13

BULK AND SOLUTION PROCESSES

Marco A. Villalobos and Jon Debling

13.1 DEFINITION

Bulk and solution polymerizations refer to polymerization systems where the polymer produced is soluble in the monomer. This is in contrast to heterogeneous polymerization where the polymer phase is insoluble in the reaction medium. In bulk polymerization, only monomer provides the liquid portion of the reactor contents, whereas in solution processes, additional solvent can be added to control viscosity and temperature. In both processes, small amounts of additional ingredients such as initiators, catalysts, chain transfer agents, and stabilizers can be added to the process, but in all cases, these are also soluble in the reactor medium. As described in more detail below, the viscosity of the reaction medium and managing the energetics of the polymerization pose the most significant challenges to operation of bulk and solution processes.

13.2 HISTORY

Given its formulation simplicity, bulk polymerization was the preferred laboratory and commercial polymerization method in the early days of polymer synthesis when scientists discovered that certain liquid substances turned into hard solids by effects of temperature, sunlight, or in the presence of other substances acting as *accelerators*. Anecdotal and documented evidence suggest that the first synthetic bulk polymer ever purposely made was poly(vinyl chloride) (PVC), first synthesized by the German chemist Eugen Baumann in 1872. A method to polymerize PVC under sunlight was first patented in 1913 by Friedrich Klatte also from Germany and in 1926,

the American Waldo Semon, working for B.F. Goodrich, invented plasticized PVC [1–3].

In 1839, the German apothecary Eduard Simon first isolated polystyrene (PS) from a natural resin. More than 85 years later, in 1922, German organic chemist Hermann Staudinger realized that Simon's material comprised long chains of styrene molecules. He described that materials manufactured by the bulk thermal processing of styrene were polymers. The first commercial bulk polymerization process for the production of PS is attributed to the German company Badische Anilin & Soda-Fabrik (BASF) working under trust to IG Farben in 1930. In 1937, the Dow Chemical company introduced PS products to the US market [1, 4–5].

Between 1930 and the onset of World War II (WWII) in 1939, several polymer families were invented and commercially developed through bulk processes. The most important ones include low density polyethylene (LDPE), poly(methyl methacrylate) (PMMA), polyurethanes (PU), poly(tetra-fluoro ethylene) (PTFE), polyamides (PAs), and polyesters (PEs). The last three are attributed to Dupont's scientists Roy Plunkett and Wallace Carothers, respectively. During WWII, bulk polymerization was still instrumental in the development and commercialization of new families of PEs such as polyethylene terephthalate (PET) developed by ICI and Dupont and unsaturated polyester resins (UPRs) [1, 6–8].

From the 1940s, the bulk polymerization technique led way to other polymerization processes suitable for the commercial production of new polymer families. The inclusion of inert solvents into the reaction mix allowed for lower viscosity operation with the consequent improvements in reactor control, turning bulk processes into solution ones.

While other polymerization processes such as emulsion, suspension, gas phase, precipitation, and interfacial polymerization were being developed, bulk polymerization evolved from its early processes of the 1930s where monomers and catalysts were loaded into a batch polymerization reactor operating at semiadiabatic conditions to temperature-programmed semicontinuous reactors and to continuous batteries of stirred and plug flow reactor trains developed in the 1970s and 1980s. Since then, advanced process control strategies, and novel stirred and plug flow reactor geometries have maintained bulk polymerization as one of the preferred manufacturing processes for a wide variety of commodity, engineering, and high performance plastics [1, 4].

## 13.3 PROCESSES FOR BULK AND SOLUTION POLYMERIZATION

13.3.1 Reactor Types

13.3.1.1 Batch/Semibatch Reactor
The simplest and arguably the oldest process vessel for polymerization and a natural extension of laboratory glassware equipment is the batch reactor. In this configuration, a reactor equipped with an agitator is charged with all of the ingredients (monomer, solvent, initiator, catalyst, etc.), heated to the desired temperature and the polymerization is allowed to proceed until completion. Safe operation of these processes requires judicious *a priori* selection of the appropriate feed formulation, batch size and cooling system to prevent uncontrollable reaction runaway and potential safety issues. A "semibatch" reactor is simply a "batch reactor" operated with a continuous or intermittent feed to the reactor instead of charging all of the material at the beginning. Often the same vessel can be used for "batch" or "semibatch" modes of operation. Metering the feed to the reactor over sufficient time allows control of the desired product quality as well as controlling the temperature from the heat of polymerization. In "semibatch" mode, it is common to stage different feeds to the process at chosen intervals over the reaction time as product needs dictate. In both the batch or semibatch processes, the product is not withdrawn until the "batch" is finished and the residence time is simply defined by the "batch" time or total process time in the "kettle."

For both batch and semibatch processes, the reactor "kettle" is often provided with heating or cooling as needed by external sources such as cooling water, tempered water, steam, oil, or electric or reflux condensers. The reaction vessel may also be put under vacuum to remove undesired volatile material. In many cases, the removal of volatiles is not simply a requirement to achieve regulatory requirements, but rather to drive the reaction to completion. For example, in condensation polymerization where equilibrium often exists, the extent of reaction is controlled by removal of a condensate; vacuum removal is critical to achieving final product molecular weight and end group concentration [9].

13.3.1.2 Continuous Stirred Tank Reactor (CSTR)
The continuous stirred tank reactor (CSTR) is a continuous process that is ideally fully back mixed such that the product leaving the reactor has the same composition and properties as the material inside the reactor. The CSTR may be considered a well-mixed "semibatch" reactor with continuous feed and product withdrawal. In many cases, the same reactor vessel used for batch/semibatch may be used as a CSTR with little modification. Figure 13.1 shows different internal configurations of CSTRs. Multiple CSTRs operating at different temperatures can be linked in a cascade of two or more in series, to achieve desired conversion of monomer and molecular weight. In between each CSTR, additional feed may be added to form unique polymers. CSTRs may also be used in combination with other reactors, such as tube reactors, to enhance monomer conversion.

Unlike batch/semibatch reactors, the mean residence time of a CSTR at steady state is defined by the ratio of volume inside the reactor to volumetric feed rate, which at equal density of feed and reactor contents is equal to the reactor space time. The advantage of the CSTR over the batch or semibatch reactor is that it is ideally suitable for long runs of continuous production of a polymer product. Once the reactor process is brought to steady state, uniform quality and consistent product is made. However, the CSTR requires several reactor turnovers (at least 3–4) before the process is at steady state and uniform product is made [10].

(a)   (b)
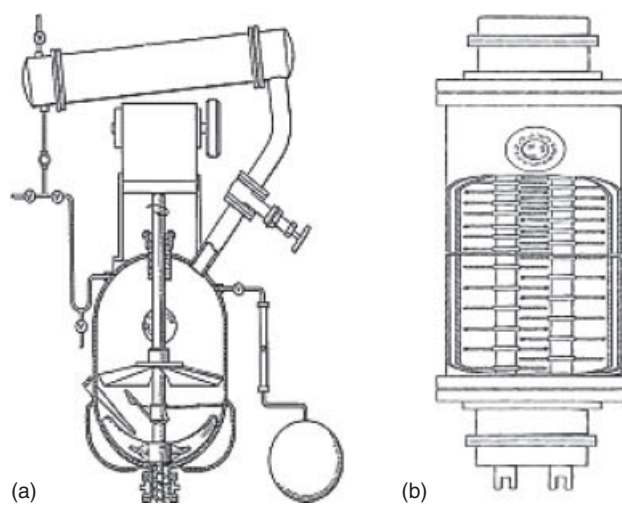
Figure 13.1 Different CSTR configurations: (a) pressure tank with condenser system and (b) vertical or horizontal intermeshing paddle mixing reactor [16, 66].

13.3.1.3 Autoclave Reactor An autoclave reactor is a batch or continuous reactor usually operating at moderate-to-high pressures >1 bar and a pressurized liquid or gaseous environment.

13.3.1.4 Tubular Reactor A tubular reactor is a continuous process where the monomer feed is charged to the inlet of a tube and the product withdrawn at the other end. The reactor has the advantage of high surface area to volume and thus good heat transfer. On the other hand, plugging and fouling must be managed as does high pressure drop. Flow through the tube is "plug flow" without significant axial mixing and thus the conversion and molecular weight of the polymer changes over the length of the tube. Sometimes axial mixing can be improved by the addition of static mixers at various places through the tube. The residence time of the reactor is defined as the tube volume divided by the volumetric feed rate. Different types of tubular reactors are shown in Figure 13.2.

13.3.1.5 Loop Reactor A loop reactor, as shown in Figure 13.3, is a tubular reactor wound around itself and operated under high recycle. It has the advantages of good heat transfer and residence time distribution of a fully back-mixed CSTR. However, loop reactors require high recycle ratios and hence significant pumping systems to provide sufficient mixing. At high recycle ratios, a loop reactor operates with the same residence time distribution as a CSTR. At low recycle ratios, it has been shown that the loop reactor residence time distribution is oscillatory [11].

13.3.1.6 Casts and Molds Polymerizations may also be carried out in molds or casts. In this process, the monomer is added to a mold and allowed to heat up to the point of self-polymerization. The resultant polymer product is removed from the pans and cooled. While this more manual process appears slightly archaic, its simplicity allows the production of a number of specialty products still in commercialization today.

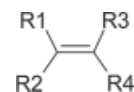### 13.3.2 Processes for Free Radical Polymerization

Free radical polymerization is a subset of the chain growth polymerization addition mechanisms between two


(a)   (b)
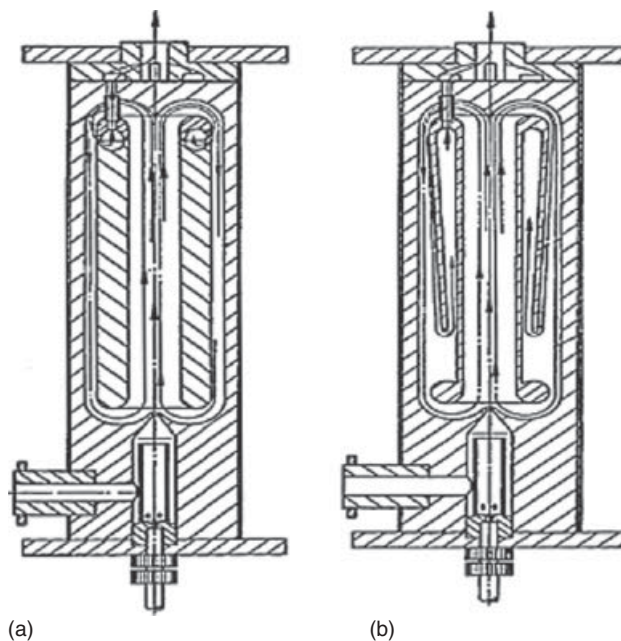
Figure 13.3 Different loop reactor configurations: (a) outlet flow is guided by a hollow ring and (b) outlet flow is guided by double walls [99].

molecules (monomers) bearing C=C double bonds. The term *homopolymerization* refers to cases where a single monomer is employed, whereas *copolymerization* refers to polymerizations where more than one monomer is present in the reaction mix. Suitable monomers for free radical polymerization include those unsaturated monomers bearing a C=C double bond of the general structure shown in Figure 13.4.

This includes α-olefins, vinyl monomers, dienes, mono- and polyunsaturated organic compounds such as alkenyl derivatives of fatty acids and alcohols. Exemplary

Figure 13.4 Suitable monomers for free radical polymerization.

(a)   (b)
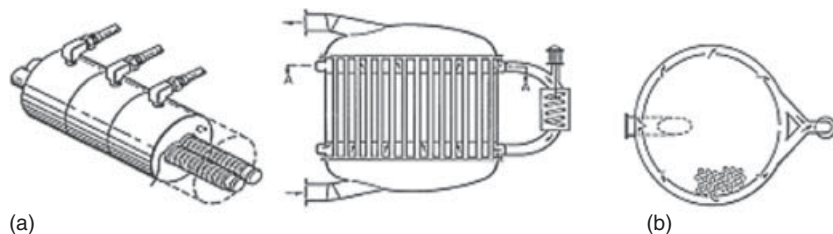
Figure 13.2 Different PFR configurations: (a) detailed of wiped surface reactor and (b) side and top view of tube bundle and shell reactors [22, 98].

monomers include styrene, α-methyl styrene, acrylic acid, and its esters (acrylates), as well as methacrylic acid and its esters (methacrylates). The chemistry of free radical polymerization is described elsewhere in this book (Chapter 4) and other references [12, 13]. The most commonly polymerized monomers and resulting polymers produced by bulk and solution processes are described below.

13.3.2.1 Polystyrene

One of the largest volume products made today through bulk addition polymerization is PS. PS repeat unit structure is shown in Figure 13.5. Developed in the 1950s, bulk polymerization of styrene monomer to make general purpose polystyrene (GPPS) originally took place in molds. In this process, styrene monomer was charged into individual molds that were assembled in a filter press like array and closed under mechanical pressure. Heating oil or steam was circulated through the individual molds, which heated the monomer about $70\,^\circ$C to sustain polymerization. Isothermal polymerization (thermal or catalyzed) took 5–14 h by progressive heating of the reaction mix at temperatures between 80 and $150\,^\circ$C. Semiadibatic polymerization was completed much faster ($t < 60$ min) with temperatures approaching $300\,^\circ$C. At the end of the polymerization, the molds were cooled and opened to remove GPPS blocks, then the polymer ground into pellets. In spite of its simplicity and relatively high reactor productivity, mold processes were abandoned in the late 1970s due to high residual styrene levels (>1 wt%), poor M_w reproducibility (due to temperature variability), and high dispersity (M_w/M_n) that affect product properties (melt flow index, tensile and impact strength, heat deformation temperature (HDT), and Vicat softening point) [14, 15].

Modern GPPS is produced by continuous bulk and solution processes developed in the mid-1950s by major PS producers, BASF, Dow Chemical, Monsanto, Union Carbide, and others. In the modern continuous GPPS process, as the one shown in Figure 13.6, styrene monomer is continuously fed to a packed column (normally alumina, silica gel, or clay) to remove moisture, impurities, and inhibitor, blended with recycled styrene monomer, peroxide initiator (normally dialkyl or diacyl peroxides, such as di-*tert*-butyl peroxide, dicumyl peroxide, or *tert*-butyl peroxibenzoate utilized at low concentrations; [I] <0.5% w/w in the feed), chain transfer agent (normally aliphatic

Figure 13.5 Polystyrene structure.

or aromatic thiols, such as *t*-dodecyl mercaptan and *n*-dodecyl mercaptan used in small concentrations [CTA] <1% w/w) and fed to a CSTR. Reactor residence times are approximately 1–3 h and typical reactor sizes in the range of 20–100 m^3 to achieve reasonable economics of scale. Normally the CSTR operates partially full (~90 %) with a vapor headspace under moderate pressure of <10 bar and isothermally at temperatures below $150\,^\circ$C. At steady state, the reaction mix in the CSTR consists of a single phase comprised of 30–40% PS in monomer with small amounts of impurities, initiator, and chain transfer agents. Conversion is purposely limited so as to achieve a manageable reactor mix viscosity and maintain isothermal conditions for high molecular weight PS (normally M_w <300,000 Da). In the end, the three variables (T, θ, and [I]) define the monomer conversion, reaction rate (and thus heat generation), and molecular weight of the PS. New process advances include adding reflux condensers, external heat exchangers, chilled jacket cooling fluids, cooling baffles, and extended area internal cooling coils and diperoxide initiators to allow an increase in reactor productivity and higher monomer conversions [16–18].

The product from the CSTR is continuously metered to a second reactor in series. Usually the second reactor is a PFR operating at higher temperature than the CSTR (up to $200\,^\circ$C) in isothermal or semiadiabatic mode. Typical residence times are between 5 and 50 min. A temperature profile may be prescribed in the PFR by segmenting the reactor jacket and allowing heating oil of different temperatures to circulate through each jacket. Semiadiabatic operation in PFRs is also possible by allowing the heat generation rate to approach the heat removal rate, thus causing the reaction mix to vary along the reactor coordinate. In any operation mode, the heat generation rate should always be less than the heat removal capacity at any point in the reactor to prevent a runaway. The higher reaction temperatures in the PFR lead to much higher reaction rates (d[M]/dt = 1–10%/min) than the CSTR and Trommsdorff and glassy effects are limited at these high reaction temperatures [18–20]. Therefore, the conditions in the PFR can be tuned to tailor the MWD of the product thus defining different GPPS grades [21–23].

The hot reaction mix leaving the second reactor is continuously pumped through a preheater operating at $T_{PH} < 300\,^\circ$C, and then to an evaporator to separate molten polymer (up to 80% of the mixture) from the unreacted volatile components. A variety of types of equipment have been used including wiped film evaporators (WFEs), wiped surface evaporators (WSEs), falling strand evaporators (FSEs), and filmtruders, described in Section 13.5.6. For PS, evaporators typically operate at high temperatures $T_{wall} \approx 250$–$300\,^\circ$C and moderate vacuum ($P \approx 1$–50 torr) with residence times in the evaporator of the order of $\theta = 2$–10 min. They are designed to minimize residual

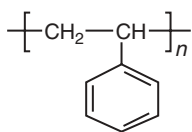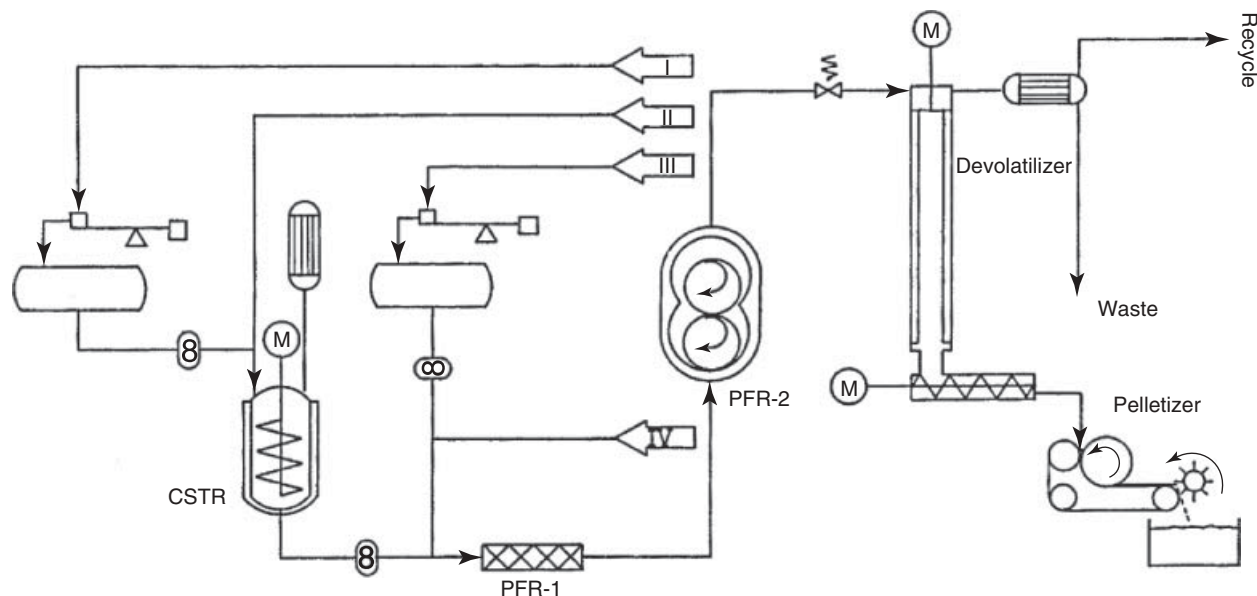**Figure 13.6** Schematic bulk continuous process for high molecular weight styrenic polymers showing a CSTR and two different PFRs in series, evaporation unit, and pelletization unit. I: monomer(s) or monomer–rubber solutions feed stream, II: initiator and additives feed, III: continuous recycled stream from evaporators, and IV: additional initiator/additives feed [21].

styrene to less than 500 ppm, but some processes include two or more evaporator stages in series to reduce volatiles to under 50 ppm. The volatile material leaving the evaporator section is recovered in a liquid separation operation, most often single- or multistage distillation most and recycled to the first reactor. The molten PS leaving the evaporator is pumped to a pelletizing line where is it is finally bagged as a solid pellet product [16, 21, 23].

Solution GPPS processes differ from bulk processes in that an inert solvent (normally ethyl benzene) is fed with the monomer. The purpose of the solvent, normally 10–30% of the reaction mix, is to reduce viscosity and aid in reactor temperature control. By reducing reactor viscosity, higher monomer conversions are possible and higher molecular weight polymer can be produced in each reactor. In addition, higher polymerization rates are possible since solvent decreases the total heat generation rate per unit mass in proportion to its content in the reaction mix. The use of solvents in sufficient levels also allows the use of multiple CSTR's in series in lieu of CSTR/PFR combinations. On the negative side, the use of solvents decreases monomer concentration and polymer production rate. For GPPS, however, the reduced monomer concentration is usually offset by higher temperature, and thus for a given reactor size, polymer productivity in bulk and solution processes is similar. Except for the presence of solvent in ppm amounts in the solution product, GPPS made through solution or bulk processes are virtually undistinguishable from one another [23–25].

A special grade of PS that is also produced commercially is low molecular weight PS. Often referred to as *oligomeric polystyrene*, this grade of material typically has an M_w from 1800 to 25,000 Da and is used for specialty applications such as additives for plastics. Low molecular weight PS can be conveniently made by a high temperature polymerization process [26–28]. At high temperatures, reaction rates and monomer conversions are extremely high and ideal for making low molecular weight oligomers. The kinetics of styrene polymerization at high temperatures has been thoroughly described by Campbell who has shown that at elevated temperatures the dominant mode of chain termination in styrene polymerization is by back biting and scission [29].

13.3.2.2 Styrene Acrylonitrile (SAN) Copolymers
Styrene–acrylonitrile copolymers are produced either by batch or continuous bulk or solution processes. SAN copolymers produced in a CSTR are clear, but in batch processes they may be hazy due to compositional drift and some degree of incompatibility between copolymers of different compositions. To prevent or minimize compositional drift, commercial batch SAN is polymerized at compositions approaching the azeotropic copolymerization condition for this monomer pair (77/23 S/AN % mol, acrylonitrile), where the instantaneous copolymer composition equals the comonomer mix composition. Around these conditions, the batch or continuous SAN processes closely follow those described for GPPS [23, 30].

13.3.2.3 High Impact Polystyrene (HIPS) (see also
Section 10.2.1.1) High impact polystyrene (HIPS) is a
composite material comprising the polymerization product
of styrene monomer in which 3–15% of polybutadiene
(PB) rubber has been dissolved before polymerization.
Designed in the 1950s to obtain ductile PS, it was originally
manufactured by a suspension polymerization process. As
demand for this ductile plastic grew during the 1960s and
1970s, continuous bulk and solution GPPS plants were
redesigned to accommodate the PB dissolution step and
to handle the normally higher reaction mix viscosities of
HIPS [25].

PB, the polymerization product of 1,3-butadiene
(CH_2=CH–CH=CH_2), is not an inert component but a
reactive one in the HIPS system. Both its total content and
its vinyl (1,2-addition unit) to linear (1,4-addition unit)
ratio are fundamental in the process design and product
characteristics. Depending on the polymerization process,
PB can be stereospecific with varying contents of cis-
and trans isomers. Normally high *cis*-PB contents are
more than 80% of the cis adduct and more than 85% of
1,4-addition units. Free radical PB is nonstereo specific.
Either one can be used to make HIPS. Typically, high
cis-PB leads to products with higher ductility and enhanced
mechanical performance. PB bales are ground in cold to
pebble size particles and added into a tank containing cold
styrene monomer and agitated at low RPM. The dissolution
is carried out below room temperature to prevent onset of
styrene polymerization [25, 31].

As in the bulk GPPS process, the single-phase solution
of PB in styrene is continuously fed into a series of
CSTRs or CSTR-PFR arrays, depending on whether the
process runs as solution or bulk. Dialkyl and diacyl
peroxide initiators are selected to optimize polymerization
rate and degree of PB grafting. Mercaptan molecular weight
regulators are added in similar proportions in the PS process
described. Prevention of extensive PB crosslinking requires
the use of antioxidant, normally hindered phenols and
hindered amines, used in <0.3% w/wp. Styrene conversion
in the first reactor is about 20–35% and 65–80% in the
second and further reactors. In this sense, HIPS and PS are
very similar processes. The major process differences arise
due to the additional reactions involving PB, noticeably
PB–PB crosslinking reactions, and PB–S copolymerization
or PB–PS grafting reactions. The higher solubility of the
styrene/PS pair than PB/styrene one causes the PB to
become insoluble in the mix and precipitate in the form
of discrete dispersed particles at conditions dependent on
styrene conversion and molecular weight, temperature, and
PB content in the mix. In this manner, the single-phase
PB/styrene solution fed to a CSTR finds at steady state
as a two-phase system where PB particles have formed a
separate phase. The PB particle formation process is still
poorly understood. The forming spherical rubber particles
are themselves composite particles with a PB continuous
phase and dispersed spherical occlusions of a polymerizing
mix of styrene and PS, and PS grafts forming on the
available S/PB internal and external interfaces [31–33].

The rubber particle size distribution (PSD) and occluded
and grafted PS fraction in HIPS are mostly controlled by
optimizing reactor agitation parameters and target reactor
conversion, solids, and viscosity. Higher agitation rates may
lead to smaller rubber particle sizes due to droplet shear
breakage. In the first reactor, the reaction mix consists
of a styrene/PS continuous phase and a PB/styrene/PS
dispersed phase. While extensive PB crosslinking renders
the PB phase ineffective to the desired toughening of
the PS matrix, total lack of crosslinking also fails to
maximize reinforcing properties. It is still an art in HIPS
polymerization to carefully craft the reactor design and
process conditions (T profile, RTD, conversion profile,
and [I]) to generate the most effective PB rubber PSD
for reinforcement (0.5–10 μm). This includes an optimal
level of PB crosslinking, measured as both swelling index
and percent gel in the product, amount of PS occluded
in the composite rubber phase (1–3 parts of PS per PB
part), and optimal degree of PS grafting in the internal
PS occlusions, and onto the PS matrix, to maximize
interfacial adhesion, and thus particle stability and HIPS
mechanical performance at a given PB content. After the
second reactor, whether a CSTR or PFR, the product is
devolatilized and separated as described before in the PS
process [31, 33–36].

13.3.2.4 Acrylonitrile/Butadiene/Styrene (ABS) Acry-
lonitrile/butadiene/styrene (ABS) polymers are not true
terpolymers. As HIPS they are multipolymer composite ma-
terials, also called *polyblends*. Continuous ABS is made by
the copolymerization of styrene and acrylonitrile (SAN) in
the presence of dissolved PB rubber. It is common to make
further physical blends of ABS with different amounts of
SAN copolymers to tailor product properties. Similar to the
bulk continuous HIPS process, in the ABS process, high
cis-PB (>50%, >85% 1,4-addition) is dissolved in styrene
monomer, or in the process solvent, and fed continuously
to a CSTR where streams of AN monomer, recycled S/AN
blends from the evaporator and separation stages, peroxide
or azo initiators, antioxidants and additives are continuously
metered according to the required mass balance to keep the
copolymer composition constant over time at steady state.

Two or three CSTRs in series or a CSTR–PFR array
can be used in mass processes. In the most common two
CSTR or CSTR/PFR arrays, the PB solution is added to the
first CSTR that operates between 20% and 40% solids at
steady state. The second CSTR operates at solid contents
between 50% and 80% depending on reactor volume and
design. In the three-CSTR array, the first reactor operates at
low conversions, X_m <20%, and the second CSTR operates

at a total solid contents of 25–40%. This process allows the choice to feed the PB rubber solution to either the first or second reactor. The addition of the PB solution to the second reactor changes the rubber PSD, the amount of SAN occluded in the PB phase, as well as the extent of SAN grafting onto the rubber particles, all instrumental parameters in defining the properties of the resulting ABS product. Ideally, a rubber content of 3–15% is desired, depending on the required impact resistance of the ABS; 3–6% PB for mid-impact grades, 6–10% for high impact grades, and 10–15% for ultrahigh impact grades, or for mid- and high impact grades that will be obtained by further dilution with bulk or suspension SAN. To maximize impact resistance, rubber particle size must be distributed between 0.5 and 10 μm. Research studies suggest that narrow rubber particle size distributions centered about 2 μm yield a better balance of impact and gloss at a given PB content. The fraction of grafted and occluded SAN in the rubber particles is also instrumental in maximizing the impact properties of ABS, with maximum properties observed at 1 : 1 to 1 : 3 ratios of PB to SAN. As in HIPS processes, minimizing PB crosslinking is also instrumental to maximize impact properties. Normally, stereospecific high *cis*-PB is preferred for high performance grades.

In ABS production, the first reactor operates at temperatures between $T_{r1} = 90–150\,^{\circ}\mathrm{C}$. The second reactor may by an isothermal CSTR operating a $T_{r2} = 110–170\,^{\circ}\mathrm{C}$, or a PFR operating on a prescribed raising temperature profile within these same limits. The far end process resembles that of PS or HIPS previously described [23, 37, 38]. The use of high T_g comonomers such as Maleic anhydride, α-methyl styrene, and *n*-phenyl maleimide in the monomer mix (<15% w/wm) has been successfully employed to increase the T_g of ABS product by 3–10 °C, producing the so-called high heat ABS grades [37–39].

13.3.2.5 Acrylics Acrylic polymers form a broad class of materials ranging from viscous liquids to hard, transparent resins. They find many applications including additives for plastics, dispersants for pigments in coatings and printing inks, overprint varnishes, adhesives, and additives for coatings, to name a few [40]. The family of acrylic monomers comprises a broad variety of vinyl monomers based on acrylic and methacrylic acid and their esters. They include acrylic and methacrylic acid and the corresponding esters of both. Functional monomers bearing hydroxyl, epoxy, and amino groups, for example, are also included in this category. Acrylic polymers range from homopolymers to copolymers containing two or more monomers. Often comonomers include styrene, and the compounds may still be referred to as *acrylics*.

PMMA is a transparent thermoplastic with high glass-transition temperature ($T_g \sim 105\,^{\circ}\mathrm{C}$), commonly used as glass replacement in windows and in colored thermoformed

parts where deep profiles, mechanical and chemical resistance is required, such as bathtubs and sinks. The cast polymerization process was developed by Rohm & Haas, and Chimey in the 1960s to make Plexiglass™ plastic windows. Although partially replaced by continuously polymerized PMMA extruded into transparent sheet, the cast process is still in use today for panels requiring thicknesses in excess of one half inch. In the PMMA cast process, MMA monomer is first polymerized slowly to low conversion (<25 wt%) in the presence of azo initiators (typically AIBN), dyes, chain transfer agents, and plasticizers, at relatively low temperatures ($T_{rx} <100\,^{\circ}\mathrm{C}$) to produce a viscous syrup [13]. The chemical structure of PMMA repeat unit is shown in Figure 13.7. Comonomers such as acrylic acid, methacrylic acid, and their alkyl esters are often employed in low proportions (<10% mol). The syrup is then transferred to a mold, sealed, and immersed in an open water pool where slow polymerization occurs over a period of hours. Slow polymerization is required to avoid self-acceleration due to the autoacceleration or Trommsdorff effect, which can lead to overheating, monomer boiling, and deterioration in product quality [19]. The mold polymerization stops when the product mixture glassifies as its T_g approaches the polymerization temperature; however, further processing is required to increase monomer conversion above 90%. The molds are therefore emptied and the product placed in convection ovens, heated above the T_g, and slowly (<1–2 %/h) polymerized to conversions above 99.9%. More recent modifications of the mold process include prepolymerization in a continuous plug flow reactor, followed by a high temperature pressurized autoclave and the use of initiator mixtures to optimize the reaction rate [41–43].

Semibatch solution polymerization is a well-established method for producing acrylic resins. In the semibatch solution process, solvent is commonly charged to the reactor and heated to the desired reaction temperature, typically 100–140 °C. Monomer, initiator, and other ingredients are slowly fed to the reactor over a period of 4–6 h to achieve a desired solids content (typically up to 70% by weight solids). During polymerization, the solvent may be refluxed to help remove the heat of polymerization [40]. At the end of the polymerization, a hold time and post charge of initiator solution are common to techniques designed to reduce

Figure 13.7 Poly(methyl methacrylate) (PMMA) repeat unit structure.

the free monomer remaining in the reactor. Many acrylic polymers, such as acrylic polyols for isocyanate cured coating, are sold as solutions in solvent. In this case, the solution is simply cooled to room temperature, additives added, and the material drummed or charged into a tanker car for shipment. Low T_g acrylic polymers can be sold as 100% solids if the reaction solvent can be removed from the vessel by vacuum distillation. In such cases, low boiling point solvents, such as acetone or isopropanol, are usually used in the polymerization process.

A wide variety of initiators may be used in the solution polymerization of acrylics and the choice depends on reaction temperature, final end-use applications, process capability (some initiators emit gaseous by-products upon decomposition), and cost. One usually selects an initiator with a suitable half-life decomposition time appropriate for the polymerization temperature and residence time to maximize initiator usage effectively. Generally, liquid initiators are used, although solid ones exist. Ideally, the initiator requires no special handling such as refrigeration; however, initiators with low half-lives temperatures usually require more extensive storage. A wide variety of Azo and organic peroxides initiators are commonly used in solution polymerization processes [44, 45]. There are more than 50 organic peroxides available including families of diacyl peroxides, t-alkyl peroxyesters, monoperoxycarbonates, di(t-alkyl) peroxides, and t-alkyl hydroperoxides, to name a few. The selection of the appropriate initiator can also have an impact on the final properties of the produced polymer. Choosing initiators that are "hot" or "active" can abstract hydrogen from the polymer backbone and lead to broader molecular weight distributions [46].

Producing high molecular weight acrylics in solution polymerization presents many of the challenges described previously for GPPS relating to heat transfer, solution viscosity, temperature control, and productivity. Making a high molecular weight acrylic often means reducing temperature and initiator content, but this requires long batch times and low solution solids. A constant trend in the market, however, is for lower VOC systems, which has resulted in a growing demand for lower molecular weight acrylic polymers. Producing low molecular weight acrylics by solution polymerization has some challenges. As temperature is raised, the pressure in the reactor increases and limits the use of volatile solvents. Making a very low molecular weight polymer by a solution process often means adding significant levels of initiator or chain transfer agents, which can add cost, regulatory hurdles, color, and odor to the final product.

To overcome the challenges described above, associated with the production of low molecular weight acrylic polymers by solution processes, a high temperature continuous polymerization processes was developed in the early 1980s by the S.C. Johnson Co. Several US patents disclose a processes for continuous bulk polymerization of acrylic monomers with styrene at elevated temperatures $>180\,^\circ$C in a CSTR at high conversions and low residence times [26–28]. At high temperatures in the presence of styrene, acrylic copolymers require little to no initiator, as styrene undergoes thermal decomposition to form free radicals. In addition, the high reaction temperatures result in low reactor viscosities and thus little or no solvent is required in these processes.

At high temperatures, the main mechanism of chain termination of styrenic and acrylate polymers is not by the classical methods of disproportionation and combination but rather by backbiting and scission [29]. This results in termination unsaturation in the final product and the presence of oligomers [47, 48]. Some monomers may be difficult to polymerize at high reaction temperatures due to depropagation. Debling and Villalobos have shown that methacrylates undergo significant depropagation at temperatures above $180\,^\circ$C but can achieve high conversion by copolymerization with acrylates or styrene [49]. At very high temperatures, acrylic acid is also prone to decarboxylation and anhydride formation reactions, which must be carefully controlled. Recent advances in understanding the kinetic mechanisms of acrylate and methacrylate polymerization at high temperatures and the modeling of these systems have been recently published [50–55].

High reaction temperatures not only favor low molecular weights at high polymerization rates but also enable slower reactions, normally not significant at lower reaction temperatures. Condensation reactions, for example, can proceed concurrently with free radical polymerization to provide uniquely modified specialty copolymers [56–59]. At the same time, deleterious side reactions that form gel can also occur and must be controlled by proper selection of solvent systems in some chemistries [60].

13.3.2.6 Water-Soluble Polymers A number of polymers useful for such applications as diaper absorbents, detergents, dispersants, thickeners, and water treatment applications are water soluble and thus may be made by aqueous polymerization processes [61–63]. Poly(methacrylic acid) and its high acid copolymers and salts, as well as poly(N-vinyl pyrrolidone), are some examples. Typically initiators include water-soluble azo compounds, hydroperoxides, persulfates, and redox systems [64]. Often, if the solubility is not complete in water, alcohol solvents are sometimes added.

13.3.3 Processes for Step-Growth Polymerization

Step-growth polymerization chemistry is based on reacting molecules having complementary reactive moieties A and B, where these react with one another to form a new chemical species given by A + B → C, wherein species

A and B contain functional groups that may react with each other to form a linkage. Sometimes, a small molecule or "condensate" is formed in the process. The most commonly functional groups in step-growth polymerization are carboxyl acids, hydroxyl, primary and secondary amines, isocyanate, oxirane, esters, and anhydride.

In contrast to addition polymerization, in step-growth polymerization, the molecular weight buildup progresses slowly with conversion and depends on the stoichiometry of the reactants. In step-growth polymerization, the monomer disappears at low conversions, and high molecular weights are achieved only at high conversions. In condensation step growth, the reactions are often reversible and thus, the removal of the condensation product becomes instrumental in reaching high group conversions and therefore high molecular weights. It is common in these systems, then, to design the reactor and operating conditions such that removal of the condensation product is facilitated. Reflux condensers with tailored fractionation separation of volatile condensates and vacuum operation are common in the step-growth commercial reactors. It should be noted that many monomers used in step-growth polymerization are solid at room temperature or form polymers with high glass-transition temperatures ($T_g > 100\,^{\circ}$C) and/or are semicrystalline, exhibiting high melting points ($T_m > 200\,^{\circ}$C). This requires processes to be run at high temperatures to avoid polymer glassification in the reactor and to deal with increasing reaction mix viscosity [65].

The use of catalyst to accelerate chain propagation steps is well documented in the art. It is important to note that the use of catalysts does not substitute the need to eliminate condensation products and impurities from the system, when present. For instance, some esterification catalysts, such as Lewis acids, are known to also catalyze hydrolysis reactions when the accumulation of moisture in the system is high.

13.3.3.1 Polyesters

In general, PEs are the high molecular weight condensation product of an aliphatic or aromatic dicarboxylic acid of general formula (HOOC-R-COOH) and an aliphatic or aromatic diol of general formula (HO-R'-OH). Because of their superior thermal, optical, and mechanical properties, the most commercially important thermoplastic PEs manufactured today are polyalkylene therephthalates, specifically PET, the condensation product of ethylene glycol (EG) with terephthalic acid (TPA) shown in Figure 13.8, and poly(butylene terephthalate) (PBT), the condensation product of butanediol with TPA, both semicrystalline polymers. Poly(ethylene naphthalate) (PEN) and poly(trimethylene terephthalate) (PTT) have gained commercial interest in the last decade [65].

PEs are produced by a variety of batch and continuous bulk processes. PET and PBT are commercially made by both continuous processes, in a series of CSTRs of varying
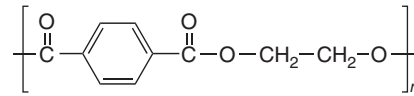
Figure 13.8 Poly(ethylene terephthalate) (PET) structure.

geometries and stirring arrays, or in batch processes. In the continuous process, the first CSTR is used to form a "prepolymer" or oligomer of 2–10 units long. In the second stage, the "prepolymer" is grown to higher molecular weight in the "melt polymerization stage." The final, "finishing" stage, often employs a long residence time reactive zone to drive off the condensate under vacuum and build molecular weight to useful levels. This is the so-called solid-state polymerization stage, which conducted while the polymer remains in the solid state.

During the prepolymerization stage, direct esterification of the diol, either EG for PET, or 1,4-butanediol (BD) for PBT, onto TPA or most commonly transesterification of the diol onto dimethyl terephthalate (DMT), is carried out to form the corresponding diol-ester. DMT is produced separately as the esterification product of TPA with methanol. The DMT route is sometimes preferred because DMT is more soluble in the reaction mix and easier to purify than TPA. Additionally, TPA is known to catalyze the cyclization of BD and is largely avoided in PBT manufacturing [65–69].

The transesterification reaction is typically carried out in a CSTR by continuously feeding a "paste" of premixed DMT/diol into a diol-ester prefilled reactor operating between 160 and 240 $^{\circ}$C. Typically DMT/diol molar ratios of 1 : 2 to 1 : 2.2 are used for PET and 1 : 1.1 to 1 : 1.5 for PBT. The reaction for PET is catalyzed by a metal acetate. Zinc acetate is commonly used, but antimony, barium, calcium, and magnesium acetates may also be used. For PBT titanium orthoesters, such as tetra-butyl titanate, are employed as catalysts. The CSTR operates at low pressures, 0.1 to 1.0 bar, allowing the condensation product (methanol) and the excess diol to be distilled out of the reactor through a system of overhead condensers and distillation columns. Typical residence times in the reactor are between 60 and 240 min. The reaction product consists of a mix of the diol-ester and some low molecular weight oligomers. This first step is shown for PET in Figure 13.9 [65].

The product of the prepolymerization stage is continuously fed into the melt polymerization reactor, where the condensation reaction of the diol-ester to form the corresponding polyalkylene terephthalate (PAT) (either PET or PBT), shown in Figure 13.10. In this self-transesterification, the ester-diol is the source of both ester and alcohol functionalities. Since these PE products are semicrystalline, the reaction must be carried out above their melting point (T_m) to prevent solidification of the
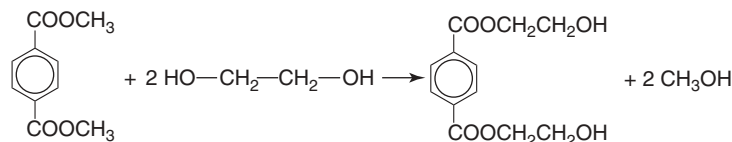
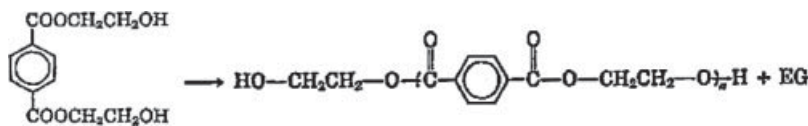**Figure 13.9** DMT transesterification (first stage).

Figure 13.10 Self-trans-esterification to produce PET.

reaction mass (T_m of PBT = 222–232 °C and T_m of PET = 255–265 °C). As with any equilibrium condensation reaction, attaining high reactive group conversions, and thus high PE molecular weights, requires the effective elimination of the diol condensation product.

Given the current high plant throughputs (50,000–300,000 tons/year), and the need for high reaction temperatures and low pressures to attain the required product molecular weight, these continuous reactor systems are complex. Reactor designs approaching plug flow performance are common. Among these, compartmentalized horizontal or vertical stirred reactors, with local stirring moving the reacting mass continuously between compartments and allowing for continuous removal of the diol by-product, are prominent in the art. Single compartmentalized reactors, or a series of reactors with enhanced ability to handle high viscosities, are common [65–68].

Melt polymerization reactors normally operate either isothermally or in prescribed upward temperature profiles at temperatures for PET between 260 and 290 °C and 230 and 260 °C for PBT. The reaction is catalyzed most commonly by antimony trioxide for PET and by titanium orthoesters for PBT, and operated at reactor pressures between 1 and 100 mbar. Temperature profile, reactor pressure, and catalyst concentration are set to minimize the residence time needed to attain a target M_w (usually 15,000 to 25,000 Da). Minimizing product exposure to extreme temperatures in these ranges is important to minimize thermal degradation, which leads to impurities and color. This is particularly important in PET used for food packaging, where small amounts of a particular degradation product, acetaldehyde (AA), may affect its organoleptic performance even at concentrations under 10 ppm. In this regard, the undesired presence of residual antimony compounds in PET food packaging is also pushing the industry toward antimony catalyst replacement. Different organo-metal compounds are being developed as suitable replacements.

The difficulty in eliminating the diol at high viscosities, the high energy requirements needed to stir and pump the viscous mass, and the need to eliminate degradation by-products set a practical limit for the maximum M_w that can be achieved in these reactors (about M_n = 15,000–20,000 Da for PET and M_n = 25,000–40,000 Da for PBT). Normally, these melt polymerization product molecular weights are measured in the industry as intrinsic viscosity, I.V. = 0.5–0.6 dl/g for PET and I.V. = 0.8–1.2 dl/g for PBT corresponding the M_n ranges above. These molecular weights confer PET and PBT PEs with sufficient mechanical properties for a wide variety of applications. More commonly, PET of this I.V. range is used in extrusion applications of fiber, film, and sheet, and PBT in injection molding applications such as electrical connectors [65–68]. Figure 13.11 shows a simplified process diagram for continuous PBT.

The molten PET or PBT products leaving the melt polymerization reactor are quenched, pelletized, and then crystallized by exposing the solid amorphous pellets to temperatures slightly under their T_g (120–140 °C and 30–50 °C, respectively) in crystallization silos. Normally, PBT crystallization rate is so high that the crystallization step can be avoided by controlled quenching of the melt polymerization product [65, 67, 68].

Demanding applications for PET, such as injection-blow molding of bottles and other food containers, and PBT-molded engineering parts, require higher molecular weights not attainable through melt polymerization. In these cases, solid-state polymerization (SSP) is employed. In a simple manner, SSP requires crystallized pellets of the melt polymerization to be exposed to high temperatures without melting, under high vacuum, and for long residence times, to remove residual diol molecules, thus allowing the equilibrium condensation reaction to proceed in the forward direction. Typically, SSP proceeds at measurable rates when temperatures approach T_m − 10 °C and pressures reach 1 to 50 mbar [70].

In batch SSP processes, crystallized PE pellets are loaded into rotating drum reactors heated to the required temperature under dry N_2, and subjected to extremely low
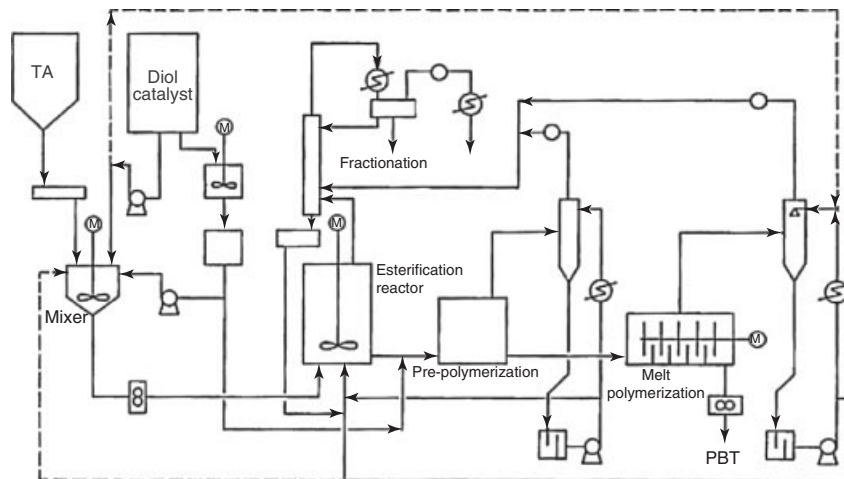
Figure 13.11 Schematic of bulk continuous polymerization process for high molecular weight PBT [67].

pressures (<50 mbar) to slowly eliminate diol promoting further polymer–polymer condensation. At these conditions, the molecular weight of PET can increase from $M_n = 20,000–50,000$ Da (I. V. $= 0.6–1.0$ dl/g) within 10–24 h residence time. This M_n allows PET to be used in food bottles and engineering applications such as tire cords. The M_w of PBT can be also increased via SSP to levels exceeding $M_n = 100,000$ Da for demanding engineering applications [65, 70].

Continuous SSP is carried out nowadays at throughputs relevant to the high melt polymerization rates so that it can be done in series to obtain high I.V. grades in a single continuous process train. Most high throughput plants are designed in this manner. In this case, the SSP reactor consists of plug flow large vertical continuous vessels where crystallized pellets are maintained under a vigorous stream of dried hot nitrogen as they slowly flow from top to bottom of the vessel. By controlling the flow and temperature of the nitrogen stream close to T_m, the SSP proceeds at rates requiring only a few hours residence time to get to the target I.V. [70, 71].

13.3.3.2 Polyamides

PAs are the polycondensation reaction product of diamines, of general formula NH_2-R-NH_2 with dicarboxylic acids of general formula HOOC-R′-COOH. Batch and continuous processes for PAs have been used over the last 70 years, since Carothers synthesized the first materials in the 1930s. Nylon 6,6 is made by a multistage process by bulk polymerization of hexamethyline diamine and adipic acid. In this process, 2 CSTRs + last stage + vacuum are employed.

Nylon-6, on the other hand, is made by the ring opening polymerization of caprolactam with water in a tubular VK column reactor [6–8]. The process consists of two main stages: (i) caprolactam hydrolysis to aminocaproic acid (ACA) and (ii) linear self-condensation polymerization of ACA and ring opening addition of caprolactam. The reaction scheme is shown in Figure 13.12 [72].

Molten caprolactam at about 80–100 °C is continuously fed into a steam-pressurized CSTR operating at temperatures between 90 and 125 °C for 30–180 min residence time. At these conditions, caprolactam hydrolyzes to ACA until equilibrium is reached at about 10 mol% of caprolactam in the mix. At these conditions, the reaction mix starts incipient A-R-B linear polycondensation of the amine and carboxylic acid moieties. A blend of ACA, caprolactam, and oligomers of polyaminocaproic polymerization and H_2O from the hydrolysis reactor, is continuously fed into a series of 2–3 CSTRs operating at temperatures between 220 and 300 °C, at very low pressures (<10 torr) under nitrogen. The average residence time in each reactor is about 1–3 h. Reactors are fitted with continuous head space purging designed to eliminate condensation water and low molecular weight oligomers from the reactor, so that reaction can proceed to high functional group conversions and high molecular weights. Catalysts, commonly phosphites, allow the polymerization to proceed toward high conversions. Molecular weight is often controlled at the right target by adding small amounts of monofunctional acids or amines. The molten PA 6 product is quenched, pelletized, and washed in a leaching tower operating with water at about 100 °C. Pellets are then dried [72–75]. The process diagram is shown in Figure 13.13.

13.3.3.3 Polycarbonates

Polycarbonates are linear PEs of carbonic acid, the vast majority of which are based on bisphenol A diol, as shown in Figure 13.14. Modern polycarbonates have a high T_g ranging from 140 to 155 °C, are tough, transparent, and thermally stable. Two important and distinct commercial manufacturing routes are used in
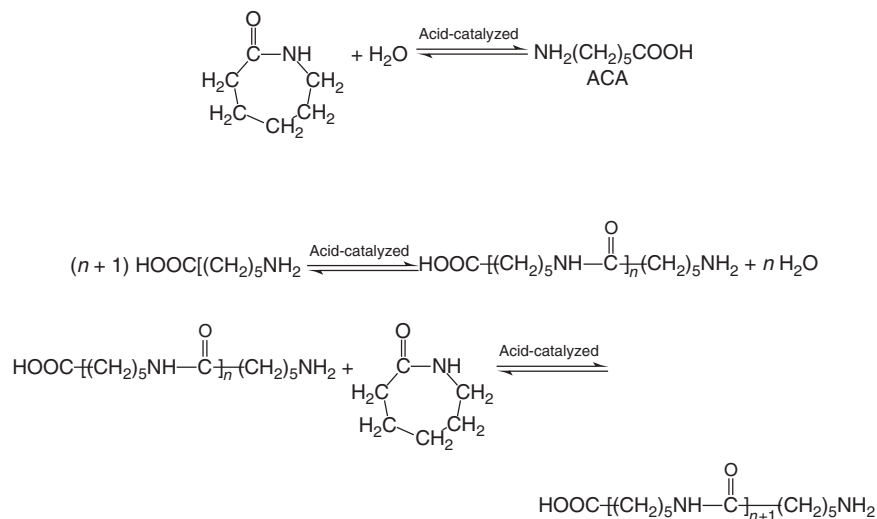
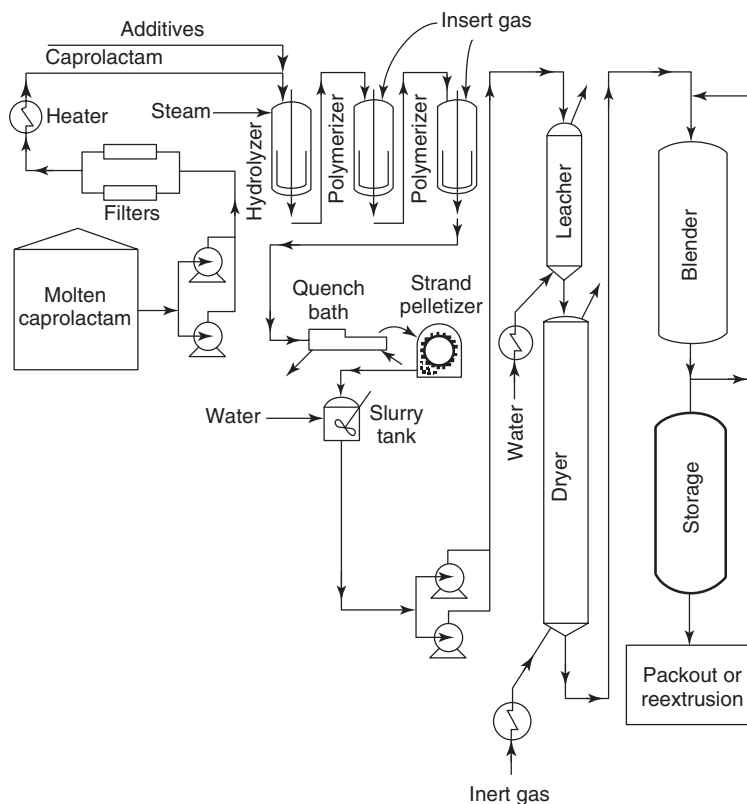**Figure 13.12**   Polyamide 6, reaction scheme.

Figure 13.13   Schematic of bulk continuous polyamide 6 process *Source*: Reproduced with permission from Welgos RJ. Polyamides, plastics. In: Kroschwitz JI, editor. High performance polymers and composites. John Wiley & Sons; 1991. p 519–527 [72]. Copyright 1991 John Wiley & Sons.

polycarbonate manufacture today. The first is an interfacial polymerization involving a Schotten–Baumann reaction of phosgene with an aromatic diol such as bisphenol A in an amine-catalyzed reaction [76]. An alternative bulk polymerization process for making polycarbonates is based on the melt transesterification of bisphenol A with diphenyl carbonate [12]. Early patents for this technology were issued to GE in 1964 [77].

In the melt transesterification process, bisphenol A and diphenyl carbonate are heated to high temperatures
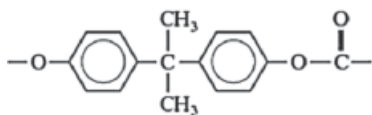
Figure 13.14   Polycarbonate (PC) repeat unit structure.

(200–300 °C) under vacuum to remove phenol under equilibrium. The reaction is generally catalyzed by basic materials such as Na, Li, and K hydroxides. During the final stages of the polymerization, the polymer melt becomes viscous, and thus, additional equipment such as WFEs or extruders are needed to remove residual phenol. Claimed advantages of the melt transesterification process for polycarbonate include stable molecular weight with thermal processing and lower oligomers [76].

13.3.3.4 Polysulfones   Polysulfones are aromatic PEs made usually by the reaction of bisphenol A and bis (4-chlorophenyl) sulfone in a nucleophilic substitution condensation reaction. The first polysulfones produced by Union Carbide in the early 1960s involved the reaction of bisphenol with and bis(4-chlorophenyl) sulfone in the presence of an alkali base (NaOH, KOH, and K carbonate) in a dipolar aprotic solvent such as NMP, DMSO, sulfolane, or dimethyl acetamide [78]. Typical temperatures are in the range of 130–160 °C. The reaction of the base with bis A generates water, which must be removed.

13.3.4   Processes for Ionic/Anionic Polymerization

Ionic polymerization systems of commercial importance employ mostly batch and continuous solution polymerization processes. Suitable monomers for ionic polymerization include conjugated dienes and vinyl aromatic. Among these, the anionic polymerization of styrene–butadiene (SB) and styrene–isoprene (SI) copolymers and the cationic polymerization of styrene are the most commercially important systems.

13.3.4.1 Anionic Polystyrene (PS), Styrene–Butadiene (SB), and Styrene–Isoprene (SI) Copolymers   Anionic addition polymerization requires monomers bearing carbon–carbon double bonds (C=C) able to form stable propagating carbanions (C–C$^-$) after their formation through an electron transfer reaction with an organo-metal compound, most commonly n-butyl-lithium, s-butyl-lithium, and t-butyl-lithium initiators. The list of monomers meeting these conditions is relatively short, yet some commercially important addition monomers like styrene, butadiene, and isoprene are part of this list.

Although stable carbanions propagate at comparable rates as their free radical counterparts, anionic polymerization presents two main mechanistic differences over free radical polymerization: (i) pseudo-instantaneous initiation, resulting in virtually all polymer chains undergoing initiation simultaneously and (ii) the absence of polymer–polymer bimolecular termination reactions. The direct result of these is that living quasi-monodispersed polymer chains of stoichiometric D_n (=moles of reacted monomer/moles of initiator) are present at any time in the reaction mix, with the final $M_n \approx M_w =$ (total moles of monomer in the mix/total moles of initiator in the mix). Importantly, the lack of polymer–polymer termination confers a living character to the polymer–lithium propagating chains allowing for the addition of comonomers to the reaction mix in manners that allow control of the copolymer microstructure. For instance, in addition to the random copolymers obtained by simultaneous addition of monomers A and B, fast addition of monomer A followed by an increased addition of a monomer B from low to high A/B ratios allows for compositionally tapered polymer chain microstructures rich in one end of monomer A and of monomer B in the other end. Moreover, the addition of monomer B to the reaction mix after monomer A has been consumed allows for nearly perfect AB block formation in every chain. The addition of monomer A after B is exhausted would further allowed for ABA triblock copolymer formation. This ability gives anionic polymerization its synthetic advantages over other addition polymerization methods that do not allow for MW monodispersed or controllable block formation [23, 79].

As main disadvantages, anionic polymerization requires the use of completely dry (moisture free) and high purity raw materials, since moisture and other impurities (acids, alcohols) deactivate anions via proton transfer destroying the living character of the chains, and requires a relatively large concentration of solvent (30–70% w/w) to control the high heat evolution caused by the instantaneous initiation. The fact that the final M_w of the polymer product is independent of the reaction rate allows for high product reproducibility in a broad range of reaction conditions of temperature ($T_{rx} = -70$–130 °C) and monomer concentration ([M] = 0.5–5 mol/l), as long as the initiator-to-monomer mole ratio is maintained the same in the initial reaction mix. This allows for highly nonisothermal conditions (semi-adiabatic conditions) to be used in anionic reactors as the temperature profile is unimportant for the final MWD of the product [79, 80].

With this in mind, the anionic polymerization of styrene (PS), styrene–butadiene (SB), or SI is typically carried out by feeding distilled and dried monomer and solvent and purified n-butyl-lithium to a CSTR operating in semicontinuous mode. The reaction mix is heated to the reaction temperature and the second monomer is fed at a programmed feed rate that allows the desired copolymer microstructure to be built, whether a block SB or SI, or tapered or random copolymers. Solution SBR is commonly
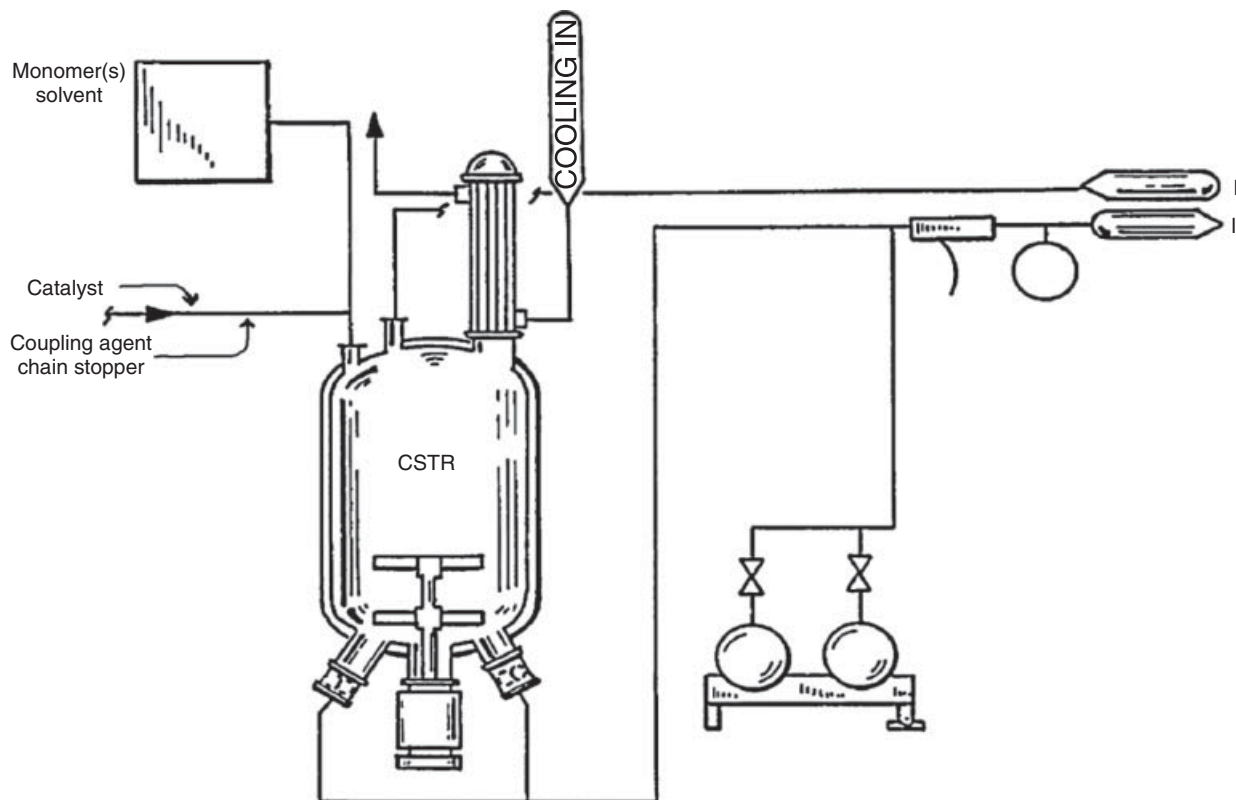
Figure 13.15   Reactor and termination stage in batch and semicontinuous anionic polymerization. I: Recycle stream from fractionator; and II: polymer product stream to devolatilization fractionation [100].

made as a random or tapered copolymer in a variety of compositions (butadiene >70% w/w/p). Thermoplastic elastomers (TPEs) normally require SB or SI blocks and a butadiene or isoprene content >50% w/w. Transparent and ductile PS grades are made as block or tapered blocks with butadiene contents under 40% (w/wp). PS is often manufactured for specialty applications such as HPLC column standards. Figure 13.15 shows a typical reaction array for batch or semicontinuous anionic polymerization.

Solvent type plays a very important role in the reactivity ratios of anionic copolymerization pairs. Hydrocarbon solvents, such as C4–C10 alkanes and cycloalkanes, are commonly used. *n*-Hexane and cyclohexane are employed in many commercial processes. Except for some SBRs with very specific microstructures made at very low temperatures ($T_{rx} < -20\,^{\circ}C$), the so-called cold rubbers, most anionic polymerization processes occur at relatively high temperatures ($T_p > 30-100\,^{\circ}C$), isothermally or semiadiabatically. Number average molecular weights for the blocks vary widely but may be most commonly maintained between 30,000 and 100,000 Da. Once all monomer has been consumed via propagation reactions, a short stopper reactant, typically alcohol or water, is added to the mix to kill the living character of the anion and

complete the polymerization process. In some instances, coupling agents such as polyepoxides, PEs, and polyhalides are added to terminate the anions, SB and SI star polymers with 2, 4, 6, or 8 SB arms, or combinations thereof are formed by adding bi, tetra, hexa, or octofunctional coupling agents, respectively [23, 79–81].

SBS and SIS triblock copolymers are alternatively made by using bifunctional initiators that create two growing anions, one on each end of the polymer chain. In these cases, the central block (PB or polyisoprene) is grown first, followed by an addition of the right ratio of styrene monomer. Owing to the need for high purity and dry monomer and solvent, the polymer separation part of the process is complex. First, the polymer is coagulated into large agglomerates (crumbs) via a solvent exchange process in a large agitated tank and then separates via centrifugation prior to be sent to dryers. Elastomers and SBRs are bagged as crumbs, and TPEs and thermoplastics as powder or pelletized particles. The solvents, unreacted monomers, by-products, and impurities from the additives system (antioxidants, stabilizers, etc.) are separated by a series of distillation columns that recover solvent and any residual monomer to be used in the next polymerization [23, 80, 81].

13.3.5 Processes for Homogenous Catalyzed Polymerization

13.3.5.1 Polyethylene   Polyethylene is produced by several commercial processes including gas-phase fluidized bed, liquid slurry CSTR or loop reactors, autoclaves, and tubes. LLDPE and HDPE grades of polyethylene have been and are still produced in a continuous solution process by companies such as Dow and DuPont using homogenous Ziegler–Natta or Metallocene catalysts. Ethylene, comonomers (1-octene, 1-hexene, and 1-butene), solvent (e.g., cyclohexane, iso-octane, and isopar E), and catalyst (Ti, V, and Cr) are provided to a CSTR operating at high temperatures (150–250 °C) and pressures from 35 to 140 bar [82]. The product is continuously charged to a flash separator to remove solvent and the polymer is subsequently pelletized [83, 84]. Compared to older processes, modern processes with high efficiency catalysts no longer require a catalyst separation stage and thus are more economical than older plants [85]. Solution processes for polyethylene have relatively small reactors, short residence times (∼10 min), and fast transitions, but there are limitations on molecular weight due to solution viscosity [86]. They are ideal for the production of rubber materials, such as EPR and other tacky copolymers that cannot be produced in traditional slurry or gas-phase polymerizations. The process is well suited for making copolymers of ethylene with higher α-olefins such as 1-octene that are difficult to make in gas phase, due to low comonomer vapor pressures.
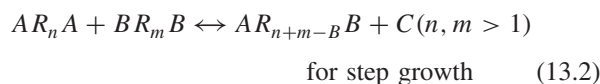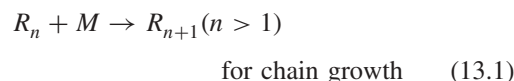
13.4 ENERGY CONSIDERATIONS

Historically, the emergence of different polymerization methods has been the result of dealing with basic engineering principles of mass and energy balances. While mass balances define the desired amounts and ratios of chemical reactants in a polymerization reactor (monomers, catalysts, initiators, etc.), the energy balance defines our ability to control the reactor operating temperature. As other chemical processes, polymerization processes can be designed to operate in batch, semicontinuous, or continuous modes. In turn, each one of these processes can be designed to operate isothermally, (semi)adiabatically, or under a prescribed temperature path. Given that elemental polymerization reactions, as many other chemical reactions, exhibit an Arrhenius-type exponential rate dependency with temperature ($k_p = A \exp(-E/RT)$), the outcome of a given polymerization recipe, namely, the extent of reaction, reaction rate, and the molecular weight distribution of the polymer, will be strongly influenced by the ability to control the reaction temperature in the prescribed manner. The simultaneous solution of mass and energy balances defines the type and size of reactor necessary to achieve the desired throughput and polymer characteristics.

TABLE 13.1   Heat of Reaction for Some Common Monomers

	kcal/mol at 25 °C
Ethylene	21.2
Propylene	19.5
Butadiene	17.6
Styrene	16.7
Vinyl chloride	22.9
Vinylidene chloride	18.0
Vinyl acetate	21.2
Methyl acrylate	18.5
Methyl methacrylate	13.2
Acrylonitrile	18.4
Formaldehyde	7.4

13.4.1 Heat of Polymerization

The elementary propagation steps for chain growth and step-growth polymerizations are shown below:

$$R_n + M \rightarrow R_{n+1} (n > 1)$$

$$\text{for chain growth} \qquad (13.1)$$

$$A R_n A + B R_m B \leftrightarrow A R_{n+m-B} B + C(n, m > 1)$$

$$\text{for step growth} \qquad (13.2)$$

The heats of polymerization for both of these steps are considerably different. For additional polymerization through the C=C, heats of reaction are in the order of 100–200 kJ/mol. While the energy on a molar basis is rather consistent, as shown in Table 13.1, on a mass balance this implies that small monomers often are more energetic than larger monomers, for example, acrylic acid versus stearyl acrylate. On the other hand, the heats of polymerization for condensation reactions are quite low because the bond energies of the monomer and products are similar. A consequence of this is that for addition polymerizations, the heats of polymerization are quite high, and thus, removing sufficient heat from the process is often the problem. On the other hand, in step polymerizations, the issue is rarely removing heat; however, adding heat to maintain a high reaction temperature can be an issue. We explore these aspects further below.

13.4.2 Adiabatic Temperature Rise

A useful way to depict how highly energetic polymerization reactions are is the computation of their adiabatic temperature rise. Adiabatic temperature rise, ΔT_a, is defined as the maximum temperature rise achieved during an exothermic chemical reaction when all heat generated by the reaction is adsorbed by the reacting mass in a closed system with

zero heat transfer to the surroundings. It can be related to the heat of polymerization, ΔH_p, and the average heat capacity of the system over the temperature interval, $\hat{C}_p$, and simply equal to the difference in the final, T_f, and initial, T_0, temperature of the system. For many materials, the heat capacity at room temperature is roughly 2 kJ/kg and decreases moderately over temperature. An average heat capacity calculated or measured with techniques such as modulated differential scanning calorimetry (MDSC) can be used to measure heat capacity with temperature:

$$\Delta T_a = T_f - T_0 = \frac{-\Delta H_p}{\hat{C}_p} \quad (13.3)$$

$$\hat{C}_p = \frac{\int_{T_0}^{T_f} C_p \, dT}{(T_f - T_0)} \quad (13.4)$$

Adiabatic temperature rise for free radical polymerizations can be substantial (hundreds of degrees Celsius). If allowed to polymerize adiabatically, many of these monomers would first yield high reactor pressures during the polymerization, followed by decomposition to gases. Thus, extremely large increases of temperature must be anticipated during adiabatic polymerization conditions. Taking into account the changes in rate of reaction, heat generation rate, and monomer vapor pressure associated with these large changes in polymerization temperature, it is clear that polymerization reactions approaching adiabatic conditions will operate in a self-accelerating mode, extremely challenging to control [87–89].

One method of handling the high adiabatic temperature rise is to provide a solvent in the formulation. In this case, some of the heat is absorbed by the solvent during the polymerization. The adiabatic temperature rise is thus a function of the solid fraction, x, in the original formulation, and the overage heat capacity of the polymer + solvent:

$$\Delta T_a = \frac{-x \Delta H_p}{\hat{C}_p} \quad (13.5)$$

13.4.3 Self-Accelerating Temperature

The temperature at which a polymerization can be self-sustaining is termed *self-accelerating temperature* (SAT). It can be conveniently measured by a calorimeter run such as a vent sizing package (VSP) or reactive safety screening tool (RSST). For polymerizations, the SAT should be measured on the feed used in the polymerization. In cases where initiator is charged to the feed, measurements must be done on the initiated feed. VSP or RSST instruments are important safety tools for studying the exothermic polymerization systems and for evaluating appropriate relief devices [90].

13.4.4 Reactor Energy Balance

The general energy balance for a reactor element can be simply expressed as

$$\text{Accumulation} = \text{In} - \text{Out} + \text{Generation} - \text{Losses} \quad (13.6)$$

Accumulation terms generally reflect the change in temperature of the process. Inflow and outflow terms measure the enthalpy of the feeds, product, and by-products leaving or entering a reactor element. The generation terms are the heats of polymerization but may include power added from mechanical equipment, such as agitators. Losses include transport of energy to the reactor surface, heat transfer to a fluid via jacket, walls or coils, and losses through uninsulated surfaces. Balances may be written at steady state when the accumulation term disappears or dynamically. We explore these further for the different chemistries and reactive systems.

13.4.4.1 CSTR For a CSTR, the energy balance for material in the reactor can be written as follows, where we have assumed heat transfer to both a jacket and losses to the atmosphere. In the case of additional coils in the reactor, a further term can be added:

$$\frac{d}{dt}\left(m\hat{C}_p T\right) = Q_{in}\hat{C}_{pin}T_{in} - Q_{out}\hat{C}_p T + m R_p \Delta H_p$$
$$-UA_t\left(T - T_{Amb}\right) - UA_j\left(T - T_j\right) \quad (13.7)$$

In Equation 13.7, m is the mass in the reactor; t is time; T, T_{in}, T_{Amb}, T_j are reactor, inlet, ambient, and jacket temperatures; $\hat{C}_p$, $\hat{C}_{pin}$ are reactor and inlet feed heat capacities; Q_{in}, Q_{out} are mass flow rates into and out of the reactor; R_p is rate of polymerization; ΔH_p is heat of polymerization; and UA_t, UA_j are heat transfer coefficients for ambient and jacket heat transfer.

In the case where the mass flows in and out of the reactor are constant and assuming average heat capacity in the reactor and the feed and constant density, we can simplify the above equation, resulting in Equation 13.8:

$$\frac{dT}{dt} = \frac{(T_{in} - T)}{\theta}$$
$$+ \frac{m R_p \Delta H_p - UA_t\left(T - T_{Amb}\right) - UA_j\left(T - T_j\right)}{m\hat{C}_p}$$
$$(13.8)$$

At steady state, the change in temperature is zero and we can rearrange the equation into a more useful form, as expressed in Equation 13.9:

$$T = T_{in} + \frac{\frac{\theta}{m\hat{C}_p}\left(mR_p\Delta H_p + UA_t\left(T_{Amb}\right) + UA_j\left(T_j\right)\right)}{\left(1 + \frac{\theta}{m\hat{C}_p}\left(UA_t + UA_j\right)\right)}$$

(13.9)

The careful reader will note that in addition to heat losses from jacket or ambient losses, heat is consumed by sensible heat of raising the temperature of the feed to the reactor temperature:

$$Q_{in}\hat{C}_p\left(T_{in} - T\right)$$

(13.10)

As reactor temperature increases, the heat load from heating the feed becomes significant. At very high operation temperatures, the process can operate at net endothermic and require heat addition. The energy balance of the system is such that at low temperatures, the CSTR operates in exothermic mode, that is, net heat must be removed from the process jacket or sometimes internal coils. At elevated process conditions, the system becomes net endothermic as a result of the considerable heat required to raise the feed to reactor temperature. The total heat of polymerization is dependent on both the energetics of the system and the conversion of monomer to polymer. This in turn is defined by the kinetics of the system [50, 91, 92].

The solvents added to the system reduce the heat load of the reactor because energy is needed to increase the temperature of the solvent to the reactor conditions (sensible heat), yet no heat of polymerization is released by the solvent. This can be an effective measure to reduce heat load at the expense of reduced polymer productivity. When the reactor system operates at elevated temperatures, the additional solvent can pose a challenge to the heating system. Because of the sensible heat effect, some processes use chilling of the monomer, as long as the chilled temperature is not too low to freeze any component.

The heat transfer coefficient UA_t for ambient temperature loss is a function of how well insulated the reactor is. Jacket heat transfer coefficient, UA_j, is a function of the reactor geometry, agitator blade design and RPMs, the viscosity of the medium, and relative amount of fouling in the reactor. The viscosity of the reaction medium as discussed before is dependent on solids level, M_w, and T_g of the polymer as well as reactor temperature. In general, removing heat from the CSTR becomes more difficult as the reactor size increases due to the surface to volume ratios.

13.4.4.2 Cascade of CSTRs In several processes, a cascade of CSTRs may be used to obtain the desired polymer properties and maximize monomer conversion. Conversion of monomer increases from reactor to reactor and thus the solids content and viscosity would increase and heat transfer coefficients decrease for each progressive reactor. For each reactor, an energy balance can be performed using Equation 13.9 by replacing the temperature

of the inlet feed with that of the exit temperature of the prior CSTR. An immediate observation is that the sensible heat available for cooling or heating (which depends on the operating temperatures of the reactors) the downstream reactor is less than available to the first reactor (51, 92). On the other hand, as one progresses from reactor 1 to 2 to 3, etc., less monomer is available to convert to polymer and less polymerization heat is given off. The overall heat load and heat removal technical challenges are thus dependent on the specific product made. Commonly, the second and third reactors in a process experience "bumps" in temperature, which are less severe than the first CSTR.

13.4.4.3 Tubular Reactors Tubular reactors can also be used for polymerizations. In general, these have high surface to volume ratios and commonly the temperature in the center of the reaction medium is higher than the outside. Larger tube diameters increase productivity but reduce heat transfer effectiveness and sometimes static mixing elements are added to increase axial mixing. Without static mixing, tubular reactors can approach zero slip at the wall surface and thus polymer may deposit over time, gel and foul the surface of the unit, thus causing a decline in heat transfer coefficient. The reader is referred to the following good references for more information [93, 94].

13.5 MASS CONSIDERATIONS

13.5.1 Reactor Size

Bulk and solution processes range from small laboratory scale vessels smaller than 100 ml to large industrial processes capable of manufacturing millions of kilograms per year of product. At the pressure rated laboratory vessels can be conveniently purchased as "off the shelf" products from a variety of suppliers. Often the reactors are certified for pressures and temperatures well above the expected manufacturing process and serve amply for research and development purposes. However, a major challenge for small-scale polymerization vessels is maintaining adequate heating and insulation on bare metal surfaces. For bulk and solution polymerization, the polymer may be ultimately separated from the unreacted monomers and solvent and thus the viscous resin must be maintained hot and flowing to avoid solidification and plugging.

Bulk and solution polymerization pilot plants are designed to mimic the manufacturing plants to facilitate accurate scale-up to the manufacturing process. Often in the liter to tens of liters sizes, they are usually built with the same quality and safety standards of a manufacturing process with Class 1, Div. 1 or Class 1 Div. 2 rated areas. The number and sizes of the pilot reactors is a function of the development activity load and the sample sizes needed for application testing.

Commercial manufacturing plants are sized to provide sufficient volume of product to satisfy market demand with provisions for reasonable growth. Maximizing the benefits of economies of scale while minimizing inventories, waste, and energy demands are key for a cost effective process. Often, the same reactor is used for multiple products and consideration of strategies for efficient product transitions, often in between chemistries is important [86]. For batch/semibatch processes, the yearly production volume is highly dependent on the reactor size and total batch time. However, it should be noted that total batch time must take into consideration all process steps such as precleaning, preheating, precharges, polymerization time, postreaction hold time, solvent stripping, cool down, product discharge, postcleaning, etc. Batch processes are generally built to be as large as possible but practical constraints such as mechanical equipment fabrication, heat and mass transfer effects, controllability, and safety limit the maximum effective reactor size. Thus, often, a batch/semibatch plant will be composed of several reactors operating independently for manufacturing the entire line of products. Continuous bulk and solution processes are ideal for making long runs of a given product grade; however, because of capital cost, they commonly produce multiple grades in a given process train. Reactor sizes are much smaller than batch/semibatch reactors and heat transfer often better. As with batch processes, many of the same issues of inventory management, grade transitions, reactor cleaning, and maintenance apply. However, the consequences of a process upset are more severe with a continuous process, which is designed to "keep running" when started up.

13.5.2 Process Residence Time, Conversion, Transients, and Steady State

The influence of the various feed flows, process kinetics, and reactor geometry on reactor productivity and product properties is complex and beyond the scope of this chapter. The interested reader is encouraged to read the other chapters of this book, or the references provided in those chapters, for more details on process modeling, kinetic mechanisms and the prediction of polymer properties. In this section, key implications of these are briefly discussed.

In Section 13.3.1, the concept of batch/reactor residence time was presented. For batch/semibatch processes, batch time is often simply dictated by the maximum polymerization rate possible for a given piece of equipment and the time required to reduce monomer residuals or end groups to within specification. For a continuous bulk or solution process, reactor residence time is simply a function of the size of the vessel and how fast monomer can be pumped

through it. Monomer conversion to polymer increases with residence time but the returns are usually diminishing. Polymer properties, such as molecular weight, may also be dependent on residence time. The task of the chemical engineering is to balance reactor productivity with properties within the range of residence times practical for the continuous process. This implies consideration of the maximum and minimum capabilities of upstream and downstream process equipment.

Process residence time has a major impact on the time required to bring a continuous process to steady state and thus making on specification product. For plug flow type processes such as tubular reactors, changes to the process take on the order of one residence time to make good product. However, for CSTRs, at least 3–4 residence times is needed during a transition before the system is at steady state. Thus, a CSTR with 5 min residence time can come to steady state in 15–20 min, whereas a CSTR with a 2 h residence time would take 6–8 h. In either case, the amount of intermediate "waste" material would equal several reactor turnovers [95].

13.5.3 Reactor Pressure

Continuous bulk and solution polymerization processes often operate at moderate-to-high pressures. Predicting the expected pressure in the reactor is critical to designing safe processes. In a closed reactor vessel, the equilibrium pressure is a function of the vapor pressure of the material in the vessel plus condensable gases. A first estimate of the vapor pressure is a simple Raoult's law summation of the vapor pressure of each remaining ingredient in the reactor such as solvent and unreacted monomer and should include any small molecules formed during polymerization such as water, alcohol condensate, and initiator by-products. Simple Antoine-type expressions usually suffice for individual vapor pressure predictions, but often a Flory–Huggins expression is needed to account for the interaction between the polymer in solution and solvents. Noncondensable gases contribute additively to the total reactor pressure. These may include precharged gases such as nitrogen and gases generated during the polymerization. Examples include nitrogen generated from azo initiators or CO_2 generated from some peroxides or by decarboxylation of monomer [95].

13.5.4 Viscosity

In bulk and solution polymerizations, the reaction mixture is homogenous (single phase) and thus the viscosity at any time is given by the viscosity of polymer solution at the given reactor temperature. During the polymerization, high solution viscosity can constrain mixing, heat and mass

transfer, and product flow from the vessel. Therefore, to maintain a manageable viscosity in the reactor, polymer solids are often limited, minimum temperature guidelines are established, or the final product properties (T_g, M_w) constrained. Consideration must also be given to the final solution viscosity after cool down if the product is supplied in solvent or the molten polymer viscosity at process temperature if the solvent is to be stripped from the resin during processing.

For amorphous polymers, the viscosity at a given temperature is a function of the T_g and M_w of the material. For many polymers, the Williams–Landry–Ferry (WLF) equation provides a good estimate of melt viscosity where η_T is melt viscosity, η_{T_g} polymer viscosity at T_g, T is the melt temperature, T_g the polymer glass-transition temperature, and b and f_g are parameters:

$$\ln\left(\frac{\eta_T}{\eta_{T_g}}\right) = \frac{\left(\frac{b}{f_g}\right)(T - T_g)}{\left(\frac{b}{f_g}\right) + (T - T_g)} \tag{13.11}$$

The WLF equation is based on the Doolittle relationship between viscosity and free volume and the assumption of a linear relationship between free volume and temperature difference from T_g, that is, the so-called iso-free volume $(T - T_g)$ condition. For many polymers, $b = 1$ and $f_g = 0.025$. Below the entanglement molecular weight, the viscosity of a linear polymer in the melt state generally follows a slope of 1 on a log scale with M_w and 3.4 above the entanglement molecular weight. The WLF equation has great utility for a given polymer and has recently been cast in a generic form for amorphous polymer to account for the T_g dependence on M_n for oligomers and also the molecular weight of the polymer [96].

In nonaqueous solvents, the viscosities of polymer solutions is often well described by a simple relationship with temperature, solids and M_w and T_g can be fit to a general semiempirical expression as described by Pezzin [97]. Essentially, higher solids, M_w and T_g and lower temperatures yield higher viscosity solutions. Secondary factors such as hydrogen bonding can also impact the solution viscosity and this must be taken into consideration when using functional monomers. Solutions in water are much more difficult to predict as neutralized polymer solutions often go through a maximum in viscosity with neutralization degree then decrease.

13.5.5 Mixing

Adequate mixing during polymerization is critical to achieving uniform product quality, heat transfer, and efficient use of initiator systems. A variety of blade designs have been used for polymerization systems ranging from pitched blade multiflight arrays to helical screws. The choice of mixing system depends on viscosity and shear requirements, power to volume ratios, as well as heat transfer needs. Often baffles can be added to the reactors to improve mixing and flow patterns in the reactor, but postcleaning must always be factored into the design.

Mixing times should be relatively short compared to reaction times. In free radical polymerization, poor mixing can lead to inefficient utilization of the initiator if it is not dispersed adequately before decomposition, which can lead to molecular weight broadening. In condensation processes, sufficient mixing is important to ensure dispersion of all ingredients and the removal of condensate by-products. Concurrent with impeller design is the proper placement of feed injection tubes. These must be placed appropriately to ensure adequate distribution of the monomer, initiators, and additives. In modern polymerization technology, the use of fluid dynamics modeling software is extremely useful in predicting flow patterns and optimizing mixing designs.

13.5.6 Polymer Purification

In bulk and solution processes, the polymer product may often need removal of unreacted monomer and solvent. Several technologies are available that use high vacuum and temperature to strip the unreacted monomer and solvent from the resin. In most cases, the unreacted material can be condensed and recycled back to the process for further use or optionally burned as fuel.

Flash devolatilization is a simple and effective method to remove the majority of solvent and unreacted monomers from the polymer solution. Product from the reactor is charged to a flash vessel and throttled to vacuum conditions whereby the volatile solvent and monomers are recovered and condensed. In the process, the polymer melt cools, sometimes considerably, due to the evaporation of volatiles. The polymer product is pumped from the bottom of the flash vessel with a gear pump or other suitable pump for viscous materials. Critical to operation of the flash devolatilization unit is prevention of air back into the unit that reduces "stripping" ability and potentially allows oxygen into the unit that can discolor products or pose a safety hazard if low autoignition temperature solvents are used. Often one flash devolatilization unit is insufficient to reduce the residual material to a sufficient level and thus additional units can be added in series [61]. In each vessel, the equilibrium concentration of volatile material in the polymer melt, is a function of the pressure and temperature the flash unit operates at, with consideration for the polymer solvent interaction effects described by the Flory–Huggins equation. Flash devolatilization units, while simple to operate, may be prone to foam development as the superheated volatiles rapidly escape from the polymer melt. Viscous polymers or polymers with mixed functionalities

can adhere to the surfaces of the vessel and discolor or form gels upon exposure to heat.

An alternative to a flash devolatilization unit is the oil heated thin film or WFE. In this equipment, the molten polymer/solvent solution is throttled to the WFE comprising a rotating set of blades that draws the melt into a thin film. In this manner, very good heat transfer from the oil heated surface is obtained and the thin film minimizes diffusion distances and allows rapid mass transfer of volatiles out of the melt. Both vertical and horizontal WFE units are in commercial production and are effective for small-to-medium-sized plants with moderate viscosity melts. Larger units require very large motors to strip viscous resins. Like flash devolatilization units, bubble formation and collapse are essential to effective mass transport of solvent from the polymer melt.

Commercial polymerization plants often use FSEs (23, 62). Often these are used as a secondary stripping stage whereby molten resin from a prior evaporation stage is preheated and then forced through a tray containing small holes. The polymer extrudes through the holes and falls by gravity into a vessel under pressure. The thin spaghetti-like strands provides good surface area for residual removal, and there are no costly moving parts in this unit. FSEs are particularly useful for high molecular weight, and high viscosity melts that have some mechanical integrity to them to prevent spattering on the vessel walls. As in other devolatilization equipment, the injection of a noncondensable gas such as nitrogen can enhance volatile stripping by reducing the partial pressure of the monomer and solvents.

Polymer devolatilization can also be accomplished by the use of single and twin screw extruders [61]. Extruders are well suited for high viscosity materials and, when equipped with appropriate vents, allow the discharge of volatiles.

Polymers made by batch and semibatch processes can also be stripped of unreacted solvents and monomers by processing through equipment described above, but commonly they are purified by vacuum stripping. In vacuum stripping, volatile solvents are pulled out at the end of the batch as much as possible. Initially the amount of solvent recovered is high; however, as the solids content increases, the melt viscosity increases and the rate of solvent recovered declines.

In all cases of polymer purification, care must be taken to avoid overheating the polymer during purification. Most polymers will discolor to a slightly amber color on extended heating especially in the presence of oxygen. Furthermore, many polymers are thermally sensitive and can degrade with excessive overheating. PS, for example, is known to degrade back to monomer upon extensive overheating [23]. Thus, increasing devolatilization temperature in PS first decreases and then increases free monomer.

REFERENCES

1. Mark HF. Chem Eng News 1976;54:176.
2. Semon WL, inventor; B.F. Goodrich, assignee. US patent 1,929,453. 1933.
3. Semon WL, inventor; B.F. Goodrich, assignee. US patent 2,188,396. 1940.
4. Dubois JH. Plastics History - *USA*. Boston: Cahners; 1971.
5. Schimdt F, inventor; Hopff H, I.G. Farbenindustrie, assignee. US patent 2,102,179. 1937.
6. Carothers WE, inventor; E.I. DuPont de Nemours, assignee. US patent 2,012,267. 1935.
7. Carothers WE, inventor; E.I. DuPont de Nemours, assignee. US patent 2,071,250. 1938.
8. Carothers WE, inventor; E.I. DuPont de Nemours, assignee. US patent 2,130,523. 1938.
9. Takamatsu T, Shioya S, Okada Y. Ind Eng Chem Res 1988;27:93.
10. Platzer N. Ind Eng Chem 1970;62:6.
11. Zacca J, Debling J, Ray WH. Chem Eng Sci 1996;51:4859.
12. Rudin A. *The Elements of Polymer Science and Engineering*. New York: Academic Press; 1982.
13. Matyjaszewski K, Davis TP. *Handbook of Radical Polymerization*. Hoboken: John Wiley and Sons; 2002.
14. Semple RB, inventor; Monsanto Chemical Co, assignee. US patent 2,367,805. 1945.
15. Glick SE, inventor; Monsanto Chemical Co, assignee. US patent 2,456,558. 1948.
16. Allen I Jr., Marshall WE, inventors; Union Carbide and Carbon Co, assignee. US patent 2,496,653. 1950.
17. Brittton EC, LeFevre WJ, inventors; The Dow Chemical Co, assignee. US patent 2,359,196. 1944.
18. Villalobos MA, Hamielec AE, Wood PE. J Appl Polym Sci 1991;42:629.
19. Trommsdorff E, Kohle H, Lagally P. Makromol Chem 1947;1:169.
20. Friis N, Hamielec AE. Polymer Prepr 1975;16:192.
21. Wingler F, Schmidt A, Liebig L, Wassmuth G, inventors; Bayer, assignee. US patent 4,141,934. 1979.
22. Kotnur TA, Barber RL, Krueger WL, inventors; Minnesota Mining and Manufacturing Co, assignee. US patent 4,619,979. 1986.
23. Scheirs J, Priddy D. *Modern Styrenic Polymers: Polystyrenes and Styrenic Copolymers*. West Sussex, England: John Wiley and Sons; 2003.
24. Wallis JPA, Ritter RA, Andre H. AIChE J 1975;21:691.
25. Doak KW, Erchak M Jr., Toekes B, inventors. US patent 3,311,675. 1967.
26. Hamielec A, Lawless G, Schultz H, inventors; S. C. Johnson, assignee. US patent 4,414,370. 1983.
27. Schmidt R, Schultz H, Wilson D, inventors; S. C. Johnson, assignee. US patent 4,529,787. 1985.
28. Brand J, Morgan L, inventors; S. C. Johnson, assignee. US patent 4,546,160. 1985.

29. Campbell D. The kinetics of high temperature polymerization of styrene [dissertation]. Zurich: Swiss Federal Institute of Technology Zurich (ETHZ); 2003.

30. Melacini P, Patron L, Moretti A, Tedesco R, inventors; Montelibre S.p.H, assignee. US patent 3,839,288. 1974.

31. Peng FM. J Appl Polym Sci 1990;40:1289.

32. Anzaldi SL, Bonifaci E, Malaguti MV, Ravanetti GP. J Mater Sci Lett 1994;13:1555.

33. Huang NJ, Sundberg DC. J Appl Polym Sci 1995;33:2571.

34. Sosa JM, Morris J, inventors; Fina Technology Inc., assignee. US patent 4,857,587. 1989.

35. Fryling CF, inventors; Koppers Company, assignee. US patent 3,144,420. 1964.

36. Estonoz DA, Meira GR, Gomez N, Oliva HM. AIChE J 1998;44:427.

37. Simon RHM, inventors; Monsanto Co., assignee. US patent 4,252,911. 1981.

38. Preti D, Rossi AG, Nocci R, Vecchini N, inventors; Enichem S.P.A., assignee. US patent 5,807,928. 1998.

39. Shinmura T, Konishi K, inventors; Denki Kagaku Kogyo Kabushiki Kaisha, assignee. US patent 5,532,317. 1996.

40. Balbour M, Clarke J, Fone D, Hoggan A, James R, Jones Grad P, Lam P, Langham C, O'Hara K, Oldring P, Raynor G, Royston I, Tuck N, Usher R. *Waterborne & Solvent Based Acrylics and Their End User Applications*. London: SITA Technology Limited; 1996.

41. Krieg M, inventor; Rohm GmbH, assignee. US patent 5,324,802. 1994.

42. Shimada K, Maeda T, Nishizawa T, Narisada T, Anzai H, Sasaki Y, inventors; Mitsubishi Rayon Co., assignee. US patent 3,900,453. 1975.

43. Van Acker EM, Bijl JM, inventors; Shell Oil Co., assignee. US patent 4,062,908. 1977.

44. Archema Peroxide Initiators. Available at http://www.arkema-inc.com. Accessed 2012 Mar.

45. Dupont Vazo Initiators. Available at http://www2.dupont.com/Vazo/en_US/. Accessed 2012 Mar.

46. Callais P, Moskal M. Higher solids higher quality acrylic coatings resins. Available at www.arkema-inc.com/literature/pdf/304.pdf. Accessed 2012 Mar.

47. Spychaj T, Hamielec A. J Appl Polym Sci 1991;42:2111.

48. Campbell D, Teymour F, Morbidelli M. Macromolecules 2003;36:5502.

49. Debling J, Villalobos M. Modelling and simulation of continuous free radical polymerization with multiple monomers exhibiting reversible propagation. DECHEMA 7th International Workshop on Polymerization Reaction Engineering; 2001; Hamburg, DE.

50. Wang W, Hutchinson RA. AIChE J 2011;57:227.

51. Leamen M, McManus N, Penlidis A. Chem Eng Sci 2006;61:7774.

52. Nising P. High temperature radical polymerization of methyl methacrylate in a continuous pilot scale process [dissertation]. Lausanne: Ecole Polytechnique Federale de Lausanne; 2006.

53. McManus N, Penlidis A, Dube M. Polymer 2002;43:1607.

54. Peck ANF, Hutchinson RA. Macromolecules 2004;37:5944.

55. Webb S. Bulk thermal copolymerization of styrene and acrylic acid in continuous flow reactors [dissertation]. Hamilton: McMaster University; 1985.

56. Andrist K, Campbell JD, Chylla R, Debling J, DeYoung D, Kaai M, Kimura T, Wilson D, inventors; S. C. Johnson Commercial Markets, assignee. US patent 6,255,403. 2001.

57. Campbell JD, Debling J, DeYoung D, Giannakitsas I, Hellwig D, Schatz D, Teymour F, Villalobos M, inventors; S. C. Johnson Commercial Markets, assignee. US patent 6,346,590. 2002.

58. Campbell JD, Debling J, DeYoung D, Giannakitsas I, Hellwig D, Schatz D, Teymour F, Villalobos M, inventors; S. C. Johnson Commercial Markets, assignee. US patent 6,689,853. 2004.

59. Andrist K, Blasko J, Calhoun G, Hansen F, Hellwig D, Hessenius K, Hurley S, Jayasuriya S, Lee M, Maccani S, Mills T, Peterson G, Sandvick P, Wilson D, Wiruth J, inventors; Johnson Polymer LLC, assignee. US patent 6,858,678. 2005.

60. Andrist K, Campbell JD, Chylla R, Popli R, inventors; S. C. Johnson and Sons, assignee. US patent 5,508,366. 1996.

61. Grulke E. *Polymer Process Engineering*. Englewood Cliffs, NJ: PTR Prentice Hall; 1994.

62. McCormick C, Ayres N, Lowe A and Herman F. Mark. Water soluble polymers. In: *Encyclopedia of Polymer Science and Technology*. John Wiley and Sons [ONLINE]; 2002.

63. Scott R, Peppas N. AIChE J 1967;43:135.

64. Swift G and Herman F. Mark. Acrylic (and methacrylate) acid polymers. In: *Encyclopedia of Polymer Science and Technology*. John Wiley & Sons [ONLINE]; Volume 1. p 79–96; 2002.

65. Jadhav YJ and Kantor SW. Polyesters, thermoplastic. In: Kroschwitz JI, editor. *High Performance Polymers and Composites*. New York: John Wiley & Sons; 1991. p 730–747.

66. Vodonik JL, inventor; Du Pont de Nemours and Co., assignee. US patent 2,758,915. 1956.

67. Heinze H, Karben W, inventors; Davy McKee A.G., assignee. US patent 4,680,376. 1987.

68. Van Endert ES, Hagen R, Atlas C, Thiele U, inventors; Inventa-Fischer GmbH & Co., assignee. US patent 7,115,701. 2006.

69. Burkhardt R, Meyer G, Schmidt R, Thewaklt K, inventors; Dynamit Nobel A.G., assignee. US patent 4,289,895. 1981.

70. Moore LD, Rule M, Wicker TH, inventors; Eastman Kodak Company, assignee. US patent 4,446,303. 1984.

71. Cavaglia G, inventor; Cavaglia G, assignee. US patent 7,557,180. 2009.

72. Welgos RJ. Polyamides, plastics. In: Kroschwitz JI, editor. *High performance polymers and composites*. New York: John Wiley & Sons; 1991. p 519–527.

73. Howell TJ, inventor; Rohm and Haas Company, assignee. US patent 3,923,749. 1975.

74. Kharkov BA, inventor; Kharkov BA, assignee. US patent 3,607,102. 1971.

75. Smith HA, inventor; The Dow Chemical Company, assignee. US patent 4,366,306. 1982.

76. Brunelle D and Herman F. Mark. Polycarbonates. In: *Encyclopedia of Polymer Science and Technology*. John Wiley & Sons [ONLINE]; 2006. p 1–33.

77. Fox D, inventor; General Electric Co., assignee. US patent 3,153,008. 1964.

78. El-Hibri J, Weinberg S, and Herman F. Mark. Polysulfones. In: *Encyclopedia of Polymer Science and Technology*. John Wiley & Sons [ONLINE]; 2006.

79. Stevens MP. *Polymer Chemistry, an Introduction*. 2nd ed. p 54–176.

80. Gunesin BZ, Nelson PJ, inventors; BASF Corporation, assignee. US patent 5,602,206. 1997

81. Warfel DR, inventor; Atlantic Richfield Company, assignee. US patent 4,346,193. 1982.

82. Jaber IA, Ray WH. J Appl Polym Sci 1993;50:217.

83. Simpson D, Vaughan G, Herman F. Mark. Ethylene polymers, LLDPE. In: *Encyclopedia of Polymer Science and Technology*. John Wiley & Sons [ONLINE]; Volume 2. p 441–482.

84. Benham E, McDaniel M, and Herman F. Mark. Ethylene polymers, HDPE. In: *Encyclopedia of Polymer Science and Technology*. John Wiley & Sons [ONLINE]; 2010. p 1–30.

85. Jaber IA, Ray WH. J Appl Polym Sci 1993;49:1695.

86. Debling J, Han C, Kuijpers F, VerBurg J, Zacca J, Ray WH. AIChE J 1994;40:506.

87. Abel O, Helbig A, Marquardt W, Zwick H, Daszkowski T. J Process Contr 2000;10:351.

88. Jacobsen LL, Ray WH. AIChE J 1992;38:911.

89. Chylla RW, Haase DR. Comput Chem Eng 1993;17:257.

90. Balchan AS, Paquet D, Klein J. Process Saf Progr 1999;18:71.

91. Henderson LS III,, Cornejo RA. Ind Eng Chem Res 1989;28:1644.

92. Lopez-Negrete R, Lopez-Rubio J, Flores-Tlacuahuac A, Saldivar-Guerra E. Ind Eng Chem Res 2006;45:1689.

93. Hill C. *An Introduction to Chemical Engineering Kinetics and Reactor Design*. New York: John Wiley and Sons; 1977.

94. Bird B, Stewart W, Lightfoot E. *Transport Phenomena*. New York: John Wiley and Sons; 1960.

95. Villa CM. Ind Eng Chem Res 2007;46:5815.

96. Kim SH, Teymour F, Debling J. J Appl Polym Sci 2006;103:2597.

97. Pezzin G. J Appl Polym Sci 1966;10:21.

98. Neudstadt FL, inventor; BASF, assignee. US patent 3,566,961. 1971.

99. Burger H, inventor. US patent 4,037,825. 1977.

100. Moore ER, Dalke BD, Malanga MT, Poindexter GM, inventors; The Dow Chemical Company, assignee. US patent 4,883,846. 1989.