Problem 56.

(a)

More negative ΔH° values are an indication of more stable species. The ΔH° is most negative for the i-propyl and 2-butyl ions, both of which contain an alkyl substituent bonded to the ionized carbon. Thus it appears that cations are stabilized by alkyl substituents. This effect is also illustrated in part b, in which both ions are derived from the same alkene.

(b)

ΔH° = -690 kJ/mol for ionization of n-propylene
ΔH° = -757 kJ/mol for ionization of isopropylene

Thus ΔH° of rearrangement is -67 kJ/mol.

These numbers indicate that the rearrangement to i-propyl ions is energetically favored.

(c)

$$\Delta H^\circ = (\Delta H^\circ_{f,X} + \Delta H^\circ_{f,H^+}) - \Delta H^\circ_{f,HX^+}$$

For 1-butene:

$$\Delta H^\circ_{f,HX^+} = (\Delta H^\circ_{f,X} + \Delta H^\circ_{f,H^+}) - \Delta H^\circ$$

$$\Delta H^\circ_{f,HX^+} = (1.6\,kJ\,/\,mol) + \Delta H^\circ_{f,H^+} - (-682\,kJ\,/\,mol)$$

$$\Delta H^\circ_{f,HX^+} = \Delta H^\circ_{f,H^+} + 683.6\,kJ\,/\,mol$$

For cis 2-butene:

$$\Delta H^\circ_{f,HX^+} = (-5.8\,kJ\,/\,mol) + \Delta H^\circ_{f,H^+} - (-782\,kJ\,/\,mol)$$

$$\Delta H^\circ_{f,HX^+} = \Delta H^\circ_{f,H^+} + 776.2\,kJ\,/\,mol$$

For rearrangement:

$$\Delta H^\circ = (\Delta H^\circ_{f,H^+} + 683.6\,kJ\,/\,mol) - (\Delta H^\circ_{f,H^+} + 776.2\,kJ\,/\,mol)$$

$$\Delta H^\circ = -93.2\,kJ\,/\,mol$$

Rearrangement goes in the same direction as the propyl ions and is more energetically favored for butyl ions than for propyl ions.

(d)

Isobutene will have three electron supplying alkyl substituents when ionized as shown below, which will provide a largely negative ΔH° as proved in part (a).

$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{}^{+}$$
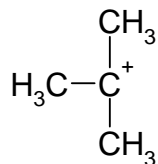
Rearrangement is unlikely, given that it would be highly unfavored energetically as proved in parts (b) and (c).

These arguments do support the notion that isobutene undergoes cationic polymerization.

Problem 57.

$$k_{app} = k_p[P\cdot] = 3.9 \times 10^{-5}\, s^{-1}$$

$$K = \frac{[P_i\cdot][CuBr_2]}{[P_iBr][CuBr]} = \frac{[P\cdot]^2}{[I]^2}$$

Generally for a free radical polymerization, k_p is approximately 10^3 M^{-1}s^{-1}. Substituting:

$$k_{app} = (10^3\, M^{-1}s^{-1})[P\cdot] = 3.9 \times 10^{-5}\, s^{-1}$$

$$[P\cdot] = 3.9 \times 10^{-8}\, M^{-1} = \frac{K^{1/2}}{(.045M)}$$

$$K = 7.51 \times 10^{-13}$$

Problem 58.

$$T_c = \frac{\Delta H^o_{poly}}{\Delta S^o_{poly} + R \ln[M]_{eq}} \qquad \text{(eqn 4.7.6)}$$

$$T_c = \frac{-22900 \; J/mol}{-41.1 \; J/molK + (8.314 \; J/molK)\ln(1)}$$

$$T_c = 557 \; K \rightarrow 284 \; ^oC$$

This value suggests that interference from equilibration is a possibility. For more evidence find the value of K ($\approx 1/[M]_{eq}$) at room temperature:

$$298 \, K = \frac{-22900 \; J/mol}{-41.1 \; J/molK + (8.314 \; J/molK)\ln([M])}$$

$$[M] = 0.014 \rightarrow K = 71$$

The equilibration constant is small enough that equilibration would be a minor problem in the polymerization of Poly(L-lactide). The following plots of T_c vs. ln[M] and ln[M] vs. 1/T (as shown in class) also illustrate this point.

Equilibration in Poly(L-Lactide) Polymerization

Equilibration in Poly(L-Lactide) Polymerization
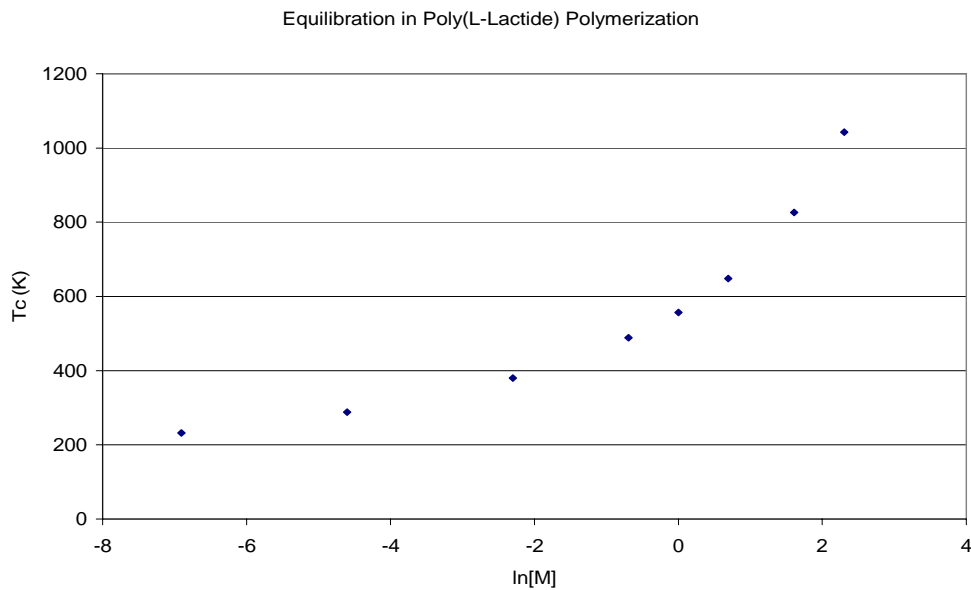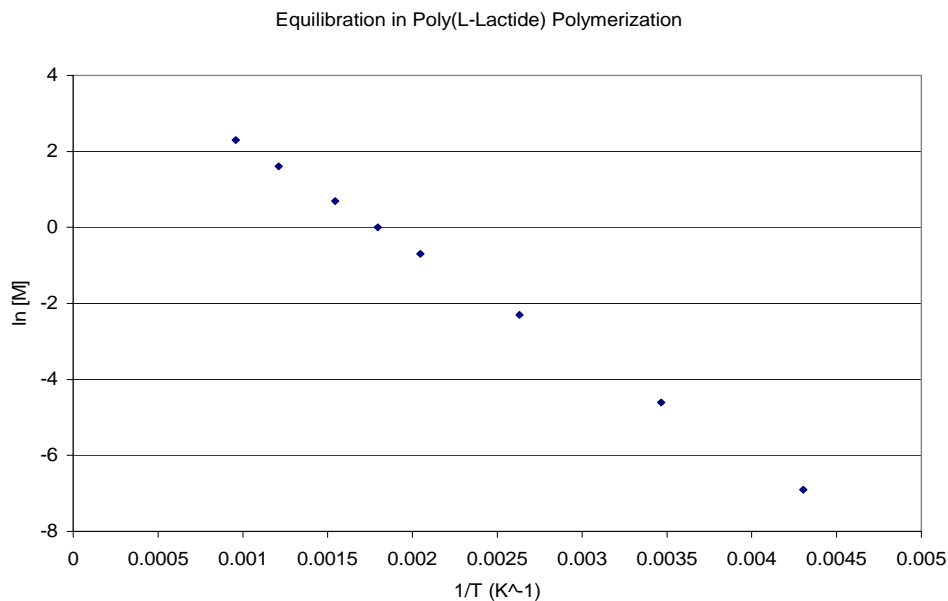
Both the ΔH° and ΔS° values for the polymerization of L-lactide are comparable to those of the majority of cyclic monomers presented in Chapter 4, although there is a discrepancy between the 6-membered alkane and L-lactide. This may seem counterintuitive since L-lactide is also a 6-membered ring, but the difference can be explained by the presence of oxygen heteroatoms in the lactide ring, which increase the ring strain slightly. As a result, L-lactide behaves more like the 5-membered alkane rings than cyclohexane.

Problem 59.

$$RT \ln[M]_{eq} = \Delta H^o_{poly} - T\Delta S^o_{poly}$$

$$[M]_{eq} = e^{\frac{\Delta H^o_{poly} - T\Delta S^o_{poly}}{RT}}$$

At 80°C:

$$[M]_{eq} = e^{\frac{(-22900)+(353)(41.1)}{(8.314)(353)}} = 0.057 \text{ M}$$

$$p = \frac{[M]_0 - [M]}{[M]_0} = \frac{1M - 0.057M}{1M} = .943$$

At 120 °C:

$$[M]_{eq} = e^{\frac{(-22900)+(393)(41.1)}{(8.314)(393)}} = 0.127 \text{ M}$$

$$p = \frac{[M]_0 - [M]}{[M]_0} = \frac{1M - 0.127M}{1M} = .873$$

Problem 60.

The kinetics of ring closing are very slow for high molecular weight polymers (large number of repeat units would lead to very large rings). Thus, in general, we do not need to worry about its effect on the polymerization. Ring closing is somewhat of a problem as the polymer is growing and has very few repeat units.
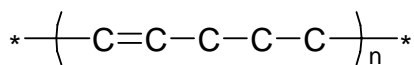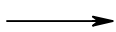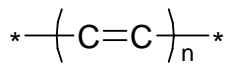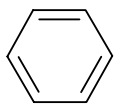
Problem 61.
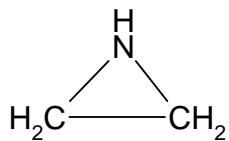
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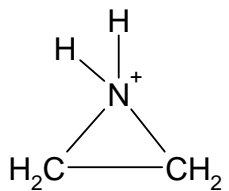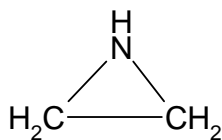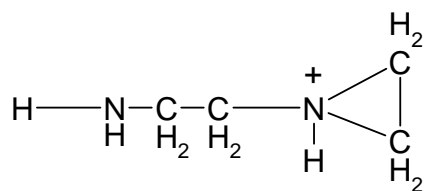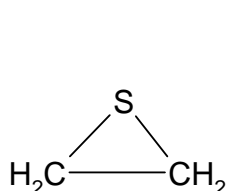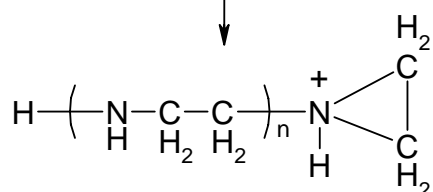
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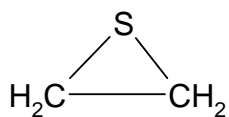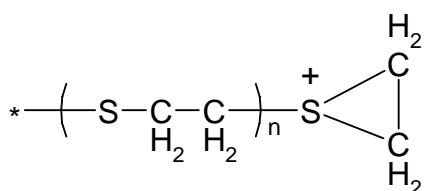
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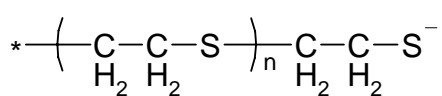
Problem 62.
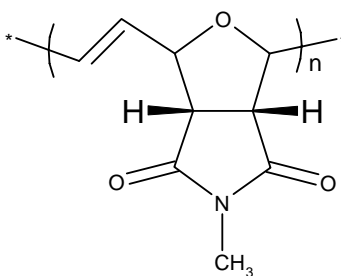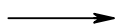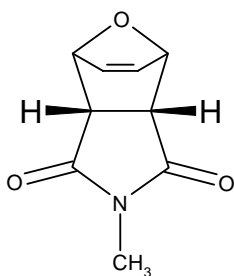
Problem 63.

For an ideal living polymerization the kinetic chain length varies linearly with conversion, and the appropriate molecular weight distribution is the Poisson distribution.

Stated mathematically:

$$\bar{v} = N_n = \frac{M_n}{M_0} = p\frac{[M]_0}{[I]_0} \qquad \rightarrow \qquad \boxed{M_n = p\frac{M_0[M]_0}{[I]_0}}$$

$$\frac{M_w}{M_n} = 1 + \frac{\bar{v}}{(1+\bar{v})^2} \qquad \rightarrow \qquad \boxed{\frac{M_w}{M_n} = 1 + \frac{\dfrac{[M]_0}{[I]_0}p}{\left(1+\dfrac{[M]_0}{[I]_0}p\right)^2}}$$

For a living polymerization, the extent of reaction varies with time as:

$$p = 1 - e^{-k_p[I]_0 t}$$

Substituting this into our equation obtained above for M_n will give us the number average molecular weight as a function of time:

$$M_n = \frac{M_0[M]_0}{[I]_0}\left(1 - e^{-k_p[I]_0 t}\right)$$

The graphs below show these relationships as compared to both free radical polymerization with termination by disproportionation and step growth polymerization.