7.1  (a) Association between the chain-end and the counterion is strongly influenced by solvent polarity.

(b) In free radical polymerization, termination (coupling and disproportionation) is bimolecular; in cationic polymerization, termination is unimolecular; in anionic polymerization, the initiator may be mono-or difunctional and the termination is unimolecular.

(c) The chloro group inductively destabilizes the intermediate carbocation and exerts an unfavorable steric effect on the propagation reaction.

(d) The former would be expected to exhibit the same steric hindrance to backside displacement (reaction 7.33) as α-methylstyrene.

(e) Li+ strongly coordinates the diene, “locking” it into the s-cis conformation during propagation (See reaction 7.57 and 7.58).

(f) Pyridine solvates the propagating anion and the counterion, syndiotactic polymer is more favored.

7.2  (a) p-methoxystyrene > p-methylstyrene > styrene > p-chlorostyrene. Carbocation stability would decrease in the order shown.

(b) 2-vinylpyridine > 4-vinylpyridine > 3-vinylpyridine > styrene. The ring nitrogen stabilizes the intermediate anion by induction in each vinylpyridine monomer in the order of distance from the carbanion site. Additionally, 2- and 4-vinylpyridine stabilize the anion by resonance delocalization, shifting the negative charge to the electronegative nitrogen atom.

7.3  Propylene:

Transfer to monomer

\[
\begin{align*}
\text{Hydride transfer} & \quad \text{CH}_2\text{CH}_3^+ + \text{CH}_2=\text{CHCH}_3 \rightarrow \text{CH}_2=\text{CHCH}_2^+ + \text{CH}_2=\text{CHCH}_3 \\
\text{Proton transfer} & \quad \text{CH}_2\text{CH}_2\text{CH}_3^+ + \text{CH}_2=\text{CHCH}_2 \\
\end{align*}
\]

Proton transfer from the growing chain to the monomer to form the isopropyl carbocation is less likely given the greater stability of the allylic carbocation.
Transfer to polymer

\[
\begin{align*}
\text{Hydride transfer} & \quad \text{CH}_3\text{CH} = \text{CH}_2 \to \text{CH}_3\text{CH}_2\text{CH}_3 \\
\end{align*}
\]

Transfer to polymer should predominate because of the greater stability of the resultant tertiary carbocation.

Isobutylene:

Transfer to monomer

\[
\begin{align*}
\text{H}^+ \text{transfer} & \quad \text{CH}_3\text{CH}_2\text{C}^+ \to \text{CH} = \text{CH}_2 \to \text{CH}_3\text{CH} = \text{CH}_3 \\
\end{align*}
\]

Hydride transfer from monomer to the growing chain to form an allylic carbocation is less likely in this case because of the greater stability of the tertiary carbocation. Transfer of a proton from a chain-end methyl group will also occur to yield a =CH\(_2\) chain end.

Transfer to polymer

\[
\begin{align*}
\text{Hydride transfer} & \quad \text{CH}_3\text{CH}_2\text{C}^+ \to \text{CH}_3\text{CH} = \text{CH}_2 \to \text{CH}_3\text{CH}_2\text{C}^+ \\
\end{align*}
\]

Transfer to monomer will predominate because of the greater stability of the tertiary carbocation.

Chain transfer to both polymer and monomer probably contribute to propylene’s failure to form high-molecular-weight polymer because both tertiary and allylic carbocations are favored over the secondary chain-end carbocation. In the case of isobutylene, the rate of propagation must be greater than the rate of transfer to monomer.

7.6 The structures are:
Their formation may be explained by a series of hydride and methyl shifts.

\[
\tilde{\nu} = \frac{[M]_0}{[I]_0} = 2.0 \times 10^3 = 2000 \\
\overline{DP} = 2\tilde{\nu} = 4000
\]

Since the molecular weight of the repeating unit is 104, \(M_n = 4000 \times 104 = 4.2 \times 10^5\)

At 25°C, \(K_p = 80\) L mol\(^{-1}\) s\(^{-1}\) (Table 7.4)

At 90% conversion, monomer concentration is reduced to 0.10 \([M]_0\).
\[ [M]_0 = [M]_0 e^{-k_p/k_0 t} \]
\[ 0.10 = e^{-80 \times 10^{-3} t} \]
\[ t = 29 \text{s} \]

7.9  
(a) Polymerize one of the monomers with butyllithium initiator at low temperature under an inert atmosphere. When the first monomer is consumed, add the second. In this case, order is not important.

(b) Same as (a) except an electron-transfer initiator such as sodium naphthalene should be used. (See reaction 7.62)

(c) Polymerize styrene with, for example, sodium naphthalene, then quench the living polymer with carbon dioxide.

7.10  
The polymer is the same as that shown in reaction (7.28). The mechanism is analogous to that given except that a delocalized carbanion is the intermediate, and electron movement is in the opposite direction.

7.11  
(a) 

(b)