5

cular conformation is quite regular. In addition to the zigzag or helical order imposed at the local level, the polymer chains are further ordered in that they fold back and forth on themselves in a regular planar arrangement. This conformational habit is shown in Figure 2–7 in an oversimplified manner for a single chain with a zigzag conformation. The plane in which the entire molecule lies is known as the *fold plane*, and in the context of this morphology we speak of *chain folding*. The plane of the zigzag may or may not lie in the fold plane.

210 Morphology and Order

This subject deals with the structure and forms exhibited by aggregates of molecules in the bulk.

The notion that a single molecule assumes random conformations leads to the premise that polymer chains in an aggregated, unordered (amorphous) state also assume random conformations. The rationale is as follows: Since a molecule is completely surrounded by like segments, there will be no net interactive forces; and, therefore, the molecule will assume random conformations. This reasoning can only lead to the premise that polymer chains are entangled under crowded conditions. In the melt, for instance, polymer chains are somewhat graphically pictured as cooked spaghetti in a bowl or as worms in a can.

Polymer single crystals are flat, platelike, well-ordered structures on the order of 100 Å thick, in which the fold planes are found packed in an orderly fashion. Bulk crystalline polymer is composed of stacks of these lamallaelike crystallites. As already noted, the importance of the crystalline form resides in the close molecular packing, which permits strong intermolecular bonding and, as a result, good mechanical-strength properties. Mechanical strength can be further enhanced by orientation of the crystallites as induced by stretching and rolling. This technique is used in fiber formation, and the phenomenon of alignment is encountered in the stretching of natural rubber.

PART II

Polymer Synthesis

The processes by which a polymer is synthesized or modified are the most important steps in producing a useful polymer artifact. It is here that all the capabilities or potential capabilities of the polymer system must be imparted. Substantially different materials can result from polymerizing the same monomer by different methods. In other instances, the nature of the monomer may be such that it can be polymerized by only one process. In general, polymerization reactions, as well as reactions of polymers, are among the most complicated and least understood of all chemical reactions.

Reaction control presents more problems in the synthesis of polymers than it does in the synthesis of many low-molecular-weight materials. Let us cite a few examples.

1. Polymer reaction environments may exhibit a rapid rise in viscosity as the reaction progresses because of increasing molecular weight and/or solids content. In such an instance, the transport properties of the reaction mixture are certain to change, thereby complicating analysis of the kinetics of the reaction system.

2. Certain reactions take place at relatively low temperatures (on the order of $-100\,°C$) in a hetereogeneous medium at rapid rates.

3. In the preparation of a resin from a set of polyfunctional reactants, conditions within the reaction vessel must be established such that

radical from the surrounding solution adds to one of the ...monomer molecules ...which facilitates rapid propagation when an initiating

difficult to remove such a polymer from the reactor, but it would also be virtually useless for further application.

4. Ultrahigh purity of the reaction ingredients is usually required for high molecular weights or for reaction to occur at all.

Molecular architecture, especially molecular weight and its distribution, becomes an even more important consideration in polymer synthesis. In low-molecular-weight compound synthesis, the molecular weights of both the reactants and products are generally monodispersed and easily defined. In polymer reactions, the molecular weight of both the product molecules and the reactant molecules (which in themselves may be product molecules) are very often changing in molecular weight as well as in molecular-weight distribution as the reaction progresses. In polymer reactor design, the engineer must consider the problem of selecting the polymerization process and optimizing the reaction conditions in terms of the desired molecular architecture of the product. Many of the molecular processes that occur during synthesis are controllable; more often than not, they are random processes that one lives with rather than controls.

CLASSIFICATION OF POLYMERS AND POLYMERIZATION MECHANISMS

Carothers (1929) suggested classifying polymers and polymerization reactions according to the stoichiometry of the reaction as either condensation or addition. Condensation polymers were formed in a process (condensation polymerization) that resulted in the splitting out of a small molecule; addition polymers were formed in a process (addition polymerization) where a small molecule did not split out. On the other hand, P. J. Flory placed the emphasis on the reaction mechanism by which the polymer was formed. Condensation polymers are usually formed by the stepwise intermolecular condensation of reactive (functional) groups; addition polymers usually result from chain reactions promoted through an active center. The preceding considerations lead to the modern terminology for these types, namely, step-reaction and chain-reaction polymerization. Inconsistencies in both systems of nomenclature arise occasionally, but these are easily recognized and cause little confusion.

The distinguishing mechanistic features of the chain-reaction and step-reaction polymerizations are tabulated below. They are presented here somewhat prematurely, but the full implications of these features will become apparent in chapters three and four. Subsequent reference should be made to them.

A particularly illuminating way to differentiate between chain-and step-

DISTINGUISHING FEATURES OF CHAIN AND STEP-REACTION POLYMERIZATION MECHANISMS[a]

Chain Polymerization	Step Polymerization
Only those molecular species containing active centers may add monomer units.	Any two potentially reactive molecular species present can react and combine.
The monomer concentration decreases steadily during the progress of the reaction.	Rapid monomer depletion occurs very soon after the reaction begins.
High-molecular-weight polymer is formed at once.	Molecular weight increases slowly as the run progresses. A high degree of conversion is required for high molecular weight.
The reaction contains at any time during the run only monomer, inactive high polymer, and about 10^{-8} parts active centers (i.e., growing chains).	At any stage of the reaction, all sizes of molecular species are present in a calculable distribution.

[a] After Billmeyer, *Textbook of Polymer Science*.

then show how the units become connected with the passage of time. Shown below are two 5×5 such "monomer-unit-matrices." The arrowheads indicate the way in which reaction occurred. Adjacent opposing arrowheads indicate step reaction, while a series of single arrowheads all pointing in the same direction along the reaction "path" indicates chain reaction.
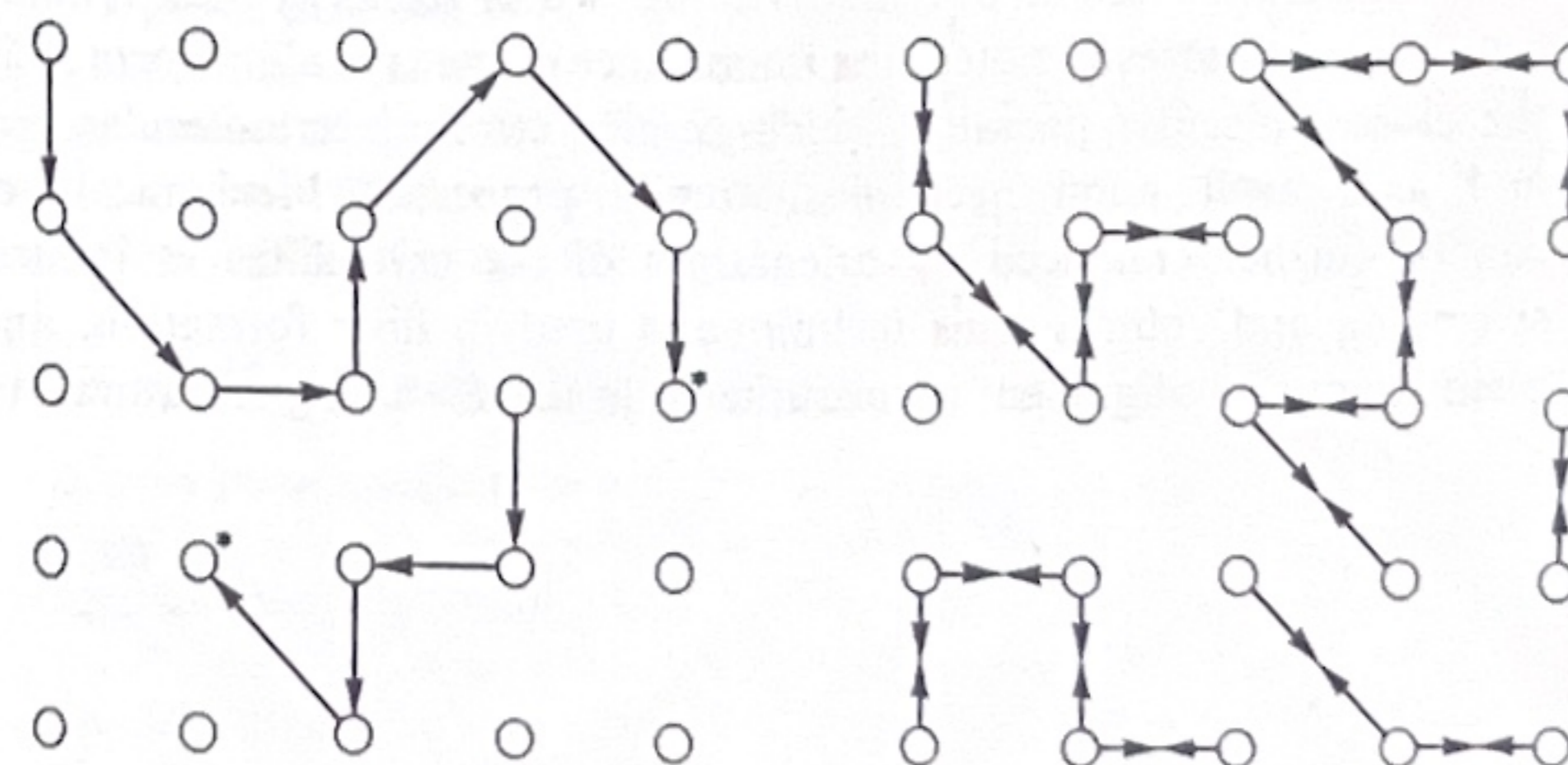
Asterisk denotes an active center.

3

Step-Reaction Polymerization

301 Chemistry of Step-Reaction Polymerization

Much of the early work of elucidating the chemistry of polymer reactions was done by Carothers. He pointed out the fact that the chemistry of condensation polymerization did not vary significantly from that of low-molecular-weight condensations.

Several common functional groups frequently arise in organic step reactions; representative of those participating in linear-condensation polymerization are the hydroxyl (—OH), carboxyl (—COOH), amine (—NH$_2$), ethylene oxide (—CH—CH$_2$), and isocyanate (—NCO). Some representative

functional group reactions are shown in Table 3–1. The interunit linkages are shown as the product of each reaction. The name for the polymer type is derived from the interunit linkage. Note that the formation of polyurethanes and polyureas involves hydrogen-transfer reactions without the emission of a low-molecular-weight by-product; they qualify as condensation polymers because of the reaction mechanism. Variations in the formation of polyesters and polyamides are introduced if the corresponding acid chlorides are substituted for the carboxyl groups.

If A and B represent two interacting functional groups on nonreacting groups R̃, R̃', or R̃'', the various reaction systems introduced in Chapter 1 can be represented as follows:

System Type	Generalized Representation
Bifunctional	ARB
Bi-bifunctional	RA$_2$ + R'B$_2$
Polyfunctional	RA$_x$ + R'B$_x$ + R''B$_x$, $h > 3$

These simple representations are useful in theoretical analyses in that reference to specific chemical systems is avoided and the results are generally applicable. Combinations other than those shown are, of course, possible.

One of the interesting facets of condensation polymerization is the enormous variety of polymers that can be generated, starting only with the few functional group reactions illustrated. This variety is obtained by manipulating the following:

1. The combinations of reacting function groups—a wide selection of A and B combinations is available.

2. The system type—use of bifunctional, bi-bifunctional, or polyfunctional systems leads to linear, branched and crosslinked networks, or copolymer systems.

3. The stoichiometric proportions—leads to control of $\overline{DP}_n$ as well as degree of branching and crosslinking.

4. The structure and compositions of the nonreactive portion—the R groups may be aromatic or aliphatic.

It is not always possible or desirable to use direct reaction, and in these

TABLE 3–1

SOME REPRESENTATIVE POLYMER FUNCTIONAL GROUPS REACTIONS

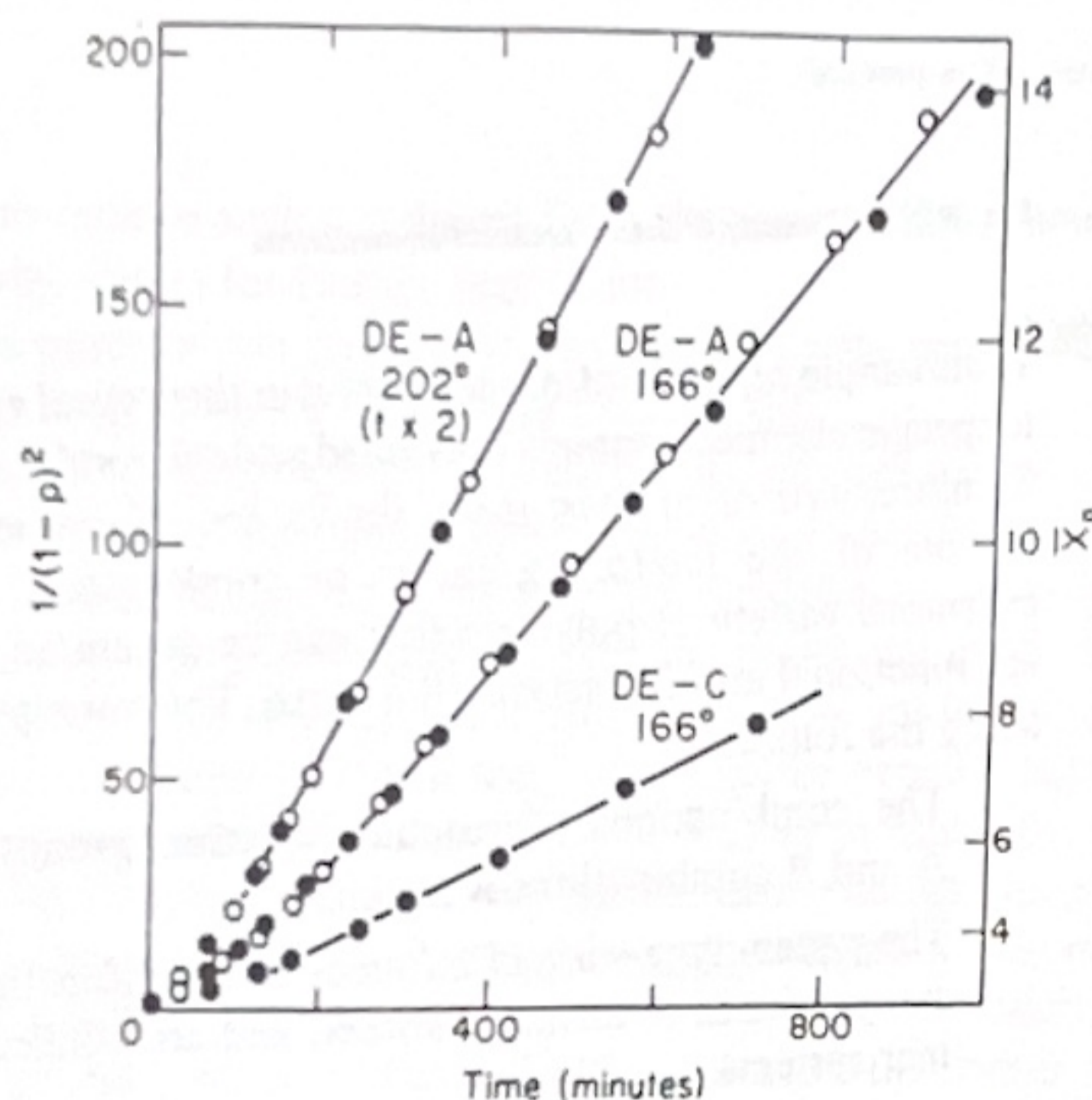| Reactants Functional Groups	Product Interunit Linkage	Polymer Type
—OH + —COOH	$-\overset{\overset{\textstyle O}{\|}}{C}-O-$	Polyester
—COOH + —NH$_2$	$-\overset{\overset{\textstyle O}{\|}}{C}-NH-$	Polyamide
—COOH + —COOH	$-\overset{\overset{\textstyle O}{\|}}{C}-O-\overset{\overset{\textstyle O}{\|}}{C}-$	Polyanhydride
—NCO + —OH	$-O-\overset{\overset{\textstyle O}{\|}}{C}-NH-$	Polyurethane
—NCO + —NH$_2$	$-NH-\overset{\overset{\textstyle O}{\|}}{C}-NH-$	Polyurea
—OH + —OH	—O—	Polyether
—CH——CH$_2$ (O)	—O—	Polyether

Figure 3–1. Reactions of diethylene glycol with adipic acid (DE-A) and of diethylene glycol with caporic acid (DE-C). Time values at 202°C have been multiplied by two. [P. J. Flory, J. Am. Chem. Soc., 62, 2261 (1940). Reprinted with permission of the copyright owner, The American Chemical Society.]
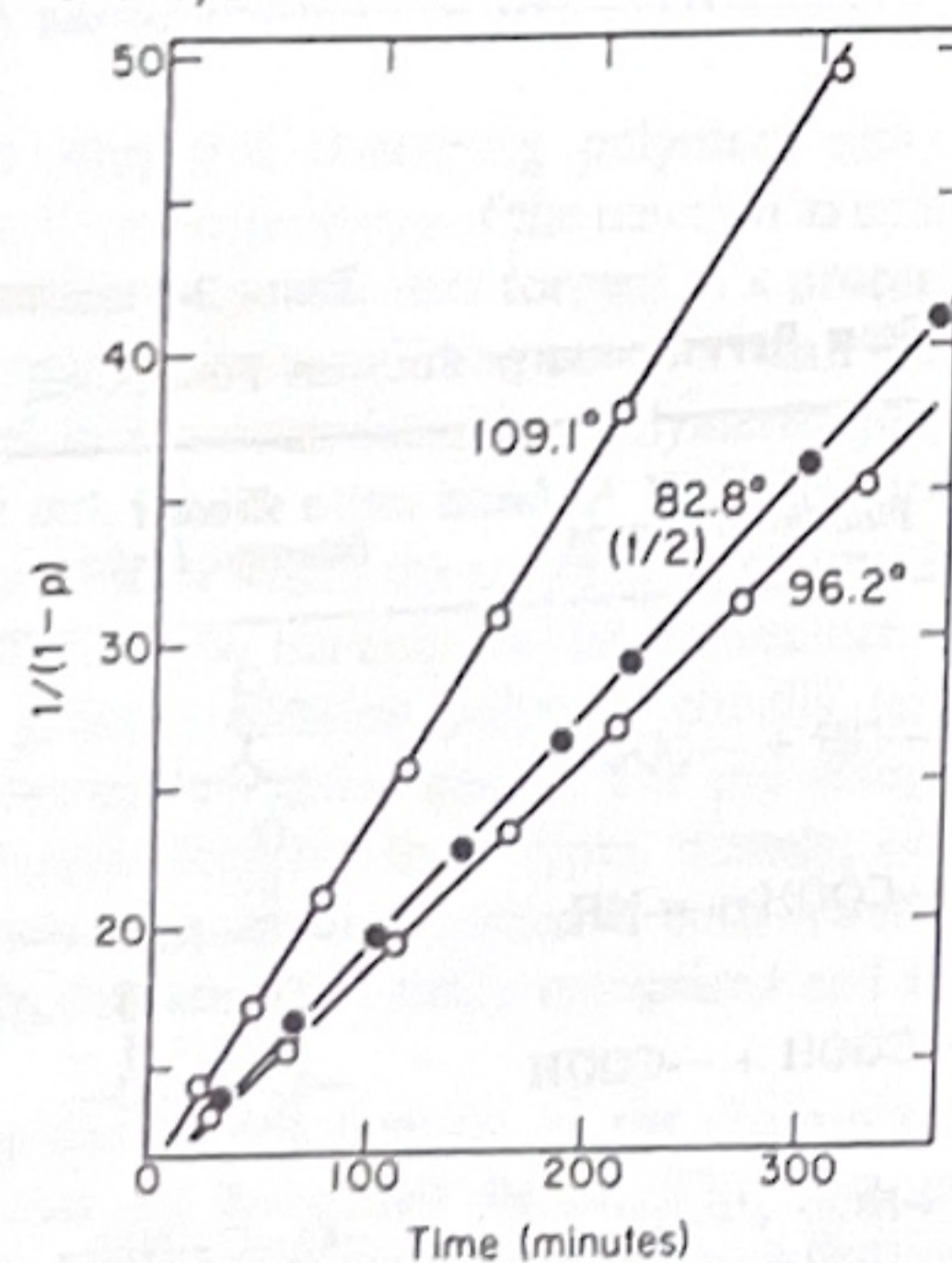

Figure 3–2. Reaction of decamethylene glycol with adipic acid at the temperature indicated, catalyzed by 0.10 equivalent percent of p-toluenesulfonic acid. [P. J. Flory, J. Am. Chem. Soc., 61, 3334 (1940). Reprinted with

305 Stoichiometry of Linear Systems

The conversion or extent of reaction is expressed as the fraction of one of the species of functional groups that has reacted, and it is usually represented by the symbol p. If we consider reacted A groups, the extent of reaction of A is represented by the symbol p_A, which is given by

$$p_A = \frac{F_A(0) - F_A(t)}{F_A(0)} \qquad (3\text{-}7)$$

where $F_A(0)$ = the number of A functions present initially and $F_A(t)$ = the number of unreacted A functions present at any time t.

In a bifunctional system ARB or in a stoichiometrically balanced bi-bifunctional system $RA_2 + R'B_2$, since the reaction is 1:1 in A and B, $p = p_A = p_B$.

In systems that are not stoichiometrically balanced, $p_A \neq p_B$, but p_A will be related to p_B as

$$\frac{F_A(0)}{F_B(0)} = \frac{p_B}{p_A} = r \qquad (3\text{-}8)$$

In practice, p is found through a combination of chemical end-group-analysis and stoichiometric balance of the reactants.

In an absolutely pure, stoichiometrically balanced reaction system, it is theoretically conceivable for the reaction to proceed indefinitely and to produce a polymer of infinite molecular weight. If there is stoichiometric imbalance, the molecular weight will not be infinite, and the polymerization reaction will be *blocked*. As a limiting example, consider a bifunctional system where the stoichiometric proportions are 2:1 as

$$2RA_2 + R'B_2 \longrightarrow ARA{-}BR'B{-}ARA$$

The product is not a high polymer at all, for the maximum average degree of polymerization is only three. Ordinarily blocking imposes unacceptable limitations in high-polymer synthesis. However, it can be employed to advantage, if controlled, to regulate molecular weight or to prevent the reaction from proceeding to the gel point in polyfunctional systems.
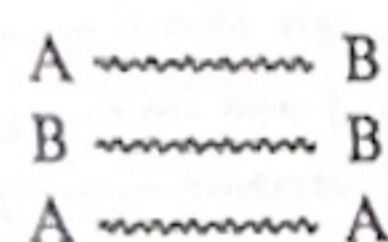
In order to take a general approach to representing the effect of stoichiometry on $\bar{X}_n$, consider the following reaction system:

$$RA_2 + (xs)R'B_2$$
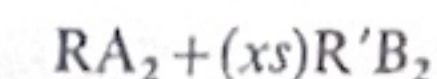
The total number of monomer units present initially can be expressed as

$$N(0) = \frac{F_A(0) + F_B(0)}{2} = \frac{F_A(0)(1 + 1/r)}{2} \tag{3-9}$$

For $p_A < 1$ there are three possible types of molecules that can form according to the terminal functional group:

$$A \;\sim\!\!\sim\!\!\sim\; B$$
$$B \;\sim\!\!\sim\!\!\sim\; B$$
$$A \;\sim\!\!\sim\!\!\sim\; A$$

Since B is in excess, it is highly unlikely that any of the last type will form. Thus the number of chain ends at any point in the reaction is, to a very good approximation, two times the number of unreacted A functions, plus the initial excess of B functions. The total number of polymer molecules, $P(t)$, at any extent of reaction of A is given by

$$P(t) = \frac{2F_A(0)(1 - p_A) + [F_B(0) - F_A(0)]}{2} \tag{3-10}$$

where the first term represents the number of chain ends associated with molecules beginning in A and ending in B (stoichiometric equivalence) and the second term represents the number of chain ends associated with molecules beginning and ending in B (stoichiometric excess). Upon rearrangement, Eq. (3-10) gives

$$P(t) = \frac{F_A(0)[2(1 - p_A) + (1 - r)/r]}{2} \tag{3-11}$$

Now recall that $\bar{X}_n = [N(0) - N(t)]/P(t)$, and observe that in step-reaction polymerization $N(t) \ll N(0)$ very soon after the reaction begins; therefore we obtain $\bar{X}_n$ as

$$\bar{X}_n = \frac{N(0)}{P(t)} \tag{3-12}$$

for step-reaction polymerizations. Combining Eqs. (3-9) and (3-11) with (3-12), we obtain the desired result, which was first derived by Flory.

$$\bar{X}_n = \frac{1 + r}{1 + r - 2rp_A} \tag{3-13}$$

A number of important lessons are to be learned from Eq. (3–13). First consider a system that is stoichiometrically balanced ($r = 1$). Then Eq. (3–13) reduces to

$$\bar{X}_n = \frac{1}{1 - p} \tag{3-14}$$

This is a result originally obtained by Carothers[*] in a slightly different fashion. It is one of the fundamental analytic representations of step-reaction polymerization. Furthermore, consider the tabulation below:

p	0	0.5	0.8	0.9	0.95	0.99	0.999	1.0
$\bar{X}_n$	1	2	5	10	20	100	1000	∞

Note that in order to achieve reasonably high molecular weights in linear-condensation polymers, the extent of reaction must exceed 99 percent. In terms of the normally anticipated industrial and laboratory yields, this is a rather stringent requirement. In its day, this was an extremely important result in that chemists were not observing good mechanical properties in their synthetic products compared to those of natural polymers. At best, resins with oil-like consistencies were obtained and subsequently discarded. Carothers showed that in order to obtain useful synthetic products, it was necessary to drive the reaction to completion.

As another limiting case, consider B functions 1 percent in excess such that $r = 100/101$. From Eq. (3–13) we find that $\bar{X}_n$ is limited to a value of 201 for $p_A = 1$. This result shows the importance of stoichiometric balance to obtain high molecular weights. As indicated previously, blocking may be used to advantage in the deliberate preparation of low-molecular-weight polymers for subsequent treatment in another process. Such materials are referred to as *prepolymers*. Also, blocking may be used to prevent gelation in polyfunctional systems, although in this case Eq. (3–13) would not be applicable.

306 Size Distribution in Linear-Condensation Systems

Flory was among the first to apply elementary statistical concepts to the analysis of polymer systems. Based on the assumption of chemical equilibrium and stoichiometric balance, he was able to develop an analytic expression to describe the size distribution in linear-polymerization systems.

* Collected Papers of Wallace H. Carothers on Polymerization

Before beginning with the derivation *per se*, the student should recall that a probability is exactly analogous to a number fraction. We make use of this point immediately in stating that the probability that any given functional group in a reaction system has reacted is simply equal to the extent of reaction of that functional group. For A groups, this would be p_A; and since equimolar quantities are present, this probability would also be equal to p_B or simply p. Suppose that we have an ARB (bifunctional) monomer to condense to polymer, and we start with one mole of reactants—that is, one mole of A groups and one mole of B. If we come to a point where the extent of reaction, p, is, say, 0.75, we know that the hypothetical chances of our encountering a reacted A or B group in the reaction vessel is 0.75 or 3 out of 4. The hypothetical chances of encountering an unreacted A or B group is simply one out of four or $(1-0.75)$. Establishment of the condition of equilibrium is necessary to remove the possibility of nonequal probability for the functional groups.

Consider the following molecule and the probability that it has formed:

$$ARB \overline{}_1 ARB \overline{}_2 ARB \overline{}_3 \ldots \overline{} ARB \overline{}_{x-1} ARB_x$$
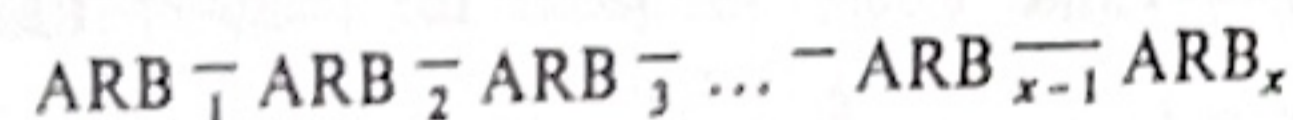
The probability that the 1st B group has reacted is p. The probability that the 2nd B group has reacted is p, and so forth up to the $(x-1)^{th}$ B group. However, the probability that the xth B group has not reacted must be accounted for, and this probability is $(1-p)$. The probability that groups 1 and 2 have reacted as $p \times p = p^2$. The probability that groups 1 through 3 have reacted is $p \times p \times p = p^3$ and so forth. The probability that groups 1 through $(x-1)$ have reacted $= p^{x-1}$. Finally, the probability, $P(x)$, that the molecule in question is exactly x units long is given by

$$P(x) = p^{x-1}(1-p) \tag{3-15}$$

which is simply the probability of all the independent events considered occurring in a consecutive fashion. By definition, this $P(x)$ is the number (or mole) fraction, n_x, of those particular molecules in the reaction system at the extent of reaction p. Hence

$$n_x = p^{x-1}(1-p) \tag{3-16}$$

This equation gives the number (or mole) fraction of each size species present in the polymer system. If $P(t)$ = the total moles of molecules at p greater than zero and $N_x(t)$ = the moles of x-mers, the following holds:

$$N_x(t) = P(t)(1-p)p^{x-1} \tag{3-17}$$

75

We can carry this derivation one step further to get the weight-fraction-distribution function w_x. With the weight fraction of any x-mer given by $xN_x(t)/N(0)$ and with $P(t) = N(0)(1-p)$, we obtain

$$w_x = x(1-p)^2 p^{x-1} \tag{3-18}$$

The distributions given by Eqs. (3-16) and (3-18) are known as the *most probable distributions*. They are shown in Figures 3-3 and 3-4 for several values of p. Note that on a mole fraction basis, the smaller species are always the most abundant. On a weight fraction basis, however, w_x passes through a maximum, which one can show occurs at $\bar{X}_n$ as $p \to 1$. They have been verified experimentally and are important aids in helping us to visualize the development of the size distributions alluded to in Chapter 1.

Other important results arise in the application of these distributions to the computation of $\bar{X}_n$ and $\bar{X}_w$. With $\bar{X}_n = \sum_{x=1}^{\infty} n_x x$ and $\bar{X}_w = \sum_{x=1}^{\infty} w_x x$, one can (via the binomial expansion theorem) show for linear-condensation systems

$$\bar{X}_n = \frac{1}{1-p} \tag{3-19}$$

and

$$\bar{X}_w = \frac{1+p}{1-p} \tag{3-20}$$

The number average is a result obtainable from stoichiometric analysis, but distribution functions are always required to compute higher-order averages.

Another important result is obtained by comparing $\bar{X}_w$ and $\bar{X}_n$ as

$$\frac{\bar{X}_w}{\bar{X}_n} = 1+p \tag{3-21}$$

This ratio gives a simple quantitative idea of the spread of the distribution curve, for as $p \to 1$, $\bar{X}_w/\bar{X}_n \to 2$ (provided that there are no side reactions).

In principle, the most probable distributions can be derived for more complicated systems by following the procedure outlined above. However, the difficulty of this task increases rapidly with increasing complexity of the reaction systems.

307 Crosslinking in Step-Reaction Systems

Phenomenologically, the *gel point* of a polyfunctional system is classically defined as that point in the reaction when the viscosity
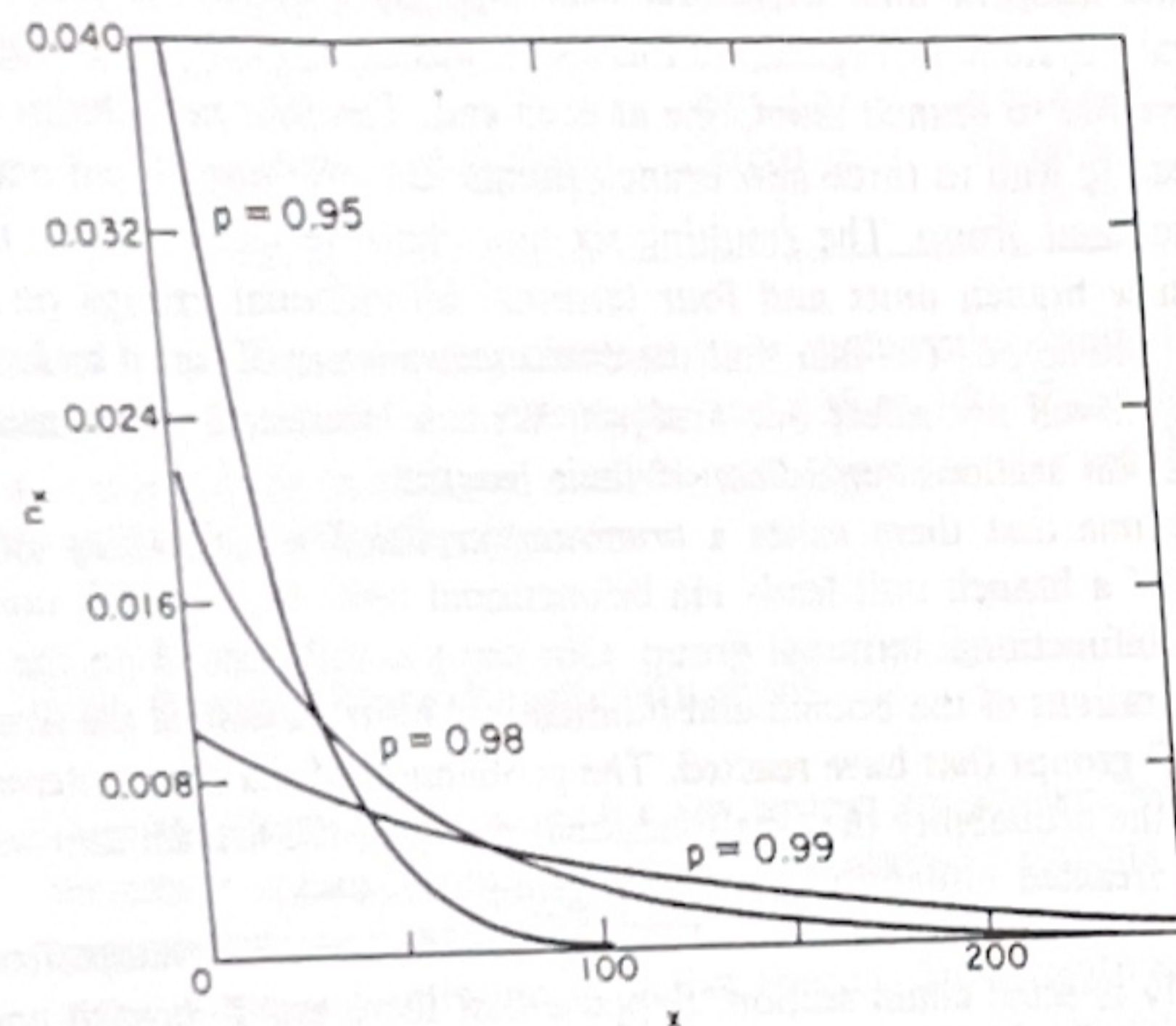
Figure 3–3. Mole fraction distribution of chain molecules in a linear condensation polymer for several extents of reaction p. [P. J. Flory, J. Am. Chem. Soc., 58, 1877 (1936). Reprinted with permission of the copyright owner, the American Chemical Society.]
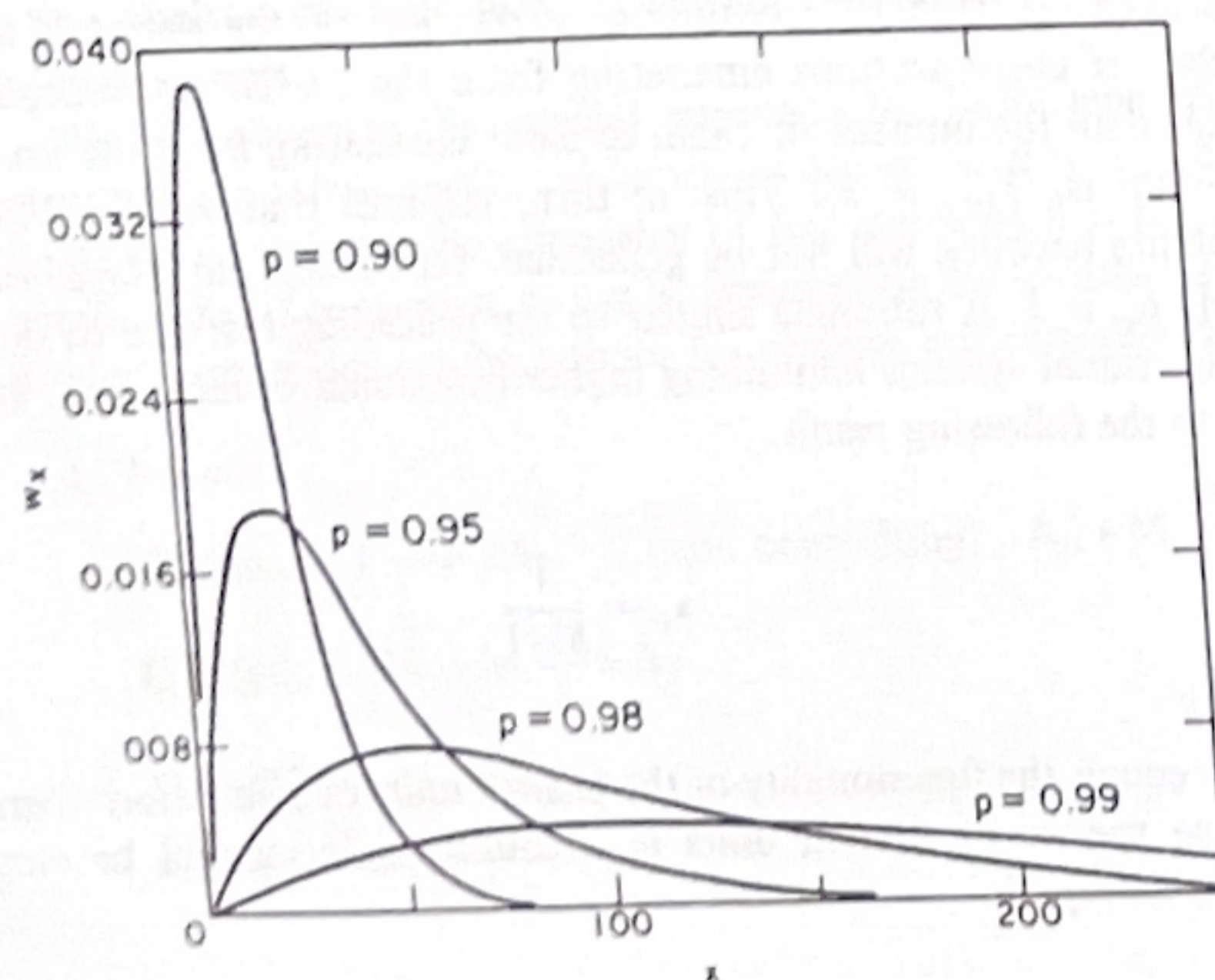

Figure 3–4. Weight fraction distribution of chain molecules in linear ... for several extents of reaction p.

the reaction medium loses all fluidity and bubbles cease to rise through it. At this point, *gelation* is said to have occurred. It is obviously important to be able to predict the onset of gelation. Figure 3–5 shows how the viscosity and extent of reaction typically vary with time in a polyfunctional system. There is, at first, a gradual rise in viscosity and then a sudden enormous rise as the gel point is approached. Also note that the reaction proceeds very slowly as the gel point is approached. These two factors make it difficult to predict the gel point well in advance by following the reaction in process with conversion or viscosity data.
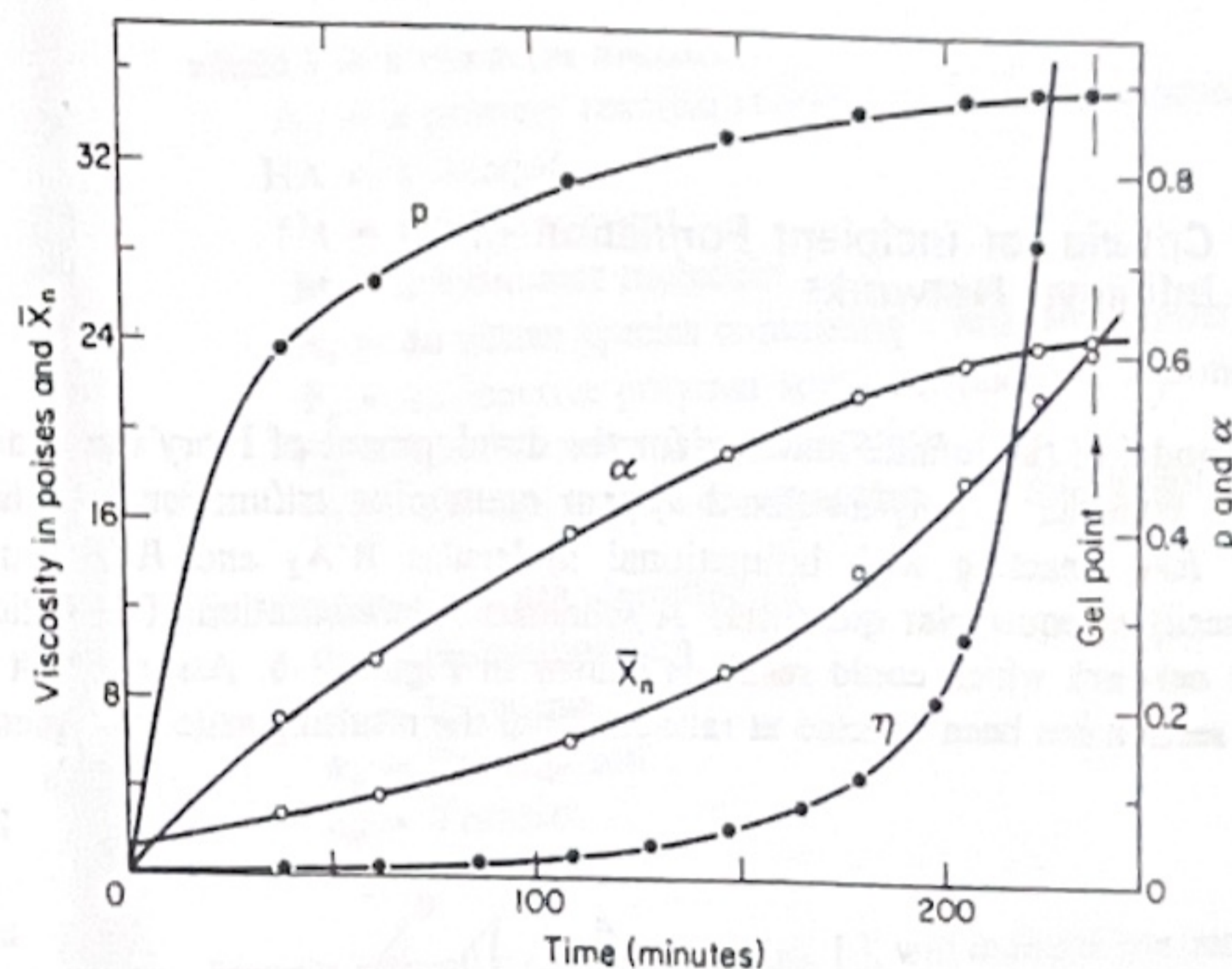

Figure 3–5. The course of typical three-dimensional polyesterification. [P. J. Flory, J. Am. Chem. Soc., 63, 3083 (1941). Reprinted with permission of the copyright owner, the American Chemical Society.]

Gelation takes place long before all the reactants are bound together, so that reaction continues even after gelation. It is common knowledge that at the gel point not all of the material is insoluble, but the gelled portion represents only a small percentage of the total reaction mixture. To amplify: if one were to attempt to dissolve in a suitable solvent the gelled polymer mass just as it exists at its gel point, all but a small portion would dissolve. Only a few very large molecules are required to induce gelation. The portion that is soluble is referred to as the *sol*, whereas the part that is insoluble is referred to as the *gel*. It will be recalled that in order to attain a three-dimensional network, one reactant must possess a functionality of 3 or more. A monomer unit posses-

of a polymeric molecule lying between two branch units or between a branch unit and an unreacted bifunctional unit will be called a *chain section*. The chain sections may vary in length, but this factor is not important at this juncture. A point in a molecule from which three or more chain sections emanate will be known as a *branch point*.

A key assumption for valid statistical treatment is that the probability that any particular functional group has reacted is independent of and uninfluenced by the number and configuration of other groups in the mole-cule to which this functional group is attached. This assumption is not always true; the secondary hydroxyl on glycerol is, for instance, less reactive than either of the primary hydroxyl groups. Also, intramolecular reaction will be assumed to be totally absent, an assumption that prevents the results from being exact.

308 Criteria for Incipient Formation of Infinitive Networks

As a model of the infinite network for the development of Flory's gel point theory, consider a polyfunctional system containing trifunctional branch units: RA_3 reacting with bifunctional molecules $R'A_2$ and $R''B_2$—not necessarily in equimolar quantities. A schematic representation of a portion of the network which could result is shown in Figure 3–6. Assume that a chain section has been selected at random from the resulting gelled polymeric
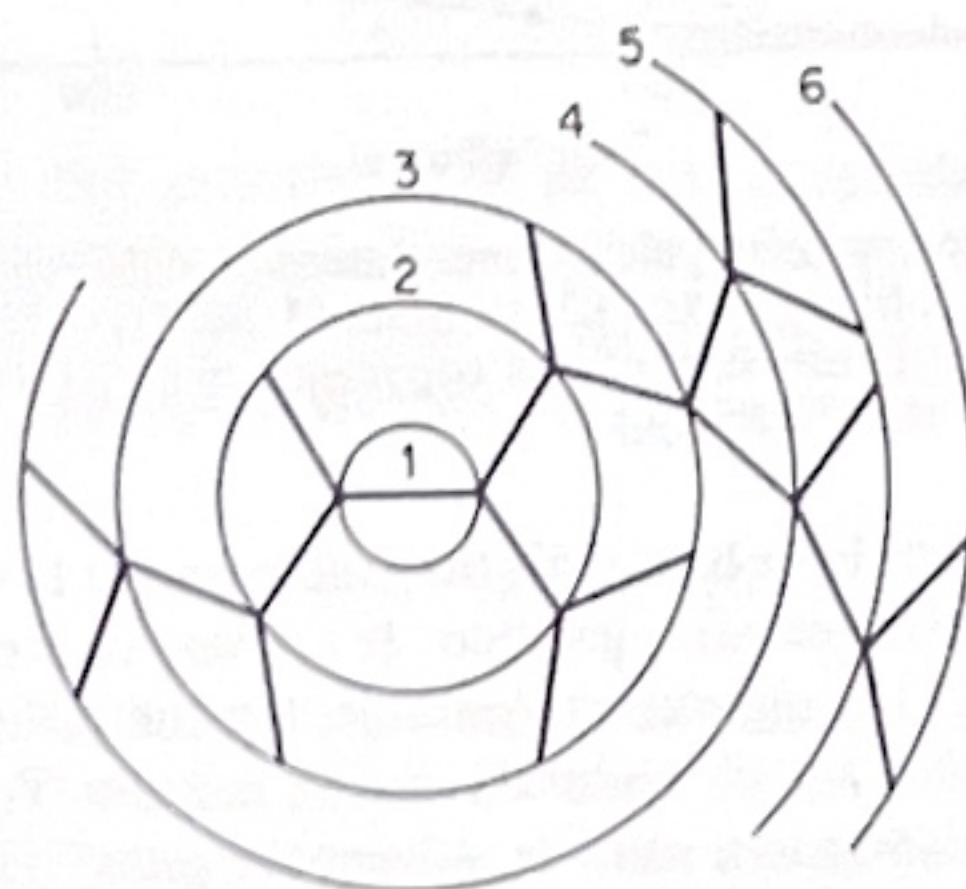

Figure 3–6. Schematic representation of a trifunctionally branched

structure and that it lies within the first envelope of Figure 3–6. The immediate problem is to determine the probability that this chain section is part of an infinite network and, therefore, that this chain section is part of a gelled polymer system. In Figure 3–6 this chain section in the first envelope happens to give rise to branch units, one at each end. The four new chains that result happen to lead to three new branch points (on envelope 2) and one terminal bifunctional group. The resulting six new chain sections happen to lead to two new branch units and four terminal bifunctional groups on envelope three, and so on. The fact that the chain sections are depicted as being equal in length will not affect our analysis. We are interested in the existence of such chain sections regardless of their lengths.

Assume that there exists a *branching probability* α that any functional group of a branch unit leads via bifunctional units to a branch unit rather than a bifunctional terminal group. Obviously α will depend on the relative concentrations of the branch and bifunctional units as well as the fraction of A and B groups that have reacted. The probability of the other alternative—that is, the probability that the functional group of the branch unit will lead to an unreacted bifunctional terminal group—is $(1-\alpha)$.

Based on the model described above, consider the *i*th envelope from the randomly selected chain section. Suppose that there are Y_i branch units on the *i*th envelope. If all the chain sections emanating from these branch units (or branch points) ended in branch units on the $i+1$th envelope, then there would be $2Y_i$ of them. However, there is only a certain probability, α, that chain sections beginning in branch units (actually all chain sections in the network begin in branch units) will end in branch units. Therefore the expected number of branch units on the $i+1$th envelope, Y_{i+1}, will be $2Y_i\alpha$. The criterion for continuous expansion of the network is that the number of chain sections emanating from the $i+1$th envelope, $2Y_{i+1}$, be greater than the number of chain sections emanating from the *i*th envelope, $2Y_i$—that is, $Y_{i+1} > Y_i$. This, in turn, requires that $\alpha > \frac{1}{2}$. When $\alpha < \frac{1}{2}$ an infinite network will not be generated. Obviously *the critical value of* α, namely α_c, is $\frac{1}{2}$. A rationale similar to the preceding can one be devised for polyfunctional systems containing higher functional branch units. Induction leads to the following result:

$$\alpha_c = \frac{1}{b-1} \tag{3-22}$$

where b equals the functionality of the branch unit. In a situation where more than one species of branch units is encountered, α_c would be computed using an average b.

TABLE 4-2

COMPARISON OF BRANCHED AND LINEAR POLYETHYLENE

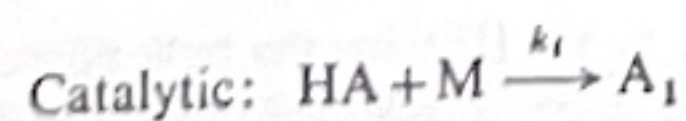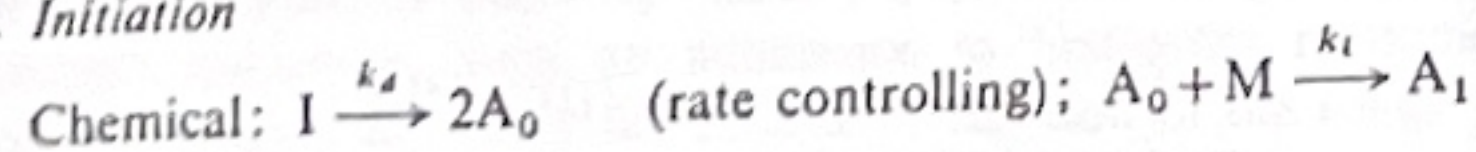|	Linear	Branched
% Crystallinity	90	50–60
Melting temperature	135°C	115°C
Density	0.95–0.97	0.91–0.94
Modulus of elasticity	100,000 psi	20,000 psi
$\bar{M}_w/\bar{M}_n$	2	20 to 50

duced via a Ziegler-Natta process at only moderately elevated pressures and temperatures, 15 to 20 atmospheres and 135 to 150 °C. Striking differences are noted in the modulus of elasticity and the molecular weight distributions as evidenced in the $\bar{M}_w/\bar{M}_n$ ratios.
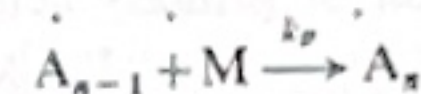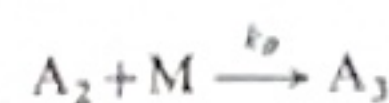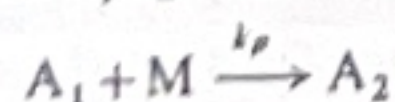
408 Steady-State Kinetic Analysis

Once the chemical processes for any system are known, we can proceed to undertake a kinetic analysis. Most elementary treatments for even homogeneous environments suffer from the fact that it is necessary to assume a steady-state concentration of active species. Such treatments are therefore valid under limited conditions. Still, considerable insight into the nature of polymerization reactions can be gained through such analyses, so they are worth pursuing. As in step-reaction polymerization, we are primarily interested in deriving relations for the rates of polymerization, the average molecular weights and/or the molecular-weight distributions. Rate expressions are easily derived. Somewhat less success is met in molecular-weight-distribution analysis of chain polymerizations compared to linear step-reaction polymerizations.

We will illustrate the general approach for homogeneous rate analysis by considering free radical polymerization, since this is the best known. First, we summarize the chemistry of the reactions just considered with a notation that is convenient to use in representing the various kinetic processes. Similar expressions can be written for systems not considered here.
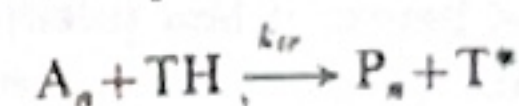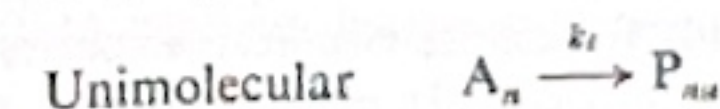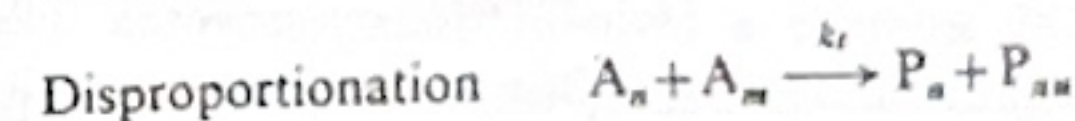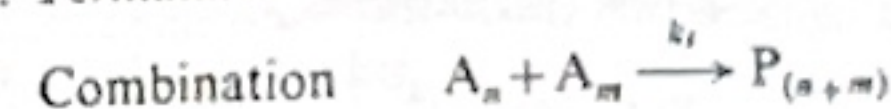
1. *Initiation*

   Chemical: $I \xrightarrow{k_d} 2A_0$ (rate controlling); $A_0 + M \xrightarrow{k_i} A_1$

   Catalytic: $HA + M \xrightarrow{k_i} A_1$

2. *Propagation*

   $A_1 + M \xrightarrow{k_p} A_2$

$A_2 + M \xrightarrow{k_p} A_3$

$\cdot \qquad \cdot \qquad \cdot$

$\cdot \qquad \cdot \qquad \cdot$

$A_{n-1} + M \xrightarrow{k_p} A_n$

3. *Transfer*

   $A_n + TH \xrightarrow{k_{tr}} P_n + T^*$

4. *Termination*

   Combination $A_n + A_m \xrightarrow{k_t} P_{(n+m)}$

   Disproportionation $A_n + A_m \xrightarrow{k_t} P_n + P_{nu}$

   Unimolecular $A_n \xrightarrow{k_t} P_{nu}$

where I = a chemical initiator
   A_0 = a primary reactive species (no added monomer)
   HA = a catalyst
   TH = a transfer agent
   M = a monomer molecule
   A_n = an active species containing n monomer units
   P_n = an inactive polymer species containing n monomer units
   P_{nu} = P_n with terminal unsaturation
   A = any active species, regardless of chain length

The rate constants are identified as
   k_d = Decomposition
   k_i = Initiation
   k_p = Propagation
   k_{tr} = Transfer
   k_t = Termination

Brackets around a chemical species, [ ], will indicate the concentration of that species in some convenient units, usually moles/liter. The letter v followed by the subscripted letters $d, i, p, tr,$ or t, will indicate the appropriate rate processes.

409 Kinetics of Homogeneous Free Radical Polymerization

The basic assumption here is that the concentration of active species is constant: $\Sigma_n[A_n]$ = constant. In order for this to be true, the rate of initiation v_i must equal the rate of termination, $v_i = v_t$. The first step is to write

the rate expressions for each of the kinetic processes based on the general expressions presented in the preceding section.

1. *Initiation*. v_i = the rate of generation of primary active species. For free radical initiation, the rate of decomposition of initiator is rate controlling and first order with respect to the initiator concentration. Hence

$$-\frac{d[I]}{dt} = k_d[I] \tag{4-1}$$

$$[I] = [I_0] \exp(-k_d t) \tag{4-2}$$

$$v_i = 2\epsilon k_d[I]^* \tag{4-3}$$

where ϵ is the initiator efficiency, which usually ranges from 0.6 to 1.0. The factor of 2 enters in Eq. (4–3) because two active species result from the decomposition of each initiator molecule. In many instances, the rate constant is so low ($\approx 10^{-4}$ to 10^{-5} min^{-1}) that very little initiator is consumed in polymerizing to 100 percent yield so that [I] is essentially constant, and v_i can also be considered constant. Initiator concentrations for radical polymerization are typically in the neighborhood of 0.1 to 0.5 weight percent based on the monomer content.

2. *Propagation*. v_p = the rate of generation of polymer; it is equivalent to the rate of loss of monomer.

$$v_p = -\frac{d[M]}{dt}$$

$$v_p = k_p[M]\Sigma[A_n] = k_p[M][A] \tag{4-6}$$

We have also assumed that all species are equally reactive, regardless of chain length, and evaluated $\Sigma[A_n]$ as [A], the total concentration of active species.

3. *Transfer*. v_{tr} = the rate of transfer of activity

$$v_{tr} = k_{tr}[TH]\Sigma[A_n] = k_{tr}[TH][A] \tag{4-7}$$

4. *Termination*. v_t = the rate of loss of active species. For bimolecular reactions,

$$v_t = 2k_t\Sigma[A_n]\Sigma[A_m] = 2k_t[A]^2 \tag{4-8}$$

To obtain the desired expression for v_p, we solve for [A] by equating v_i and v_t and insert this into the equation for v_p. We must also assume that either trans-

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* This expression should not be equated to the rate of change in the concentration of primary active species, $d[A_0]/dt$. We do not, at this point consider their fate, only the fact that they are being generated at a specified rate.

fer is absent, or that if it does occur, the transferred species is as reactive as the original species. Thus

$$v_p = k_p\left(\frac{\epsilon k_d[I]}{k_t}\right)^{\frac{1}{2}}[M] \tag{4-9}$$

Equation (4–9) holds in the early stages of reaction for a large number of free radical polymerizations, but it should not be considered valid beyond 10 to 15 percent conversion, without experimental verification. Analogous equations can be derived for the cationic and anionic polymerizations
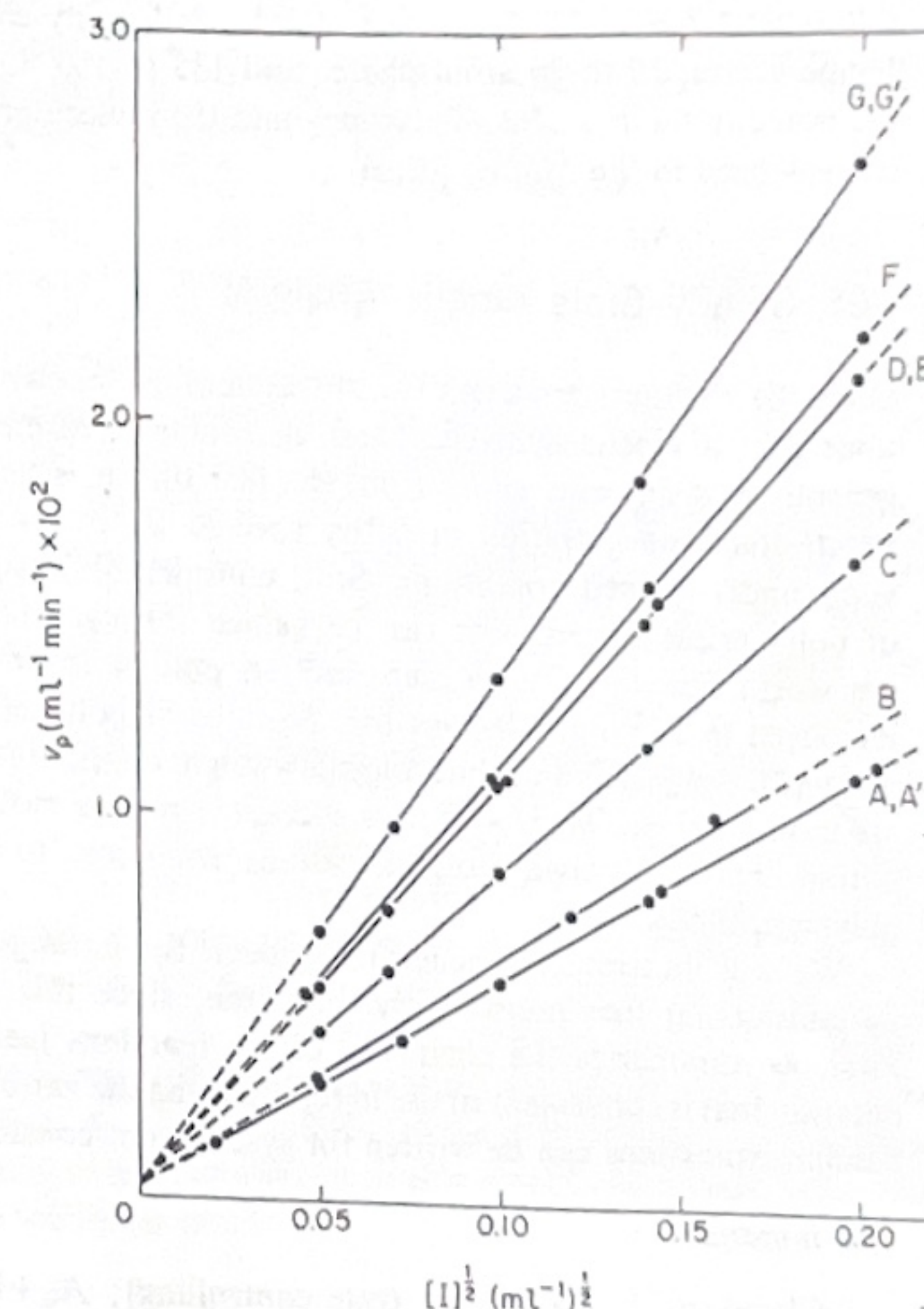

Figure 4–2. Plot of initial v_p vs. $[I]^{1/2}$ for the bulk polymerization of styrene at 70°C. A, bis(p-chlorobenzoyl)peroxide; A', Luperco BDB; B, benzoyl peroxide; C, acetyl peroxide in dimethyl phthalate; D, lauroyl peroxide; E, myristoyl peroxide; F, caprylyl peroxide; G, bis(2,4-dichloro-benzoyl)peroxide; G', Luperco CDB. [A. I. Lowell and I. R. Price, I. Polymer Sci., 43, 1 (1960).]

discussed, but they may be valid in even a more limited number of instances because the reactions proceed so rapidly that it is unlikely that steady state can be established.

The proportionality predicted by Eq. (4-9) between the rate of polymerization and the square root of the initiator concentration has been abundantly confirmed for low extents of reaction for numerous monomer-initiator pairs. Figure 4-2 is a log-log plot of the initial rates of polymerization against initiator concentration for styrene with various peroxide initiators. If the initiator efficiency for these reactions is constant, the ratio of $v_p/[M][I]^{\frac{1}{2}}$ should be constant for initial rates at various stages of dilution with an inert solvent. This ratio usually decreases but only slowly even over a tenfold dilution range. If this fact is coupled with a close adherence to kinetics that
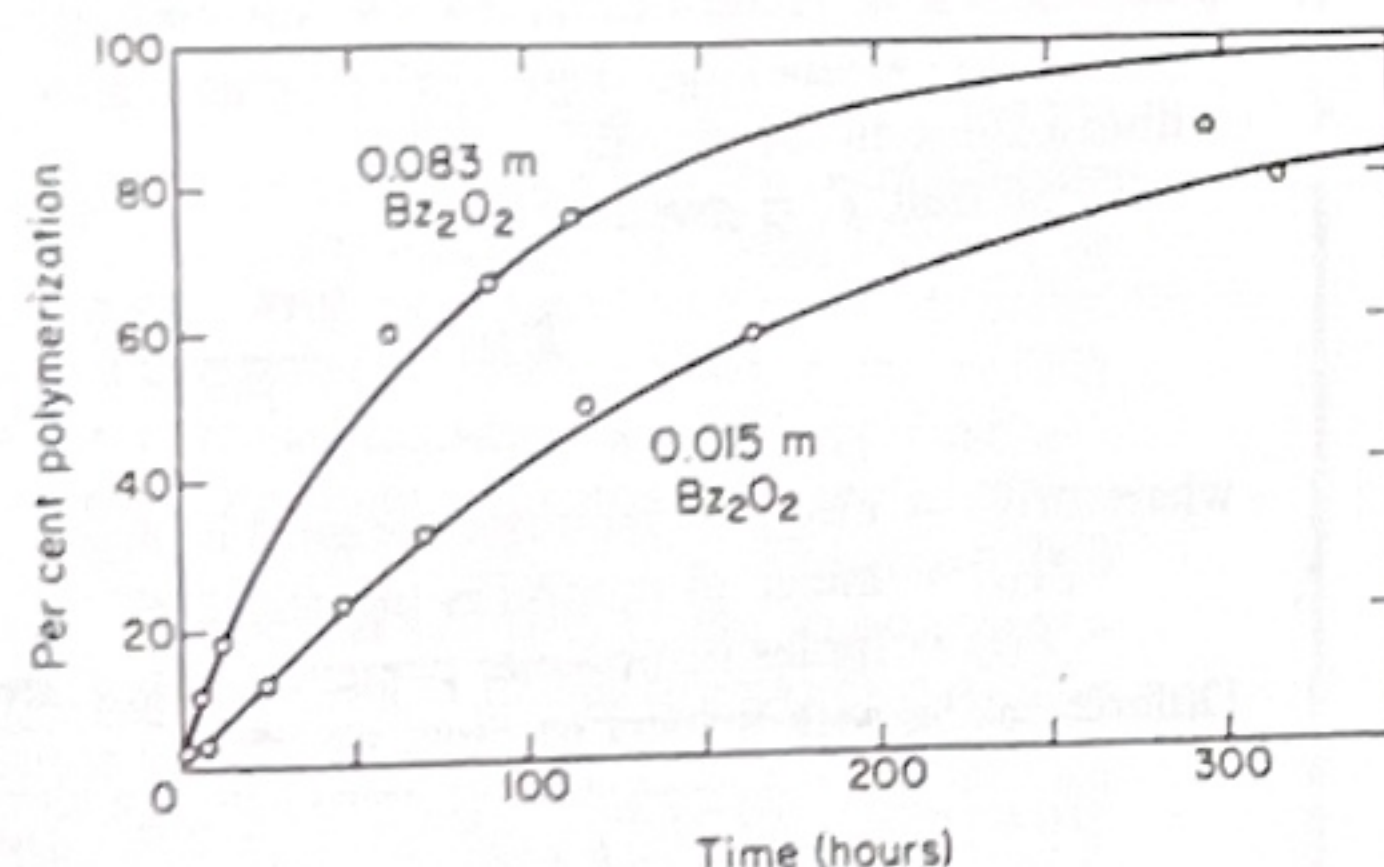

Figure 4-3. Polymerization of 40 percent styrene in toluene at 50°C in the presence of the amounts of benzoyl peroxide indicated. [G. V. Schulz and E. Husemann, Z. physik. Chem., B39, 246 (1938).]

are first order in monomer, an efficiency of unity is indicated for polymerization in undiluted monomer. Such an adherence to first-order monomer kinetics, however, is rare, especially for extents of reaction in the range of practical interest.

Figure 4-3 shows data for styrene polymerized with benzoyl peroxide, 40 percent monomer in toluene. In this instance, the assumptions of a constant initiator concentration and 100 percent radical efficiency are well justified over a broad extent of reaction. We note, in general, that v_p should decrease as monomer is consumed. In the polymerization of certain monomers, either undiluted or in concentrated solution, a point in the reaction is reached where there is a marked increase in both reaction rate and molecular _ _ _ _ _ This effect may be termed the *autoacceleration*, the *Trommsdorff*, or

concentrations of monomer in benzene. It is particularly pronounced with methyl methacrylate, methyl acrylate, and acrylic acid. It occurs independently of initiator and is caused by a physical factor that we have heretofore ignored: the rise in viscosity brought about by the continuous generation of high-molecular-weight polymer. This rise in viscosity causes the reaction to become diffusion, rather than chemically, controlled, and valid rate expressions must reflect this situation.

Physically, autoacceleration involves a complex series of events that develop as the reaction enters the diffusion-controlled regime. As the viscosity of the reaction medium increases, monomer diffusion decreases much less
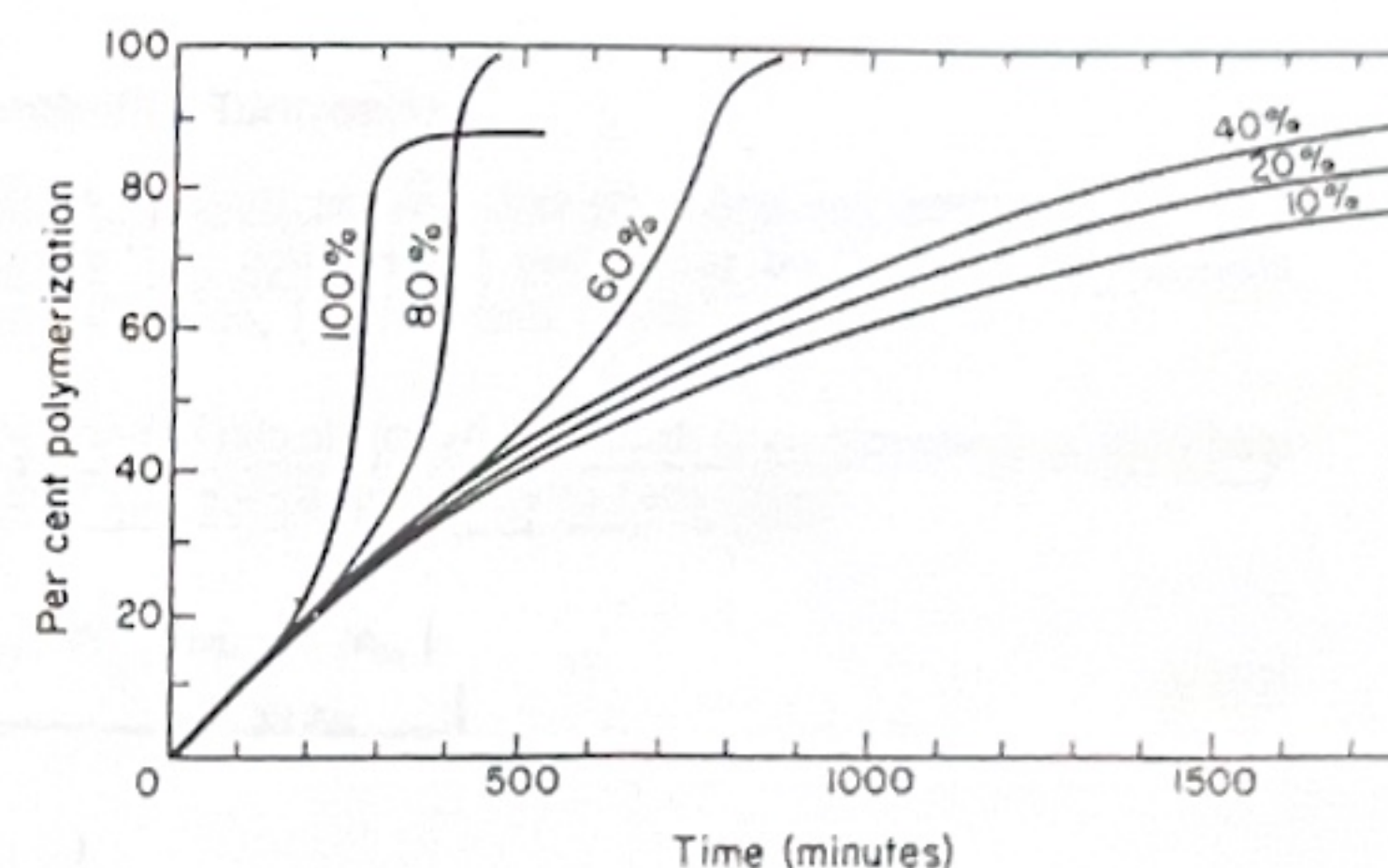

Figure 4-4. The course of polymerization of methyl methacrylate at 50°C in the presence of benzoyl peroxide at various concentrations of monomer in benzene. [G. V. Shulz and G. Harborth, Macromol. Chem., 1, 106 (1947). Reprinted with permission; Hüthig and Werpf, publishers.]

rapidly than does diffusion of the growing polymer chains. Thus propagation at a particular site diminishes slightly, if at all, but its chances of termination by another active species decrease markedly. At the same time, radicals are being generated at a near normal rate. Since the overall rate of termination is decreasing, the result is an increase in the number of active sites—an unsteady state condition—with an overall increase in the rate of polymerization. Since many chain polymerizations are highly exothermic, this polymerization rate increase is most capable of setting off another round of rate increases through a rapid rise in temperature. This is obviously a potentially dangerous situation, and precautions must be taken, especially on the industrial scale, to limit the risk of a runaway reaction and subsequent explosion.

Reference to Figure 4-4 shows that the rates decrease at conversions on

Fig. 3-19   Effect of conversion on polymerization rate.

consistency below 90 °C, and the propagation rate becomes monomer diffusion controlled.

Other manifestations of a gel effect, or of a diffusion-controlled mechanism, are encountered in heterogeneous reactions as well. The phenomenon is thus generally important. Reference to these will be made at the appropriate places in the sections on the production of addition polymers.

410 Instantaneous Number-Average Degree of Polymerization

The problem of deriving analytic expressions for molecular weight and molecular-weight distributions in chain polymerization is much more cumbersome than for linear condensation polymerization. This situation is true even for the simplest case of linear polymerization under steady state conditions. In practice, the problem is compounded by the frequently encountered phenomenon of chain branching. In this section we develop an expression for the number-average degree of polymerization that is being generated within a short time interval.

Recall that $\bar{X}_n$ is given by

$$\bar{X}_n(t) = \frac{M(0) - M(t)}{P(t)}$$

where $M(0)$ = moles of monomer present initially
$M(t)$ = moles of monomer present at any time t
$P(t)$ = moles of polymer present at any time t
Differentiating with respect to time, we get

$$P(t)\frac{d\bar{X}_n(t)}{dt} + \bar{X}_n(t)\frac{dP(t)}{dt} = \frac{-dM(t)}{dt}$$

During a short time interval, the *instantaneous number-average degree of polymerization*, $\bar{X}_{ni}$, will be constant, and we will obtain

$$\bar{X}_{ni} = \frac{-dM(t)/dt}{dP(t)/dt} \tag{4-10}$$

In the absence of chain transfer and for termination by combination, $dP/dt = \frac{1}{2}v_t$, whereas for termination by disproportionation or unimolecular termination, $dP/dt = v_t$. For termination by combination,

$$\bar{X}_{ni} = \frac{2v_p}{v_t} = \frac{2v_p}{v_i} \tag{4-11}$$

The ceiling temperature phenomenon is observed because ΔH is highly exothermic, while ΔS is mildly exoentropic. The opposite type of phenomenon occurs in rare instances where ΔS is endoentropic ($\Delta S = +$) and ΔH is very small (either $+$ or $-$) or zero. Under these conditions, there will be a *floor temperature* T_f below which polymerization is not possible. This behavior has been observed in only three cases—the polymerizations of cyclic sulfur and selenium octamers and octamethylcyclotetrasiloxane to the corresponding linear polymers (Secs. 7-11a). ΔH is 9.5, 13.5, and nearly 0 kJ/mole, respectively, and ΔS is 27, 31, and 6.7 J/K-mole, respectively, for the three systems [Brandrup and Immergut, 1989; Lee and Johannson, 1966, 1976].

3-10 AUTOACCELERATION

3-10a Course of Polymerization

Radical chain polymerizations are characterized by the presence of an *autoacceleration* in the polymerization rate as the reaction proceeds [North, 1974]. One would normally expect a reaction rate to fall with time (i.e., the extent of conversion), since the monomer and initiator concentrations decrease with time. However, the exact opposite behavior is observed in many polymerizations—the reaction rate increases with conversion. A typical example is shown in Fig. 3-18 for the polymerization of methyl methacrylate in benzene solution [Schulz and Haborth, 1948]. The curve for the 10% methyl methacrylate solution shows the behavior that would generally be expected. The curve for neat (pure) monomer shows a dramatic autoacceleration in the polymerization rate. Such behavior is referred to as the *gel effect*. (The term *gel* as used here is different from its usage in Sec. 2-10; it does not refer to the formation of a crosslinked polymer.) The terms *Trommsdorf effect* and *Norrish-Smith effect* are also used in recognition of the early workers in the field. Similar behavior has been observed for a variety of monomers, including styrene, vinyl acetate, and methyl methacrylate [Abuin and Lissi, 1977; Balke and Hamielec, 1973; Cardenas and O'Driscoll, 1976, 1977; Small, 1975; Turner, 1977; Yamamoto and Sugimoto, 1979]. It turns out that

the gel effect is the "normal" behavior for most polymerizations. The gel effect should not be confused with the autoacceleration that would be observed if a polymerization were carried out under nonisothermal conditions such that the reaction temperature increased with conversion (since ΔH is negative). The gel effect is observed under isothermal reaction conditions.

A more critical analysis of accurate polymerization data indicates that the situation is complicated; three stages can be distinguished in some polymerizations when $R_p/[M][I]^{1/2}$ is plotted against time (or conversion) (Fig. 3-19) [Dionisio et al., 1979; Dionisio and O'Driscoll, 1980; Sack et al., 1988]. Plotting $R_p/[M][I]^{1/2}$ instead of percent conversion takes into account the concentration changes in monomer and initiator with time. *Stage I* involves either a constant rate (IA) or declining rate (IB) with time. *Stage II* constitutes the autoaccelerative gel effect region. *Stage III* involves either a constant (IIIA) or declining (IIIB) rate.

3-10b Diffusion-Controlled Termination

An understanding of this behavior requires that we appreciate termination is a diffusion-controlled reaction best described as proceeding by the three-step process [Mahabadi and O'Driscoll, 1977a, 1977b; North, 1974]:

1 *Translational diffusion* of two propagating radicals (i.e., movement of the whole radicals) until they are in close proximity to each other:

$$\underbrace{M_n{}^{\cdot} + M_m{}^{\cdot} \; \frac{k_1}{k_2} \; [M_n{}^{\cdot} \text{---} M_m{}^{\cdot}]}_{\text{XLIIa}} \tag{3-197}$$
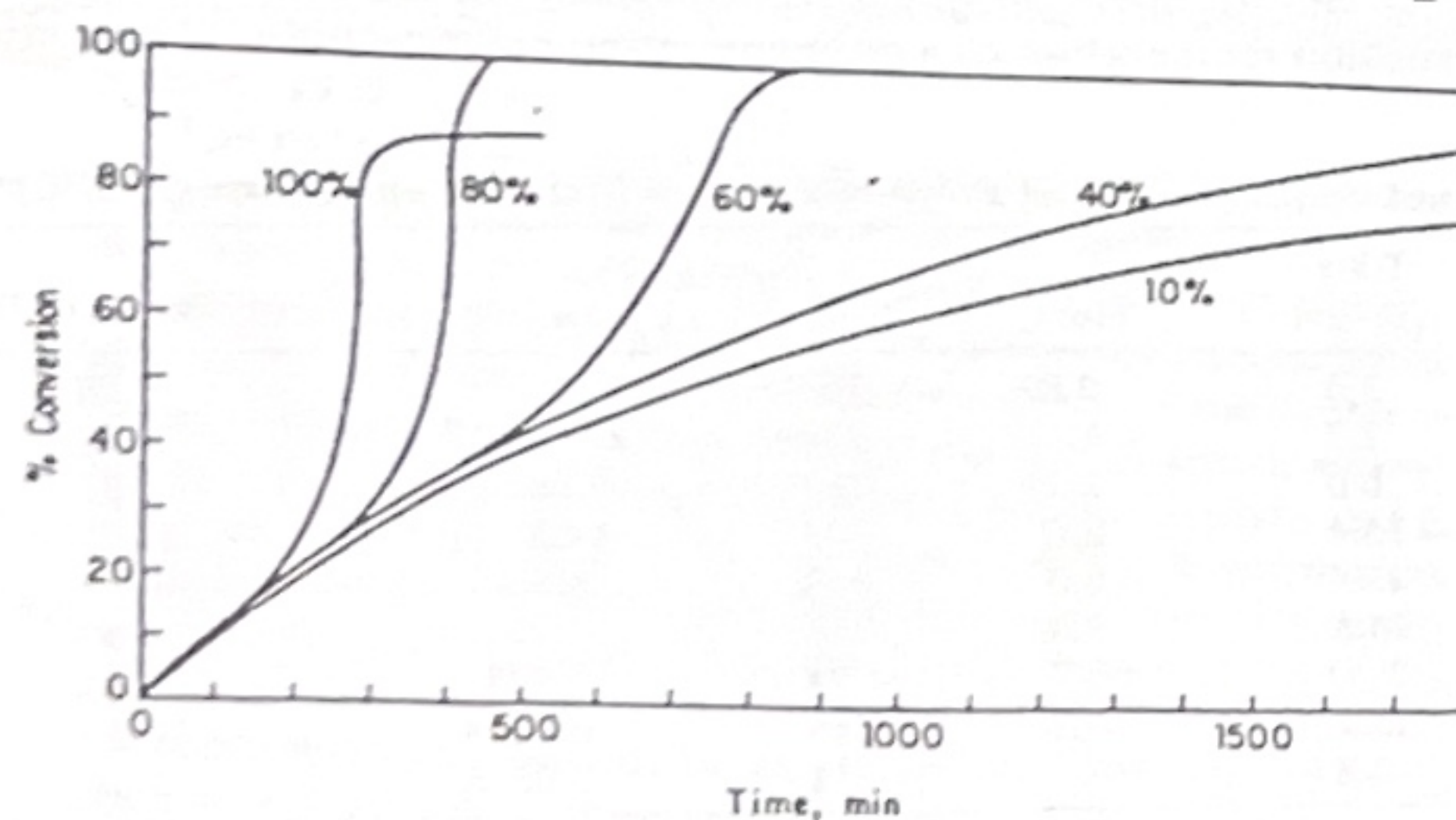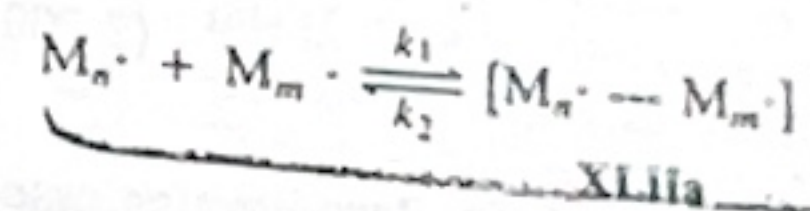

Fig. 3-18 Autoacceleration in the benzoyl peroxide initiated polymerization of methyl methacrylate in benzene at 50°C. The different plots represent various concentrations of monomer in solvent. After Schulz and Haborth [1948] (by permission of Huthig and Wepf Verlag, Basel).
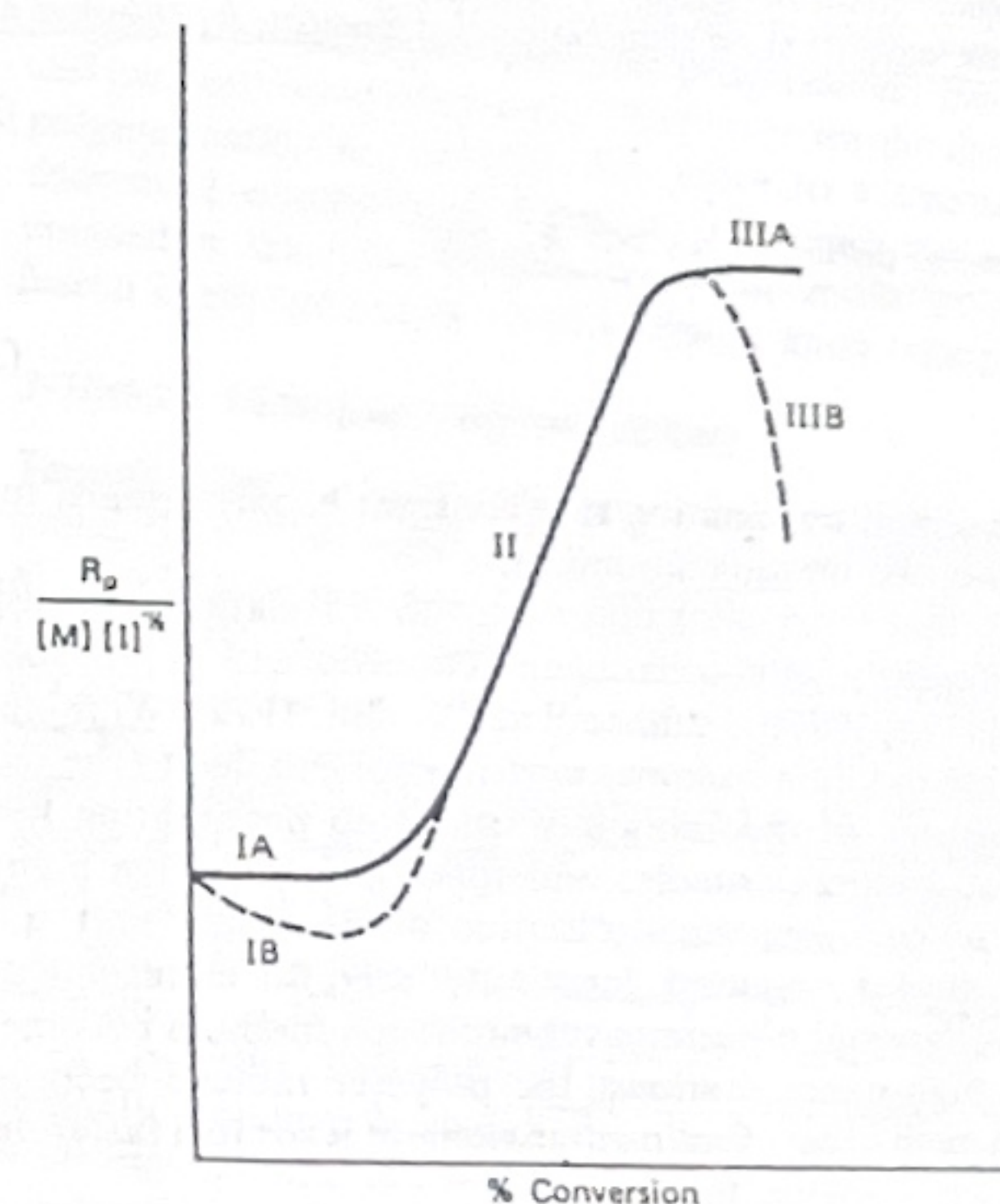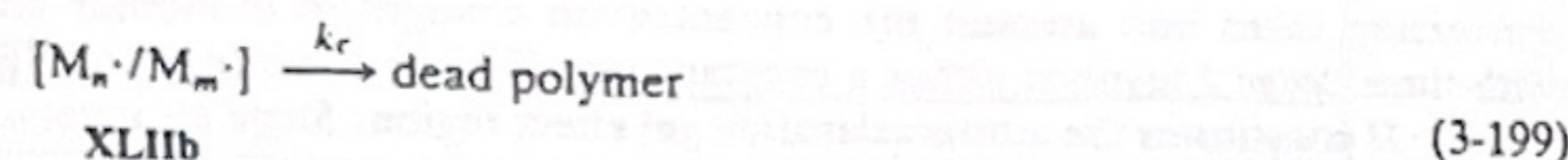

Fig. 3-19 Effect of conversion on polymerization rate.

2 Rearrangement of the two chains so that the two radical ends are sufficiently close for chemical reaction, which occurs by *segmental diffusion* of the chains, that is, by the movement of segments of a polymer chain relative to other segments

$$[M_n \cdot - M_m \cdot] \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [M_n \cdot / M_m \cdot]$$

XLIIa   XLIIb   (3-198)

3 Chemical reaction of two radical ends

$$[M_n \cdot / M_m \cdot] \xrightarrow{k_c} \text{dead polymer}$$

XLIIb   (3-199)

Theoretical considerations indicate that k_c would be very large, about 8×10^9 liters/mole-sec, in low viscosity media (such as bulk monomer) for the reaction between two radicals. The rate constants for reactions of small radicals (e.g., methyl, ethyl, propyl) are close to this value (being about 2×10^9 liters/mole-sec) [Ingold, 1973]. Experimentally determined k_t values for radical polymerizations, however, are considerably lower, usually by two orders of magnitude or more (see Table 3-11). Thus diffusion is the rate-determining process for termination, $k_c \gg k_4$ and one obtains

$$R_t = \frac{k_1 k_3 [M \cdot]^2}{k_2 + k_3}$$ (3-200)

by assuming steady-state concentrations of both **XLIIa** and **XLIIb**. Two limiting cases of termination arise. For the case of slow translational diffusion, $k_3 \gg k_2$, and

$$R_t = k_1 [M \cdot]^2$$ (3-201a)

For the case of slow segmental diffusion, $k_2 \gg k_3$, and

$$R_t = \frac{k_1 k_3 [M \cdot]^2}{k_2}$$ (3-201b)

Thus the experimentally observed termination rate constant k_t corresponds to k_1 and $k_1 k_3/k_2$, respectively, for the two limiting situations.

Recent work has shown that segmental diffusion and translational diffusion are expected to be affected differently with conversion [Dionisio and O'Driscoll, 1980; Mahabadi and O'Driscoll, 1977a, 1977b; Mahabadi and Rudin, 1979]. With increasing conversion the polymerization medium becomes a poorer solvent due to the increased polymer concentration. The size of the randomly coiled up propagating radical in solution (referred to as *coil*) becomes smaller and there is an effective higher concentration gradient across the coil. Segmental diffusion of the radical end out of the coil to encounter another radical is increased. Simultaneously, the increasing polymer concentration decreases translational diffusion as the reaction medium becomes more viscous and, at sufficiently high concentrations, the polymer radicals become more crowded and entangled with each other. Chain entanglement leads to a faster decrease

in translational diffusion relative to the decrease with increasing viscosity. Stage IA behavior corresponds to the situation observed for many monomers where the increase in segmental diffusion is apparently exactly counterbalanced by the decrease in translational diffusion (i.e., k_t remains constant). When the initial increase in segmental diffusion is greater than the decrease in translational diffusion, k_t increases and the polymerization rate decreases (Stage IB). Moderate Stage IB behavior has been observed in several polymerizations (styrene, methyl methacrylate [Abuin et al., 1978; High et al., 1979]). At this time, no system has been observed with more than a moderate decrease in $R_p/[M][I]^{1/2}$ with conversion.

At some point, translational diffusion decreases faster than the increase in segmental diffusion and rapid autoacceleration occurs—Stage II—the gel effect. As the polymerization proceeds the viscosity of the system increases with subsequent chain entanglement [Lachinov et al., 1979] and termination becomes increasingly slower. Although propagation is also hindered, the effect is much smaller, since k_p values are smaller than k_t values by a factor of 10^4–10^5. Termination involves the reaction of two large polymer radicals, while propagation involves the reaction of small monomer molecules and only one large radical. High viscosity affects the former much more than the latter. Therefore, the quantity $k_p/k_t^{1/2}$ increases and the result in accordance with Eq. 3-25 is an increase in R_p with conversion. A second consequence of this effect is an increase in molecular weight with conversion as required by Eq. 3-105. These conclusions have been verified by the quantitative evaluation of the k_p and k_t values as a function of the percent conversion. Thus, Table 3-16 shows data on the polymerization of methyl methacrylate [Hayden and Melville, 1960]. It is seen that k_p is relatively unaffected until 50% conversion (of monomer to polymer) has been reached, whereas k_t has decreased by almost two orders of magnitude in the same span. The $k_p/k_t^{1/2}$ ratio and the polymerization rate simultaneously increase rapidly at first and then taper off as k_p is also affected in the later stages of reaction. The attention of the reader is also called to the data showing the increase in the radical lifetime with increasing conversion.

At very high (e.g., above 50% conversion for the system in Table 3-16), k_p becomes sufficiently affected that the $R_p/[M][I]^{1/2}$ begins to level off (Stage IIIA behavior) or decrease (Stage IIIB behavior). Stage IIIB behavior is much more common than Stage IIIA. The decrease in rate during Stage IIIB, sometimes referred to as the *glass or vitrification effect*, can be extremely pronounced depending on the reaction temperature. The glass transition temperature of a polymerization reaction mixture increases

TABLE 3-16   Effect of Conversion on the Polymerization of Methyl Methacrylate (22.5°C)[a]

% Conversion	Rate (%/hr)	τ (sec)	k_p	$k_t \times 10^{-5}$	$(k_p/k_t^{1/2}) \times 10^2$
0	3.5	0.89	384	442	5.78
10	2.7	1.14	234	273	4.58
20	6.0	2.21	267	72.6	8.81
30	15.4	5.0	303	14.2	25.5
40	23.4	6.3	368	8.93	38.9
50	24.5	9.4	258	4.03	40.6
60	20.0	26.7	74	0.498	33.2
70	13.1	79.3	16	0.0564	21.3
80	2.8	216	1	0.0076	3.59

[a]Data from Hayden and Melville [1960].

with conversion of monomer to polymer. Polymerization can stop appreciably short of full conversion if the reaction system has a percent conversion whose glass transition temperature exceeds the reaction temperature [Friis and Hamielec, 1976; Mita and Horie, 1987; Sundberg and James, 1978]. For example, this occurs in the polymerization of pure methyl methacrylate in Fig. 3-18 since the polymerization temperature (50°C) is considerably below the glass transition temperature of poly(methyl methacrylate (105°C).

Recent work indicates that variations in initiator efficiency f are also important in understanding the effect of conversion on rate and degree of polymerization. The calculations of k_p and k_t in Table 3-16 were carried out with the assumption of a constant f independent of conversion, but it is known that f varies with conversion. The initiator efficiency decreases with conversion in an approximately linear manner until the high conversions of the Stage IIIB region are reached; thereafter, there is a much steeper drop in f with conversion [Russell et al., 1988; Sack et al., 1988]. Thus, the behavior in Stage IIIB is a consequence of decreases in both k_p and f, not just a decrease in k_p. If one corrects the calculations of rate constants in previous work (e.g., Table 3-16) for the variation in f with conversion, the trends for k_t and k_p are essentially unchanged.

3-10c Effect of Reaction Conditions

The rate of segmental diffusion is predicted to increase (with a corresponding increase in k_t and decreases in rate and degree of polymerization) by any factor that decreases the coil size of the propagating radical. Thus segmental diffusion will increase with decreasing polymer molecular weight and goodness of reaction solvent and with increasing conversion [Mahabadi, 1987; Olaj and Zifferer, 1987]. The various factors affecting segmental diffusion are interrelated. At zero or very low conversion, k_t is larger in a poor solvent compared to k_t in a good solvent. It is possible to observe a "crossover" at somewhat higher conversion whereby the k_t in the good solvent is larger than k_t in the poor solvent. This occurs because coil size decreases with increasing polymer concentration, but the decrease is steeper in better solvents [Mahabadi and Rudin, 1979]. Many of these predictions for the course of polymerization in Stage I have been verified [Abuin et al., 1978; Dionisio and O'Driscoll, 1980; Ludwico and Rosen, 1975, 1976].

The behavior in Stage II is dominated by the decreased rate of translational diffusion caused by the increasing viscosity of the reaction system. Viscosity increases with increasing polymer molecular weight and solvent goodness. Increased polymer molecular weight also leads to earlier chain entanglements. These expectations have been verified in a number of studies. Lower polymer molecular weights moderate the gel effect (Stage II behavior) by shifting the conversion at which the gel effect begins and the steepness of the subsequent increase in rate [Abuin and Lissi, 1977; Cardenas and O'Driscoll, 1976, 1977]. Vinyl acetate yields a lower-molecular-weight polymer due to chain transfer to monomer and does not show as dramatic a gel effect as styrene or methyl methacrylate. Temperature also plays a large role—higher temperatures decrease the viscosity of the reaction medium. This delays the gel effect and the autoacceleration may not be as pronounced. Similar effects are observed in the presence of solvents and chain transfer agents. Solvents lower the viscosity of the medium directly, while chain transfer agents do so by lowering the polymer molecular weight. The effect of solvent in methyl methacrylate polymerization is seen in Fig. 3-19. The

effect of viscosity on the gel effect has also been examined by adding polymer to a monomer prior to initiating polymerization; R_p increases with viscosity (which increases with polymer concentration) [Kulkarni et al., 1979].

The percent conversion for the onset of the gel effect varies considerably depending on the monomer and the reaction conditions (which determine coil size, viscosity, entanglements). In some systems the gel effect has been reported as occurring at only a few percent conversion, in others, not until 60–70% conversion. Further, there is considerable difficulty in obtaining sufficiently accurate data to allow a precise evaluation of the onset of the gel effect, especially if the onset occurs gradually.

3-10d Related Phenomena

3-10d-1 Occlusion (Heterogeneous) Polymerization

Autoacceleration of the gel effect type is observed for the polymerization of monomers whose polymers are insoluble or weakly soluble in their own monomers. Examples of this type of behavior are acrylonitrile, vinyl chloride, trifluorochloroethylene, and vinylidene chloride [Billingham and Jenkins, 1976; Gromov et al., 1980; Guyot, 1987; Jenkins, 1967; Olaj et al., 1977a, 1977b; Talamini and Peggion, 1967]. Similar effects are observed in other polymerizations when one uses solvents which are nonsolvents for the polymer [e.g., methanol for polystyrene, hexane for poly(methyl methacrylate)]. The accelerative effects observed in these instances of heterogeneous polymerization are similar to the gel effect and are caused by a decrease in k_t relative to k_p. The growing polymeric radicals become coiled up, since they are essentially insoluble or on the verge of insolubility in the solvent or in their own monomer. Termination between radicals again becomes progressively more difficult, while propagation may still proceed reasonably well. The reason for the decrease in occlusion or heterogeneous polymerization is probably due more to a decrease in segmental diffusion than to decreased translational diffusion. Although the propagating radical coil size is decreased in the poor reaction medium, unlike homogeneous systems, segmental diffusion is not enhanced, since diffusion must take place in a poor medium.

3-10d-2 Template Polymerization

Template (matrix) polymerization involves the polymerization of a monomer in the presence of a polymer, often a polymer derived from a different monomer [Gons et al., 1978; Matuszewska-Czerwik and Polowinski, 1990; Srivstava et al., 1987; Tan and Challa, 1987, 1988; Tewari and Srivastava, 1989; van de Grampel et al., 1988]. The original polymer and formed polymer are often referred to as parent and daughter polymer, respectively. Examples include acrylic acid with polyethyleneimine or poly(N-vinylpyrrolidinone), N-vinylimidazole with poly(methacrylic acid), acrylonitrile with poly(vinyl acetate), and methyl methacrylate with poly(methyl methacrylate). Many of these polymerizations proceed with rate enhancements relative to the corresponding polymerizations in the absence of polymer. The rate enhancements are typically by a factor no larger than 2–5, although a few larger enhancements have been observed. Two types of mechanisms appear to be operative depending on how strongly monomer is absorbed to polymer. A zip mechanism occurs when monomer is strongly complexed with the parent polymer. The complexed monomer molecules are lined up next to each other, which facilitates rapid propagation when an initiating radical from the surrounding solution adds to one of the absorbed monomers.

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Ionic Chain-Reaction and Complex Coordinative Polymerization (Addition Polymerization)

In contrast to the slow step-reaction polymerization discussed in Chap. 7, chain-reaction polymerization is usually rapid, and the initiated species continue to propagate until termination. Thus, in the extreme case, *one* could produce one initiating species which would produce *one* high molecular weight polymer molecule, leaving all the other monomer molecules unchanged. In any case, the concentration of the monomer, which is usually a derivative of ethylene, decreases continuously throughout the reaction. In contrast to stepwise polymerization, the first species produced is a high molecular weight polymer.

A kinetic chain reaction usually consists of at least three steps, namely, initiation, propagation, and termination. The initiator may be an anion, a cation, a free radical, or a coordination catalyst. While coordination catalysts are the most important commercially, the ionic initiators will be discussed first in an attempt to simplify the discussion of *chain-reaction polymerization*.

8.1 CATIONIC POLYMERIZATION

The art of cationic polymerization, like many other types of polymerization, is at least a century old. However, the mechanisms for the early reactions were not understood, and, of course, the early scientists did not understand the modern concept of macromolecules. Nevertheless, it is of interest to note that turpentine, styrene, isobutylene, and ethyl vinyl ether were polymerized over a century ago by the use of cationic initiators such as sulfuric acid, tin(IV)chloride, boron trifluoride, and iodine.

The first species produced in these reactions are carbocations, and these were unknown as such prior to World War II. It is now known that pure Lewis acids, such as boron

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