

Average lifetime of a radical from generation to its capture by a polymer particle is

$$\frac{\text{concentration of radicals}}{\text{rate of radical generation}} = \frac{10^8 \text{ radicals cm}^{-3}}{10^{13} \text{ radicals cm}^{-3} \text{ s}^{-1}} = 10^{-5} \text{ s}$$

d. Degree of Polymerization

Whenever a primary radical enters an inactive polymer particle, polymerization occurs as it would in normal homogeneous polymerization. In this case the rate of polymerization is given by

$$r_p = k_p [M] \quad (10.2)$$

where k_p is the propagation rate constant. The rate of capture of primary radicals is given by

$$r_c = \frac{r_i}{N} \quad (10.3)$$

where r_i is the rate of generation of primary radicals (in radicals per milliliter per second). From our discussion in the previous section, the growth of a polymer is terminated immediately following the entry of another radical. Therefore the rate of termination should be essentially equal to the rate of capture of primary radicals. The degree of polymerization, in the absence of transfer, should then be the ratio of the rate of polymer growth to the rate of capture of primary radicals.

$$\overline{X}_n = \frac{r_p}{r_c} = \frac{k_p[M]}{r_i/N} \quad (10.4)$$

$$\overline{X}_n = \frac{k_p N [M]}{r_i}$$

Both the degree of polymerization and the rate of polymerization show a direct variation with the number of polymer particles N . However, unlike the rate of polymerization, the degree of polymerization varies indirectly with the rate of generation of primary radicals. This is as should be expected intuitively since the greater the rate of radical generation, the greater the frequency of alternation between polymer particle growth and dormancy and therefore the lower the chain length.

e. The Number of Particles

Equations 10.1 and 10.4 show that the number of polymer particles is crucial in determining both the rate and degree of polymerization. The mechanism of polymer particle formation indicates clearly that the number of polymer particles will depend on the emulsifier, its initial concentration (which determines the number of micelles), and the rate of generation of primary radicals. Smith and Ewart³ have shown that

$$N = k \left(\frac{r_i}{\mu} \right)^{0.4} (a_s [E])^{0.6} \quad (10.5)$$

where k is a constant with a value between 0.4 and 0.53; μ is the rate of increase in volume of a polymer particle, a_s is the interfacial area occupied by an emulsifier molecule; and $[E]$ is the soap or emulsifier concentration. Note that all the units are in cgs. Equations 10.1, 10.4, and 10.5 establish the quantitative

relations between the rate and degree of polymerization and the rate of generation of primary radicals and the emulsifier concentration.

In bulk polymerization, the rate of polymerization depends directly on the rate of initiation. However, the degree of polymerization is inversely related to the rate of initiation. Consequently, an increase in the rate of initiation results in a high rate of polymerization but a decrease in the degree of polymerization. This constitutes a major difference between bulk and emulsion polymerization. In emulsion polymerization, it is possible to increase the rate of polymerization by increasing the concentration of polymer radicals through a high initial emulsifier concentration. If the rate of initiation (generation of primary radicals) is kept constant, the degree of polymerization is increased as well.

f. Deviations from Smith-Ewart Kinetics

The Smith-Ewart kinetic theory of emulsion polymerization is simple and provides a rational and accurate description of the polymerization process for monomers such as styrene, butadiene, and isoprene, which have very limited solubility in water (less than 0.1%). However, there are a number of exceptions. For example, as we indicated earlier, large particles (> 0.1 to 0.5 cm diameter) may and can contain more than one growing chain simultaneously for appreciable lengths of time. Some initiation in, followed by polymer precipitation from the aqueous phase may occur for monomers with appreciable water solubility (1 to 10%), such as vinyl chloride. The characteristic dependence of polymerization rate on emulsifier concentration and hence N may be altered quantitatively by the absorption of emulsifier by these particles. Polymerization may actually be taking place near the outer surface of a growing particle due to chain transfer to the emulsifier.

Emulsion polymerization has a number of unique advantages compared with other polymerization methods. The viscosity of the reaction mass is relatively much less than that of a comparable true solution of polymers in the same molecular weight range. This, coupled with the increased heat capacity due to the presence of water, results in excellent heat transfer and creates a physical state that is much easier to control. Efficient removal of heat of polymerization is one of the factors determining the rate at which polymer may be produced on a commercial scale: efficient heat transfer permits faster rates to be used without overheating the mass and thus avoiding possible polymer degradation. As indicated above, it is possible to obtain both high rates of polymerization and relatively high-molecular-weight polymers through high emulsifier concentration and low initiator concentration. In bulk, solution, or suspension polymerization, rapid polymerization rates can be attained only at the expense of lower-molecular-weight polymers, except in anionic polymerization. In contrast to suspension polymerization, where there is a high risk of agglomeration of polymer particles into an intractable mass, emulsion polymerization is suitable for producing very soft and tacky polymers. Relatively low viscosity with high polymeric solids is advantageous in many applications. The latex product from emulsion polymerization can be used either directly or through master-batching to obtain uniform compounds that find useful applications in coatings, finishes, floor polishes, and paints. Emulsion polymerization, however, has some drawbacks. The large surface area presented by the tiny surfaces of a large number of small particles is ideal for absorption of impurities, thus making the product polymer impure. For example, the presence of water-soluble surface-active agents used in the polymerization process results in some degree of water sensitivity of the polymer itself, while ionic materials such as surfactants and inorganic salts result in poor electrical properties of the final polymer. Only free-radical-type initiators can be used in emulsion polymerization. This precludes the possibility of producing stereoregular polymers by this method.

Example 10.6: From the data given below for the emulsion polymerization of styrene in water at 60°C :

- Calculate the rate of polymerization.
- Show that the number average degree of polymerization \bar{X}_n is 3.52×10^3 .
- Estimate the number of polymer chains in each. Data:

$$k_p = 176 \text{ l mol}^{-1} \text{ s}^{-1}$$

$$r_i = 5 \times 10^{12} \text{ radicals cc}^{-1} \text{ s}^{-1}$$

$$N = 10^{13} \text{ particles cc}^{-1}$$

$$[M] = 10 \text{ M}$$

$$\text{Latex particle size} = 0.10 \mu\text{m}$$

$$\text{Particle density} = 1.2 \text{ g/cc}$$

Solution: a. $R_p = k_p \cdot \frac{N}{2} [M]$

$$k_p = \frac{176 l}{mol \cdot s} = 176 \left(\frac{1000 cc}{1} \right) \left(\frac{1}{mol \cdot s} \right) = 1.76 \times 10^5 \frac{cc}{mol \cdot s}$$

$$N = 10^{13} \frac{particles}{cm^3} = 10^{13} \left(\frac{particle}{cm^3} \right) \left(\frac{1 mol}{6.023 \times 10^{23} particles} \right)$$

$$= 1.66 \times 10^{-11} \frac{mol}{cm^3}$$

$$[M] = 10 M = \frac{10 mol}{1} = 10 \frac{mol}{1} \left(\frac{1 l}{1000 cc} \right) = 10^{-2} mol cc^{-1}$$

$$R_p = \left(\frac{1.76}{2} \times 10^5 \frac{cm^3}{mol \cdot s} \right) \left(1.66 \times 10^{-11} \frac{mol}{cm^3} \right) \left(10^{-2} \frac{mol}{cm^3} \right)$$

$$= 1.46 \times 10^{-8} mol cc^{-1} s^{-1}$$

b. $\overline{X}_n = k_p N \frac{[M]}{r_i}$

$$r_i = 5 \times 10^{-12} \frac{radicals}{cm^3 s} \left(\frac{1 mol}{6.023 \times 10^{23} radicals} \right)$$

$$= 8.30 \times 10^{-12} \frac{mol}{cm^3 \cdot s}$$

$$\overline{X}_n = \left(1.76 \times 10^5 \frac{cm^3}{mol \cdot s} \right) \left(1.66 \times 10^{-11} \frac{mol}{cm^3} \right) \left(10^{-2} \frac{mol}{cm^3} \right) \left(\frac{10^{12}}{8.30} \frac{cm^3 \cdot s}{mol} \right)$$

$$= 3.52 \times 10^3$$

c. Volume of a particle = $\frac{4}{3} \pi r^3$, $r = 0.05 \mu m = 0.05 \times 10^{-4} cm$

$$= 4.19 r^3 = 4.19 \times (5 \times 10^{-6} cm)^3$$

$$= 5.24 \times 10^{-16} cm^3$$

Density of each particle = 1.2 g/cc

$$\text{Mass of each particle} = (1.2 \text{ g/cm}^3) (5.24 \times 10^{-16} \text{ cm}^3)$$

$$= 6.29 \times 10^{-16} g$$

Molecular wt of styrene = 104

Each particle contains

$$6.29 \times 10^{-16} \text{ g} \left(\frac{1 \text{ g mol}}{104 \text{ g}} \right) \text{ monomer units}^{**}$$

$$= 6.05 \times 10^{-18} \text{ g mol monomer units}$$

$$= (6.05) \times 10^{-18} \text{ g-mol monomer units)$$

$$\left(6.023 \times 10^{23} \frac{\text{monomer}}{\text{g-mol monomer}} \right)$$

$$= 3.64 \times 10^6 \text{ monomers}$$

Since $\bar{X}_n = 3.5 \times 10^3$ or 3.52×10^3 monomer per chain

$$\text{Chains per particle} = (3.64 \times 10^6 \text{ monomers}) \left(\frac{10^{-3} \text{ chains}}{3.25 \text{ monomer}} \right)$$

$$= 103 \times 10^3 \text{ chains}$$

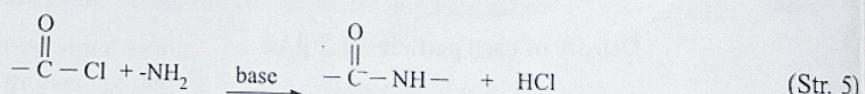
3. Precipitation Polymerization

Precipitation polymerization, also known as slurry polymerization, involves solution systems in which the monomer is soluble but the polymer is not. It is probably the most important process for the coordination polymerization of olefins. The process involves, essentially, a catalyst preparation step and polymerization at pressures usually less than 50 atm and low temperatures (less than 100°C). The resultant polymer, which is precipitated as fine flocs, forms a slurry consisting of about 20% polymer suspended in the liquid hydrocarbon employed as solvent. The polymer is recovered by stripping off the solvent, washing off the catalyst, and if necessary, extracting any undesirable polymer components. Finally, the polymer is compounded with additives and stabilizers and then granulated.

The suspension of the polymer flocs in the solvent produces a physical system of low viscosity that is easy to stir. However, problems may arise due to settling of the polymer and the formation of deposits on the stirrer and reactor walls. Most industrial transition-metal catalysts are insoluble, and consequently polymerization occurs in a multiphase system and may be controlled by mass transfer. Therefore, the type of catalyst employed exerts a larger influence on parameters and reactor geometry.

4. Interfacial and Solution Polycondensations

Monomers that are very reactive are capable of reacting rapidly at low temperatures to yield polymers that are of higher molecular weight than would be produced in normal bulk polycondensations. The best and most widely used reactants are organic diacid chlorides and compounds containing active hydrogens (Table 10.5):



In interfacial polymerization a pair of immiscible liquids is employed, one of which is usually water while the other is a hydrocarbon or chlorinated hydrocarbon such as hexane, xylene, or carbon tetrachloride. The aqueous phase contains the diamine, diol, or other active hydrogen compound and the acid receptor or base (e.g., NaOH). The organic phase, on the other hand, contains the acid chloride. As the name suggests, this type of polymerization occurs interfacially between the two liquids. In contrast to high-temperature polycondensation reactions, these reactions are irreversible because there are no significant reactions between the polymer product and the low-molecular-weight by-product at the low

Unit Operations in Polymer Processing

I. INTRODUCTION

Polymer processing may be divided into two broad areas. The first is the processing of the polymer into some form such as pellets or powder. The second type describes the process of converting polymeric materials into useful articles of desired shapes. Our discussion here is restricted to the second method of polymer processing. The choice of a polymer material for a particular application is often difficult given the large number of polymer families and even larger number of individual polymers within each family. However, with a more accurate and complete specification of end-use requirements and material properties the choice becomes relatively easier. The problem is then generally reduced to the selection of a material with all the essential properties in addition to desirable properties and low unit cost. But then there is usually more than one processing technique for producing a desired item from polymeric materials or, indeed, a given polymer. For example, hollow plastic articles like bottles or toys can be fabricated from a number of materials by blow molding, thermoforming, and rotational molding. The choice of a particular processing technique is determined by part design, choice of material, production requirements, and, ultimately, cost-performance considerations.

The number of polymer processing techniques increases with each passing year as newer methods are invented and older ones modified. This chapter is limited to the most common polymer processing unit operations, but only extrusion and injection molding, the two predominant polymer processing methods, are treated in fairly great detail. Our discussion is restricted to general process descriptions only, with emphasis on the relation between process operating conditions and final product quality. Table 11.1 summarizes some polymer processing operations, their characteristics, and typical applications.

II. EXTRUSION¹

Extrusion is a processing technique for converting thermoplastic materials in powdered or granular form into a continuous uniform melt, which is shaped into items of uniform cross-sectional area by forcing it through a die. As shown in Table 11.1, extrusion end products include pipes for water, gas, drains, and vents; tubing for garden hose, automobiles, control cable housings, soda straws; profiles for construction, automobile, and appliance industries; film for packaging; insulated wire for homes, automobiles, appliances, telephones and electric power distribution; filaments for brush bristles, rope and twine, fishing line, tennis rackets; parisons for blow molding. Extrusion is perhaps the most important plastics processing method today.

A simplified sketch of the extrusion line is shown in Figure 11.1. It consists of an extruder into which is poured the polymer as granules or pellets and where it is melted and pumped through the die of desired shape. The molten polymer then enters a sizing and cooling trough or rolls where the correct size and shape are developed. From the trough, the product enters the motor-driven, rubber-covered rolls (puller), which essentially pull the molten resin from the die through the sizer into the cutter or coiler where final product handling takes place.

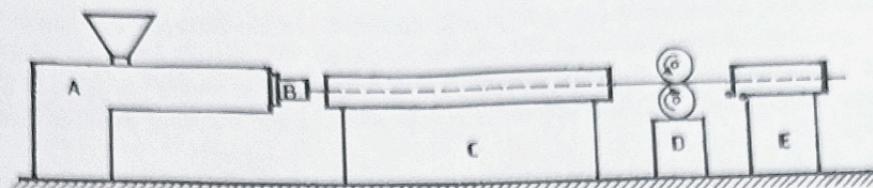
A. THE EXTRUDER

Figure 11.2 is a schematic representation of the various parts of an extruder. It consists essentially of the barrel, which runs from the hopper (through which the polymer is fed into the barrel at the rear) to the die at the front end of the extruder. The screw, which is the moving part of the extruder is designed to pick up, mix, compress, and move the polymer as it changes from solid granules to a viscous melt. The screw turns in the barrel with power supplied by a motor operating through a gear reducer.

The heart of the extruder is the rotating screw (Figure 11.3). The thread of an extruder screw is called a flight, and the axial distance from the edge of one flight to the corresponding edge on the next flight is called the pitch. The pitch is a measure of the coarseness of the thread and is related to the helix

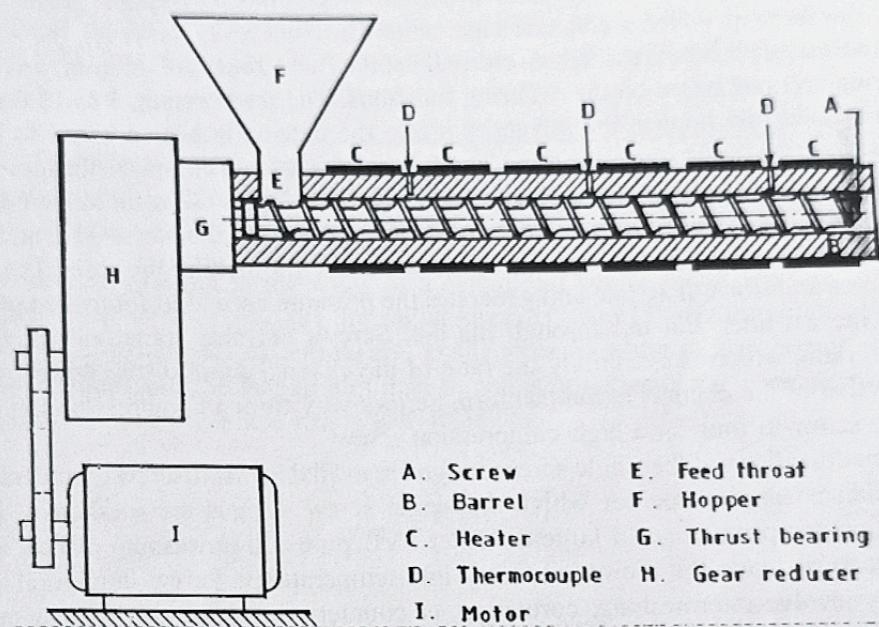
Table 11.1 Some Unit Operations in Polymer Processing and Typical Products

Process	Characteristics	Resin Employed	Typical Products
Extrusion	A process for making indeterminate length of thermoplastics with constant cross-section	Most thermoplastics including PE, PP, PVC, ABS, PS	Pipes and tubing used for soda straws, gas hose, drains and vents, control cable, housings, gas and water pipes; profiles, auto trim, home siding, storm windows, sheets used for window glazing, refrigerator liners, signs, plates, lighting; films for bag coverings, laminates, packaging; fibers, filaments for brush bristles, rope, fishing line; insulated wire for homes, automobile, appliances, telephone and electric power distribution; coated paper for milk carton, meat packaging
Injection molding	Versatile process, most suitable for high speed, low cost molding of intricate plastic parts required in high volume	Virtually all thermoplastics and some thermosets; most common are commodity plastics such as PVC, PE, PP, and PS; others include ABS, nylon, cellulosics, acrylics	Automobile parts, appliance housings, camera cases, knobs, gears, grilles, fan blades, bowls, spoons, lenses, flowers, wastebaskets and garbage cans
Blow molding	Process used for making bottles and other hollow plastic parts having relatively thin walls	Several thermoplastics with PE (particularly LDPE, HDPE) having the largest volume; others include PVC, PP, PS, ABS, acrylics, nylons, acrylonitrile, acetates, and PC	Bottles, watering cans, hollow toys, gas tanks for automobiles and trucks
Rotational molding	Economical process for the production of hollow seamless parts with heavy walls and/or complex shapes	PE, (highest volume) PP, PVC together account for almost all plastics used; others include a number of engineering thermoplastics, including ABS, acetal copolymers, nylon (6 and 11), polycarbonate	Hollow balls, squeeze toys, storage and fuel tanks, automobile dashboards, door liners and gearshift covers, industrial storage tanks and shipping containers, whirlpool tubs, recreational boats, canoes and camp tops, hobby horses, heater ducts, auto armrest skins, athletic balls, portable toilets
Thermoforming	Process for forming moderately complex shapes that are not readily amenable to injection molding	Almost all thermoplastics but most commonly used include ABS, PP, PS, PVC polyesters; others include acrylics, polycarbonate, cellulosic, nitrile resins	Automobile, airline and mass transportation industries for such uses as auto headliners, fender walls, overhead panels, aircraft canopies; construction industry for exterior and interior paneling, bathtubs, shower stalls; outdoor signs; appliances, e.g., refrigerator liners, freezer panels; packaging trays for meat packing, egg cartons, fast-food disposables and carryouts, blister packages, suitcases, tool boxes, cups, and containers
Compression and transfer molding	Most widely used techniques for molding thermosets	Phenolic (largest volume), urea, melamines, epoxy, rubber, diallyl phthalate, alkyds	Pot handles, electrical connectors, radio cases, television cabinets, bottle closures, buttons, dinnerware, knobs, handles, replacement for metal parts in electrical, automotive, aircraft industries
Casting	Process for converting liquid resins into rigid objects of desired shape	Polyesters, nylons, polyurethanes, silicones, epoxies, phenolics, acrylics	Tooling and metal-forming industries' cast epoxy dies used to produce airplane and missile skins, automobile panels and truck parts; epoxies used by artists and architects for outdoor sculpture, churches, homes and commercial buildings, and encapsulation in electronic industry; cast acrylic sheets used in airplanes, helicopters, schools



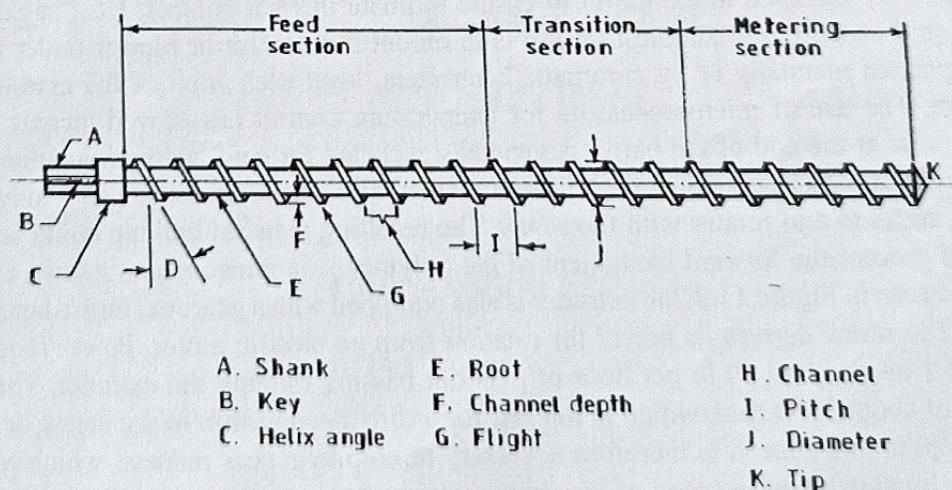
A. Extruder C. Sizer cooler
B. Die (water trough) D. Pull rolls
E. Cutter (coiler)

Figure 11.1 Sketch of an extrusion line. (From Richards, P.N., *Introduction to Extrusion*, Society of Plastics Engineers, CT, 1974. With permission.)



A. Screw E. Feed throat
B. Barrel F. Hopper
C. Heater G. Thrust bearing
D. Thermocouple H. Gear reducer
I. Motor

Figure 11.2 Parts of an extruder. (From Richards, P.N., *Introduction to Extrusion*, Society of Plastics Engineers, CT, 1974. With permission.)



A. Shank E. Root H. Channel
B. Key F. Channel depth I. Pitch
C. Helix angle G. Flight J. Diameter
K. Tip

Figure 11.3 Parts of an extruder screw. (From Richards, P.N., *Introduction to Extrusion*, Society of Plastics Engineers, CT, 1974. With permission.)