R7.1 Polymerization

10^{11} 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 repeat- ing units of ethylene are used to make electrical insulation:

$$nCH_2—CH_2 \longrightarrow —[CH_2—CH_2—]_n$$

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).

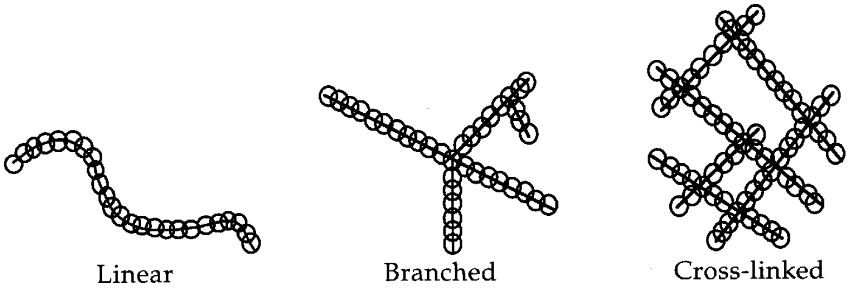

Figure R7-1-1 Types of polymer chains.

Homopolymers are polymers consisting of a single repeating unit, such as [—CH_2—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 polyfunc- tional monomers, while chain reactions require the presence of an initiator.

$$n\,HO\overbrace{R_1}^{\text{Unit 1}}OH \quad n\,\overset{\text{Unit 2}}{HOOCR_2COOH} \longrightarrow HO\,\underbrace{(\overbrace{R_1}^{\text{Unit 1}}\overset{\text{Unit 2}}{OOCR_2COO})_n}_{\text{Repeating Unit}}\,H \quad (2n \quad 1)\,H_2O$$

$$n\,AR_1A \quad n\,BR_2\,B \longrightarrow A\,(R_1 \quad R_2)_n\,B \quad (2n \quad 1)\,AB$$

Copolymers are polymers made up of two or more repeating units. There are five basic categories of copolymers that have two different repeating units Q and S. They are

Categories of Copolymers

1. *Alternating*: –Q–S–Q–S–Q–S–Q–S–Q–S–
2. *Block*: –Q–Q–Q–Q–Q–S–S–S–S–S–
3. *Random*: –Q–Q–S–Q–S–S–Q–S–S–S–
4. *Graft*: –Q–Q–Q–Q–Q–Q–Q–Q–Q–Q–
   └ S–S–S–S–S–S–
5. *Statistical* (follow certain addition laws)

Examples of each can be found in Young and Lovell.[1]

R7.1.1 Step Polymerization

Step polymerization requires that there is at least a reactive functional group on each end of the monomer that will react with functional groups with other monomers. For example, amino-caproic acid

$$NH_2\text{—}(CH_2)_5\text{—}COOH$$

has an amine group at one end and a carboxyl group at the other. Some common functional groups are —OH , —COOH , —COCl , $\text{—}NH_2$.

In step polymerization the molecular weight usually builds up slowly

$$\text{Dimer}\qquad 2H\overbrace{(NH\text{—}R\text{—}CO)}^{\text{Structural Unit}}OH \longrightarrow H\overbrace{(NH\text{—}R\text{—}CO)_2}^{\text{Repeating Unit}}OH \quad H_2O$$

For the preceding case the structural unit and the repeating unit are the same.

Letting A H, R NH—R_1—CO, and B OH, AB H_2O. We can write the preceding reaction as

$$\begin{array}{lrrcll}
\text{Dimer} & ARB & ARB & \longrightarrow & A\text{—}R_2\text{—}B & AB \\
\text{Trimer} & ARB & A\text{—}R_2\text{—}B & \longrightarrow & A\text{—}R_3\text{—}B & AB \\
\text{Tetramer} & ARB & A\text{—}R_3\text{—}B & \longrightarrow & A\text{—}R_4\text{—}B & AB \\
 & A\text{—}R_2\text{—}B & A\text{—}R_2\text{—}B & \longrightarrow & A\text{—}R_4\text{—}B & AB \\
\text{Pentamer} & ARB & A\text{—}R_4\text{—}B & \longrightarrow & A\text{—}R_5\text{—}B & AB \\
 & A\text{—}R_2\text{—}B & A\text{—}R_3\text{—}B & \longrightarrow & A\text{—}R_5\text{—}B & AB \\
\text{Hexamer} & ARB & A\text{—}R_5\text{—}B & \longrightarrow & A\text{—}R_6\text{—}B & AB \\
 & A\text{—}R_2\text{—}B & A\text{—}R_4\text{—}B & \longrightarrow & A\text{—}R_6\text{—}B & AB \\
 & A\text{—}R_3\text{—}B & A\text{—}R_3\text{—}B & \longrightarrow & A\text{—}R_6\text{—}B & AB
\end{array}$$

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[1] R. J. Young and P. A. Lovell, *Introduction to Polymers*, 2nd ed. (New York: Chapman & Hall, 1991).

etc.

$$\text{overall:}\quad n\,\mathrm{NH_2RCOOH} \longrightarrow \mathrm{H(NHRCO)}_n\,\mathrm{OH} \quad (\mathrm{n} \quad 1)\mathrm{H_2O}$$

$$n\,\mathrm{ARB} \longrightarrow \mathrm{A{—}R_n{—}B} \quad (n \quad 1)\mathrm{AB}$$

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.

$$n\,\mathrm{HO}\overbrace{\mathrm{R_1}}^{\text{Unit 1}}\mathrm{OH} \quad n\,\overbrace{\mathrm{HOOCR_2COOH}}^{\text{Unit 2}} \longrightarrow \mathrm{HO}\,\underbrace{(\overbrace{\mathrm{R_1}}^{\text{Unit 1}}\overbrace{\mathrm{OOCR_2COO}}^{\text{Unit 2}})}_{\text{Repeating Unit}}{}_n\,\mathrm{H} \quad (2n \quad 1)\,\mathrm{H_2O}$$

$$n\,\mathrm{AR_1A} \quad n\,\mathrm{BR_2\,B} \longrightarrow \mathrm{A\,(R_1 \quad R_2)}_n\,\mathrm{B} \quad (2n \quad 1)\,\mathrm{AB}$$

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_1A plus $BR_2\,B$ 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

$$\mathrm{A{—}R_2{—}B} \quad \mathrm{A{—}R_3{—}B} \longrightarrow \mathrm{A{—}R_5{—}B} \quad \mathrm{AB} \quad \mathrm{A{—}R_5{—}}$$
$$\mathrm{B} \quad \mathrm{A{—}R_5{—}B} \longrightarrow \mathrm{A{—}R_{10}{—}B} \quad \mathrm{AB}$$

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

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

M concentration of either A or B functional groups (mol/dm^3)

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

$$\frac{d[A]}{dt} \quad k[A][B] \tag{R7.1-1}$$

For equal molar feed we have

$$[A] \quad [B] \quad M$$

$$\frac{dM}{dt} \quad kM^2$$

$$M \quad \frac{M_o}{1 \quad M_o kt} \tag{R7.1-2}$$

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

$$\frac{1}{1 \quad p} \quad M_o kt \quad 1 \tag{R7.1-3}$$

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

Degree of polymerization

$$\boxed{\overline{X}_n \quad \frac{1}{1 \quad p}} \tag{R7.1-4}$$

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

$$\overline{M}_n \quad \overline{X}_n \overline{M}_s \quad M_{eg}$$

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

$$\boxed{\overline{M}_n \quad \overline{X}_n \overline{M}_s} \tag{R7.1-5}$$

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

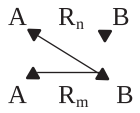
Letting P_1 A—R—B, P_2 A—R_2—B, … ,P_j A—R_j—B and omitting the water condensation products AB for each reaction we have

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

$$(3) \qquad P_1 \quad P_3 \rightarrow P_4 \qquad r_{3P_1} \quad r_{3P_3} \quad r_{3P_4} \quad 2kP_1P_3$$

$$(4) \qquad P_2 \quad P_2 \rightarrow P_4 \qquad r_{4P_2} \quad 2kP_2^2, \quad r_{4P_4} \quad \frac{r_{4P_2}}{2} \quad kP_2^2$$

The factor of 2 in the disappearance term (e.g., $r_{3P_3} \quad 2kP_1P_3$) 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

$$r_1 \quad r_{P_1} \qquad 2kP_1^2 \quad 2kP_1P_2 \quad 2kP_1P_3 \tag{RE7.1-1}$$

$$r_2 \quad r_{P_2} \quad kP_1^2 \quad 2kP_1P_2 \quad 2kP_2^2 \tag{RE7.1-2}$$

$$r_3 \quad r_{P_3} \quad 2kP_1P_2 \quad 2kP_1P_3 \quad 2kP_2P_3 \tag{RE7.1-3}$$

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

$$r_{P_1} \qquad 2kP_1 \quad \underset{j\quad 1}{P_j} \tag{RE7.1-4}$$

However, we note that $\underset{j\quad 1}{P_j}$ is just the total concentration of functional groups of either A or B, which is $M \left(M \quad \underset{j\quad 1}{P_j}\right)$.

$$r_{P_1} \qquad 2kP_1M \tag{RE7.1-5}$$

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

$$\boxed{r_j \quad k \underset{i\quad 1}{\overset{j\quad 1}{\quad}} P_iP_{j\quad i} \quad 2kP_jM} \tag{RE7.1-6}$$

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

$$\frac{dP_1}{dt} \quad 2kP_1M \quad 2kP_1\frac{M_o}{1 \quad M_okt} \tag{RE7.1-7}$$

which solves to

$$P_1 \quad M_o\left(\frac{1}{1 \quad M_okt}\right)^2 \tag{RE7.1-8}$$

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

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

$$kM_o^2\left(\frac{1}{1 \quad M_okt}\right)^4 \quad 2Mk_o\left(\frac{1}{1 \quad M_okt}\right) \qquad \text{(RE7.10)}$$

with $P_2 \quad 0$ at $t \quad 0$

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

Continuing we find that, in general[2]

$$\boxed{P_j \quad M_o\left(\frac{1}{1 \quad M_okt}\right)^2\left(\frac{M_okt}{1 \quad M_okt}\right)^{j \quad 1}} \qquad \text{(RE7.1-12)}$$

Recalling $p \quad \frac{M_o \quad M}{M_o}$

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

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

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

Recalling $M \quad M_o(1 \quad p)$, we obtain

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

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.

$$\begin{aligned} I \quad M &\longrightarrow R_1 \\ M \quad R_1 &\longrightarrow R_2 \\ M \quad R_2 &\longrightarrow R_3 \\ M \quad R_3 &\longrightarrow R_4 \\ M \quad R_4 &\longrightarrow R_5\text{, etc.} \end{aligned}$$

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