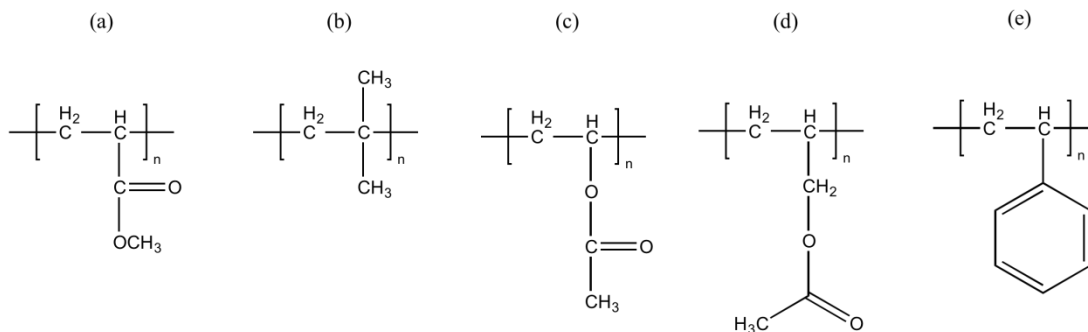


## Rudin & Choi: The Elements of Polymer Science & Engineering, 3rd Edition

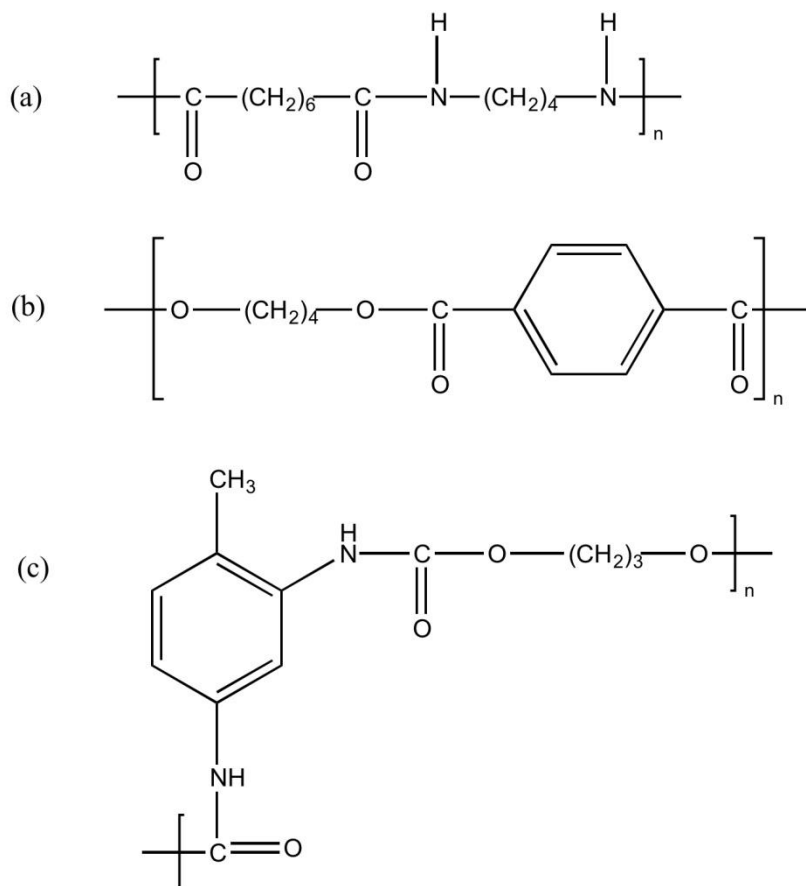
### Chapter 1

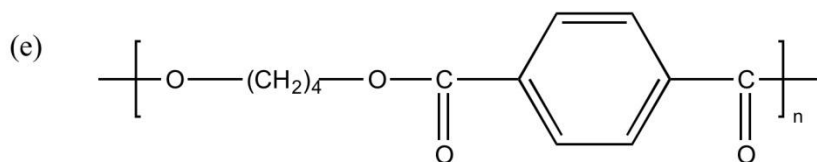
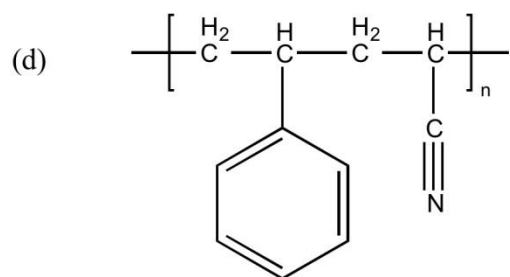
#### Solutions Manual

#### 1-1



#### 1-2

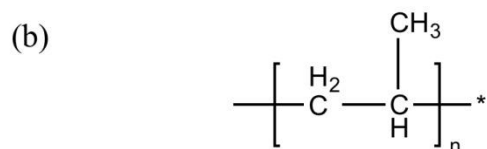
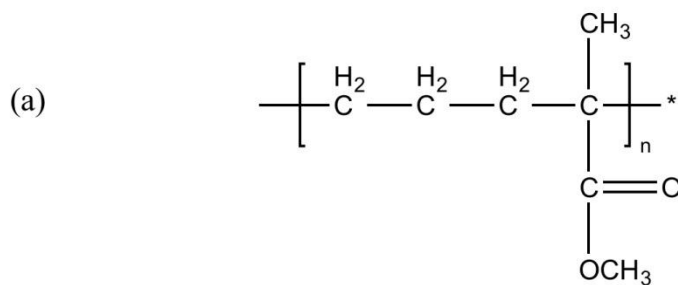


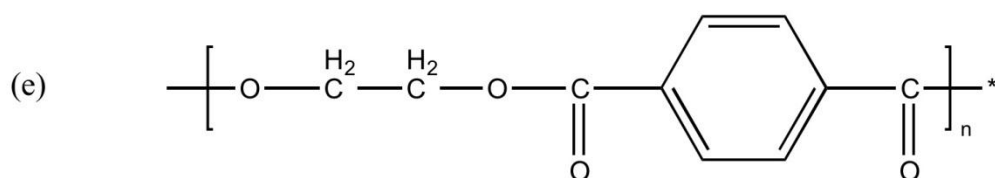
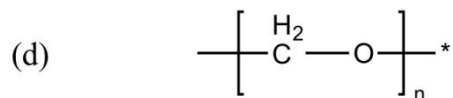
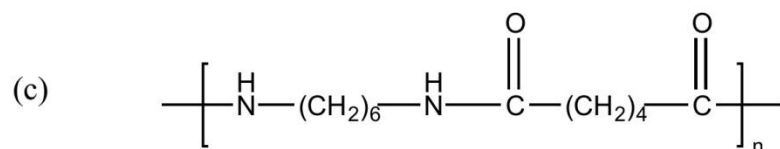
**1-3**

- (a)  $100,000 / 113 = 885$   
 (b)  $100,000 / 192 = 521$   
 (c)  $100,000 / 97 = 1,031$   
 (d)  $100,000 / 162 = 617$

**1-4**

- (a) (i) 2 (ii) 2 (iii) 0 (iv) 4  
 (b) same as in (a)

**1-5**

**1-6**

- (a) polyisobutene (polyisobutylene)
- (b) poly(vinyl chloride) (PVC)
- (c) poly(tetramethylene terephthalate) (poly(butylene terephthalate))
- (d) poly(ethyl methacrylate)
- (e) poly(vinyl acetate)
- (f) poly(methyl acrylate)
- (g) polycaprolactam (nylon 6)
- (h) poly(phenylene oxide)
- (i) poly(para-bromostyrene)
- (j) poly(ethylene-2,5-toluene-urethane) (poly(ethylene-2,5-tolyl-urethane))

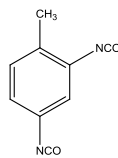
**1-7**

- (a) is too weak mechanically while (c) is too difficult to shape into pipe form. The correct answer is (b).

**1-8**

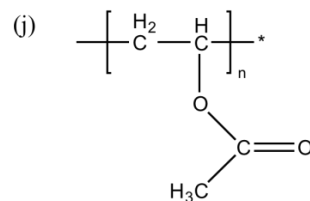
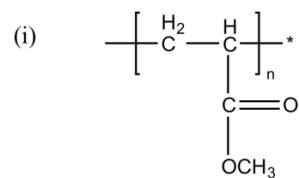
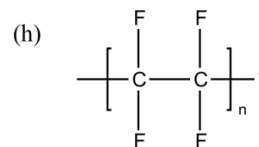
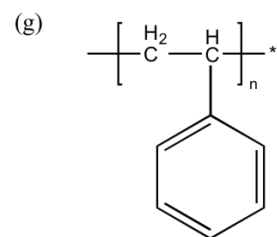
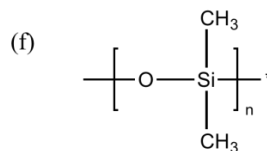
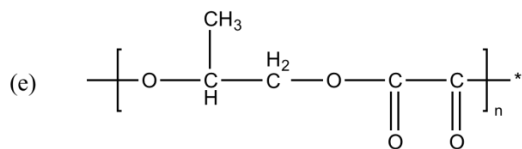
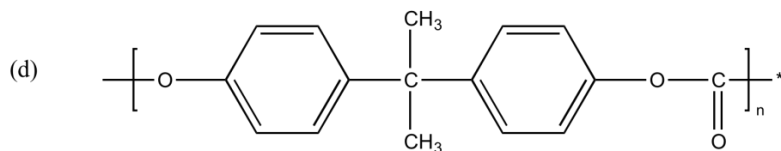
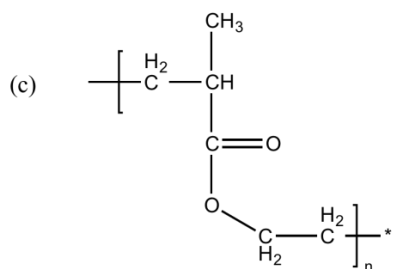
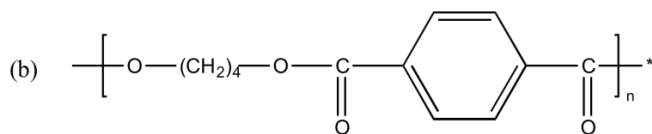
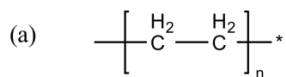
The functionality of glycerol is 3 in every case listed.

## 1-9



React 1 mole of  $\text{HOCH}_2\text{CH}_2\text{OH}$  with 2 moles as in reaction (1-12). Then react the product of this reaction with  $\text{H}-(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{O})_m-\text{H}$  as in reaction (1-13).

## 1-10



**1-11**

The polyisobutene requires a fairly high molecular weight for use in inner tubes and cable coatings, in order to ensure good mechanical strength. Reasonably low viscosity is needed in adhesive and oil additive applications and this calls for lower molecular polymers.

**1-12**

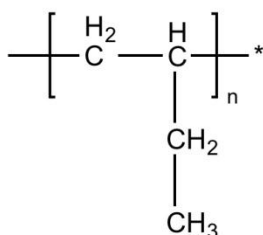
- (a) 4
- (b) 2
- (c) 1

**1-13**

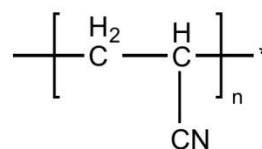
- (a) 2
- (b) The functionality of (2) is 5 since there are 5 active hydrogens on the nitrogens.
- (c) Yes.

**1-14**

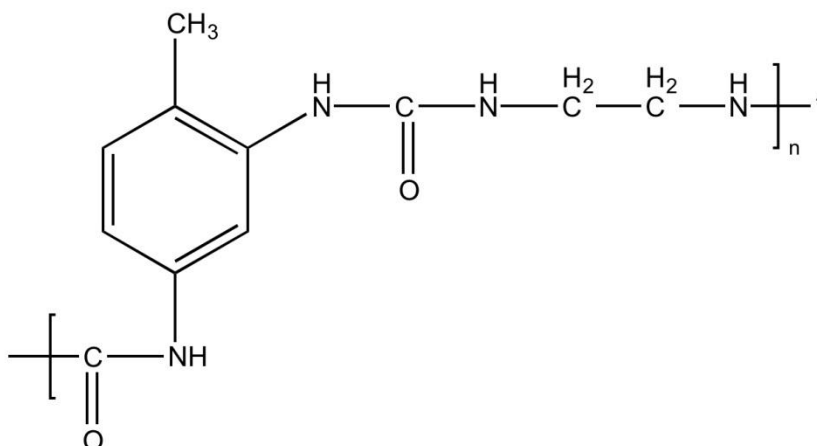
(a)



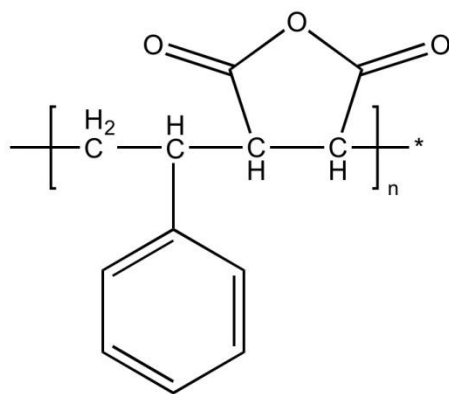
(b)



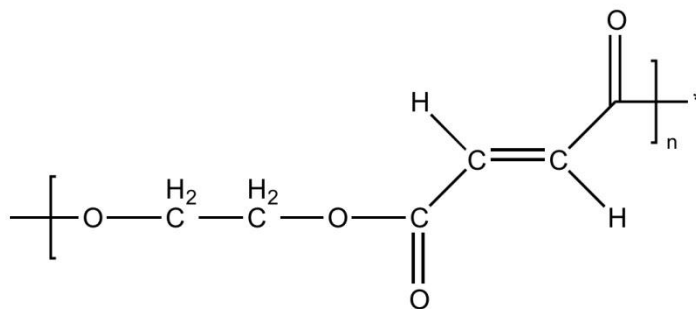
(c)



(d)



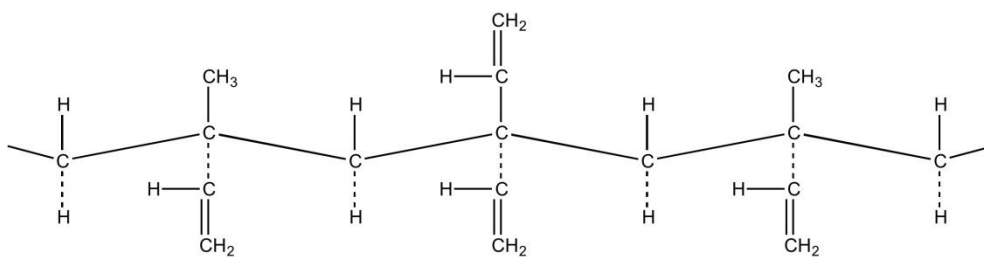
(e)

**1-15**

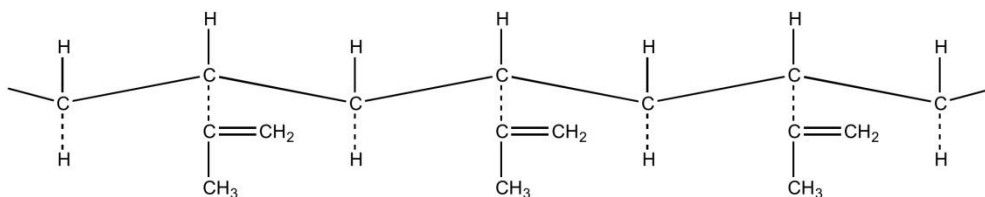
(a) and (d).

**1-16**

(a)



(b)

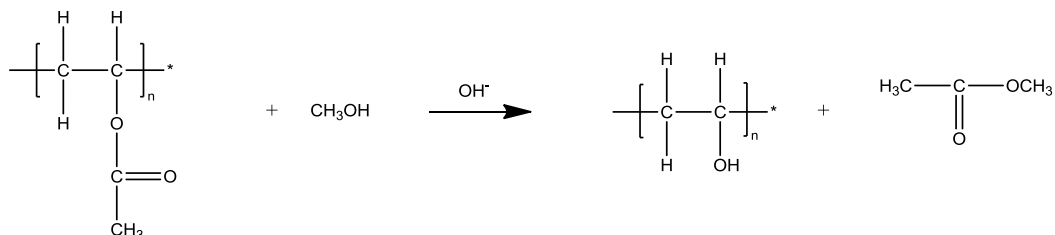


## 1-17

Polyethylene crystallizes very rapidly because its structure is regular and symmetrical and the chain carries no bulky substituents (see also Sect. 4.3). Polyisobutene is amorphous (Sect. 4.5.1) and can therefore exhibit recovery from high extensions.

## 1-18

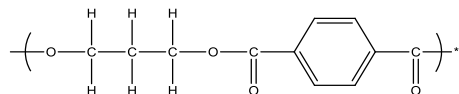
(a)



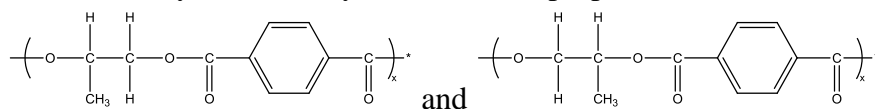
(b) There are a few head-to-head linkages in the poly(vinyl acetate) which produce 1,2-diol structures on alcoholysis to poly(vinyl alcohol). There are insufficient head-to-head placements to register in terms of  $\text{HIO}_4$  consumption but it only takes an average of one such linkage per macromolecule to result in a halving of the molecular weight, as shown. In this case the average number of vinyl alcohol repeating units in the initial macromolecule is  $250,000 / 44 = 5700$  (where the formula weight of the repeating unit is 44 g/mol). It only requires about 1 head-to-head linkage out of an average of 2300 such bonds to result in the observed reduction in molecular weight.

## 1-19

The glycol should be 1,3-propane diol. This molecule is symmetrical and would produce polyester structures like



which will crystallize. Polymers from 1,2-propane diol have the following structures:



A mixture of such structures in the polymer chains would inhibit crystallization because of the different steric requirements of the two positional isomers.

## 1-20

- (a) Formula weight for propylene = 42.  
 Degree of polymerization =  $10^5 / 42 = 2376$ .  
 Number of C-C bonds =  $2 \times 2376 = 4752$  (there are 2 bonds in the main chain per repeating unit).

$$\langle d^2 \rangle = \sigma l^2 \frac{1 + \cos \theta}{1 - \cos \theta}$$

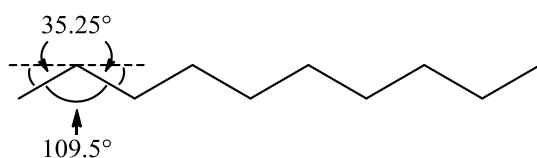
$$\theta = 180 - 109.5 = 70.5^\circ$$

$$\cos \theta = 0.33$$

$$\langle d^2 \rangle = 4753(1.54 \times 10^{-8})^2 \left( \frac{1+0.33}{1-0.33} \right)$$

$$\sqrt{\langle d^2 \rangle} = 150 \times 10^{-8} \text{ cm (rms end-to-end distance)}$$

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



The projection of the bond length on the chain length direction is  $(1.54 \times 10^{-8}) \cos 35.25^\circ = 1.26 \times 10^{-8} \text{ cm}$ .

For  $\sigma = 4753$  the end-to-end distance of the fully extended chain =  $4753(1.26 \times 10^{-8}) = 5989 \times 10^{-8} \text{ cm}$ .

Extensibility =  $(5989 - 150) / 150 = 39$  times.

- (c) Because of the lack of rotational freedom of the real chain and because two segments of the chain cannot occupy the same space (excluded volume effect) the real macromolecule will have a longer rms end-to-end distance than that calculated in part (a) (cf. equation (1-31)). The ratio calculated in part (b) will therefore be lower. Conclusion: the real chain is less extensible.

1-21  $\sqrt{\langle d^2 \rangle} = \sqrt{x l_a^2 + y l_b^2}$

This is a straightforward extension of the ideas behind equation (1-28).

## 1-22

For polyethylene, the torsional potential energy difference between the trans and gauche states (i.e.,  $\Delta e$ ) is 2,100 J/mol (see example 1-2).

At 200°C (473K), the fraction of bonds in the trans state is given by:

$$\frac{\exp\left(-\frac{0}{R \times 473}\right)}{\exp\left(-\frac{0}{R \times 433}\right) + 2 \exp\left(-\frac{2100}{R \times 473}\right)} = \frac{1}{1 + 2 \times 0.5863} = 0.46$$

where  $R = 8.314 \text{ J/(mol-K)}$ .

The fraction of bonds in the gauche states is  $1 - 0.46 = 0.54$  (0.27 for each gauche state).

$$\therefore \langle \cos \phi \rangle = 0.46 \cos 0^\circ + 0.27 \cos 120^\circ + 0.27 \cos 240^\circ = 0.19$$

For polyethylene,  $\theta \approx 71^\circ$  (see Example 1-3).

$$C_\infty = \left( \frac{1 + \cos 71^\circ}{1 - \cos 71^\circ} \right) \left( \frac{1 + 0.19}{1 - 0.19} \right) = 2.89$$

The Kuhn length,  $l_e = \frac{C_\infty l}{\cos(\theta/2)}$ . Here  $l = 0.154 \text{ nm}$ .

$$l_e = \frac{2.89 \times 0.154}{\cos(71^\circ/2)} = 0.55 \text{ nm}$$

## 1-23

For polyethylene, when temperature increases, the number of bonds in *gauche* conformation increases and chain dimension decreases. For silicon polymers, when temperature increases, the number of bonds in *trans* conformation increases, and chain dimension increases.

## 1-24

$$\begin{aligned} \text{(a)} \quad r \rightarrow 0, \quad P(r)4\pi r^2 &= 0 \\ r \rightarrow \infty, \quad P(r)4\pi r^2 &= 0 \end{aligned}$$

In order to determine the  $r$  at which  $P(r)4\pi r^2$  is maximum, let  $k_1 = \left(\frac{3}{2\pi n l^2}\right)^{\frac{3}{2}}$  and

$$k_2 = \frac{3}{2n l^2} \text{ and } k_1' = 4\pi k_1.$$

$$\begin{aligned} \therefore P(r)4\pi r^2 &= 4\pi r^2 k_1 e^{-k_2 r^2} \\ &= k_1' r^2 e^{-k_2 r^2} \end{aligned}$$

$$\begin{aligned} \frac{d}{dr} [P(r)4\pi r^2] &= k_1' r^2 \frac{d}{dr} (e^{-k_2 r^2}) + e^{-k_2 r^2} \frac{d}{dr} (k_1' r^2) \\ &= -k_2 k_1' r^2 e^{-k_2 r^2} \cdot 2r + 2r k_1' e^{-k_2 r^2} \\ &= e^{-k_2 r^2} r (-2k_2 k_1' r^2 + 2k_1') \end{aligned}$$

$$\text{Let } \frac{d}{dr} [P(r)4\pi r^2] = 0.$$

$$e^{-k_2 r^2} = 0 \text{ or } r = 0 \text{ or } -2k_2 k_1' r^2 + 2k_1' = 0$$

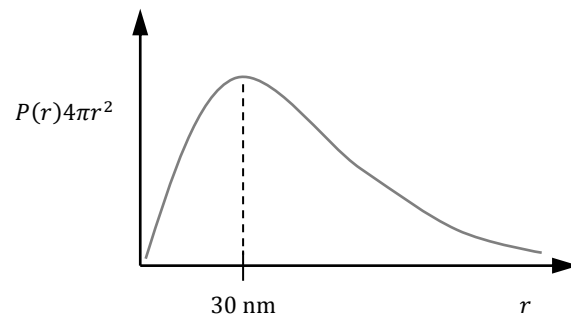
$$\Rightarrow r = \infty$$

$$\text{From } -2k_2 k_1' r^2 + 2k_1' = 0,$$

$$k_2 r^2 = 1$$

$$r^2 = \frac{1}{k_2}$$

$$r = \sqrt{\frac{2nl^2}{3}} = 30 \text{ nm}$$



$$\begin{aligned} \text{(b) } \langle r^2 \rangle &= \frac{\int_0^\infty r^2 P(r)4\pi r^2 dr}{\int_0^\infty P(r)4\pi r^2 dr} \text{ (denominator = 1)} \\ &= 4\pi \int_0^\infty r^4 P(r) dr \\ &= 4\pi \int_0^\infty r^4 \left(\frac{3}{2\pi nl^2}\right)^{\frac{3}{2}} e^{-\frac{3r^2}{2nl^2}} dr \\ &= 4\pi \left(\frac{3}{2\pi nl^2}\right)^{\frac{3}{2}} \int_0^\infty r^4 e^{-\frac{3r^2}{2nl^2}} dr \\ &= 4\pi \left(\frac{3}{2\pi nl^2}\right)^{\frac{3}{2}} \frac{1}{4\pi} \left(\frac{2\pi}{3}\right)^{\frac{3}{2}} (nl^2)^{\frac{5}{2}} \\ &= nl^2 \end{aligned}$$

$$\begin{aligned} \text{(c) } \langle r^2 \rangle &= nl^2 = \frac{900 \times 3}{2} \\ \langle r \rangle &= \sqrt{\frac{900 \times 3}{2}} = 36.7 \text{ nm} \end{aligned}$$

$$\text{(d) } c_\infty = \frac{nl^2}{nl^2} = 1.$$