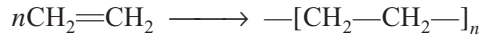


### R7.1 Polymerization

10<sup>11</sup> lb/yr

Polymers are finding increasing use throughout our society. Well over 100 billion pounds of polymer are produced each year, and it is expected that this figure will double in the coming years as higher-strength plastics and composite materials replace metals in automobiles and other products. Consequently, the field of polymerization reaction engineering will have an even more prominent place in the chemical engineering profession. Because there are entire books on this field (see *Supplementary Reading*), it is the intention here to give only the most rudimentary thumbnail sketch of some of the principles of polymerization.

A polymer is a molecule made up of repeating structural (monomer) units. For example, polyethylene is used for such things as tubing, and repeating units of ethylene are used to make electrical insulation:



where  $n$  may be 25,000 or higher.

*Everyday Examples*

- Polyethylene
  - Softdrink cups
  - Sandwich bags
- Poly (vinyl chloride)
  - Pipes
  - Shower curtains
  - Tygon tubing
- Poly (vinyl acetate)
  - Chewing gum

Polymerization is the process in which monomer units are linked by chemical reaction to form long chains. These long chains set polymers apart from other chemical species and give them their unique characteristic properties. The polymer chains can be linear, branched, or cross-linked (Figure R7-1-1).

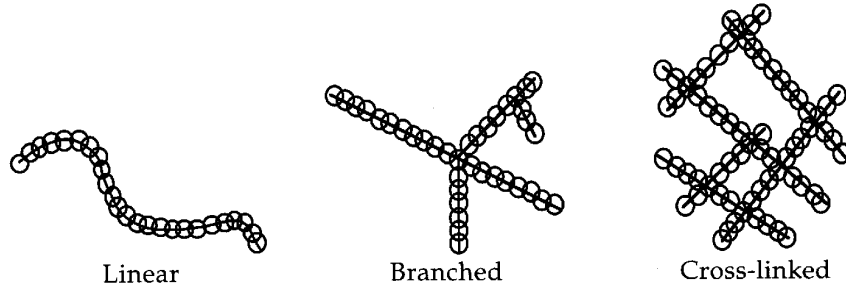
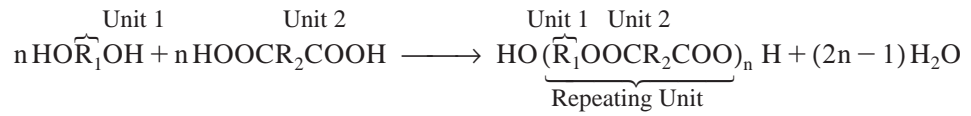


Figure R7-1-1 Types of polymer chains.

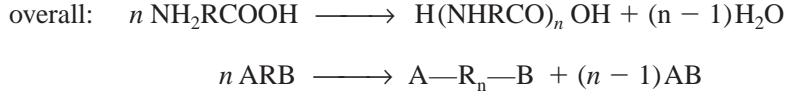
Homopolymers are polymers consisting of a single repeating unit, such as  $[-\text{CH}_2-\text{CH}_2-]$ . Homopolymers can also be made from two different monomers whose structural units form the repeating unit such as the formation of a polyamide (e.g., nylon) from a diamine and a diacid.

Polymerization reactions are divided into two groups known as **step reactions** (also called condensation reactions) and **chain reactions** (also known as addition reactions). Step reactions require bifunctional or polyfunctional monomers, while chain reactions require the presence of an initiator.



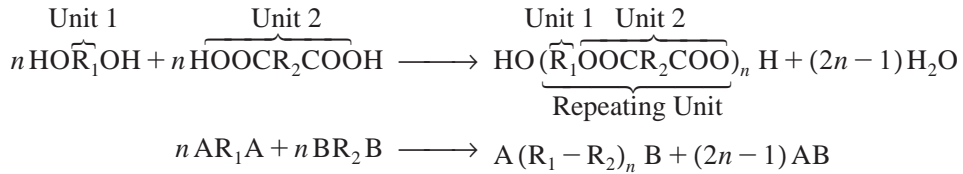


etc.



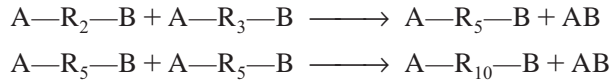
We see that from tetramers on, the *-mer* can be formed by a number of different pathways.

The A and B functional groups can also be on different monomers such as the reaction for the formation of polyester (shirts) from diols and dibasic acids.



By using diols and diacids we can form polymers with two different structural units which together become the repeating unit. An example of an AR<sub>1</sub>A plus BR<sub>2</sub>B reaction is that used to make Coca-cola bottles (i.e., terephthalic acid plus ethylene glycol to form poly [ethylene glycol terephthalate]).

When discussing the progress of step polymerization, it is not meaningful to use conversion of monomer as a measure because the reaction will still proceed even though all the monomer has been consumed. For example, if the monomer A—R—B has been consumed. The polymerization is still continuing with



because there are both A and B functional groups that can react. Consequently, we measure the progress by the parameter  $p$ , which is the fraction of functional groups, A, B, that have reacted. We shall only consider reaction with equal molar feed of functional groups. In this case

$$p = \frac{M_o - M}{M_o} = \text{fraction of functional groups of either A or B that have reacted}$$

$M$  = concentration of either A or B functional groups (mol/dm<sup>3</sup>)

As an example of step polymerization, consider the polyester reaction in which sulfuric acid is used as a catalyst in a batch reactor. Assuming the rate of disappearance is first order in A, B, and catalyst concentration (which is constant for an externally added catalyst). The balance on A is

$$\frac{-d[A]}{dt} = k[A][B] \quad (\text{R7.1-1})$$

For equal molar feed we have

$$[A] = [B] = M$$

$$\frac{dM}{dt} = -kM^2$$

$$M = \frac{M_o}{1 + M_o kt} \quad (\text{R7.1-2})$$

In terms of the fractional conversion of functional groups,  $p$ ,

$$\frac{1}{1-p} = M_o kt + 1 \quad (\text{R7.1-3})$$

The number-average degree of polymerization,  $\bar{X}_n$ , is the average number of structural units per chain:

Degree  
of polymerization

$$\bar{X}_n = \frac{1}{1-p} \quad (\text{R7.1-4})$$

The number-average molecular weight,  $\bar{M}_n$ , is just the average molecular weight of a structural unit,  $\bar{M}_s$ , times the average number of structural unit per chain,  $\bar{X}_n$ , plus the molecular weight of the end groups,  $M_{eg}$ :

$$\bar{M}_n = \bar{X}_n \bar{M}_s + M_{eg}$$

Since  $M_{eg}$  is usually small (18 for the polyester reaction), it is neglected and

$$\bar{M}_n = \bar{X}_n \bar{M}_s \quad (\text{R7.1-5})$$

In addition to the conversion of the functional groups, the degree of polymerization, and the number average molecular weight we are interested in the distribution of chain lengths,  $n$  (i.e. molecular weights  $M_n$ ).

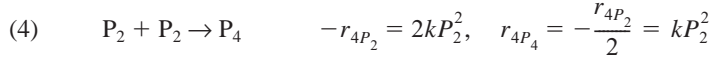
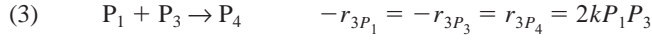
**Example R7-1 Determining the Concentrations of Polymers for Step Polymerization**

Determine the concentration and mole fraction of polymers of chain length  $j$  in terms of initial concentration of ARB,  $M_o$ , the concentration of unreacted functional groups  $M$ , the propagation constant  $k$  and time  $t$ .

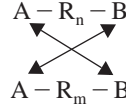
*Solution*

Letting  $P_1 = A-R-B$ ,  $P_2 = A-R_2-B$ , ...,  $P_j = A-R_j-B$  and omitting the water condensation products AB for each reaction we have

	Reaction	Rate Laws
(1)	$2P_1 \rightarrow P_2$	$-r_{1P_1} = 2kP_1^2, \quad r_{1P_2} = -\frac{r_{1P_1}}{2} = kP_1^2$
(2)	$P_1 + P_2 \rightarrow P_3$	$-r_{2P_1} = -r_{2P_2} = r_{2P_3} = 2kP_1P_2$



The factor of 2 in the disappearance term (e.g.,  $-r_{3P_3} = 2kP_1P_3$ ) comes about because there are two ways A and B can react.



The net rate of reaction of  $P_1$ ,  $P_2$  and  $P_3$  for reactions (1) through (4) are

$$r_1 \equiv r_{P_1} = -2kP_1^2 - 2kP_1P_2 - 2kP_1P_3 \quad (RE7.1-1)$$

$$r_2 \equiv r_{P_2} = kP_1^2 - 2kP_1P_2 - 2kP_2^2 \quad (RE7.1-2)$$

$$r_3 \equiv r_{P_3} = 2kP_1P_2 - 2kP_1P_3 - 2kP_2P_3 \quad (RE7.1-3)$$

If we continue in this way, we would find that the net rate of formation of the  $P_1$  is

$$r_{P_1} = -2kP_1 \sum_{j=1}^{\infty} P_j \quad (RE7.1-4)$$

However, we note that  $\sum_{j=1}^{\infty} P_j$  is just the total concentration of functional groups of

either A or B, which is  $M \left( M = \sum_{j=1}^{\infty} P_j \right)$ .

$$r_{P_1} = -2kP_1M \quad (RE7.1-5)$$

Similarly we can generalize reactions (1) through (4) to obtain the net rate of formation of the  $j$ -mer, for  $j \geq 2$ .

$$r_j = k \sum_{i=1}^{j-1} P_i P_{j-i} - 2kP_jM \quad (RE7.1-6)$$

For a batch reactor the mole balance on  $P_1$  and using Equation (RE7.1-2) to eliminate  $M$  gives

$$\frac{dP_1}{dt} = -2kP_1M = -2kP_1 \frac{M_o}{1 + M_o kt} \quad (RE7.1-7)$$

which solves to

$$P_1 = M_o \left( \frac{1}{1 + M_o kt} \right)^2 \quad (RE7.1-8)$$

Having solved for  $P_1$  we can now use  $r_j$  to solve successively for  $P_j$

$$\frac{dP_2}{dt} = r_2 = kP_1^2 - 2kP_2M \quad (\text{RE7-1.9})$$

$$= kM_o^2 \left( \frac{1}{1 + M_o kt} \right)^4 - 2M_o k \left( \frac{1}{1 + M_o kt} \right) \quad (\text{RE7.10})$$

with  $P_2 = 0$  at  $t = 0$

$$P_2 = M_o \left( \frac{1}{1 + M_o kt} \right)^2 \left( \frac{M_o kt}{1 + M_o kt} \right) \quad (\text{RE7.1-11})$$

Continuing we find that, in general<sup>2</sup>

$$P_j = M_o \left( \frac{1}{1 + M_o kt} \right)^2 \left( \frac{M_o kt}{1 + M_o kt} \right)^{j-1} \quad (\text{RE7.1-12})$$

Recalling  $p = \frac{M_o - M}{M_o}$

$$P_j = M_o (1 - p)^2 p^{j-1} \quad (\text{RE7.1-13})$$

The mole fraction of polymer with a chain length  $j$  is just

$$y_j = \frac{P_j}{M}$$

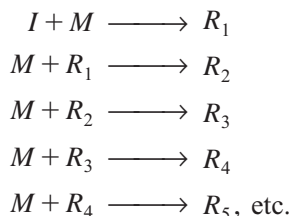
Recalling  $M = M_o(1 - p)$ , we obtain

$$y_j = (1 - p) p^{j-1} \quad (\text{R.1-6})$$

This is the Flory–Schulz distribution. We discuss this distribution further after we discuss chain reactions.

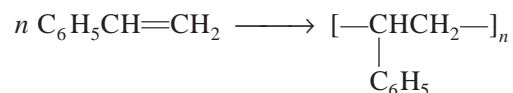
### 7.1.2 Chain Polymerizations Reactions

Chains (i.e., addition) polymerization requires an initiator ( $I$ ) and proceeds by adding one repeating unit at a time.

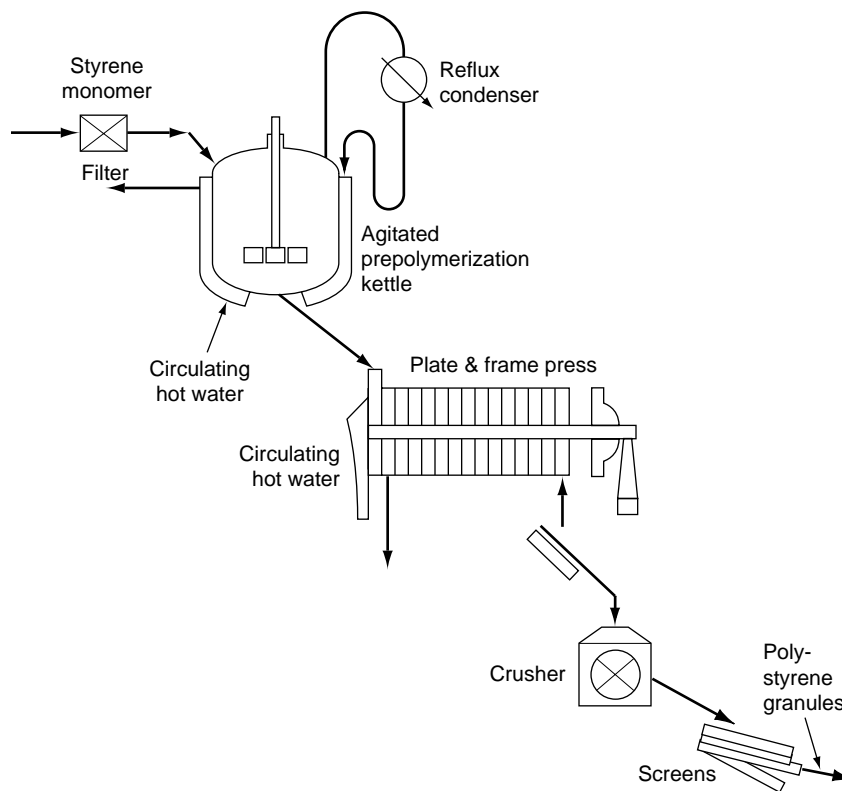


<sup>2</sup> N. A. Dotson, R. Galván, R. L. Lawrence, and M. Tirrell, *Polymerization Process Modeling*, New York: VCH Publishers (1996).

Here the molecular weight in a chain usually builds up rapidly once a chain is initiated. The formation of polystyrene,



is an example of chain polymerization. A batch process to produce polystyrene for use in a number of molded objects is shown in Figure R7.1-2.



**Figure R7.1-2** Batch bulk polystyrene process. (From *Chemical Reactor Theory*, p. 543, Copyright © 1977, Prentice Hall. Reprinted by permission of Prentice Hall, Upper Saddle River, NJ)

We can easily extend the concepts described in the preceding section to polymerization reactions. In this section we show how the rate laws are formulated so that one can use the techniques developed in Chapter 6 for multiple reactions to determine the molecular weight distribution and other properties. In the material that follows we focus on *free-radical polymerization*.

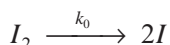
Polystyrene  
Coffee Cups

## R7.1.2.1 Steps in Free-Radical Polymerization

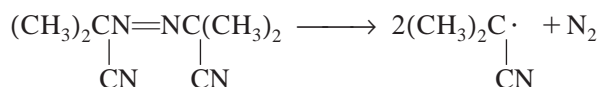
The basic steps in free-radical polymerization are initiation, propagation, chain transfer, and termination.

**Initiation.** Chain polymerization reactions are different because an initiation step is needed to start the polymer chain growth. Initiation can be achieved by adding a small amount of a chemical that decomposes easily to form free radicals. Initiators can be monofunctional and form the same free radical:

Initiation

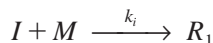


For example, 2,2-azobisisobutyronitrile:

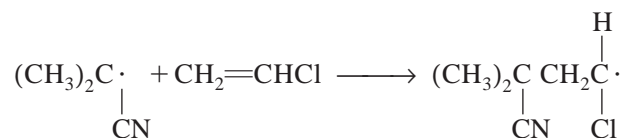


or they can be multifunctional and form different radicals. Multifunctional initiators contain more than one labile group<sup>3</sup> [e.g., 2,5 dimethyl-2,5-bis(benzoylperoxy)hexane].

For monofunctional initiators the reaction sequence between monomer  $M$  and initiator  $I$  is

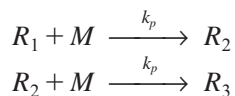


For example,

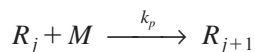


**Propagation.** The propagation sequence between a free radical  $R_1$  with a monomer unit is

Propagation



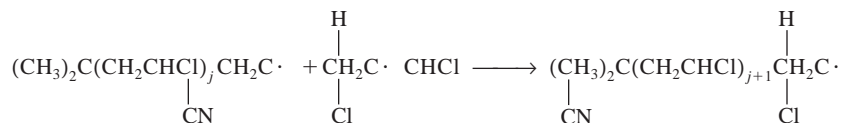
In general,

Assumption of equal  
reactivity

<sup>3</sup> J. J. Kiu and K. Y. Choi, *Chem. Eng. Sci.*, 43, 65 (1988); K. Y. Choi and G. D. Lei, *AIChE J.*, 33, 2067 (1987).



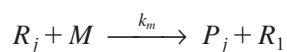
For example,



The specific reaction rates  $k_p$  are assumed to be identical for the addition of each monomer to the growing chain. This is usually an excellent assumption once two or more monomers have been added to  $R_1$  and for low conversions of monomer. The specific reaction rate  $k_i$  is often taken to be equal to  $k_p$ .

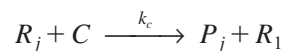
**Chain Transfer.** The transfer of a radical from a growing polymer chain can occur in the following ways:

1. Transfer to a monomer:



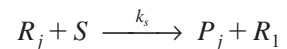
Here a *live* polymer chain of  $j$  monomer units transfers its free radical to the monomer to form the radical  $R_1$  and a *dead* polymer chain of  $j$  monomer units.

2. Transfer to another species:



Chain  
transfer

3. Transfer of the radical to the solvent:



The species involved in the various chain transfer reactions such as  $\text{CCl}_3\cdot$  and  $\text{C}_6\text{H}_5\text{CH}_2\cdot$  are all assumed to have the same reactivity as  $R_1$ . In other words, all the  $R_1$ 's produced in chain transfer reactions are taken to be the same. However, in some cases the chain transfer agent may be too large or unreactive to propagate the chain. The choice of solvent in which to carry out the polymerization is important. For example, the solvent transfer specific reaction rate  $k_s$  is 10,000 times greater in  $\text{CCl}_4$  than in benzene.

The specific reaction rates in chain transfer are all assumed to be independent of the chain length. We also note that while the radicals  $R_1$  produced in each of the chain transfer steps are different, they function in essentially the same manner as the radical  $R_1$  in the propagation step to form radical  $R_2$ .





TABLE R7.1-1

		Rate Law
Initiation:	$I_2 \xrightarrow{k_0} 2I$ $I + M \xrightarrow{k_i} R_1$	$\begin{cases} -r_{I_2} = k_0 I_2 \\ r_{I_f} = 2fk_0 I_2 \\ -r_i = k_i MI \end{cases}$
Propagation:	$R_j + M \xrightarrow{k_p} R_{j+1}$	$-r_j = k_p MR_j$
Chain transfer to: Monomer:	$R_j + M \xrightarrow{k_m} P_j + R_1$	$-r_{mj} = k_m MR_j$
Another species:	$R_j + C \xrightarrow{k_c} P_j + R_1$	$-r_{cj} = k_c CR_j$
Solvent:	$R_j + S \xrightarrow{k_s} P_j + R_1$	$-r_{sj} = k_s SR_j$
Termination: Addition:	$R_j + R_k \xrightarrow{k_{ta}} P_{j+k}$	$-r_{aj} = k_{ta} R_j R_k$
Disproportionation:	$R_j + R_k \xrightarrow{k_{td}} P_j + P_k$	$-r_{dj} = k_{td} R_j R_k$

$$r_{I_f} = 2fk_0(I_2)$$

where  $f$  is the fraction of initiator free radicals successful in initiating chaining and has a typical value in the range 0.2 to 0.7. The rate law for the formation of  $R_1$  in the initiation step is

$$r_{R1} = -r_i = k_i(M)(I) \tag{R7.1-7}$$

Using the PSSH for the initiator free radical,  $I$ , we have

$$r_I = 2fk_0(I_2) - k_i(M)(I) = 0$$

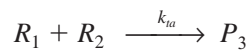
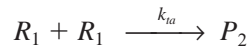
$$(I) = \frac{2fk_0(I_2)}{(M)k_i} \tag{R7.1-8}$$

Then

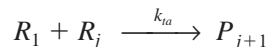
Rate of initiation

$$-r_i = 2fk_0(I_2) \tag{R7.1-9}$$

Before writing the rate of disappearance of  $R_1$ , we need to make a couple of points. First, the radical  $R_1$  can undergo the following termination sequence by addition.



Termination of  $R_1$  In general,



Consequently, the total loss of  $R_1$  radicals in the preceding reactions is found by adding the loss of  $R_1$  radicals in each reaction so that the rate of disappearance by termination addition is given by

$$-r_{1t} = k_{ta}R_1^2 + k_{ta}R_1R_2 + k_{ta}R_1R_3 + \cdots + k_{ta}R_1R_j + \cdots$$

$$-r_{1t} = k_{ta}R_1 \sum_{j=1}^{\infty} R_j$$

Net rate of disappearance of radicals of chain length one

Free radicals usually have concentrations in the range  $10^{-6}$  to  $10^{-8}$  mol/dm<sup>3</sup>. We can now proceed to write the net rate of disappearance of the free radical,  $R_1$ . [ $R_1 \equiv (R_1) \equiv C_{R_1}$ .]

$$\begin{aligned} -r_1 = -r_i + k_p R_1 M + k_{ta} R_1 \sum_{j=1}^{\infty} R_j + k_{td} R_1 \sum_{j=1}^{\infty} R_j \\ - k_m M \sum_{j=2}^{\infty} R_j - k_c C \sum_{j=2}^{\infty} R_j - k_s S \sum_{j=2}^{\infty} R_j \end{aligned} \quad (\text{R7.1-10})$$

Net rate of disappearance of radicals of chain length  $j$

In general, the net rate of disappearance of live polymer chains with  $j$  monomer units (i.e., length  $j$ ) for ( $j \geq 2$ ) is

$$\begin{aligned} -r_j = k_p M (R_j - R_{j-1}) + (k_{ta} + k_{td}) R_j \sum_{i=1}^{\infty} R_i \\ + k_m M R_j + k_c C R_j + k_s S R_j \end{aligned} \quad (\text{R7.1-11})$$

At this point one could use the techniques developed in Chapter 6 on multiple reactions to follow polymerization process. However, by using the PSSH, we can manipulate the rate law into a form that allows closed-form solutions for a number of polymerization reactions.

First, we let  $R^*$  be the total concentration of the radicals  $R_j$ :

$$R^* = \sum_{j=1}^{\infty} R_j \quad (\text{R7.1-12})$$

and  $k_t$  be the termination constant  $k_t = (k_{ta} + k_{td})$ . Next we sum Equation (R7.1-11) over all free-radical chain lengths from  $j = 2$  to  $j = \infty$ , and then add the result to Equation (R7.1-10) to get

$$\sum_{j=1}^{\infty} -r_j = -r_i + k_t(R^*)^2$$

The total rate of termination is just

$$r_t = k_t(R^*)^2 \tag{R7.1-13}$$

Using the PSSH for all free radicals, that is,  $\sum_{j=1}^{\infty} -r_j = 0$ , the total free-radical concentration solves to

Total free-radical concentration

$$R^* = \sqrt{\frac{-r_i}{k_t}} = \sqrt{\frac{2k_0(I_2)f}{k_t}} \tag{R7.1-14}$$

We now use this result in writing the net rate of monomer consumption. As a first approximation we will neglect the monomer consumed by monomer chain transfer. The net rate of monomer consumption,  $-r_M$ , is the rate of consumption by the initiator plus the rate of consumption by all the radicals  $R_j$  in each of the propagation steps ( $r_p$ ).

$$-r_M = -r_i + -r_p = -r_i + k_p M \sum_{j=1}^{\infty} R_j$$

We now use the long-chain approximation (LCA). The LCA is that the rate of propagation is much greater than the rate of initiation:

Long-chain approximation (LCA)

$$\frac{r_p}{r_i} \gg 1$$

Substituting for  $r_p$  and  $r_i$ , we obtain

$$\begin{aligned} \frac{r_p}{r_i} &= \frac{-k_p M R^*}{-k_i M I} = \frac{k_p (2k_0 f(I_2)/k_t)^{1/2}}{k_i (2k_0 f(I_2)/M k_i)} \\ &= \frac{M}{I_2^{1/2}} \sqrt{\frac{k_p^2}{2k_0 f k_t}} \end{aligned}$$

Consequently, we see that the LCA is valid when both the ratio of monomer concentration to initiator concentration and the ratio of  $k_p^2$  to  $(k_0 f k_t)$  are high. Assume that the LCA gives

Rate of  
disappearance  
of monomer

$$-r_M = k_p M \sum_{j=1}^{\infty} R_j = k_p M R^* \quad (\text{R7.1-15})$$

Using Equation (R7.1-14) to substitute for  $R^*$ , the rate of disappearance of monomer is

$$-r_M = k_p M \sqrt{\frac{2k_0(I_2)f}{k_t}} \quad (\text{R7.1-16})$$

The rate of disappearance of monomer,  $-r_M$ , is also equal to the rate of propagation,  $r_p$ :

$$r_p = -r_M$$

Finally, the net rate of formation of dead polymer  $P_j$  by addition is

$$r_{P_j} = 0.5k_{ta} \sum_{k=1}^{k=j-1} R_k R_{j-k} \quad (\text{R7.1-17})$$

The rate of formation of all dead polymers is

$$r_P = \sum_{j=1}^{\infty} r_{P_j}$$

$$r_P = 0.5k_{ta}(R^*)^2$$

Rate of formation of  
dead polymers

### R7.1.3 Modeling a Batch Polymerization Reactor

To conclude this section we determine the concentration of monomer as a function of time in a batch reactor. A balance on the monomer combined with the LCA gives

$$-\frac{dM}{dt} = k_p M \sum R_j = k_p M R^* = k_p M \sqrt{\frac{2k_0(I_2)f}{k_t}} \quad (\text{R7.1-18})$$

A balance on the initiator  $I_2$  gives

$$-\frac{dI_2}{dt} = k_0 I_2$$

Initiator  
balance

Integrating and using the initial condition  $I_2 = I_{20}$  at  $t = 0$ , we obtain the equation of the initiator concentration profile:

$$I_2 = I_{20} \exp(-k_0 t) \quad (\text{R7.1-19})$$

Substituting for the initiator concentration in Equation (R7.1-18), we get

$$\frac{dM}{dt} = -k_p M \left( \frac{2k_0 I_{20} f}{k_t} \right)^{1/2} \exp\left(-\frac{k_0}{2} t\right) \quad (\text{R7.1-20})$$

Integration of Equation (R7.1-20) gives

$$\ln \frac{M}{M_0} = \left( \frac{8k_p^2 f I_{20}}{k_0 k_t} \right)^{1/2} \left[ \exp\left(-\frac{k_0}{2} t\right) - 1 \right] \quad (\text{R7.1-21})$$

One notes that as  $t \longrightarrow \infty$ , there will still be some monomer left unreacted. Why?

A plot of monomer concentration is shown as a function of time in Figure R7-5 for different initiator concentrations.

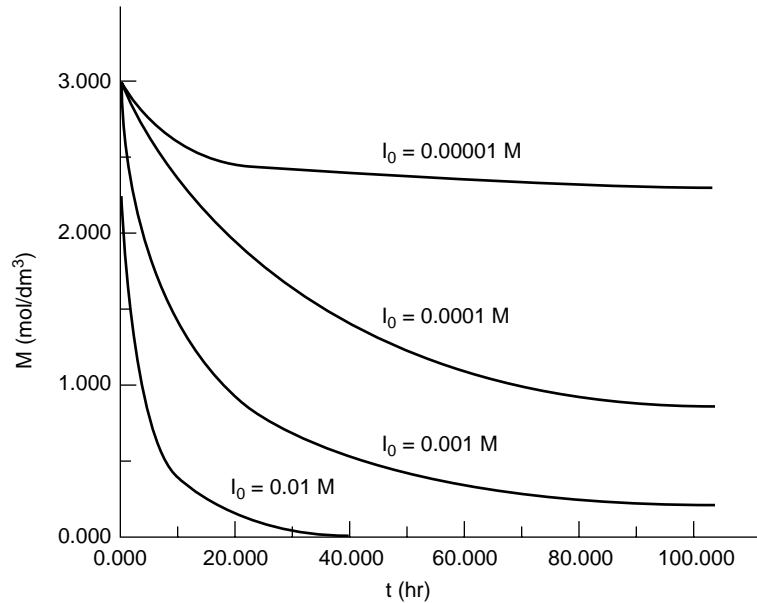


Figure R7.1-3 Monomer concentration as a functional time.

The fractional conversion of a monofunctional monomer is

$$X = \frac{M_0 - M}{M_0}$$

We see from Figure R7.1-3 that for an initiator concentration 0.001 M, the monomer concentration starts at 3 M and levels off at a concentration of 0.6 M, corresponding to a maximum conversion of 80%.

Now that we can determine the monomer concentration as a function of time, we will focus on determining the distribution of dead polymer,  $P_j$ . The concentrations of dead polymer and the molecular weight distribution can be derived in the following manner.<sup>5</sup> The probability of propagation is

$$\beta = \frac{\text{Rate of propagation}}{\text{Rate of propagation} + \text{Rate of termination}} = \frac{r_p}{r_p + r_t}$$

$$\beta = \frac{k_p MR^*}{k_p MR^* + k_s SR^* + k_m MR^* + k_c CR^* + k_t (R^*)^2}$$

Simplifying

$$\beta = \frac{k_p M}{k_p M + k_m M + k_c C + k_s S + \sqrt{2k_t k_\alpha f(I_2)}} \quad (\text{R7.1-22})$$

In the absence of chain transfer, the monomer concentration,  $M$ , can be determined from Equation (R7.1-22) and concentration of initiator,  $I_2$ , from Equation (R7.1-19). Consequently we have  $\beta$  as a function of time. We now set

$$\beta = p$$

to use in the Flory distribution.

It can be shown that in the absence of termination by combination, the mole fractions  $y_j$  and weight fraction  $w_j$  are exactly the same as those for step polymerization. That is, we can determine the dead polymer concentrations and molecular weight distribution of dead polymer in free radical polymerization for the Flory distributions. For example, the concentration of dead polymer of chain length  $n$  is

$$P_n = y_n \left( \sum_{j=2}^{\infty} P_j \right) = \left( \sum_{j=2}^{\infty} P_j \right) (1-p) p^{n-1}$$

where  $\left( \sum_{n=2}^{\infty} P_n \right)$  is the total dead polymer concentration and

$$y_n = (1-p) p^{n-1} \quad (\text{R7.1-6})$$



which is the same as the mole fraction obtained in step polymerization, i.e. Equation (R7.1-6).

If the termination is only by disproportionation, the dead polymer  $P_j$  will have the same distribution as the live polymer  $R_j$ .

<sup>5</sup> E. J. Schork, P. B. Deshpande, and K. W. Leffew, *Control of Polymerization Reactor* (New York: Marcel Dekker, 1993).



We will discuss the use of the Flory equation after we discuss molecular weight distributions.

#### R7.1.4 Molecular Weight Distribution

Although it is of interest to know the monomer concentration as a function of time (Figure R7.1-3), it is the polymer concentration, the average molecular weight, and the distribution of chain lengths that give a polymer its unique properties. Consequently, to obtain such things as the average chain length of the polymer, we need to determine the molecular weight distribution of radicals (live polymer),  $R_j$ , and then dead polymers  $P_j$  as well as the molecular weight distribution. Consequently, we need to quantify these parameters. A typical distribution of chain lengths for all the  $P_j$  ( $j = 1$  to  $j = n$ ) is shown in Figure R7.1-4. Gel permeation chromatography is commonly used to determine the molecular weight distribution. We will now explore some properties of these distributions. If one divides the  $y$ -axis by the total concentration of polymer (i.e.,  $\sum P_j$ ), that axis simply becomes the mole fraction of polymer with  $j$  repeating units embedded in it (i.e.,  $y_j$ ).

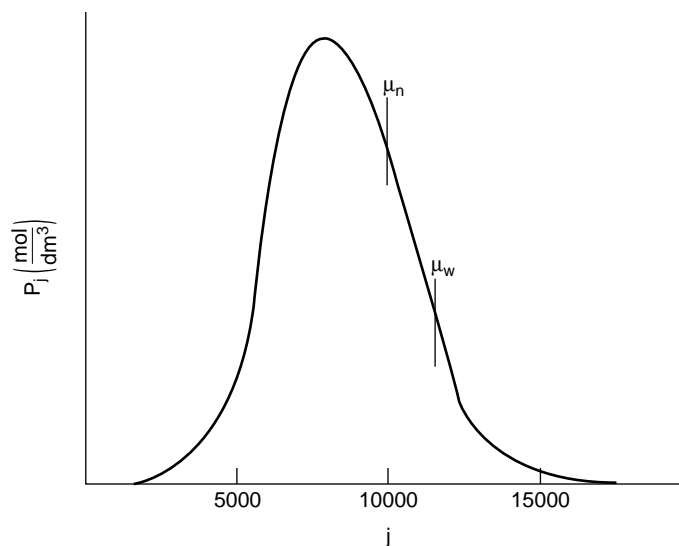


Figure R7.1-4 Distribution of concentration of dead polymers of length  $j$ .

**Properties of the Distribution.** From the distribution of molecular weights of polymers, we can use some of the parameters to quantify the distribution shown in Figure R7.1-4. Their relationships follow.

1. The moments of the distribution

$$\lambda_n = \sum_{j=1}^{\infty} j^n P_j \quad (\text{R7.1-23})$$

2. The zeroth moment is just the total polymer concentration:

$$\lambda_0 = \sum_{j=1}^{\infty} P_j = P \quad (\text{R7.1-24})$$

3. The first moment is related to the total number of monomer units (i.e., mass):

$$\lambda_1 = \sum_{j=1}^{\infty} j P_j \quad (\text{R7.1-25})$$

4. The first moment divided by the zeroth moment gives the *number-average chain length* (NACL),  $\mu_n$ :

$$\text{NACL} = \mu_n = \frac{\lambda_1}{\lambda_0} = \frac{\sum j P_j}{\sum P_j} \quad (\text{R7.1-26})$$

For step-reaction polymerization, the NACL is also sometimes referred to as the *degree of polymerization*. It is the average number of structural units per chain and can also be calculated from

$$\mu_n \equiv \bar{X}_n = \frac{1}{1-p}$$

5. The number-average molecular weight is

$$\bar{M}_n = \mu_n \bar{M}_s \quad (\text{R7.1-27})$$

where  $\bar{M}_s$  is the average molecular weight of the structural units. In chain polymerization, the average molecular weight of the structural unit is just the molecular weight of the monomer,  $M_M$ .

6. The second moment gives emphasis to the larger chains:

$$\lambda_2 = \sum_{j=1}^{\infty} j^2 P_j \quad (\text{R7.1-28})$$

7. The mass per unit volume of each polymer species is just  $\bar{M}_s j P_j$ . The weight (mass) average chain length (WACL) is just the ratio of moment 2 to moment 1:

$$\text{WACL} = \frac{\lambda_2}{\lambda_1} = \mu_w = \frac{\sum j^2 P_j}{\sum j P_j} \quad (\text{R7.1-29})$$

8. The weight-average molecular weight is

$$\bar{M}_w = \bar{M}_n \mu_w \tag{R7.1-30}$$

9. The number-average variance is

$$\sigma_n^2 = \frac{\lambda_2}{\lambda_0} - \left( \frac{\lambda_1}{\lambda_0} \right)^2 \tag{R7.1-31}$$

10. The polydispersity index ( $D$ ) is

$$D = \frac{\mu_w}{\mu_n} = \frac{\lambda_0 \lambda_2}{\lambda_1^2} \tag{R7.1-32}$$

A polydispersity of 1 means that the polymers are all the same length and a polydispersity of 3 means that there is a wide distribution of polymer sizes. The polydispersity of typical polymers ranges from 2 to 10.

**Example R7-2 Parameters Distributions of Polymers**

A polymer was fractionated into the following six fractions:

Fraction	Molecular Weight	Mole Fraction
1	10,000	0.1
2	15,000	0.2
3	20,000	0.4
4	25,000	0.15
5	30,000	0.1
6	35,000	0.05

The molecular weight of the monomer was 25 Daltons.

Calculate NA<sub>CL</sub>, WA<sub>CL</sub>, the number variance, and the polydispersity.

*Solution*

MW	$j$	$y$	$jy$	$j^2y$
10,000	400	0.1	40	16,000
15,000	600	0.2	120	72,000
20,000	800	0.4	320	256,000
25,000	1000	0.15	150	150,000
30,000	1200	0.1	120	144,000
35,000	1400	0.05	70	98,000
			820	736,000

The number-average chain length, Equation (R7.1-26), can be rearranged as

$$\begin{aligned} \text{NACL} &= \frac{\sum j P_j}{\sum P_j} = \sum j \frac{P_j}{\sum P_j} = \sum j y_j \\ &= \mu_n = 820 \text{ structural (monomer) units} \end{aligned} \quad (\text{RE7-2.1})$$

The number-average molecular weight is

$$\bar{M}_n = \mu_n M_M = 820 \times 25 = 20,500$$

Recalling Equation (7-50) and rearranging, we have

$$\begin{aligned} \text{WACL} = \mu_w &= \frac{\sum j^2 P_j}{\sum j P_j} = \frac{\sum j^2 (P_j / \sum P_j)}{\sum j (P_j / \sum P_j)} \\ &= \frac{\sum j^2 y}{\sum j y} = \frac{736,000}{820} = 897.5 \text{ monomer units.} \end{aligned} \quad (\text{RE7-2.2})$$

The mass average molecular weight is

$$\bar{M}_w = M_M \mu_w = 25 \times 897.5 = 22,434$$

The variance is

$$\begin{aligned} \sigma_n^2 &= \frac{\lambda_2}{\lambda_0} - \left( \frac{\lambda_1}{\lambda_0} \right)^2 = 736,000 - (820)^2 \\ &= 63,600 \\ \sigma_n &= 252.2 \end{aligned} \quad (\text{RE7-2.3})$$

The polydispersity index  $D$  is

$$D = \frac{\bar{M}_w}{\bar{M}_n} = \frac{22,434}{20,500} = 1.09 \quad (\text{RE7-2.4})$$

**Flory Statistics of the Molecular Weight Distribution.** The solution to the complete set ( $j = 1$  to  $j = 100,000$ ) of coupled-nonlinear ordinary differential equations needed to calculate the distribution is an enormous undertaking even with the fastest computers. However, we can use probability theory to estimate the distribution. This theory was developed by Nobel laureate Paul Flory. We have shown that for step polymerization and for free-radical polymerization in which termination is by disproportionation the mole fraction of polymer with chain length  $j$  is

Flory mole fraction  
distribution

$$y_j = (1 - p) p^{j-1} \quad (\text{R7.1-6})$$

In terms of the polymer concentration

$$P_j = y_j M = M_o (1 - p)^2 p^{j-1} \quad (\text{R7.1-33})$$

The number-average molecular weight

Termination other  
than by combination

$$\begin{aligned}\bar{M}_n &= \sum_{j=1}^{\infty} y_j M_j = \sum_{j=1}^{\infty} y_j j \bar{M}_s \\ &= \bar{M}_s (1-p) \sum_{j=1}^{\infty} j p^{j-1} = \bar{M}_s (1-p) \frac{1}{(1-p)^2}\end{aligned}$$

and we see that the number-average molecular weight is identical to that given by Equation (R7-1.5)

$$\bar{M}_n = \bar{X}_n \bar{M}_s = \frac{\bar{M}_s}{1-p} \quad (\text{R7.1-5})$$

The weight fraction of polymer of chain length  $j$  is

$$\begin{aligned}w_j &= \frac{P_j M_j}{\sum_{j=1}^{\infty} P_j M_j} = \frac{P_j j \bar{M}_s}{\bar{M}_s \sum_{j=1}^{\infty} j P_j} = \frac{j P_j}{\sum_{j=1}^{\infty} j P_j} \\ w_j &= \frac{j(1-p)^2 p^{j-1}}{(1-p)^2 \underbrace{\sum_{j=1}^{\infty} j p^{j-1}}_1} \\ &= \frac{j(1-p)^2 p^{j-1}}{(1-p)^2}\end{aligned}$$

Flory weight  
fraction distribution

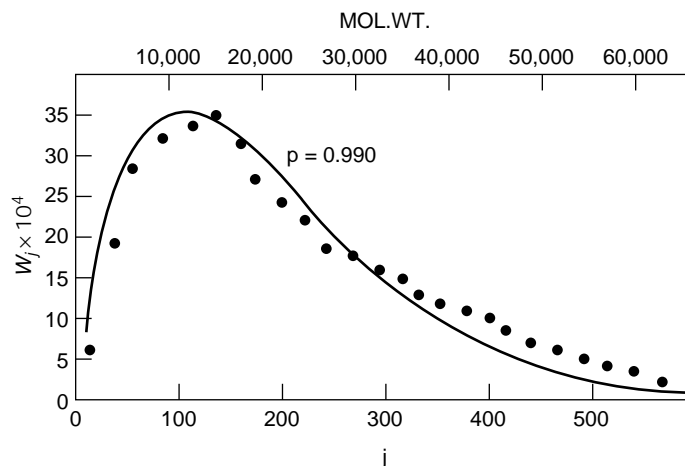
$$w_j = j(1-p)^2 p^{j-1} \quad (\text{R7-1-35})$$

The weight fraction is shown in Figure R7-7 as a function of chain length.  
The weight average molecular weight is

$$\bar{M}_w = \sum_{j=1}^{\infty} w_j M_j = \bar{M}_s \sum_{j=1}^{\infty} j w_j$$

$$\bar{M}_w = \bar{M}_s \frac{(1+p)}{(1-p)}$$

These equations will also apply for AR<sub>1</sub>A and BR<sub>2</sub>B polymers if the monomers are fed in stoichiometric portions. Equations (R7.1-33) through (R7.1-35) also can be used to obtain the distribution of concentration and molecular weights for radical reactions where termination is by chain transfer or by disproportionation if by  $p$  is given by Equation (R7.1-22). However, they cannot be used for termination by combination.



**Figure 7-1** Molecular distribution. [Adapted from G. Tayler, *Journal of the American Chemical Society*, 69, p. 638, 1947. Reprinted by permission.]

Figure R7.1-5 compares the molecular weight distribution for poly(hexamethylene adipamide) calculated from Flory's most probable distribution<sup>6</sup> [Equation (R7.1-35)] for a conversion of 99% with the experimental values obtained by fractionation. One observes that the comparison is reasonably favorable.

For termination by combination, the mole fraction of polymers with  $j$  repeating units is

Termination by  
combination

$$y_j = (j-1)(1-p)^2 p^{j-2} \quad (\text{R7.1-36})$$

while the corresponding weight fraction is

$$w_j = \frac{1}{2} j (1-p)^3 (j-1) p^{j-2} \quad (\text{R7.1-37})$$

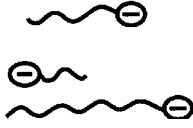
where  $p$  is given by Equation (R7.1-22) [i.e.,  $p = B$ ].

### 7.1.5 Anionic Polymerization

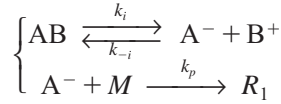
To illustrate the development of the growth of live polymer chains with time, we will use anionic polymerization. In anionic polymerization, initiation takes place by the addition of an anion, which is formed by dissociation of strong bases such as hydroxides, alkylolithium, or alkoxides that react with the monomer to form an active center,  $R_1^-$ . The dissociation of the initiator is very rapid and essentially at equilibrium. The propagation proceeds by the addition of monomer units to the end of the chain with the negative charge. Because the live ends of the polymer are negatively charged, termination can occur only by charge transfer to either the monomer or the solvent or by the addition of a

<sup>6</sup> P. J. Flory, *Principles of Polymer Chemistry*, (Ithaca, N.Y.: Cornell University Press, 1953).

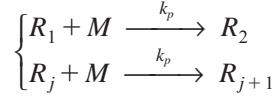
neutralizing agent to the solution. Let  $R_j^- \equiv R_j$  and the sequence of reactions for anionic polymerization becomes



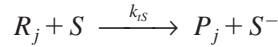
Initiation:



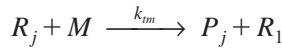
Propagation:



Chain transfer to solvent:



Transfer to monomer:

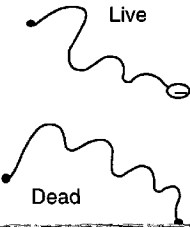


Batch reactor calculations

The corresponding combined batch reactor mole balances and rate laws are:

For the initiator:

$$\frac{dA^-}{dt} = k_i AB - k_{-i} A^- B^+ - k_p A^- M$$



For the **live** polymer:

$$\begin{aligned} \frac{dR_1}{dt} &= k_p A^- M - k_p R_1 M + k_{tm} M \sum_{j=1}^n R_j \\ \frac{dR_j}{dt} &= k_p (R_{j-1} - R_j) M - k_{tS} S R_j - k_{tm} M R_j \end{aligned}$$

For the **dead** polymer:

$$\frac{dP_j}{dt} = k_{tS} S R_j + k_{tm} M R_j$$

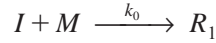
“Houston, we have a problem!”  
—Apollo 13

In theory one could solve this coupled set of differential equations. However, this process is very tedious and almost insurmountable if one were to carry it through for molecular weights of tens of thousands of Daltons, even with the fastest of computers. Fortunately, for some polymerization reactions there is a way out of this dilemma.

**Some Approximations.** To solve this set of coupled ODEs, we need to make some approximations. There are a number of approximations that could be made, but we are going to make ones that allow us to obtain solutions that provide insight on how the live polymerization chains grow and dead polymer

chains form. First, we neglect the termination terms ( $k_{ts}SR_j$  and  $k_{tm}R_jM$ ) with respect to propagation terms in the mole balances. This assumption is an excellent one as long as the monomer concentration remains greater than the live polymer concentration.

For this point, we can make several assumptions. We could assume that the initiator ( $I = A^-$ ) reacts slowly to form  $R_1$  (such is the case in Problem CDP7-P<sub>B</sub>).



$$\text{Initiation} \quad \frac{dR_1}{dt} = k_0MI - k_pR_1M$$

Another assumption is that the rate of formation of  $R_1$  from the initiator is instantaneous and that at time  $t = 0$  the initial concentration of live polymer is  $R_{10} = I_0$ . This assumption is very reasonable for this initiation mechanism. Under the latter assumption the mole balances become

$$\text{Propagation} \quad \frac{dR_1}{dt} = -k_pMR_1 \quad (\text{R7.1-38})$$

$$\frac{dR_2}{dt} = k_pM(R_1 - R_2) \quad (\text{R7.1-39})$$

$$\vdots$$

$$\frac{dR_j}{dt} = k_p(R_{j-1} - R_j)M \quad (\text{R7.1-40})$$

For the live polymer with the largest chain length that will exist, the mole balance is

$$\frac{dR_n}{dt} = k_pMR_{n-1} \quad (\text{R7.1-41})$$

If we sum Equations (R7-1.38) through (R7-1.41), we find that

$$\sum_{j=1}^n \frac{dR_j}{dt} = \frac{dR^*}{dt} = 0$$

Consequently, we see the total free live polymer concentration is a constant at  $R^* = R_{10} = I_0$ .

There are a number of different techniques that can be used to solve this set of equations, such as use of Laplace transforms, generating functions, statistical methods, and numerical and analytical techniques. We can obtain an analytical solution by using the following transformation. Let

$$d\Theta = k_pM dt \quad (\text{R7.1-42})$$



Then Equation (R7.1-38) becomes

$$\frac{dR_1}{d\Theta} = -R_1 \quad (\text{R7.1-43})$$

Using the initial conditions that when  $t = 0$ , then  $\Theta = 0$  and  $R_1 = R_{10} = I_0$ , Equation (R7.1-43) solves to

$$R_1 = I_0 e^{-\Theta} \quad (\text{R7.1-44})$$

Next we transform Equation (R7.1-39) to

$$\frac{dR_2}{d\Theta} = R_1 - R_2$$

and then substitute for  $R_1$ :

$$\frac{dR_2}{d\Theta} + R_2 = I_0 e^{-\Theta}$$

With the aid of the integrating factor,  $e^\Theta$ , along with the initial condition that at  $t = 0$ ,  $\Theta = 0$ ,  $R_2 = 0$ , we obtain

$$R_2 = I_0 (\Theta e^{-\Theta})$$

In a similar fashion,

$$R_3 = I_0 \left( \frac{\Theta^2}{2 \cdot 1} e^{-\Theta} \right)$$

$$R_4 = I_0 \left( \frac{\Theta^3}{3 \cdot 2 \cdot 1} e^{-\Theta} \right)$$

In general,

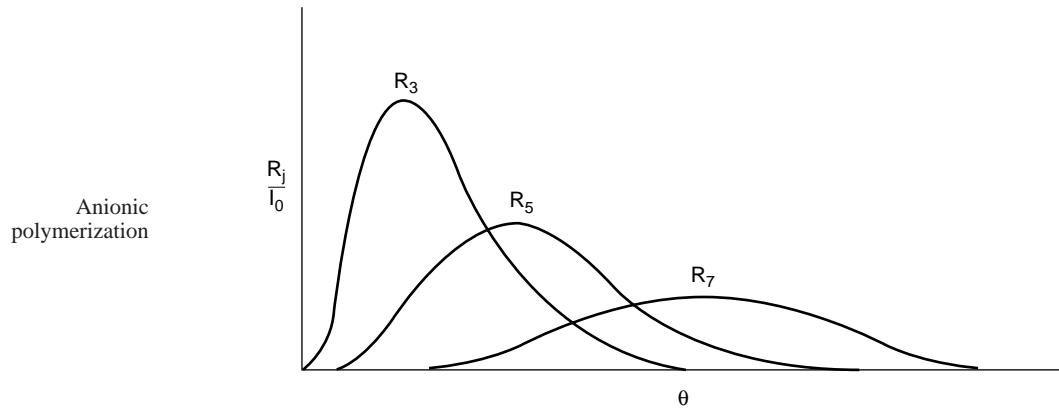
Concentration of  
live polymer of  
chain length  $j$

$$R_j = I_0 \frac{\Theta^{j-1}}{(j-1)!} e^{-\Theta} \quad (\text{R7.1-45})$$

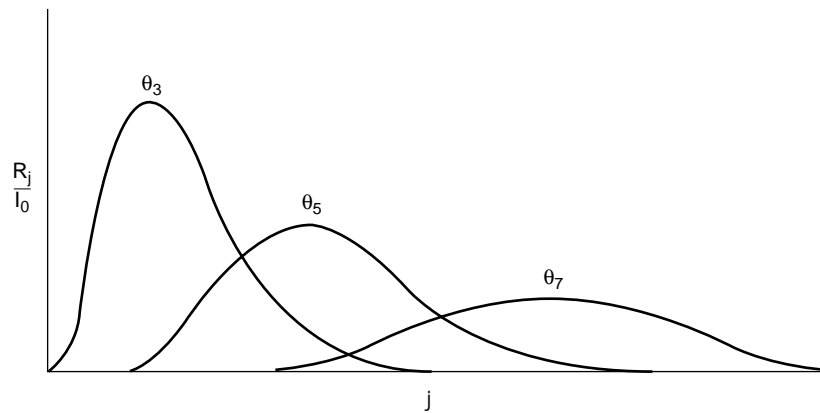
The live polymer concentrations are shown as a function of time and of chain length and time in Figures R7.1-6 and R7.1-7, respectively.

Neglecting the rate of chain transfer to the monomer with respect to the rate of propagation, a mole balance on the monomer gives

$$\frac{dM}{dt} = -k_p M \sum_{i=1}^n R_i = -k_p M R_{10} = -k_p M I_0 \quad (\text{R7.1-46})$$



**Figure R7.1-6** Live polymer concentration as a function of scaled time.



**Figure R7.1-7** Live polymer concentration as a function of chain length at different scaled times.

Knowing the initial monomer concentration,  $M_0$ , we can solve for the monomer concentration at any time:

$$M = M_0 e^{-I_0 k_p t} \quad (\text{R7.1-47})$$

We can also evaluate the scaled time  $\Theta$ :

$$\begin{aligned} \Theta &= \int_0^t k_p M dt = M_0 k_p \int_0^t e^{-I_0 k_p t} dt \\ &= + \frac{M_0 k_p}{k_p I_0} (e^{-I_0 k_p t}) \Big|_0^t \end{aligned}$$

Relationship  
between the scaled  
time,  $\Theta$ , and real  
time  $t$

$$\boxed{\Theta = \frac{M_0}{I_0} (1 - e^{-I_0 k_p t})} \quad (\text{R7.1-48})$$

One can now substitute Equation (R7.1-48) into Equation (R7.1-45) to determine the live polymer concentrations at any time  $t$ .

For anionic polymerization, termination can occur by neutralizing the live polymer  $R_j$  to  $P_j$ .

**Example R7-3 Calculating the Distribution Parameters from Analytical Expressions for Anionic Polymerization**

Calculate  $\mu_n$ ,  $\mu_m$ , and  $D$  for the live polymer chains  $R_j$ .

*Solution*

$$R_j = I_0 \frac{\Theta^{j-1}}{(j-1)!} e^{-\Theta} \quad (\text{R7.1-45})$$

We recall that the zero moment is just the total radical concentrations:

$$\lambda_0 = \sum_{j=1}^{\infty} R_j = I_0 \quad (\text{RE7-3.1})$$

The first moment is

$$\lambda_1 = \sum_{j=1}^{\infty} jR_j = I_0 \sum_{j=1}^{\infty} \frac{j\Theta^{j-1}e^{-\Theta}}{(j-1)!} \quad (\text{RE7-3.2})$$

Let  $k = j - 1$ :

$$\lambda_1 = I_0 \sum_{k=0}^{\infty} (k+1) \frac{\Theta^k e^{-\Theta}}{k!} \quad (\text{RE7-3.3})$$

Expanding the  $(k + 1)$  term gives

$$\lambda_1 = I_0 \left( \sum_{k=0}^{\infty} \frac{\Theta^k e^{-\Theta}}{k!} + \sum_{k=0}^{\infty} \frac{k\Theta^k e^{-\Theta}}{k!} \right) \quad (\text{RE7-3.4})$$

Recall that

$$\sum_{k=0}^{\infty} \frac{\Theta^k}{k!} = e^{+\Theta} \quad (\text{RE7-3.5})$$

Therefore,

$$\lambda_1 = I_0 \left( 1 + e^{-\Theta} \sum_{k=0}^{\infty} \frac{k\Theta^k}{k!} \right) \quad (\text{RE7-3.6})$$

Let  $l = k - 1$ :

$$\lambda_1 = I_0 \left( 1 + e^{-\Theta} \Theta \sum_{l=0}^{\infty} \frac{\Theta^l}{l!} \right) = I_0 (1 + e^{-\Theta} \Theta e^{\Theta}) \quad (\text{RE7-3.7})$$

The first moment is

$$\lambda_1 = I_0 (1 + \Theta) \quad (\text{RE7-3.8})$$

The number-average length of growing polymer radical (i.e., live polymer) is

$$\mu_n = \frac{\lambda_1}{\lambda_0} = 1 + \Theta \quad (\text{RE7-3.9})$$

$$\lambda_2 = I_0 \sum_{j=0}^{\infty} j^2 R_j = I_0 \sum_{j=0}^{\infty} j^2 \frac{\Theta^{j-1}}{(j-1)!} \quad (\text{RE7-3.10})$$

Realizing that the  $j = 0$  term in the summation is zero and after changing the index of the summation and some manipulation, we obtain

$$\lambda_2 = I_0 (1 + 3\Theta + \Theta^2) \quad (\text{RE7-3.11})$$

$$\mu_w = \frac{\lambda_2}{\lambda_1} = \frac{1 + 3\Theta + \Theta^2}{1 + \Theta} \quad (\text{RE7-3.12})$$

$$D = \frac{\mu_w}{\mu_n} = \frac{1 + 3\Theta + \Theta^2}{(1 + \Theta)^2} \quad (\text{RE7-3.13})$$

Plots of  $\mu_n$  and  $\mu_w$  along with the polydispersity,  $D$ , are shown in Figure RE7-3.1.

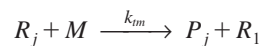
We note from Equation (R7.1-48) that after a long time the maximum value of  $\Theta$ ,  $\Theta_M$ , will be reached:

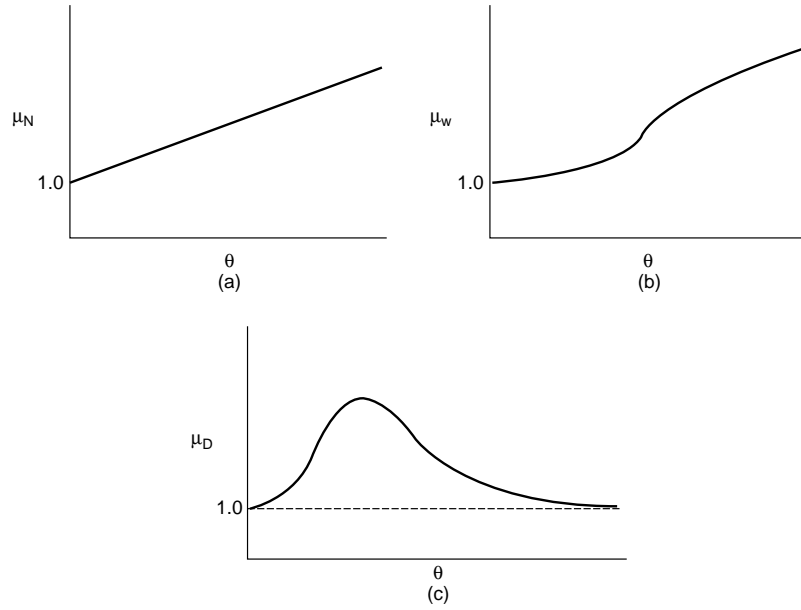
$$\Theta_M = \frac{M_0}{I_0}$$

The distributions of live polymer species for an anionic polymerization carried out in a CSTR are developed in Problem P7-19.

**Example R7-4 Determination of Dead Polymer Distribution When Transfer to Monomer Is the Main Termination Mechanism**

Determine an equation for the concentration of polymer as a function of scaled time. After we have the live polymer concentration as a function of time, we can determine the dead polymer concentration as a function of time. If transfer to monomer is the main mechanism for termination,





**Figure RE7-3.1** Moments of live polymer chain lengths: (a) number-average chain length; (b) weight-average chain length; (c) polydispersity.

Anionic polymerization

A balance of dead polymer of chain length  $j$  is

$$\frac{dP_j}{dt} = k_{tm} R_j M \tag{RE7-4.1}$$

As a *very* first approximation, we neglect the rate of transfer to dead polymer from the live polymer with respect to the rate of propagation:

$$(k_{tm} M R_j \ll k_p M R_j)$$

so that the analytical solution obtained in Equation (R7.1-4.2) can be used. Then

$$\frac{dP_j}{d\Theta} = \frac{k_{tm}}{k_p} R_j = \frac{k_{tm}}{k_p} I_0 \frac{\Theta^{j-1} e^{-\Theta}}{(j-1)!} \tag{RE7-4.2}$$

Integrating, we obtain the dead polymer concentrations as a function of scaled time from CRC Mathematical Tables integral number 521:

$$= \frac{k_{tm}}{k_p} I_0 \left[ 1 - e^{-\Theta} \sum_{n=0}^{j-1} \frac{\Theta^{j-1-n}}{(j-1-n)!} \right] \tag{RE7-4.3}$$

We recall that the scaled time  $\Theta$  can be calculated from

$$\Theta = \frac{M_0}{I_0} (1 - e^{-I_0 k_p t'})$$

In many instances termination of anionic polymerization is brought about by adding a base to neutralize the propagating end of the polymer chain.

**Other Useful Definitions.** The number-average kinetic chain length,  $V_N$ , is the ratio of the rate of the propagation rate to the rate of termination:

$$V_N = \frac{r_p}{r_t} \quad (\text{R7.1-49})$$

Most often, the PSSH is used so that  $r_t = r_i$ :

$$V_N = \frac{r_p}{r_i}$$

The long-chain approximation holds when  $V_N$  is large.

Excellent examples that will reinforce and expand the principles discussed in this section can be found in Holland and Anthony,<sup>7</sup> and the reader is encouraged to consult this text as the next step in studying polymer reaction engineering.

For the free-radical polymerization in which termination is by transfer to the monomer or a chain transfer agent and by addition, the kinetic chain length is

$$V_N = \frac{r_p}{r_t} = \frac{k_p MR^*}{k_{tm} MR^* + k_t (R^*)^2 + k_{ct} R^* C} = \frac{k_p M}{k_{tm} M + k_t R^* + k_{ct} C}$$

$$\boxed{V_N = \frac{k_p M}{k_{tm} M + (2k_t k_o I_2 f)^{1/2} + k_{ct} C}} \quad (\text{R7-1.50})$$

For termination by combination

$$\bar{M}_n = 2V_N M_M$$

and for termination by disproportionation

$$\bar{M}_n = V_N M_M$$

<sup>7</sup> C. D. Holland and R. G. Anthony, *Fundamentals of Chemical Reaction Engineering*, 2nd ed. (Upper Saddle River, N.J.: Prentice Hall, 1977) p. 457.