

# Polymer Reaction Engineering

## I. INTRODUCTION

Several important differences exist between the industrial production of polymers and low-molecular-weight compounds:<sup>6,7</sup>

- Generally, polymers of industrial interest have high molecular weights, usually in the range of  $10^4$  to  $10^7$ . Also, in contrast to simple compounds, the molecular weight of a polymer does not have a unique value but, rather, shows a definite distribution. The high molecular weight of polymers results in high solution or melt viscosities. For example, in solution polymerization of styrene, the viscosity can increase by over six orders of magnitude as the degree of conversion increases from zero to 60%.
- The formation of a large polymer molecule from small monomer results in a decrease in entropy. It follows therefore from elementary thermodynamic considerations that the driving force in the conversion process is the negative enthalpy gradient. This means, of course, that most polymerization reactions are exothermic. Consequently, heat removal is imperative in polymerization reactions — a problem that is accentuated by the high medium viscosity that leads to low heat transfer coefficients in stirred reactors.
- In industrial formulations, the steady-state concentration of chain carriers in chain and ionic polymerization is usually low. These polymerization reactions are therefore highly sensitive to impurities that could interfere with the chain carriers. Similarly, in step-growth polymerization, a high degree of conversion is required in order to obtain a product of high molecular weight (Chapters 6 and 7). It is therefore necessary to prevent extraneous reactions of reactants and also exclude interference of impurities like monofunctional compounds.
- The quality of a product from a low-molecular-weight compound can be usually improved by such processes as distillation, crystallization, etc. However, if the performance of a product from a polymerization process is inadequate, it is virtually impossible to upgrade its quality by subsequent processing.

Given these possible differences in the production processes between polymers and low-molecular-weight compounds, it is vitally important to choose the most suitable reactor and operating conditions to obtain the required polymer properties from a polymerization reaction. This demands a detailed knowledge of the phenomena that occur in the reactor. This, in turn, requires an accurate model of the polymerization kinetics, the mass and heat transfer characteristics of the polymerization process. Our approach in this chapter is largely qualitative, and our treatment involves a discussion of the various polymerization processes, followed by a brief review of polymerization reactors. It is hoped that this approach will enable the reader to gain insight into the complex problem of selecting a reactor for a specific polymerization reaction.

## II. POLYMERIZATION PROCESSES

Polymerization processes may be conveniently classified as homogeneous or heterogeneous. In homogeneous polymerization, as the name suggests, all the reactants, including monomers, initiators, and solvents, are mutually soluble and compatible with the resulting polymer. On the other hand, in heterogeneous systems, the catalyst, the monomer, and the polymer product are mutually insoluble. Homogeneous polymerization comprises bulk (mass) or solution systems while heterogeneous polymerization reactions may be categorized as bulk, solution, suspension precipitation, emulsion, gas phase, and interfacial polymerization.

### A. HOMOGENEOUS SYSTEMS

#### 1. Bulk (Mass) Polymerization

In bulk polymerization the reaction mixture consists essentially of the monomer and, in the case of chain growth polymerization, a soluble initiator and possibly modifiers. In the case of homogeneous bulk

**Table 10.1** *Heats of Polymerization of Some Monomers*

| Monomer             | Heat of Polymerization, Btu/lb <sup>a</sup> |
|---------------------|---|
| Ethylene            | 1530–1660 (gas to solid)                    |
| Propylene           | 860   |
| Isobutylene         | 370   |
| Butadiene           | 620 (1,4 addition)                          |
| Vinyl chloride      | 650   |
| Vinyl acetate       | 445 (at 170°F)                              |
| Acrylic acid        | 400 (at 166°F)                              |
| Ethyl acrylate      | 340   |
| Methyl methacrylate | 245   |
| Styrene             | 290   |
| Isoprene            | 470   |
| Vinylidene chloride | 330   |
| Acrylonitrile       | 620   |

<sup>a</sup> Value given for liquid monomer converted to a condensed solid polymer at 77°F unless indicated otherwise.

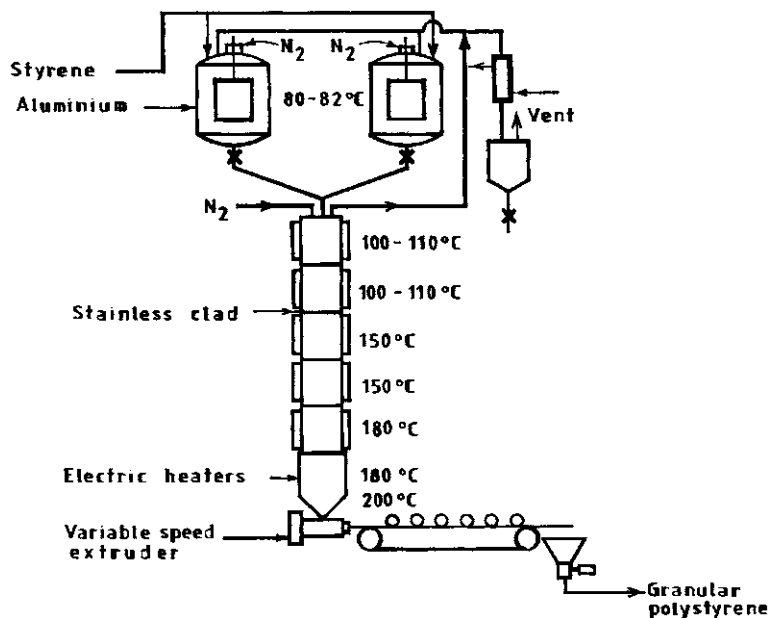
polymerization, the product polymer and monomer are miscible. Since polymerization reactions are generally exothermic, the temperature of polymerization depends on the polymerization system. Mixing and heat transfer become difficult as the viscosity of the reaction mass increases.

Bulk polymerization is widely practiced in the manufacture of step-growth polymers. However, since condensation reactions are not very exothermic and since the reactants are usually of low activity, high temperatures are required for these polymerization processes. Even though medium viscosities remain low throughout most of the course of polymerization, high viscosities are generally experienced at later stages of the reaction. Such high viscosities cause not only problems with the removal of volatile by-products, but also a possible change in the kinetics of the reaction from a chemical-controlled regime to a diffusion-controlled one. To obtain a product of an appropriate molecular weight, therefore, proper cognizance must be given to this problem in the design of the reactor.

Organic systems have low heat capacities and thermal conductivities. Free-radical reactions are highly exothermic in nature. This coupled with the extremely viscous reaction media for these systems prevents effective convective (mixing) heat transfer, leading, as a consequence, to very low overall heat transfer coefficients. The problem of heat removal is accentuated at higher conversions because the rates of polymerization and heat generation are usually enhanced at these stages of reaction. This leads to the development of localized hot spots or runaway reactions, which if uncontrolled may be ultimately disastrous. The occurrence of local hot spots could result in the discoloration and even possible degradation of the polymer product, which usually has a broadened molecular weight distribution due to chain transfer to polymer.

Because of the above heat transfer problems, bulk polymerization of vinyl monomers is restricted to those with relatively low reactivities and enthalpies of polymerization. This is exemplified by the homogeneous bulk polymerization of methyl methacrylate and styrene (Table 10.1). Some polyurethanes and polyesters are examples of step-reaction polymers that can be produced by homogeneous bulk polymerizations. The products of these reactions might be a solid, as in the case with acrylic polymers; a melt, as produced by some continuous polymerization of styrene; or a solution of polymer in monomer, as with certain alkyd-type polyesters.

Sheets, rods, slabs, and other desired shapes of objects are produced from poly(methyl methacrylate) in batch reactors by keeping at least one dimension of the reaction mass thin, thereby facilitating heat transfer. Typically, the monomer containing a small amount of an initiator such as benzoyl peroxide is poured between two glass plates separated by a flexible gasket of poly(vinyl chloride) tubing and held together by spring clips to compensate for shrinkage. Depending upon the thickness, the filled mold is heated from 45 to 90°C for about 12 to 24 h. After cooling, the molds are stripped from the casting and the sheets are annealed at 140 to 150°C. The resulting sheet has good optical properties, but the process



**Figure 10.1** Vertical column reactor for the continuous bulk polymerization of styrene. (From Winding, C.C. and Hiatt, G.D., *Polymeric Materials*, McGraw-Hill, New York, 1961. With permission.)

suffers from a number of problems. These include possible bubbles from dissolved gases, long curing times, and large shrinkage (about 21%). These problems may be overcome by using prepolymerized syrup rather than the pure monomer. The syrup is prepared by carefully heating methyl methacrylate monomer containing 0.02 to 0.1% benzoyl peroxide or azo-bis-isobutyronitrile in a well-agitated stainless steel vessel to initiate polymerization. A good syrup is obtained after a prepolymerization cycle of 5 to 10 min at a batch temperature of 90°C.

Another way of circumventing the heat transfer problems is by continuous bulk polymerization. An example is the polymerization of polystyrene, which is carried out in two stages. In the first stage, styrene is polymerized at 80°C to 30 to 35% monomer conversion in a stirred reactor known as a prepolymerizer. The resulting reaction mass — a viscous solution or syrup of polymer in monomer — subsequently passes down a tower with increasing temperature. The increasing temperature helps to keep the viscosity at manageable levels and also enhances conversion, which reaches at least 95% at the exit of the tower (Figure 10.1). By removal of the heat of polymerization at the top of the tower and proper temperature control of the finished polymer at the bottom of the tower, an optimum molecular weight may be achieved and channeling of the polymer may be minimized.

Bulk polymerization is ideally suited for making pure polymeric products, as in the manufacture of optical grade poly(methyl methacrylate) or impact-resistant polystyrene, because of minimal contamination of the product. However, removal of the unreacted monomer is usually necessary, and this can be a difficult process. This may be achieved in vacuum extruders where the molten polymer is extruded under vacuum to suck off the residual monomer.

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**Example 10.1:** Explain why bulk polymerization is generally more suited for step-growth polymerization than for chain-growth polymerization.

**Solution:** The major problems in bulk polymerization are heat removal and mixing. Both step-growth and chain-growth polymerization are exothermic. But the enthalpy of polymerization for chain-growth reactions is of the order of 15 to 20 kcal/g mol compared with 2 to 6 kcal/g mol for step-growth polymerization. Also, chain-growth polymerization is characterized by high viscosities even at low conversions due to the generation of polymers early in the reaction, whereas viscosities are generally low in step-growth polymerization until the later stages of the reaction (high conversions). Thus the

much higher exothermic nature of chain-growth polymerization, coupled with the difficulty of mixing the reaction mixture due to high viscosities, leads to much lower heat transfer efficiencies in chain-growth polymerization than in step-growth polymerization.

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**Example 10.2:** Purified styrene monomer is charged along with initiators into an aluminum prepolymerization vessel. Polymerization is carried out at about 90°C to 30% conversion. The resulting syrup is then poured into molds where the reaction is completed. Comment on the probable molecular weight distribution of the product polymer.

**Solution:** This process is essentially batch polymerization of styrene. Most of the conversion takes place in the finishing trays. Because of the relatively poor heat transfer in these trays, the polymerizing mass may reach high temperatures at some spots. Consequently, the resulting polystyrene will have a broad molecular weight distribution, with very high molecular weights being produced at low temperatures and lower molecular weights produced at high temperature.

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## B. Solution Polymerization

In solution polymerization, the monomer, initiator, and resulting polymer are all soluble in the solvent. Solution polymerization may involve a simple process in which a monomer, catalyst, and solvent are stirred together to form a solution that reacts without the need for heating or cooling or any special handling. On the other hand, elaborate equipment may be required. For example, a synthetic rubber process using a coordination catalyst requires rigorous exclusion of air (to less than 10 ppm); moisture; carbon dioxide; and other catalyst deactivators from the monomer, solvent, and any other ingredient with which the catalyst will come in contact before the reaction. In addition, exclusion of air prevents the tendency to form dangerous peroxides. To avoid product contamination and discoloration, materials of construction also need to be selected with the greatest care.

Polymerization is performed in solution either batchwise or continuously. Batch reaction takes place in a variety of ways. The batch may be mixed and held at a constant temperature while running for a given time, or for a time dictated by tests made during the progress of the run. Alternatively, termination is dictated by a predetermined decrease in pressures following monomer consumption. A continuous reaction train, on the other hand, consists of a number of reactors, usually up to about ten, with the earlier ones overflowing into the next and the later ones on level control, with transfer from one to the next by pump.

As the reaction progresses, solution polymerization generally involves a pronounced increase in viscosity and evolution of heat. The viscosity increase demands higher power and stronger design for pumps and agitators. The reactor design depends largely on how the heat evolved is dissipated. Reactors in solution polymerization service use jackets; internal or external coils; evaporative cooling with or without compression of the vapor or simple reflux-cooling facilities, a pumped recirculation loop through external heat exchanger; and combinations of these. A typical reactor has agitation, cooling, and heating facilities; relief, temperature level, and pressure connections; and, frequently, cleanout connections in addition to inlet and outlet fittings.

Solution polymerization has certain advantages over bulk, emulsion, and suspension polymerization techniques. The catalyst is not coated by polymer so that its efficiency is sustained and removal of catalyst residues from the polymer, when required, is simplified. Solution polymerization is one way of reducing the heat transfer problems encountered in bulk polymerization. The solvent acts as an inert diluent, increasing overall heat capacity without contributing to heat generation. By conducting the polymerization at the reflux temperature of the reaction mass, the heat of polymerization can be conveniently and efficiently removed. Furthermore, relative to bulk polymerization, mixing is facilitated because the presence of the solvent reduces the rate of increase of reaction medium viscosity as the reaction progresses.

Solution polymerization, however, has a number of drawbacks. The solubility of polymers is generally limited, particularly at higher molecular weights. Lower solubility requires that vessels be larger for a given production capacity. The use of an inert solvent not only lowers the yield per reactor volume but also reduces the reaction rate and average chain length since these quantities are proportional to monomer concentration. Another disadvantage of solution polymerization is the necessity of selecting an inert solvent to eliminate the possibility of chain transfer to the solvent. The solvent frequently presents

hazards of toxicity, fire, explosion, corrosion, and odor problems not associated with the product itself. Also, solvent handling and recovery and separation of the polymer involve additional costs, and removal of unreacted monomer can be difficult. Complete removal of the solvent is difficult in some cases. With certain monomers (e.g., acrylates) solution polymerization leads to a relatively low reaction rate and low-molecular-weight polymers as compared with aqueous emulsion or suspension polymerization. The problem of cleaning equipment and disposal of dirty solvent constitutes another disadvantage of solution polymerization.

Solution polymerization is of limited commercial utility in free-radical polymerization but finds ready applications when the end use of the polymer requires a solution, as in certain adhesives and coating processes [i.e., poly(vinyl acetate) to be converted to poly(vinyl alcohol) and some acrylic ester finishes]. Solution polymerization is used widely in ionic and coordination polymerization. High-density polyethylene, polybutadiene, and butyl rubber are produced this way. [Table 10.2](#) shows the diversity of polymers produced by solution polymerization, while [Figure 10.2](#) is the flow diagram for the solution polymerization of vinyl acetate.

## C. HETEROGENEOUS POLYMERIZATION

### 1. Suspension Polymerization

Suspension polymerization generally involves the dispersion of the monomer, mainly as a liquid in small droplets, into an agitated stabilizing medium usually consisting of water containing small amounts of suspension and dispersion agents. The catalyst or initiator is dissolved in the monomer if the monomer is a liquid or included in the reaction medium if a gaseous monomer is used. The ratio of monomer to dispersing medium ranges from 10 to 40% suspension of monomer or total solids content of polymer at the finish of polymerization. When polymerization is completed, the polymer suspension is sent to a blowdown tank or stripper where any remaining monomer is removed, using a vacuum or antifoaming agent if necessary. Several stripped batches are transferred and blended in a hold tank. The slurry mixture is finally pumped to a continuous basket-type centrifuge or vibrating screen where the polymer is filtered, washed, and dewatered. The wet product, which may still contain as much as 30% water or solvent, is dried in a current of warm air (66 to 149°C) in a dryer. It is then placed in bulk storage or transferred to a hopper for bagging as powdered resin or put through an extruder for forming into a granular pellet product. [Figure 10.3](#), which shows a flow sheet of the suspension polymerization of methyl methacrylate, is typical of many suspension polymerization processes for the production of thermoplastic resins.

For the monomer to be dispersible in the suspension system, it must be immiscible or fairly insoluble in the reaction medium. In some instances, partially polymerized monomers or prepolymers are used to decrease the solubility and also increase the particle size of the monomer. The initiators employed in the polymerization reaction are mainly of the peroxide type and, in some cases, are azo and ionic compounds. Examples include benzoyl, diacetyl, lauroyl, and *t*-butyl-peroxides. Azo-bis-isobutyronitrile (AIBN) is one of the most frequently used azo initiators, while aluminum and antimony alkyls, titanium chloride, and chromium oxides are typical ionic initiators. The amount of catalyst used depends on the reactivity of the monomer and the degree of polymerization, varying from 0.1 to 0.5% of the weight of the monomer.

Apart from the monomer itself, the most important ingredient in suspension polymerization is the suspension agent. Even though it is used in relatively small amounts (0.01 to 0.50% weight of monomer), it is vital to the successful control of the polymerization process and the uniformity of the product obtained. The major problem in suspension polymerization is in the formation and the maintenance of the stability of the thermodynamically unstable droplets as they are slowly transformed from a highly mobile immiscible liquid, through the viscous, sticky stage to the final solid beads (rigid granules) without their coalescence or agglomeration into a conglomerate mass. During the transformation of the liquid monomer droplet to the solid resin, the viscous or sticky phase first appears when 10 to 20% conversion has occurred. This phase persists for up to 75 to 80% conversion before the particles take on a nonsticky solid appearance. The tendency for agglomeration of the particles, which is particularly critical at the stage when the particles become sticky, is prevented by proper agitation and the use of suspending agents. The stabilizing agents are employed in two ways. (1) Surface-acting agents (surfactants) such as fatty acids and some inorganic salt such as magnesium and calcium carbonates, calcium phosphate, titanium and aluminum oxides reduce the surface tension between water and the monomer droplets, thus providing greater stability for this interface. They also reduce the surface viscosity of the

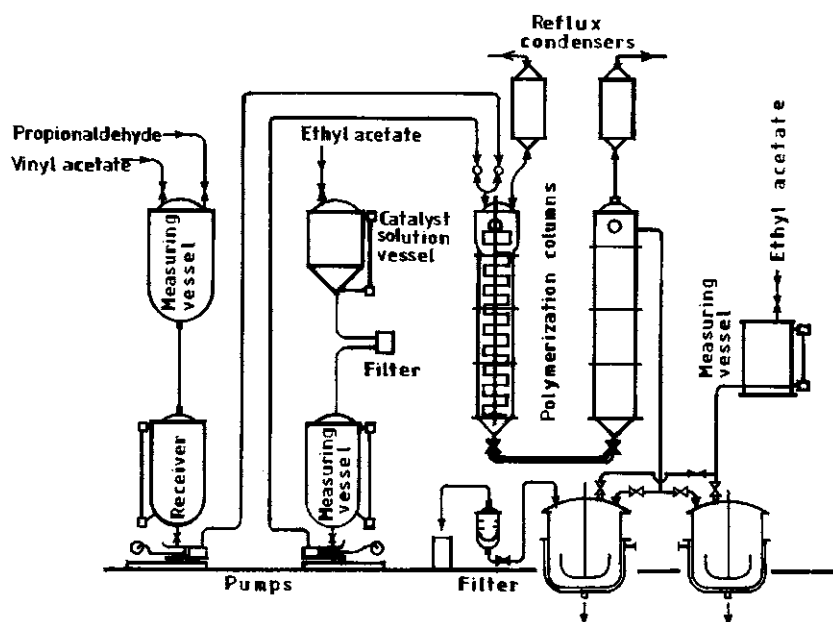
**Table 10.2** *Typical Solution-Polymerization Processes*

| Monomer                                      | Product                                 | Solvent                         | Catalyst                                   | Pressure (Psig)     | Temperature (°F)                   | Isolation  |
|--|---|---------------------------------|--|---------------------|------------------------------------|--|
| Conjugated diene <sup>a</sup>                | Synthetic rubber                        | Various <sup>b</sup>            | Coordination, <sup>c</sup> or alkyllithium | 40                  | 50                                 | Steam coagulation, slurring in hot water, extrusion into hot water, evaporation of solvent on drum, or dryer |
| Isobutylene + isoprene                       | Butyl rubber                            | Methyl chloride                 | AlCl <sub>3</sub>                          | Atm                 | -140                               | Slurring in hot water  |
| Ethylene alone, or with 1-butene             | Linear polyethylene, homo- or copolymer | Cyclohexane, pentane, or octane | Chrome oxide on silica alumina base        | 400–500             | 275–375                            | Precipitation with water then steam stripping  |
| Ethylene                                     | Polyethylene                            | Ethylene                        | Peroxygenic                                | 500–2,000 atm       | 210–480                            |  |
| Vinyl acetate                                | Polyvinyl acetate                       | Alcohol, ester, or aromatic     | Peroxygenic compound                       |                     | Precipitation                      |  |
| Urea-formaldehyde                            | Resin                                   | Water                           |  |                     |                                    |  |
| Bisphenol A + phosgene                       | Polycarbonate resin                     |                                 |  |                     | to 104                             | Precipitation  |
| Dimethyl terephthalate + ethylene glycol     | Polyester resin                         | Ethylene glycol                 | Various <sup>d</sup>                       |                     | 320–570                            | Distillation of solvent and recovery of the polymer as a melt  |
| Resorcinol + formaldehyde                    | Latex adhesive for tire cord            | Water                           | NaOH                                       | Atm                 | Ambient                            | Not isolated but used as a solution  |
| Melamine + formaldehyde                      | Laminating resin                        | Water NH <sub>4</sub> OH        |  |                     | Spray dried, or used as a solution |  |
| Acrylamide + acrylonitrile                   | Resin                                   | Water                           | Ammonium persulfate                        | Atm                 | 165–175                            |  |
| Acrylate                                     | Adhesive coating                        | Ethyl acetate                   | Free-radical initiator                     | Atm                 | Refluxing temperature              | Not isolated but used as a solution  |
| Maleic anhydride + styrene + divinylbenzene  | Water-soluble thickener                 | Acetone or benzene              | Benzoyl peroxide                           | Atm                 | Refluxing temperature              | Neutralized with ammonium hydroxide and used as a solution, or precipitated with petroleum ether             |
| Ethylene + propylene + a diene               | EPT rubber                              | Hydrocarbon                     | Coordination                               | 200–500             | 100                                | Steam coagulation  |
| Epichlorohydrin                              | Polyepichlorohydrin elastomer           | Cyclohexane, or ether           | Organo-aluminum compound                   | Autogenous pressure | -20 to 210                         |  |
| Phenol + drying oil + hexamethylenetetramine | Thermosetting resin                     | Ester-alcohol mixture           | H <sub>3</sub> PO <sub>4</sub>             | Atm                 | 350, 200, and 185 in stages        | Not isolated but used as solution for paint vehicle  |
| Propylene <sup>e</sup>                       | Polypropylene                           | Hexane                          | Coordination                               | 175                 | 150–170                            | Precipitates as formed   |
| Formaldehyde                                 | Polyoxymethylene                        | Hexane                          | Anionic type <sup>f</sup>                  | Atm                 | -60 to 160                         | Precipitates as formed   |

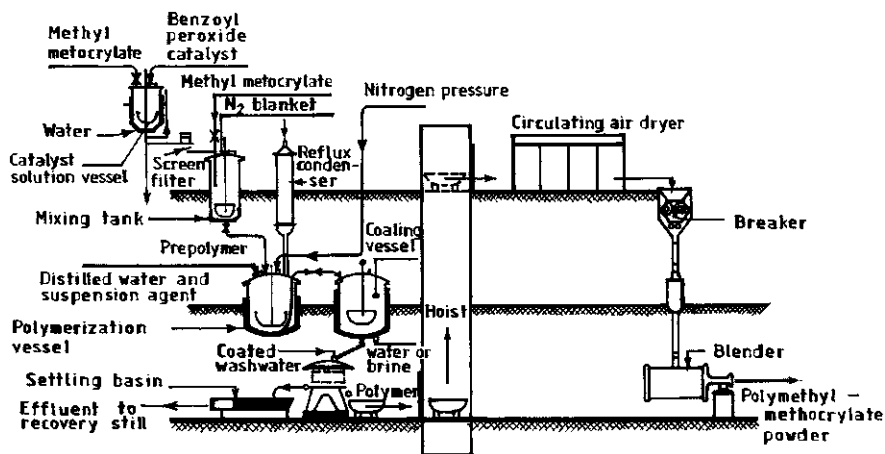
**Table 10.2 (continued)** *Typical Solution-Polymerization Processes*

- <sup>a</sup> For example, 1,3-butadiene or isoprene
- <sup>b</sup> Includes hexane, heptane, an olefin, benzene, or a halogenated hydrocarbon. Must be free from moisture, oxygen, and other catalyst deactivators.
- <sup>c</sup>  $TiCl_4$ , an aluminium, alkyl, and cobalt halide are reported to be used to make Ameripol CB *cis*-polybutadiene.
- <sup>d</sup> In the transesterification step, inorganic salts, alkali metals or their alkoxides, or Cu, Cr, Pb, or Mn metal are used. In the next step, the catalyst is not disclosed.
- <sup>e</sup> Isotactic polymers are not usually formed completely in solution but precipitate in the course of reaction.
- <sup>f</sup> Amines, cyclic nitrogen compounds, arsine, stibine, or phosphine.

From Back, A.L., *Chem. Eng.*, p. 65, August 1, 1966.



**Figure 10.2** *Continuous process for production of low viscosity polyvinyl acetate in solution. (From Back, A.L., Chem. Eng., p. 65, August 1, 1966. With permission.)*



**Figure 10.3** *Flow sheet for the suspension polymerization of methyl methacrylate. (From Church, J.M., Chem. Eng., p. 79, August 1, 1966.)*

**Table 10.3** *Composition and Reaction Conditions for Some Suspension Polymerization Systems*

| Polymer                     | Suspension Medium <sup>a</sup>   | Catalyst System <sup>a</sup>                                | Temperature | Pressure     | Time Cycle | Polymer Slurry |
|-----------------------------|--|---|-------------|--------------|------------|----------------|
| Polyethylene (low density)  | 1,000 water<br>100 benzene   | 0.1 oxygen (air), or<br>0.5 di- <i>tert</i> -butyl peroxide | 350–400 F   | 800–1000 atm | 1–2 min    | 10%            |
| Polyethylene (high density) | 500 cyclohexane or<br>heptane  | 0.3 aluminum triethyl<br>or chromium oxide                  | 180–250 F   | 150–200 psi  | 1–3 h      | 20%            |
| Polyvinyl chloride          | 300 water<br>0.2 polyvinyl alcohol,<br>or 0.5 gelatin<br>0.05 emulsifier | 0.2 lauroyl peroxide  | 130–140 F   | 100–200 psi  | 10–12 h    | 18%            |
| Polymethylmethacrylate      | 350 water<br>0.8 polyacrylic acid<br>0.7 lauryl sulfonate                | 0.5 benzoyl peroxide  | 160–180 F   | —            | 6–8 h      | 23%            |
| Polystyrene                 | 400 water<br>0.5 methyl cellulose<br>0.2 calcium phosphate               | 0.3 diacetyl peroxide                                       | 190–200 F   | —            | 3–4 h      | 20%            |
| Polytetrafluoroethylene     | 600 water<br>0.3 polyvinyl alcohol<br>0.1 lauryl sulfonate               | 0.1 isobutylazobitrile                                      | 80–140 F    | —            | 2–3 h      | 12%            |

<sup>a</sup> Concentrations expressed as part of materials per 100 parts of monomer.

From Church, J.M., *Chem. Eng.*, p. 79, August 1, 1966.

droplets. (2) Water-soluble polymers like gelatin, methyl cellulose, poly(vinyl alcohol), starches, gums, and poly(acrylic acids) and their salts raise the viscosity of the suspending aqueous medium and act as protective coatings.

Suspension polymerization reactors are generally vertical, agitated (or stirred tank) vessels usually made of stainless steel or glass-lined carbon steel. Reactors are provided with agitators with a paddle or anchor-type stirrer of speed in the range 20 to 60 rpm, with baffles in some cases to enhance dispersion. The most important design for the suspension polymerization reactor is the temperature control, which must ensure a close degree of accuracy. Reactors must therefore be capable of removing the heat of polymerization, which may be quite appreciable. For example, the heats of polymerization for vinyl chloride and styrene are 650 Btu/lb and about 300 Btu/lb, respectively (Table 10.1). This heat is released over a relatively short period (5 to 10 h). Consequently, reactors are jacketed and water cooled. The overall heat transfer coefficient for a glass-lined steel unit is 55 to 70 Btu/h · ft<sup>2</sup> · °F. The difference in the heat transfer coefficients between the two reactor types is due to the additional heat transfer resistance offered by the glass layer. Glass lining, of course, helps to reduce reactor fouling problems, but glass thickness must be minimized so as not to compromise reactor heat transfer capability.

As the reactor size increases, problems are generally encountered with heat transfer surfaces. Even when dimensional similarity is maintained, heat transfer area does not increase in direct proportion to the reactor volume. For example, for a cylindrical vessel, the increase in jacket heat-transfer area for the straight side is proportional to the volume raised to the 0.67 power. Therefore it is frequently necessary to provide additional heat transfer surface. This is commonly achieved by using the baffles required for agitation as cooling aids. However, extreme care must be exercised in the design of supplemental baffles to avoid creation of dead volumes. Polymer buildup in these spots contributes to poor product properties and creates operational problems such as the plugging of valves, lines, and pipes by chunks of polymers from these spots. Chilled or refrigerated water is often used for heat removal in lieu of adding supplementary heat-transfer area. Hot water or low-pressure steam may also be used to heat up reactants to initiate polymerization. Table 10.3 summarizes the typical composition and reaction conditions for a number of suspension polymerization systems.

We indicated in our discussion of bulk polymerization that one way of reducing heat transfer problems is to conduct the reaction in thin sections. In suspension polymerization, this concept is utilized practically in its extreme by dispersing and suspending monomer droplets (0.0001 to 0.50 cm diameter) in an inert nonsolvent, which is almost always water. This is achieved by maintaining an adequate degree of



turbulence and an interfacial tension between the monomer droplets and the water. This way, the monomer droplets and the resulting viscous polymer form the discontinuous (dispersed) phase in the continuous aqueous phase. This, combined with the added heat capacity of water, enhances the overall heat transfer efficiency. Kinetically, therefore, each of the suspended particles has the characteristics of a miniature bulk reactor without a mechanism for internal mixing but with a good surface-to-volume ratio for efficient heat removal.

Suspension polymerization, also known as bead, pearl, or granular polymerization because of the physical nature of the product polymer, has numerous attractive features. First, the use of water as the heat exchange medium is more economical than the organic solvents used in most solution polymerizations. Second, with water as the dispersed phase acting as the heat-transfer medium, the removal of the excessive heat of polymerization presents minimal problems, and control of temperature is relatively simple. Another advantage is the quality of the product obtained. Separation and handling of the polymer product are relatively easier than in emulsion and solution polymerizations. The product is far easier to purify than emulsion systems; very little contamination occurs, with only trace amounts of catalyst, suspension, and dispersing agents remaining in the resin. Only a minimum amount of these ingredients are used in the polymerization process and much of these are removed in the subsequent purification steps.

Suspension polymerization is the most widely used process for making plastic resins both in terms of the number of polymer products and in tonnage production. Practically all of the common thermo-plastic resins, including some of the newer polymers, are made by this method. Styrene, methyl methacrylate, vinyl chloride, vinylidene chloride, vinyl acetate, the fluorocarbons, and some gaseous monomers, including ethylene, propylene and formaldehyde, may be polymerized by the suspension polymerization process.

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**Example 10.3:** Describe briefly the potential implications with respect to process operation and/or the resulting product of the following problems.

- a. Power or equipment failure in solution polymerization
- b. Addition of excess amount of initiator in suspension polymerization

**Solution:**

- a. The reaction must be stopped in an appropriate way depending on the nature of the reactants. Failure to stop a highly exothermic polymerization during an extended power loss can be potentially dangerous since agitators and compressors stop functioning and the necessary heat transfer to the coolant is effectively terminated. The reaction may proceed to a violent stage or a completely solidified mass depending on the reactants. A deactivator such as a ketone, an alcohol, or water is effective with a coordination-type initiator. In some cases, e.g., the phenolic type, the reaction is effectively terminated by lowering the temperature and adding more solvent. For a free-radical polymerization reaction, a free-radical acceptor (“shot stop”) halts the polymerization. These additives are charged into the reactor where necessary or, preferably, after the batch leaves the reactor. In the case of a train of reactors, the reactor in which the rate of polymerization is highest is dumped into an off-grade vessel and terminated there.
- b. An excess of initiator should be avoided because of the undesirable effects it has on process control and product quality. Some of these adverse effects include low-molecular-weight polymer formation resulting from chain termination, difficult control of temperature due to enhanced reaction rate and exothermic heat resulting in gel formation and agglomeration, and decreased thermal stability of the product polymer due to the presence of the excess peroxide causing degradation of the product at processing temperatures.

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**Example 10.4:** Explain the following observation. The use of internal cooling coils or an external circulating loop and exchanger is generally not an appropriate means of providing supplemental heat-transfer area in suspension polymerization.

**Solution:** Polymer fouling is generally a problem in suspension polymerization reactors. Supplemental heat-transfer area in the form of coils is generally avoided because of the difficulty encountered in cleaning the area between coils and the vessel wall.

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The use of an external circulating loop and exchanger requires that a portion of the reaction mass is pumped through an external heat exchanger and cooled and returned to the reactor. In suspension polymerization, a controlled degree of agitation is imperative to prevent agglomeration and maintain the desired polymer particle size. It is difficult to design the equipment and the recirculating loop to avoid zones of too little agitation, where the coalescence of monomer droplets occurs. When the reaction slurry is pumped through an external loop, the pump may impose an order-of-magnitude increase in the shear rate, thereby forcefully agglomerating polymer particles as they pass through a sticky phase of polymerization. Also, some polymer buildup is inevitable and an external circulating cooling loop will present cleaning problems.

## 2. Emulsion Polymerization

Emulsion polymerization was developed in the U.S. during World War II for the manufacture of GR-S rubber (Government-Rubber-Styrene) or SBR (styrene-butadiene rubber) when the Japanese cut off the supply of rubber from the East. Emulsion polymerization is now widely used commercially for the production of a large variety of polymers. All polymers made by this process are addition polymers rather than condensation polymers and require free-radical initiators. In general, an emulsion polymerization system would consist of the following ingredients: monomer(s), dispersing medium, emulsifying agent, water-soluble initiator, and, possibly, a transfer agent. Water serves as the dispersing medium in which the various components are suspended by the emulsifying agent. The water also acts as a heat transfer medium. Monomers such as styrene, acrylates, methacrylates, vinyl chloride, butadiene, and chloroprene used in emulsion polymerization show only a slight solubility in water.

Reactors for the emulsion polymerization process vary in size from 1000 to 4000 gal depending upon production requirements. Reactors may be glass lined or made of stainless steel. Glass-lined reactors are preferred for the production of acrylic polymer emulsions, while stainless steel is usually preferred for the manufacture of poly(vinyl acetate) because it can be cleaned easily with a boiling solution of dilute caustic. Both types of reactors have been employed in the production of butadiene-styrene copolymers and poly(vinyl chloride). Reactors are necessarily jacketed for heat control purposes. In processes [e.g., poly(vinyl acetate) manufacture] where monomer, catalyst, and surfactant are added to the reactor incrementally and the available jacket heat-transfer area is not initially available for cooling, supplemental cooling is both necessary and attractive. This involves the use of reflux cooling. Here, the heat of polymerization vaporizes unreacted monomer, and the monomer vapor is condensed in a reflux condenser and returned to the reactor. In this case, however, the foaming characteristics of the latex must be determined first since a stable foam carried into the reflux condenser will foul the exchanger surface. Reactors must also be rated to withstand a minimum internal pressure ranging from 50 psi for acrylic, methacrylic and acrylic-styrene vinyl acetate and its copolymers to at least 300 psi for vinyl chloride homopolymers and copolymers. Figure 10.4 shows a flow sheet for a typical emulsion polymerization plant.

In order to understand the quantitative relations governing emulsion polymerization kinetics, it is necessary to give a qualitative description of the process.

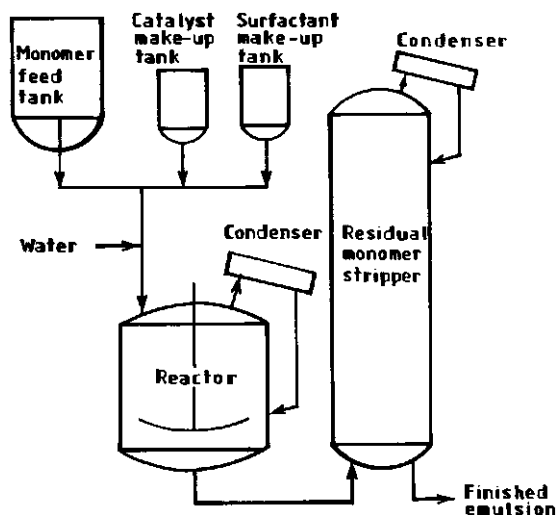
### a. Distribution of Components

A typical recipe for emulsion polymerization in parts by weight consists of 180 parts of water, 100 parts of monomer, 5 parts of fatty acid soap (emulsifying agent), and 0.5 parts of potassium persulfate (water-soluble initiator). The question, of course, is how these components are distributed within the system. By definition, soaps are sodium or potassium salts of organic acids, for example, sodium stearate:



When a small amount of soap is added to water, the soap ionizes and the ions move around freely. The soap anion consists of a long oil-soluble portion (R) terminated at one end by the water-soluble portion.





**Figure 10.4** Flow sheet of typical emulsion polymerization plant. (From Gellner O., *Chem. Eng.*, p. 74, August 1, 1966.)

In other words, soap anions consist of both hydrophilic and hydrophobic groups. In water containing a partially soluble monomer molecule, the soap anion molecules orient themselves at the water–monomer interfaces with the hydrophilic ends facing the water, while the hydrophobic ends face the monomer phase. Each monomer droplet therefore has a protective coat of negative charge. Consequently, the emulsified monomer droplet is stabilized not only by the reduction of surface tension but also by the repulsive forces between the negative charges on its surface.

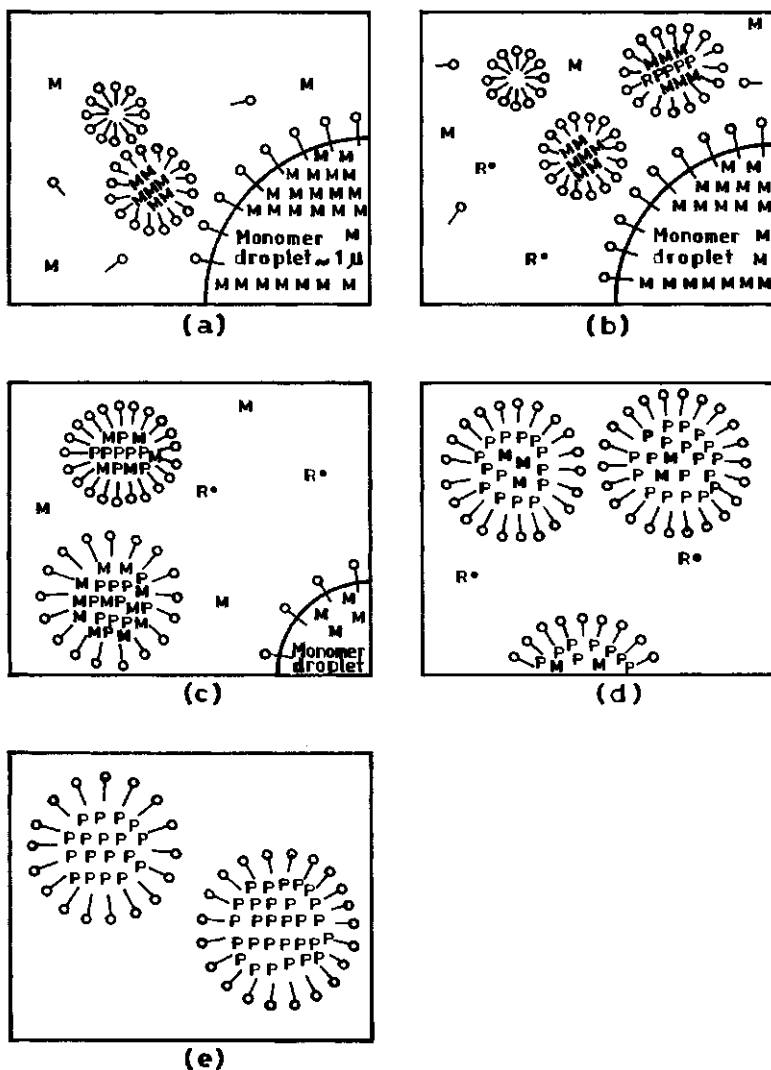
Above a critical concentration of the emulsifying agent known as the critical micelle concentration (CMC), only a small fraction of the emulsifying agent is dissolved in the water. The bulk of the emulsifier molecules arrange themselves into colloidal particles called micelles. The micelles remain in dynamic equilibrium with the soap molecules dissolved in water. Arguments persist with regard to the shape of the micellar aggregate, but energy considerations favor a spherical arrangement with the hydrophilic (polar) groups on the surface facing the aqueous phase while the hydrophobic chains are arranged somewhat irregularly at the interior. Each micelle consists of 50 to 100 soap molecules. Proposed rodlike-shaped micelles range in length from 1000 to 3000 Å and have diameters that are approximately twice the length of each soap molecule. The number and size of micelles depend on the relative amounts of the emulsifier and the monomer. Generally, large amounts of emulsifier result in larger numbers of smaller size particles.

The presence of soap or emulsifying agents considerably enhances the solubility of a water insoluble or sparingly soluble monomer. It has been demonstrated by X-ray and light scattering measurements that in the presence of monomers, micelles increase in size, a clear manifestation of the occupation of the hydrophobic interior part of the micelles. Meanwhile, a very small portion of the monomer remains dissolved. However, the bulk of the monomer is dispersed as droplets are stabilized, as discussed above, by the emulsifier. Consequently, when a slightly water-soluble monomer is emulsified in water with the aid of soap and agitation, three phases are present: the aqueous phase with small amounts of dissolved soap and monomer, the emulsified monomer droplets, and the monomer-swollen micelles. The level of agitation dictates the size of the monomer droplets, but they are generally at least 1 μm in diameter. The emulsifier in micelle form and monomer concentrations would typically be in the range of 10<sup>18</sup> micelles per ml and 10<sup>10</sup> to 10<sup>11</sup> droplets per ml, respectively. Figure 10.5 is a schematic representation of the components of the reaction medium at various stages of emulsion polymerization.

### ***b. Locus and Progress of Polymerization***

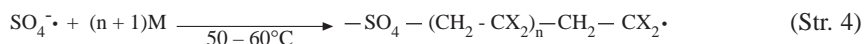
When the water-soluble initiator potassium persulfate is added to an emulsion polymerization system, it undergoes thermal decomposition to form sulfate radical anion:



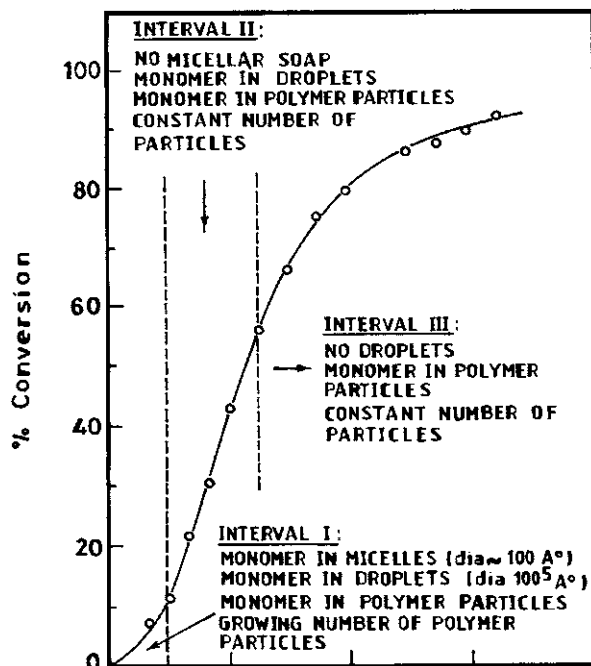


**Figure 10.5** Representation of stages of an ideal emulsion polymerization. (–O) An emulsifier molecule; (M), a monomer molecule; (P) a polymer molecule; and (R•) a free radical. (a) Prior to initiation; (b) polymerization stage 1; shortly after initiation; (c) polymerization stage 2; all emulsifier micelles consumed; (d) polymerization stage 3; monomer droplets disappear; and (e) end polymerization.

The water-soluble radical anions react with monomer dissolved in aqueous phase to form soap-type free radicals:



Given the three phases present in an emulsion polymerization system, the locus of polymerization can conceivably be in the monomer droplets, in the aqueous phase within the micelles, or possibly at an interface. Some polymerization obviously takes place in the aqueous phase but with a limited contribution to the overall polymerization because of the low solubility of the monomer in water. The monomer droplets also do not provide the loci for polymerization because the negatively charged sulfate anions find the soap-stabilized monomer droplets virtually impossible to penetrate. Also, the primary sulfate radical anions are oil insoluble. The absence of polymerization in the monomer droplets has been verified



**Figure 10.6** Stages in an emulsion polymerization. (From Rudin, A., *The Elements of Polymer Science and Engineering*, Academic Press, New York, 1982. With permission.)

experimentally. Consequently, emulsion polymerization takes place almost exclusively in the micelles. This is because of two reasons: (1) A micelle has a dimension in the range 50 to 100 Å while, as we said earlier, the dimension of the monomer droplet is at least 1 μm (10,000 Å). Since the surface/volume ratio of a sphere is 3/R and even though the total volume of micelles is considerably less than that of the droplets, the micelles present a much greater total surface area. (2) The concentration of the micelles is higher than that of the monomer droplets ( $10^{18}$  vs.  $10^{11}$ ).

Emulsion polymerization is considered to take place in three stages (Figure 10.6).

- **Stage I:** — Polymerization is initiated in only a small number (about 0.1%) of the micelles present initially. As polymerization proceeds, the active micelles consume the monomers within the micelle. Monomer depletion within the micelle is replenished first from the aqueous phase and subsequently from the monomer droplets. The active micelles grow in size with polymer formation and monomers contained therein, resulting in a new phase: monomer-polymer particles. To preserve their stability, these growing monomer-swollen polymer particles absorb the soap of the parent micelles. As the number of micelles converted to monomer-swollen particles increases and as these particles grow larger than the parent micelles, soap from the surrounding (existing micelles and emulsified monomer droplets) is rapidly absorbed. At about 13 to 20% conversion, the soap concentration decreases to a level below that required to form and sustain micelles (i.e., CMC). Consequently, the inactive micelles (those without a growing polymer) become unstable and disappear. As evidence for this, the initially low surface tension of the aqueous emulsion rises rather suddenly due to the decrease in the soap concentration, and if agitation is stopped at this stage the monomer droplets will coalesce because they are no longer stable. This marks the completion of stage I, which is characterized by a continuous increase in the overall rate of polymerization (Figure 10.6).
- **Stage II** — At the end of stage I, the locus of further polymerization is shifted exclusively to the monomer-swollen polymer particles since the micelles (the site of generation of new polymer particles) have all disappeared. Polymerization proceeds homogeneously in the polymer particles by the maintenance of a constant monomer concentration within the particles through the diffusion of monomers from the monomer droplets, which, in effect, serve as monomer reservoirs. As the polymer particles increase in size, the size of the monomer droplets disappears. Since there is no new particle nucleation

**Table 10.4** *Characteristics of Various Stages of Emulsion Polymerization*

| Stage                            | Characteristics   |
|----------------------------------|---|
| Prior to initiation              | Dispersing medium, usually water, containing small amount of dissolved soap (emulsifier) and monomer.<br>Monomer droplets each of size ca. 10,000 Å separate due to stabilization by a coat of emulsifier molecules whose hydrophilic ends face the aqueous phase; concentration of monomer droplets $10^{10}$ – $10^{11}$ per ml.<br>Beyond CMC, emulsifier molecules number 50–100 form spherically shaped micelles each of size 40–50 Å; some micelles are swollen by monomer and have dimensions 50–100 Å; micelle concentration is about $10^{18}$ per ml.<br>Low surface tension due to emulsifier concentration. |
| Stage I<br>(12–20% conversion)   | Polymerization initiated in ca. 0.1% of initially present micelles.<br>As monomers in active micelles are consumed, and then replenished by diffusion of monomers from the aqueous phase and subsequently from monomer droplets, the micelles form swollen particles that are stabilized by their absorbing soap molecules from neighboring inactive micelles and emulsified monomer droplets.<br>End of stage marked by disappearance of inactive micelles and increase in surface tension; agitation needed to prevent coalescence of monomer droplets.   |
| Stage II<br>(25–50% conversion)  | Low concentration of dissolved monomer molecules.<br>No dissolved emulsifier or emulsifier micelles.<br>Polymerization occurs exclusively in monomer-swollen polymer (latex) particles through diffusion of monomers from monomer droplets.<br>Polymer particles grow while monomer droplets decrease in size.<br>No new particle nucleation (i.e., number of latex particles is constant) and since monomer concentration within particles is constant, rate of polymerization is constant.<br>End of stage marked by disappearance of monomer droplets.   |
| Stage III<br>(50–80% conversion) | No dissolved monomer, dissolved emulsifier, emulsifier micelles, monomer droplets or monomer-swollen micelles.<br>Since monomer droplets have disappeared, a supply of monomers from the monomer reservoir (i.e., monomer droplets) is exhausted, hence rate of polymerization drops with depletion of monomers in latex particles.<br>At end of polymerization (i.e., 100% conversion) system contains polymer particles, i.e., 400–800 Å dispersed in aqueous phase.  |

at this stage, the number of polymer particles remains constant. As a result of this and the constant monomer concentration within the particles, this stage is characterized by a constant rate of reaction.

- **Stage III** — At an advanced stage of the polymerization (50 to 80% conversion), the supply of excess monomer becomes exhausted due to the disappearance of the monomer droplets. The polymer particles contain all the unreacted monomers. As the concentration of monomer in the polymer particles decreases, the rate of polymerization decreases steadily and deviates from linearity. The characteristics of various stages of emulsion polymerization are summarized in Table 10.4.

### ***c. Kinetics of Emulsion Polymerization***

A number of questions need to be resolved from the qualitative description of emulsion polymerization given in the previous section. For example, it is necessary to consider whether the diffusion of monomers to the polymer particles is high enough to sustain polymerization given the low solubility of monomer in the aqueous phase. It is also important to know the average radical concentration in a polymer particle. Also, the validity of the assumption that only the monomer–polymer particles capture the radicals generated by the initiator needs to be established convincingly. The answers to these questions were provided by Smith and Ewart<sup>3</sup> and this forms the basis for the quantitative treatment of the steady-state portion of emulsion polymerization.

#### **(1) Rate of Emulsion Polymerization**

In emulsion polymerization, the rate of generation of free radicals is about  $10^{13}$ /m-s while the number of monomer–polymer particles for typical recipes,  $N$ , is in the range  $10^{13}$  to  $10^{15}$  particles/ml of the aqueous phase. Consequently, if all the initiator radicals are captured by the monomer–polymer particles, each particle will acquire, at the most, a radical every 1 to 100 s. It can be shown that if a particle contains two radicals, mutual annihilation of radical activity will occur within a time span of the order

of  $10^{-13}$  s. This is much smaller than the interval between radical entry into the polymer particle. It is, therefore, perfectly safe to assume that the entry of a second radical with an active polymer particle results in immediate bimolecular termination. The particle remains dormant until another radical enters about 1 to 100 s later to reactivate polymerization. The activity of the particle will once again be terminated after 1 to 100 s due to the entry of another radical and the cycle is repeated. It follows, therefore, that at any given point in time a particle will either have one or zero radicals. This, in turn, means that a given particle will be active half of the time and dormant the other half of the time. By extension of this argument, at any given instant of time, one half of the polymer particles will contain a single radical and be active while the other half will remain dormant. The polymerization rate is given by:

$$R_p = k_p [M] [M\cdot].$$

Therefore, the polymerization rate per cubic centimeter of water is given by

$$R_p = k_p \frac{N}{2} [M] \quad (10.1)$$

where  $N$  = number of polymer particles per cubic centimeter of aqueous phase

$k_p$  = homogeneous propagation rate constant

$[M]$  = monomer concentration in the polymer particles

Notice that Equation 10.1 predicts a direct dependence of the polymerization rate on the number of particles but not on the rate of radical generation. The equation holds true, of course, only when the radicals are being produced. Again, since the derivation of the equation is pivoted on the argument that each particle does not contain more than one radical at a given time, it follows that the particle size is not large enough to violate this condition.

Figure 10.7 is an experimental verification of the linear dependence of the rate of polymerization on the number of particles and monomer concentration. The polymerization rate increases with an increase in soap concentration due to the increase in  $N$  with soap concentration.

**Example 10.5:** The rate of diffusion,  $I$ , into a sphere of radius  $r$  is given by

$$I = D4\pi r\Delta C$$

where  $D$  = diffusion coefficient ( $\text{cm}^2/\text{s}$ )

$\Delta C$  = concentration difference between the surface of the sphere and the surroundings

In the emulsion polymerization of styrene at  $60^\circ\text{C}$  the diffusion coefficient is  $10^{-10} \text{ cm}^2 \text{ s}^{-1}$  and the termination rate constant is  $3 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ . Show that the rate of termination of the initiating radicals in the aqueous phase is of the order  $10^3$  radicals/ml/s. What is the average lifetime of a radical in the aqueous phase? Assume that the concentration of the radicals at the surface of the polymer particles is zero.

**Solution:** The rate of termination  $R_t$  is given by

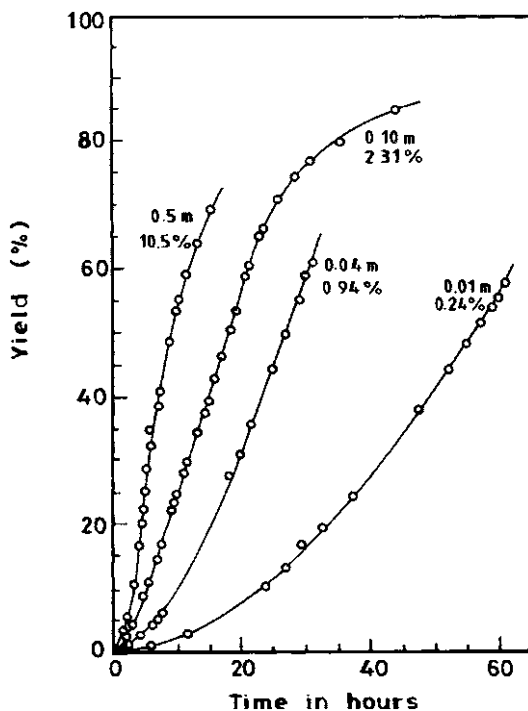
$$R_t = 2k_t [M\cdot]^2$$

where  $[M\cdot]$  = the overall concentration of radicals.

Since the concentration of radicals within and at the surface of the polymer particles is zero then

$\Delta C = [M\cdot]$  = the concentration of radicals in the surrounding aqueous phase

$[M\cdot] = I/D4\pi r$



**Figure 10.7** Polymerization of isoprene in emulsion at 50°C using 0.3 g of  $K_2S_2O_8$  per 100 g of monomer, and with the amounts of soap (potassium chlorate) indicated in weight percent and in molality  $m$ . (From Harkins, H.B., *J. Am. Chem. Soc.*, 69, 1428, 1947. With permission.)

For emulsion polymerization, the rate of generation of radicals from the initiator is of the order of  $10^{13}$  radicals/cm<sup>3</sup>/s; the number of polymer particles is about  $10^{14}$  particles/cm<sup>3</sup>; and the average diameter of polymer particles is 1000 Å. The rate of diffusion of radicals to the polymer surface is

$$\begin{aligned}
 I &= \frac{\text{rate of generation of radicals}}{\text{concentration of polymer particles}} \\
 &= \left( 10^{13} \frac{\text{radicals}}{\text{cm}^3 \text{ s}} \right) \left( \frac{1}{10^{14}} \frac{\text{cm}^3}{\text{particle}} \right) = 10^{-1} \text{ radicals s}^{-1} \\
 r &= \frac{1}{2} \times 1000 \text{ \AA} = 5 \times 10^{-6} \text{ cm} \\
 [M.] &= \frac{10^{-1} \text{ radicals s}^{-1}}{(10^{-5} \text{ cm}^2 \text{ s}^{-1})(4\pi)(5 \times 10^{-6} \text{ cm})} \\
 &= 10^8 \text{ radicals cm}^{-3} \\
 k_t &= 3 \times 10^7 \frac{1}{\text{mol-s}} = 3 \times 10^7 \left( \frac{1000 \text{ cm}^3}{1} \right) \left( \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ molecules}} \right) \left( \frac{1}{\text{s}} \right) \\
 &= 5 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \\
 R_t &= 2 \left( 5 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \right) \left[ 10^8 \text{ radicals cm}^3 \right]^2 \\
 &= 10^3 \text{ radicals cm}^{-3} \text{ s}^{-1}
 \end{aligned}$$



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

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

#### **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.

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

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 Ewart<sup>3</sup> have shown that

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

where  $k$  is a constant with a value between 0.4 and 0.53;  $\mu_s$  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 differences 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.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$= 3.52 \times 10^3$$

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

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

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

Density of each particle = 1.2 g/cc

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

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

Molecular wt of styrene = 104

Each particle contains

$$\begin{aligned}
 & 6.29 \times 10^{-16} \text{ g} \left( \frac{1 \text{ g mol}}{104 \text{ g}} \right) \text{ monomer units} \\
 & = 6.05 \times 10^{-18} \text{ g mol monomer units} \\
 & = (6.05) \times 10^{-18} \text{ g-mol monomer units)} \\
 & \left( 6.023 \times 10^{23} \frac{\text{monomer}}{\text{g-mol monomer}} \right) \\
 & = 3.64 \times 10^6 \text{ monomers} \\
 & \text{Since } \bar{X}_n = 3.5 \times 10^3 \text{ or } 3.52 \times 10^3 \text{ monomer per chain} \\
 & \text{Chains per particle} = (3.64 \times 10^6 \text{ monomers}) \left( \frac{10^{-3} \text{ chains}}{3.25 \text{ monomer}} \right) \\
 & = 103 \times 10^3 \text{ chains}
 \end{aligned}$$


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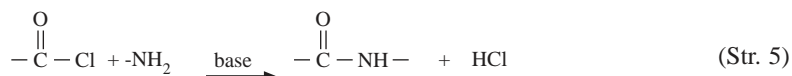
### 3. Precipitation Polymerization

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

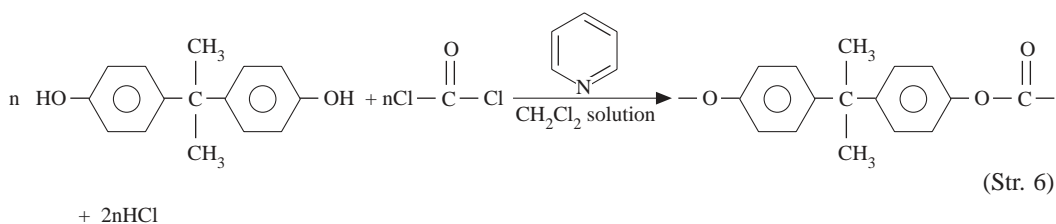
**Table 10.5** Typical Interfacial/Solution Polycondensation Reactions

| Active Hydrogen Compound | Acid Halide   | Product   |               |
|--------------------------|---|---|---------------|
| -NH <sub>2</sub>         | $\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{Cl} \end{array}$          | $\begin{array}{c} \text{O} \quad \text{H} \\    \quad   \\ -\text{C}-\text{N}- \end{array}$                                 | Polyamide     |
| -NH <sub>2</sub>         | $\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{Cl} \end{array}$          | $\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \\   \quad    \quad   \\ -\text{N}-\text{C}-\text{N}- \end{array}$ | Polyurea      |
| -NH <sub>2</sub>         | $\begin{array}{c} \text{O} \\    \\ \text{Cl}-\text{C}-\text{O}- \end{array}$ | $\begin{array}{c} \text{H} \quad \text{O} \\   \quad    \\ -\text{N}-\text{C}-\text{O}- \end{array}$                        | Polyurethane  |
| -OH                      | $\begin{array}{c} \text{O} \\    \\ \text{Cl}-\text{C}- \end{array}$          | $\begin{array}{c} \text{O} \\    \\ -\text{O}-\text{C}- \end{array}$  | Polyester     |
| -OH                      | $\begin{array}{c} \text{O} \\    \\ \text{Cl}-\text{C}-\text{Cl} \end{array}$ | $\begin{array}{c} \text{O} \\    \\ -\text{O}-\text{C}-\text{O}- \end{array}$   | Polycarbonate |

From Williams, D.J., *Polymer Science and Engineering*, Prentice-Hall, Englewood Cliffs, NJ, 1971. With permission.

temperatures employed. Consequently, the molecular weight distribution is a function of the kinetics of the polymerization system; it is not determined statistically as in normal equilibrium polycondensations. The rate of reaction is controlled by the rate of monomer diffusion to the interface. This obviates the necessity to start the reaction with stoichiometric quantities of reactants. Since the reactions are irreversible, high conversions are not necessarily required to obtain high-molecular-weight polymers.

In solution polycondensation, all the reactants are dissolved in a simple, inert solvent. However, for some solution polymerizations, the solvent can facilitate the reaction. For example, a tertiary amine such as pyridine is an acid acceptor in the solution phosgenation in polycarbonate manufacture.



Interfacial and solution polycondensations are commercially important. For example, an unstirred interfacial polycondensation reaction is utilized in the production of polyamide fibers. Another important application of interfacial polycondensation is the enhancement of shrink resistance of wool. The wool is immersed first in a solution containing one of the reactants and subsequently in another solution containing the other reactant. The polymer resulting from the interfacial reaction coats the wool and improves its surface properties.

### III. POLYMERIZATION REACTORS

The course of a polymerization reaction and hence the properties of the resultant polymer are determined by the nature of the polymerization reaction and the characteristics of the reactor employed in the reaction. In other words, the reactor is essentially the heart of any polymerization process. The reactor

**Table 10.6** *Characteristics, Advantages and Disadvantages of Various Polymerization Types*

| Polymerization Process | Characteristics  | Advantages   | Disadvantages   |
|------------------------|--|--|---|
| Bulk                   | Reaction mixture consists essentially of monomer; and initiator in the case of chain reaction polymerization<br>Monomer acts as solvent for polymers                           | Products relatively pure due to minimum contamination<br>Enhanced yield per reactor volume   | Exothermic nature of polymerization reactions (particularly chain reaction polymerizations) makes temperature control of system difficult<br>Product has broad molecular weight distribution<br>Removals of tracers of unreacted monomer difficult  |
| Solution               | Solvent miscible with monomer, dissolves polymer   | Heat transfer efficiency greatly enhanced resulting in better process control<br>Resulting polymer solution may be directly usable   | Necessary to select an inert solvent to avoid possible transfer to solvent<br>Lower yield per reactor volume<br>Reduction of reaction rate and average chain length<br>Not particularly suitable for production of dry or relatively pure polymer due to difficulty of complete solvent removal |
| Suspension             | Monomer and polymer insoluble in water, initiator soluble in monomer   | Heat removal and temperature control relatively easier<br>Polymer obtained in a form that is convenient and easily handled<br>Resulting polymer suspension or granules may be directly usable                                      | Need to maintain stability of droplets requires continuous and a minimum level of agitation<br>Possibility of polymer contamination by absorption of stabilizer on particle surface<br>Continuous operation of system difficult   |
| Emulsion               | Monomer and polymer insoluble in water, initiator soluble in water<br>Emulsifier needed for stabilization of system component particularly at initial stages of polymerization | Physical state of the system enhances heat transfer efficiency<br>Possible to obtain high rates of polymerization and high average chain lengths<br>Narrow molecular weight distribution<br>Latex (emulsion) often directly usable | Difficult to get pure polymer due to contamination from other components of polymerization system<br>Difficult and expensive if solid polymer product is required<br>Presence of water lowers yield per reactor volume  |
| Precipitation          | Polymer insoluble in monomer or monomer miscible with precipitant for polymer  | Physical state of system permits easy agitation<br>Relatively low temperatures employed  | Separation of product difficult and expensive<br>Catalyst systems are special and need careful preparation<br>Molecular weight distribution depends on type of catalyst   |
| Interfacial            | Polymerization occurs at interface of two immiscible solvents, usually water and an organic solvent  | Polymerization is rapid and occurs at low temperatures<br>High conversions are not necessarily required to obtain high molecular weight<br>Unnecessary to start with stoichiometric quantities of reactants                        | Limited to highly reactive systems<br>Need appropriate choice of solvent to dissolve reactants  |

affects the conversion of the monomer to the polymer. The reactor also effectively establishes the ultimate properties of the polymer such as polymer structure, molecular weight, molecular weight distribution, and copolymer composition. To perform its functions satisfactorily, the reactor must remove the heat of polymerization, provide the necessary residence time, provide good temperature control and reactant homogeneity, control the degree of back-mixing in a continuous polymerization, and provide surface exposure. In addition, the reactor must be applicable to mass production and economical to operate.

Therefore, the control of polymer properties requires a careful selection of a reactor appropriate for the particular polymerization process.

We dealt with various polymerization processes in the previous sections. We now consider polymerization reactors. Our treatment of this subject is essentially qualitative; the principal focus is to highlight salient features of each reactor type.

Reactors may be divided into three simple, idealized model categories: batch reactor, tubular or plug flow reactor, and the continuous stirred tank reactor (CSTR).

## A. BATCH REACTORS

In the case of the batch reactor, the reactants are charged into the reactor and mixed properly for the duration of the reaction and then the product is discharged. The batch reactor has essentially the following characteristics:

- It is simple and does not need extensive supporting equipment.
- It is ideal for small-scale operations.
- The operation is an unsteady-state operation, with composition varying with time.

Now let us discuss how these features affect the various polymerization reactions and the resultant polymer. We start by considering the general material balance equation for the batch reactor:

$$\begin{array}{l} \text{Rate of} \\ \text{monomer flow} \\ \text{into the reactor} \end{array} = \begin{array}{l} \text{Rate of} \\ \text{monomer flow} \\ \text{out of the reactor} \end{array} + \begin{array}{l} \text{Rate of monomer loss} \\ \text{due to reaction} \\ \text{within the reactor} \end{array} + \begin{array}{l} \text{Rate of monomer} \\ \text{accumulation} \\ \text{within the reactor} \end{array} \quad (10.6)$$

For a batch reactor, the first two terms of Equation 10.6 are equal to zero since by definition nothing flows in or out of the reactor. Consequently, the equation reduces to

$$\begin{array}{l} \text{Rate of monomer loss} \\ \text{due to reaction} \\ \text{within the reactor} \end{array} = \begin{array}{l} \text{Rate of accumulation} \\ \text{monomer} \\ \text{within the reactor} \end{array} \quad (10.7)$$

$$-\frac{dM}{dt} = R_p \quad (10.8)$$

$$\int_0^t dt = - \int_{[M_0]}^{[M]} \frac{dM}{R_p} \quad (10.9)$$

For free radical polymerization,

$$R_p = k_p \left( \frac{f k_d}{k_t} \right)^{1/2} [I]^{1/2} [M].$$

If  $f$  is independent of monomer concentration and the initiator concentration remains constant, then the above operation is first order in monomer concentration and may be rewritten:

$$R_p = k[M] \quad (10.10)$$

where  $k = k_p \left( \frac{f k_d}{k_t} \right)^{1/2} [I]^{1/2}$ . On substitution of Equation 10.10, Equation 10.9 becomes

$$\int_0^t dt = - \int_{[M_0]}^{[M]} \frac{dM}{kM} \quad (10.11)$$

Integrating this equation yields

$$\ln \frac{[M]}{[M]_o} = -kt \quad (10.12)$$

or

$$[M] = [M]_o e^{-kt} \quad (10.13)$$

$$\text{Percent Conversion} = 100 \frac{[M]_o - [M]}{[M]_o} = 100(1 - e^{-kt}) \quad (10.14)$$

The derivation of Equation 10.13 assumes that the composition of the reaction mixture is uniform throughout the reactor at any instant of time and the initiator concentration is constant. Good mixing is an important way to ensure not only uniform concentration but also uniform temperature and prevents the occurrence of localized inhomogeneities. However, the mixing efficiency for bulk polymerizations in batch reactors, while difficult to generalize, usually varies with conversion because the viscosity and density of the reaction mass changes continuously with reaction time. For example, the viscosity of styrene at 150°C increases by an order of three at 60% conversion. The corresponding changes in emulsion and suspension polymerizations are less drastic. An important assumption made in the derivation of Equation 10.10 is that the initiator concentration remains constant. This assumption may not be realistic under industrial conditions beyond a few percentage points of conversion. A more accurate expression is obtained by assuming a first-order decay of the initiator:

$$[I] = [I]_o e^{-k_d t} \quad (10.15)$$

---

**Example 10.7:** Calculate the time required for 10% polymerization of pure styrene at 60°C with benzoyl peroxide as the initiator in a batch reactor. Assume that the initiator concentration remains constant. Data:

$$f = 1$$

$$k_p^2/k_t = 0.95 \times 10^{-3} \text{ l/mol-s}$$

$$[I] = 4.0 \times 10^{-3} \text{ mol/l}$$

$$k_d = 1.92 \times 10^{-6} \text{ s}^{-1}$$

**Solution:** Since the initiator remains constant, Equation 10.12 is applicable:

$$\ln \frac{[M]}{[M]_o} = -kt$$

$$k = k_p \left( \frac{f k_d}{k_t} \right)^{1/2} [I]^{1/2}$$

or

$$k^2 = \frac{k_p^2}{k_t} (f k_d) [I]$$

$$= \left( 0.95 \times 10^{-3} \frac{\text{l}}{\text{mol-s}} \right) \left( 1.92 \times 10^{-6} \frac{1}{\text{s}} \right) \left[ 4.0 \times 10^{-3} \frac{\text{mol}}{\text{l}} \right]$$

$$= 7.30 \times 10^{-12} \text{ s}^{-2}$$



$$k = 2.70 \times 10^{-6} \text{ s}$$

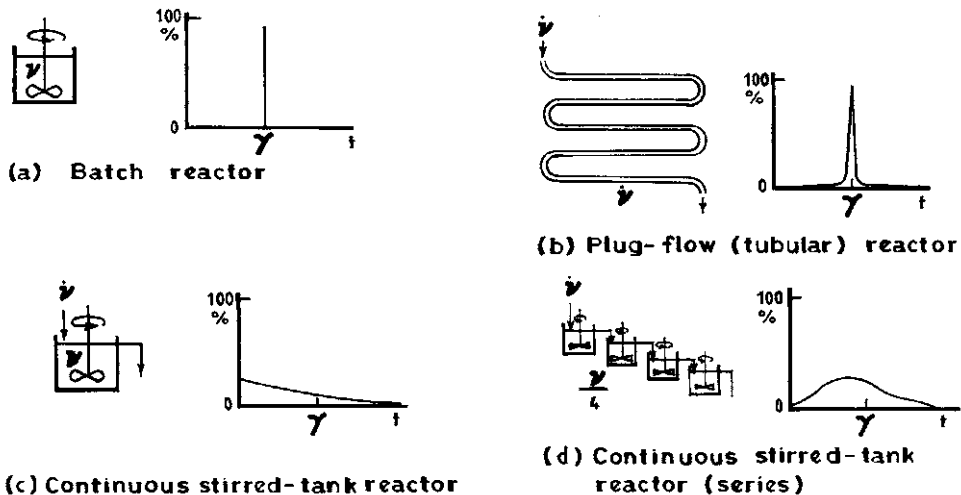
$$\ln \frac{[M]}{[M_o]} = -2.70 \times 10^{-6} t$$

$$\frac{[M_o] - [M]}{[M_o]} = 0.10, \text{ i.e., } \frac{[M]}{[M_o]} = 0.9$$

$$\ln 0.9 = -2.70 \times 10^{-6} t$$

$$t = 8.10 \text{ h}$$

In chain growth reactions, temperature control is a major problem in bulk polymerization and, to a lesser extent, in solution polymerization in batch reactors. This is due to the large increase in viscosity of the reaction medium with conversion. The heat transfer to a jacket in a vessel varies approximately inversely with the one-third power of the viscosity. For example, in a stirred batch (tank) reactor with thick walls and unfavorable surface-to-volume ratio, polymerization essentially proceeds adiabatically. A variety of methods are employed for heat removal, including heat transfer to a jacket, the internal cooling loop, and, in the case of a vaporizable constituent, an overhead condenser through reflux. While reactors are almost always jacketed, the use of additional heat removal devices is generally necessary as the size of the reactor increases since the heat transfer area of the reactor increases with reactor volume to the two-thirds power, while the rate of heat generation varies directly with the reactor volume. As we said earlier, the use of external cooling devices, of course, depends on the polymerization. Where the viscosity is relatively low and/or the latex stable, a portion of the reaction mixture is recycled through a heat exchanger. This is impossible in suspension polymerization where a continuous and minimum level of agitation is required to ensure the stability of the particles and avoid the formation of coagulate and wall deposits in the dead volumes. Also, the high viscosity in bulk polymerization precludes the use of external heat exchangers because the poor agitation would lead to wall deposits and a rapid loss of cooling efficiency. The use of internal cooling coils is restricted to low viscosity reactions to avoid poor product quality resulting from improper mixing. The idealized model batch reactor together with its residence time is shown in Figure 10.8a.



**Figure 10.8** Idealized reactors and their associated residence time distribution. (From Gerrens, H., *Chem. Technol.*, p. 380, June 1982.)

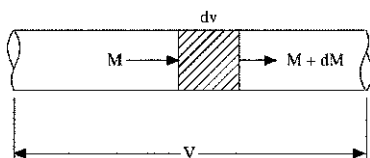
## B. TUBULAR (PLUG FLOW) REACTOR

The tubular or plug flow reactor, as the name suggests, is essentially a tube or unstirred vessel with very high length/diameter ( $l/d$ ) ratio. Fluid flow in the ideal plug flow reactor is orderly, with no element of fluid overtaking any other element. The description of a tubular reactor as plug flow connotes that each element moves through the tube as a plug with no axial diffusion along the flow path and no difference in the velocity of any two elements flowing through the reactor (i.e., no lateral or back-mixing). For the ideal plug flow reactor, therefore, the residence time for all elements flowing through the tube is the same.

In principle, the tubular reactor has a favorable surface-to-volume ratio and relatively thin walls — features that should enhance heat-transfer efficiency. In addition, like the batch reactor, it is suited for achieving high conversions. However, tubular reactors have limited application in polymer production. The high viscosities characteristic of polymerization reaction media present temperature control problems. In addition, the material temperature increases from the tube wall to its radius. This broad distribution of temperature leads to a broad molecular weight distribution — a situation that is accentuated in chain-growth polymerizations by the decrease in initiator and monomer concentrations with increasing conversions. Since the reactor walls are cooler than the center of the reactor, there is a tendency to form a slow-moving polymer layer on the walls. This reduces the production capacity and aggravates the heat-transfer problems. A typical idealized-model tubular reactor together with the residence time distribution and concentration profile for a first-order reaction is shown in [Figure 10.8b](#).

**Example 10.8:** The production of high-pressure low-density polyethylene is carried out in tubular reactors of typical dimensions 2.5 cm diameter and 1 km long at 250°C and 2500 atm. The conversion per pass is 30% and the flow rate is 40,000 kg/h. Assuming that the polymerization reaction is first order in ethylene concentration, estimate the value of the polymerization rate constant.

**Solution:** Consider a mass balance about an elemental volume of the reactor.



On substitution:

$$vM_o dp = R_p dV$$

$$\int_o^V \frac{dV}{vM_o} = \int_o^p \frac{dp}{R_p}$$

Now,

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

$$dp = -\frac{dM}{M_o}$$

$$\int_o^V \frac{dV}{vM_o} = \int_{M_o}^M -\frac{dM}{M_o R_p}$$

$$\frac{V}{v} = \int_{M_o}^M -\frac{dM}{R_p}$$

$$R_p = k[M]$$

$$\frac{V}{v} = -\int_{M_o}^M \frac{dM}{kM}$$

$$k \frac{V}{v} = -\int_{M_o}^M \frac{dM}{M} \text{ or } k\tau = -\int_{M_o}^M \frac{dM}{M}$$

where  $\tau = \frac{V}{v}$  = mean residence time.

$$\ln \frac{M}{M_o} = -k\tau$$

or

$$M = M_o e^{-k\tau}$$

$$k = -\frac{1}{\tau} \ln \frac{M}{M_o}$$

For a conversion of 30%

$$\frac{M_o - M}{M_o} = 0.3$$

or

$$\frac{M}{M_o} = 0.7$$

$$k = \frac{1}{\tau} \ln 0.7$$

$$\begin{aligned} V &= \pi R^2 L = \pi \left( \frac{2.5}{2} \times 10^{-2} \right)^2 \times 1.0 = \pi (1.25)^2 \times 10^{-4} \\ &= 4.9 \times 10^{-4} \text{ m}^3 \end{aligned}$$

Assume, for simplicity, under the conditions of polymerization ethylene behaves as an ideal gas

$$pv = nRT$$

or

$$v = \frac{nRT}{P}$$

$$n = 40,000 \text{ kg/h} = \frac{40,000}{28} \text{ kg mol/h}$$

$$= 1.43 \times 10^3 \text{ kg mol/h}$$

$$R = 0.08206 \text{ (l)(atm)/(g mol)(K)}$$

$$= 0.08206 \left( 1 \times 10^{-3} \frac{\text{m}^3}{\text{l}} \right) (\text{atm}) / (\text{kg mol} \times 10^3) (\text{K})$$

$$= 0.08206 \text{ (m}^3\text{)(atm)/(kg mol)(K)}$$

$$T = 273 + 250\text{K} = 523\text{K}$$

$$v = \left( 1.43 \times 10^3 \frac{\text{kg mol}}{\text{h}} \right) \left( 0.08206 \frac{(\text{m}^3)(\text{atm})}{(\text{kg mol})(\text{K})} \right) (523 \text{ K}) \left( \frac{1}{2500 \text{ atm}} \right)$$

$$= 24.55 \text{ m}^3/\text{h}$$

Assuming the flow rate is constant along the entire length of the reactor, then

$$\tau = \frac{V}{v} = \frac{4.91 \times 10^{-4} \text{ m}^3}{24.55 \text{ m}^3/\text{h}} = 2.0 \times 10^{-5} \text{ h}$$

$$k = -\frac{1}{\tau} \ln 0.7 = \frac{1}{2.0 \times 10^{-5} \text{ h}} \ln 0.7$$

$$k = 1.78 \times 10^4 \text{ h}^{-1}$$

$$= 4.95 \text{ s}^{-1}$$

### C. CONTINUOUS STIRRED TANK REACTOR (CSTR)

The ideal continuous stirred tank reactor is a reactor with well-stirred and back-mixed contents. As a result, instant blending of the feed with the reactor contents is assumed to occur. The composition of the contents of the reactor is uniform throughout the reactor. Consequently, the exit stream from the reactor has the same composition and temperature as the reactor contents.

During polymerization with a CSTR, the monomer and the other components of the polymerization recipe are fed continuously into the reactor while the polymerization product mixture is continually withdrawn from the reactor. The application of the CSTR in suitable polymerization processes reduces, to some extent, the heat removal problems encountered in batch and tubular reactors due to the cooling effect from the addition of cold feed and the removal of the heat of reaction with the effluent. Even though the supporting equipment requirements may be relatively substantial, continuous stirred tank reactors are economically attractive for industrial production and consistent product quality.

In a CSTR, each element of monomer feed has an equal chance of being withdrawn from the reactor at any instant regardless of the time it has been in the reactor. Therefore, in a CSTR, unlike in batch and tubular reactors, the residence time is variable. The contents of a well-stirred tank reactor show an exponential distribution of residence times of the type shown in Equation 10.15.

$$R(t) = e^{-t/\tau} \quad (10.16)$$

where  $R(t)$  is the residence time distribution and  $t$  is the mean residence time, which, as we said previously, is the ratio of the reactor volume to the volumetric flow rate. The residence time distribution influences the degree of mixing of the reaction mixture. This, in turn, determines the uniformity of the composition and temperature of the reactor contents. As a consequence, the polymer product properties are influenced by the residence time distribution. Figure 10.8c shows an ideal CSTR with its residence time distribution and concentration profile. Tables 10.7 and 10.8 summarize polymerization reactions and processes, industrially employed reactors, and resulting polymer products.

**Table 10.7** *Polymerization Processes and Industrially Employed Reactors*

| Polymerization Reaction | Polymerization Process | Reactor |           |      |
|-------------------------|------------------------|---------|-----------|------|
|                         |                        | Batch   | Plug Flow | CSTR |
| Chain                   | Bulk                   | X       |           | X    |
|                         | Solution               | X       | X         | X    |
|                         | Suspension             | X       |           |      |
|                         | Emulsion               | X       |           | X    |
|                         | Precipitation          | X       |           | X    |
| Ionic                   | Solution               | X       |           |      |
|                         | Precipitation          | X       | X         | X    |
| Step growth             | Solution               | X       | X         |      |
|                         | Interfacial            | X       |           |      |

**Table 10.8** *Polymerization Reactions and Processes and Some Polymer Products*

| Reactor      | Polymerization Reaction | Polymerization Process                 | Example  |  |   |
|--------------|-------------------------|--|--|--|---|
| Batch        | Free radical            | Solution                               | Paint resins by polymerization and often also copolymerization of acrylates and methacrylates<br>Vinylacetate in methanol with subsequent alcoholysis to poly(vinyl alcohol)<br>Polyacrylonitrile spinning solution in dimethylformamide   |  |   |
|              |                         | Precipitation                          | Acrylonitrile in water<br>Azeotropic copolymerization of styrene and acrylonitrile in methanol   |  |   |
|              |                         | Suspension (bead)                      | Poly(vinylchloride)<br>Expanded polystyrene<br>Poly(methyl methacrylate)   |  |   |
|              |                         | Emulsion                               | Poly(vinyl acetate)<br>Water soluble paints<br>Poly(vinyl acetate)   |  |   |
|              |                         | Ionic                                  | Solution   | Butadiene<br>Isoprene<br>Ethylene or propylene and their copolymers<br>Block copolymers such as butadiene-styrene or styrene-butadiene-styrene<br>Polyether polyols block copolymers prepared from reaction of ethylene oxide or propylene oxide with polyhydric alcohols used for polyurethane preparation<br>Polymerization of $\epsilon$ -caprolactam<br>Polyethylene-propylene copolymer |   |
|              | Condensation            |  | Precipitation  | Formaldehyde resin (UF, MF, PF)  |   |
|              |                         |  | Solution   | Nylon 6,6<br>Polyurethanes   |   |
|              |                         |  |  | Interfacial  | Heat resistant aromatic polyamides and polyimides     |
|              | Plug Flow               |  | Free radical   | Solution   | High pressure polymerization of ethylene to give LDPE |
|              |                         | Ionic                                  | Precipitation  | Polymerization of isobutene in liquid ethylene with $\text{BF}_3$ catalyst<br>Polymerization of trioxane with $\text{BF}_3$ etherate as catalyst to produce polyoxymethylene   |   |
| Condensation |                         |  | Solution   | Continuous manufacture of polyurethane foam blocks<br>Production of nylon 6,6 on the extruder reactor as the last stage  |   |
| CSTR         | Free radical            | Solution<br>Precipitation<br>Emulsions | Vinyl acetate esters of acrylic acid acrylonitrile<br>Acrylonitrile<br>Polymerization of vinyl chloride<br>Polyacrylates and polymethacrylates<br>Butadiene, isoprene and then copolymers  |  |   |
|              |                         | Precipitation                          | Cationic copolymerization of isobutene-isoprene with slurry $\text{AlCl}_3$ as the initiator and methyl chloride as diluent<br>$\text{AlCl}_3$ slurry polymerization of propylene in the presence of transition methyl catalyst and excess monomer as a diluent<br>Fluidized bed reactor is used in the gas phase polymerization; a powdered polymer is produced in a gaseous monomer-low pressure polymerization of ethylene (HDPE) and propylene |  |   |

**Example 10.9:** Explain the molecular weight distribution shown in the following table.

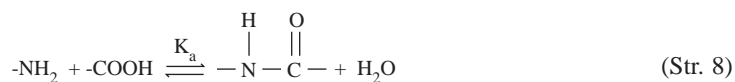
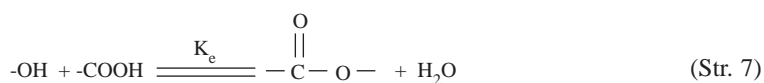
| Reactor                         | Polymerization Reaction              |                                      |
|---------------------------------|--------------------------------------|--------------------------------------|
|                                 | Chain-Growth                         | Step-Reaction                        |
| Batch or plug flow              | Wider than Schulz-Flory distribution | Schulz-Flory distribution            |
| Continuous stirred tank reactor | Schulz-Flory distribution            | Much wider Schulz-Flory distribution |

**Solution:** In radical chain reactions, the overall rate of polymerization,  $R_p$ , and the number-average degree of polymerization,  $\bar{X}_n$ , are functions of the initiator concentration  $[I]$ , the monomer concentration  $[M]$ , and also the temperature via the temperature dependence of the individual rate constants. At constant  $[M]$  and  $[I]$ , the Schulz-Flory MWD is produced. However, if  $[M]$  and  $[I]$  vary with time, a number of Schulz-Flory distributions overlap and thus a broader MWD is produced. In the ideal CSTR  $[M]$  and  $[I]$  are constant and the temperature is relatively uniform. Consequently, chain polymerizations in CSTR produce the narrowest possible MWD. In the batch reactor,  $[M]$  and  $[I]$  vary with time (decrease with conversion) while in the tubular reactor  $[M]$  and  $[I]$  vary with position in the reactor and the temperature increases with tube radius. These variations cause a shift in  $\bar{X}_n$  with conversion and consequently a broadening of MWD.

The molecular weight distribution also depends on the relative lifetime of the growing macromolecule and the mean residence time. In step-growth polymerization, even though monomers disappear very early in the reaction, high conversions are required to generate high  $\bar{X}_n$ . In general, therefore, the lifetime of a growing macromolecule is much higher than the residence time in step-growth polymerizations. For the CSTR, the composition of the product is not altered by increasing the duration of the polymerization process. In addition, because the residence time in CSTR is variable, there is an equal chance of finding both small and large molecules in the polymerization product. Consequently, there is a relatively broad molecular weight distribution. On the other hand, for step-growth polymerization in batch and tubular reactors, narrow MWD with increasing  $\bar{X}_n$  is generated with increasing conversion.

#### IV. PROBLEMS

10.1. Polyesters and polyamides are prepared according to the following equilibrium reactions.



$K_e$  and  $K_a$  are 10 and 400, respectively.

In the manufacture of linear polyesters, the final stages of polymerization are carried out at pressures of about 1 mm Hg and temperatures of 280°C. On the other hand, the reaction for the manufacture of nylon 6,6 is completed at 240 to 280°C and atmospheric pressure. Explain.

- 10.2. Repeat Example 10.7 in this chapter but assume that the initiator concentrations show a first-order decay.
- 10.3. Calculate the time required for 80% conversion of pure styrene at 60°C with benzoyl peroxide as the initiator in a batch reactor. Assume that the initiator concentration remains constant. Use the data given in Example 10.7 in this chapter and comment on your result.

- 10.4. It has been proposed that to avoid possible health problems, the polystyrene used for drinking cups must contain less than 1% monomer. Polystyrene was prepared at 100°C by the thermal polymerization of 10 M styrene in toluene in a batch reactor. The shift operator stopped the reaction after 2.5 h. Is the product from this operation suitable for producing drinking cups without further purification?

Data:

$$\frac{k_p^2}{k_t} = 8.5 \times 10^{-3} \text{ l/mol-s}$$

$$k_i = 4.2 \times 10^{-11} \text{ l/mol-s}$$

- 10.5. Estimate the adiabatic increase in temperature for the batch polymerization of butadiene.

Data:

$$\Delta H_p = -18.2 \text{ kcal/g mol}$$

$$\text{Heat capacity} = 29.5 \text{ cal/g mol } ^\circ\text{C}$$

- 10.6. For the bulk polymerization of methyl methacrylate at 77°C with azo-bis-isobutyronitrile as the initiator, the initial rate of polymerization was  $1.94 \times 10^{-4}$  mol/l-s. The concentrations of the monomer and initiator were 9 mol/l and  $2.35 \times 10^{-4}$  mol/l, respectively. To reduce the heat transfer problems, the polymerization was repeated in a solution of benzene by the addition of 4.5 l of benzene with an initiator concentration of  $2.11 \times 10^{-4}$  l/mol. Assuming that the rate constants are the same for both the bulk and solution polymerizations, calculate the rate of solution polymerization of methyl methacrylate. If there is no transfer to the solvent and the initial rate of initiation is  $4 \times 10^{-4}$  mol/l-s, what is the ratio of the number-average degree of polymerization for bulk-to-solution polymerization? Comment on your results.
- 10.7. It has been found that the polymer from a certain toxic monomer has excellent mechanical properties as a food wrap. To ensure maximum conversion and obtain a relatively pure product, the monomer was bulk polymerized in a batch reactor. Do you agree with the decision to use this polymer as a food wrap?
- 10.8. A typical emulsion polymerization recipe consists of 180 g water, 100 g monomer, 5 g soap, and 0.5 g potassium persulfate. Estimate the ratio of the total surface area of micelles to that of monomer droplets. Assume that the relative volume of micelle to a droplet is equal to the ratio of their volumes in the polymerization recipe. The density of a micelle is 0.2 g/cc and that of a droplet is 0.8 g/cc.
- 10.9. The following data were found for the emulsion polymerization of vinyl acetate at 60°C:

$$N = 12.04 \times 10^{14} \text{ particles/ml}$$

$$R_i = 1.1 \times 10^{12} \text{ radicals/ml-s}$$

$$k_p = 550 \text{ l/mol-s}$$

$$[M] = 5 \text{ M}$$

$$\text{Polymer particle density} = 1.25 \text{ g/cm}^3$$

- a. Assuming that the Smith–Ewart kinetics is valid for emulsion polymerization up to 80% conversion, how much time was required to obtain this conversion?
- b. What is the average size of the latex polymer particles if, on the average, each particle contains 133 chains?
- 10.10. A batch reactor of length 2.5 m and diameter 5.046 m is filled with vinyl acetate monomer. Polymerization is carried out isothermally at 50°C. The reactor is jacketed for heat removal. What is the temperature of the coolant?

Data:

$$\text{Rate of polymerization} = 10^{-4} \text{ mol/l-s}$$

$$\Delta H_p = 21.3 \text{ kcal/mol}$$

$$\text{Overall heat-transfer coefficient} = 0.0135 \text{ cal/cm}^2 \text{ s } ^\circ\text{K}$$

- 10.11. In an emulsion polymerization of styrene in a  $50 \text{ m}^3$  CSTR, the feed contains 5.845 mol of styrene per liter. For an average conversion of 75% in the reactor and assuming the Smith–Ewart behavior is followed, estimate:
- The mean residence time
  - The volumetric flow rate
- Data:
- $$k_p = 2200 \text{ l/mol-s}$$
- $$N = 1.80 \times 10^{14} \text{ particles/cm}^3$$
- 10.12. The bulk polymerization of a polymer in a plug flow reactor had been found to follow first-order kinetics. The flow rate is  $3.14 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$ , while the reaction rate constant and residence time are  $10^{-2} \text{ s}^{-1}$  and  $10^2 \text{ s}$ , respectively. Calculate:
- The conversion
  - The length of the reactor if its diameter is  $2 \times 10^{-2} \text{ m}$
- 10.13. The bulk polymerization of the poly(ethylene terephthalate) or polyisobutylene is to be carried out. For which of these polymerizations would it be more favorable to use a plug flow reactor?
- 10.14. Explain why a continuous stirred tank reactor (CSTR) is not normally used in industry in the production of nylon 6,6. What modification is needed to make (CSTR) suitable for the preparation of nylon 6,6?
- 10.15. The specific heats of polymerization of styrene and butene monomers are 160 and 300 kcal/kg, respectively. For which of these monomers would solution polymerization be more appropriate?
- 10.16. In certain *cis*-butadiene processes, the volume of the diluting solvent is sufficiently high that cooling is achieved by feeding cold diluent solvent to the reactor. For an end-use application, the final polymer concentration was 10%. The specific heat of the solvent is 0.96 Btu/lb°F. If the final reaction temperature is 122°F, at what temperature should the solvent be fed into the reactor so as to remove all of the heat of polymerization?

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