

3

Chain-growth polymerization

3.1 Introduction

We indicated in Chapter 1 that the category of addition polymers is best characterized by the mechanism of the polymerization reaction, rather than by the addition reaction itself. This is known to be a chain mechanism, so in the case of addition polymers we have chain reactions producing chain molecules. One thing to bear in mind is the two uses of the word *chain* in this discussion. The word *chain* continues to offer the best description of large polymer molecules. A chain reaction, on the other hand, describes a whole series of successive events triggered by some initial occurrence. We sometimes encounter this description of highway accidents in which one traffic mishap on a fogbound highway results in a pileup of colliding vehicles that can extend for miles. In nuclear reactors a cascade of fission reactions occurs which is initiated by the capture of the first neutron. In both of these examples some initiating event is required. This is also true in chain-growth polymerization.

In the above examples the size of the chain can be measured by considering the number of automobile collisions that result from the first accident, or the number of fission reactions which follow from the first neutron capture. When we think about the number of monomers that react as a result of a single initiation step, we are led directly to the degree of polymerization of the resulting molecule. In this way the chain mechanism and the properties of the polymer chains are directly related.

Chain reactions do not go on forever. The fog may clear and the improved visibility ends the succession of accidents. Neutron-scavenging control rods may be inserted to shut down a nuclear reactor. The chemical reactions which terminate polymer chain growth are also an important part of the polymerization mechanism. Killing off the reactive intermediate that keeps the chain going is the essence of a termination reaction. Some interesting polymers can be

formed when this termination process is suppressed; these are called "living" polymers, and will be discussed extensively in Chapter 4.

The kind of reaction which produces a "dead" polymer from a growing chain depends on the nature of the reactive intermediate. These intermediates may be free radicals, anions, or cations. We shall devote the rest of this chapter to a discussion of the free-radical mechanism, since it readily lends itself to a very general treatment. Furthermore, it is by far the most important chain-growth mechanism from a commercial point of view; examples include polyethylene (specifically, low density polyethylene, LDPE), polystyrene, polyvinylchloride, and polyacrylates and methacrylates. Anionic polymerization plays a central role in Chapter 4, where we discuss so-called "living" polymerizations. In this chapter we deal exclusively with homopolymers. The important case of copolymers formed by chain-growth mechanisms is taken up in both Chapters 4 and 5; block copolymers in the former, statistical or random copolymers in the latter.

3.2 Chain-growth and step-growth polymerizations: some comparisons

Our primary purpose in this section is to point out some of the similarities and differences between step-growth and chain-growth polymerizations. In so doing we shall also have the opportunity to indicate some of the different types of chain-growth systems.

In Chapter 2 we saw that step-growth polymerizations occur, one step at a time, through a series of relatively simple organic reactions. By treating the reactivity of the functional groups as independent of the size of the molecule carrying the group, the entire course of the polymerization is described by the conversion of these groups to their condensation products. Two consequences of this are that both high yield and high molecular weight require the reaction to approach completion. In contrast, chain-growth polymerization occurs by introducing an active growth center into a monomer, followed by the addition of many monomers to that center by a chain-type kinetic mechanism. The active center is ultimately killed off by a termination

step. The (average) degree of polymerization that characterizes the system depends on the frequency of addition steps relative to termination steps. Thus high molecular weight polymer can be produced almost immediately. The only thing that is accomplished by allowing the reaction to proceed further is an increased yield of polymer; the molecular weight of the product is relatively unaffected. (This simple argument tends to break down at high extents of conversion. For this reason we shall focus attention in this chapter on low to moderate conversions to polymer, except where noted.)

Step-growth polymerizations can be schematically represented by one of the individual reaction steps $A + B \rightarrow ab$, with the realization that the species so connected can be any molecules containing A and B groups. Chain-growth polymerization, by contrast, requires at least three distinctly different kinds of reactions to describe the mechanism. These three types of reactions will be discussed in the following sections in considerable detail; for now our purpose is just to introduce some vocabulary. The principal steps in the chain growth mechanism are the following:

1. Initiation. An active species I^* is formed by the decomposition of an initiator molecule I:

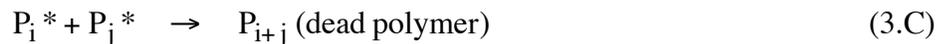


2. Propagation. The initiator fragment reacts with a monomer M to begin the conversion to polymer; the center of activity is retained in the adduct. Monomers continue to add in some way until polymers P_i are formed with degree of polymerization i:



If i is large enough, the initiator fragment – an endgroup – need not be written explicitly.

3. Termination. By some reaction, generally involving two polymers containing active centers, the growth center is deactivated, resulting in dead polymer:



Elsewhere in the chapter we shall see that other reactions – notably, chain transfer and chain inhibition – also need to be considered to give a more fully developed picture of chain-growth polymerization, but we shall omit these for the time being. Most of this chapter examines the kinetics of these three mechanistic steps. We shall describe the rates of the three general kinds of reactions by the notation R_i , R_p , and R_t for initiation, propagation, and termination, respectively.

In the last chapter we presented arguments supporting the idea that reactivity is independent of molecular size. Although the chemical reactions are certainly different between this chapter and the last, we shall also adopt this *assumption of equal reactivity* for addition polymerization. For step-growth polymerization this assumption simplified the discussion tremendously and at the same time needed careful qualification. We recall that the equal reactivity premise is valid only after an initial size dependence for smaller molecules. The same variability applies to the propagation step of addition polymerizations for short-chain oligomers, although things soon level off and the assumption of equal reactivity holds. We are thus able to treat all propagation steps by the single rate constant k_p . Since the total polymer may be the product of hundreds or even thousands of such steps, no serious error is made in neglecting the variation that occurs in the first few steps.

In Section 2.3 we rationalized that, say, the first 50% of a step-growth reaction might be different from the second 50% because the reaction causes dramatic changes in the polarity of the reaction mixture. We shall see that, under certain circumstances, the rate of addition polymerization accelerates as the extent of conversion to polymer increases, due to a composition-dependent effect on termination. In spite of these deviations from the assumption

of equal reactivity at all extents of reaction, we continue to make this assumption because of the simplification it allows. We will then seek to explain the deviations from this ideal or to find experimental conditions – low conversions to polymer – under which the assumptions apply. This approach is common in chemistry; for example, most discussions of gases begin with the ideal gas law, and describe real gases as deviating from the ideal at high pressures and approaching the ideal as pressure approaches zero.

In the last chapter we saw that two reactive groups per molecule are the norm for the formation of linear step-growth polymers. A pair of monofunctional reactants might undergo essentially the same reaction, but no polymer is produced because no additional functional groups remain to react. On the other hand, if a molecule contains more than two reactive groups, then branched or cross-linked products can result from step-growth polymerization. By comparison, a wide variety of unsaturated monomers undergo chain-growth polymerization. A single kind of monomer suffices – more than one yields a copolymer – and more than one double bond per monomer may result in branching or crosslinking. For example, the 1,2-addition reaction of butadiene results in a chain which has a substituent vinyl group capable of branch formation. Divinyl benzene is an example of a bifunctional monomer which is used as a crosslinking agent in chain-growth polymerizations. We shall be primarily concerned with various alkenes as the monomers of interest; however, the carbon-oxygen double bond in aldehydes and ketones can also serve as the unsaturation required for addition polymerization. The polymerization of alkenes yields a carbon atom backbone, whereas the carbonyl group introduces carbon and oxygen atoms into the backbone, thereby illustrating the inadequacy of backbone composition as a basis for distinguishing between addition and condensation polymers.

It might be noted that most (but not all) alkenes are polymerizable by the chain mechanism involving free-radical intermediates, whereas the carbonyl group is generally not polymerized by the free-radical mechanism. Carbonyl groups and some carbon-carbon double bonds are polymerized by ionic mechanisms. Monomers display far more specificity where the

ionic mechanism is involved than with the free-radical mechanism. For example, acrylamide will polymerize through an anionic intermediate but not a cationic one, *N*-vinyl pyrrolidones by cationic but not anionic intermediates, and halogenated olefins by neither ionic species. In all of these cases free-radical polymerization is possible.

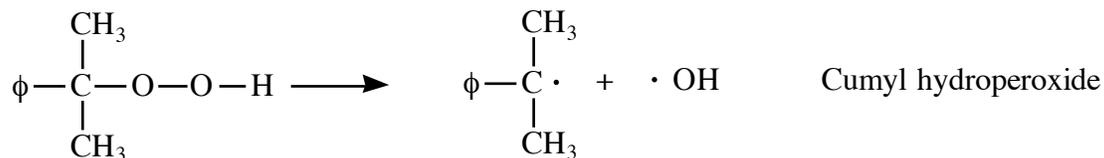
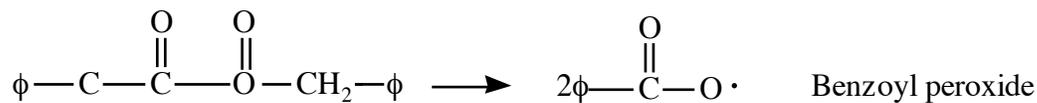
The initiators used in addition polymerizations are sometimes called "catalysts", although strictly speaking this is a misnomer. A true catalyst is recoverable at the end of the reaction, chemically unchanged. This is not true of the initiator molecules in addition polymerizations. Monomer and polymer are the initial and final states of the polymerization process, and these govern the thermodynamics of the reaction; the nature and concentration of the intermediates in the process, on the other hand, determine the rate. This makes initiator and catalyst synonyms for the same material: the former term stresses the effect of the reagent on the intermediate, and the latter its effect on the rate. The term catalyst is particularly common in the language of ionic polymerizations, but this terminology should not obscure the importance of the initiation step in the overall polymerization mechanism.

In the next three sections we consider initiation, termination, and propagation steps in the free-radical mechanism for addition polymerization. As noted above two additional steps, inhibition and chain transfer, are being ignored at this point. We shall take up these latter topics in Section 3.8.

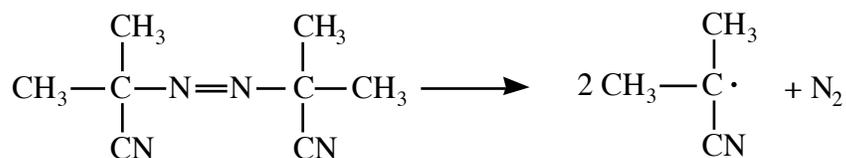
3.3 Initiation

In this section we shall discuss the initiation step of free-radical polymerization. This discussion is centered around initiators and their decomposition behavior. The first requirement for an initiator is that it be a source of free radicals. In addition, the radicals must be produced at an acceptable rate at convenient temperatures; have the required solubility behavior; transfer their activity to monomers efficiently; be amenable to analysis, preparation, purification, and so on.

1. Organic peroxides or hydroperoxides:



2. Azo compounds:

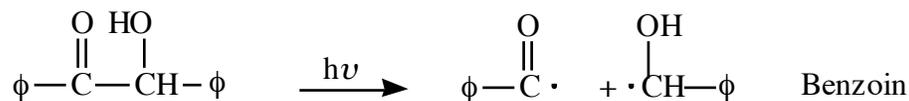
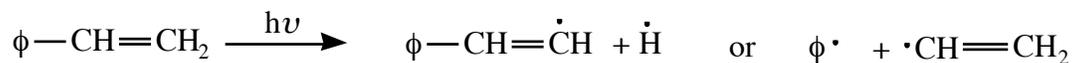


2,2'-Azobisisobutyronitrile (AIBN)

3. Redox systems:



4. Electromagnetic radiation:

**Table 3.1** Examples of free radical initiation reactions

3.3A Initiation reactions

Some of the most widely used initiator systems are listed below, and Table 3.1 illustrates their behavior by typical reactions:

1. Organic peroxides or hydroperoxides.
2. Azo compounds.
3. Redox systems.
4. Thermal or light energy.

Peroxides and hydroperoxides are useful as initiators because of the low dissociation energy of the O–O bond. This very property makes the range of possible compounds somewhat limited because of the instability of these reagents. In the case of azo compounds the homolysis is driven by the liberation of the very stable N₂ molecule, despite the relatively high dissociation energy of the C–N bond. The redox systems listed in Table 3.1 have the advantage of water solubility, although redox systems which operate in organic solvents are also available. One advantage of redox reactions as a source of free radicals is the fact that these reactions often proceed more rapidly and at lower temperatures than the thermal homolysis of the peroxide and azo compounds.

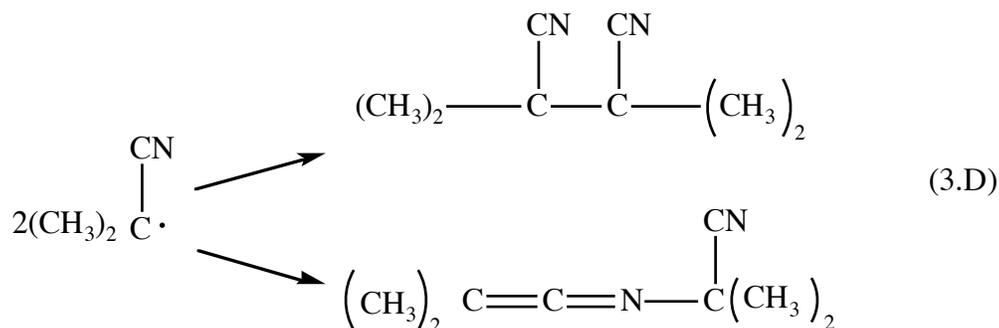
The initiation reactions shown under the heading of electromagnetic radiation in Table 3.1 indicate two possibilities out of a large number of examples that might be cited. One mode of photochemical initiation involves the direct excitation of the monomer with subsequent bond rupture. The second example cited is the photolytic fragmentation of initiators such as alkyl halides and ketones. Because of the specificity of light absorption, photochemical initiators include a wider variety of compounds than those which decompose thermally. Photosensitizers can also be used to absorb and transfer radiation energy to either monomer or initiator molecules. Finally we note that high-energy radiation such as x-rays and γ -rays and particulate radiation such as α or β particles can also produce free radicals. These latter sources of radiant energy are

nonselective and produce a wider array of initiating species. Even though such high-energy radiation produces both ionic and free-radical species, the polymerizations that are so initiated follow the free-radical mechanism almost exclusively, except at very low temperatures, where ionic intermediates become more stable. We shall not deal further with these higher energy sources of initiating radicals, but we shall return to light as a photochemical initiator because of its utility in the evaluation of kinetic rate constants.

3.3B Fate of free radicals

All of the reactions listed in Table 3.1 produce free radicals, so we are presented with a number of alternatives for initiating a polymerization reaction. Our next concern is in the fate of these radicals or, stated in terms of our interest in polymers, the efficiency with which these radicals initiate polymerization. Since these free radicals are relatively reactive species, there are a variety of processes they can undergo as alternatives to adding to monomers to commence the formation of polymer.

In discussing mechanism (2.F) in the last chapter we noted that the entrapment of two reactive species in the same solvent cage may be considered a transition state in the reaction of these species. Reactions such as the thermal homolysis of peroxides and azo compounds result in the formation of two radicals already trapped together in a cage that promotes direct recombination, as with the 2-cyanopropyl radicals from 2,2'-azobisisobutyronitrile (AIBN),

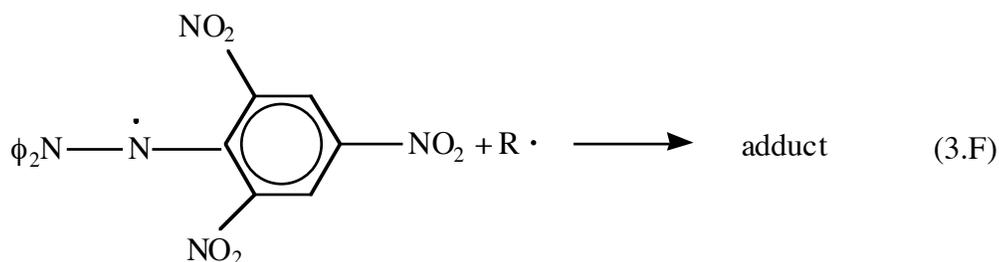


The significant thing about these, and numerous other side reactions that could be described, is the fact that they lower the efficiency of the initiator in promoting polymerization. To quantify this concept we define the initiator efficiency f to be the following fraction:

$$f \equiv \frac{\text{radicals incorporated into polymer}}{\text{radicals formed by initiator}} \quad (3.3.1)$$

The initiator efficiency is not an exclusive property of the initiator, but depends on the conditions of the polymerization experiment, including the solvent. In many experimental situations, f lies in the range of 0.3–0.8. The efficiency should be regarded as an empirical parameter whose value is determined experimentally. Several methods are used for the evaluation of initiator efficiency, the best being the direct analysis for initiator fragments as endgroups compared to the amount of initiator consumed, with proper allowances for stoichiometry. As an endgroup method, this procedure is difficult in addition polymers, where molecular weights are higher than in condensation polymers. Research with isotopically labeled initiators is particularly useful in this application. Since the quantity is so dependent on the conditions of the experiment, it should be monitored for each system studied.

Scavengers such as diphenylpicrylhydrazyl radicals [II] react with other radicals and thus provide an indirect method for analysis of the number of free radicals in a system:



[II]

The diphenylpicrylhydrazyl radical itself is readily followed spectrophotometrically, since it loses an intense purple color on reacting. Unfortunately, this reaction is not always quantitative.

3.3C Kinetics of initiation

We recall some of the ideas of kinetics from the summary given in Section 2.2 and recognize that the rates of initiator decomposition can be developed in terms of the reactions listed in Table 3.1. Using the change in initiator radical concentration $d[I\bullet]/dt$ to monitor the rates, we write the following:

1. For peroxides and azo compounds

$$\frac{d[I\bullet]}{dt} = 2k_d[I] \quad (3.3.2)$$

where k_d is the rate constant for the homolytic decomposition of the initiator and $[I]$ is the concentration of the initiator. The factor of 2 appears because of the stoichiometry in these particular reactions.

2. For redox systems

$$\frac{d[I\bullet]}{dt} = k[Ox][Red] \quad (3.3.3)$$

where the bracketed terms describe the concentrations of oxidizing and reducing agents and k is the rate constant for the particular reactants.

3. For photochemical initiation

$$\frac{d[I\bullet]}{dt} = 2\phi' I_{abs} \quad (3.3.4)$$

where I_{abs} is the intensity of the light absorbed and the constant ϕ' is called the quantum yield. The factor of 2 is again included for reasons of stoichiometry.

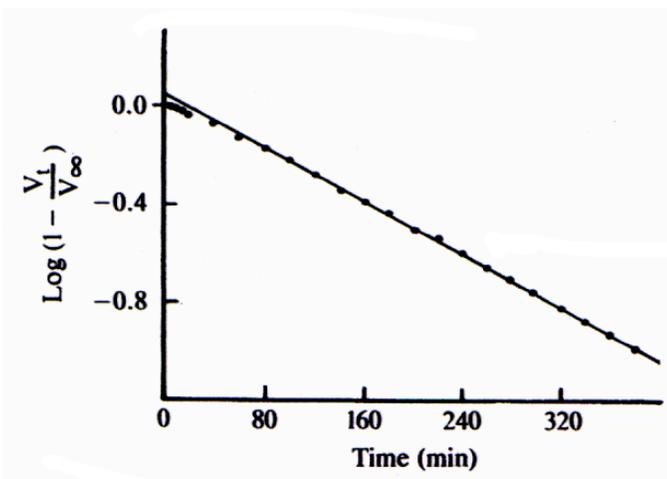


Figure 3.1

Volume of nitrogen evolved from the decomposition of AIBN at 77 °C plotted according to the first-order rate law as discussed in Example 3.1. Reprinted with permission from L. M. Arnett, *J. Am. Chem. Soc.* 74, 2027 (1952).

Since $(1/2)d[I\bullet]/dt = -d[I]/dt$ in the case of the azo initiators, eq 3.3.2 can also be written as $-d[I]/dt = k_d[I]$ or, by integration, $\ln([I]/[I]_0) = -k_d t$, where $[I]_0$ is the initiator concentration at $t = 0$. Figure 3.1 shows a test of this relationship for AIBN in xylene at 77 °C. Except for a short induction period, the data points fall on a straight line. The evaluation of k_d from these data is presented in the following example.

Example 3.1

The decomposition of AIBN in xylene at 77 °C was studied by measuring the volume of N_2 evolved as a function of time. The volumes obtained at time t and $t = \infty$ are V_t and V_∞ , respectively. Show that the manner of plotting used in Figure 3.1 is consistent with the integrated first-order rate law and evaluate k_d .

Solution

The ratio $[I]/[I]_0$ gives the fraction of initiator remaining at time t . The volume of N_2 evolved is:

1. $V_0 = 0$ at $t = 0$, when no decomposition has occurred.
2. V_∞ at $t = \infty$, when complete decomposition has occurred.
3. V_t at time t , when some fraction of initiator has decomposed.

The fraction decomposed at t is given by $(V_t - V_0)/(V_\infty - V_0)$ and the fraction remaining at t is $1 - (V_t - V_0)/(V_\infty - V_0) = (V_\infty - V_t)/(V_\infty - V_0)$. Since $V_0 = 0$, this becomes $(V_\infty - V_t)/V_\infty$ or $[I]/[I]_0 = 1 - V_t/V_\infty$. Therefore a plot of $\ln(1 - V_t/V_\infty)$ versus t is predicted to be linear with slope $-k_d$. (If logarithms to base 10 were used, the slope would equal $-k_d/2.303$). From Figure 3.1,

$$\text{Slope} = \frac{-0.4 - (-0.8)}{160 - 320} = -2.5 \times 10^{-3} \text{ min}^{-1} = \frac{-k_d}{2.303}$$

$$k_d = 5.8 \times 10^{-3} \text{ min}^{-1}$$

Next we assume that only a fraction f of these initiator fragments actually reacts with monomer to transfer the radical functionality to monomer:



As indicated in the last section, we regard the reactivity of the species $IP_i \cdot$ to be independent of the value of i . Accordingly, all subsequent additions to $IM \cdot$ in reaction (3.G) are propagation steps and reaction (3.G) represents the initiation of polymerization. Although it is premature at

this point, we disregard endgroups and represent the polymeric radicals of whatever size by the symbol $P\bullet$. Accordingly, we write the following for the initiation of polymer radicals:

1. By peroxide and azo compounds,

$$\frac{d[P\bullet]}{dt} = 2fk_d[I] \quad (3.3.5)$$

2. By redox system,

$$\frac{d[P\bullet]}{dt} = fk[Ox][Red] \quad (3.3.6)$$

3. By photochemical initiation,

$$\frac{d[P\bullet]}{dt} = 2f\phi'I_{abs} = 2\phi I_{abs} \quad (3.3.7)$$

where we have combined the factors of f and ϕ' into a composite quantum yield ϕ , since both of the separate factors are measures of efficiency.

Any one of these expressions gives the rate of initiation R_i for the particular catalytic system employed. We shall focus attention on the homolytic decomposition of a single initiator as the mode of initiation throughout most of this chapter, since this reaction typifies the most widely used free-radical initiators. Appropriate expressions for initiation which follow eq 3.3.6 are readily derived.

3.3D Photochemical initiation

An important application of photochemical initiation is in the determination of the rate constants which appear in the overall analysis of the chain-growth mechanism. Although we outline this method in Section 3.6, it is worthwhile to develop eq 3.3.7 somewhat further at this point. It is not feasible to give a detailed treatment of light absorption here. Instead, we summarize some pertinent relationships and refer the reader who desires more information to standard textbooks of analytical or physical chemistry.

1. The intensity of light transmitted (subscript t) through a sample I_t depends on the intensity of the incident (subscript o) light I_o , the thickness of the sample b , and the concentration $[c]$ of the absorbing species,

$$I_t = I_o e^{-\epsilon[c]b} \quad (3.3.8)$$

where the proportionality constant ϵ is called the absorption coefficient (or molar absorptivity if $[c]$ is in moles/liter) and is a property of the absorber. The reader may recognize this equation as a form of the famous "Beer's Law".

2. The absorbance A as measured by spectrophotometers is defined as

$$A = \log_{10} \left(\frac{I_o}{I_t} \right) \quad (3.3.9)$$

The variation in absorbance with wavelength reflects the wavelength dependence of ϵ .

3. Since I_{abs} equals the difference $I_o - I_t$,

$$I_{\text{abs}} = I_o \left(1 - e^{-\epsilon[c]b} \right) \quad (3.3.10)$$

If the exponent in eq 3.3.10 is small – which in practice means dilute solutions, since most absorption experiments are done where ϵ is large – then the exponential can be expanded (see Appendix), $e^x \cong 1 + x + \dots$, with only the leading terms retained to give

$$I_{\text{abs}} = I_0(\epsilon[c]b) \quad (3.3.11)$$

4. Substituting this result into eq 3.3.7 gives

$$\frac{d[\text{P}\cdot]}{dt} = 2\phi I_0 \epsilon [c] b \quad (3.3.12)$$

where $[c]$ is the concentration of monomer or initiator for the two reactions shown in Table 3.1.

3.3E Temperature dependence of initiation rates

Note that although eqs 3.3.5 and 3.3.12 are both first order rate laws, the physical significance of the proportionality factors is quite different in the two cases. The rate constants shown in eqs 3.3.5 and 3.3.6 show a temperature dependence described by the Arrhenius equation:

$$k = Ae^{-E^*/RT} \quad (3.3.13)$$

where E^* is the activation energy, which is interpreted as the height of the energy barrier to a reaction, and A is the prefactor. Activation energies are evaluated from experiments in which rate constants are measured at different temperatures. Taking logarithms of both sides of eq

3.3.13 gives $\ln k = \ln A - E^*/RT$. Therefore E^* is obtained from the slope of a plot of $\ln k$ against $1/T$. As usual, T is in Kelvin and R and E^* are in (the same) energy units.

Since E^* is positive according to this picture, the form of the Arrhenius equation assures that k gets larger as T increases. This means that a larger proportion of molecules have sufficient energy to surmount the energy barrier at higher temperatures. This assumes, of course, that thermal energy is the source of E^* , something that is not the case in photoinitiated reactions. The effective first-order rate constants k and $I_0 \epsilon b$ – for thermal initiation and photoinitiation, respectively – do not show the same temperature dependence. The former follows the Arrhenius equation, whereas the latter cluster of terms in eq 3.3.12 is essentially independent of T .

The activation energies for the decomposition (subscript d) reaction of several different initiators in various solvents are shown in Table 3.2. Also listed are values of k_d for these systems at the temperature shown. The Arrhenius equation can be used in the form $\ln(k_{d,1}/k_{d,2}) = -(E^*/R)(1/T_1 - 1/T_2)$ to evaluate k_d values for these systems at temperatures different from those given in Table 3.2.

3.4 Termination

The formation of initiator radicals is not the only process that determines the concentration of free radicals in a polymerization system. Polymer propagation itself does not change the radical concentration; it merely converts one radical to another. Termination steps also occur, however, and these remove radicals from the system. We shall discuss *combination* and *disproportionation* reactions as the two principal modes of termination.

3.4A Combination and disproportionation

Termination by combination results in the simultaneous destruction of two radicals by direct coupling:

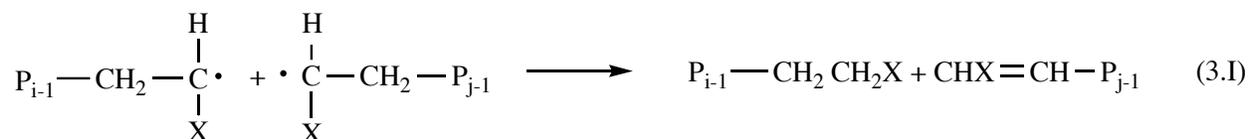


| Initiator | Solvent | T(°C) | $k_d(\text{sec}^{-1})$ | $E_d^*(\text{kJ mol}^{-1})$ |
|-------------------------------|----------------|-------|------------------------|-----------------------------|
| 2,2'-Azobisisobutyronitrile | Benzene | 70 | 3.17×10^{-5} | 123.4 |
| | CCl_4 | 40 | 2.15×10^{-7} | 128.4 |
| | Toluene | 100 | 1.60×10^{-3} | 121.3 |
| <i>t</i> -Butyl peroxide | Benzene | 100 | 8.8×10^{-7} | 146.9 |
| Benzoyl peroxide | Benzene | 70 | 1.48×10^{-5} | 123.8 |
| | Cumene | 60 | 1.45×10^{-6} | 120.5 |
| <i>t</i> -Butyl hydroperoxide | Benzene | 169 | 2.0×10^{-5} | 170.7 |

Table 3.2 Rate constants (at given temperature) and activation energies for some initiator decomposition reactions. Data from J. C. Masson in [1].

The degrees of polymerization i and j in the two combining radicals can have any values, and the molecular weight of the product molecule will be considerably higher on the average than the radicals so terminated. The polymeric product molecule contains two initiator fragments per molecule by this mode of termination. Note also that for a vinyl monomer, such as styrene or methylmethacrylate, the combination reaction produces a single "head-to-head" linkage, with the side groups attached to adjacent backbone carbons instead of every other carbon.

Termination by disproportionation comes about when an atom, usually hydrogen, is transferred from one polymer radical to another:



This mode of termination produces a negligible effect on the molecular weight of the reacting species, but it does produce a terminal unsaturation in one of the dead polymer molecules. Each polymer molecule contains one initiator fragment when termination occurs by disproportionation.

Kinetic analysis of the two modes of termination is quite straightforward, since each mode of termination involves a bimolecular reaction between two radicals. Accordingly, we write the following:

1. For general termination,

$$R_t = -\frac{d[\text{P}\cdot]}{dt} = 2k_t[\text{P}\cdot]^2 \quad (3.4.1)$$

where R_t and k_t are the rate and rate constant for termination (subscript t) and the factor of 2 enters (by convention) because two radicals are lost for each termination step.

2. The polymer radical concentration in eq 3.4.1 represents the total concentration of all such species, regardless of their degree of polymerization; that is,

$$[P\cdot] = \sum_{\text{all } i} [P_i\cdot] \quad (3.4.2)$$

3. For combination,

$$R_t = -\frac{d[P\cdot]}{dt} = 2k_{t,c}[P\cdot]^2 \quad (3.4.3)$$

where the subscript c specifically indicates termination by combination.

4. For disproportionation,

$$R_t = -\frac{d[P\cdot]}{dt} = 2k_{t,d}[P\cdot]^2 \quad (3.4.4)$$

where the subscript d specifically indicates termination by disproportionation.

5. In the event that the two modes of termination are not distinguished, eq 3.4.1 represents the sum of eqs 3.4.3 and 3.4.4, or

$$k_t = k_{t,c} + k_{t,d} \quad (3.4.5)$$

Combination and disproportionation are competitive processes and do not occur to the same extent for all polymers. For example, at 60 °C termination is virtually 100% by combination for polyacrylonitrile and 100% by disproportionation for poly(vinyl acetate). For

polystyrene and poly(methyl methacrylate), both reactions contribute to termination, although in different proportions. Both of the rate constants for termination individually follow the Arrhenius equation, so the relative amounts of termination by the two modes is given by

$$\begin{aligned} \frac{\text{termination by combination}}{\text{termination by disproportionation}} &= \frac{k_{t,c}}{k_{t,d}} = \frac{A_{t,c} e^{-E_{t,c}^*/RT}}{A_{t,d} e^{-E_{t,d}^*/RT}} \\ &= \frac{A_{t,c}}{A_{t,d}} \exp\left(\frac{-(E_{t,c}^* - E_{t,d}^*)}{RT}\right) \end{aligned} \quad (3.4.6)$$

Since the disproportionation reaction requires bond breaking, which is not required for combination, $E_{t,d}^*$ is expected to be greater than $E_{t,c}^*$. This causes the exponential to be large at low temperatures, making combination the preferred mode of termination under these circumstances. Note that at higher temperatures this bias in favor of one mode of termination over another decreases as the difference in activation energies becomes smaller relative to the thermal energy RT . The experimental results on modes of termination cited above make it apparent that this qualitative argument must be applied cautiously. The actual determination of the partitioning between the two modes of termination is best accomplished by analysis of endgroups, using the difference in endgroup distribution noted above.

Table 3.3 lists the activation energies for termination (these are overall values, not identified as to mode) of several different radicals. The rate constants for termination at 60 °C are also given. We shall see in Section 3.6 how these constants are determined.

| Monomer | E_t^* (kJ mol ⁻¹) | $k_{t,60^\circ} \times 10^{-7}$ (liter mol ⁻¹ sec ⁻¹) |
|---------------------|---------------------------------|---------------------------------------------------------------------------------|
| Acrylonitrile | 1.5 | 78.2 |
| Methyl acrylate | 22.2 | 0.95 |
| Methyl methacrylate | 11.9 | 2.55 |
| Styrene | 8.0 | 6.0 |
| Vinyl acetate | 21.9 | 2.9 |
| 2-Vinyl pyridine | 21.0 | 3.3 |

Table 3.3 Rate constants at 60 °C and activation energies for some termination reactions. Data from R. Korus and K. F. O'Driscoll in [1].

3.4B Effect of termination on conversion to polymer

The assumption that k values are constant over the entire duration of the reaction breaks down for termination reactions in bulk polymerizations. Here, as in Section 2.2, we can consider the termination process – whether by combination or disproportionation – to depend on the rates at which polymer molecules can diffuse into (characterized by k_i) or out of (characterized by k_o) the same solvent cage and the rate at which chemical reaction between them (characterized by k_r) occurs in that cage. In Chapter 2 we saw that two limiting cases of eq 2.2.8 could be readily identified:

1. Rate of diffusion > rate of reaction (eq 2.2.9):

$$k_t = \frac{k_i}{k_o} k_r \quad (3.4.7)$$

2. This situation seems highly probable for *step-growth* polymerization because of the high activation energy of many condensation reactions. The constants for the diffusion-dependent steps, which might be functions of molecular size or the extent of the reaction, cancel out.
3. Rate of reaction > rate of diffusion (eq 2.2.10):

$$k_t = k_i \quad (3.4.8)$$

4. This situation is expected to apply to radical termination, especially by combination, because of the high reactivity of the trapped radicals. Only one constant appears which depends on the diffusion of the polymer radicals, so it cannot cancel out and may contribute to a dependence of k_t on the extent of reaction or degree of polymerization.

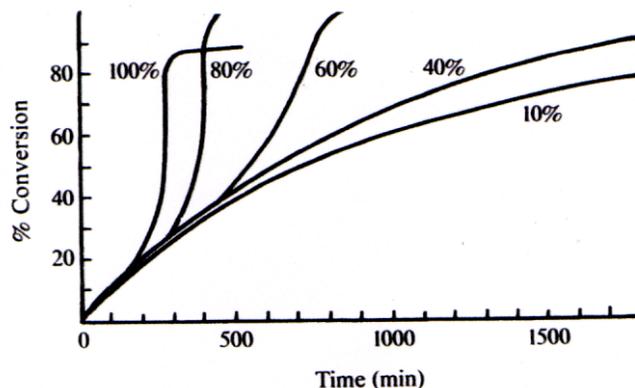


Figure 3.2

Acceleration of the polymerization rate for methyl methacrylate at the concentrations shown in benzene at 50 °C. Reprinted from G. V. Schulz and G. Harborth, *Makromol. Chem.* **1**, 106 (1948).

Figure 3.2 shows how the percent conversion of methyl methacrylate to polymer varies with time. These experiments were carried out in benzene at 50 °C. The different curves

correspond to different concentrations of monomer. Up to about 40% monomer the conversion varies smoothly with time, gradually slowing down at higher conversions owing to the depletion of monomer. At high concentrations, however, the polymerization starts to show an acceleration between 20 and 40% conversion. This behavior, called the Trommsdorff effect [2], is attributed to a decrease in the rate of termination with increasing conversion. This, in turn, is due to the increase in viscosity which has an adverse effect on k_t through eq 3.4.8. Considerations of this sort are important in bulk polymerizations where high conversion is the objective, but this complication is something we will avoid. Hence we shall be mainly concerned with solution polymerization and/or low degrees of conversion where k_t may be justifiably treated as a true constant. We shall see in Section 3.8 that the introduction of solvent is accompanied by some complications of its own, but we shall ignore this for now.

3.4C Stationary state radical concentration

Polymer propagation steps do not change the total radical concentration, so we recognize that the two opposing processes, initiation and termination, will eventually reach a point of balance. This condition is called the *stationary state*, and is characterized by a constant total concentration of free radicals. Under stationary-state conditions (subscript s) the net rate of initiation must equal the rate of termination. Using eq 3.3.2 for the rate of initiation (that is, two radicals per initiator molecule) and eq 3.4.1 for termination, we write

$$2fk_d[I] = 2k_t[P\bullet]_s^2 \quad (3.4.9)$$

or

$$[P\bullet]_s = \left(\frac{fk_d}{k_t}\right)^{1/2} [I]^{1/2} \quad (3.4.10)$$

This important equation shows that the stationary-state free-radical concentration increases with $[I]^{1/2}$ and varies directly with $k_d^{1/2}$ and inversely with $k_t^{1/2}$. The concentration of free radicals determines the rate at which polymer forms and the eventual molecular weight of the polymer, since each radical is a growth site. We shall examine these aspects of eq 3.4.10 in the next section. We conclude this section with a numerical example illustrating the stationary-state radical concentration for a typical system.

Example 3.2

For an initiator concentration which is constant at $[I]_0$, the *non-stationary-state* radical concentration varies with time according to the following expression:

$$\frac{[P\cdot]}{[P\cdot]_s} = \frac{\exp\left[\left(16fk_d k_t [I]_0\right)^{1/2} t\right] - 1}{\exp\left[\left(16fk_d k_t [I]_0\right)^{1/2} t\right] + 1}$$

Calculate $[P\cdot]_s$ and the time required for the free-radical concentration to reach 99% of this value, using the following as typical values for constants and concentrations: $k_d = 1.0 \times 10^{-4} \text{ sec}^{-1}$, $k_t = 3 \times 10^7 \text{ liter mol}^{-1} \text{ sec}^{-1}$, $f = 1/2$, and $[I]_0 = 10^{-3} \text{ M}$. Comment on the assumption $[I] = [I]_0$ that is made in deriving the non-stationary-state equation.

Solution

Use eq 3.4.10 to evaluate $[P\cdot]_s$ for the system under consideration:

$$\begin{aligned}
 [\text{P}\cdot]_s &= \left(\frac{fk_d}{k_t} [\text{I}]_o \right)^{1/2} = \left(\frac{(1/2)(1.0 \times 10^{-4})(10^{-3})}{3 \times 10^7} \right)^{1/2} = (1.67 \times 10^{-15})^{1/2} \\
 &= 4.08 \times 10^{-8} \text{ mol liter}^{-1}
 \end{aligned}$$

This low concentration is typical of free-radical polymerizations. Next we inquire how long it will take the free-radical concentration to reach $0.99[\text{P}\cdot]_s$, or $4.04 \times 10^{-8} \text{ mol liter}^{-1}$ in this case. Let $a = (16fk_d k_t [\text{I}]_o)^{1/2}$ and rearrange the expression given to solve for t when $[\text{P}\cdot]/[\text{P}\cdot]_s = 0.99$: $0.99(e^{at} + 1) = e^{at} - 1$, or $1 + 0.99 = e^{at}(1 - 0.99)$. Therefore the product $at = \ln(1.99/0.01) = \ln 199 = 5.29$, and $a = [16(1/2)(1. \times 10^{-4})(3 \times 10^7)(10^{-3})]^{1/2} = 4.90 \text{ sec}^{-1}$. Hence $t = 5.29/4.90 = 1.08 \text{ sec}$.

This short period is also typical of the time required to reach the stationary state. The assumption that $[\text{I}] = [\text{I}]_o$ maybe assessed by examining the integrated form of eq 3.3.2 for this system and calculating the ratio $[\text{I}]/[\text{I}]_o$ after 1.08 sec:

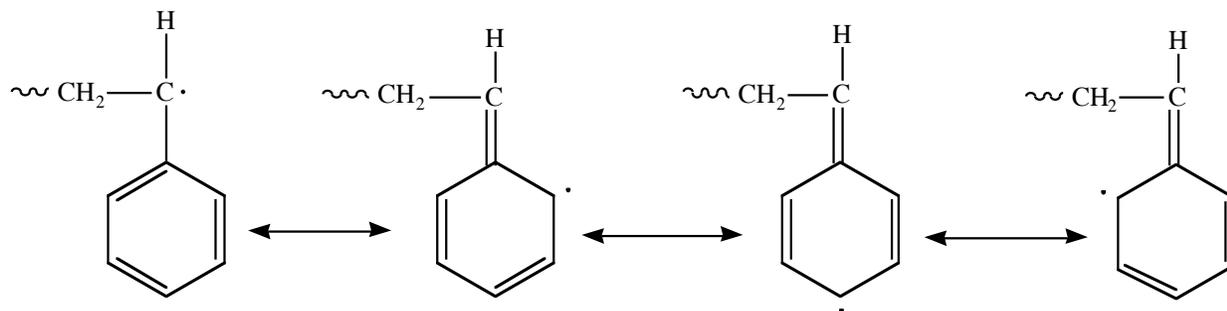
$$\begin{aligned}
 \ln \left(\frac{[\text{I}]}{[\text{I}]_o} \right) &= k_d t = -(1.0 \times 10^{-4})(1.08) = -1.08 \times 10^{-4} \\
 \frac{[\text{I}]}{[\text{I}]_o} &= 0.99989
 \end{aligned}$$

Over the time required to reach the stationary state, the initiator concentration is essentially unchanged. As a matter of fact, it would take about 100 sec for $[\text{I}]$ to reach $0.99 [\text{I}]_o$ and about 8.5 min to reach $0.95 [\text{I}]_o$, so the assumption that $[\text{I}] = [\text{I}]_o$ is entirely justified over the short times involved.

3.5 Propagation

The propagation of polymer chains is easy to consider under stationary-state conditions. As the preceding example illustrates, the stationary state is reached very rapidly, so we lose only a brief period at the start of the reaction by restricting ourselves to the stationary state. Of course, the stationary-state approximation breaks down at the end of the reaction also, when the radical concentration drops toward zero. We shall restrict our attention to relatively low conversion to polymer, however, to avoid the complications of the Trommsdorff effect. Therefore deviations from the stationary state at long times need not concern us.

It is worth taking a moment to examine the propagation step more explicitly in terms of the reaction mechanism itself. As an example, consider the case of styrene as a representative vinyl monomer. The polystyryl radical is stabilized on the terminal substituted carbon by resonance delocalization:



Consequently, the addition of the next monomer is virtually exclusively in a "head-to-tail" arrangement, leading to an all-carbon backbone with substituents (X) on alternating backbone atoms:



This should be contrasted with the single head-to-head linkage that results from termination by recombination (recall reaction (3.H)).

3.5A Rate laws for propagation

Consideration of reaction (3.B) leads to

$$-\frac{d[M]}{dt} = k_p[M][P\cdot] \quad (3.5.1)$$

as the expression for the rate at which monomer is converted to polymer. In writing this expression, we assume the following:

1. The radical concentration has the stationary-state value given by eq 3.4.10.
2. k_p is a constant independent of the size of the growing chain and the extent of conversion to polymer.
3. The rate at which monomer is consumed is equal to the rate of polymer formation R_p :

$$-\frac{d[M]}{dt} = \frac{d[\text{polymer}]}{dt} = R_p \quad (3.5.2)$$

Combining eqs 3.4.10 and 3.5.1 yields

$$R_p = k_p[M] \left(\frac{fk_d}{k_t} \right)^{1/2} [I]^{1/2} = k_{app}[M][I]^{1/2} \quad (3.5.3)$$

in which the second form reminds us that an experimental study of the rate of polymerization yields a single apparent rate constant (subscript app) which the mechanism reveals to be a composite of three different rate constants. Equation 3.5.3 shows that the rate of polymerization is first order in monomer and half order in initiator and depends on the rate constants for each of the three types of steps – initiation, propagation, and termination – that make up the chain

mechanism. Since the concentrations change with time, it is important to realize that eq 3.5.3 gives an instantaneous rate of polymerization at the concentrations considered. The equation can be applied to the initial concentrations of monomer and initiator in a reaction mixture only to describe the initial rate of polymerization. Unless stated otherwise, we shall assume the initial conditions apply when we use this result.

The initial rate of polymerization is a measurable quantity. The amount of polymer formed after various times in the early stages of the reaction can be determined directly by precipitating the polymer and weighing. Alternatively, some property such as the volume of the system (or the density, the refractive index, or the viscosity) can be measured. Using an analysis similar to that followed in Example 3.1, we can relate the values of the property measured at t , $t = 0$ and $t = \infty$ to the fraction of monomer converted to polymer. If the rate of polymerization is measured under known and essentially constant concentrations of monomer and initiator, then the cluster of constants $(fk_p^2k_d/k_t)^{1/2}$ can be evaluated from the experiment. As noted above, f is best investigated by endgroup analysis. Even with the factor f excluded, experiments on the rate of polymerization still leave us with three unknowns. Two other measurable relationships among these unknowns must be found if the individual constants are to be resolved. In anticipation of this development, we list values of k_p and the corresponding activation energies for several common monomers in Table 3.4.

| Monomer | E_p^* (kJ mol ⁻¹) | $k_{p,60^\circ} \times 10^{-3}$ (liter mol ⁻¹ sec ⁻¹) |
|---------------------|---------------------------------|---------------------------------------------------------------------------------|
| Acrylonitrile | 16.2 | 1.96 |
| Methyl acrylate | 29.7 | 2.09 |
| Methyl methacrylate | 26.4 | 0.515 |
| Styrene | 26.0 | 0.165 |
| Vinyl acetate | 18.0 | 2.30 |
| 2-vinyl pyridine | 33.0 | 0.186 |

Table 3.4 Rate constants at 60 °C and activation energies for some propagation reactions
Data from R. Korus and K. F. O'Driscoll in [1].

Equation 3.5.3 is an important result which can be expressed in several alternate forms:

1. The variation in monomer concentration may be taken into account by writing the equation in the integrated form and treating the initiator concentration as constant at $[I]_0$ over the interval considered:

$$\ln \left(\frac{[M]}{[M]_0} \right) = - \left(\frac{f k_p^2 k_d}{k_t} [I]_0 \right)^{1/2} t \quad (3.5.4)$$

where $[M] = [M]_0$ at $t = 0$.

2. Instead of using $2fk_d [I]$ for the rate of initiation, we can simply write this latter quantity as R_i , in which case the stationary-state radical concentration is

$$[P\cdot]_s = \left(\frac{R_i}{2k_t} \right)^{1/2} \quad (3.5.5)$$

and the rate of polymerization becomes

$$R_p = \left(\frac{k_p^2}{2k_t} \right)^{1/2} R_i^{1/2} [M] \quad (3.5.6)$$

If the rate of initiation is investigated independently, the rate of polymerization measures a combination of k_p and k_t .

3. Alternatively, eqs 3.3.6 and 3.3.7 can be used as expressions for R_i in eq 3.5.6 to describe redox or photoinitiated polymerization.

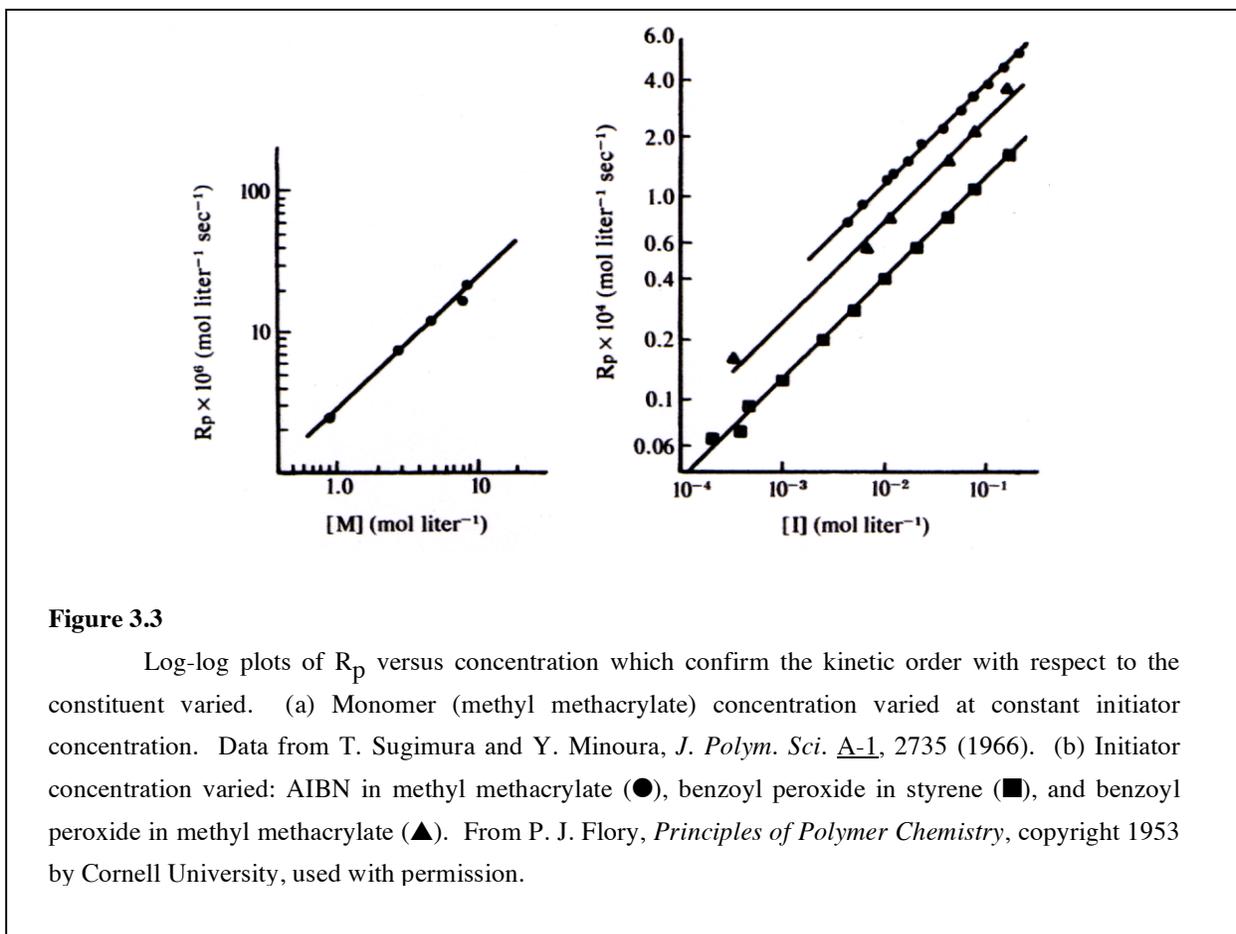


Figure 3.3 shows some data which constitute a test of eq 3.5.3. In Figure 3.3a, R_p and $[M]$ are plotted on a log–log scale for a constant level of redox initiator. The slope of this line, which

indicates the order of the polymerization with respect to monomer, is unity, showing that the polymerization of methyl methacrylate is first order in monomer. Figure 3.3b is a similar plot to the initial rate of polymerization – which essentially maintains the monomer at constant concentration – versus initiator concentration for several different monomer-initiator combinations. Each of the lines has a slope of 1/2, indicating a half-order dependence on [I] as predicted by eq 3.5.3.

3.5B Temperature dependence of propagation rates

The apparent rate constant in eq 3.5.3 follows the Arrhenius equation and yields an apparent activation energy:

$$\ln k_{\text{app}} = \ln A_{\text{app}} - \frac{E_{\text{app}}^*}{RT} \quad (3.5.7)$$

The mechanistic analysis of the rate of polymerization and the fact that the separate constants individually follow the Arrhenius equations means that

$$\begin{aligned} \ln k_{\text{app}} &= \ln k_p \left(\frac{k_d}{k_t} \right)^{1/2} \\ &= \ln A_p \left(\frac{A_d}{A_t} \right)^{1/2} - \frac{E_p^* + E_d^*/2 - E_t^*/2}{RT} \end{aligned} \quad (3.5.8)$$

This enables us to identify the apparent activation energy in eq 3.5.7 with the difference in E^* values for the various steps:

$$E_{\text{app}}^* = E_p^* + \frac{E_d^*}{2} - \frac{E_t^*}{2} \quad (3.5.9)$$

Equation 3.5.9 allows us to conveniently assess the effect of temperature variation on the rate of polymerization. This effect is considered in the following example.

Example 3.3

Using typical activation energies from Tables 3.2–3.4, estimate the percent change in the rate of polymerization with a 1 °C change in temperature at 50 °C, for both thermally initiated and photoinitiated polymerization.

Solution

Write eq 3.5.3 in the form

$$\ln R_p = \ln k_{\text{app}} + \ln[M] + 1/2 \ln[I]$$

Take the derivative, treating [M] and [I] as constants with respect to T while k is a function of T:

$$d \ln R_p = \frac{dR_p}{R_p} = d \ln k_{\text{app}}$$

Expand $d \ln k_{\text{app}}$ by means of the Arrhenius equation via eq 3.5.8:

$$\frac{dR_p}{R_p} = d \ln A_{\text{app}} - d \left(\frac{E_{\text{app}}^*}{RT} \right) = \frac{E_{\text{app}}^*}{RT^2} dT$$

Substitute eq 3.5.9 for E_{app}^* :

$$\frac{dR_p}{R_p} = \frac{E_p^* + E_d^*/2 - E_t^*/2}{RT^2} dT$$

Finally we recognize that a 1°C temperature variation can be approximated as dT and that $(dR_p/R_p) \times 100$ gives the approximate percent change in the rate of polymerization. Taking average values of E^* from the appropriate tables, we obtain $E_d^* = 145$, $E_t^* = 16.8$, and $E_p^* = 24.9$ kJ mol⁻¹. For thermally initiated polymerization

$$\frac{dR_p}{R_p} = \frac{(2.49 + 145/2 - 16.8/2)(10^3)(1)}{(8.314)(323)^2} = 0.103$$

or 10.3% per degree Celsius.

For photoinitiation there is no activation energy for the initiator decomposition; hence

$$\frac{dR_p}{R_p} = \frac{(2.49 - 16.8/2)(10^3)(1)}{(8.314)(323)^2} = 1.90 \times 10^{-2}$$

or 1.90% per degree Celsius. Note that the initiator decomposition makes the largest contribution to E^* ; therefore photoinitiated processes display a considerably lower temperature dependence for the rate of polymerization.

3.5C Kinetic Chain Length

Suppose we consider the ratio

$$R_p / R_i = \frac{-d[M]/dt}{-d[I]/dt}$$

under conditions where an initiator yields one radical, where $f = 1$, and where the final polymer contains one initiator fragment per molecule. For this set of conditions the ratio gives the number of monomer molecules polymerized per chain initiated, which is the degree of polymerization. A more general development of this idea is based on a quantity called the *kinetic chain length* $\bar{\nu}$. The kinetic chain length is defined as the ratio of the number of propagation steps to the number of initiation steps, regardless of the mode of termination:

$$\bar{\nu} = \frac{R_p}{R_i} = \frac{R_p}{R_t} \quad (3.5.10)$$

where the second form of this expression uses the stationary-state condition $R_i = R_t$. The significance of the kinetic chain length is seen in the following statements:

1. For termination by disproportionation

$$\bar{\nu} = N_n \quad (3.5.11)$$

where N_n is the number average degree of polymerization.

2. For termination by combination

$$\bar{\nu} = \frac{N_n}{2} \quad (3.5.12)$$

3. \bar{v} is an average quantity – indicated by the overbar – since not all kinetic chains are identical any more than all molecular chains are.

Using eqs 3.5.3 and 3.4.4 for R_p and R_t , respectively, we write

$$\bar{v} = \frac{k_p[\text{P}\cdot][\text{M}]}{2k_t[\text{P}\cdot]^2} = \frac{k_p[\text{M}]}{2k_t[\text{P}\cdot]} \quad (3.5.13)$$

This may be combined with eq 3.4.10 to give the stationary-state value for \bar{v} :

$$\bar{v} = \frac{k_p[\text{M}]}{2k_t(fk_d[\text{I}]/k_t)^{1/2}} = \frac{k_p[\text{M}]}{2(fk_tk_d[\text{I}])^{1/2}} \quad (3.5.14)$$

As with the rate of polymerization, we see from eq 3.5.14 that the kinetic chain length depends on the monomer and initiator concentrations and on the constants for the three different kinds of kinetic processes that constitute the mechanism. When the initial monomer and initiator concentrations are used, eq 3.5.14 describes the initial polymer formed. The initial degree of polymerization is a measurable quantity, so eq 3.5.14 provides a second functional relationship, distinct from eq 3.5.3, among experimentally available quantities – N_n , $[\text{M}]$, $[\text{I}]$ – and theoretically important parameters – k_p , k_t , and k_d . Note that the mode of termination, which establishes the connection between \bar{v} and N_n , and the value of f are both accessible through endgroup characterization. Thus we have a second equation with three unknowns; one more and the evaluation of the individual kinetic constants from experimental results will be feasible.

There are several additional points about eq 3.5.14 that are worthy of comment. First it must be recalled that we have intentionally ignored any kinetic factors other than initiation, propagation, and termination. We shall see in Section 3.8 that another process, chain transfer,

has significant effects on the molecular weight of a polymer. The result we have obtained, therefore, is properly designated as the kinetic chain length without transfer. A second observation is that \bar{v} depends not only on the nature and concentration of the monomer, but also on the nature and concentration of the initiator. The latter determines the number of different sites competing for the addition of monomer, so it is not surprising that \bar{v} is decreased by increases in either k_d or $[I]$. Finally, we observe that both k_p and k_t are properties of a particular monomer. The relative molecular weight that a specific monomer tends towards – all other things being equal – is characterized by the ratio $k_p/k_t^{1/2}$ for a monomer. Using the values in Table 3.3 and 3.4, we see that $k_p/k_t^{1/2}$ equals 0.678 for methyl acrylate and 0.0213 for styrene at 60 °C. The kinetic chain length for poly(methyl acrylate) is thus expected to be about 32 times greater than for polystyrene if the two are prepared with the same initiator (k_d) and the same concentrations $[M]$ and $[I]$. Extension of this type of comparison to the degree of polymerization requires that the two polymers compared show the same proportion of the modes of termination. Thus for vinyl acetate (subscript V) relative to acrylonitrile (subscript A) at 60 °C, with the same provisos as above, $\bar{v}_V/\bar{v}_A = 6$ while $N_{n,V}/N_{n,A} = 3$ because of the differences in the mode of termination for the two.

The proviso “all other things being equal” in discussing the last point clearly applies to temperature as well, since the kinetic constants can be highly sensitive to temperature. To evaluate the effect of temperature variation on the molecular weight of an addition polymer, we follow the same sort of logic as was used in Example 3.3:

1. Take logarithms of eq 3.5.14:

$$\ln \bar{v} = \ln k_p (k_t k_d)^{-1/2} + \ln \left(\frac{[M]}{2(f[I])^{1/2}} \right) \quad (3.5.15)$$

2. Differentiate with respect to T , assuming the temperature dependence of the concentrations is negligible compared to that of the rate constants:

$$\frac{d\bar{v}}{\bar{v}} = d \ln k_p - 1/2 d \ln (k_t k_d) \quad (3.5.16)$$

3. By the Arrhenius equation $d \ln k = -d (E^*/RT) = (E^*/RT^2) dT$; therefore

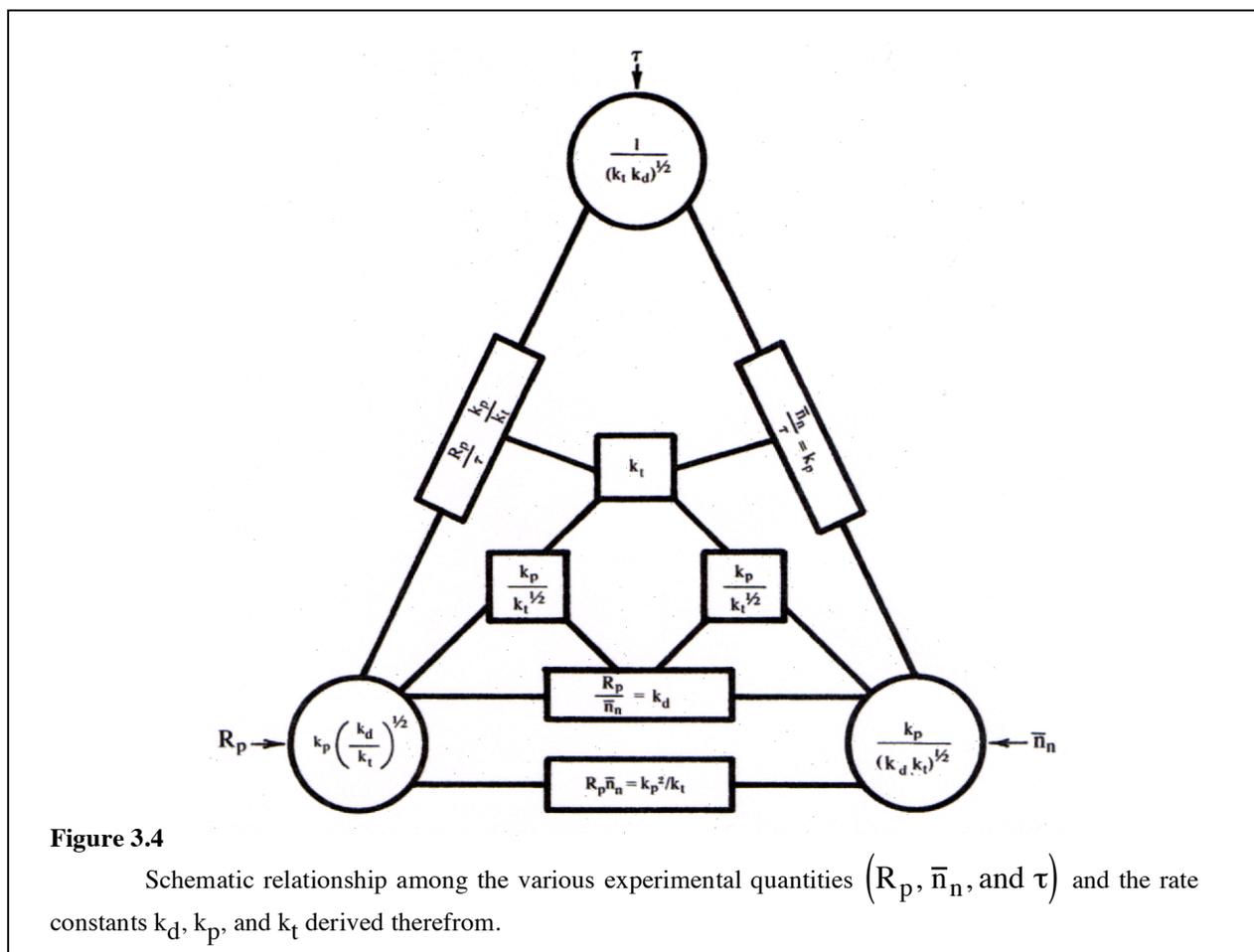
$$\frac{d\bar{v}}{\bar{v}} = \frac{E_p^* - E_t^*/2 - E_d^*/2}{RT^2} dT \quad (3.5.17)$$

It is interesting to compare the application of this result to thermally initiated and photoinitiated polymerizations as we did in Example 3.3. Again using the average values of the constants from Tables 3.2–3.4 and taking $T = 50^\circ\text{C}$, we calculate that \bar{v} *decreases* by about 6.5% per degree C for thermal initiation and *increases* by about 2% per degree for photoinitiation. It is clearly the large activation energy for initiator dissociation which makes the difference. This term is omitted in the case of photoinitiation, where the temperature increase produces a bigger effect on propagation than on termination. On the other hand, for thermal initiation an increase in temperature produces a large increase in the number of growth centers, with the attendant reduction of the average kinetic chain length.

Photoinitiation is not as important as thermal initiation in the overall picture of free-radical chain-growth polymerization. The foregoing discussion reveals, however, that the contrast between the two modes of initiation does provide insight into, and confirmation of, various aspects of addition polymerization. The most important application of photoinitiated polymerization is in providing a third experimental relationship among the kinetic parameters of the chain mechanism. We shall consider this in the next section.

3.6 Radical lifetime

In the preceding section we observed that both the rate of polymerization and the degree of polymerization under stationary-state conditions can be interpreted to yield some cluster of the constants k_p , k_t , and k_d . The situation is summarized diagrammatically in Figure 3.4. The circles at the two bottom corners of the triangle indicate the particular grouping of constants obtainable from the measurement of R_p or \bar{N}_n , as shown. By combining these two sources of data in the manner suggested in the boxes situated along the lines connecting these circles k_d can be evaluated, as well as the ratio k_p^2/k_t . Using this stationary-state data, however, it is not possible to further resolve the propagation and termination constants. Another relationship is needed to do this. A quantity called the radical lifetime $\bar{\tau}$ supplies the additional relationship and enables us to move off the base of Figure 3.4.



To arrive at an expression for the radical lifetime, we return to eq 3.5.1, which may be interpreted as follows:

1. $d[M]/dt$ gives the rate at which monomers enter polymer molecules. This, in turn, is given by the product of number of growth sites, $[P\bullet]$, and the rate at which monomers add to each growth site. On the basis of eq 3.5.1, the rate at which monomers add to a radical is given by $k_p[M]$.
2. If $k_p[M]$ gives the number of monomers added per unit time, then $1/k_p[M]$ equals the time elapsed per monomer addition.
3. If we multiply the time elapsed per monomer added to a radical by the number of monomers in the average chain, then we obtain the time during which the radical exists. This is the definition of the radical lifetime. The number of monomers in a polymer chain is, of course, the degree of polymerization. Therefore we write

$$\bar{\tau} = \frac{N_n}{k_p[M]} \quad (3.6.1)$$

4. The degree of polymerization in eq 3.6.1 can be replaced with the kinetic chain length, and the resulting expression simplified. To proceed, however, we must choose between the possibilities described in eqs 3.5.11 and 3.5.12. Assuming termination by disproportionation, we replace N_n by $\bar{\nu}$, using eq 3.5.14:

$$\bar{\tau} = \frac{k_p[M]}{2(f k_t k_d [I])^{1/2}} \frac{1}{k_p[M]} = \frac{1}{2(f k_t k_d [I])^{1/2}} \quad (3.6.2)$$

5. The radical lifetime is an average quantity, as indicated by the overbar.

We shall see presently that the lifetime of a radical can be measured. When such an experiment is conducted with a known concentration of initiator, then the cluster of constants $(k_t k_p)^{-1/2}$ can be evaluated. This is indicated at the apex of the triangle in Figure 3.4.

There are several things about Figure 3.4 that should be pointed out:

1. In going from the experimental quantities R_p , N_n and $\bar{\tau}$ to the associated clusters of kinetic constants, it has been assumed that the monomer and initiator concentrations are known and essentially constant. In addition, the efficiency factor f has been left out, the assumption being that still another type of experiment has established its value.
2. By following the lines connecting two sources of circled information, the boxed result in the perimeter of the triangle may be established. Thus k_p is evaluated from $\bar{\tau}$ and N_n .
3. Here k_p can be combined with one of the various k_p/k_t ratios to permit the evaluation of k_t .

We can use the constants tabulated elsewhere in the chapter to get an idea of a typical radical lifetime. Choosing 10^{-3} M AIBN as the initiator ($k_d = 0.85 \times 10^{-5} \text{ sec}^{-1}$ at 60°C) and vinyl acetate as the monomer (terminates entirely by disproportionation, $k_t = 2.9 \times 10^7 \text{ liter mol}^{-1} \text{ sec}^{-1}$ at 60°C), and taking $f = 1$ for the purpose of calculation, we find $\bar{\tau} = 0.5[(1.0)(2.9 \times 10^7)(0.85 \times 10^{-5})(10^{-3})]^{-1/2} = 1.01 \text{ sec}$. This figure contrasts sharply with the times required to obtain high molecular weight molecules in step-growth polymerizations.

Since the radical lifetime provides the final piece of information needed to independently evaluate the three primary kinetic constants – remember, we are still neglecting chain transfer – the next order of business is a consideration of the measurement of $\bar{\tau}$. A widely used technique for measuring radical lifetime is based on photoinitiated polymerization using a light source which blinks on and off at regular intervals. In practice, a rotating opaque disk with a wedge sliced out of it is interposed between the light and the reaction vessel. Thus the system is in darkness when the solid part of the disk is in the light path and is illuminated when the notch passes. With this device, called a rotating sector or chopper, the relative lengths of light and dark

periods can be controlled by the area of the notch, and the frequency of the flickering by the velocity of rotation of the disk. We will not describe the rotating sector experiments in detail. It is sufficient to note that, with this method, the rate of photoinitiated polymerization is studied as a function of the time of illumination with the rapidly blinking light. The results show the rate of polymerization dropping from one plateau value at slow blink rates ("long" bursts of illumination) to a lower plateau at fast blink rates ("short" periods of illumination). A plot of the rate of polymerization versus the duration of an illuminated interval resembles an acid-base titration curve with a step between the two plateau regions. Just as the "step" marks the end point of a titration, the "step" in rotating sector data identifies the transition between relatively long and short periods of illumination. Here is the payoff: "long" and "short" times are defined relative to the average radical lifetime. Thus $\bar{\tau}$ may be read from the time axis at the midpoint of the transition between the two plateaus.

This qualitative description enables us to see that the radical lifetime described by eq 3.6.2 is an experimentally accessible quantity. More precise values of $\bar{\tau}$ may be obtained by curve fitting since the non-stationary state kinetics of the transition between plateaus have been analyzed in detail. To gain some additional familiarity with the concept of radical lifetime and to see how this quantity can be used to determine the absolute value of a kinetic constant, consider the following example:

Example 3.4

The polymerization of ethylene at 130 °C and 1500 atm was studied using different concentrations of the initiator, 1-*t*-butylazo-1-phenoxy-cyclohexane. The rate of initiation was measured directly and radical lifetime were determined using the rotating sector method. The following results were obtained (data from T. Takahashi and P. Ehrlich, *Polym. Prepr., Am. Chem. Soc. Polym. Chem. Div.* 22, 203 (1981)).

| Run | $\bar{\tau}$ (sec) | $R_i \times 10^9$ (mol liter ⁻¹ sec ⁻¹) |
|-----|--------------------|----------------------------------------------------------------|
| 5 | 0.73 | 2.35 |
| 6 | 0.93 | 1.59 |
| 8 | 0.32 | 12.75 |
| 12 | 0.50 | 5.00 |
| 13 | 0.29 | 14.95 |

Demonstrate that the variations in the rate of initiation and $\bar{\tau}$ are consistent with free-radical kinetics, and evaluate k_t .

Solution

Since the rate of initiation is measured, we can substitute R_i for the terms $(2fk_d[I])^{1/2}$ in eq 3.6.2 to give

$$\bar{\tau} = \frac{1}{(2k_t R_i)^{1/2}} \quad \text{or} \quad k_t = \frac{1}{2\bar{\tau}^2 R_i}$$

If the data follow the kinetic scheme presented here, the values of k_t calculated for the different runs should be constant:

| Run | 5 | 6 | 8 | 12 | 13 | Average |
|-------------------------------------------------------------------|------|------|------|------|------|---------|
| $k_t \times 10^{-8}$ (liter mol ⁻¹ sec ⁻¹) | 3.99 | 3.64 | 3.83 | 4.00 | 3.98 | 3.89 |

Even though the rates of initiation span almost a 10-fold range, the values of k_t show a standard deviation of only 4%, which is excellent in view of the inevitable experimental errors. Note that the rotating sector method can be used in high-pressure experiments and other unusual situations, a highly desirable characteristic it shares with many optical methods in chemistry.

3.7 Distribution of molecular weights

Until this point in the chapter we have intentionally avoided making any differentiation among radicals on the basis of the degree of polymerization of the radical. Now we seek a description of the molecular weight distribution of addition polymer molecules. Toward this end it becomes necessary to consider radicals of different i values.

3.7A Distribution of i -mers: termination by disproportionation

We begin by writing a kinetic expression for the concentration of radicals of degree of polymerization i , which we designate $[P_i \bullet]$. This rate law will be the sum of three contributions:

1. An increase which occurs by addition of monomer to the radical $P_{i-1} \bullet$.
2. A decrease which occurs by addition of a monomer to the radical $P_i \bullet$.
3. A decrease which occurs by the termination of $P_i \bullet$ with any other radical $P \bullet$.

The change in $[P_i \bullet]$ under stationary-state conditions equals zero for all values of i ; hence we can write

$$\frac{d[P_i \bullet]}{dt} = k_p[M][P_{i-1} \bullet] - k_p[M][P_i \bullet] - 2k_t[P_i \bullet][P \bullet] = 0 \quad (3.7.1)$$

which can be rearranged to

$$\frac{[P_i \bullet]}{[P_{i-1} \bullet]} = \frac{k_p[M]}{k_p[M] + 2k_t[P \bullet]} \quad (3.7.2)$$

Dividing the numerator and denominator of eq 3.7.2 by $2k_t[P\bullet]$ and recalling the definition of \bar{v} provided by eq 3.5.13 enables us to express this result more succinctly as

$$\frac{[P_i\bullet]}{[P_{i-1}\bullet]} = \frac{\bar{v}}{1 + \bar{v}} \quad (3.7.3)$$

Next let us consider the following sequence of multiplications:

$$\frac{[M_i\bullet]}{[M_{i-1}\bullet]} \frac{[P_{i-1}\bullet]}{[P_{i-2}\bullet]} \frac{[P_{i-2}\bullet]}{[P_{i-3}\bullet]} \dots \frac{[P_{i-(i-2)}\bullet]}{[P_{i-(i-1)}\bullet]} = \frac{[P_i\bullet]}{[P_1\bullet]} \quad (3.7.4)$$

This shows that the number of i -mer radicals relative to the number of the smallest radicals is given by multiplying the ratio $[P_i\bullet]/[P_{i-1}\bullet]$ by $i-2$ analogous ratios. Since each of the individual ratios is given by $\bar{v}/(1 + \bar{v})$, we can rewrite eq 3.7.4 as

$$\frac{[P_i\bullet]}{[P_1\bullet]} = \frac{[P_i\bullet]}{[P_{i-1}\bullet]} \left(\frac{\bar{v}}{1 + \bar{v}} \right)^{i-2} \quad (3.7.5)$$

or

$$[P_{i-1}\bullet] = [P_1\bullet] \left(\frac{\bar{v}}{1 + \bar{v}} \right)^{(i-1)-1} \quad (3.7.6)$$

Since it is more convenient to focus attention on i -mers than $(i - 1)$ -mers, the corresponding expression for the i -mer is written by analogy:

$$[P_i \bullet] = [P_1 \bullet] \left(\frac{\bar{v}}{1 + \bar{v}} \right)^{i-1} \quad (3.7.7)$$

Dividing both sides of eq 3.7.7 by $[P \bullet]$, the total radical concentration, gives the number (or mole) fraction of i -mer radicals in the total radical population. This ratio is the same as the number of i -mers n_i in the sample containing a total of n (no subscript) polymer molecules:

$$\frac{n_i}{n} = \frac{[P_i \bullet]}{[P \bullet]} = \frac{[P_1 \bullet]}{[P \bullet]} \left(\frac{\bar{v}}{1 + \bar{v}} \right)^{i-1} \quad (3.7.8)$$

The ratio $[P_1 \bullet]/[P \bullet]$ in eq 3.7.8 can be eliminated by applying eq 3.7.1 explicitly to the P_1 radical:

1. Write eq 3.7.1 for $P_1 \bullet$, remembering in this case that the leading term describes initiation:

$$\frac{d[P_1 \bullet]}{dt} = R_i - k_p[M][P_1 \bullet] - 2k_t[P_1 \bullet][P \bullet] = 0 \quad (3.7.9)$$

2. Rearrange under stationary-state conditions:

$$[P_1 \bullet] = \frac{R_i}{k_p[M] + 2k_t[P \bullet]} \quad (3.7.10)$$

The total radical concentration under stationary-state conditions can be similarly obtained:

3. Write eq 3.4.9 using the same notation for initiation as in eq 3.7.9:

$$\frac{d[\text{P}\cdot]}{dt} = R_i - 2k_t[\text{P}\cdot]^2 = 0 \quad (3.7.11)$$

4. Rearrange under stationary-state conditions:

$$[\text{P}\cdot] = \frac{R_i}{2k_t[\text{P}\cdot]} \quad (3.7.12)$$

5. Take the ratio of eq 3.7.10 to eq 3.7.12:

$$\frac{[\text{P}_1\cdot]}{[\text{P}\cdot]} = \frac{2k_t[\text{P}\cdot]}{k_p[\text{M}] + 2k_t[\text{P}\cdot]} = \frac{1}{1 + \bar{\nu}} \quad (3.7.13)$$

Combining eq 3.7.13 with eq 3.7.8 gives

$$x_i = \frac{n_i}{n} = \frac{1}{1 + \bar{\nu}} \left(\frac{\bar{\nu}}{1 + \bar{\nu}} \right)^{i-1} = \frac{1}{\bar{\nu}} \left(\frac{\bar{\nu}}{1 + \bar{\nu}} \right)^i \quad (3.7.14)$$

This expression gives the number fraction or mole fraction, x_i , of i -mers in the polymer and is thus equivalent to eq 2.4.2 for step-growth polymerization.

The kinetic chain length \bar{v} may also be viewed as merely a cluster of kinetic constants and concentrations which was introduced into eq 3.7.13 to simplify the notation. As an alternative, suppose we define for the purposes of this chapter a fraction p such that

$$p \equiv \frac{\bar{v}}{1 + \bar{v}} = \frac{k_p[M]}{k_p[M] + 2k_t[P\bullet]} \quad (3.7.15)$$

It follows from this definition that $1/(1 + \bar{v}) = 1 - p$, so eq 3.7.14 can be rewritten as

$$x_i = \frac{n_i}{n} = (1 - p)p^{i-1} \quad (3.7.16)$$

This change of notation now expresses eq 3.7.14 in exactly the same form as its equivalent in Section 2.4. In other words, the distribution of chain lengths is the Most Probable Distribution, just as was the case for step-growth polymerization! Several similarities and differences should be noted in order to take full advantage of the parallel between this result and the corresponding material for condensation polymers in Chapter 2:

1. In Chapter 2, p was defined as the fraction (or probability) of functional groups that had reacted at a certain point in the polymerization. According to the current definition provided by eq 3.7.15, p is the fraction (or probability) of propagation steps among the combined total of propagation and termination steps. The quantity $1-p$ is therefore the fraction (or probability) of termination steps. An addition polymer with degree of polymerization i has undergone $i-1$ propagation steps and one termination step. Therefore it makes sense to describe its probability in the form of eq 3.7.16.

2. It is apparent from eq 3.7.15 that $p \rightarrow 1$ as $\bar{v} \rightarrow \infty$; hence those same conditions which favor the formation of a high molecular weight polymer also indicate p values close to unity.
3. In Chapter 2 all molecules – whether monomer or i-mers of any i – carry functional groups; hence the fraction described by eq 2.4.1 applies to the entire reaction mixture. Equation 3.7.16, by contrast, applies *only to the radical population*. Since the radicals eventually end up as polymers, the equation also describes the polymer produced. Unreacted monomers are specifically excluded, however.
4. Only one additional stipulation needs to be made before adapting the results that follow from eq 2.4.1 to addition polymers. The mode of termination must be specified to occur by disproportionation to use the results of Section 2.4 in this chapter, since termination by combination obviously changes the size distribution. We shall return to the case of termination by combination presently.
5. For termination by disproportionation (subscript d), we note that $p = k_p[M]/(k_p[M] + 2k_{t,d}[P\bullet])$, and therefore by analogy with eqs 2.4.5, 2.4.9, and 2.4.10,

$$(N_n)_d = \frac{1}{1-p} \quad (3.7.17)$$

$$(N_w)_d = \frac{1+p}{1-p} \quad (3.7.18)$$

$$\left(\frac{N_w}{N_n}\right)_d = 1+p \rightarrow 2 \quad \text{as } p \rightarrow 1 \quad (3.7.19)$$

By virtue of eq 3.7.15, $(N_n)_d$ can also be written as $1 + \bar{v} \cong \bar{v}$ for large $e \bar{v}$, which is the result already obtained in eq 3.5.11. Figures 2.5 and 2.6 also describe the distribution by number and weight of addition polymers, if the provisos enumerated above are applied.

| Reaction | Rate Law |
|-------------------------------------------------|-------------------------------------------------------------|
| $P_{i-1} \bullet + P_1 \bullet \rightarrow P_i$ | $\frac{d[P_i]}{dt} = k_{t,c}[P_{i-1} \bullet][P_1 \bullet]$ |
| $P_{i-2} \bullet + P_2 \bullet \rightarrow P_i$ | $\frac{d[P_i]}{dt} = k_{t,c}[P_{i-2} \bullet][P_2 \bullet]$ |
| $P_{i-3} \bullet + P_3 \bullet \rightarrow P_i$ | $\frac{d[P_i]}{dt} = k_{t,c}[P_{i-3} \bullet][P_3 \bullet]$ |
| ... | |
| $P_{i-j} \bullet + P_j \bullet \rightarrow P_i$ | $\frac{d[P_i]}{dt} = k_{t,c}[P_{i-j} \bullet][P_j \bullet]$ |

Table 3.5 Some free radical combination reactions which yield i-mers and their rate laws

3.7B Distribution of i-mers: termination by combination

To deal with the case of termination by combination, it is convenient to write some reactions by which an i-mer might be formed. Table 3.5 lists several specific chemical reactions and the corresponding rate expressions as well as the general form for the combination of an (i – j)-mer and a j-mer. On the assumption that all $k_{t,c}$ values are the same, we can write the total rate of change of $[P_i]$:

$$\left(\frac{d[P_i]}{dt}\right)_{\text{tot}} = k_{t,c} \sum_{j=1}^{i-1} [P_{i-j} \bullet][P_j \bullet] \quad (3.7.20)$$

The fraction of i -mers formed by combination may be evaluated by dividing $d[P_i]/dt$ by $\sum_i d[P_i]/dt$. Assuming that termination occurs exclusively by combination, then

$$\sum_i \frac{d[P_i]}{dt} = k_{t,c} [P \bullet]^2 \quad (3.7.21)$$

and the number or mole fraction of i -mers formed by combination (subscript c) is

$$\left(\frac{n_i}{n}\right)_c = \frac{d[P_i]/dt}{\sum_i d[P_i]/dt} = \frac{k_{t,c} \sum_{j=1}^{i-1} [P_{i-j} \bullet][P_j \bullet]}{k_{t,c} [P \bullet]^2} \quad (3.7.22)$$

Equation 3.7.16 can be used to relate $[P_{i-j} \bullet]$ and $[P_j \bullet]$ to the total radical concentration:

$$[P_{i-j} \bullet] = (1-p) p^{(i-j)-1} [P \bullet] \quad (3.7.23)$$

and

$$[P_j \bullet] = (1-p) p^{(j-1)} [P \bullet] \quad (3.7.24)$$

Therefore

$$\begin{aligned} \left(\frac{n_i}{n}\right)_c &= \frac{k_{t,c} \sum_{j=1}^{i-1} (1-p) p^{i-j-1} [P\bullet] (1-p) p^{j-1} [P\bullet]}{k_{t,c} [P\bullet]^2} \\ &= \sum_{j=1}^{i-1} (1-p)^2 p^{i-2} \end{aligned} \quad (3.7.25)$$

The index j drops out of the last summation; we compensate for this by multiplying the final result by $i-1$ in recognition of the fact that the summation adds up $i-1$ identical terms. Accordingly, the desired result is obtained:

$$\left(\frac{n_i}{n}\right)_c = x_i = (i-1) (1-p)^2 p^{i-2} \quad (3.7.26)$$

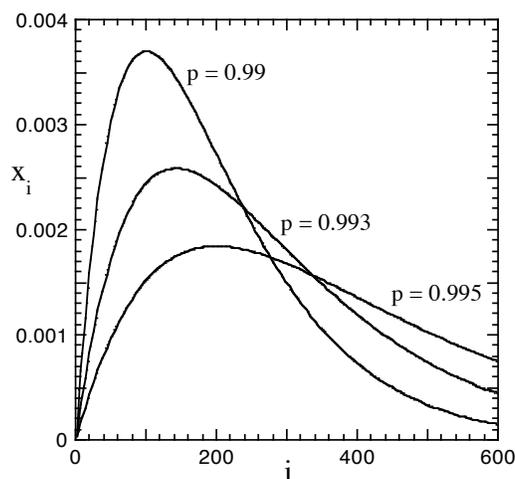


Figure 3.5

Mole fraction of i -mers as a function of i for termination by combination, according to eq 3.7.26, for various values of p .

This expression is plotted in Figure 3.5 for several large values of p . Although it shows the number distribution of polymers terminated by combination, the distribution looks quite different from Figure 2.5, which described the number distribution for termination by disproportionation. In the latter x_i decreases monotonically with increasing i . With combination, however, the curves go through a maximum which reflects the fact that the combination of two very small or two very large radicals is a less probable event than a more random combination.

Expression for the various averages are readily derived from eq 3.7.26 by procedures identical to those used in Section 2.4 (see Problem 3.6). We only quote the final results for the case where termination occurs exclusively by combination:

$$(\overline{N}_n)_c = \frac{2}{1-p} \quad (3.7.27)$$

$$(\overline{N}_w)_c = \frac{2+p}{1-p} \quad (3.7.28)$$

$$\left(\frac{\overline{N}_w}{\overline{N}_n}\right)_c = \frac{2+p}{2} \quad (3.7.29)$$

These various expressions differ from their analogs in the case of termination by disproportionation by the appearance of occasional 2's. These terms arise precisely because two chains are combined in this mode of termination. Again using eq 3.7.15, we note that $(\overline{N}_n)_c = 2(1 + \bar{v}) \cong 2\bar{v}$ for large \bar{v} , a result which was already given as eq 3.5.12.

One rather different result that arises from the case of termination by combination is seen by examining the limit of eq 3.7.29 for large values of p :

$$\frac{N_w}{N_n} \rightarrow \frac{2+1}{2} = 1.5 \quad \text{as} \quad p \rightarrow 1 \quad (3.7.30)$$

This contrasts with a limiting ratio of 2 for the case of termination by disproportionation. Since M_n and M_w can be measured, the difference is potentially a method for determining the mode of termination in a polymer system. In most instances, however, termination occurs by some proportion of both modes. Furthermore, other factors in the polymerization such as transfer, autoacceleration, etc., will also contribute to the experimental molecular weight distribution, so in general it is risky to draw too many conclusions about mechanisms from the measured distributions. Also, we have used p and \bar{v} to describe the distribution of molecular weights, but it must be remembered that these quantities are defined in terms of various concentrations and therefore change as the reactions proceed. Accordingly, the results presented here are most simply applied at the start of the polymerization reaction when the initial concentrations of monomer and initiator can be used to evaluate p or \bar{v} .

3.8 Chain transfer

The three-step mechanism for free-radical polymerization represented by reactions (3.A)–(3.C) does not tell the whole story. Another type of free-radical reaction, called chain transfer, may also occur. This is unfortunate in the sense that it complicates the neat picture presented until now. On the other hand, this additional reaction can be turned into an asset in actual polymer practice. One consequence of chain transfer reactions is a lowering of the kinetic chain length and hence the molecular weight of the polymer, without necessarily affecting the rate of polymerization. A certain minimum average molecular weight is often needed to achieve a desired physical property, but further increases in chain length simply make processing more difficult.

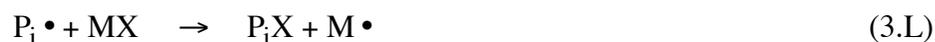
3.8A Chain transfer reactions

Chain transfer arises when hydrogen or some other atom X is transferred from a molecule in the system to the polymer radical. This terminates the growth of the original radical but replaces it with a new one: the fragment of the species from which X was extracted. These latter molecules will be designated by attaching the letter X to their symbol in this discussion. Thus if chain transfer involves an initiator molecule, we represent the latter as IX in this section. Chain transfer can occur with any molecule in the system. The following reactions specifically describe transfer to initiator, monomer, solvent, and polymer molecules, respectively:

1. Transfer to initiator, IX:



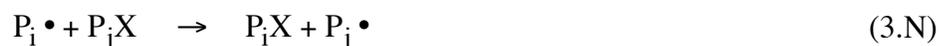
2. Transfer to monomer, MX:



3. Transfer to solvent, SX:



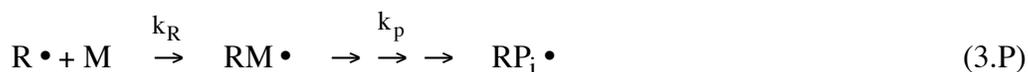
4. Transfer to polymer, P_jX:



5. General transfer to RX:



It is apparent from these reactions how chain transfer lowers the molecular weight of a chain-growth polymer. The effect of chain transfer on the rate of polymerization depends on the rate at which the new radicals reinitiate polymerization:



If the rate constant k_R is comparable to k_p , the substitution of a polymer radical with a new radical has little or no effect on the rate of polymerization. If $k_R \ll k_p$, the rate of polymerization will be decreased by chain transfer.

The kinetic chain length acquires a slightly different definition in the presence of chain transfer. Instead of being simply the ratio R_p / R_t , it is redefined to be the rate of propagation relative to the rates of *all* other steps that compete with propagation; specifically, termination and transfer (subscript tr):

$$\bar{v}_{tr} = \frac{R_p}{R_t + R_{tr}} \quad (3.8.1)$$

The transfer reactions follow second-order kinetics, the general rate law being

$$R_{tr} = k_{tr} [P_i \bullet][RX] \quad (3.8.2)$$

where k_{tr} is the rate constant for chain transfer to a specific compound RX. Since chain transfer can occur with several different molecules in the reaction mixture, eq 3.8.1 becomes

$$\begin{aligned} \bar{v}_{tr} &= k_p [P\cdot][M] / \{2k_t [P\cdot]^2 + k_{t,IX} [P\cdot][IX] + k_{tr,MX} [P\cdot][MX] \\ &\quad + k_{tr,SX} [P\cdot][SX] + k_{tr,P_iX} [P\cdot][P_iX]\} \end{aligned} \quad (3.8.3)$$

$$= \frac{k_p [M]}{2k_t [P\cdot] + \sum k_{tr,RX} [RX]}$$

where the summation is over all pertinent RX species. It is instructive to examine the reciprocal of this quantity:

$$\frac{1}{\bar{v}_{tr}} = \frac{2k_t [P\cdot]}{k_p [M]} + \frac{\sum k_{tr,RX} [RX]}{k_p [M]} \quad (3.8.4)$$

Since the first term on the right-hand side is the reciprocal of the kinetic chain length in the absence of transfer, this becomes

$$\frac{1}{\bar{v}_{tr}} = \frac{1}{\bar{v}} + \frac{\sum k_{tr,RX} [RX]}{k_p [M]} \quad (3.8.5)$$

This notation is simplified still further by defining the ratio of constants

$$\frac{k_{tr,RX}}{k_p} = C_{RX} \quad (3.8.6)$$

which is called the chain transfer constant for the monomer in question to molecule RX:

$$\frac{1}{\bar{v}_{tr}} = \frac{1}{\bar{v}} + \sum_{\text{all RX}} C_{RX} \frac{[RX]}{[M]} \quad (3.8.7)$$

It is apparent from this expression that the larger the sum of chain transfer terms becomes, the smaller will be \bar{v}_{tr} .

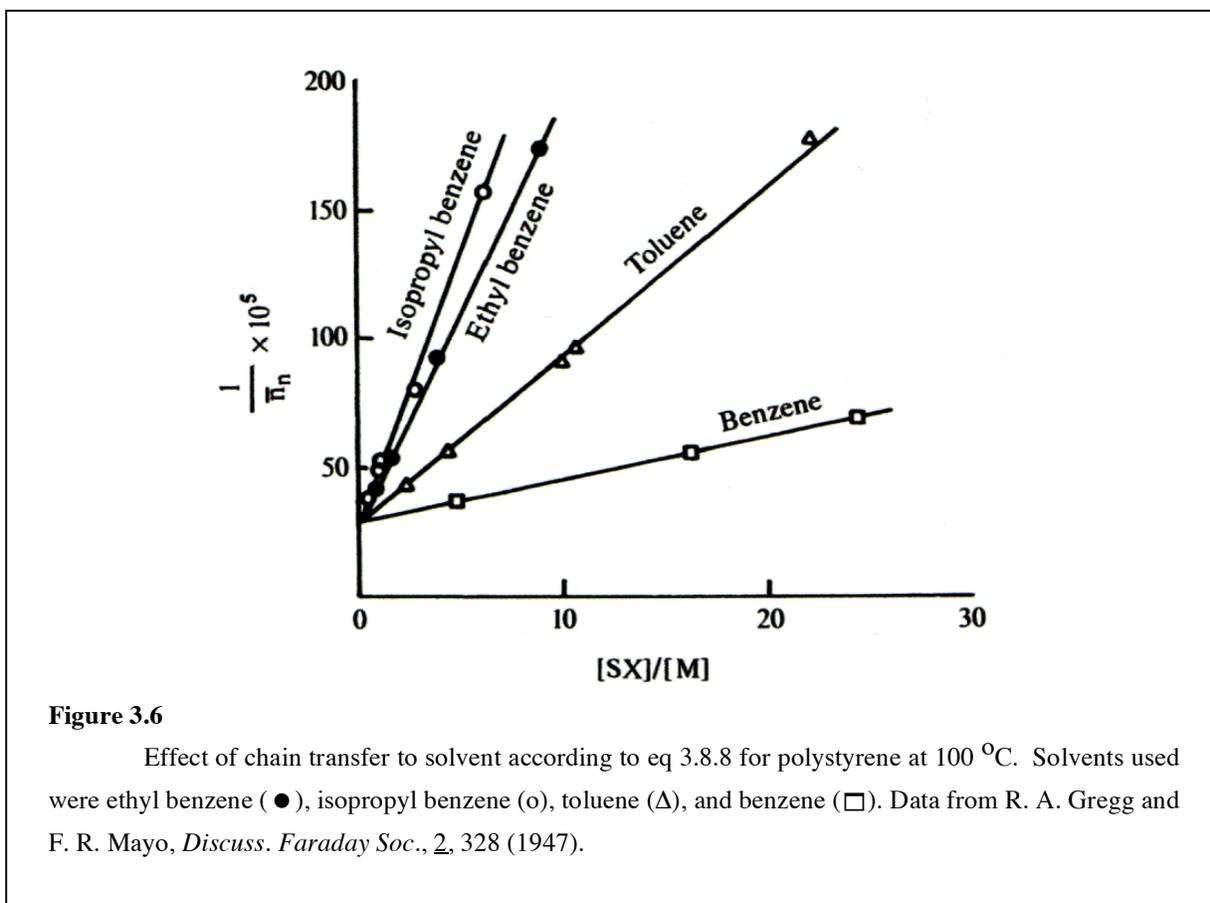
The magnitude of the individual terms in the summation depends on both the specific chain transfer constants and the concentrations of the reactants under consideration. The former are characteristics of the system and hence quantities over which we have little control; the latter can often be adjusted to study a particular effect. For example, chain transfer constants are generally obtained under conditions of low conversion to polymer where the concentration of polymer is low enough to ignore the transfer to polymer. We shall return below to the case of high conversions where this is not true.

3.8B Evaluation of chain transfer constants

If an experimental system is investigated in which only one molecule is significantly involved in transfer, then the chain transfer constant to that material is particularly easy to obtain. If we assume that species SX is the only molecule to which transfer occurs, eq 3.8.7 becomes

$$\frac{1}{\bar{v}_{tr}} = \frac{1}{\bar{v}} + C_{SX} \frac{[SX]}{[M]} \quad (3.8.8)$$

This suggests that polymerizations should be conducted at different ratios of $[SX]/[M]$ and the resulting molecular weight measured for each. Equation 3.8.8 indicates that a plot of $1/\bar{v}_{tr}$ versus $[SX]/[M]$ should be a straight line with slope C_{SX} . Figure 3.6 shows this type of plot for the polymerization of styrene at 100 °C in the presence of four different solvents. The fact that all show a common intercept as required by eq 3.8.8 shows that the rate of initiation is unaffected by the nature of the solvent. The following example examines chain transfer constants evaluated in this situation.



Example 3.5

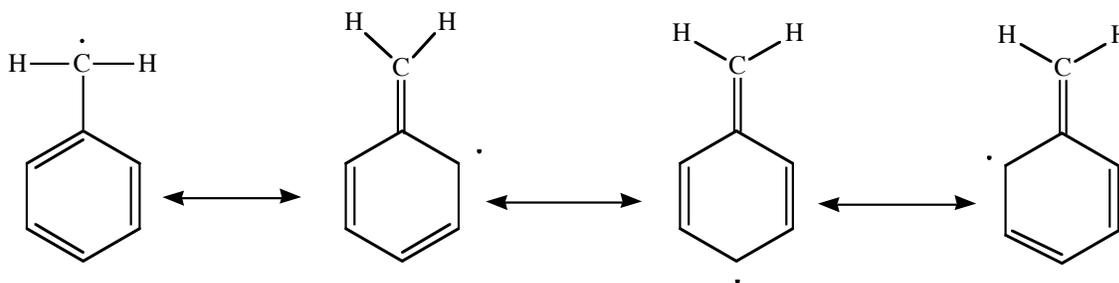
Estimate the chain transfer constants for styrene to isopropylbenzene, ethylbenzene, toluene, and benzene from the data presented in Figure 3.6. Comment on the relative magnitude of these constants in terms of the structure of the solvent molecules.

Solution

The chain transfer constants are given by eq 3.8.8 as the slopes of the lines in Figure 3.6. These are estimated to be as follows (note that X = H in this case):

| SX | <i>i</i> -C ₃ H ₇ (C ₆ H ₅) | C ₂ H ₅ (C ₆ H ₅) | CH ₃ (C ₆ H ₅) | H(C ₆ H ₅) |
|-----------------------------------|--------------------------------------------------------------------------|----------------------------------------------------------------|--------------------------------------------------|-----------------------------------|
| C _{SX} × 10 ⁴ | 2.08 | 1.38 | 0.55 | 0.16 |

The relative magnitudes of these constants are consistent with the general rule that benzylic hydrogens are more readily abstracted than those attached directly to the ring. The reactivity of the benzylic hydrogens themselves follows the order tertiary > secondary > primary, which is a well-established order in organic chemistry. The benzylic radical resulting from hydrogen abstraction is resonance stabilized. For toluene, as an example,



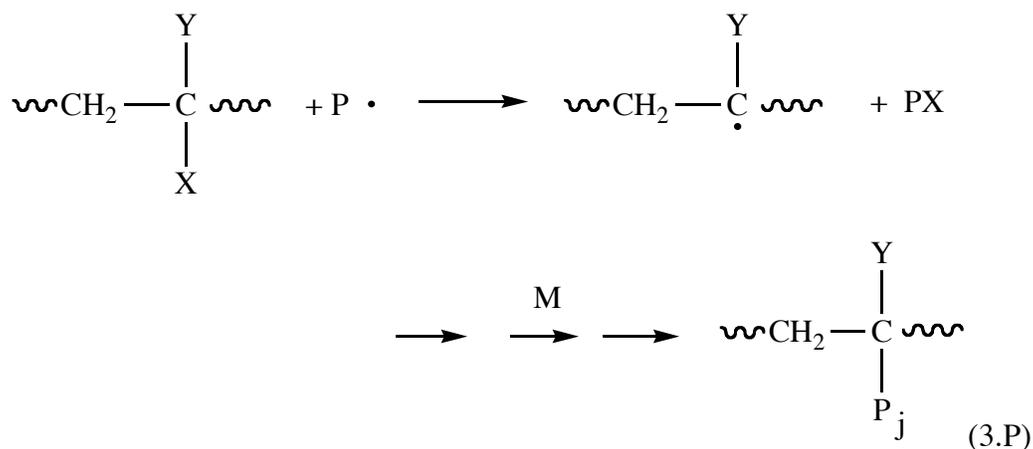
In certain commercial processes it is essential to regulate the molecular weight of the polymer either for ease of processing or because low molecular weight products are desirable for particular applications such as lubricants or plasticizers. In such cases the solvent or chain transfer agent is chosen and its concentration selected to produce the desired value of \bar{v}_{tr} .

Certain mercaptans have particularly large chain transfer constants for many common monomers and are especially useful for molecular weight regulation. For example, styrene has a chain transfer constant for *n*-butyl mercaptan equal to 21 at 60 °C. This is about 10^7 times larger than the chain transfer constant to benzene at the same temperature.

Chain transfer to initiator or monomer cannot always be ignored. It may be possible, however, to evaluate these transfer constants by conducting a similar analysis on polymerizations without added solvent or in the presence of a solvent for which C_{SX} is known to be negligibly small. Fairly extensive tables of chain transfer constants have been assembled on the basis of investigations of this sort. For example, the values of C_{MX} for acrylamide at 60 °C is 6×10^{-5} , and that for vinyl chloride at 30 °C is 6.3×10^{-4} . Likewise, for methyl methacrylate at 60 °C, C_{IX} is 0.02 to benzoyl peroxide and 1.27 to *t*-butyl hydroperoxide.

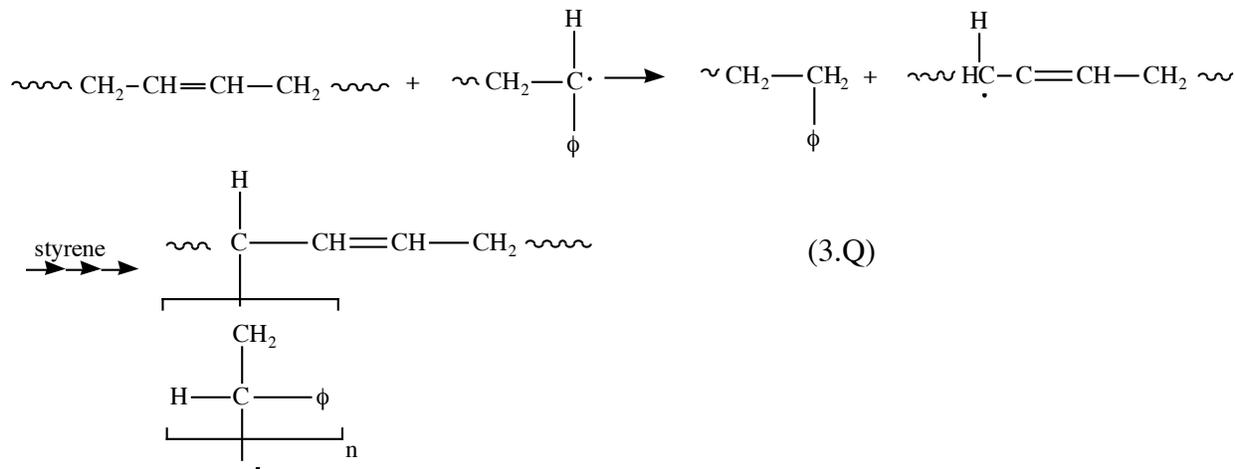
3.8C Chain transfer to polymer

As noted above, chain transfer to polymer does not interfere with the determination of other transfer constants, since the latter are evaluated at low conversions. In polymer synthesis, however, high conversions are desirable and extensive chain transfer can have a dramatic effect on the properties of the product. This comes about since chain transfer to polymer introduces branching into the product:



A moment's reflection reveals that the effect on \bar{v} of transfer to polymer is different from the effects discussed above inasmuch as the overall degree of polymerization is not decreased by such transfers. Investigation of chain transfer to polymer is best handled by examining the extent of branching in the product. We shall not pursue the matter of evaluating the transfer constants, but shall consider describe two important specific examples of transfer to polymer.

Remember from Section 1.3 that *graft copolymers* have polymeric side chains which differ in the nature of the repeat unit from the backbone. These can be prepared by introducing a pre-polymerized sample of the backbone polymer into a reactive mixture – i.e., one containing a source of free radicals – of the side-chain monomer. As an example, consider introducing poly(1,4)-butadiene into a reactive mixture of styrene:

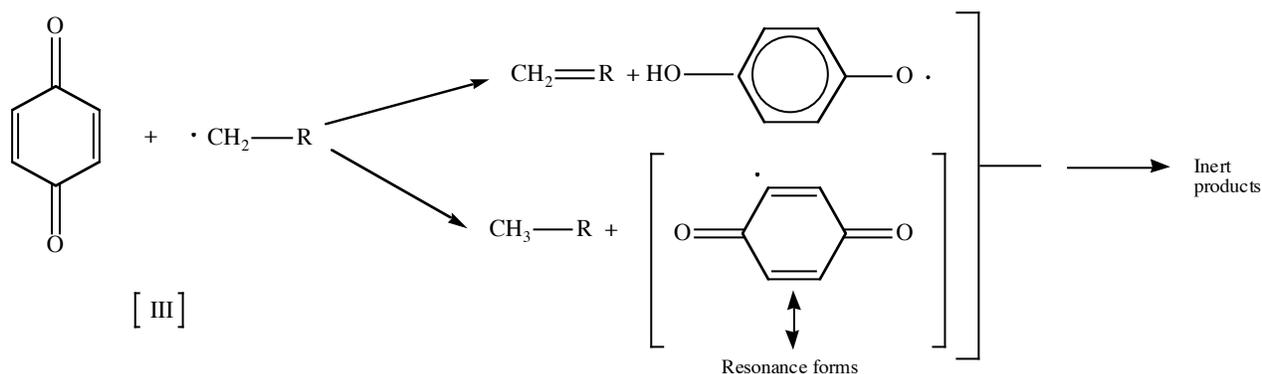


This procedure is used commercially to produce rubber-modified or high impact polystyrene (HIPS). The polybutadiene begins to segregate from the styrene as it polymerizes (see Chapter 7 to learn why!), but is prevented from undergoing macroscopic phase separation due to the covalent linkages to polystyrene chains. Consequently, small (micron-sized) domains of polybutadiene rubber are distributed throughout the glassy polystyrene matrix. These "rubber

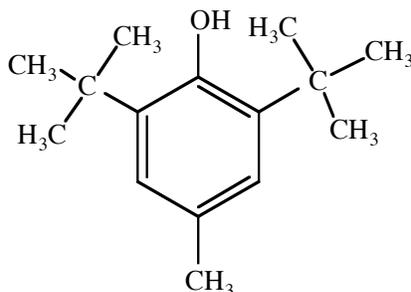
3.8D Suppressing polymerization

We conclude this section by noting an extreme case of chain transfer, a reaction which produces radicals of such low reactivity that polymerization is effectively suppressed. Reagents that accomplish this are added to commercial monomers to prevent their premature polymerization during storage. These substances are called either retarders or inhibitors, depending on the degree of protection they afford. Such chemicals must be removed from monomers prior to use, and failure to achieve complete purification can considerably affect the polymerization reaction. Inhibitors and retarders differ in the extent to which they interfere with polymerization, but not in their essential activity. An *inhibitor* is defined as a substance which blocks polymerization completely until it is either removed or consumed. Thus failure to totally eliminate an inhibitor from purified monomer will result in an induction period in which an inhibitor is first converted to an inert form before polymerization can begin. A *retarder* is less efficient and merely slows down the polymerization process by competing for radicals.

Benzoquinone [III] is widely used as an inhibitor:



The resulting radical is stabilized by electron delocalization and eventually reacts with either another inhibitor radical by combination (dimerization) or disproportionation or with an inhibitor or other radical. Another commonly used inhibitor is 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxy toluene, or BHT):



which is also known as an *antioxidant*. Such free radical "scavengers" often act as antioxidants, in that the first stage of oxidative attack generates a free radical.

Molecular oxygen contains two unpaired electrons and has the distinction of being capable of both initiating and inhibiting polymerization. It functions in the latter capacity by forming the relatively unreactive peroxy radical:



Inhibitors are characterized by inhibition constants which are defined as the ratio of the rate constant for transfer to inhibitor to the propagation constants for the monomer in analogy with eq 3.8.6 for chain transfer constants. For styrene at 50 °C the inhibition constant of *p*-benzoquinone is 518, and that for O₂ is 1.5 x 10⁴. The Polymer Handbook [1] is an excellent source for these and most other rate constants discussed in this chapter.

CHAPTER SUMMARY

In this chapter we have explored chain growth or addition polymerization, as exemplified by the free radical mechanism. This particular polymerization route is the most prevalent from a commercial perspective, and is broadly applicable to a wide range of monomers, especially those

containing carbon-carbon double bonds. The main points of the discussion may be summarized as follows.

1. In comparison with step-growth polymerization, free radical polymerization can lead to much higher molecular weights and in much shorter times, although the resulting distributions of molecular weight are comparably broad.
2. There are three essential reaction steps in a chain-growth polymerization: initiation, propagation, and termination. A wide variety of free radical initiators are available; the most common act by thermally-induced cleavage of a peroxide or azo linkage. Propagation occurs by head-to-tail addition of a monomer to a growing polymer radical, and is typically very rapid. Termination occurs by reaction between two radicals, either by direct combination or by disproportionation.
3. A fourth class of reactions, termed transfer reactions, is almost always important in practice. The primary effect of transfer of a radical from a growing chain to another molecule is to reduce the average degree of polymerization of the resulting polymer chains, but in some cases it can also lead to interesting architectural consequences in the final polymer.
4. The kinetic analysis of the distribution of chain lengths is made tractable by three key assumptions. The steady-state approximation requires that the net rates of initiation and termination be equal; thus the total concentration of radicals is constant. The same approximation extends to the concentration of each radical species individually. The principle of equal reactivity asserts that a single rate constant describes each propagation step and each termination step, independent of the degree of polymerization of the radicals involved. Thirdly, transfer reactions are assumed to be absent.

5. The aforementioned assumptions are most successful in describing the early stages of polymerization, before a host of competing factors become significant, such as depletion of reactants, loss of mobility of chain radicals, etc. Under these assumptions explicit expressions for the number and weight distribution of polymer chains can be developed. In the case that termination occurs exclusively by disproportionation, the result is a most probable distribution of molecular weights, just as with step-growth polymerization. Termination by recombination, on the other hand, leads to a somewhat narrower distribution, with $M_w/M_n \approx 1.5$ rather than 2.

References

- [1]. Brandrup, J. and Immergut, E. H., Eds., *Polymer Handbook*, 3rd Edition, Wiley, New York (1989).
- [2]. Trommsdorff, E., Kohle, H., and Lagally, P., *Makromol. Chem.* 1, 169 (1948).

Further information on chain-growth polymerization may be found in the following books:

Allcock, H. R., and Lampe, F. W., *Contemporary Polymer Chemistry*, 2nd Edition, Prentice Hall, Englewood Cliffs, NJ, 1990.

North, A. M., *The Kinetics of Free Radical Polymerization*, Pergamon, New York (1966).

Odian, G., *Principles of Polymerization*, 2nd Ed., Wiley, New York, 1981.

Rempp, P., and Merrill, E. W., *Polymer Synthesis*, 2nd Ed., Hüthig & Wepf, Basel. 1991.

Problems

1. The efficiency of AIBN in initiating polymerization at 60 °C was determined (Bevington, Bradbury, and Burnett, *J. Polym. Sci.*, **12**, 469 (1954)) by the following strategy. They measure R_p and \bar{v} and calculated $R_i = R_p/\bar{v}$. The constant k_d was measured directly in the system, and from this quantity and the measured ratio R_p/\bar{v} the fraction f could be determined. The following results were obtained for different concentrations of initiator:

| [I] (g L ⁻¹) | $R_p/\bar{v} \times 10^8$ (mol L ⁻¹ s ⁻¹) |
|--------------------------|---------------------------------------------------------------------|
| 0.0556 | 0.377 |
| 0.250 | 1.57 |
| 0.250 | 1.72 |
| 1.00 | 6.77 |
| 1.50 | 10.9 |
| 2.50 | 17.1 |

Using $k_d = 0.0388 \text{ hr}^{-1}$, evaluate f from these data.

2. AIBN was synthesized using ¹⁴C-labeled reagents and the tagged compound was used to initiate polymerization to methyl methacrylate and styrene. Samples of initiator and polymers containing initiator fragments were burned to CO₂. The radioactivity of uniform (in sample size and treatment) CO₂ samples was measured in counts per minute (cpm) by a suitable Geiger counter. A general formulas for the poly(methylmethacrylate) with its initiator fragments is (C₅H₈O₂)_n(C₄H₆N)_m, where n is the degree of polymerization for the polymer and m is either 1 or 2, depending on the mode of termination. The specific activity measured in the CO₂ resulting from combustion of the polymer relative to that produced by the initiator is

$$\frac{\text{Activity of C in polymer}}{\text{activity of C in initiator}} = \frac{4m}{5n + 4m} \cong \frac{4m}{5n}$$

From the ratio of activities and measured values of n , the average number of initiator fragments per polymer can be determined.

Carry out a similar argument for the ratio of activities for polystyrene and evaluate the average number of initiator fragments per molecule for each polymer from the following data (Bevington, Melville, and Taylor, *J. Polym. Sci.* **12**, 449 (1954)). For both sets of data, the radioactivity from the labeled initiator gives 96,5000 cpm when converted to CO₂.

| Methyl methacrylate | | Styrene | |
|---------------------|-------------------|-------------|-------------------|
| \bar{M}_n | Counts per minute | \bar{M}_n | Counts per minute |
| 444,000 | 20.6 | 383,000 | 25.5 |
| 312,000 | 30.1 | 117,000 | 86.5 |
| 298,000 | 29.0 | 114,000 | 89.5 |
| 147,000 | 60.5 | 104,000 | 96.4 |
| 124,000 | 76.5 | 101,000 | 113.5 |
| 91,300 | 103.4 | | |
| 89,400 | 104.6 | | |

3. In the research described in Example 3.4, the authors measured the following rates of polymerization:

| Run number | $R_p \times 10^4$ (mol L ⁻¹ s ⁻¹) |
|------------|-------------------------------------------------------------|
| 5 | 3.40 |
| 6 | 2.24 |
| 8 | 6.50 |
| 12 | 5.48 |
| 13 | 7.59 |

They also reported a k_p value of 1.2×10^4 L mol⁻¹ s⁻¹, but the concentrations of monomer in each run were not given. Use these values of R_p and k_p and the values of $\bar{\tau}$ and k_t given in Example 3.4 to evaluate $[M]$ for each run. As a double check, evaluate $[M]$ from these values of R_p (and k_p) and the values of R_i and k_t given in the example.

4. Arnett (*J. Am. Chem. Soc.* **74**, 2027 (1952)) initiated the polymerization of methyl methacrylate in benzene at 77 °C with AIBN and measured the initial rates of polymerization for the concentrations listed:

| $[M]$ (mol L ⁻¹) | $[I]_0 \times 10^4$ (mol L ⁻¹) | $R_p \times 10^3$ (mol L ⁻¹ min ⁻¹) |
|---------------------------------|-----------------------------------------------|---------------------------------------------------------------|
| 9.04 | 2.35 | 11.61 |
| 8.63 | 2.06 | 10.20 |
| 7.19 | 2.55 | 9.92 |
| 6.13 | 2.28 | 7.75 |
| 4.96 | 3.13 | 7.31 |
| 4.75 | 1.92 | 5.62 |
| 4.22 | 2.30 | 5.20 |
| 4.17 | 5.81 | 7.81 |
| 3.26 | 2.45 | 4.29 |
| 2.07 | 2.11 | 2.49 |

Use these data to evaluate the cluster of constants $(fk_d/k_t)^{1/2} k_p$ at this temperature. Evaluate $k_p/k_t^{1/2}$ using Arnett's finding that $f = 1.0$ and assuming the k_d value determined in Example 3.1 for AIBN at 77 °C in xylene also applies in benzene.

5. The lifetime of polystyrene radicals at 50 °C was measured (Matheson, Auer, Bevilacqua, and Hart, *J. Am. Chem. Soc.* 73, 1700 (1951)) as a function of the extent of conversion to polymer. The following results were obtained:

| Percent conversion | $\bar{\tau}$ (sec) |
|--------------------|--------------------|
| 0 | 2.29 |
| 32.7 | 1.80 |
| 36.3 | 9.1 |
| 39.5 | 13.1 |
| 43.8 | 18.8 |

Propose an explanation for the variation observed.

6. Derive eqs 3.7.27 and 3.7.28.
7. The equations derived in Section 3.7 are based on the assumption that termination occurs exclusively by either disproportionation or combination. This is usually not the case; some proportion of each is more common. If α equals the fraction of chains for which termination occurs by disproportionation, it can be shown that

$$N_n = \frac{\alpha}{1-p} + \frac{(1-\alpha)2}{1-p} = \frac{2-\alpha}{1-p}$$

and

$$\frac{N_w}{N_n} = \frac{4-3\alpha-\alpha p+2p}{(2-\alpha)^2}$$

From measurements of N_n and N_w/N_n it is possible *in principle* to evaluate A and p . May and Smith (*J. Phys. Chem.* 72, 216 (1968)) have done this for a number of polystyrene samples. A selection of their data for which this approach seems feasible is presented below. Since p is very close to unity, it is adequate to assume this value and evaluate A from N_w/N_n and then use the value of A so obtained to evaluate a better value of p from N_n .

| N_n | N_w/N_n |
|-------|-----------|
| 1129 | 1.60 |
| 924 | 1.67 |
| 674 | 1.73 |
| 609 | 1.74 |

8. Derive the two equations given in the previous problem. It may be helpful to recognize that for any distribution taken as a whole, $w_i = i x_i/N_n$
9. In the research described in problem 7, the authors determined the following distribution of molecular weights by a chromatographic procedure (w_i is the weight fraction of i -mer):

| i | $w_i \times 10^4$ | i | $w_i \times 10^4$ |
|-----|-------------------|------|-------------------|
| 100 | 3.25 | 800 | 6.88 |
| 200 | 5.50 | 900 | 6.10 |
| 300 | 6.80 | 1200 | 4.20 |
| 400 | 7.45 | 1500 | 2.90 |
| 500 | 7.91 | 2000 | 1.20 |
| 600 | 7.82 | 2500 | 0.50 |
| 700 | 7.18 | 3000 | 0.20 |

They asserted that the points are described by the expression

$$w_i = \alpha i(1-p)^2 p^{i-1} + 0.5(1-\alpha)i(i-1)(1-p)^3 p^{i-2}$$

with $\alpha = 0.65$ and $p = 0.99754$. Calculate some representative points for this function and plot the theoretical and experimental points on the same graph. From the expression given extract the weight fraction i -mer resulting from termination by combination.

10. In fact, the expression in the previous problem is slightly incorrect. Derive the correct expression, and see if the implied values of α and p are significantly different. The solution to problem 8 provides part of the solution.
11. Palit and Das (*Proc. Roy. Soc. London*, 226A, 82 (1954)) measured \bar{v}_{tr} at 60 °C for different values of the ratio $[SX]/[M]$ and evaluated C_{SX} and \bar{v} for vinyl acetate undergoing chain transfer with various solvents. Some of their measured and derived results are tabulated below (the same concentrations of AIBN and monomer were used in each run). Assuming that no other transfer reactions occur, calculate the values missing from the table. Criticize or defend the following proposition: The \bar{v} values obtained from the limit $[SX] / [M] \rightarrow 0$ show that the AIBN initiates polymerization identically in all solvents.

| Solvent | \bar{v} | \bar{v}_{tr} | [SX] / [M] | $C_{SX} \times 10^4$ |
|------------------------|-----------|----------------|------------|----------------------|
| τ -Butyl alcohol | 6580 | 3709 | - | 0.46 |
| Methyl isobutyl ketone | 6670 | 510 | 0.492 | - |
| Diethyl ketone | 6670 | - | 0.583 | 114.4 |
| Chloroform | - | 93 | 0.772 | 125.2 |

12. Gregg and Mayo (*J. Am. Chem. Soc.*, 70, 2373 (1948)) studied the chain transfer between styrene and carbon tetrachloride at 60 and 100 °C. A sample of their data is given below for each of the temperatures.

| <u>At 60 °C</u> | | <u>At 100 °C</u> | |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| [CCl ₄] / [styrene] | $\bar{v}_{tr}^{-1} \times 10^5$ | [CCl ₄] / [styrene] | $\bar{v}_{tr}^{-1} \times 10^5$ |
| 0.00614 | 16.1 | 0.00582 | 36.3 |
| 0.0267 | 35.9 | 0.0222 | 68.4 |
| 0.0393 | 49.8 | 0.0416 | 109 |
| 0.0704 | 74.8 | 0.0496 | 124 |
| 0.1000 | 106 | 0.0892 | 217 |
| 0.1643 | 156 | | |
| 0.2595 | 242 | | |
| 0.3045 | 289 | | |

Evaluate the chain transfer constant (assuming that no other transfer reactions occur) at each temperature. By means of an Arrhenius analysis, estimate $E_{tr}^* - E_p^*$ for this reaction. Are the values of \bar{v} in the limit of no transfer in the order expected for thermal polymerization? Explain.

13. Most simple olefins, including ethylene, propylene, and 1-butene, are readily polymerized by a free radical route. On the other hand, isobutylene is usually polymerized by a cationic mechanism. Explain.