

Montogue



## GATE Polymer Science and Engineering

### ◆ 20 Practice Questions

Lucas Monteiro Nogueira

Here's a set of 20 fully solved problems for applicants to the GATE Polymer Science and Engineering sub-exam. The problems were taken from a carefully researched assortment of textbooks. All problems are solved step by step. Enjoy! ■

#### ► PROBLEMS

**Problem 1.** The following is a list of 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 on 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 2.** Match the polymers in column A to the corresponding applications in column B.

Column A	Column B
<b>P.</b> Nylon	<b>I.</b> Keyboard keycaps
<b>Q.</b> Polyethylene	<b>II.</b> Automotive tires
<b>R.</b> Cis-1,4-polyisoprene	<b>III.</b> Pipes
<b>S.</b> Acrylonitrile-butadiene-styrene	<b>IV.</b> Packaging

- (A)** P-III; Q-IV; R-II; S-I
- (B)** P-IV; Q-III; R-II; S-I
- (C)** P-IV; Q-II; R-III; S-I
- (D)** P-III; Q-IV; R-I; S-II

**Problem 3.** Match the polymers in column A to the corresponding polymerization methods in column B.

Column A	Column B
<b>P.</b> Bisphenol A polycarbonate	<b>I.</b> Cationic
<b>Q.</b> Polyethylene	<b>II.</b> Step-growth
<b>R.</b> Poly(styrene-b-butadiene)	<b>III.</b> Coordination
<b>S.</b> Butyl rubber	<b>IV.</b> Anionic

- (A)** P-III; Q-IV; R-II; S-I
- (B)** P-II; Q-III; R-IV; S-I
- (C)** P-II; Q-III; R-I; S-IV
- (D)** P-III; Q-IV; R-I; S-II

**Problem 4.** Two monodisperse polystyrenes are mixed in equal quantities by weight. One polymer has a molecular weight of 39,000 and the other has a molecular weight of 292,000. What is the intrinsic viscosity of the blend in benzene at 25°C? The Mark-Houwink-Sakurada constants for polystyrene/benzene are  $K = 9.18 \times 10^{-5}$  dL/g and  $a = 0.74$ .

- (A) 0.386 (dL/g)
- (B) 0.443 (dL/g)
- (C) 0.623 (dL/g)
- (D) 0.871 (dL/g)

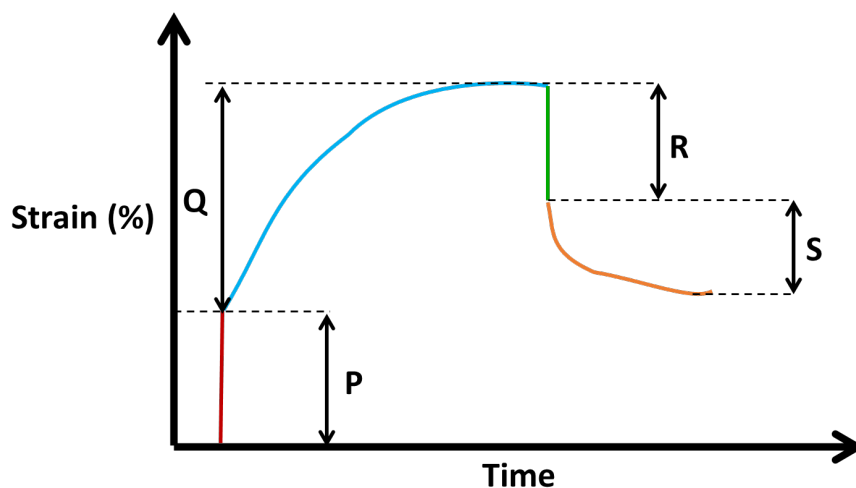
**Problem 5.** The use of universal calibration curves in gel permeation chromatography is based upon the principle that the product  $[\eta]M$ , the hydrodynamic volume, is the same for all polymers at equal elution volumes. If the retention volume for a monodisperse polystyrene (PS) sample of 50,000 molecular weight is 100 mL in toluene at 25°C, what is the molecular weight of a fraction of poly(methyl methacrylate) at the same elution volume in toluene at 25°C? The Mark-Houwink parameters,  $K$  and  $a$ , for PS are given as  $7.54 \times 10^{-3}$  mL·g<sup>-1</sup> and 0.783, respectively; the corresponding values for PMMA are  $8.12 \times 10^{-3}$  mL·g<sup>-1</sup> and 0.71.

- (A) 76,000
- (B) 88,000
- (C) 102,000
- (D) 114,000

**Problem 6.** Solution viscosities for a particular polymer and solvent are plotted in the form  $(\eta - \eta_0)/(c\eta_0)$  against  $c$ , where  $\eta$  is the viscosity of a solution of polymer with concentration  $c$  g·cm<sup>-3</sup> and  $\eta_0$  is the solvent viscosity. The plot is a straight line with an intercept of 1.50 cm<sup>3</sup>·g<sup>-1</sup> and a slope of 0.9 cm<sup>6</sup>·g<sup>-2</sup>. The value of Huggins's constant for this polymer-solvent pair is:

- (A) 0.2
- (B) 0.3
- (C) 0.4
- (D) 0.5

**Problem 7.** A plot of strain (%) versus time for a given polymer is shown below. Match the segments specified in the plot to definitions I – IV.



- I. Viscoelastic deformation
- II. Elastic deformation
- III. Viscoelastic recovery
- IV. Elastic recovery

- (A) P.I; Q.IV; R.III; S.II
- (B) P.I; Q.III; R.II; S.IV
- (C) P.II; Q.I; R.III; S.IV
- (D) P.II; Q.I; R.IV; S.III

**Problem 8.** The ratio of extensional viscosity to dynamic viscosity for a Troutonian polymer equals:

- (A) 1/6
- (B) 1/3
- (C) 3
- (D) 6

**Problem 9.** What is, most nearly, the percent volume change that is expected at 100% elongation of a natural rubber sample with Poisson's ratio equal to 0.49? Assume that no crystallization occurs during deformation.

- (A) 0.9%
- (B) 1.4%
- (C) 1.9%
- (D) 2.4%

**Problem 10.** Match the rubber additives in column A to the corresponding functions in column B.

Column A	Column B
P. Tetramethyl thiuram disulfide	I. Peptizer
Q. Xylyl mercaptan	II. Antiozonant
R. Sulfur	III. Accelerator
S. Microcrystalline wax	IV. Cross-linking agent

- (A) P-III; Q-IV; R-I; S-II
- (B) P-II; Q-III; R-IV; S-I
- (C) P-III; Q-I; R-IV; S-II
- (D) P-I; Q-III; R-IV; S-II

**Problem 11.** An ideal rubber is stretched to 1.10 times its unstretched length at 27°C (300 K) while supporting a stress of 150 psi. After aging for 10 days in air at 127°C, the stress at 1.10 times its unstretched length is only 100 psi. If the original polymer contained 0.015 mol of cross-links per unit volume, how many moles of cross-links per unit volume were lost or gained on aging?

- (A) The rubber lost 0.0075 mol of cross-links per unit volume.
- (B) The rubber lost 0.005 mol of cross-links per unit volume.
- (C) The rubber lost 0.0025 mol of cross-links per unit volume.
- (D) The rubber gained 0.0025 mol of cross-links per unit volume.

**Problems 12 and 13**

**12.** Calculate the copolymer composition formed at an early stage of the reaction of methyl methacrylate (monomer 1) at 5 mol/liter and 5-ethyl-2-vinyl pyridine (monomer 2) at 1 mol/liter concentration. Reactivity ratios are  $r_1 = 0.40$  and  $r_2 = 0.69$ .

- (A) The copolymer shall have 1.32 moles of monomer 1 for every mole of monomer 2.
- (B) The copolymer shall have 2.64 moles of monomer 1 for every mole of monomer 2.
- (C) The copolymer shall have 3.96 moles of monomer 1 for every mole of monomer 2.
- (D) The copolymer shall have 4.15 moles of monomer 1 for every mole of monomer 2.

**13.** What molar ratio of monomers in the feed produces a copolymer composition which is the same as the feed composition?

- (A) [monomer 1]/[monomer 2] = 0.41
- (B) [monomer 1]/[monomer 2] = 0.52
- (C) [monomer 1]/[monomer 2] = 0.66
- (D) [monomer 1]/[monomer 2] = 0.84

### Problems 14 and 15

**14.** Consider the free-radical polymerization of styrene (molar mass = 104 g/mol) initiated by di-*t*-butyl peroxide at 60°C. For a solution of 0.01 M peroxide and 1.0 M styrene in benzene, the initial rate of polymerization is  $1.5 \times 10^{-7}$  mol/liter·sec, the rate of termination is  $10^8$  liter/mol·sec, and the number-average molecular weight  $\bar{M}_n$  of the polymer produced is 138,000. What is the propagation rate constant for this system?

- (A)  $k_p = 46.5$  L/(mol·s)
- (B)  $k_p = 53.7$  L/(mol·s)
- (C)  $k_p = 89.5$  L/(mol·s)
- (D)  $k_p = 141$  L/(mol·s)

**15.** What is the average lifetime of a macroradical during initial stages of polymerization in this system?

- (A) 1.1 s
- (B) 2.6 s
- (C) 4.7 s
- (D) 8.3 s

**Problem 16.** Consider a free-radical polymerization initiation reaction that uses as initiator a peroxide with half-life equal to 0.24 sec. The initial concentration of peroxide is  $0.06 \text{ mol L}^{-1}$ . Assuming an efficiency of 75%, the initiation reaction proceeds at a rate equal to \_\_\_\_\_ (◆  $\text{mol L}^{-1} \text{ s}^{-1}$ , rounded to two decimal places).

**Problem 17.** Suppose that a hypothetical polymer P undergoes a crystallization process that can be modeled with Avrami kinetics. The crystalline growth parameter is 2 and the rate constant is  $0.01 \text{ s}^{-2}$  at 90°C. After 10 seconds, the percent crystallinity of P is \_\_\_\_\_ (◆ %, rounded to one decimal place).

**Problem 18.** A polymer sample of  $0.50 \text{ cm}^3$  volume described by the following rheological model ( $\dot{\gamma}$  in  $\text{sec}^{-1}$ ,  $\tau$  in Pa) is placed in a parallel plate viscometer with a plate separation of 0.01 cm. A weight of 0.500 g is applied to the movable plate by appropriate pulleys, so that, after 10 seconds, the plate will be displaced by a distance of \_\_\_\_\_ (◆  $\mu\text{m}$ , rounded to one decimal place).

$$\text{Model: } \dot{\gamma} = 2.00 \times 10^{-2} \tau^2$$

**Problem 19.** Suppose that three Maxwell viscoelastic elements described by the following parameters are associated in parallel. The relaxation modulus, 10 seconds after a stress has been applied to this system, is \_\_\_\_\_ (◆ GPa, rounded to two decimal places).

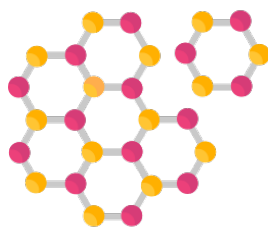
$$E_1 = 0.1 \text{ GPa}; \tau_1 = 10 \text{ s}$$

$$E_2 = 1.0 \text{ GPa}; \tau_2 = 20 \text{ s}$$

$$E_3 = 10 \text{ GPa}; \tau_3 = 30 \text{ s}$$

( $E$  = Elastic modulus,  $\tau$  = Relaxation time)

**Problem 20.** Vinyl acetate was polymerized in a free-radical reaction. The initial monomer concentration was 1 mol/liter and its concentration after 1 h was 0.85 mol/liter. Chloroform was present as a chain transfer agent, with concentrations of 0.01 mol/liter at time zero and 0.007 mol/liter after 1 h. The chain transfer constant  $C$  in this case is \_\_\_\_\_ (◆ Dimensionless, rounded to two decimal places).



**Answer key is on the next page! Problem solutions also begin on the next page.**

## ▶ ANSWER KEY

Problem	Answer	Problem	Answer
I	D	II	A
2	B	12	B
3	B	13	B
4	C	14	D
5	A	15	C
6	C	16	0.24 – 0.28
7	D	17	62.0 – 64.0
8	C	18	18.0 – 20.0
9	B	19	7.50 – 8.50
10	C	20	2.00 – 2.40

## ▶ SOLUTIONS

### 1 → D

All molecular modifications mentioned in the problem increase the glass transition temperature of a polymer chain. The modifications reduce the freedom of movement or reduce backbone flexibility, thereby raising  $T_g$ . Polyethylene, a polymer with a very flexible backbone, has a  $T_g$  of about  $-20^\circ\text{C}$ , whereas polytetrafluoroethylene (PTFE), a polymer with an exceptionally rigid backbone, has a  $T_g$  of  $115^\circ\text{C}$ .

### 2 → B

Nylon and its many variants are commonly used in soft packaging. Polyethylene, much like other commodity plastics such as PVC, is commonly used in pipe manufacturing. Polyisoprene is a prominent type of rubber employed in automotive tires. ABS is a reliable plastic for applications such as automotive dashboards, instrument panels, and keyboard keycaps.

### 3 → B

Bisphenol A polycarbonate is produced by condensation (step-growth) polymerization of bisphenol A and carbonic acid. Polyethylene is a commodity plastic that can be produced by coordination polymerization, which is a type of addition polymerization catalyzed by transition metal complexes such as the so-called Ziegler-Natta catalysts. Polymerization of styrene and butadiene is the most well-known example of anionic polymerization. Butyl rubber, more properly known as polyisobutylene, is synthesized by cationic polymerization of isobutylene.

### 4 → C

We first compute the viscosity-average molecular weight,

$$\bar{M}_V = \left[ \sum (w_i M_i^a) \right]^{\frac{1}{a}}$$

$$\therefore \bar{M}_V = \left( 0.5 \times 39,000^{0.74} + 0.5 \times 292,000^{0.74} \right)^{\frac{1}{0.74}} = 150,600$$

Substituting in the MHS equation, we get

$$[\eta] = K\bar{M}_V^a = (9.18 \times 10^{-5}) \times 150,600^{0.74} = \boxed{0.623 \text{ (dL/g)}}$$

### 5 → A

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

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

$$\begin{aligned} \therefore (7.54 \times 10^{-3}) \times (5 \times 10^4)^{1+0.783} &= (8.12 \times 10^{-3}) \times M_v^{1+0.71} \\ \therefore 1.80 \times 10^6 &= (8.12 \times 10^{-3}) \times M_v^{1.71} \\ \therefore M_v &= \left( \frac{1.80 \times 10^6}{8.12 \times 10^{-3}} \right)^{\frac{1}{1.71}} = \boxed{76,000} \end{aligned}$$

### 6 → C

The plot in question is based on the linear relationship

$$\frac{1}{c} \left( \frac{\eta - \eta_0}{\eta_0} \right) = [\eta] + k_H [\eta]^2 c$$

Clearly, the intercept with the vertical axis gives the intrinsic viscosity  $[\eta]$ ,

$$[\eta] = 1.50 \text{ cm}^3 \cdot \text{g}^{-1}$$

In turn, the slope gives Huggins's constant  $k_H$ ,

$$\begin{aligned} k_H [\eta]^2 &= 0.9 \rightarrow k_H = \frac{0.9}{[\eta]^2} \\ \therefore k_H &= \frac{0.9}{1.5^2} = \boxed{0.40} \end{aligned}$$

### 7 → D

Region P is the linear deformation region. Region Q is the viscoelastic deformation region. Region R is the elastic recovery region. Region S is the viscoelastic recovery region.

### 8 → C

The ratio of extensional viscosity to dynamic viscosity is known as Trouton's ratio,  $Tr$ . For so-called Troutonian polymers, the extensional viscosity equals 3 times the dynamic viscosity, hence  $Tr = 3$ .

### 9 → B

At 100% deformation, the longitudinal strain is

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

Taking a Poisson ratio  $\nu = 0.49$  for natural rubber, the volumetric strain may be determined as

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

### 10 → C

Tetramethyl thiuram disulfide acts as an accelerator in rubber synthesis. Xylyl mercaptan is a peptizing agent (i.e., a chemical additive that facilitates rubber plasticization and thereby shortens the time required for industrial plastification). Sulfur is of course the oldest cross-linking agent in rubber vulcanization practice. Microcrystalline waxes are used to protect rubber articles from static ozone attack.

### 11 → A

In either stretched configuration, we may write

$$\sigma = KT(N/2)$$

where  $N/2$  is the density of cross-links per unit volume. When the rubber is originally stretched to  $\alpha = 1.10$ , we have

$$\sigma = 150 = K \times 300 \times 0.015 \quad (\text{I})$$

After aging for 10 days at  $T = 400 \text{ K}$ , we have

$$\sigma = 100 = K \times 400 \times (N/2)_0 \quad (\text{II})$$

Dividing (II) by (I) and solving for  $(N/2)$ ,

$$\frac{100}{150} = \frac{\cancel{K} \times 400 \times (N/2)_0}{\cancel{K} \times 300 \times 0.015}$$

$$\therefore (N/2)_0 = \frac{100}{150} \times \frac{300}{400} \times 0.015 = 0.0075 \text{ mol/vol.}$$

Therefore, the rubber lost  $0.015 - 0.0075 = 0.0075$  mol of cross-links per unit volume.

### 12 → B

The copolymer composition ratio is given by equation (9-13),

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_2[M_2] + [M_1])} = \frac{5.0 \times (0.40 \times 5.0 + 1.0)}{1.0 \times (0.69 \times 1.0 + 5.0)} = 2.64$$

The copolymer shall have 2.64 moles of methyl methacrylate for every mole of 5-ethyl-2-vinyl pyridine.

### 13 → B

The azeotropic composition ratio is given by

$$\left( \frac{[M_1]}{[M_2]} \right)_{\text{azeotrope}} = \frac{1-r_2}{1-r_1} = \frac{1-0.69}{1-0.40} = \boxed{0.517}$$

### 14 → D

The number-average degree of polymerization for the polymer in question is  $\overline{DP}_n = 138,000/104 = 1330$ . Solving for propagation rate constant  $k_p$ , we obtain

$$\overline{DP}_n = 1330 = \frac{k_p^2 [M]^2}{k_t R_p} = \frac{k_p^2 \times 1.0^2}{10^8 \times (1.5 \times 10^{-7})}$$

$$\therefore 1330 = 0.0667 k_p^2$$

$$\therefore k_p = \sqrt{\frac{1330}{0.0667}} = \boxed{141 \text{ L}/(\text{mol} \cdot \text{s})}$$

### 15 → C

The radical lifetime can be estimated as

$$\tau = \frac{k_p [M]}{2k_t R_p} = \frac{141 \times 1.0}{2 \times 10^8 \times (1.5 \times 10^{-7})} = \boxed{4.7 \text{ s}}$$

### 16 → 0.24 – 0.28

The rate associated with the initiation reaction is

$$\frac{d[M]}{dt} = 2fK_d [I]$$

where  $f = 0.75$  is the reaction efficiency,  $[I]$  is the concentration of initiator, and  $K_d$  is the rate constant, which, noting that the initiation reaction is first-order, can be determined from the half-life  $t_{1/2} = 0.24$  sec,

$$K_d = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{0.24} = 2.89 \text{ sec}^{-1}$$

so that

$$\frac{d[M]}{dt} = 2 \times 0.75 \times 2.89 \times 0.06 = \boxed{0.26 \text{ mol L}^{-1} \text{ s}^{-1}}$$

**17 → 62.0 – 64.0**

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

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

**18 → 18.0 – 20.0**

The area of the polymer specimen is  $A = \text{volume}/\text{thickness} = 0.50/0.01 = 50 \text{ cm}^2 = 5 \times 10^{-3} \text{ m}^2$ . The corresponding shear is

$$\tau = \frac{mg}{A} = \frac{(0.5 \times 10^{-3}) \times 9.81}{5 \times 10^{-3}} = 0.981 \text{ Pa}$$

Using the given formula, the shear rate is found as

$$\dot{\gamma} = 2.00 \times 10^{-2} \tau^2 = (2.0 \times 10^{-2}) \times 0.981^2 = 0.0192 \text{ s}^{-1}$$

However, for a parallel-plate viscometer, the shear rate is given by the ratio of sliding velocity  $u$  to plate separation  $y$ , so that

$$\dot{\gamma} = \frac{u}{y} \rightarrow u = \dot{\gamma} y$$

$$\therefore u = 0.0192 \times 0.01 = 1.92 \times 10^{-4} \text{ cm/s}$$

In  $\Delta t = 10$  sec, the plate will be displaced by a distance  $d$  such that

$$d = u \times \Delta t = (1.92 \times 10^{-4}) \times 10 = 1.92 \times 10^{-3} \text{ cm}$$

$$\therefore \boxed{d = 19.2 \mu\text{m}}$$

**19 → 7.50 – 8.50**

The relaxation modulus 10 seconds after the stress has been applied is

$$E(t=10) = 0.1 \times e^{-10/10} + 1.0 \times e^{-10/20} + 10 \times e^{-10/30} = \boxed{7.81 \text{ GPa}}$$

**20 → 2.00 – 2.40**

We first write kinetic differential equations for the monomer M and the transfer agent TH,

$$-\frac{d}{dt}[\text{TH}] = k_{tr} [\text{M}^*][\text{TH}] \quad (\text{I})$$

$$-\frac{d}{dt}[\text{M}] = k_p [\text{M}][\text{M}^*] \quad (\text{II})$$

Dividing (I) by (II), separating variables and integrating,

$$\frac{-d[\text{TH}]/dt}{-d[\text{M}]/dt} = \frac{k_{tr} \cancel{[\text{M}^*]}[\text{TH}]}{k_p [\text{M}] \cancel{[\text{M}^*]}}$$

$$\therefore \frac{d[\text{TH}]}{d[\text{M}]} = \frac{k_{tr} [\text{TH}]}{\underbrace{k_p}_{=C} [\text{M}]}$$

$$\therefore \frac{d[\text{TH}]}{[\text{TH}]} = C \frac{d[\text{M}]}{[\text{M}]}$$

$$\therefore \ln\left(\frac{[\text{TH}]}{[\text{TH}]_0}\right) = C \times \ln\left(\frac{[\text{M}]}{[\text{M}]_0}\right)$$

$$\therefore C = \frac{\ln([\text{TH}]/[\text{TH}]_0)}{\ln([\text{M}]/[\text{M}]_0)} = \frac{\ln(0.007/0.01)}{\ln(0.85/1.0)} = \boxed{2.19}$$



## ► REFERENCES

- CARRAHER, C.E. (2018). *Carraher's Polymer Chemistry*. 10th edition. CRC Press.
- CHANDA, M. (2013). *Introduction to Polymer Science and Chemistry: A Problem-Solving Approach*. 2nd edition. CRC Press.
- FRIED, J.R. (2014). *Polymer Science and Technology*. 3rd edition. Prentice-Hall.
- RODRÍGUEZ, F., COHEN, C., OBER, C.K. and ARCHER, L.A. (2015). *Principles of Polymer Systems*. 6th edition. CRC Press.
- RUDIN, A. (1998). *The Elements of Polymer Science and Engineering*. 2nd edition. Academic Press.



Visit [www.montoguequiz.com](http://www.montoguequiz.com) for more materials on all things science/engineering!