000,000, is contaminated with 3% by weight of an impurity with molecular weight 30,000. What effects does this contamination have on the average molar masses determined by light scattering and membrane osmometry?

Statement 1: The molar mass measured by membrane osmometry will change by more than 10%.

Statement 2: The molar mass measured by light scattering will change by more than 10%.

A) Both statements are true.
B) Statement 1 is true and statement 2 is false.
C) Statement 2 is true and statement 1 is false.
D) Both statements are false.

Problem 5 (Modified from Chanda, 2013)

Two monodisperse polystyrenes are mixed in equal quantities by weight. One polymer has molar mass of 39,000 and the other 300,000. The Mark-Houwink-Sakurada constants for polystyrene/benzene are K = 9.18×10^{-5} dL/g and a = 0.75. What is the intrinsic viscosity of the blend in benzene at 25°C?

A) $[\eta]$ = 0.188 dL/g
B) $[\eta]$ = 0.311 dL/g
C) $[\eta]$ = 0.717 dL/g
D) $[\eta]$ = 1.03 dL/g

Problem 6.1

The relative flow times of a poly(methyl methacrylate) polymer in chloroform are shown below.

Concentration (g/dL)	t/t_0
0.20	1.290
0.40	1.632
0.60	2.026
0.80	2.310
1.00	2.628
1.20	2.989

The intrinsic viscosity can be established by the Huggins equation,

$$\frac{\eta_{\text{sp}}}{c} = \frac{1}{c}\left(\frac{t}{t_0} - 1\right) = [\eta] + k_H [\eta]^2 c + k'_H [\eta]^3 c^2 + \ldots$$

where c is concentration; or the Kraemer equation,

$$\eta_{\text{inh}} = \frac{\ln(\eta/\eta_0)}{c} = [\eta] - k_1 [\eta]^2 c - k'_1 [\eta]^3 c^2 - \ldots$$

Determine $[\eta]$ by plotting η_{sp}/c and η_{inh} against c.

Problem 6.2

Find the viscosity-average molar mass if the Mark-Houwink-Sakurada fit for this polymer is $[\eta]$ = 3.52×10$^{-5}M_v^{0.80}$. dL/g.

A) $\bar{M}_V$ = 83,900
B) $\bar{M}_V$ = 168,000
C) $\bar{M}_V$ = 325,000
D) $\bar{M}_V$ = 537,000

Problem 7

Rank the following three types of polymer structure in terms of their ability to crystallize.

X. Atactic polymers
Y. Isotactic polymers
Z. Syndiotactic polymers

A) Y > X > Z
B) X > Z > Y
C) Y > Z > X
D) Z > Y > X

Problem 8

Associate the polymer additives with the correct application.

Additive	Application
P. 2,6-Di-t-butyl-4-methyl phenol (BHT)	**1.** Antioxidant
Q. Hydrated alumina	**2.** Ultraviolet stabilizer
R. 2-Mercaptobenzothiazole	**3.** Vulcanization accelerator
S. 2(2-hydroxyphenyl) 2H-benzotriazole derivatives	**4.** Flame retardant

A) P-1, Q-4, R-2, S-3
B) P-2, Q-3, R-1, S-4
C) P-3, Q-1, R-2, S-4
D) P-1, Q-4, R-3, S-2

Problem 9

The following is a list of possible molecular structural modifications in a polymer chain.

P. Increased molecular weight
Q. Increased symmetry
R. Addition of polar groups
S. Increased crosslink density

What are the effects of each of these structural changes in the glass transition temperature (T_g) of an amorphous polymer?

A) P: increases T_g; Q: decreases T_g; R: increases T_g; S: decreases T_g
B) P: decreases T_g; Q: increases T_g; R: decreases T_g; S: increases T_g
C) P: decreases T_g; Q: decreases T_g; R: increases T_g; S: increases T_g
D) P: increases T_g; Q: increases T_g; R: increases T_g; S: increases T_g

Problem 10.1 **(Rudin, 1982, w/permission)**

An elastomer has $\bar{M}_n$ = 100,000 before crosslinking, The density of the vulcanizate (without fillers) with 24 mol% styrene in the polymer is 0.97 g/cm³. Assume the average molar mass between crosslinks to be 8000 and take the temperature to be 30°C. Calculate the stress at 100% elongation of the elastomer. Use $R = 8.3\times10^7$ ergs·mol·K^{-1} and then express your result in MN/m².

A) τ = 0.233 MN/m²
B) τ = 0.534 MN/m²
C) τ = 0.798 MN/m²
D) τ = 0.985 MN/m²

Problem 10.2

Estimate Young's modulus for the elastomer introduced in the previous problem.

A) E = 0.915 MN/m²
B) E = 1.31 MN/m²
C) E = 1.68 MN/m²
D) E = 2.08 MN/m²

Problem 11

The ratio of elongational viscosity to shear viscosity for a Troutonian polymer is:

A) $\mu_{\text{el}}/\mu_{\text{sh}} = 1/3$

B) $\mu_{\text{el}}/\mu_{\text{sh}} = 1/2$

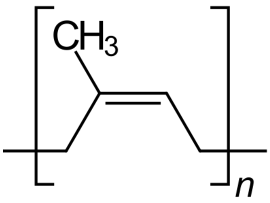
C) $\mu_{\text{el}}/\mu_{\text{sh}} = 2$

D) $\mu_{\text{el}}/\mu_{\text{sh}} = 3$

Problem 12

Regarding aspects of polymer technology, true or false?

1.( ) About one out of every 160 chain carbon atoms is cross-linked in a typical natural rubber (cis-polyisoprene, monomer structure shown below) compound with good properties. The density of such a vulcanizate is 0.96 g/cm³ at a temperature of 30°C. The modulus of this rubber sample at low extensions is greater than 2.5 MPa. Use $R = 8.3\times10^{7}$ ergs·mol·K^{-1}.



2.( ) Random copolymers generally do not crystallize, especially when the number of one of the monomers outstrips that of the other monomer by one order of magnitude or more.

3.( ) The theoretical density of 100% crystalline polyethylene is 1 g/cm³, while the density of amorphous polyethylene is 0.86 g/cm³. The crystallinity of a sample of density 0.92 g/cm³ can be estimated to be greater than 40%.

4.( ) The root-mean-square end-to-end distance of a polymer chain takes account of the average distance between the first and the last segment in the macromolecule. The radius of gyration of a polymer macromolecule, in turn, is the root-mean-square distance of the elements of a polymer chain from its center of gravity. The rms end-to-end distance d is and the radius of gyration r are related by an expression of the form $d = \sqrt{6}r$.

5.( ) It has been found that the glass transition temperature of a polymer is associated to the number-average molar mass of a polymer by an expression of the form $T_g = T_g^{\infty} - K/\bar{M}_n$, where T_g^{∞} is the glass transition temperature at infinite molecular weight and K is a constant. Suppose we have a polystyrene compound with $\bar{M}_n = 2500$. Knowing that $T_g^{\infty} = 100^{\text{o}}$C and $K = 200{,}000$ for polystyrene, we surmise that the glass transition temperature of this system is greater than 18°C..

6.( ) The molar mass of a polymer can be determined by a light scattering experiment because it is proportional to the intensity of scattering. The scattering intensity of a light beam in such a procedure is directly proportional to the fourth power of wavelength, which is to say that, the greater the wavelength of the incident source, the larger the scattering.

7.( ) Raw rubber is not elastic until it has been slightly crosslinked. This is generally achieved by the addition of a small amount of phosphorus, of the order of a few percent by weight, together with an appropriate accelerator, followed by heating. The process in question is known as vulcanization.

8.( ) If natural rubber is treated with a proton donor such as sulfuric acid or stannic chloride, the product is cyclized rubber, of which the empirical formula is $-C_5H_8-$. This polymer is inelastic, has high density, and dissolves in hydrocarbon solvents only.

9.( ) The limiting oxygen index (LOI) is a quantitative means of evaluating the flammability of polymers and other organic materials. Values of LOI are found to be reasonably reproducible and they give an excellent indication of a material's thermal performance in actual fires. The higher the LOI, the greater will be the flammability of the polymer.

10.( ) Advantages of solution polymerization include the fact that polymer synthesis can be carried out at high temperatures, with correspondingly high reaction rates. In addition, chain transfer is generally not a problem for this polymer synthesis procedure.

11.( ) One of the drawbacks of cationic polymerization is the low reaction rate, especially at high temperatures, since the carbocation involved in the polymerization process is generally much less reactive than, say, a free radical under the same conditions.

12.( ) Anionic polymerization features a high frequency of side reactions and, consequently, anionic polymers have broader molecular weight and branching distributions than polymers produced via free radical mechanisms.

13.( ) Many physical properties of polymers change profoundly at the glass transition temperature, including coefficient of thermal expansion, mechanical damping, and electrical properties. All of these are dependent on the relative degree of freedom for molecular motion within a given polymeric material and each can be used to monitor the point at which the glass transition occurs. Fortunately, the glass transition temperature has a constant value for a given material and different characterization techniques in general yield the same value for it.

14.( ) A polyblend consisting of a 55% mass fraction of PVC (glass transition temperature = 80°C) and 45% mass fraction of PTFE (T_g = 115°C) has a glass transition temperature greater than 90°C.

15.( ) Most polymers exhibit shear-thinning behavior, that is, they are such that the shear viscosity decreases with increasing rates of deformation.

16.( ) A PVC sample has glass transition temperature of 353 K and corresponding viscosity of 10^{12} Pa·s. Assuming that the constants in the Williams-Landel-Ferry (WLF) equation are C_1 = 17.44 and C_2 = 51.6 K, we surmise that the viscosity of this polymer at a temperature of 400 K is greater than 4500 Pa·s.

17.( ) The transfer constant to the solvent for the polymerization of styrene in benzene at 60°C is 0.15×10^{-4}. We conclude that the dilution factor required to halve the molar mass of the polymer is greater than 15. Use $1/\bar{X}_{no} = 2.5\times10^{-4}$ as the reciprocal of the degree of polymerization in the absence of a solvent.

18.( ) A polypropylene specimen had its storage shear modulus determined to be 100 kPa, while the loss shear modulus was established as 120 kPa. The phase angle of the deformation delay between stress and strain is 39.8°.

Problem 13

A nylon sample of 0.03 m^2 cross-sectional area is subjected to a creep load of 10 kN. The load is removed after 60 seconds. Assuming that Young's modulus and the coefficient of viscosity for polystyrene are E = 1 GPa and η = 300 GP, true or false? Assume that the viscoelastic behavior of the polymer can be represented by a Maxwell element.

1.( ) The compliance of the specimen is greater than 2.5×10^{-9} m^2/N.
2.( ) The deformation recovered upon removal of the load is greater than 5.0×10^{-4}.
3.( ) The permanent set upon removal of the load is greater than 6.0×10^{-4}.

SOLUTIONS

P.1 ■ Solution

1. True. The number-average molar mass is given by

$$\bar{M}_n = \frac{\Sigma W_i}{\Sigma\left(W_i/M_i\right)}$$

where W_i is the mass of species i and M_i is the molecular mass. Accordingly,

$$\bar{M}_n = \frac{\Sigma W_i}{\Sigma\left(W_i/M_i\right)} = \frac{1.2+2.0+3.6+5.0}{\frac{1.2}{75,000}+\frac{2.0}{56,000}+\frac{3.6}{40,000}+\frac{5.0}{25,000}} = \boxed{34,500\ \text{g/mol}}$$

2. False. The number of molecules in 1 gram of polymer follows as

$$N = \frac{N_A}{\bar{M}_n} = \frac{6.02\times10^{23}}{34,500} = \boxed{1.74\times10^{19}\ \text{molec}}$$

3. True. The mass-average molecular mass is given by

$$\bar{M}_w = \Sigma w_i M_i$$

where $w_i = W_i/W$. Accordingly,

$$\bar{M}_w = \frac{(75,000\times1.2+56,000\times2.0+40,000\times3.6+25,000\times5.0)}{1.2+2.0+3.6+5.0} = \boxed{39,900\text{ g/mol}}$$

4. False. The polydispersivity of the polymer is calculated with the ratio

$$PD = \frac{\bar{M}_w}{\bar{M}_n} = \frac{39,900}{34,500} = \boxed{1.16}$$

P.2 ■ Solution

Vapor phase osmometry is suitable for compound X, as it is the technique of choice for determining the number-average molar mass soluble polymers usually contained in the interval 4000 < $\bar{M}_n$ < 50,000. Light scattering is particularly tailored for compound Y, since this method is used to compute the weight-average molar mass over a wide range, e.g. such that 10,000 < $\bar{M}_w$ < 10,000,000. Lastly, membrane osmometry may be the best choice for establishing the number-average molar mass of a compound that includes some unknown content of a second or third polymer, since, much like light scattering in the determination of $\bar{M}_w$, membrane osmometry covers a wide range of molar masses (50,000 ≲ $\bar{M}_n$ ≲ 1,000,000). The correct association is X-3, Y-1, Z-2.

◆ The correct answer is **C**.

P.3 ■ Solution

The osmotic pressure in atm is Π = 12.0/760 = 0.0158 atm. For water, the density at 25°C and the molecular weight are 0.997 g/cm³ and 18.0 g/mol, respectively. The molar volume of water is V_A^o = 18.0/0.997 = 18.05 cm³/mol. The number of moles in 100 g of water is n_A = 100/18.0 = 5.56 mol. The number of moles of solute (protein) is then

$$n_B = \frac{\Pi V_A^o n_A}{RT} = \frac{0.0158\times18.05\times5.56}{82.1\times298} = 6.48\times10^{-5}\text{ mol}$$

The molecular weight of the protein follows as

$$M = \frac{0.75}{6.48\times10^{-5}} = \boxed{11,600\text{ g/mol}}$$

◆ The correct answer is **A**.

P.4 ■ Solution

The number-average molar mass will be shifted to

$$\bar{M}_n = \frac{1}{\Sigma\left(\frac{w_i}{M_i}\right)} = \left(\frac{0.97}{430,000}+\frac{0.03}{30,000}\right)^{-1} = 307,100$$

which represents a decrease of about 29%. Membrane osmometry measures $\bar{M}_n$, and hence the molar mass measurement obtained from this technique will be affected substantially. The weight-average molar mass, in turn, will be shifted to

$$\bar{M}_w = \Sigma w_i M_i = 0.97\times10^6 + 0.03\times30,000 = 970,900$$

which represents a decrease of approximately 3%. Light scattering measures $\bar{M}_w$, and hence the molar mass measurement yielded by this technique will not be affected appreciably. Statement 1 is true and statement 2 is false.

◆ The correct answer is **B**.

P.5 ■ Solution

To begin, we find the value of M_V.

$$\bar{M}_V = \left(\Sigma w_i M_i^{\,a}\right)^{1/a} = (0.5\times39,000^{0.75}+0.5\times300,000^{0.75})^{1/0.75} = 155,000$$

The intrinsic viscosity follows from the MHS equation,

$$[\eta] = KM_V^a = \left(9.18\times10^{-5}\right)\times155,000^{0.75} = \boxed{0.717\text{ dL/g}}$$

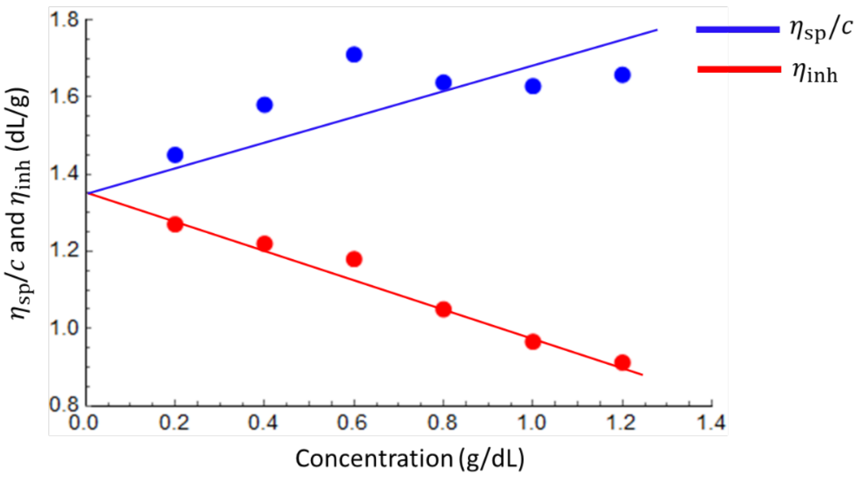
◆ The correct answer is **C**.

P.6 ■ Solution

Part 1: The data processed with the Huggins and Kraemer equations are summarized below.

Conc. (g/dL)	t/t_0	$\left(\frac{t}{t_0}-1\right)/c$	$\frac{\ln(t/t_0)}{c}$
0.20	1.290	1.45	1.27
0.40	1.632	1.58	1.22
0.60	2.026	1.71	1.18
0.80	2.310	1.64	1.05
1.00	2.628	1.63	0.966
1.20	2.989	1.66	0.912

The Huggins line is obtained by plotting the data in the blue column versus the data in the yellow column; the Kraemer line, in turn, is obtained by plotting the data in the red column versus the data in the yellow column. The lines are extrapolated to the vertical axis, yielding $[\eta]$ = 1.35 dL/g.



Part 2: All we have to do is substitute $[\eta]$ = 1.35 dL/g in the MHS equation and solve for M_v,

$$[\eta] = 3.52\times10^{-5} M_V^{0.80} \rightarrow M_V = \left(\frac{[\eta]}{3.52\times10^{-5}}\right)^{1/0.80}$$

$$\therefore M_V = \left(\frac{1.35}{3.52\times10^{-5}}\right)^{1/0.80} = \boxed{537,000}$$

♦ The correct answer is **D**.

P.7 ■ Solution

Due to their regular nature, isotactic polymers will readily crystallize from the molten state when thermodynamic conditions are favorable. Syndiotactic polymers can crystallize, but do so fairly slowly due to steric interference and the fact that repeat units comprising two monomers are required to organize into repeating arrays. Lastly, the nearly random placement of side groups in atactic polymers prevents them from developing regular structures. The correct order is then Y > Z > X.

♦ The correct answer is **C**.

P.8 ■ Solution

Brief comments on each compound follow. BHT, along with 4-isopropenyl phenol, is an antioxidant that polymerizes readily with isoprene, butadiene, styrene, and methyl methacrylate. The resulting copolymers are good antioxidants for their parent polymers at copolymer compositions of only 10 to 15 mol% of polimerizable antioxidants. Hydrated alumina is a common inorganic flame retardant, but there are also viable organic retardants; most are halogen-containing materials such as 2,4,6-tribromophenyl and pentabromophenyl. 2-mercaptobenzothiazole is an example of moderately fast primary vulcanization accelerator (in contrast to, say, its derivative zinc-2-mercaptobenzothiazole, which is a *very fast* accelerator). Lastly, the derivatives of 2(2-hydroxyphenyl) 2H-benzotriazole have been recognized to be the most effective compounds for protecting polymeric materials from photodegradation. The correct association is P-1, Q-4, R-3, S-2.

♦ The correct answer is **D**.

P.9 ▪ Solution

All molecular modifications increase the glass transition temperature of a polymer chain. The modifications in question all reduce the freedom of movement or reduce backbone flexibility, thereby increasing T_g. Polyethylene, a polymer with very flexible backbone, has a T_g of about -20°C, whereas PTFE, a polymer with an exceptionally rigid backbone, has a T_g of 115°C.

♦ The correct answer is **D**.

P.10 ▪ Solution

Part 1: The stress is given by the relation

$$\tau = \frac{\rho RT}{M}\left(\Lambda - \frac{1}{\Lambda^2}\right)$$

In the case at hand, the strain is ε = 100% and the extension ratio $\Lambda = 1 + \varepsilon = 2.0$. Substituting the pertaining variables in the equation above, we obtain

$$\tau = \frac{\rho RT}{M}\left(\Lambda - \frac{1}{\Lambda^2}\right) = \frac{0.97\times\left(8.3\times10^7\right)\times303}{8000}\times\left(2.0-\frac{1}{2.0^2}\right) = 5.34\times10^6\ \text{dyn/cm}^2$$

$$\therefore \boxed{\tau = 0.534\ \text{MN/m}^2}$$

♦ The correct answer is **B.**

Part 2: Young's modulus can be estimated with the relation

$$E = \frac{3\rho RT}{M} = \frac{3\times0.97\times\left(8.3\times10^7\right)\times303}{8000} = 9.15\times10^6\ \text{dyn/cm}^2$$

$$\therefore \boxed{E = 0.915\ \text{MN/m}^2}$$

♦ The correct answer is **A**.

P.11 ▪ Solution

For a Troutonian polymer, the elongational (or tension) viscosity is independent of the elongational flow rate and equals three times the shear viscosity, i.e., $\mu_{\text{el}} = 3\mu_{\text{sh}}$. Polymers may exhibit other forms of mechanical behavior with respect to tensile stress. If the elongational viscosity increases with tensile stress, the material is said to exhibit *tension stiffening*; this is analogous to shear thickening in shear flow. In turn, if the elongational viscosity decreases with tensile stress, the material is said to exhibit *tension thinning*; this is analogous to shear thinning in shear flow.

♦ The correct answer is **D**.

P.12 ▪ Solution

1. True. There are 150 carbon atoms between crosslinks on average. Referring to the structure of cis-isoprene, the number of monomer units between crosslinks is 160/4 = 40. The mass between crosslinks is then 40×68 = 2720 g/mol. Accordingly, Young's modulus can be estimated as (the same formula used in Problem 10.2)

$$E = \frac{3\rho RT}{M} = \frac{3\times0.96\times\left(8.3\times10^7\right)\times303}{2720} = 2.66\times10^7\ \text{dyn/cm}^2$$

$$\therefore \boxed{E = 2.66\ \text{MN/m}^2}$$

2. False. While it is true that random copolymers with equal numbers of different monomers do not crystallize, such a process is indeed possible when the one of the monomers is sufficiently superior to that of the other. When one comonomer dominates, the other comonomer can be considered as a source of defects that separate homopolymer sequences of the major comonomer. If the homopolymer sequences are sufficiently long, they may be capable of crystallizing.

3. True. If the biphasic model (amorphous phase + crystalline phase) is accepted for a semicrystalline sample, the specific volume can be written as

$$v = x_c v_c + \left(1 - x_c\right) v_a$$

where v = 1/0.92 cm³/g, v_c = 1/1.0 cm³/g, and v_a = 1/0.86 cm³/g are the specific volumes of the semicrystalline sample, the hypothetical 100% crystalline polymer, and the amorphous polymer, respectively, and x_c is the degree of crystallinity of the sample. Substituting and solving for x_c, we obtain

$$v = x_c v_c + (1 - x_c) v_a$$

$$\therefore 0.92^{-1} = x_c \times 1.0^{-1} + (1 - x_c) \times 0.86^{-1}$$

$$\therefore \boxed{x_c = 46.6\%}$$

4. True. Indeed, the rms end-to-end distance equals the square root of 6 times the radius of gyration.

5. True. All we have to do is substitute the pertinent data in the equation we were given,

$$T_g = T_g^{\infty} - \frac{K}{\bar{M}_n} = 100 - \frac{200{,}000}{2500} = \boxed{20^{\circ}\mathrm{C}}$$

6. False. In actuality, Rayleigh has shown that

$$\frac{I}{I_0} = \frac{8\pi^4\alpha^2}{\lambda^4 r^2}\left(1 + \cos^2\theta\right)$$

where I_0 is the intensity of the incident beam, I is the intensity of the scattering radiation at a distance r from the particle and an angle of θ to the incident beam, λ is the wavelength of the radiation, and α is the polarizability of the particle. As can be seen, the intensity of the scattered radiation is *inversely* proportional to the fourth power of wavelength. The polarizability α of the molecule is proportional to the refractive index increment dn/dc (where c is concentration) and to the relative molar mass of the molecule in question; that is,

$$\alpha = \frac{1}{2\pi}\frac{dn}{dc}\frac{M}{N_A}$$

Accordingly, I/I_0 is dependent on the relative molar mass of the molecules involved in the light scattering. At this point, we define the Rayleigh ratio

$$R_\theta = \frac{Ir^2}{I_0}$$

so that we can restate the first equation as

$$R_\theta = \frac{8\pi^4\alpha^2\left(1 + \cos^2\theta\right)}{\lambda^4}$$

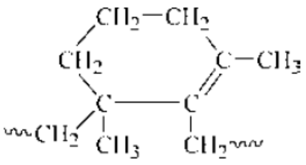
Taking all the constants in a single super constant K and including the expression for α presented above, we obtain

$$R_\theta = K\left(1 + \cos^2\theta\right)Mc$$

where c is the concentration of molecules. This latter equation indicates that we can determine the molar mass of the molecule from the experimental measurement of the Rayleigh ratio in a light scattering experiment.

7. False. Vulcanization is achieved by the addition of sulfur, not phosphorus, to the polymer. Ordinary vulcanized natural rubber contains 0.5 – 5 parts (by weight) of combined sulfur vulcanizing agent per 100 parts of rubber. Approximately one of every few hundred chain atoms is crosslinked in a typical rubber with good properties.

8. True. Indeed, cyclized rubber results when natural rubber is treated with acids such as H_2SO_4. The rubber is usually natural rubber, but another diene rubber, such as synthetic polyisoprene, may also be used. The molecular structure of a cyclized rubber is illustrated below.



9. False. On the contrary, a large LOI is associated with lower flammability. The values of LOI for selected polymers are listed below. The statement is also not entirely correct when it posits that LOI values are solid indicators of a material's behavior under fire; their use in this respect is limited because real fires differ in important respects from the conditions of the LOI test. For example, real fires often generate a considerable velocity of air, which sweeps away degradation products that may otherwise suppress combustion. Secondly, the temperature of the air in real fires may rapidly become very high. Hot, well-oxygenated air is more likely to initiate substantial damage to organic polymers than the gaseous mixture used in the LOI test.

Limiting oxygen index of some polymers	LOI (%)
Poly(methyl methacrylate)	17.3
Poly(propylene)	17.4
Poly(ethylene)	17.4
Poly(vinyl alcohol)	22.5
Poly(vinyl chloride)	45.0
Poly(vinylidene chloride)	60.0
PTFE	95.0

10. False. On the contrary, the temperatures achieved in solution polymerization – and, as a consequence, the reaction rates achieved – are inevitably limited by the boiling point of the solvent. Another drawback of this process is the possibility of chain transfer and subsequent contamination of the product, which makes it hard to attain a high-purity polymer.

11. False. On the contrary, a carbocation is in general much more reactive than a free radical, *especially* at high temperatures. One example of cationic polymerization is the production of poly(isobutylene), which, catalyzed with BF_3, can yield polymers of molar mass well in excess of one million in just a few seconds. The inherently fast reaction rate associated with cationic polymerization is not always an asset, since it can lead to undesirable side reactions.

12. False. Anionic polymerization is in fact associated with a very low frequency of side reactions, which leads to narrower molecular weight distributions than those associated with free radical polymerization.

13. False. In certain cases, the measured glass transition temperature can vary widely according to the technique being used to measure it. One extreme example is that of the measured T_g values of poly(methyl methacrylate), which range from 110°C using dilatometry (i.e., a technique in which volume changes are monitored) to 160°C using a rebound elasticity technique. Nevertheless, this is an outstanding case; in general, the variation of measured T_g values is contained within a small temperature range.

14. True. The glass transition temperature of the polyblend can be calculated as

$$\frac{1}{T_g} = \frac{M_{PVC}}{\left(T_g\right)_{PVC}} + \frac{M_{PTFE}}{\left(T_g\right)_{PTFE}} \rightarrow \frac{1}{T_g} = \frac{0.55}{80} + \frac{0.45}{115}$$

$$\therefore \boxed{T_g = 92.7^\circ\mathrm{C}}$$

15. True. The shear viscosity of most polymers decreases with increasing strain rates. One simplistic explanation for this property is that the molecular chains are disentangled and stretched out at high rates of deformation and can therefore slide past each other with more ease, so that, in macroscopic terms, a reduced bulk viscosity is observed.

16. True. Appealing to the WLF equation, we have

$$\log_{10}\frac{\eta(T)}{\eta\left(T_g\right)} = -\frac{C_1\left(T-T_g\right)}{C_2+\left(T-T_g\right)} \rightarrow \log_{10}\frac{\eta(400)}{10^{12}} = -\frac{17.44\times(400-353)}{51.6+(400-353)}$$

$$\therefore \boxed{\eta(400) = 4860\ \mathrm{Pa\cdot s}}$$

17. True. The general expression for transfer in the presence of a solvent is

$$\frac{1}{\bar{X}_n} = \frac{1}{\bar{X}_{no}} + \frac{C_S[\mathrm{S}]}{[\mathrm{M}]}$$

For the molar mass to be halved, then $1/\bar{X}_n$ becomes $2/\bar{X}_{no}$. Accordingly,

$$\frac{2}{\bar{X}_{no}}-\frac{1}{\bar{X}_{no}}=\frac{C_S[\mathrm{S}]}{[\mathrm{M}]}\rightarrow[\mathrm{S}]=\frac{1}{C_S\bar{X}_{no}}[\mathrm{M}]$$

$$\therefore[\mathrm{S}]=\frac{2.5\times10^{-4}}{0.15\times10^{-4}}[\mathrm{M}]=16.7[\mathrm{M}]$$

18. False. The loss tangent is the ratio of the loss modulus to the storage modulus; that is,

$$\tan\delta=\frac{G''}{G'}=\frac{120}{100}=1.2$$

The phase angle is then arctan 1.2 = 50.2°. The result would have been about 39.8 degrees had we computed $\tan\delta$ as the incorrect ratio 100/120.

P.13 ■ Solution

1. True. The creep equation for a Maxwell element is such that

$$\varepsilon(t)=\sigma_0\left(\frac{1}{E}+\frac{t}{\eta}\right)\rightarrow J=\frac{\varepsilon(t)}{\sigma_0}=\frac{1}{E}+\frac{t}{\eta}$$

$$\therefore J=\frac{1}{1.0\times10^9}+\frac{60}{\left(300\times10^9\right)\times0.1}=\boxed{3.0\times10^{-9}\ \mathrm{m}^2/\mathrm{N}}$$

2. False. The normal stress in the specimen is calculated as

$$\sigma_0=\frac{F}{A}=\frac{10\times10^3}{0.03}=333\ \mathrm{kPa}$$

The deformation recovered follows from Hooke's law,

$$\sigma_0=E\varepsilon_s\rightarrow\varepsilon_s=\frac{\sigma_0}{E}$$

$$\therefore\varepsilon_s=\frac{333\times10^3}{10^9}=\boxed{3.33\times10^{-4}}$$

3. True. The permanent set is due to viscous flow and can be calculated as

$$\varepsilon_d=\frac{\sigma_0 t}{\eta}=\frac{\left(333\times10^3\right)\times60}{\left(300\times10^9\right)\times0.1}=\boxed{6.66\times10^{-4}}$$

ANSWER SUMMARY

Problem 1		T/F
Problem 2		C
Problem 3		A
Problem 4		B
Problem 5		C
Problem 6	**6.1**	Open-ended pb.
	6.2	D
Problem 7		C
Problem 8		D
Problem 9		D
Problem 10	**10.1**	B
	10.2	A
Problem 11		D
Problem 12		T/F
Problem 13		T/F

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