5

Copolymers, Microstructure, and Stereoregularity

5.1 Introduction

All polymer molecules have unique features of one sort or another at the level of individual repeat units. Occasional head-to-head or tail-to-tail orientations, random branching, and the distinctiveness of chain ends are all examples of such details. In this chapter we shall focus attention on two other situations which introduce structural variation at the level of the repeat unit: the presence of two different monomers, or the regulation of configuration of successive repeat units. In the former case copolymers are produced, and in the latter polymers with differences in tacticity. In the discussion of these combined topics, we use statistics extensively because the description of microstructure requires this kind of approach. This is the basis for merging a discussion of copolymers and stereoregular polymers into a single chapter. In other respects these two classes of materials and the processes which produce them are very different and their description leads us into some rather diverse areas.

The formation of copolymers involves the reaction of (at least) two kinds of monomers. This means that each must be capable of undergoing the same propagation reaction, but it is apparent that quite a range of reactivities is compatible with this broad requirement. We shall examine such things as the polarity of monomers, the degree of resonance stabilization they possess, and the steric hindrance they experience in an attempt to understand these differences in reactivity. There are few reactions for which chemists are successful in explaining all examples with general concepts such as these, and polymerization reactions are no exception. Even for the specific case of free-radical copolymerization, we shall see that reactivity involves the interplay of all these considerations.

To achieve any sort of pattern in configuration among successive repeat units in a polymer chain, the tendency toward random addition must be overcome. Although temperature effects are pertinent here – remember that high temperature is the great randomizer – real success in regulating the pattern of successive addition involves the use of catalysts which "pin down" both the monomer and the growing chain so that their reaction is biased in favor of one mode of addition or another. We shall discuss the Ziegler-Natta catalysts which accomplish this, and shall discover these to be complicated systems for which no single mechanism is entirely satisfactory. We shall also compare these to the more recently developed "single-site" catalysts, which offer great potential for controlling multiple aspects of polymer structure.

For both copolymers and stereoregular polymers, experimental methods for characterizing the products often involve spectroscopy. We shall see that nuclear magnetic resonance (NMR) spectra are particularly well suited for the study of tacticity. This method is also used for the analysis of copolymers.

In spite of the assortment of things discussed in this chapter, there are also related topics that could be included but which are not owing to space limitations. We do not discuss copolymers formed by the step-growth mechanism, for example, or the use of Ziegler-Natta catalysts to regulate geometrical isomerism in, say, butadiene polymerization. Some other important omissions are noted in passing in the body of the chapter.

5.2 Copolymer composition

We begin our discussion of copolymers by considering the free-radical polymerization of a mixture of two monomers, M_1 and M_2. This is already a narrow view of the entire field of copolymers, since more than two repeat units can be present in copolymers and, in addition, mechanisms other than free-radical chain growth can be responsible for copolymer formation. The essential features of the problem are introduced by this simpler special case, and so we shall restrict our attention to this system.

5.2A Rate laws

The polymerization mechanism continues to include initiation, termination, and propagation steps, and we ignore transfer reactions for simplicity. This time, however, there are four distinctly different propagation reactions:

$$-M_1\bullet + M_1 \xrightarrow{k_{11}} -M_1M_1\bullet \tag{5.A}$$

$$-M_1\bullet + M_2 \xrightarrow{k_{12}} -M_1M_2\bullet \tag{5.B}$$

$$-M_2\bullet + M_1 \xrightarrow{k_{21}} -M_2M_1\bullet \tag{5.C}$$

$$-M_2\bullet + M_2 \xrightarrow{k_{22}} -M_2M_2\bullet \tag{5.D}$$

Each of these reactions is characterized by a propagation constant which is labeled by a two-digit subscript: the first number identifies the terminal repeat unit in the growing radical, and the second identifies the added monomer. The rate laws governing these four reactions are

$$R_{p,11} = k_{11}[M_1\bullet][M_1] \tag{5.2.1}$$

$$R_{p,12} = k_{12}[M_1\bullet][M_2] \tag{5.2.2}$$

$$R_{p,21} = k_{21}[M_2\bullet][M_1] \tag{5.2.3}$$

$$R_{p,22} = k_{22}[M_2\bullet][M_2] \tag{5.2.4}$$

In writing eqs 5.2.1 – 5.2.4 we make the customary assumption that the kinetic constants are independent of the size of the radical, and we indicate the concentration of all radicals ending with the M_1 repeat unit, whatever their chain length, by the notation $[M_1\bullet]$. This formalism therefore assumes that only the nature of the radical chain end influences the rate constant for propagation. We refer to this as the *terminal control mechanism.* If we wished to consider the effect of the next-to-last repeat unit in the radical, each of these reactions and the associated rate laws would be replaced by two alternatives. Thus reaction (5.A) becomes

$$-M_1M_1\bullet + M_1 \xrightarrow{k_{111}} -M_1M_1M_1\bullet \tag{5.E}$$

$$-M_2M_1\bullet + M_1 \xrightarrow{k_{211}} -M_2M_1M_1\bullet \tag{5.F}$$

and eq 5.2.1 becomes

$$R_{p,111} = k_{111}[M_1M_1\bullet][M_1] \tag{5.2.5}$$

$$R_{p,211} = k_{211}[M_2M_1\bullet][M_1] \tag{5.2.6}$$

where the effect of the next-to-last, or *penultimate*, unit is considered. For now we shall restrict ourselves to the simpler case where only the terminal unit determines behavior, although systems in which the penultimate effect is important are well known.

The magnitude of the various k values in eqs 5.2.1 – 5.2.4 describes the intrinsic differences between the various modes of addition, and the k's plus the concentration of the different species determine the rates at which the four kinds of addition occur. It is the proportion of different steps which determines the composition of the copolymer produced.

Monomer M_1 is converted to polymer by reactions (5.A) and (5.C); therefore the rate at which this occurs is the sum of $R_{p,11}$ and $R_{p,21}$:

$$-\frac{d[M_1]}{dt} = k_{11}[M_1\bullet][M_1] + k_{21}[M_2\bullet][M_1] \qquad (5.2.7)$$

Likewise, reactions (5.B) and (5.D) convert M_2 to polymer, and the rate at which this occurs is the sum of $R_{p,12}$ and $R_{p,22}$:

$$-\frac{d[M_2]}{dt} = k_{12}[M_1\bullet][M_2] + k_{22}[M_2\bullet][M_2] \qquad (5.2.8)$$

The ratio of eqs 5.2.7 and 5.2.8 gives the relative rates of the two monomer additions and, hence, the ratio of the two kinds of repeat units in the copolymer:

$$\frac{d[M_1]/dt}{d[M_2]/dt} = \frac{k_{11}[M_1\bullet][M_1] + k_{21}[M_2\bullet][M_1]}{k_{12}[M_1\bullet][M_2] + k_{22}[M_2\bullet][M_2]} \qquad (5.2.9)$$

We saw in Chapter 3 that the stationary-state approximation is applicable to free-radical homopolymerizations, and the same is true of copolymerizations. Of course, it takes a brief time for the stationary-state radical concentration to be reached, but this period is insignificant compared to the total duration of a polymerization reaction. If the total concentration of radicals is constant, this means that the rate of crossover between the different types of terminal units is also equal, or that $R_{p,12} = R_{p,21}$:

$$k_{12}[M_1\bullet][M_2] = k_{21}[M_2\bullet][M_1] \tag{5.2.10}$$

or

$$\frac{[M_1\bullet]}{[M_2\bullet]} = \frac{k_{21}[M_1]}{k_{12}[M_2]} \tag{5.2.11}$$

Combining eqs 5.2.9 and 5.2.11 yields one form of the important *copolymer composition equation* or *copolymerization equation*:

$$\frac{d[M_1]/dt}{d[M_2]/dt} = \frac{[M_1]}{[M_2]}\ \frac{(k_{11}/k_{12})[M_1]+[M_2]}{(k_{22}/k_{21})[M_2]+[M_1]} \tag{5.2.12}$$

Although there are a total of four different rate constants for propagation, eq 5.2.12 shows that the relationship between the relative amounts of the two monomers incorporated into the polymer and the composition of the monomer feedstock involves only two ratios of different pairs of these constants. Accordingly, we simplify the notation by defining *reactivity ratios:*

$$r_1 = \frac{k_{11}}{k_{12}} \tag{5.2.13}$$

and

$$r_2 = \frac{k_{22}}{k_{12}} \tag{5.2.14}$$

With these substitutions, eq 5.2.12 becomes

$$\frac{d[M_1]/dt}{d[M_2]/dt} = \frac{[M_1]}{[M_2]}\frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]} = \frac{1+r_1[M_1]/[M_2]}{1+r_2[M_2]/[M_1]} \tag{5.2.15}$$

The ratio $(d[M_1]/dt)/(d[M_2]/dt)$ is the same as the ratio of the numbers of each kind of repeat unit in the polymer formed from the solution containing M_1 and M_2 at concentrations $[M_1]$ and $[M_2]$, respectively. Since the composition of the monomer solution changes as the reaction progresses, eq 5.2.15 applies to the feedstock as prepared only during the initial stages of the polymerization. Subsequently, the instantaneous concentrations in the prevailing mixture apply unless monomer is added continuously to replace that which has reacted and maintain the original composition of the feedstock. We shall assume that it is the initial product formed that we describe when we use eq 5.2.15 so as to remove uncertainty as to the monomer concentrations.

5.2B Composition versus feedstock

As an alternative to eq 5.2.15, it is convenient to describe the composition of both the polymer and the feedstock in terms of the mole fraction of each monomer. Defining F_i as the mole fraction of the ith component in the polymer and f_i as the mole fraction of component i in the monomer solution, we observe that

$$F_1 = 1 - F_2 = \frac{d[M_1]/dt}{d[M_1]/dt + d[M_2]/dt} \qquad (5.2.16)$$

and

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_2] + [M_2]} \qquad (5.2.17)$$

Combining eqs 5.2.15 and 5.2.16 into 5.2.17 yields another form of the copolymer composition equation

$$F_1 = \frac{r_1 f_1{}^2 + f_1 f_2}{r_1 f_1{}^2 + 2 f_1 f_2 + r_2 f_2{}^2} \qquad (5.2.18)$$

This equation relates the composition of the copolymer formed to the instantaneous composition of the feedstock and to the reactivity ratios r_1 and r_2 which characterize the specific system.

Figure 5.1 shows a plot of F_1 versus f_1 – the mole fractions of monomer 1 in the copolymer and in the mixture, respectively – for several values of the reactivity ratios. Inspection of Figure 5.1 brings out the following points:

1. If $r_1 = r_2 = 1$, the copolymer and the feed mixture have the same composition at all times. In this case eq 5.2.18 becomes

$$F_1 = \frac{f_1(f_1 + f_2)}{(f_1 + f_2)^2} = f_1 \qquad (5.2.19)$$

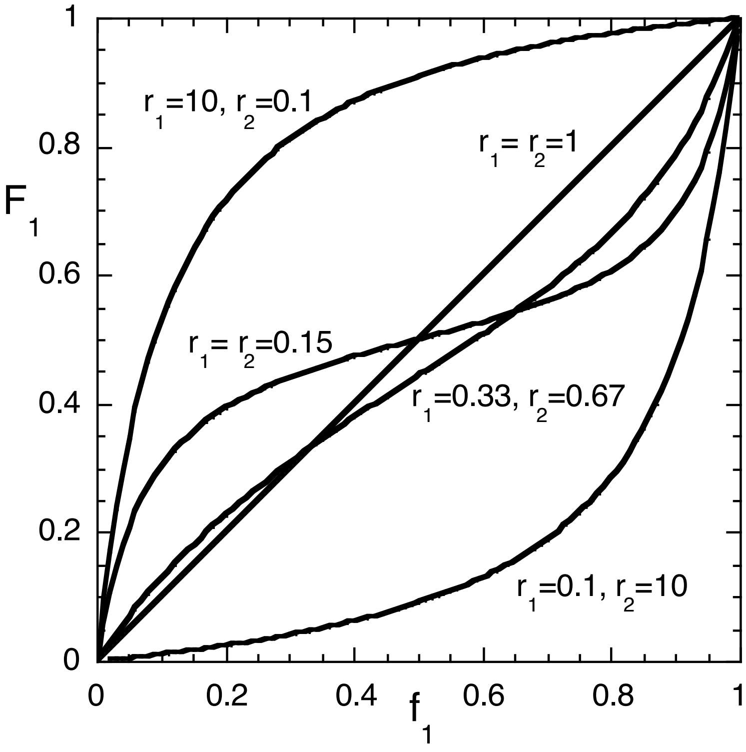


Figure 5.1

Mole fraction of component 1 in the copolymer as a function of feedstock composition, for various reactivity ratios.

2. If $r_1 = r_2$, the copolymer and the feed mixture have the same composition at $f_1 = 0.5$. In this case eq 5.2.18 becomes $F_1 = (r + 1)/2(r + 1) = 0.5$.

3. If $r_1 = r_2$, with both values less than unity, the copolymer is richer in component 1 than the feed mixture for $f_1 < 0.5$, and richer in component 2 than the feed mixture for $f_1 > 0.5$.

4. If $r_1 = r_2$, with both values greater than unity, an S-shaped curve passing through the point (0.5, 0.5) would also result, but in this case reflected across the 45° line compared to item (3).

5. If $r_1 \neq r_2$, with both values less than unity, the copolymer starts out richer in monomer 1 than the feed mixture and then crosses the 45° line, and is richer in component 2 beyond

this crossover point. At the crossover point the copolymer and feed mixture have the same composition. The monomer ratio at this point is conveniently solved by eq 5.2.15:

$$\left(\frac{[M_1]}{[M_2]}\right)_{\text{cross}} = \frac{1 - r_2}{1 - r_1} \tag{5.2.20}$$

For the case of $r_1 = 0.33$ and $r_2 = 0.67$ shown in Figure 5.1, $[M_1]/[M_2]$ equals 0.5 and $f_1 = 0.33$. This mathematical analysis shows that a comparable result is possible with both r_1 and r_2 greater than unity, but is not possible for $r_1 > 1$ and $r_2 < 1$.

6. When $r_1 = 1/r_2$, the copolymer composition curve will be either convex or concave when viewed from the F_1 axis, depending on whether r_1 is greater or less than unity. The further removed from unity r_1 is, the farther the composition curve will be displaced from the 45° line. This situation where $r_1r_2 = 1$ is called an *ideal copolymerization*. The example below explores the origin of this terminology.

There is a parallel between the composition of a copolymer produced from a certain feed and the composition of a vapor in equilibrium with a two-component liquid mixture. The following example illustrates this parallel when the liquid mixture is an ideal solution and the vapor is an ideal gas.

Example 5.1

An ideal gas obeys Dalton's law; that is, the total pressure is the sum of the partial pressures of the components. An ideal solution obeys Raoult's law; that is, the partial pressure of the ith component above a solution is equal to the mole fraction of that component in the solution times the vapor pressure of pure component i. Use these relationships to relate the mole fraction of component 1 in the equilibrium vapor to its mole fraction in a two-component solution and relate the result to the ideal case of the copolymer composition equation.

Solution

We define F_1 to be the mole fraction of component 1 in the vapor phase and f_1 to be its mole fraction in the liquid solution. Here p_1 and p_2 are the vapor pressures of components 1 and 2 in equilibrium with an ideal solution, and p_1^o and p_2^o are the vapor pressures of the two pure liquids. By Dalton's law, $p_{tot} = p_1 + p_2$ and $F_1 = p_1/p_{tot}$, since these are ideal gases and p is proportional to the number of moles. By Raoult's law, $p_1 = f_1p_1^o$, $p_2 = f_2p_2^o$, and $p_{tot} = f_1p_1^o + f_2p_2^o$. Combining the two gives

$$F_1 = \frac{f_1p_1^o}{f_1p_1^o + f_2p_2^o} = \frac{f_1\left(p_1^o/p_2^o\right)}{f_1\left(p_1^o/p_2^o\right) + f_2}$$

Now examine eq 5.2.18 for the case of $r_1 = 1/r_2$:

$$F_1 = \frac{r_1f_1^2 + f_1f_2}{r_1f_1^2 + 2f_1f_2 + (1/r_1)f_2^2} = \frac{r_1f_1(r_1f_1 + f_2)}{(r_1f_1 + f_2)^2} = \frac{r_1f_1}{r_1f_1 + f_2}$$

This is identical to the ideal liquid-vapor equilibrium if r_1 is identified with p_1^o/p_2^o.

The vapor pressure ratio measures the intrinsic tendency of component 1 to enter the vapor phase relative to component 2. Likewise r_1 measures the tendency of M_1 to add to M_1• relative to M_2 adding to M_2•. In this sense there is a certain parallel, but it is based on M_1• as a reference radical and hence appears to be less general than the vapor pressure ratio. Note, however, that $r_1 = 1/r_2$ means $k_{11}/k_{12} = k_{21}/k_{22}$. In this case the ratio of rate constants for monomer 1 relative to monomer 2 is the same regardless of the reference radical examined. This shows the parallelism to be exact.

Because of the analogy with liquid-vapor equilibrium, copolymers for which $r_1 = 1/r_2$ are said to be ideal. For those nonideal cases in which the copolymer and feedstock happen to have the same composition, the reaction is called an *azeotropic polymerization*. Just as in the case of azeotropic distillation, the composition of the reaction mixture does not change as copolymer is formed if the composition corresponds to the azeotrope. The proportion of the two monomers at this point is given by eq 5.2.20.

In this section we have seen that the copolymer composition depends to a large extent on the four propagation constants, although it is sufficient to consider these in terms of the two reactivity ratios r_1 and r_2. In the next section we shall examine these ratios in somewhat greater detail.

5.3 Reactivity ratios

The parameters r_1 and r_2 are the vehicles by which the nature of the reactants enter the copolymer composition equation. We shall call these *radical* reactivity ratios simply reactivity ratios, although similarly defined ratios also describe copolymerizations that involve ionic intermediates. There are several important things to note about reactivity ratios:

1. The single subscript used to label r is the index of the radical.
2 r_1 is the ratio of two propagation constants involving radical 1: the ratio always compares the propagation constant for the same monomer adding to the radical relative to the

propagation constant for the addition of the other monomer. Thus if $r_1 > 1$, $M_1\bullet$ adds M_1 in preference to M_2; if $r_1 < 1$, $M_1\bullet$ adds M_2 in preference to M_1.

3. Although r_1 is descriptive of radical $M_1\bullet$, it also depends on the identity of monomer 2; the pair of parameters r_1 and r_2 are both required to characterize a particular system and the product r_1r_2 is used to quantify this by a single parameter.

4. The reciprocal of a radical reactivity ratio can be used to quantify the reactivity of monomer M_2 by comparing its rate of addition to radical $M_1\bullet$ relative to the rate of M_1 adding $M_1\bullet$.

5. As the ratio of two rate constants, a radical reactivity ratio follows the Arrhenius equation with an apparent activation energy equal to the difference in the activation energies for the individual constants. Thus for r_1, $E_{app}{}^* = E_{p,11}{}^* - E_{p,12}{}^*$. Since the activation energies for propagation are not large to begin with, their difference is even smaller. Accordingly, the temperature dependence of r is relatively small.

5.3A Effects of r values

The reactivity ratios of a copolymerization system are the fundamental parameters in terms of which the system is described. Since the copolymer composition equation relates the compositions of the product and the feedstock, it is clear that values of r can be evaluated from experimental data in which the corresponding compositions are measured. We shall consider this evaluation procedure in Section 5.6, where it will be found that this approach is not as free of ambiguity as might be desired. For now we shall simply assume that we know the desired r values for a system; in fact, extensive tabulations of such values exist. An especially convenient source of this information is the *Polymer Handbook* [1]. Table 5.1 lists some typical r values at 60 °C.

Although Table 5.1 is rather arbitrarily assembled, note that it contains no system for which r_1 and r_2 are *both* greater than unity. Indeed, such systems are very rare. We can understand this by recognizing that, at least in the extreme case of very large r's, these monomers would tend to simultaneously homopolymerize. Because of this preference toward homopolymerization, any copolymer that does form in systems with r_1 and r_2 both greater than unity will be a block-type polymer with very long sequences of a single repeat unit. Since such systems are only infrequently encountered, we shall not consider them further.

M_1	M_2	r_1	r_2	r_1r_2
Acrylonitrile	Methyl vinyl ketone	0.61	1.78	1.09
	Methyl methacrylate	0.13	1.16	0.15
	α-Methyl styrene	0.04	0.20	0.008
	Vinyl acetate	4.05	0.061	0.25
Methyl methacrylate	Styrene	0.46	0.52	0.24
	Methacrylic acid	1.18	0.63	0.74
	Vinyl acetate	20	0.015	0.30
	Vinylidene chloride	2.53	0.24	0.61
Styrene	Vinyl acetate	55	0.01	0.55
	Vinyl chloride	17	0.02	0.34
	Vinylidene chloride	1.85	0.085	0.16
	2-Vinyl pyridine	0.55	1.14	0.63
Vinyl acetate	1-Butene	2.0	0.34	0.68
	Isobutylene	2.15	0.31	0.67
	Vinyl chloride	0.23	1.68	0.39
	Vinylidene chloride	0.05	6.7	0.34

Table 5.1

Values of reactivity ratios r_1 and r_2 and the product r_1r_2 for a few copolymers at 60 °C; data from L. J. Young in [1].

Table 5.1 also lists the product r_1r_2 for the systems included. These products lie in the range between zero and unity, and it is instructive to consider the character of the copolymer produced toward each of these extremes.

In the extreme case where $r_1r_2 = 0$ because both r_1 *and* r_2 equal zero, the copolymer adds monomers with perfect alternation. This is apparent from the definition of r, which compares the addition of the same monomer to the other monomer for a particular radical. If both r's are zero, there is no tendency for a radical to add a monomer of the same kind as the growing end, whichever species is the terminal unit. When only one of the r's is zero, say r_1, then alternation occurs whenever the radical ends with an $M_1\bullet$ unit. There is thus a tendency toward alternation in this case, although it is less pronounced than in the case where both r's are zero. Accordingly, we find increasing tendency toward alternation as $r_1 \rightarrow 0$ and $r_2 \rightarrow 0$, or, more succinctly, as the product $r_1r_2 \rightarrow 0$.

At the other end of the commonly encountered range we find the product $r_1r_2 \rightarrow 1$. As noted above, this limit corresponds to ideal copolymerization and means the two monomers have the same relative tendency to add to both radicals. Thus if $r_1 \rightarrow 10$, monomer 1 is 10 times more likely to add to $M_1\bullet$ than monomer 2. At the same time $r_2 = 0.1$, which also means that monomer 1 is 10 times more likely to add to M_2. In this case the radicals exert the same influence, so the monomers add at random in the proportion governed by the specific values of the r's.

Recognition of these differences in behavior points out an important limitation on the copolymer composition equation. The equation describes the overall composition of the copolymer, but gives no information whatsoever about the *distribution* of the different kinds of repeat units within the polymer. While the overall composition is an important property of the copolymer, the detailed microstructural arrangement is also a significant feature of the molecule. It is possible for copolymers with the same overall composition to have very different properties because of the differences in microstructure. Reviewing the three categories presented in Chapter 1, we see the following:

1. Alternating structures are promoted by $r_1 \rightarrow 0$ and $r_2 \rightarrow 0$, e.g.:

$$M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2$$

2. Random structures are promoted by $r_1r_2 \rightarrow 1$, e.g.:

$$M_1M_2M_2M_2M_1M_1M_2M_1M_1M_2M_1M_2M_1M_2M_1M_2M_2M_1M_1M_2$$

3. "Blocky" structures are promoted by $r_1r_2 > 1$, e.g.:

$$M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_2M_2M_2M_2M_2M_2M_2M_2M_2M_2$$

Each of these polymers has a 50:50 proportion of the two components, but the products probably differ in properties. As examples of such differences, we note the following:

4. Alternating copolymers, while relatively rare, are characterized by combining the properties of the two monomers along with structural regularity. We will see in Chapter 13 that a very high degree of regularity – extending all the way to stereoregularity in the configuration of the repeat units – is required for crystallinity to develop in polymers.

5. Random copolymers tend to average the properties of the constituent monomers in proportion to the relative abundance of the two comonomers.

6. Block copolymers are closer to blends of homopolymers in properties, but without the latter's tendency to undergo phase separation. As a matter of fact, diblock copolymers can be used as surfactants to bind immiscible homopolymer blends together and thus improve their mechanical properties. Block copolymers are generally prepared by sequential addition of monomers to living polymers, rather than by depending on the improbable $r_1r_2 > 1$ criterion in monomers, as was discussed in Chapter 4.

Returning to the data of Table 5.1, it is apparent that there is a good deal of variability among the r values displayed by various systems. We have already seen the effect this produces on the overall copolymer composition; we shall return to this matter of microstructures in Section 5.5. First, however, let us consider the obvious question. What factors in the molecular structure of two monomers govern the kinetics of the different addition steps? This question is considered in the following sections; for now we look for a way to systematize the data as the first step toward an answer.

5.3B Relation of reactivity ratios to chemical structure

We noted above that the product r_1r_2 can be used to locate a copolymer along an axis between alternating and random structures. It is by means of this product that some values from Table 5.1, supplemented by other results for additional systems, have been organized in Figure 5.2. Figure 5.2 has been constructed according to the following general principles:

1. Various monomers are listed along the base of the triangle.
2. The triangle is subdivided into an array of diamonds by lines drawn parallel to the two sides of the triangle.
3. The spacing of the lines is such that each monomer along the base serves as a label for a row of diamonds.

4. Each diamond marks the intersection of two such rows and therefore corresponds to two comonomers.

5. The r_1r_2 product for the various systems is the number entered in each diamond.

6. The individual monomers have been arranged in such a way as to achieve to the greatest extent possible the values of r_1r_2 that approach zero toward the apex of the triangle and values of r_1r_2 which approach unity toward the base of the triangle.

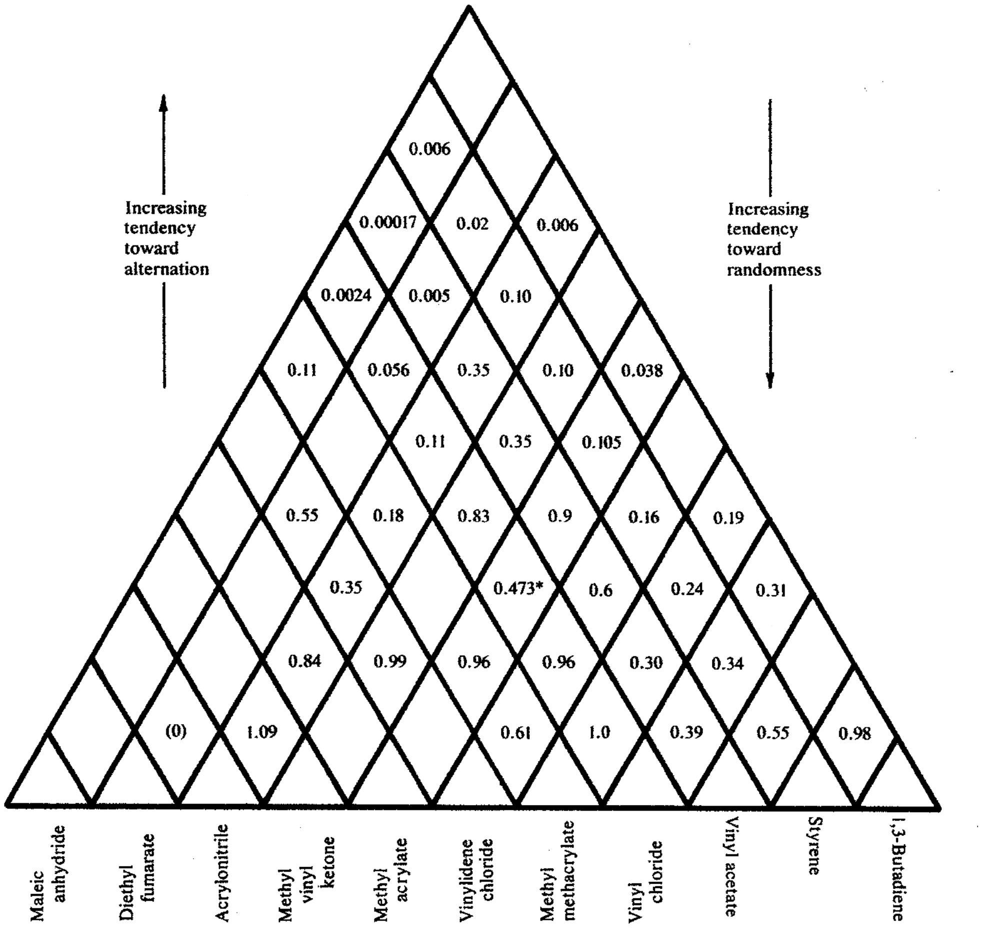


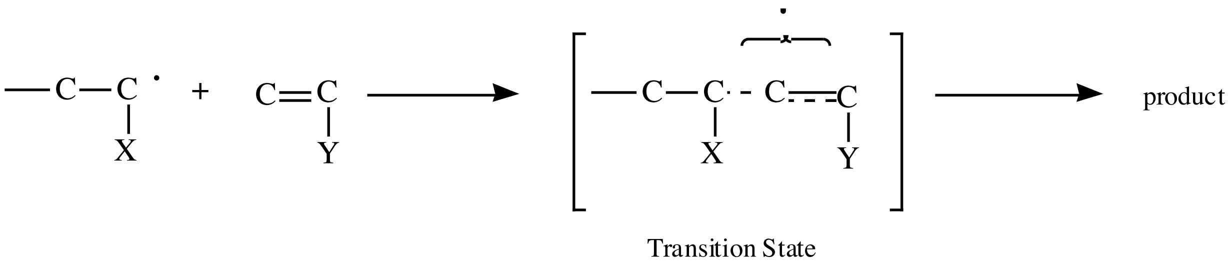
Figure 5.2

The product r_1r_2 for copolymers whose components define the intersection where the numbers appear. The value marked * is determined in Example 5.4; other values are from [1].

Before proceeding with a discussion of this display, it is important to acknowledge that the criteria for monomer placement can be met only in part. For one thing, there are combinations for which data are not readily available. Incidentally, not all of the r_1r_2 values in Figure 5.2 were measured at the same temperature, but, as noted above, temperature effects are expected to be relatively unimportant. Also, there are outright exceptions to the pattern sought: generalizations about chemical reactions always seem to be plagued by these. In spite of some reversals of ranking, the predominant trend moving upward from the base along any row of diamonds is a decrease in r_1r_2 values.

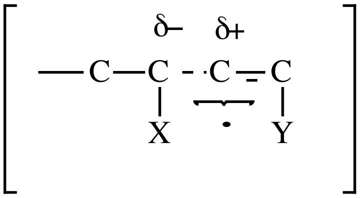
From the geometry of this triangular display, it follows immediately – if one overlooks the exceptions – that the more widely separated a pair of comonomers are in Figure 5.2, the greater is their tendency toward randomness. We recognize a parallel here to the notion that widely separated elements in the periodic table will produce more polar bonds than those which are closer together, and vice versa. This is a purely empirical and qualitative trend. The next order of business is to seek an explanation for its origin in terms of molecular structure. If we focus attention on the electron-withdrawing or electron-donating attributes of the substituent(s) on the double bond, we find that the substituents of monomers which are located toward the right-hand corner of the triangle in Figure 5.2 are recognized as electron donors. Likewise, the substituents in monomers located toward the left-hand corner of the triangle are electron acceptors. The demarcation between the two regions of behavior is indicated in Figure 5.2 by reversing the direction of the lettering at this point. Pushing this point of view somewhat further, we conclude that the sequence acetoxy < phenyl < vinyl is the order of increase in electron-donating tendency. Chloro < carbonyl < nitrile is the order of increase in electron-withdrawing tendency. The positions of diethyl fumarate and vinylidene chloride relative to their mono-substituted analogs indicates that “more is better” with respect to these substituent effects. The location of methyl methacrylate relative to methyl acrylate also indicates additivity, this time with partial compensation of opposing effects.

The reactivity ratios are kinetic in origin, and therefore reflect the mechanism or, more specifically, the transition state of a reaction. The transition state for the addition of a vinyl monomer to a growing radical involves the formation of a partial bond between the two species, with a corresponding reduction of the double-bond character of the vinyl group in the monomer:

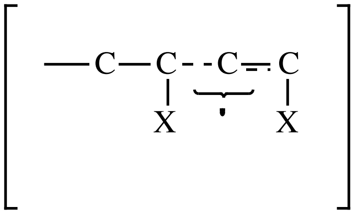


(5.G)

If substituent X is an electron donor and Y an electron acceptor, then the partial bond in the transition state is stabilized by a resonance form [I] which attributes a certain polarity to the emerging bond:



[I]



[II]

The contribution of this polar structure to the bonding lowers the energy of the transition state. This may be viewed as a lower activation energy for the addition step and thus a factor which promotes this particular reaction. The effect is clearly larger the greater difference in the donor-acceptor properties of X and Y. The transition state for the successive addition of the same monomer (whether X or Y substituted) is structure [II]. This involves a more uniform distribution of charge because of the identical substituents and thus lacks the stabilizing effect of the polar resonance form. The activation energy for this mode of addition is greater than that for alternation, at least when X and Y are sufficiently different.

Although we use the term *resonance* in describing the effect of polarity in stabilizing the transition state in alternating copolymers, the emphasis of the foregoing is definitely on polarity rather than resonance *per se*. It turns out, however, that resonance plays an important role in free-radical polymerization, even when polarity effects are ignored. In the next section we examine some evidence for this and consider the origin of this behavior.

5.4 Resonance and reactivity

The tendency toward alternation is not the only pattern in terms of which copolymerization can be discussed. The reactivities of radicals and monomers may also be examined as a source of insight into copolymer formation. The reactivity of radical 1 copolymerizing with monomer 2 is measured by the rate constant k_{12}. The absolute value of this constant can be determined from copolymerization data (r_1) and studies yielding absolute homopolymerization constants (k_{11}):

$$k_{12} = \frac{k_{11}}{r_1} \tag{5.4.1}$$

Table 5.2 lists a few cross-propagation constants calculated by eq 5.4.1. Far more extensive tabulations than this have been prepared by correlating copolymerization and homopolymerization data for additional systems.

Examination of Table 5.2 shows that the general order of increasing *radical* activity isstyrene < acrylonitrile < methyl acrylate < vinyl acetate. An additional observation is that any one of these species shows the reverse order of reactivity for the corresponding monomers. As *monomers*, the order of reactivity in Table 5.2 is styrene > acrylonitrile > methyl acrylate >

vinyl acetate. These and similar rankings based on more extensive comparisons are summarized in terms of substituents in Table 5.3.

	Radical			
Monomer	Styrene	Acrylonitrile	Methyl acrylate	Vinyl acetate
Styrene	145	49,000	14,000	230,000
Acrylonitrile	435	1,960	2,510	46,000
Methyl acetate	203	1,310	2,090	23,000
Vinyl acetate	2.9	230	230	2,300

Table 5.2

Values of the cross-propagation constants k_{12} for four monomer-radical combinations in liter/mol sec, from [1].

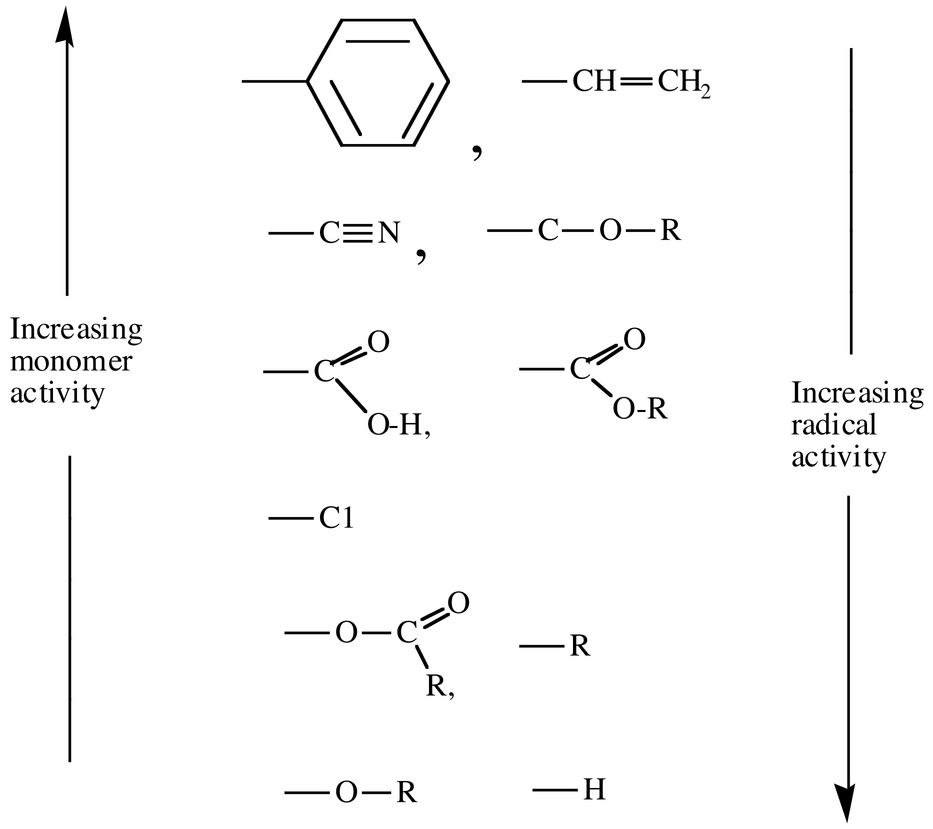


Table 5.3

List of substituents ranked in terms of their effects on monomer and radical reactivity.

An important pattern to recognize among the substituents listed in Table 5.3 is this: those which have a double bond conjugated with the double bond in the olefin are the species which are more stable as radicals and more reactive as monomers. The inverse relationship between the stability of monomers and radicals arises precisely because monomers gain (or lose) stability by converting to the radical: the greater the gain (or loss), the greater (or less) the incentive for the monomer to react. It is important to realize that the ability to form conjugated structures is associated with a substituent, whether it is in a monomer or a radical. Conjugation allows greater electron delocalization, which, in turn, lowers the energy of the system that possesses this feature.

Comparison of the range of k_{12} along rows and columns in Table 5.2 suggests that resonance stabilization produces a bigger effect in the radical than in the monomer. After all, the right- and left-hand columns in Table 5.2 (various radicals) differ by factors of 100–1000, while the top and bottom rows (various monomers) differ only by the factors of 50–100. In order to examine this effect in more detail, consider the addition reaction of monomer M to a reactant radical R• to form a product radical P•. What distinguishes these species is the presence or absence of resonance stabilization (subscript rs). If the latter is operative, we must also consider which species benefit from its presence. There are four possibilities:

1. Unstabilized monomer converts stabilized radical to unstabilized radical:

$$R_{rs} \bullet + M \rightarrow P \bullet \tag{5.H}$$

There is an overall loss of resonance stabilization in this reaction. Since it is a radical which suffers the loss, the effect is larger than in the reaction in which…

2. Stabilized monomer converts stabilized radical to another stabilized radical:

$$R_{rs}\bullet + M_{rs} \rightarrow P_{rs}\bullet \qquad (5.I)$$

Here too there is an overall loss of resonance stabilization, but it is monomer stabilization which is lost, and this is energetically less costly than reaction (5.H).

3. Unstabilized monomer converts unstabilized radical to another unstabilized radical:

$$R\bullet + M \rightarrow P\bullet \qquad (5.J)$$

This reaction suffers none of the reduction in resonance stabilization that is present in reactions (5.H) and (5.I). It is energetically more favored than both of these, but not as much as the reaction in which…….

4. Stabilized monomer converts unstabilized radical to stabilized radical:

$$R\bullet + M_{rs} \rightarrow P_{rs}\bullet \qquad (5.K)$$

This reaction converts the less effective resonance stabilization of a monomer to a more effective form of radical stabilization. This is the most favorable of the four reaction possibilities.

In summary, we can rank these reactions in terms of their propagation constants as follows:

$$R_{rs}\bullet + M < R_{rs}\bullet + M_{rs} < R\bullet + M < R\bullet + M_{rs}$$

Systems from Table 5.2 which correspond to these situations are the following:

Radical:	styrene		styrene		vinyl acetate		vinylacetate
	+	<	+	<	+	<	+
Monomer:	vinylacetate		styrene		vinylacetate		styrene

Note that this inquiry into copolymer propagation rates also increases our understanding of the differences in free-radical homopolymerization rates. Recall that in Chapter 3 a discussion of this aspect of homopolymerization was deferred until copolymerization was introduced. The trends under consideration enable us to make some sense out of the rate constants for propagation in free-radical homopolymerization as well. For example, in Table 3.4 we see that k_p values at 60 °C for vinyl acetate and styrene are 2300 and 165 liter mol^{-1} sec^{-1}, respectively. The relative magnitude of these constants can be understood in terms of the sequence above.

Resonance stabilization energies are generally assessed from thermodynamic data. If we define ε_1 to be the resonance stabilization energy of species i, then the heat of formation of that species will be less by an amount ε_1 than for an otherwise equivalent molecule without resonance. Likewise, the change in enthalpy ΔH for a reaction which is influenced by resonance effects is less by an amount Δε (Δ is the usual difference: products minus reactants) that the ΔH for a reaction which is otherwise identical except for resonance effects:

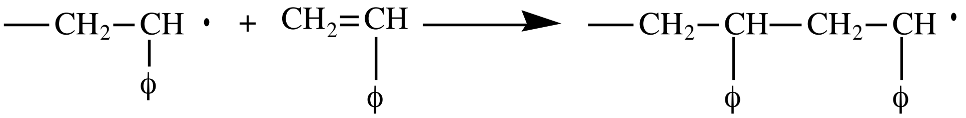
$$\Delta H_{rs} = \Delta H_{no\ rs} - \Delta\varepsilon \tag{5.4.2}$$

Thus if we consider the homopolymerization of ethylene (no resonance possibilities),

$$-CH_2-CH_2\bullet + CH_2=CH_2 \rightarrow -CH_2CH_2CH_2CH_2\bullet \tag{5.L}$$

$$\Delta H_{no\ rs} = -88.7\ \mathrm{kJ\ mol}^{-1}$$

as a reference reaction, and compare it with the homopolymerization of styrene (resonance effects present)



$$-\mathrm{CH_2}-\underset{\phi}{\mathrm{CH}}\cdot + \mathrm{CH_2}{=}\underset{\phi}{\mathrm{CH}} \longrightarrow -\mathrm{CH_2}-\underset{\phi}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\phi}{\mathrm{CH}}\cdot$$

$$\Delta H_{rs} = -69.9 \text{ kJ mol}^{-1} \qquad (5.M)$$

we find a value of $\Delta\varepsilon = -19$ kJ mol^{-1}, according to eq 5.4.2. Reaction (5.M) is a specific example of the general reaction (5.I), and the negative value of $\Delta\varepsilon$ in this example indicates the overall loss of resonance stabilization which is characteristic of (5.I).

Although it is not universally true that the activation energies of reactions parallel their heats of reaction, this is approximately true for the kind of addition reaction we are discussing. Accordingly, we can estimate $E^* = \alpha\,\Delta H$, with α an appropriate proportionally constant. If we consider the difference between two activation energies by combining this idea with eq 5.4.2, the contribution of the nonstabilized reference reaction drops out of eq 5.4.2 and we obtain

$$\begin{aligned} E_{11}{}^* - E_{12}{}^* &= \alpha\left[-\Delta\varepsilon_{11} - \left(-\Delta\varepsilon_{12}\right)\right] \\ &= -\left(\varepsilon_{P_1\bullet} - \varepsilon_{R_1\bullet} - \varepsilon_{M_1}\right) + \left(\varepsilon_{P_2\bullet} - \varepsilon_{R_1\bullet} - \varepsilon_{M_2}\right) \end{aligned} \qquad (5.4.3)$$

In writing the second version of this relation the proportionality constant has been set equal to unity as a simplification. Note that the resonance stabilization energy of the reference radical $R_1\bullet$ also cancels out of this expression.

The temperature dependence of the reactivity ratio r_1 also involves the $E_{11}{}^* - E_{12}{}^*$ difference through the Arrhenius equation; hence

$$r_1 \quad \propto \quad \exp\left(\frac{\varepsilon_{p_1\bullet} - \varepsilon_{M1}}{RT}\right)\exp\left(\frac{-\left(\varepsilon_{p_2\bullet} - \varepsilon_{M2}\right)}{RT}\right) \tag{5.4.4}$$

An analogous expression can be written for r_2:

$$r_2 \quad \propto \quad \exp\left(\frac{\varepsilon_{p_2\bullet} - \varepsilon_{M2}}{RT}\right)\exp\left(\frac{-\left(\varepsilon_{p_1\bullet} - \varepsilon_{M1}\right)}{RT}\right) \tag{5.4.5}$$

According to this formalism, the following applies:

1. The reactivity ratios are proportional to the product of two exponentials.
2. Each exponential involves the difference between the resonance stabilization energy of the radical and monomer of a particular species.
3. The positive exponent is associated with the same species as identifies the r (i.e., for r_1, $M_1 \rightarrow P_1\bullet$), while the negative exponent is associated with the other species (for r_1, $M_2 \rightarrow P_2\bullet$).

We might be hard-pressed to estimate the individual resonance stabilization energies in eqs 5.4.4 and 5.4.5, but the quantitative application of these ideas is not difficult. Consider once again the styrene–vinyl acetate system:

1. Define styrene to be monomer 1 and vinyl acetate to be monomer 2.
2. The difference in resonance stabilization energy $\varepsilon_{p_1\bullet} - \varepsilon_{M_1} > 1$, since styrene is resonance stabilized and the effect is larger for the radical than the monomer.
3. The difference $\varepsilon_{p_2\bullet} - \varepsilon_{M_2} \cong 0$, since neither the radical nor the monomer of vinyl acetate shows appreciable stabilization.

4. Therefore, according to eqs 5.4.4 and 5.4.5, $r_1 > 1$ while $r_2 < 1$.
5. The experimental values for this system are $r_1 = 55$ and $r_2 = 0.01$.

Although this approach does correctly rank the parameters r_1 and r_2 for the styrene-vinyl acetate system, this conclusion was already reached qualitatively above, using the same concepts and without any mathematical manipulations. One point that the quantitative derivation makes clear is that explanations of copolymer behavior based exclusively on resonance concepts fail to describe the full picture. All that we need to do is examine the product r_1r_2 as given by eqs 5.4.4 and 5.4.5, and the shortcoming becomes apparent. According to these relationships, the product r_1r_2 always equals unity, yet we saw in the last section that experimental r_1r_2 values generally lie between zero and unity. We also saw that polarity effects could be invoked to rationalize the r_1r_2 product.

The situation may be summarized as follows:

1. If resonance effects *alone* are considered, it is possible to make some sense of the ranking of various propagation constants.
2. In this case only random microstructure is predicted.
3. If polarity effects *alone* are considered, it is possible to make some sense out of the tendency toward alternation.
4. In this case homopolymerization is unexplained.

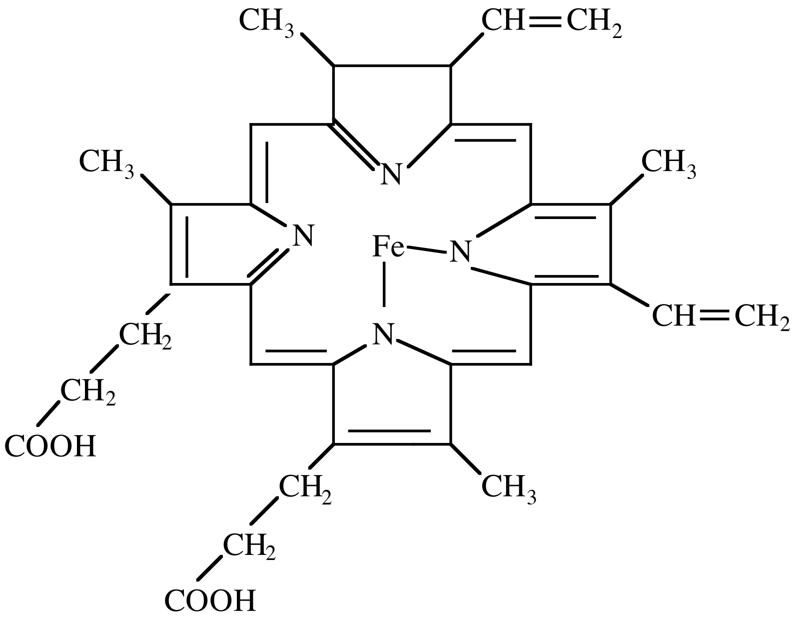
The way out of this apparent dilemma is easily stated, although not easily acted upon. It is not adequate to consider any *one* of these approaches for the explanation of something as complicated as these reactions. Polarity effects and resonance are *both* operative, and, if these still fall short of explaining all observations, there is another old standby to fall back on: steric effects. Resonance, polarity, and steric considerations are all believed to play an important role in copolymerization chemistry, just as in the other areas of organic chemistry. Things are obviously simplified if only one of these is considered, but it must be remembered that doing this necessarily reveals only one facet of the problem. Nevertheless, there are times, particularly before launching an experimental investigation of a new system, when some guidelines are very useful. The following example illustrates this point.

Example 5.2

It is proposed to polymerize the vinyl group of the hemin molecule with other vinyl comonomers to prepare model compounds to be used in hemoglobin research. Considering hemin and styrene to be species 1 and 2, respectively, use the resonance concept to rank the reactivity ratios of r_1 and r_2.

Solution

Hemin is the complex between protoporphyrin and iron in the +3 oxidation state. Iron is in the +2 state in the heme of hemoglobin. The molecule has the following structure:



It is apparent from the size of the conjugated system here that numerous resonance possibilities exist in this species in both the radical and the molecular form. Styrene also has resonance structures in both forms. On the principle that these effects are larger for radicals than monomers, we conclude that the difference $\varepsilon_{p\bullet} - \varepsilon_M > 0$ for both hemin and styrene. On the principle that greater resonance effects result from greater delocalization, we expect the difference to be larger for hemin than for styrene. According to eq 5.4.4, $r_1 \propto e^{\text{larger}} e^{-\text{smaller}} > 1$. According to eq 5.4.5, $r_2 \propto e^{\text{smaller}} e^{-\text{larger}} < 1$. Experimentally, the values for these parameters turn out to be $r_1 = 65$ and $r_2 = 0.18$.

5.5 A closer look at microstructure

In Section 5.3 we noted that variations in the product $r_1 r_2$ led to differences in the polymer microstructure, even when the overall compositions of two systems are the same. In this section we shall take a closer look at this variation, using the approach best suited for this kind of detail: statistics.

5.5A Sequence distributions

Suppose we define as p_{ij} the probability that a unit of type i is followed in the polymer by a unit of type j, where both i and j can be either 1 or 2. Since an i unit must be followed by either an i or a j, the fraction of ij sequences out of all possible sequences defines p_{ij}:

$$p_{ij} = \frac{\text{number of ij sequences}}{\text{number of ij sequences} + \text{number of ii sequences}} \tag{5.5.1}$$

This equation can also be written in terms of the propagation rates of the different types of addition steps which generate the sequences:

$$p_{ij} = \frac{R_{ij}}{R_{ij} + R_{ii}} = \frac{k_{ij}[M_i \bullet][M_j]}{k_{ij}[M_i \bullet][M_j] + k_{ii}[M_i \bullet][M_i]} \tag{5.5.2}$$

For the various possible combinations in a copolymer, eq 5.5.2 becomes

$$p_{11} = \frac{k_{11}[M_1 \bullet][M_1]}{k_{11}[M_1 \bullet][M_1] + k_{12}[M_1 \bullet][M_2]} = \frac{r_1[M_1]}{r_1[M_1] + [M_2]} \tag{5.5.3}$$

$$p_{12} = \frac{[M_2]}{r_1[M_1] + [M_2]} \tag{5.5.4}$$

$$p_{22} = \frac{k_{22}[M_2 \bullet][M_2]}{k_{22}[M_2 \bullet][M_2] + k_{21}[M_2 \bullet][M_1]} = \frac{r_2[M_2]}{r_2[M_2] + [M_1]} \tag{5.5.5}$$

$$p_{22} = \frac{[M_1]}{r_2[M_2] + [M_1]} \tag{5.5.6}$$

Note that $p_{11} + p_{12} = p_{22} + p_{21} = 1$. In writing these expressions we make the assumption that only the terminal unit of the radical influences the addition of the next monomer. This same assumption was made in deriving the copolymer composition equation. We shall have more to say below about this particular assumption.

Next let us consider the probability of finding a sequence of repeat units in a copolymer which is exactly ν units of M_1 in length. This may be represented as $M_2(M_1)_\nu M_2$. Working from left to right in this sequence, we note the following:

1. If the addition of monomer M_1 to a radical ending with M_2 occurs L times in a sample, then there will be a total of L sequences, of unspecified length, of M_1 units in the sample.

2. If $\nu - 1$ consecutive M_1 monomers add to radicals capped by M_1 units, the total number of such sequences is expressed in terms of p_{11} to be $Lp_{11}^{\nu-1}$.

3. If the sequence contains exactly ν units of type M_1, then the next step must be the addition of an M_2 unit. The probability of such an addition is given by p_{12}, and the number of sequences is $Lp_{11}^{\nu-1}p_{12}$.

Since L equals the total number of M_1 sequences of any length, the fraction of sequences of length ν, ϕ_ν, is given by

$$\phi_\nu = p_{11}^{\nu-1} p_{12} \tag{5.5.7}$$

The similarity of this derivation to those in Sections 2.4 and 3.7 should be apparent. Substitution of the probabilities given by eqs 5.5.3 and 5.5.4 leads to

$$\phi_\nu = \left(\frac{r_1[M_1]}{r_1[M_1]+[M_2]}\right)^{\nu-1}\left(\frac{[M_2]}{r_1[M_1]+[M_2]}\right) \tag{5.5.8}$$

A similar result can be written for ϕ_μ, where μ denotes the length of a sequence of M_2 units. These expressions give the fraction of sequences of specified length in terms of the reactivity ratios of the copolymer system and the composition of the feedstock. Figure 5.3 illustrates by means of a bar graph how ϕ_ν varies with ν for two polymer systems prepared from equimolar solutions of monomers. The shaded bars in Figure 5.3 describe the system for which $r_1r_2 = 0.03$ and the unshaded bars describe $r_1r_2 = 0.30$.

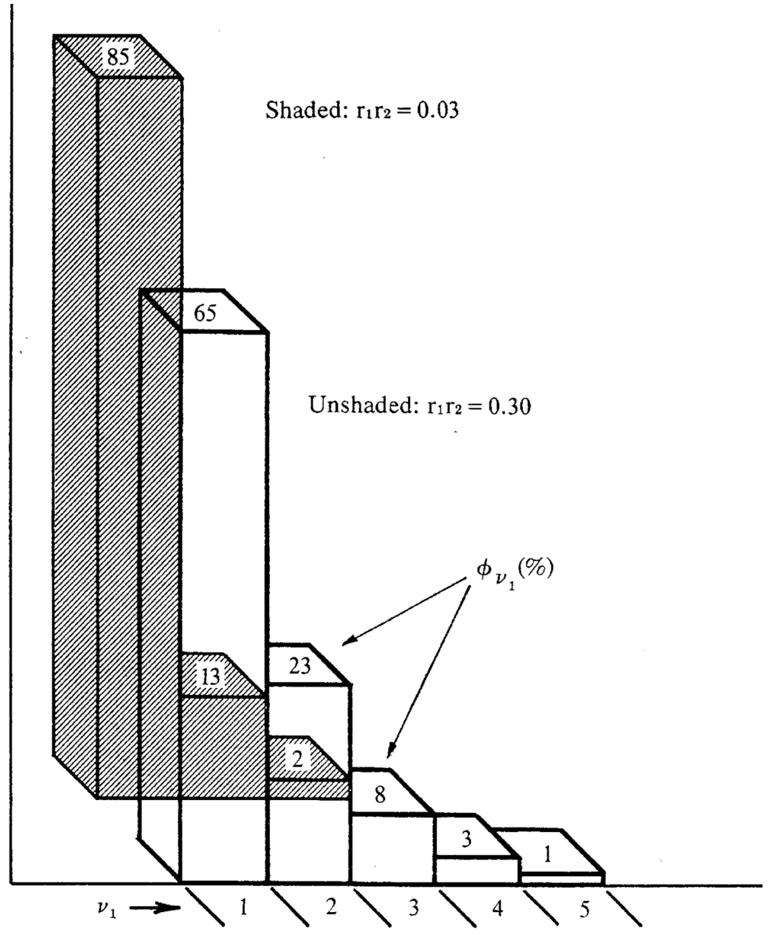


Figure 5.3
Fraction of sequences of the indicated length for copolymers prepared from equimolar feedstocks with $r_1r_2 = 0.03$ (shaded) and $r_1r_2 = 0.30$ (unshaded). Data from C. Tosi, *Adv. Polym. Sci.* 5, 451 (1968).

Table 5.4 shows the effect of variations in the composition of the feedstock for the system $r_1r_2 = 1$. The following observations can be made concerning Figure 5.3 and Table 5.4:

1. In all situations, the fraction ϕ_ν decreases with increasing ν.

2. Figure 5.3 shows that for $r_1r_2 = 0.03$, about 85% of the M_1 units are sandwiched between two M_2's. We have already concluded that low values of the r_1r_2 product indicate a tendency toward alternation.

3. Figure 5.3 also shows that the proportion of alternating M_1 units decreases, and the fraction of longer sequences increases, as r_1r_2 increases. The 50 mol % entry in Table

5.4 shows that the distribution of sequence lengths gets flatter and broader for $r_1r_2 = 1$, the ideal case.

4. Table 5.4 also shows that increasing the percentage of M_1 in the monomer solution flattens and broadens the distribution of sequence lengths. Similar results are observed for lower values of r_1r_2, but the broadening is less pronounced when the tendency toward alternation is high.

$\nu \backslash f_1$	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**
1	90	80	70	60	50	40	30	20	10
2	9	16	21	24	25	24	21	16	9
3	0.9	3.2	6.3	9.6	12.5	14.4	14.7	12.8	8.1
4	0.09	0.64	1.89	3.84	6.25	8.64	10.3	10.2	7.29
5		0.13	0.57	1.54	3.13	5.18	7.20	8.19	6.56
6			0.17	0.62	1.56	3.11	5.04	6.55	5.90
7			0.05	0.25	0.78	1.87	3.53	5.24	5.31
8				0.10	0.39	1.12	2.47	4.19	4.78
9				0.04	0.20	0.67	1.73	3.36	4.30
10					0.10	0.40	1.21	2.68	3.87
11					0.05	0.24	0.85	2.15	3.59
12						0.14	0.59	1.72	3.23

Table 5.4
Percentage of sequences of length ν for copolymers prepared from different feedstocks f_1 with $r_1r_2 = 1$.

Next we consider the average value of a sequence length of M_1, $\bar{\nu}$. Combining eqs 1.7.7 and 5.5.7 gives

$$\bar{\nu} = \frac{\sum_{\nu=1}^{\infty} \nu\, \phi_\nu}{\sum_{\nu=1}^{\infty} \phi_\nu} = \frac{\sum_{\nu=1}^{\infty} \nu\, p_{11}{}^{\nu-1}\, p_{12}}{\sum_{\nu=1}^{\infty} p_{11}{}^{\nu-1}\, p_{12}} \qquad (5.5.9)$$

Simplifying this result involves the same infinite series that we examined in connection with eq 2.4.5; therefore we can write immediately

$$\bar{\nu} = \frac{1}{1 - p_{11}} = \frac{1}{p_{12}} \qquad (5.5.10)$$

By combining eqs 5.5.4 and 5.5.10, we obtain

$$\bar{\nu} = 1 + r_1 \frac{[M_1]}{[M_2]} \qquad (5.5.11)$$

A value of $\bar{\mu}$ is obtained by similar operations:

$$\bar{\mu} = 1 + r_2 \frac{[M_2]}{[M_1]} \qquad (5.5.12)$$

The following example demonstrates the use of some of these relationships pertaining to microstructure.

Example 5.3

The hemoglobin molecule contains four heme units. It is proposed to synthesize a hemin (molecule 1)–styrene (molecule 2) copolymer such that $\bar{\nu} = 4$ in an attempt to test some theory concerning hemoglobin. As noted in Example 5.2, $r_1 = 65$ and $r_2 = 0.18$ for this system. What should be the proportion of monomers to obtain this average hemin sequence length? What is the average styrene sequence length at this composition? Does this system seem like a suitable model if the four hemin clusters are to be treated as isolated from one another in the theory being tested? Also evaluate ϕ_ν for several ν bracketing $\bar{\nu}$ to get an idea of the distribution of these values.

Solution

Use eq 5.5.11 to evaluate $[M_1]/[M_2]$ for $r_1 = 65$ and $\bar{\nu} = 4$:

$$\frac{[M_1]}{[M_2]} = \frac{\bar{\nu} - 1}{r_1} = \frac{4 - 1}{65} = 0.046 \quad \text{and} \quad \frac{[M_2]}{[M_1]} = 21.7$$

Use this ratio of concentration in eq 5.5.12 to evaluate $\bar{\mu}$:

$$\bar{\mu} = 1 + r_2 \frac{[M_2]}{[M_1]} = 1 + 0.18\,(21.7) = 4.9$$

The number of styrene units in an average sequence is a little larger than the length of the average hemin sequence. It is not unreasonable to describe the hemin clusters as isolated, on the average, in this molecule. The product $r_1 r_2 = 11.7$ in this system, which also indicates a tendency toward block formation. Use eq 5.5.8 with $[M_1]/[M_2] = 0.046$ and the r_1 and r_2 values to evaluate ϕ_ν:

$$\phi_\nu = \left(\frac{65\,(0.046)}{65\,(0.046) + 1}\right)^{\nu-1} \left(\frac{1}{65\,(0.046) + 1}\right)$$

$$= \left(\frac{2.99}{3.99}\right)^{\nu-1} \left(\frac{1}{3.99}\right) = (0.0749)^{\nu-1}\,(0.251)$$

Solving for several values of ν, we conclude that the distribution of sequence length is quite broad:

ν	1	2	3	4	5	6
ϕ_ν	0.251	0.188	0.140	0.105	0.079	0.059

For the systems represented in Figure 5.3 and the equimolar case in Table 5.4, the average lengths are $\bar{\nu}$ = 1.173 for r_1r_2 = 11.7 for r_1r_2 = 0.03, $\bar{\nu}$ = 1.548 for r_1r_2 = 0.30, and $\bar{\nu}$ = 2.000 for r_1r_2 = 1.0. ___________________

Equations 5.5.11 and 5.5.12 suggest a second method for the experimental determination of reactivity ratios, in addition to the copolymer composition equation. If the average sequence length can be determined for a feedstock of known composition, then r_1 and r_2 can be evaluated. We shall return to this possibility in the next section. In anticipation of applying this idea, let us review the assumptions and limitation to which eqs 5.5.11 and 5.512 are subject:

1. The instantaneous monomer concentration must be used. Except at the azeotrope, this changes as the conversion of monomers to polymer progresses. As in Section 5.2, we assume that either the initial conditions apply (little change has taken place) or that monomers are continuously being added (replacement of reacted monomer).
2. The kinetic analysis described by eqs 5.5.3 and 5.54 assumes that no repeat unit in the radical other than the terminal unit influences the addition. The penultimate unit in the radical as well as those still further from the growing end are assumed to have no effect.
3. Item (2) requires that each event in the addition process be independent of all others. We have consistently assumed this throughout this chapter, beginning with the copolymer composition equation. Until now we have said nothing about testing this assumption. Consideration of copolymer sequence length offers this possibility.

5.5B Terminal and penultimate models

We have suggested above that both the copolymer composition equation and the average sequence length offer possibilities for experimental evaluation of the reactivity ratios. Note that in so doing we are finding parameters which fit experimental results to the predictions of a model. Nothing about this tests the model itself. It could be argued that obtaining the same values of r_1 and r_2 from the fitting of composition and microstructure data would validate the model. It is not likely, however, that both types of data would be available and of sufficient quality to make this unambiguous. We shall examine the experimental side of this in the next section.

Statistical considerations make it possible to test the assumption of independent additions. Let us approach this topic by considering an easier problem: coin tossing. Under conditions where two events are purely random – as in tossing a fair coin – the probability of a specific sequence of outcomes is given by the product of the probabilities of the individual events. The probability of tossing a head followed by a head – indicated HH – is given by

$$p_{HH} = p_H p_H \tag{5.5.13}$$

If the events are not independent, provision must be made for this, so we define a quantity called the *conditional probability*. For the probability of a head *given the prior event* of a head, this is written $p_{H/H}$, where the first quantity in the subscript is the event under consideration and that following the slash mark is the prior condition. Thus $p_{T/H}$ is the probability of a tail following a head. If the events are independent, $p_{H/H} = p_H$; if not, then $p_{H/H}$ must be evaluated as a separate quantity. If the coin being tossed were biased, that is, if successive events are not independent, eq 5.5.13 would become

$$p_{HH} = p_{H/H}\, p_H \tag{5.5.14}$$

We recall that the fraction of times a particular outcome occurs is used to estimate probabilities. Therefore we could evaluate $p_{H/H}$ by counting the number of times N_H the first toss yielded a head and the number of times N_{HH} two tosses yielded a head followed by a head and write

$$p_{H/H} = \frac{p_{HH}}{p_H} = \frac{N_{HH}}{N_H} \qquad (5.5.15)$$

This procedure is readily extended to three tosses. For a fair coin the probability of three heads is the cube of the probability of tossing a single head:

$$p_{HHH} = p_H p_H p_H \qquad (5.5.16)$$

If the coin is biased, conditional probabilities must be introduced:

$$p_{HHH} = p_{H/HH} p_{H/H} p_H \qquad (5.5.17)$$

Using eq 5.5.15 to eliminate $p_{H/H}$ from the last result gives

$$p_{HHH} = p_{H/HH} \left(\frac{p_{HH}}{p_H} \right) p_H \qquad (5.5.18)$$

or

$$p_{H/HH} = \frac{p_{HHH}}{p_{HH}} = \frac{N_{HHH}}{N_{HH}} \qquad (5.5.19)$$

If we were testing whether a coin were biased or not, we would use ideas like these as the basis for a test. We could count, for example, HHH and HH sequences and divide them according to eq 5.5.19. If $p_{H/HH} \neq p_H$, we would be suspicious!

A similar logic can be applied to copolymers. The story is a bit more complicated to tell, so we only outline the method. If penultimate effects operate, then the probabilities $p_{11,}$ p_{12}, etc., defined in eqs 5.5.3 – 5.5.6 should be replaced by conditional probabilities. As a matter of fact, the kind of conditional probabilities needed must be based on the two preceding events. Thus reactions (5.E) and (5.F) are two of the appropriate reactions, and the corresponding probabilities are $p_{1/11}$ and $p_{1/21}$. Rather than work out all of the probabilities in detail, we summarize the penultimate model as follows:

1. A total of eight different reactions are involved, since each reaction like (5.A) is replaced by a pair of reactions like (5.E) and (5.F).
2. There are eight different rate laws and rate constants associated with these reactions. Equation 5.2.1, for example, is replaced by eqs 5.2.5 and 5.2.6.

3 The eight rate constants are clustered in four ratios which define new reactivity ratios. Thus r_1 as defined in eq 5.2.13 is replaced by $r_1' = k_{111}/k_{112}$ and $r_1'' = k_{211}/k_{212}$ while r_2 is replaced by $r_2' = k_{222}/k_{221}$ and $r_2'' = k_{122}/k_{121}$.

4. The probability p_{11} as given by eq 5.5.3 is replaced by the conditional probability $p_{1/11}$, which is defined as

$$p_{1/11} = \frac{k_{111}[M_1M_1\bullet][M_1]}{k_{111}[M_1M_1\bullet][M_1] + k_{112}[M_1M_1\bullet][M_2]} = \frac{r_1'[M_1]/[M_2]}{1 + r_1'[M_1]/[M_2]} \tag{5.5.20}$$

There are eight of these conditional probabilities, each associated with the reaction described in item (1).

5. The probability p_{11} can be written as the ration $N_{M_1M_1}/N_{M_1}$ using eq 5.5.15. This is replaced by $p_{1/11}$, which is given by the ratio $N_{M_1M_1M_1}/N_{M_1M_1}$ according to eq 5.5.19.
6. Equation 5.5.4 shows that p_{11} is constant for a particular copolymer if the terminal model applies; therefore the ratio $N_{M_1M_1}/N_{M_1}$ also equals this constant. Equation 5.5.20 shows that $p_{1/11}$ is constant for a particular copolymer if the penultimate model applies; therefore the ratio $N_{M_1M_1M_1}/N_{M_1M_1}$ also equals this constant, but the ratio $N_{M_1M_1}/N_{M_1}$ does not have the same value.

These observations suggest how the terminal mechanism can be proved to apply to a copolymerization reaction if experiments exist which permit the number of sequences of a particular length to be determined. If this is possible, we should count the number of M_1's (this is given by the copolymer composition) and the number of M_1M_1 and $M_1M_1M_1$ sequences. Specified sequences, of any definite composition, of two units are called dyads; those of three units, triads; those of four units, tetrads; those of five units, pentads; and so on. Next we examine the ratio $N_{M_1M_1}/N_{M_1}$ and $N_{M_1M_1M_1}/N_{M_1M_1}$. If these are the same, then the mechanism is shown to have terminal control; if not, it *may* be penultimate control. To prove the penultimate model it would also be necessary to count the number of M_1 tetrads. If the tetrad/triad ratio were the same as the triad/dyad ratio, the penultimate model is established.

This situation can be generalized. If the ratios do not become constant until the ratio of pentads to tetrads is considered, then the unit before the next to last – called the antepenultimate unit – plays a role in the addition. This situation has been observed, for example, for propylene oxide-maleic anhydride copolymers. The foregoing discussion has been conducted in terms of M_1 sequences. Additional relationships of the sort we have been considering also exist for dyads, triads, and so forth, of different types of specific composition. Thus an ability to investigate microstructure experimentally allows some rather subtle mechanistic effects to be studied. In the next section we shall see how such information is obtained.

5.6 Copolymer composition and microstructure: experimental aspects

As we have already seen, the reactivity ratios of a particular copolymer system determine both the composition and microstructure of the polymer. Thus it is important to have reliable values for these parameters. At the same time it suggests that experimental studies of composition and microstructure can be used to evaluate the various r's.

5.6A Evaluating reactivity ratios from composition data

Evaluation of reactivity ratios from the copolymer composition equation requires only composition data – that is, relatively straightforward analytical chemistry – and has been the method most widely used to evaluate r_1 and r_2. As noted in the last section, this method assumes terminal control and seeks the best fit of the data to that model. It offers no means for testing the model, and as we shall see, is subject to enough uncertainty to make even self-consistency difficult to achieve. Microstructure studies, by contrast, offer both a means both to evaluate the reactivity ratios and also to test the model. The capability to investigate this level of structural detail was virtually nonexistent until the advent of modern instrumentation, and even now is limited to sequences of rather modest length.

In this section we shall use the evaluation of reactivity ratios as the unifying theme; the experimental methods constitute the new material introduced. The copolymer composition equation 5.2.18 relates the r's to the mole fractions of the monomers in the feedstock and in the copolymer. To use the equation to evaluate r_1 and r_2, the composition of a copolymer resulting from a feedstock of known composition must be measured. The composition of the feedstock itself must also be known, but we assume this poses no problems. The copolymer specimen must be obtained by proper sampling procedures, and purified of extraneous materials. Remember that monomers, initiators, and possibly solvents and soluble catalysts are involved in these reactions also, even though we have been focusing attention on the copolymer alone. The proportions of the two kinds of repeat unit in the copolymer is then determined by either chemical or physical methods. Elemental analysis is a widely used chemical method, but spectroscopic analysis (UV-visible, IR, NMR, and mass spectrometry) for functional groups is commonly employed.

Since the copolymer equation involves both r_1 and r_2 as unknowns, at least two polymers prepared from different feedstocks must be analyzed. It is preferable to use more than this minimum number of observations, and it is helpful to rearrange the copolymer composition equation into a linear form so that simple graphical methods can be employed to evaluate the r's. Several ways to linearize the equation exist:

1. Rearrange eq 5.2.18 to give

$$\frac{f_1(1-2F_1)}{F_1(1-f_1)} = r_1\left(\frac{f_1^2\,(F_1-1)}{F_1\,(1-f_1)^2}\right) + r_2 \qquad (5.6.1)$$

This is the equation of a straight line, so r_1 and r_2 can be evaluated from the slope and intercept of an appropriate plot.

2. In terms of ratios rather than fractions, eq 5.6.1 may be written as

$$\frac{[M_1]/[M_2]}{n_1/n_2}\left(\frac{n_1}{n_2}-1\right) = r_1\,\frac{([M_1]/[M_2])^2}{n_1/n_2} - r_2 \qquad (5.6.2)$$

where n_i refers to the number of repeat units in the polymer. This expression is also of the form y = mx + b if $x = ([M_1]/[M_2])^2/(n_1/n_2)$ and $y = ([M_1]/[M_2])/(n_1/n_2)\,/(n_1/n_2 - 1)$, so the slope and intercept yield r_1 and r_2, respectively. This type of analysis is known as a Finemann-Ross plot.

3. This last expression can be rearranged in several additional ways which yield linear plots:

$$\frac{y}{x} = -r_2\frac{1}{x} + r_1 \tag{5.6.3}$$

$$x = \frac{1}{r_1}y + \frac{r_2}{r_1} \tag{5.6.4}$$

$$\frac{x}{y} = \frac{r_1}{r_2}\frac{1}{y} + \frac{1}{r_1} \tag{5.6.5}$$

Each of these forms weigh the errors in various data points differently, so some may be more suitable than others, depending on the precision of the data. Ideally all should yield the same values of the reactivity ratios. The following example illustrates the use of eq 5.6.1 to evaluate r_1 and r_2.

Example 5.4

The data in Table 5.5 list the mole fraction of methyl acrylate in the feedstock and in the copolymer for the methyl acrylate (M_1)-vinyl chloride (M_2) system. Use eq 5.6.1 as the basis for the graphical determination of the reactivity ratios which describe this system.

f_1	F_1	f_1	F_1
0.075	0.441	0.421	0.864
0.154	0.699	0.521	0.900
0.237	0.753	0.744	0.968
0.326	0.828	0.867	0.983

Table 5.5

Values of F_1 as a function for f_1 for the methyl acrylate (M_1)-vinyl chloride (M_2) system; data from E. L. Chapin, G. Ham, and R. Fordyce, *J. Am. Chem. Soc.* 70, 538 (1948). These data are also plotted in Figure 5.4.

Solution

We calculate the variables to be used as ordinate and abscissa for the data in Table 5.5 using eq 5.6.1:

$f_1(1-2F_1)/F_1(1-f_1)$	0.0217	-0.1036	-0.2087	-0.3832	-0.6127	-0.9668	-2.8102	-6.4061
$f_1^2(F_1-1)/F_1(1-f_1)^2$	-0.0083	-0.0143	-0.0316	-0.0486	-0.0832	-0.1315	-0.2792	-0.7349

Least-square analysis of these values gives a slope $r_1 = 8.929$ and an intercept $r_2 = 0.053$. Figure 5.4b shows these data plotted according to eq 5.6.1. The line is drawn with the least-squares slope and intercept. The last point on the left is Figure 5.4a, which this line passes through, corresponds to $F_1 = 0.983$ and $f_1 = 0.867$. Because the functional form plotted involves the small differences $F_1 - 1$ and $1 - f_1$, this point is also subject to the largest error. This illustrates the value of having alternate methods for analyzing the data. The authors of this research carried out several different analyses of the same data; the values they obtained for r_1 and r_2 averaged over the various methods were $r_1 = 9.616 \pm 0.603$ and $r_2 = 0.0853 \pm 0.0239$. The standard deviations of about 6 and 28% in r_1 and r_2 analyzed *from the same data* indicate the hazards of this method for determining r values.

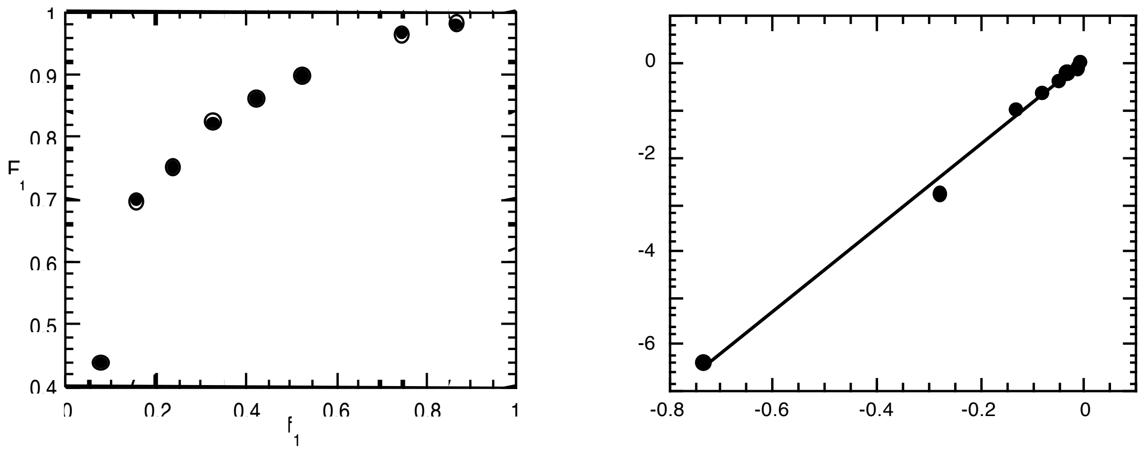


Figure 5.4.

(a) Mole fraction of methylacrylate in copolymers with vinyl chloride as a function of feedstock composition, and (b) Finemann-Ross plot to extract reactivity ratios, as describe in Example 5.4.

5.6B Spectroscopic techniques

In spite of the compounding of errors to which it is subject, the foregoing method was the best procedure for measuring reactivity ratios until the analysis of microstructure became feasible. Let us now consider this development. Most of the experimental information concerning copolymer microstructure has been obtained by modern instrumental methods. Techniques such as ultraviolet (UV), visible, and infrared (IR) spectroscopy, NMR spectroscopy, and mass spectroscopy have all been used to good advantage in this type of research. Advances in instrumentation have made these physical methods particularly suitable to answer the question we pose: with what frequency do particular sequences of repeat units occur in a copolymer? The choice of the best method for answering this question is governed by the specific nature of the system under investigation. Few general principles exist beyond the importance of analyzing a representative sample of suitable purity. Our approach is to consider some specific examples. In view of the diversity of physical methods available and the number of copolymer combinations which exist, a few samples barely touch the subject. They will suffice to illustrate the concepts involved, however. The simpler question – what is the mole fraction of each repeat unit in the polymer sample? – can usually be answered via the same instrumental techniques.

Spectroscopic techniques based on the absorption of UV, visible, or IR radiation depend on the excitation from one quantum state to another. References in physical and/or analytical chemistry should be consulted for additional details, but a brief summary will be sufficient for our purposes:

1. The excitation energy ΔE reflects the separation between the final (subscript f) and initial (subscript i) quantum states:

$$\Delta E = E_f - E_i \qquad (5.6.6)$$

   The difference is positive for absorbed energy.

2. The energy absorbed is proportional to the frequency of the radiation via Planck's constant ($h = 6.63 \times 10^{-34}$ J sec):

$$\Delta E = h\nu = h\frac{c}{\lambda} \qquad (5.6.7)$$

   In the second version of this equation c is the speed of light, and λ the wavelength of the radiation.

3 The more widely separated two states are in energy, the shorter the wavelength of the radiation absorbed. Transitions between electronic states have higher energies, and

correspond to UV-visible wavelengths, whereas vibrational quantum states are more closely spaced and are induced by IR radiation.

4. Different light-absorbing groups, called *chromophores*, absorb characteristic wavelengths, opening the possibility of qualitative analysis based on the location of an absorption peak.

5. If there is no band overlap in a spectrum, the absorbance at a characteristic wavelength is proportional to the concentration of chromophores present. This is the basis of quantitative analysis using spectra. With band overlap, things are more complicated but still possible.

6. The proportionality between the concentration of chromophores and the measured absorbance is given by Beer's Law (recall the discussion in Chapter 3.3D):

$$A = \varepsilon\, b\, c \qquad (5.6.8)$$

where A is the (dimensionless) absorbance, b is the sample thickness, c is the chromophore concentration, and ε is the absorptivity. Usually quantitative measurements are facilitated by calibration with standards of known concentrations, so that ε, b and various other instrumental parameters need not be determined individually.

7. For copolymers, or any other mixture of chromophores, the measured absorbance is given by the sum of individual Beer's Law terms:

$$A = \varepsilon_1\, b\, c_1 + \varepsilon_2\, b\, c_2 + \varepsilon_3\, b\, c_3 + \ldots \qquad (5.6.9)$$

Recalling that ε depends on the chromophore and on the wavelength, measurements at different wavelengths can be used to extract the concentrations of each component. For a copolymer with two monomers, at least two wavelengths would be needed, and ideally they should be chosen to such that if ε_1 is large at λ_1, then ε_2 is large at λ_2.

$$\begin{aligned} A(\lambda_1) &= \varepsilon_1(\lambda_1)\, b\, c_1 + \varepsilon_2(\lambda_1)\, b\, c_2 \\ A(\lambda_2) &= \varepsilon_1(\lambda_2)\, b\, c_1 + \varepsilon_2(\lambda_2)\, b\, c_2 \end{aligned} \tag{5.6.10}$$

These relations amount to a system of two equations with two unknowns, c_1 and c_2, which can be solved in a straightforward manner.

Nuclear magnetic resonance (NMR) spectroscopy is especially useful for microstructure studies, because of the sensitivity to the chemical environment of a particular nucleus. We shall consider its application to copolymers now and to questions of stereoregularity in Section 5.7. NMR has become such an important technique (actually a family of techniques) in organic chemistry that contemporary textbooks in the subject discuss its principles quite thoroughly, as do texts in physical and analytical chemistry, so here also we note only a few pertinent highlights:

1. Nuclei with an odd number of protons plus neutrons – especially ^{1}H and ^{13}C – possess magnetic moments and show two quantum states ("spin up" and "spin down") in a strong magnetic field.

2. If energy of the proper frequency is supplied, a transition between these quantum states occurs with the absorption of an amount of energy equal to the separation of the states, just as in UV-visible and IR absorption. For NMR the frequency of the absorbed radiation lies in the radio-frequency range, and depends on the local magnetic field at the atom in question.

3. The electrons in a molecule also have magnetic moments and set up secondary magnetic fields which partly screen each atom from the applied field. Thus atoms in different chemical environments display resonance at slightly different magnetic fields.

4. The displacement δ of individual resonances from that of a standard are small, and are measured in parts per million (ppm) relative to the applied field. These so-called *chemical shifts* are characteristic of a proton or carbon in a specific environment.

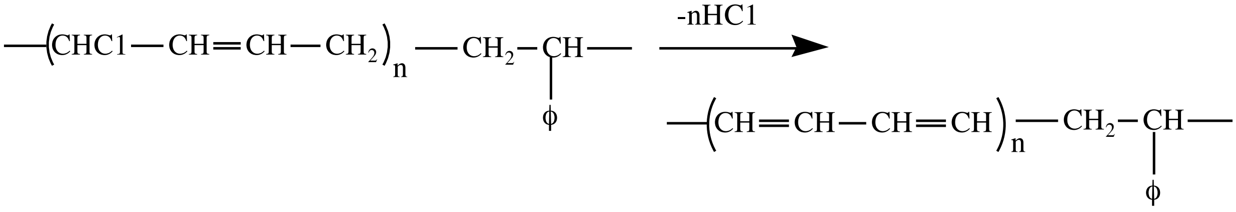
5. The interaction between nuclei splits resonances into multiple peaks, the number and relative intensity of which also assist in qualitative identification of the proton responsible for the absorption. For protons splitting is most commonly caused by the interaction of protons on adjacent carbons with the proton of interest. If there are m equivalent hydrogens on an adjacent carbon, the proton of interest produces m + 1 peaks by this coupling.

6. More distant coupling is revealed in high magnetic fields. Unresolved fine structures in a field of one strength may be resolved at higher field where more subtle long-range influences can be probed. The use of NMR spectroscopy to characterize copolymer microstructure takes advantage of this last ability to discern environmental effects which extend over the length of several repeat units. This capability is extremely valuable in analyzing the stereoregularity of a polymer, and we shall have more to say about it in that context in Section 5.7.

7. In NMR spectroscopy the "absorptivities" are, in essence, all the same, so that the integrated area under a peak is directly proportional to the number of nuclei of that type in the sample. Thus if different repeat units have identifiably different peaks, as is almost always the case, the relative abundance of each type can be extracted by peak integration without any additional calibration.

5.6C Sequence distribution: experimental determination

As suggested in the foregoing, the analysis for overall composition in a copolymer sample is by now a relatively straightforward affair. The analysis for sequence distribution, however, is not. The primary difficulty is that the energy of a particular transition, be it electronic, vibrational, or nuclear, is determined primary by the immediate chromophore of interest, and only weakly influenced by chemically bonded neighbors. NMR offers the most promise in this respect, especially with the advent of higher magnetic fields; this feature can provide sufficient resolution to detect the influence of repeat units up to about five monomers down the chain. Nevertheless, there are cases where UV-visible spectroscopy can help. An elegant example is the copolymer of styrene (molecule 1) and 1-chloro-1,3-butadiene (molecule 2). These molecules quantitatively degrade with the loss of HCl upon heating in base solution. This restores 1,3-unsaturation to the butadiene repeat unit:



$$-\left(\mathrm{CHC1-CH=CH-CH_2}\right)_n-\mathrm{CH_2-}\underset{\phi}{\mathrm{CH}}- \xrightarrow{\text{-nHC1}} -\left(\mathrm{CH=CH-CH=CH}\right)_n-\mathrm{CH_2-}\underset{\phi}{\mathrm{CH}}-$$

(5.N)

It is these conjugated double bonds that are the chromophores of interest in this system. What makes this particularly useful is the fact that the absorption maximum for this chromophore is displaced to longer wavelengths the more conjugated bonds there are in a sequence. Qualitatively, this can be understood in terms of a one-dimensional particle-in-a-box model for which the energy level spacing is inversely proportional to the square of the length of the box. In this case the latter increases with the length of the conjugated polyene system. This in turn depends on the number of consecutive butadiene repeat units in the copolymer. For an isolated butadiene molecule dehalogenation produces one pair of conjugated double bonds; two adjacent butadienes, four conjugated double bonds; three adjacent butadienes, six conjugated double bonds; and so on. Sequences of these increasing lengths are expected to absorb at progressively longer wavelengths.

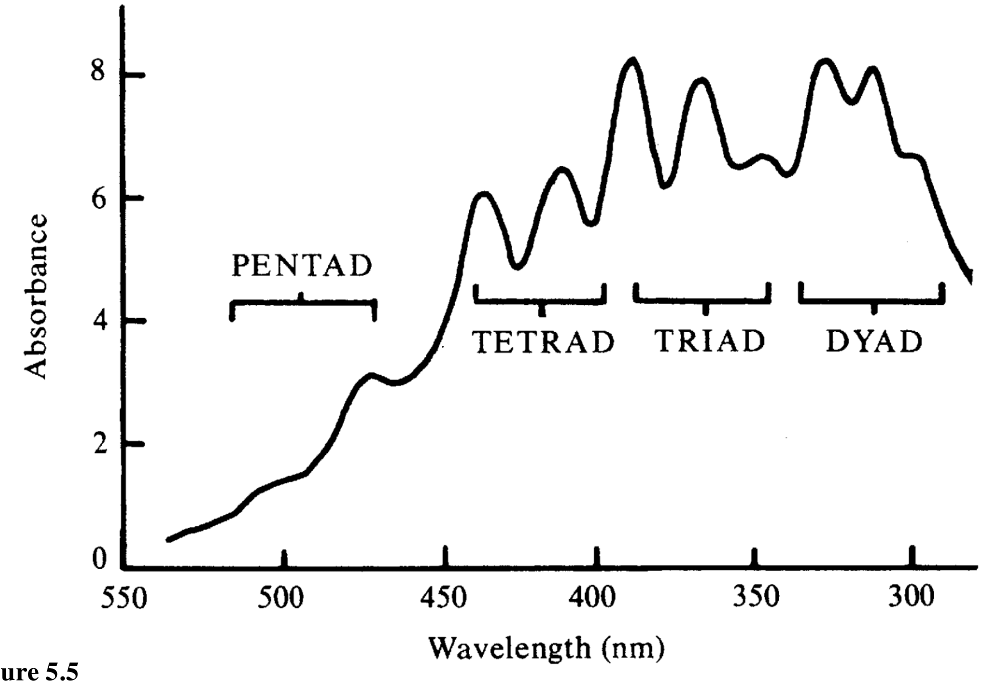


Figure 5.5

Ultraviolet-visible spectrum of dehydrohalogenated copolymers of styrene-1-chloro-1,3-butadiene. [Redrawn with permission from A. Winston and P. Wichacheewa, *Macromolecules* 6, 200 (1973)]

Figure 5.5 shows the appropriate portion of the spectrum for a copolymer prepared from a feedstock for which $f_1 = 0.153$. It turns out that each polyene produces a set of three bands: the dyad is identified with the peaks at $\lambda = 298$, 312, and 327 nm; the triad, with $\lambda = 347$, 367, and 388 nm; the tetrad with $\lambda = 412$ and 437 nm. Apparently one of the tetrad bands overlaps that of the triad and is not resolved. Likewise, only one band (at 473 nm) is observed for the pentad. The identification of these features can be confirmed with model compounds and the location and *relative* intensities of the peaks have been shown to be independent of copolymer composition. Once these features have been identified, the spectra can be interpreted in terms of the numbers of dyads, triads, tetrads, and maybe pentads of the butadiene units and compared with predicted sequences of various lengths. Further consideration of this system is left for Problems 5.3–5 at the end of the chapter.

We now illustrate the application of NMR to gather copolymer sequence information. Suppose we consider the various triads of repeat units. There are six possibilities: $M_1M_1M_1$, $M_1M_1M_2$, $M_2M_1M_2$, $M_2M_2M_2$, $M_2M_2M_1$, and $M_1M_2M_1$. These can be divided into two groups of three, depending on the identity of the central unit. Thus the center of a triad can be bracketed by two monomers identical to itself, different from itself, or by one of each. In each of these cases the central repeat unit is in a different environment, and a characteristic proton in that repeat unit is in a different location, depending on the effect of that environment. As a specific example, consider the methoxy group in poly(methyl methacrylate). The hydrogens in the group

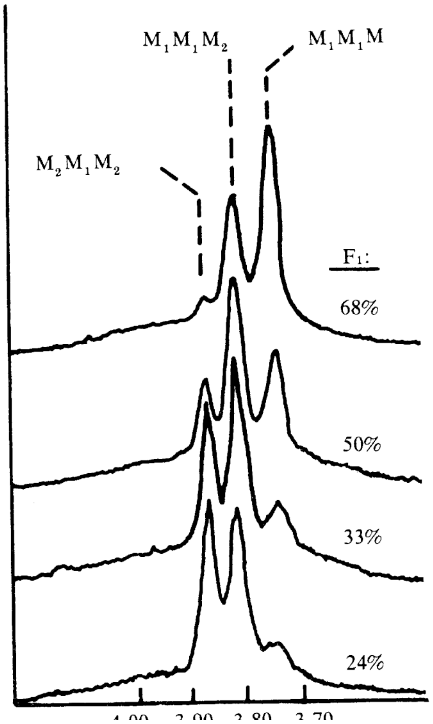


Figure 5.6

Chemical shift (from hexamethyldisiloxane) for acrylonitrile-methyl methacylate copolymers of the indicated methyl methacylate (M_1) content. Methyoxyl resonances are labeled as to the triad source. [From R. Chujo, H. Ubara and A. Nishioka, *Polym. J.* 3, 670 (1972)] are magnetically equivalent and hence produce a single resonance at $\delta = 3.74$ ppm. Now suppose we look for the same resonance feature in the copolymer of methyl methacrylate (M_1) and acrylonitrile (M_2). Figure 5.6 shows that 60-MHz spectrum of several of these copolymers in the neighborhood of the methoxy resonance. Three resonance peaks rather than one are observed. Figure 5.6 also lists the methyl methacrylate content of each of these polymers. As the methyl methacrylate content decreases, the peak on the right decreases and the left increases. We therefore identify the peak on the right with the $M_1M_1M_1$ sequence, the left-hand peak with $M_2M_1M_2$, and the peak in the center with $M_1M_1M_2$. The $M_1M_1M_1$ peak occurs at the same location as in the methyl methacrylate homopolymer.

The areas under the three peaks give the relative proportions of three sequences. In the following example we consider some results on dyad sequences determined by comparable procedures in vinylidene chloride-isobutylene copolymers.

Example 5.5

The mole fractions of various dyads in the vinylidine chloride (M_1)-isobutylene (M_2) system were determined by NMR spectroscopy (J. B. Kinsinger, T. Fischer, and C. W. Wilson, *Polym. Lett.* 5, 285 (1967)). A selection of the values obtained are listed below, as well as the compositions of the feedstocks from which the copolymers were prepared; assuming terminal control, evaluate r_1 from each of the first three sets of data, and r_2 from each of the last three.

Mole fraction of dyads

f_1	11	12	22
0.584	0.68	0.29	—
0.505	0.61	0.36	—
0.471	0.59	0.36	—
0.130	—	0.67	0.08
0.121	—	0.66	0.10
0.083	—	0.64	0.17

Solution

Equations 5.5.3 and 5.5.5 provide the method for evaluating the r's from the data given. We recognize that a 12 dyad can come about from 1 adding to 2 as well as from 2 adding to 1; therefore we use half the number of 12 dyads as a measure of the number of additions of monomer 2 to chain end 1. Accordingly, by eq 5.5.1,

$$p_{11} = \frac{N_{11}}{N_{11} + (1/2)\,N_{12}} = \frac{N_{12}}{2N_{11} + N_{12}} \quad \text{and} \quad p_{22} = \frac{2N_{22}}{2N_{22} + N_{12}}$$

Since $[M_1]/[M_2] = f_1/(1 - f_1)$, eq 5.5.2 can be written

$$p_{11} = \frac{r_1[f_1/(1-f_1)]}{1 + r_1[f_1/(1-f_1)]} \quad \text{and} \quad p_{22} = \frac{r_2[(1-f_1)/f_1]}{1 + r_2[(1-f_1)/f_1]}$$

Particularly when r values are close to zero, this method for evaluating small r's is superior to the graphical analysis of composition data (compare Example 5.4 and Figure 5.4).

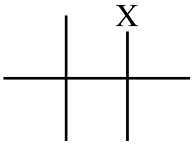
From $\frac{2N_{11}}{2N_{11}+N_{12}} = \frac{r_1[f_1/(1-f_1)]}{1+r_1[f_1/(1-f_1)]}$		From $\frac{2N_{22}}{2N_{22}+N_{12}} = \frac{r_2[(1-f_1)/f_1]}{1+r_2[(1-f_1)/f_1]}$	
f_1	**r_1**	**f_1**	**r_2**
0.584	3.33	0.130	0.036
0.505	3.32	0.121	0.042
0.471	3.48	0.083	0.048
Average	3.38	Average	0.042

By making measurements at higher magnetic fields, it is possible to resolve spectral features arising from still longer sequences. As a matter of fact, the authors of the research described in the last example were able to measure the fractions of tetrads of different composition in the same vinylidene chloride-isobutylene copolymer. Based on the longer sequences, they concluded that the penultimate model describes this system better than the terminal model, although the shortcomings of the latter are not evident in the example. Problems 7 and 8 at the end of the chapter also refer to this system.

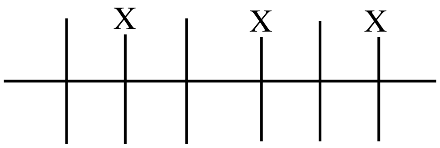
5.7 Characterizing stereoregularity

We introduced the concept of stereoregularity in Section 1.6. Figure 1.3 illustrates isotactic, syndiotactic, and atactic structures of a vinyl polymer in which successive repeat units along the fully extended chain lie, respectively, on the same side, alternating sides, or at random with respect to the backbone. It is important to appreciate the fact that these different structures – different configurations – have their origin in the bonding of the polymer, and no amount of rotation around bonds – changes in conformation – will convert one structure into another.

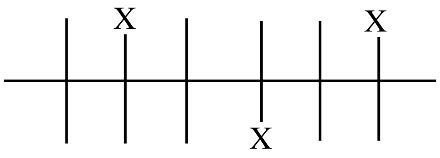
Our discussion of stereoregularity in this chapter is primarily concerned with polymers of monosubstituted ethylene repeat units. We shall represent these by



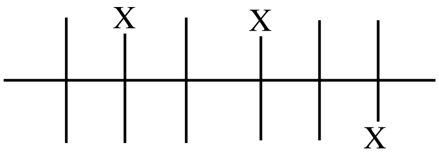
In this representation the X indicates the substituent; other bonds involve only hydrogens. This formalism also applies to 1,1-disubstituted ethylenes in which the substituents are different. With these symbols, the isotactic, syndiotactic, and atactic structures shown in Figure 1.3 are represented by structures [III] – [V], respectively:



[III]



[IV]

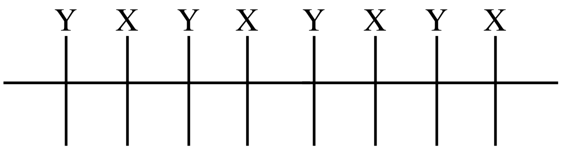


[V]

The carbon atoms carrying the substituents are not truly asymmetric, since the two chain sections – while generally of different length – are locally the same on either side of any carbon atom, except near the ends of the chain. As usual, we ignore any uniqueness associated with chain ends.

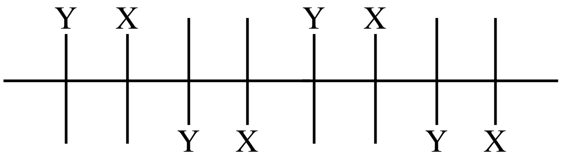
There are several topics pertaining to stereoregularity which we shall not cover, to simplify the presentation:

1. Stereoregular copolymers. We shall restrict our discussion to stereoregular homopolymers.
2. Complications arising from other types of isomerism. Positional and geometrical isomerism, also described in Section 1.6, will be excluded for simplicity. In actual polymers these are not always so easily ignored.
3. Polymerization of 1,2-disubstituted ethylenes. Since these introduce two different "asymmetric" carbons into the polymer backbone (second substituent Y), they have the potential to display ditacticity. Our attention to these is limited to the illustrations of some terminology which is derived from carbohydrate nomenclature (structures [VI-IX])



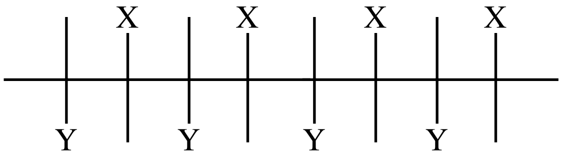
Erythro-di-isotactic

[VI]



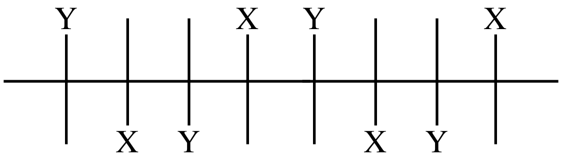
Erythro-di-syndiotactic

[VII]



Threo-di-isotactic

[VIII]



Threo-di-syndiotactic

[IX]

The successive repeat units in structures [III]-[V] are of two different kinds. If they were labeled M_1 and M_2, we would find that, as far as microstructure is concerned, isotactic polymers are formally the same as alternating copolymers, and atactic polymers are formally the same as random copolymers. The analog of block copolymers, stereoblock polymers, also exist. Instead of using M_1 and M_2 to differentiate between the two kinds of repeat units, we shall use the letters D and L as we did in Chapter 1.

The statistical nature of polymers and polymerization reactions has been illustrated at many points throughout this volume. It continues to be important in the discussion of stereoregularity. Thus it is generally more accurate to describe a polymer as, say, predominantly isotactic rather than perfectly isotactic. More quantitatively, we need to be able to describe a polymer in terms of the percentage of isotactic, syndiotactic, and atactic sequences.

Certain bulk properties of polymers also reflect differences in stereoregularity. We will see in Chapter 13 that cystallinity is virtually impossible unless a high degree of stereoregularity is present in a polymer. Since crystallinity plays such an important part in determining the mechanical properties of polymers, stereoregularity manifests itself in these other behaviors also. These gross, bulk properties provide qualitative evidence for differences in stereoregularity, but, as with copolymers, it is the microstructural details that quantitatively characterize the tacticity of a polymer. We shall examine the statistics of this situation in the next section, and the application of NMR in Section 5.9.

The analogy between stereoregular polymers and copolymers can be extended still further. We can write chemical equations for propagation reactions leading to products which differ in configuration along with the associated rate laws. We do this without specifying anything – at least for now – about the mechanism. There are several things that need to be defined to do this:

1. These are addition polymerizations in which chain growth is propagated through an active center. The latter could be a free radical or an ion; we shall see that a coordinated intermediate is the more usual case.
2. The active-center chain end is open to front or rear attack in general; hence the configuration of a repeat unit is not fixed until the next unit attaches to the growing chain.
3. The reactivity of a growing chain is, as usual, assumed to be independent of chain length. In representing this schematically, as either DM* or LM*. The M* indicates the terminal active center, and the D or L, the penultimate units of fixed configuration. From a kinetic point of view, we ignore what lies further back along the chain.
4. As in Chapters 3 and 4, the monomer is represented by M.

With these definitions in mind, we can write

$$—DM^* + M \begin{array}{l} \nearrow DDM^* \\ \searrow DLM^* \end{array} \qquad \text{or} \qquad —LM^* + M \begin{array}{l} \nearrow LLM^* \\ \searrow LDM^* \end{array} \tag{5.O}$$

What is significant about these reactions is that only two possibilities exist: addition with the same configuration (D → DL or L → LL) or addition with the opposite configuration (D → DL or L → LD). We shall designate these isotactic (subscript i) or syndiotactic (subscript s) additions, respectively, and shall define the rate constants for the two steps k_i and k_s. Therefore the rates of isotactic and syndiotactic propagation become

$$R_{p,i} = k_i[M^*][M] \tag{5.7.1}$$

and

$$R_{p,s} = k_s[M^*][M] \tag{5.7.2}$$

and, since the concentration dependences are identical, the relative rate of the two processes is given by the ratio of the rate constants. This same ratio also gives the relative number of dyads having the same or different configurations:

$$\frac{R_{p,i}}{R_{p,s}} = \frac{R_{p,i}}{R_{p,s}} = \frac{k_i}{k_s} = \frac{\text{number dyads with same configuration}}{\text{number dyads with different configurations}} \tag{5.7.3}$$

The Arrhenius equation enables us to expand on this still further:

$$\frac{\text{iso dyads}}{\text{syndio dyads}} = \frac{A_i}{A_e} e^{-(E_i^* - E_s^*)/RT} \tag{5.7.4}$$

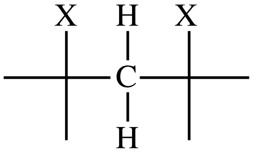
The main conclusion we wish to draw from this line of development is that the difference between E_i^* and E_s^* could vary widely, depending on the nature of the active center. If the active center in a polymerization is a free radical unencumbered by interaction with any surrounding species, we would expect $E_i^* - E_s^*$ to be small. Experiment confirms this expectation; for vinyl chloride it is on the order of 1.3 kJ mol^{-1}. Thus at the temperatures usually encountered in free-radical polymerizations (ca. 60 °C), the exponential in eq 5.7.4 is small and the proportions of isotactic and syndiotactic dyads are roughly equal. This is the case for polyvinyl chloride, for which $k_i / k_s = 0.63$ at 60 °C. The preference for syndiotactic addition is greater than this (that is, $E_i^* - E_s^*$ is larger) in some systems, apparently because there is less repulsion between substituents when they are staggered in the transition state. In all cases, whatever difference in activation energies exists manifests itself in product composition to a greater extent at low temperatures. At high temperatures small differences in E* value are leveled out by the high average thermal energy available.

The foregoing remarks refer explicitly to free-radical polymerizations. If the active center is some kind of associated species – an ion pair or a coordination complex – then predictions based on encumbered intermediates are irrelevant. It turns out that the Ziegler-Natta catalysts – which won their discoverers the Nobel Prize – apparently operate in this way. The active center of the chain coordinates with the catalyst in such a way as to block one mode of addition. High levels of stereoregularity are achieved in this case. Although these substances also initiate the polymerization, the term *catalyst* is especially appropriate in the present context, since the activation energy for one mode of addition is dramatically altered relative to the other by these materials. We shall discuss the chemical makeup of Ziegler-Natta catalysts and some ideas about how they work in Section 5.10. For now it is sufficient to recognize that these catalysts introduce a real bias into eq 5.7.4 and thereby favor one pattern of addition.

In the next section we take up the statistical description of various possible sequences.

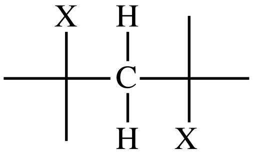
5.8 A statistical description of stereoregularity

Since it is unlikely that a polymer will possess perfect stereoregularity, it is desirable to assess this property quantitatively, both to describe the polymer and to evaluate the effectiveness of various catalysts in this regard. In discussing tacticity in terms of microstructure, it has become conventional to designate a dyad as *meso* if the repeat units have the same configuration, and as *racemic* if the configuration is reversed. The terminology is derived from the stereochemistry of small molecules; its basis is seen by focusing attention on the methylene group in the backbone of the vinyl polymer. This methylene lies in a plane of symmetry in the isotactic molecule [X],



[X]

and thereby defines a meso (subscript m) structure as far as the dyad is concerned. Considering only the dyad, we see that these two methylene protons are in different environments. Therefore each will show a different chemical shift in an NMR spectrum. In addition, each proton splits the resonance of the other into a doublet, so a quartet of peaks appears in the spectrum. Still considering only the dyad, we see that the methylene in a syndiotactic grouping [XI] contains two protons in identical environments:



[XI]

These protons show a single chemical shift in the NMR spectrum. This is called a racemic (subscript r) structure, since it contains equal amounts of D and L character. In the next section we shall discuss the NMR spectra of stereoregular polymers in more detail.

If we define p_m and p_r as the probability of addition occurring in the meso and racemic modes, respectively, then $p_m + p_r = 1$, since there are only two possibilities. The probability p_m is the analog of p_{ij} for copolymers; hence, by analogy with eq 5.5.1, this equals the fraction of isotactic dyads among all dyads. In terms of the kinetic approach of the last section, p_m is equal to the rate of an iso addition divided by the combined rates of iso and syndio additions:

$$p_m = \frac{k_i}{k_i + k_s} \tag{5.8.1}$$

This expression is the equivalent of eq 5.5.2 for copolymers.

The system of notation we have defined can readily be extended to sequences of greater length. Table 5.6 illustrates how either m or r dyads can be bracketed by two additional repeat units to form a tetrad. Each of the outer units is either m or r with respect to the unit it is attached to, so the meso dyad generates three tetrads. Note that the tetrads mmr and rmm are equivalent and are not distinguished. A similar set of tetrads is generated from the r dyad.

The same system of notation can be extended further by focusing attention on the backbone substituents rather than on the methylenes. Consider bracketing a center *substituent* with a pair of monomers in which the substituents have either the same or opposite configurations as the central substituents. Thus the probabilities of the resulting triads are obtained from the probabilities of the respective m or r additions. The following possibilities exist:

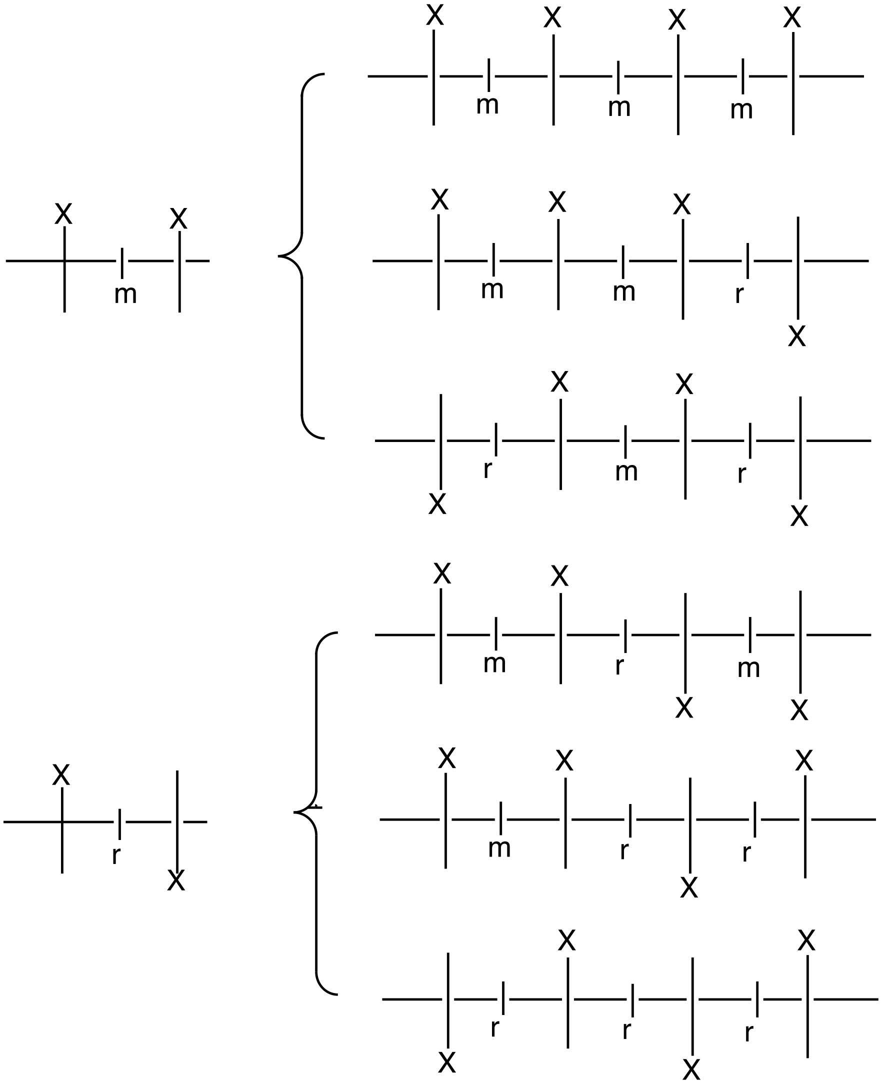
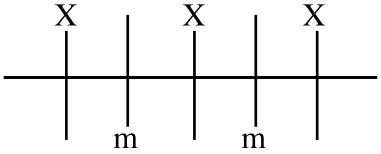


Table 5.6

The splitting of meso and racemic dyads into six tetrads.

1. An isotactic triad [XII] is generated by two successive meso additions:

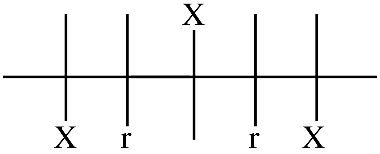


[XII]

The probability of the isotactic triad is

$$p_i = p_m^2 \tag{5.8.2}$$

2. A syndiotactic triad [XIII] is generated by two successive racemic additions:

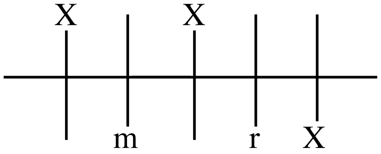


[XIII]

The probability of the syndiotactic triad is given by p_r^2, which becomes

$$P_s = (1 - p_m)^2 \tag{5.8.3}$$

3. A heterotactic triad [XIV] is generated by mr and rm sequences of additions:



[XIV]

The probability of a heterotactic (subscript h) triad is

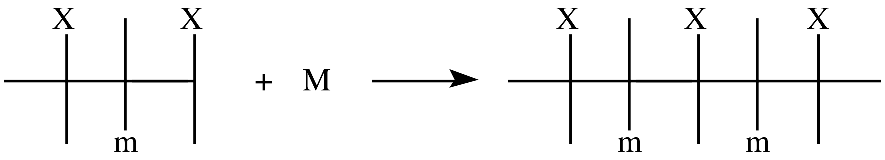
$$p_h = 2p_m(1 - p_m) \tag{5.8.4}$$

The factor 2 arises because this particular sequence can be generated in two different orders.

These triads can also be bracketed by two more units to generate 10 different pentads following the pattern established in Table 5.6. It is left for the reader to verify this number by generating the various structures.

The probabilities of the various dyad, triad, and other sequences that we have examined have all been described by single probability parameter p_m. When we used the same kind of statistics for copolymers, we called the situation one of terminal control. We are considering similar statistics here, but the idea that the stereochemistry is controlled by the terminal unit is inappropriate. The active center of the chain end governs the *chemistry* of the addition, but not the *stereochemistry*. Equations 5.7.1 and 5.7.2 merely state that an addition must be of one kind or another, but that the rates are not necessarily identical.

A mechanism in which the stereochemistry of the growing chain does exert an influence on the addition might exist, but at least two repeat units in the chain are required to define any such stereochemistry. Therefore this possibility is equivalent to the penultimate mechanism in copolymers. In this case the addition would be described in terms of conditional probabilities, just as eq 5.5.20 does for copolymers. Thus the probability of an isotactic triad controlled by the stereochemistry of the growing chain would be represented by the reaction.



(5.P)

and described by the probability

$$p_{\text{control}} = p_m p_{m/m} \qquad (5.8.5)$$

where $p_{m/m}$, a conditional probability, is the probability of an m addition, given the fact of a prior m addition. As with copolymers, triads must be considered in order to *test* whether the simple statistics apply. Still longer sequences need to be examined to test whether stereochemical control is exerted by the chain. Although such situations are known, we shall limit our discussion to the simple case where the single probability p_m is sufficient to describe the various additions. The latter, incidentally, may be called *zero-order Markov (or Bernoulli) statistics* to avoid the vocabulary of terminal control. The case where the addition is influenced by whether the last linkage in the chain is m or r is said to follow a first-order Markov process.

The number of m or r linkages in an "n-ad" is n – 1. Thus dyads are characterized by a single linkage (either m or r), triads by two linkages (either mm, mr, or rr), and so forth. The m and r notation thus reduces by 1 the order of the description from what is obtained when the repeat units themselves are described. For this reason the terminal control mechanism for copolymers is a first-order Markov process and the penultimate model is a second-order Markov process. Note that the compound probabilities which describe the probability of an n-ad in terms of p_m are also of order n – 1. In the following example we calculate the probability of various triads on the basis of zero-order Markov statistics.

Example 5.6

Use zero-order Markov statistics to evaluate the probability of isotactic, syndiotactic, and heterotactic triads for the series of p_m values spaced at intervals of 0.1. Plot and comment on the results.

Solution

Evaluate eqs 5.8.2-5.8.4 for p_m between zero and unity; these results are plotted in Figure 5.7.

p_m	p_m^2	$(1 - p_m)^2$	$2p_m(1 - p_m)$
0	0	0	0
0.1	0.01	0.81	0.18
0.2	0.04	0.64	0.32
0.3	0.09	0.49	0.42
0.4	0.16	0.36	0.48
0.5	0.25	0.25	0.50
0.6	0.36	0.16	0.48
0.7	0.49	0.09	0.42
0.8	0.64	0.04	0.32
0.9	0.81	0.01	0.18
1.0	1.0	0	0

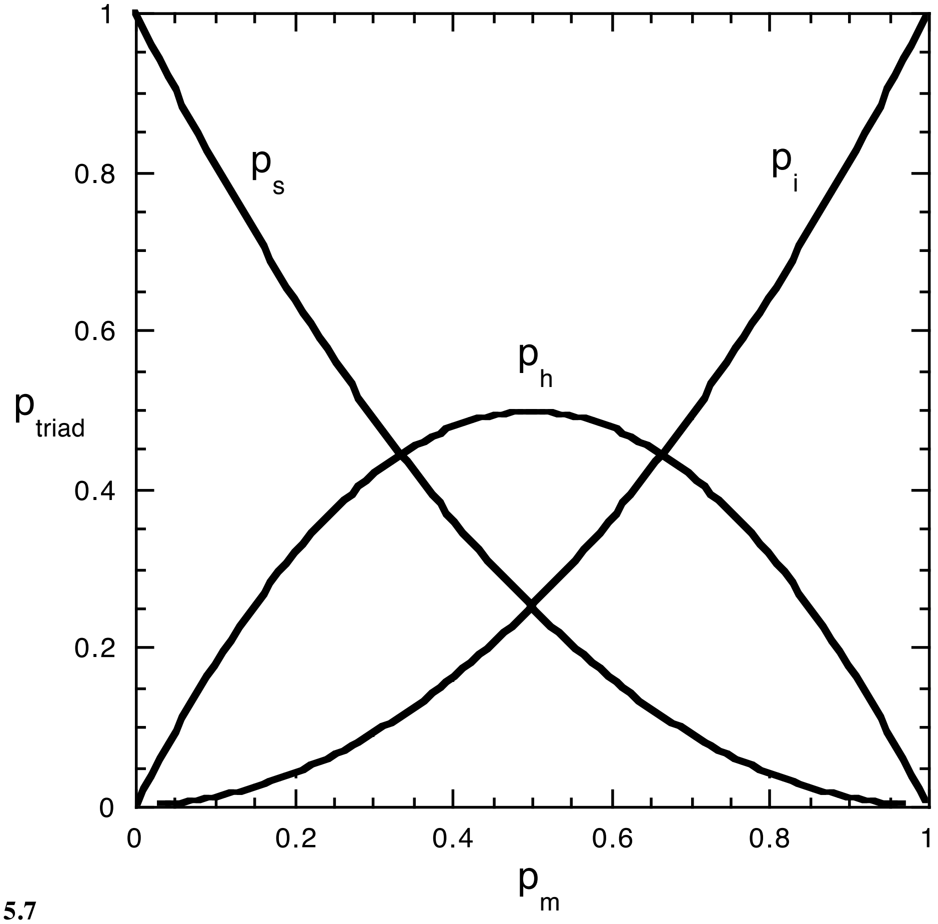


Figure 5.7

Fractions of iso, syndio, and hetero triads as a function of p_m, calculated assuming zero-order Markov statistics in Example 5.6.

The following observations can be made from these calculations:

1. The probabilities give the fractions of the three different types of triads in the polymer.
2. If the fractions of triads could be measured, they either would or would not lie on a single vertical line in Figure 5.7. If they did occur at a single value of p_m, this would not only give the value of p_m (which could be obtained from the fraction of one kind of triad), but would also prove the statistics assumed. If the fractions were not consistent with a single p_m value, higher-order Markov statistics are indicated.
3. The fraction of isotactic sequences increases as p_m increases, as required by the definition of these quantities.
4. The fraction of syndiotactic sequences increases as $p_m \rightarrow 0$, which corresponds to $p_r \rightarrow 1$.
5. The fraction of heterotactic triads is a maximum at $p_m = p_r = 0.5$ and drops to zero at either extreme.
6. For an atactic polymer the proportions of isotactic, syndiotactic, and heterotactic triads are 0.25:0.25:0.50

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To investigate the triads by NMR, the resonances associated with the chain substituent are examined, since structures [XII]-[XIV] show that it is these that experience different environments in the various triads. If dyad information is sufficient, the resonances of the methylenes in the chain backbone are measured. Structures [X] and [XI] show that these serve as probes of the environment in dyads. In the next section we shall examine in more detail how this type of NMR data is interpreted.

5.9 Assessing stereoregularity by NMR

It is not the purpose of this book to discuss in detail the contribution of NMR spectroscopy to the determination of molecular structure. This is a specialized field in itself and a great deal has been written on the subject. In this section we shall consider only the application of NMR to the elucidation of stereoregularity in polymers. Numerous other applications of this powerful technique have also been made in polymer chemistry, including the study of positional and geometrical isomerism (Section 1.6) and copolymers (Section 5.7. We shall also make no attempt to compare the NMR spectra of various different polymers; instead, we shall examine primarily the NMR spectra of different poly(methyl methacrylate) preparations to illustrate the capabilities of the method, using the first system that was investigated by this technique as the example.

Figure 5.8 shows the 60-MHz spectra of poly(methyl methacrylate) prepared with different catalysts so that predominately isotactic, syndiotactic, and atactic products are formed. The three spectra in Figure 5.8 are identified in terms of this predominant character. It is apparent that the spectra are quite different, especially in the range of δ values between 1 and 2 ppm. Since the atactic polymer has the least regular structure, we concentrate on the other two to make the assignment of the spectral features to the various protons.

Several observations from the last section provide the basis of interpreting these spectra:

1. The hydrogens of the methylene group in the backbone of the poly(methyl methacrylate) produce a single peak in a racemic dyad, as illustrated by structure [XIII].
2. The same group of hydrogens in a meso dyad [X] produce a quartet of peaks: two different chemical shifts, each split into two by the two hydrogens in the methylene.
3. The peaks centered at $\delta = 1.84$ ppm – a singlet in the syndiotactic and a quartet in the isotactic polymers – are thus identified with these protons. This provides an unambiguous identification of the predominant stereoregularity of these samples.

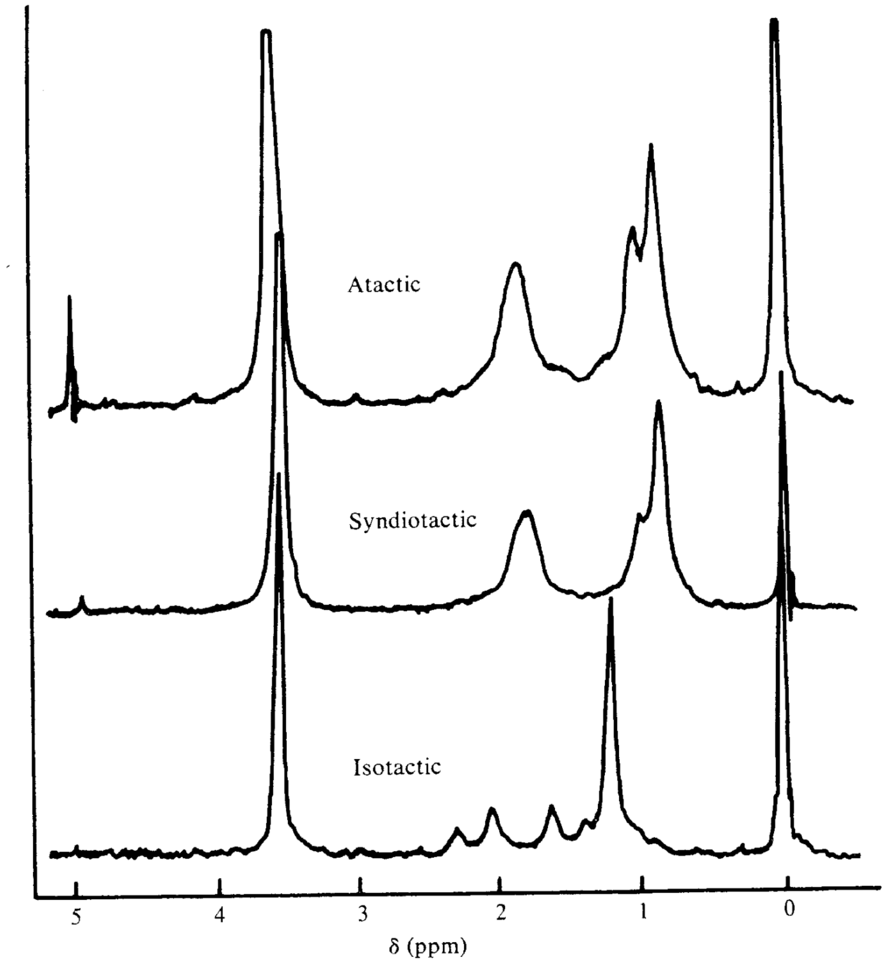


Figure 5.8

Nuclear magnetic resonance spectra of three poly(methyl methacrylate) samples. Curves are labeled according to the predominant tacticity of samples. [From D.W. McCall and W. P. Slichter, in *Newer Methods of Polymer Characterization*, B. Ke (Ed.), Interscience, New York, 1964, used with permission]

4. The features that occur near $\delta = 1.0$ ppm are associated with the protons of the α-methyl group. The location of this peak depends on the configurations of the nearest neighbors.

5. Working from the methylene assignments, we see that the peak at $\delta = 1.22$ ppm in the isotactic polymer arises from the methyl in the center of an isotactic triad, the peak at $\delta = 0.87$ ppm from a syndiotactic triad, and the peak at $\delta = 1.02$ ppm from a homotactic triad.

6. The peak at $\delta = 3.5$ ppm is due to the methoxy group.

Once these assignments are made, the areas under the various peaks can be measured to determine the various fractions:

1. The area under the methylene peaks is proportional to the dyad concentration: the singlet gives the racemic dyads and the quartet gives the meso dyads.
2. The area under one of the methyl peaks is proportional to the concentration of the corresponding triad.
3. It is apparent that it is not particularly easy to determine the exact areas of these features when the various contributions occur together to any significant extent. This is clear from the atactic spectrum, in which slight shoulders on both the methylene and methyl peaks are the only evidence of meso methylenes and iso methyls.

The spectra shown in Figure 5.8 were early attempts at this kind of experiment, and the measurement of peak areas in this case was a rather subjective affair. We shall continue with an analysis of these spectra, even though improved instrumentation has resulted in greatly improved spectra. One development that has produced better resolution is the use of higher magnetic fields. As the magnetic field increases, the chemical shifts for the various features are displaced proportionately. The splitting caused by spin-spin coupling, on the other hand, is unaffected. This can produce a considerable sharpening of the NMR spectrum. Other procedures such as spin decoupling, isotopic substitution, computerized stripping of superimposed spectra, and ^{13}C-NMR also offer methods for identifying and quantifying NMR spectra.

Table 5.7 lists the estimated fractions of dyads of types m and r and the fractions of triads of types i, s and h from Figure 5.8. These fractions represent the area under a specific peak (or four peaks in the case of the meso dyads) divided by the total area under all of the peaks in either the dyad or triad category. As expected for the sample labeled isotactic, 89% of the triads are of type i and 87% of the dyads are of type m. Likewise, in the sample labeled syndiotactic, 68% of the triads are s and 83% of the dyads are r.

The sample labeled in Figure 5.8 was prepared by a free-radical mechanism and is expected to follow zero-order Markov statistics. As a test for this, we examine Figure 5.7 to see whether the values of p_i, p_s, and p_h given by the fractions in Table 5.7 agree with a single set of p_m values. When this is done, it is apparent that these proportions are consistent with this type of statistics within experimental error and that $p_m \cong 0.25$ for poly(methyl methacrylate). Under the conditions of this polymerization, the free-radical mechanism is biased in favor of syndiotactic additions over isotactic additions by about 3:1, according to eq 5.8.1. Presumably this is due to steric effects involving the two substituents on the α-carbon.

	Dyads		Triads		
Sample	Meso	Racemic	Iso	Syndio	Hetero
Atactic	0.22	0.78	0.07	0.55	0.38
Syndiotactic	0.17	0.83	0.04	0.68	0.28
Isotactic	0.87	0.13	0.89	0.04	0.07

Table 5.7

The fractions of meso and racemic dyads and iso, syndio, and hetero triads for the data in Figure 5.8. Data from D. W. McCall and W. P. Slichter in *Newer Methods of Polymer Characterization*, B. Ke (Ed.), Interscience, New York, 1964.

With this kind of information it is not difficult to evaluate the average lengths of isotactic and syndiotactic sequences in a polymer. As a step toward this objective, we define the following:

1. The number of isotactic sequences containing n_i iso repeat units is N_{n_i}.

2. The number of syndiotactic sequences containing n_s syndio repeat units is N_{n_s} .

3. Since isotactic and syndiotactic sequences must alternate, it follows that

$$N_{n_i} = N_{n_s} \tag{5.9.1}$$

4. The number of iso triads in a sequence of n_i iso repeat units is $n_i - 1$, and the number of syndio triads in a sequence of n_s syndio repeat units is $n_s - 1$. We can verify these relationships by examining a specific chain segment:

   –DDLDLDLDLD*DDDDDDDDL–

   In this example both the iso and syndio sequences consist of eight repeat units, with seven triads in each. The repeat unit marked * is counted as part of each type of triad, but is itself the center of a hetero triad.

5. The number of racemic dyads in a sequence is the same as the number of syndiotactic units n_s. The number of meso dyads in a sequence is the same as the number of iso units n_i. These can also be verified from structure above.

With these definitions in mind, we can immediately write expressions for the ratio of the total number of ν of iso triads to the total number of syndio triads:

$$\frac{\nu_i}{\nu_s} = \frac{\sum N_{n_i}(n_i - 1)}{\sum N_{n_s}(n_s - 1)} = \frac{\sum N_{n_i}(n_i) - \sum N_{n_i}}{\sum N_{n_s}(n_s) - \sum N_{n_s}} \tag{5.9.2}$$

In this equation the summations are over all values of n of the specified type. Also remember that the ν's and n's in this discussion (with subscript i or s) are defined differently from the ν's and n's defined earlier in the chapter for copolymers. Using eq 5.9.1 and remembering the definition of an average provided by eq 1.7.7, we see that eq 5.9.2 becomes

$$\frac{\nu_i}{\nu_s} = \frac{\bar{n}_i - 1}{\bar{n}_s - 1} \tag{5.9.3}$$

where the overbar indicates the average length of the indicated sequence.

A similar result can be written for the ratio of the total number (ν) of dyads of the two types (m and r), using item 5 above:

$$\frac{\nu_m}{\nu_r} = \frac{\sum N_{n_i}(n_i)}{\sum N_{n_s}(n_s)} = \frac{\bar{n}_i}{\bar{n}_s} \tag{5.9.4}$$

Equations 5.9.3 and 5.9.4 can be solved simultaneously for $\bar{n}_i$ and $\bar{n}_s$ in terms of the total number of dyads and triads:

$$\bar{n}_i = \frac{1 - \nu_i/\nu_s}{1 - (\nu_i/\nu_s)(\nu_r/\nu_m)} \tag{5.9.5}$$

and

$$\bar{n}_s = \frac{1 - \nu_i/\nu_s}{(\nu_m/\nu_t) - (\nu_i/\nu_s)} \tag{5.9.6}$$

Use of these relationships is illustrated in the following example:

Example 5.7

Use the dyad and triad fractions in Table 5.7 to calculate the average lengths of isotactic and syndiotactic sequences for the polymers of Figure 5.8. Comment on the results.

Solution

Since the total numbers of dyads and triads always occur as ratios in eqs 5.9.3 and 5.9.4, both the numerators and denominators of these ratios can be divided by the total number of dyads or triads to convert these total numbers into fractions, i.e.,

$$\nu_i / \nu_s = \left(\nu_i / \nu_{tot}\right) / \nu_s / \nu_{tot} = p_i / p_s .$$

Thus the fractions in Table 5.7 can be substituted for the ν's in eqs 5.9.3 and 5.9.4. The values of $\bar{n}_i$ and $\bar{n}_s$ so calculated for the three polymers are:

	$\bar{n}_i$	$\bar{n}_s$
Atactic	1.59	5.64
Syndiotactic	1.32	6.45
Isotactic	9.14	1.37

This` analysis adds nothing new to the picture already presented by the dyad and triad probabilities. It is somewhat easier to visualize an average sequence, however, although it must be remembered that the latter implies nothing about the distribution of sequence length.

We conclude this section via Figure 5.9, which introduces the use of ^{13}C NMR obtained at 100 MHz for the analysis of steroeregularity in polypropylene. This spectrum shows the carbons on the pendant methyl groups for an atactic polymer. Individual peaks are resolved for all the possible pentad sequences. Polypropylene also serves as an excellent starting point for the next section, in which we examine some of the catalysts which are able to control stereoregularity in such polymers.

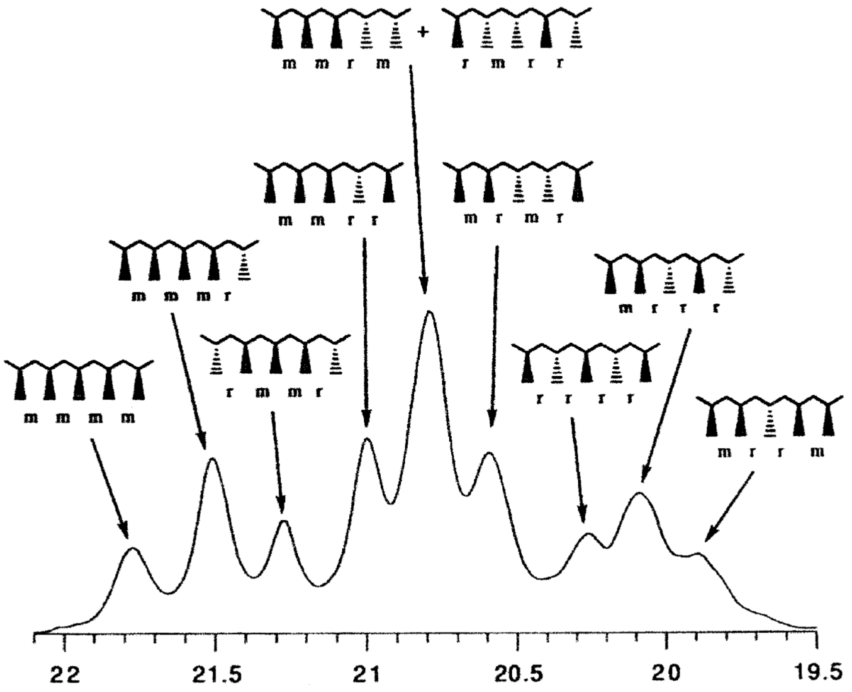


Figure 5.9
^{13}C NMR assignments for polypropylene. From M. D. Bruce and R. M. Waymouth, *Macromolecules* 31, 2707 (1998).

5.10 Ziegler-Natta catalysts

In this discussion we consider Ziegler-Natta catalysts and their role in achieving stereoregularity. This is a somewhat restrictive view of the situation, since there are other catalysts – such as phenyl magnesium bromide, a Grignard reagent – which can produce stereoregularity; the Ziegler-Natta catalysts are also used to produce polymers – unbranched polyethylene to name one – which lack stereoregularity. However, Ziegler-Natta catalysts are historically the most widely used and best-understood stereoregulating systems, so the loss of generality in this approach is not of great consequence.

The fundamental Ziegler-Natta recipe consists of two components: a halide or some other compound of a transition metal from among the group IVB to VIIIB elements, and an organometallic compound of a representative metal from groups IA to IIIA. Some of the transition metal compounds that have been studied include $TiCl_4$, $TiCl_3$, VCl_4, VCl_3, $ZrCl_4$, $CrCl_3$, $MoCl_5$, and CuCl. Some of the representative organometallics include $(C_2H_5)_3Al$, $(C_2H_5)_2Mg$, C_4H_9Li and $(C_2H_5)_2Zn$. These are only a few of the possible compounds, so the number of combinations is very large.

The individual components of the Ziegler-Natta system can separately account for the initiation of some forms of polymerization reactions, but not for the fact of stereoregularity. For example, butyl lithium can initiate anionic polymerization (see Section 4.3) and $TiCl_4$ can initiate cationic polymerization (see Section 4.5). In combination, still another mechanism for polymerization, coordination polymerization, is indicated. When the two components of the Ziegler-Natta system are present together, complicated exchange reactions are possible. Often the catalyst must age to attain maximum effectiveness; presumably this allows these exchange reactions to occur. Some possible exchange equilibria are

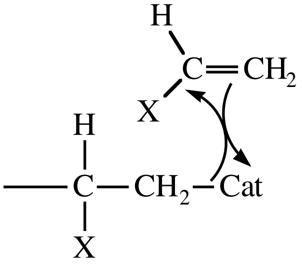
$$\begin{aligned} &2\,Al(C_2H_5)_3 \;\Leftrightarrow\; Al_2(C_2H_5)_6 \;\Leftrightarrow\; [Al(C_2H_5)_2]^+\,[Al(C_2H_5)_4]^- \\ &TiCl_4 + [Al(C_2H_5)_2]^+ \;\Leftrightarrow\; C_2H_5TiCl_3 + [Al(C_2H_5)Cl]^+ \qquad (5.Q) \end{aligned}$$

The organotitanium halide can then be reduced to $TiCl_3$:

$$C_2H_5TiCl_3 \;\rightarrow\; TiCl_3 + C_2H_5\bullet \qquad (5.R)$$

Among other possibilities reactions, these free radicals can initiate ordinary free-radical polymerization. The Ziegler-Natta systems are thus seen to encompass several mechanisms for the initiation of polymerization. Neither ionic nor free-radical mechanisms account for stereoregularity, however, so we must look further for the mechanism whereby the Ziegler-Natta systems produce this interesting effect.

The stereoregularity capability of Ziegler-Natta catalysts is believed to depend on a coordination mechanism in which both the growing polymer chain and the monomer coordinate with the catalyst. The addition then occurs by insertion of the monomer between the growing chain and the catalysts by a concerted mechanism [XV]:



[XV]

Since the coordination almost certainly involves the transition metal atom, there is a resemblance here to anionic polymerization. The coordination is an important aspect of the present picture, since it is this feature which allows the catalyst to serve as a template for stereoregulation.

The assortment of combination of components is not the only variable to consider in describing Ziegler-Natta catalysts. Some other variables include the following:

1. Catalyst solubility. Polymerization systems may consist of one or two phases. Titanium-based catalysts are the most common of the heterogeneous systems; vanadium-based catalysts are the most common homogeneous systems. Since the catalysts functions as a template for the formation of a stereoregular product, it follows that the more extreme orienting effect of a solid surface (i.e., heterogeneous catalysts) are required for those monomers which interact only weakly with the catalyst. The latter are nonpolar

monomers. Polar monomers interact more strongly with catalysts, and dissolved catalysts are able to exert sufficient control for stereoregularity.

2. Crystal structure of solids. The α-crystal from of $TiCl_3$ is an excellent catalyst and has been investigated extensively. In this particular crystal form of $TiCl_3$, the titanium ions are located in an octahedral environment of chloride ions. It is believed that the stereoactive titanium ions in this crystal are located at the edges of the crystal, where chloride ion vacancies in the coordination sphere allow coordination with the monomer molecules.

3. Tacticity of products. Most solid catalysts produce isotactic products. This is probably because of the highly orienting effect of the solid surface, as noted in item (1). The preferred isotactic configuration produced at these surfaces is largely governed by steric and electrostatic interactions between the monomer and the ligands of the transition metal. Syndiotacticity is mostly produced by soluble catalysts. Syndiotactic polymerizations are carried out at low temperatures, and even the catalyst must be prepared at low temperatures; otherwise specificity is lost. With polar monomers syndiotacticity is also promoted by polar reaction media. Apparently the polar solvent molecules compete with monomer for coordination sites, and thus indicate more loosely coordinated reactive species.

4. Rate of polymerization. The rate of polymerization for homogeneous systems closely resembles anionic polymerization. For heterogeneous systems the concentration of alkylated transition metal sites on the surface appears in the rate law. The latter depends on the particle size of the solid catalyst and may be complicated by sites of various degrees of activity. There is sometimes an inverse relationship between the degree of stereoregularity produced by a catalyst and the rate at which polymerization occurs.

The catalysts under consideration both initiate the polymerization and regulate the polymer formed. There is general agreement that the mechanism by which these materials exert their regulatory role involves coordination of monomer with the transition metal atom, but proposed details beyond this are almost as numerous and specific as the catalysts themselves. We shall return to a description of two specific mechanisms below. The general picture postulates an interaction between monomer and catalyst such that a complex is formed between the π elements of the olefin and the d orbitals of the transition metal. Figure 5.10 shows that the overlap between the filled orbitals of the monomer can overlap with vacant $d_{x^2-y^2}$ orbitals of the metal. Alternatively, hybrid orbitals may be involved on the metal. There is a precedent for such bonding is simple model compounds. It is known, for example, that Pt^{2+} complexes with ethylene by forming a dsp^2 hybrid-π sigma bond and a dp hybrid-π^* pi bond. A crucial consideration in the coordination is maximizing the overlap of the orbitals involved. Titanium (III) ions seem ideally suited for this function; higher effective nuclear charge on the metal results in less spatial extension of d orbitals and diminished overlap.

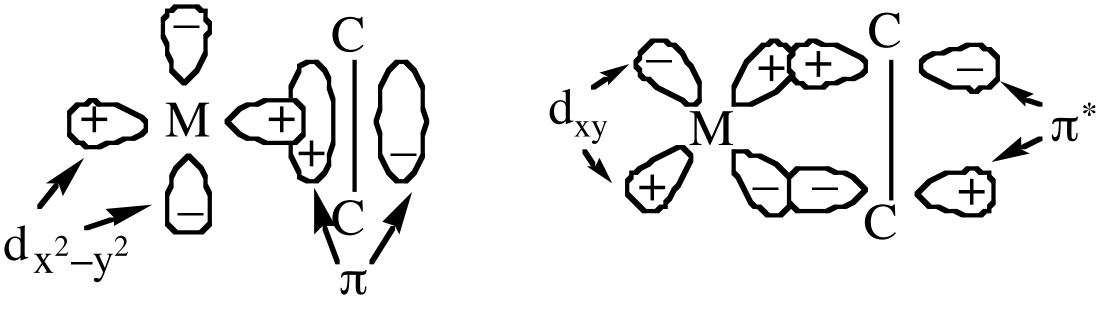


Figure 5.10

Possible orbital overlaps between a transition metal and an olefin

Many mechanisms have been proposed that elaborate on this picture. These are often so specific that they cannot be generalized beyond the systems for which they are proposed. Two schemes that do allow some generalization are presented here. Although they share certain common features, these mechanisms are distinguished by the fact that one – the monometallic model – does not include any participation by the representative metal in the mechanism. The second – the bimetallic model – does assume the involvement of both metals in the mechanism.

The monometallic mecahnism is illustrated by Figure 5.11. It involves the monomer coordinating with an alkylated titanium atom. The insertion of the monomer into the titanium-carbon bond propagates the chain. As shown in Figure 5.11 this shifts the vacancy – represented by the square – in the coordination sphere of the titanium to a different site. Syndiotactic regulation occurs if the next addition takes place via this newly created vacancy. In this case the monomer and the growing chain occupy alternating coordination sites in successive steps. For the more common isotactic growth the polymer chain must migrate back to its original position.

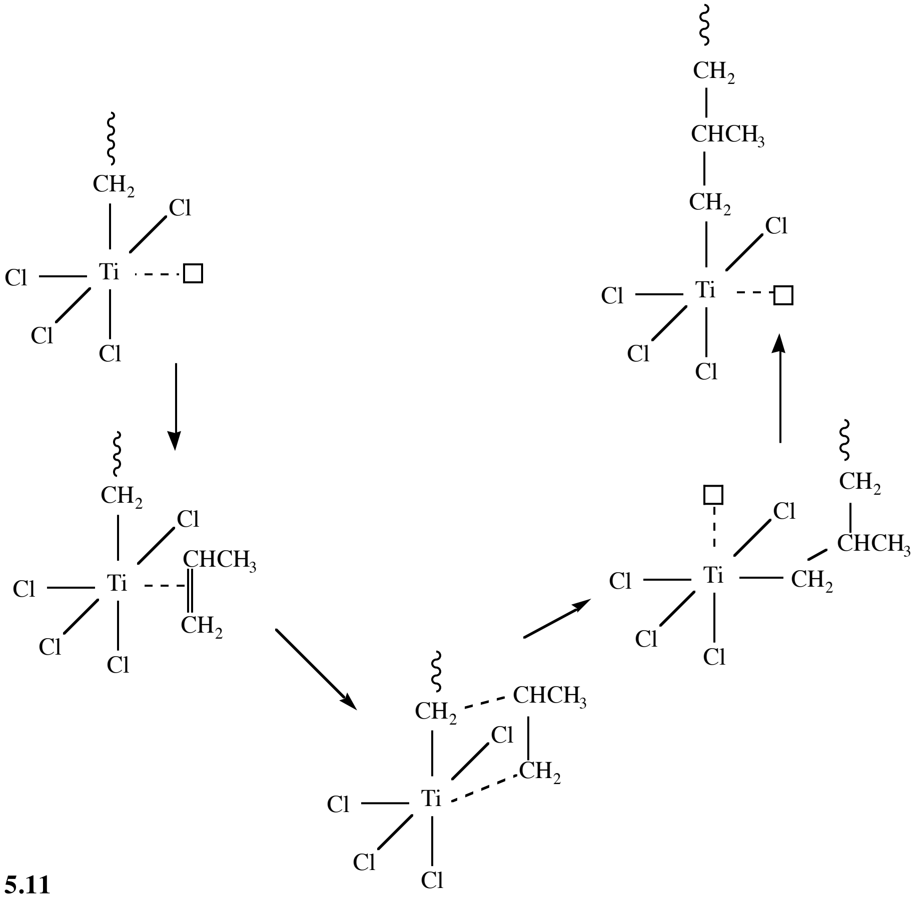


Figure 5.11

Monometallic mechanism. The square indicates a vacant ligand site.

The bimetallic mechanism is illustrated in Figure 5.12; the bimetallic active center is the distinguishing feature of this mechanism. The precise distribution of halides and alkyls is not spelled out because of the exchanges described by reaction (5.Q). An alkyl bridge is assumed based on observation of other organometallic compounds. The pi coordination of the olefin with the titanium is followed by insertion of the monomer into the bridge to propagate the reaction.

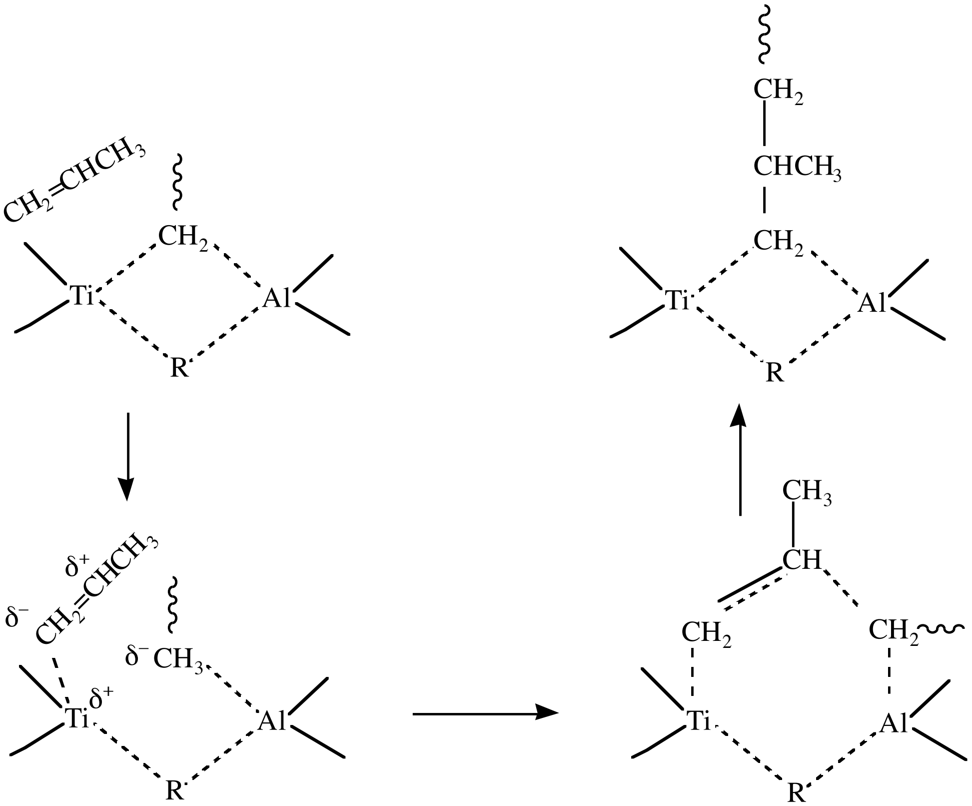


Figure 5.12
The bimetallic mechanism.

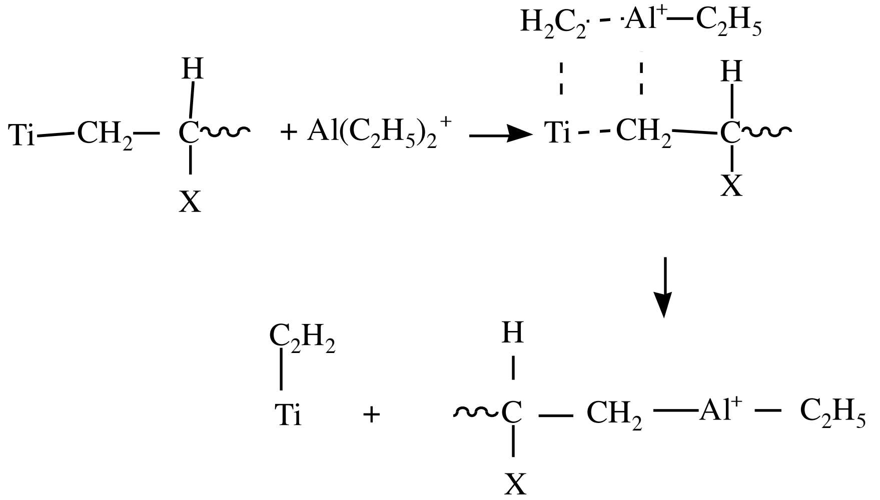
At present it is not possible to determine which of these mechanisms or their variations most accurately represents the behavior of Ziegler-Natta catalysts. In view of the number of variables in these catalyzed polymerizations, both mechanisms may be valid, each for different specific systems. In the following example the termination step of coordination polymerizations is considered.

Example 5.8

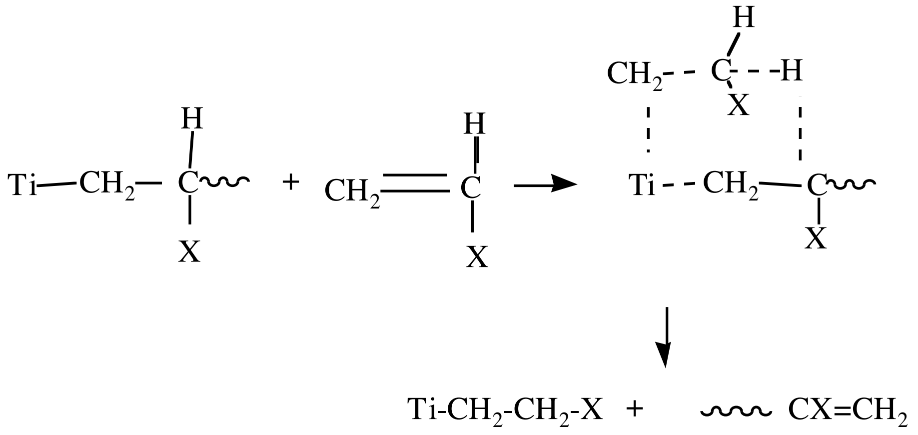
Polypropylene polymerized with triethyl aluminum and titanium trichloride has been found to contain various kinds of chain ends. Both terminal vinylidene unsaturation and aluminum-bound chain ends have been identified. Propose two termination reactions which can account for these observations. Do the termination reactions allow any discrimination between the monometallic and bimetallic propagation mechanisms?

Solution

A reaction analogous to the alkylation step of reactions (4.Q) can account for the association of an aluminum species with chain ends:



The transfer of a tertiary hydrogen between the polymer chain and a monomer can account for the vinylidene group in the polymer:



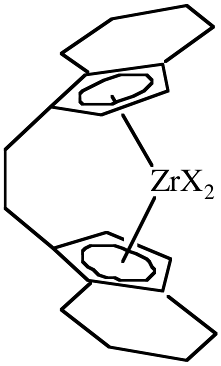
These reactions appear equally feasible for titanium in either the monometallic or bimetallic intermediate. Thus they account for the different types of end groups in the polymer, but do not differentiate between propagation intermediates. In the commercial process for the production of polypropylene by Ziegler-Natta catalysts, hydrogen is added to terminate the reaction, so neither of these reactions is pertinent in this case.

5.11 Single-site catalysts

The discussion in the preceding section indicates that Ziegler-Natta catalysts represent a rather complicated subject. This complexity is often reflected in the structure of the polymers produced. For example, the different ways that the two metal centers may or may not interact during an addition step suggests that there are, in fact multiple catalytic sites active in a given polymerization. This can lead to sites with greatly different propagation rates, different stereoselectivity, and different propensities to incorporate any co-monomers present. The net result is that polymer materials produced by Ziegler-Natta catalysts, especially under commercial conditions, tend to be highly heterogeneous at the molecular level. A broad strategy to overcome this limitation is based on the concept of a single-site catalyst, i.e., one that has a single, well-defined catalytic geometry that can control the desired aspect of propagation. In this section we briefly consider some examples of such catalysts for stereochemical control in the polymerization of α-olefins. We begin with a little more consideration of catalysis in general.

The majority of catalysts in commercial use are *heterogeneous*. In this usage, the term heterogeneous means that the phase of the catalyst (e.g., solid) is distinct from that of the reagents and products (usually gases and liquids). When the catalyst is a relatively small molecule, it is retained in the solid phase by immobilization on some kind of inert, robust *support*. The reaction(s) of interest therefore take place at the solid/liquid or solid/gas interface. The fact of immobilization can itself contribute to the multiple site nature of heterogeneous catalysts, for example by exposing different faces of the catalytically active metal center, by restricting accessibility of reagents to catalyst particles deep within a porous support, and by presenting a distribution of different cluster sizes of catalytic particles. Given these disadvantages, one might ask why heterogeneous catalysis is the norm? The answer is simple: it is much easier to separate (and possibly regenerate) heterogeneous catalysts from products and unreacted reagents. Note that if the activity of a catalyst is sufficiently high (in terms of grams polymer produced per gram catalysts employed), then separation and/or recovery of the catalyst may not be necessary. In contrast, single-site polymerization catalysts are usually *homogenous*: they are molecularly dispersed within the reaction medium. This situation leads to better defined products, and is much more amenable to detailed studies of mechanism. Furthermore, strategies for immobilizing such catalysts are available, making them also of potential commercial interest.

Most single-site catalysts have the general formula [L_nMP], where L_n represents a set of ligands, M is the active metal center, and P is the growing polymer. Furthermore, a common motif is for two of the ligands to contain cyclopentadienyl (Cp) rings, which may themselves be covalently-linked or bridged. The example shown below [XVI] was one of the first such *metallocene* systems, and produces highly isotactic polypropylene.



[XVI]

However, this representation is not complete. Just as Ziegler-Natta catalysts always involve a mixture of at least two active ingredients, single-site catalysts involve another component. The most common is a partially hydrolyzed tri-methyl aluminum species, methylaluminoxane (MAO). The active center is more properly denoted $[L_nMP]^+[X]^-$, where the metal site is cationic by virtue of being coordinatively unsaturated, and the counterion contains MAO and a displaced ligand, such as chloride.

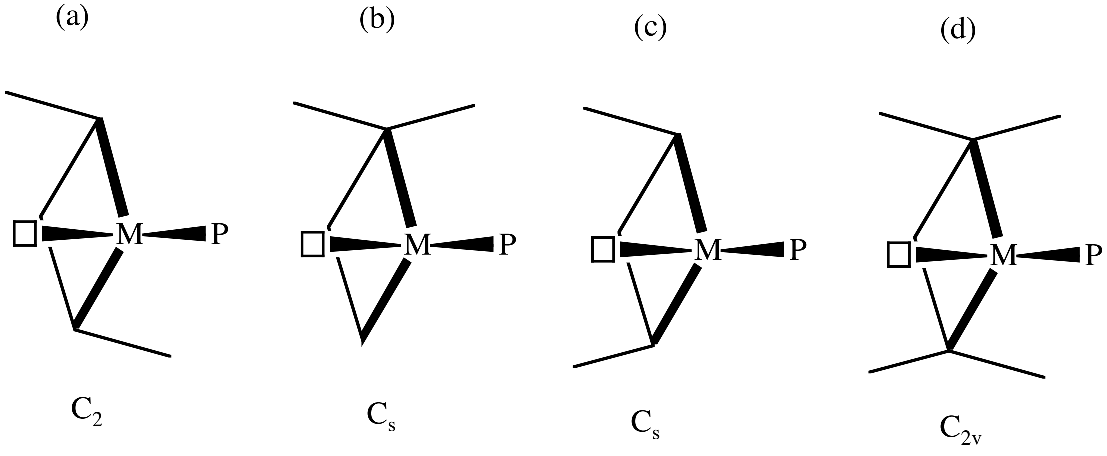


Figure 5.13

Role of catalyst symmetry in stereocontrol, following G. W. Coates, *Chem. Rev.* 100, 1223 (2000). The open square represents the unsaturated site for monomer addition, and the Cp rings are represented by the pendant lines. A catalyst of type (a) is isospecific and (b) is syndiospecific, when under site control; (c) and (d) can be either iso- or syndiospecific, under chain-end control.

The choice of metal, ligands and design of the overall constraining geometry provide a rich palette from which catalysts may be designed. In general, the stereoregulation of monomer addition can be achieved through one of two modes. Under *chain-end control*, the addition of a monomer is influenced most by the configuration of the previous repeat unit, which is reminiscent of the terminal model of copolymerization. To appreciate how this can happen, it is important to realize that the growing polymer remains bound to the metal center during the addition step. Alternatively, under *site control* the ligand set may be chosen to provide a chiral confining environment, which exerts a dominant influence on the stereochemistry of addition. The symmetry of the catalyst is often strongly correlated with the mode and effect of stereo control. This is summarized in Figure 5.13. Catalysts with a plane of symmetry, or C_s, tend to produce syndiotactic polymers under site control, but either iso- or syndiotactic polymers under chain-end control. When the symmetry is C_2, i.e., identical after rotation by 180° about a single axis, the addition is isospecific under site control. When a further mirror plane exists, in C_{2v} symmetry, chain end control leads to either iso- or syndiospecific addition.

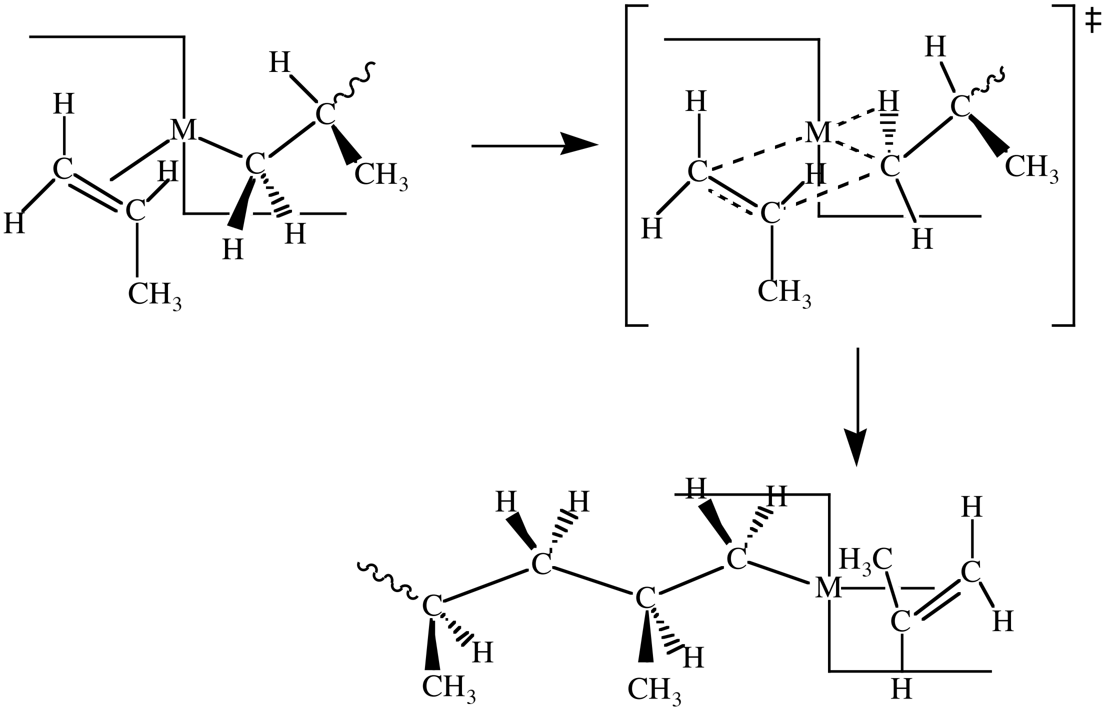
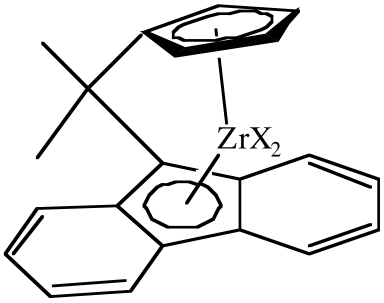


Figure 5.14

Proposed mechanism of isospecific polymerization of polypropylene; following G. W. Coates, *Chem. Rev.* 100, 1223 (2000).

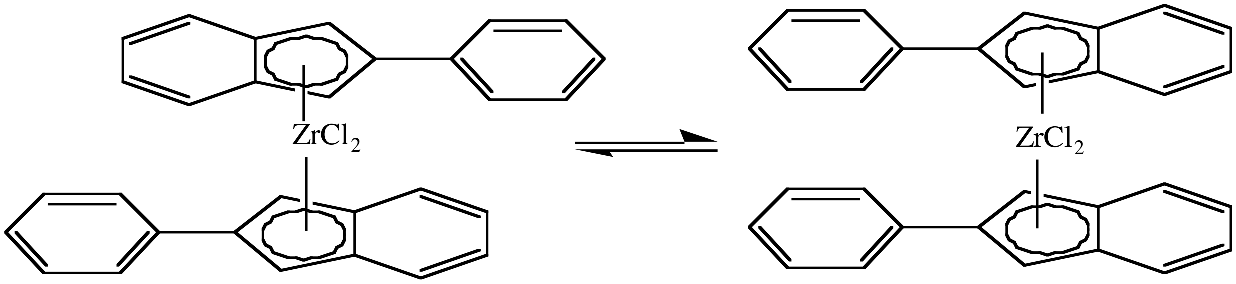
We now illustrate these phenomena with two particular catalysts, and a cartoon sketch of the mechanism of monomer insertion. The monomer in question is polypropylene, the commercially most important stereogenic polyolefin, and the most studied model system. However, it should be noted that the flexibility of design for single-site catalysts offers the possibility of more tolerance toward monomer polarity or functionality than in the Ziegler-Natta analogs, thereby enabling stereocontrol of many different monomers or comonomers. The catalyst [XVI] has C_2 symmetry, and is isospecific under site control. The mechanism is illustrated in Figure 5.14, where for simplicity the Cp-containing ligands are represented by horizontal lines. The polymer chain is bound to the metal through the unsubstituted backbone carbon, and the orientation of the incoming monomer is influenced by the location of the Cp ligand. In the transition state the unsubstituted carbon of the new monomer coordinates with the metal, and will become the new terminal carbon of the growing chain. A key role is thought to be played by a so-called "α-agostic" interaction between the metal and the hydrogen on the terminal carbon of the polymer chain, which stabilizes the particular geometry of the transition state. After the incorporation of the monomer, the polymer chain (or a last few repeat units thereof) has "flipped" to the other side of the metal center, in a process which is often compared to the action of a windshield wiper.

In contrast, the following zirconocene [XVII] is syndiospecific, consistent with its C_s symmetry. The mechanism is analogous to that illustrated in Figure 5.14, except that the inversion of the position of the bulky ligand inverts the preferred orientation of the incoming monomer.



[XVII]

The range of possibilities afforded by this class of catalysts is vast. As one last example, consider the following zirconocene [XVIII], developed by Coates and Waymouth [2]:



[XVIII]

As indicated by the double arrows, the catalyst actually oscillates between two isomeric structures. The structure on the left is chiral with C_2 symmetry, and gives isotactic polypropylene (note that the chloride ligands are not in the plane of the page). The structure on the right, however, is achiral, and actually leads to random stereochemistry, i.e. atactic polypropylene. Now, consider the interesting situation where the rate of monomer insertion is more rapid than the rate of exchange between the two structures, say by a factor of 20. In such a case the resulting polymer would be a "stereoblock copolymer", with alternating sequences of isotactic and atactic polypropylene, where the average sequence length would be about 20. Such a polymer has some very appealing properties. The isotactic blocks can crystallize, as will be discussed at length in Chapter 13, whereas the atactic blocks cannot. The result is that for temperatures above the glass transition of the atactic block (about –10 ^{o}C, see Chapter 12) but below the melting temperature of the stereoregular block (about 140 ^{o}C) the material acts as a crosslinked elastomer (see Chapter 10). The crystallites tie the different molecules together, imparting mechanical strength, but the atactic blocks can be stretched appreciably without breaking, like a rubbery material. The mechanical response is sensitive to the relative lengths of the two blocks, which can be tuned through monomer concentration and polymerization temperature. The result is an appealing situation in which an inexpensive monomer can be used to produce a variety of different products by straightforward modification to the reaction conditions.

CHAPTER SUMMARY

This chapter has covered a broad range of issues relating to the structure of polymer chains at the level of a few repeat units. The two main topics have been copolymerization and stereoregularity. These topics share many features in common, including (i) the importance of the relative reactivity of a growing chain end to addition of a particular monomer, or a monomer in a particular configuration; (ii) the use of statistics in describing composition, average sequence lengths, and sequence length distribution; (iii) the central role of spectroscopic methods, and especially NMR, in characterizing structural details.

1. The key parameters in copolymerization are the reactivity ratios, which influence the relative rates at which a given radical will add the same monomer versus a comonomer. Thus a given reactivity ratio is specific to a particular pair of monomers, and copolymerization of two monomer system requires specification of two reactivity ratios.
2. The copolymerization equation relates the mole fraction of monomers in polymer to the composition of the feedstock, via the reactivity ratios. Different classes of behavior may be assigned based on the product of the reactivity ratios, including an "ideal" copolymerization when the two reactivity ratios are reciprocals.
3. The relative magnitudes of reactivity ratios can be understood at least qualitatively, by considering the contributions of resonance stabilization, polarity differences, and possible steric effects.
4. Statistical considerations give predictions for the average sequence length and sequence length distributions in a copolymer on the basis of reactivity ratios and feedstock composition. However, the probability of adding a given monomer to a growing chain end may be determined by the last, the last plus next-to-last, or even the last, next-to-last and second-to-last monomers added. These mechanisms are referred to as terminal, penultimate, and antepenultimate control, respectively.

5. Steroeregularity may be viewed as a subset of copolymerization, in which addition of a monomer with an asymmetric center may follow the same stereochemistry as the previous repeat unit, thereby forming a meso dyad, or by the opposite stereochemistry, forming a racemic dyad. Isotactic, syndiotactic, and atactic polymers thus correspond to predominantly meso dyads, predominantly racemic dyads, or random mixtures of the two, respectively.

6. Copolymer sequence lengths (dyads, triads, tetrads, etc.) can be determined by NMR methods. These in turn may be used to discriminate among terminal, penultimate, and antepenultimate control mechanisms. Similarly NMR gives access to stereochemical information, being sensitive to sequences of meso dyads, racemic dyads, and even longer sequences.

7. Stereoregularity is obtained by coordination polymerization in the presence of particular catalysts. The most commonly used systems for the polyermization of α-olefins are referred to as Ziegler-Natta catalysts, a class which actually spans a large variety of particular compiounds. The mechanism(s) of action of these catalysts are typically rather complicated. More recently there have been rapid advances in the development of "single-site" catalysts, which usually are based on metallocenes: a metal center coordinated to one or more cyclopentadienyl ligands. The terminology refers to the presence of a well-defined catalytic site throughout the polymerization medium, leading to more homogenous products. These systems are capable of being fined-tuned to regulate a variety of structural features, including stereochemistry and comonomer addition.

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Suggestions for further reading on copolymerization, stereoregularity, and characterization of microstructure:

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Problems

1. Write structural formulas for maleic anhydride (M_1) and stilbene (M_2). Neither of these monomers homopolymerize to any significant extent, presumably owing to steric effects. These monomers form a copolymer, however, with $r_1 = r_2 = 0.03$. (F. M. Lewis and F. R. Mayo, *J. Am. Chem. Soc.* 70, 1533 (1948)). Criticize or defend the following proposition: the strong tendency toward alternation in this copolymer suggests that polarity effects offset the steric hindrance and permit copolymerization of these monomers.

2. Styrene and methyl methacylate have been used as comonomers in many investigations of copolymerization. Use the following list of r_1 values for each of these copolymerizing with the monomers listed below to rank the latter with respect to reactivity. To the extent that the data allow, suggest where these substituents might be positioned in Table 7.3.

M_2	Styrene as M_1	Methyl methacrylate as M_1
Acrylonitrile	0.41	1.35
Allyl acetate	90	23
1, 2-bichloropropene-2	5	5.5
Methacrylonitrile	0.30	0.67
Vinyl chloride	17	12.5
Vinylidene chloride	1.85	2.53
2-Vinyl pyridine	0.55	0.395

3. As part of the research described in Figure 5.5, Winston and Wichacheewa measured the percentages of carbon and chlorine in copolymers of styrene (molecule 1) and 1-chloro-1,3-butadiene (molecule 2) prepared from various feedstocks. A portion of their data is given below. Use these data to calculate F_1, the mole fraction of styrene in these copolymers.

f_1	Percent C	Percent Cl
0.892	81.80	10.88
0.649	71.34	20.14
0.324	64.95	27.92
0.153	58.69	34.79

4. Additional data from the research of the last problem yield the following pairs of f_l, F_1 values (remember that styrene is component 1 in the styrene1-chloro-1,3-butadiene system). Use the form suggested by eq 5.6.1 to prepare a graph based on these data and evaluate r_1 and r_2.

f_1	F_1	f_1	F_1
0.947	0.829	0.448	0.362
0.861	0.688	0.247	0.207
0.698	0.515	0.221	0.200
0.602	0.452		

5. The reactivity ratios for the styrene (M_r)-1-chloro-1,3-butadiene (M_2) system were found to be r_1 = 0.26 and r_2 = 1.02 by the authors of the research described in the last two problems using the results of all their measurements. Use these r values and the feed compositions listed below to calculate the fraction expected in the copolymer of 1-chlorobutadiene sequences of lengths ν = 2, 3, or 4. From these calculated results, evaluate the ratios N_{222}/N_{22} and N_{2222}/N_{222}. Copolymers prepared from these feedstocks were dehydrohalogenated to yield the polyenes like that whose spectrum is shown in Figure 5.5. The absorbance at the indicated wavelengths was measured for 1% solutions of the products after HCL elimination:

	Absorbance		
f_1	λ = 312 nm	367 nm	412 nm
0.829	74	13	-
0.734	71	19	-
0.551	154	77	20
0.490	151	78	42

As noted in Section 5.6, these different wavelengths correspond to absorbance by sequences of different lengths. Compare the appropriate absorbance ratios with the theoretical sequence length ratios calculated above and comment briefly on the results.

6. Use the values determined in Example 7.5 for the vinylidene chloride (M_1) – isobutylene (M_2) system to calculate F_1, for various values of f_1, according to the terminal mechanism. Prepare a plot of the results. On the same graph, plot the following experimentally measured values of f_t and F_l. Comment on the quality of the fit.

f_1	F_1	f_1	F_1
0.548	0.83	0.225	0.66
0.471	0.79	0.206	0.64
0.391	0.74	0.159	0.61
0.318	0.71	0.126	0.58
0.288	0.70	0.083	0.52

7. Some additional dyad fractions from the research cited in the last problem are reported at intermediate feedstock concentrations (M_1 = vinylidene chloride; M_z = isobutylene) (J. B. Kinsinger, T. Fischer, and C. W. Wilson, *Polym. Lett*. 5, 285 (1967)). Still assuming terminal control, evaluate r_1 and r_z from these data. Criticize or defend the following proposition: The copolymer composition equation does not provide a very sensitive test for the terminal control mechanism. Dyad fractions are more sensitive, but must be examined over a wide range of compositions to provide a valid test.

	Mole fraction of dyads		
f_1	11	12	22
0.418	0.55	0.43	0.03
0.353	0.48	0.49	0.04
0.317	0.44	0.52	0.04
0.247	0.38	0.58	0.04
0.213	0.34	0.62	0.04
0. 198	0.32	0.64	0.05

8. Fox and Schnecko carried out the free-radical polymerization of methyl methacrylate between –40 and 250 ºC. By analysis of the α-methyl peaks in the NMR spectra of the products, they determined the following values of β, the probability of an isotactic placement in the products prepared at the different temperatures:

T (ºC)	250	150	100	95	60	30	0	–20	–40
β	0.36	0.33	0.27	0.27	0.24	0.22	0.20	0.18	0.14

Evaluate $E_i^* - E_s^*$ by means of an Arrhenius plot of these data using $\beta/(1-\beta)$ as a measure of k_i/k_s. Briefly justify this last relationship.

9. A hetero triad occurs at each interface between iso and syndio triads. The total number of hetero triads, therefore, equals the total number of sequences of all other types:

$$\nu_h = \Sigma N_{n_i} + \Sigma N_{n_s}$$

Use this relationship and eq 5.9.1 to derive the expression

$$p_h = \frac{\nu_h}{\nu_h + \nu_i + \nu_s} = \frac{2}{\bar{n}_i} + \bar{n}_s$$

Criticize or defend the following proposition: The sequence DL– is already two-thirds of the way to becoming a hetero triad, while the sequence DD– is two-thirds of the way toward an iso triad. This means that the fraction of heterotactic triads is larger when the average length of syndio sequences is greater than the average length of iso sequences.

10. Randall used ^{13}C-NMR to study the methylene spectrum of polystyrene (J. C. Randall, *J. Polym. Sci., Polym. Phys. Ed.* 13, 889 (1975)). In 1,2,4-trichlorobenzene at 120 °C, nine resonances were observed. These were assumed to arise from a combination of tetrads and hexads. Using m and r notation, extend Table 5.6 to include all 20 possible hexads. Criticize or defend the following proposition. Assuming that none of the resonances are obscured by overlap, there is only one way that nine methylene resonances can be produced, namely, by one of the tetrads being split into hexads while the remaining tetrads remain unsplit.

11. In the research described in the preceding problem, Randall was able to assign the five peaks associated with tetrads in the ^{13}C-NMR spectrum on the basis of their relative intensities, assuming zero-order Markov statistics with $p_m = 0.575$. The five tetrad intensities and their chemical shifts from TMS are as follows:

^{13}C δTMS (ppm)	Relative area under peak
45.38	0.10
44.94	0.28
44.25	0.13
43.77	0.19
42.84	0.09

The remaining 21% of the peak area is distributed among the remaining hexad features. Use the value of p_m given to calculate the probabilities of the unsplit tetrads (see problem 10) and on this basis assign the features listed above to the appropriate tetrads. Which of the tetrads appears to be split into hexads?

12. The fraction of sequences of the length indicated below have been measured for a copolymer system at different feed ratios (K. Ito and Y. Yamashita, *J. Polym. Sci.* 3A, 2165 (1965). From appropriate ratios of these sequence lengths, what conclusions can be drawn concerning terminal versus penultimate control of addition?

$[M_1][M_2]$	$P(M_1)$	$P(M_1M_1)$	$P(M_1M_1M_1)$
3	0.168	0.0643	0.0149
4	0.189	0.0563	0.0161
9	0.388	0.225	0.107
19	0.592	0.425	0.278

13. The following are experimental tacticity fractions of polymers prepared from different monomers and with various catalysts. On the basis of Figure 5.7, decide whether these preparations are adequately described (remember to make some allowance for experimental error) by a single parameter p_m or whether some other type of statistical description is required. On the basis of these observations, criticize or defend the following proposition: Regardless of the monomer used, zero-order Markov statistics apply to all free radical, anionic, and cationic polymerizations, but not to Ziegler-Natta catalyzed systems. MMA data from K. Hatada, K. Ota, and H. Yuki, *Polym. Lett.* 5, 225 (1967), and αMS data from S. Brownstein, S. Bywater, and O. J. Worsfold, *Makromol. Chem.* 48, 127 (1961).

			Fraction of polymer		
Catalyst	Solvent	T, °C	Iso	Hetero	Syndio
Methyl methacrylate					
Thermal	Toluene	60	8	33	59
n-Butyl lithium	Toluene	–78	78	16	6
n-Butyl lithium	Methyl isobutyrate	–78	21	31	48
α-Methyl styrene					
$TiCl_4$	Toluene	–78	–	19	81
$Et_3Al/TiC1_4$	Benzene	25	3	35	62
n-Butyl lithium	Cyclohexane	4	–	31	69

14. Replacing one of the alkyl groups in R_3Al with a halogen increases the stereospecificity of the Ziegler-Natta catalyst in the order l > Br > Cl > R. Replacement of a second alkyl by halogen decreases specificity. Criticize or defend the following proposition on the basis of these observations: The observed result of halogen substitution is consistent with the effect on the ease of alkylation produced by substituents of different electronegativity. This evidence thus adds credence to the monometallic mechanism, even though the observation involves the organometallic.

15. The weight percent propylene in ethylene-propylene copolymers for different Ziegler-Natta catalysts was measured for the initial polymer produced from identical feedstocks (F. J. Karol and W. L. Carrick, *J. Am. Chem. Soc.* 83, 585 (1960)). The following results were obtained. Interpret these results in terms of the relative influence of the two components of the catalyst on the product found.

Catalyst components	Weight percent propylene	Catalyst components	Weight percent propylene
$VC1_4$, plus		$Al(i\text{-}BU)_3$, plus	
$Al(i\text{-}Bu)_3$	4.5	$HfC1_4$	0.7
CH_3TiC1_3	4.5	ZrCl4	0.8
$Zn(C_2H_5)_2$	4.5	$VOC1_3$	2.4
$Zn(n\text{-}Bu)_2$	4.5		

16. Imagine a given single-site catalyst for polypropylene introduced a stereodefect on average once every ten monomer additions. Furthermore, assume the catalyst was supposed to be highly isospecific. Explain how measurements of triad populations (e.g, mmm, mmr, etc.) could be used to distinguish between chain-end control and site-control.