

the average chain length and weight fraction of gel during network formation in the copolymerization of methyl methacrylate and ethylene glycol dimethacrylate [2.140].

3. Polymerization Processes and Reactor Modeling

3.1. Introduction

The polymer reactor model is now becoming accepted as a valuable tool whose use contributes significantly to all aspects of process technology for polymer manufacture. This includes process design, optimization, state estimation, and control. Through process design, polymers with a unique and desirable combination of properties can often be obtained. Process parameters such as residence time distribution (RTD) are usually not considered by polymer synthesis chemists, although RTD can influence chemical composition distribution (CCD), molecular mass distribution (MWD), long-chain branching (LCD) and gel/sol ratios. In the early days of the polymer industry, the chemist played the major role in product and process development and scale-up. This has changed, with the process engineer now playing a significant role in all phases of commercialization of new and improved polymer products. His broad experience with process fundamentals and computer modeling are essential to obtain high-quality products, safely and economically.

Dynamic reactor models can be used in a variety of ways. Stability and control of polymer reactors should be considered at the design stage and control problems minimized then, rather than take corrective action after the plant is built. Complex interactions which are involved in polymerization (highly nonlinear temperature and concentration effects) preclude optimal design based on experimentation alone because the cost would be prohibitive. Models can be used to identify potential sources of product variability and strategies to minimize their effects. Models can be used to store information on process technology in a concise and readily retrievable and modifiable form.

Process models can be used to train chemists, chemical engineers, and plant operators and give them a feel for the dynamics of the polymerization process.

The most expensive aspect of model development is experimental estimation of model parameters; highly instrumented bench-, pilot-scale, and plant-scale reactors are required. Statistically designed experiments should be performed to permit efficient parameter estimation and model development. Modeling is an iterative process and the very act of developing a deterministic model permits a greater understanding of the relevant microscopic processes which occur during polymerization or polymer modification. As additional data (plant, pilot-plant, and bench-scale) become available, model structure and parameters can be updated.

This section considers recent developments in polymerization/polymer modification processes and discusses advances in polymer reactor modeling, state estimation, and control.

3.2. Processes and Reactor Modeling for Step-Growth Polymerization

3.2.1. Types of Reactors and Reactor Modeling

In step-growth polymerization, high molecular mass polymers are usually not produced until the final stage of reactions, so that thermal control and mixing of the reaction mixture do not present serious problems in the earlier stages. However, since the final stage of polymerization is very important for the production of polymers with high molecular mass, handling of very high viscosities and temperatures and high interfacial area to remove small molecules are required. Various polymerization processes and reactor types, both for batch and continuous production, have been proposed. Examples of reactors for high viscosities are shown in Figures 19 and 20. Careful selection of the polymerization reactor is very important to produce high-quality polymers [3.1], [3.2].

The batch reactor is the most versatile reactor type and is used extensively for specialty polymers at low production volumes. Some examples of step-growth polymerizations carried out in such reactors are nylon 6, phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde. In polycondensation reactions, it may be necessary to remove condensation products to attain sufficient conversion. When the volume of the reaction mass decreases continuously with time, such reactors are called

semi-batch reactors. (A tank-type reactor which does not operate at steady state is defined as a semi-batch reactor). For example, in the produc-

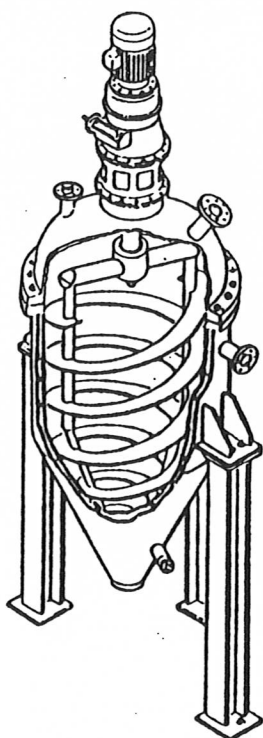


Figure 19. Vertical cone ribbon blade reactor (Mitsubishi Heavy Industries)

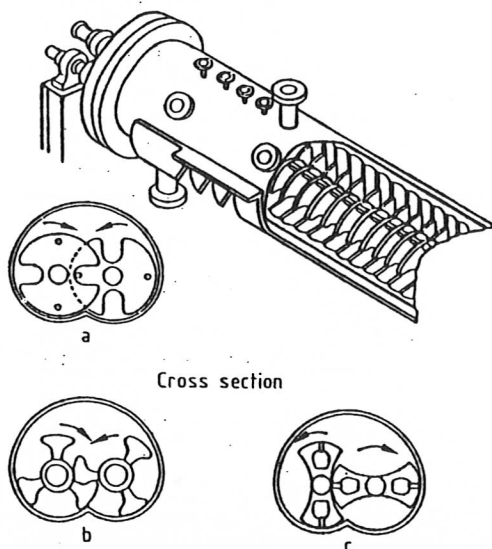


Figure 20. Horizontal high-viscosity reactor

tion of poly(ethylene terephthalate), PETP, since methanol or ethylene glycol evaporates during polymerization, the batchwise production of PETP is considered a semi-batch operation.

On the other hand, newer high-capacity plants often use continuous processes. The first approximation for a continuous process is a model that consists of plug flow reactors (PFR) and continuous stirred-tank reactors (CSTR) in various combinations (Fig. 21), although various nonideal effects such as flow pattern in the reactor, mass- and heat-transfer limitations, and residence time distribution must be considered for a detailed analysis and design of real reactors [3.3]–[3.7].

Molecular mass distribution of linear polymers produced by step-growth polymerization in a batch or a PFR basically follows the most probable distribution [3.8]. (Note that batch reactor and PFR are, in principle, equivalent). The molecular mass distribution may be controlled by varying its reaction path if the reaction system is in a nonequilibrium state. Assuming irreversible step-growth polymerization without interchange reactions, the effect of reactor types, such as homogeneous CSTR, segregated CSTR and PFR with a recycle loop, on molecular mass distribution have been considered [3.6], [3.7], [3.9], [3.10]. An important feature of step-growth polymerization is that the variance of the molecular mass distribution is smallest in a batch reactor or PFR and is largest in a homogeneous CSTR, which is quite contrary to that for chain-growth polymerization. This result may be disappointing, since it is, in principle, impossible to produce polymers whose polydispersity index M_w/M_n is smaller than two in step-growth polymerization at sufficiently high conversions. The polydispersity index of polymers produced in a batch reactor is given by $1 + p$, as shown in Section 2.1.1., where p is the conversion of the functional group. However, in commercial polymeric materials, polymers with narrower distributions are not always superior to those with broader distributions, since various levels of properties are required at the same time. The use of a cascade of CSTRs and/or PFRs with recycle loops may be one method to obtain a molecular mass distribution with a polydispersity index larger than two. However, in practice, these methods may have shortcomings because they need a long start-up period and, therefore, problems may occur with the stability of the reaction system. Recently, a new method in which additional

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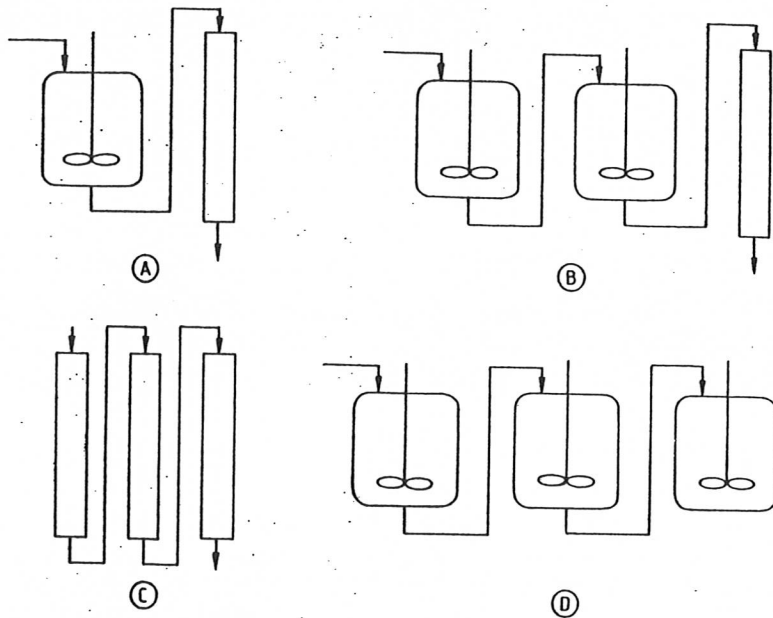


Figure 21. Representative models for polymerization reactors
 A) CSTR + PFR; B) CSTR + CSTR + PFR; C) PFRs; D) CSTRs

monomers are fed intermediately to a batch reactor or a PFR has been proposed [3.11]. Theoretical analysis of this intermediate monomer feed method has also been carried out [3.12], and it has been shown that the polydispersity index can be easily controlled over a wide range with values greater than 2.

In a batch reactor, the reverse reactions and the interchange reactions (redistribution reactions) do not change the MWD from the most probable distribution [3.8], [3.13]–[3.15]. However, these reactions do change the MWD of polymers produced in CSTR, PFR with a recycle loop, and intermediate monomer feed method. Some consideration of these reactions in a CSTR is given in [3.16]. Qualitatively, these effects lower the polydispersity and make the MWD approach the most probable distribution. This result seems reasonable, since any MWD approaches the most probable distribution with a polydispersity index of two when polymer chains are severed randomly [3.17], [3.18].

Other than the common reactor types discussed above, other special types of reactor system may be applied. For example, in the polymerization of urethanes, the reaction rates are so high that reaction takes place even when the monomers are being mixed and pumped into

molds. In situ polymerization to form the desired articles directly from monomeric liquids is known as reaction injection molding (RIM) [3.19], [3.20]. A schematic of the RIM process is shown in Figure 22. The RIM processing of polyesters, epoxy resins, polyamides, and dicyclopentadienes has also been introduced, although more than 95% of the total produced by RIM is polyurethane [3.20]. In the RIM process, the reaction is almost complete by the time the material fills the mold, and therefore the mixing and flow equations must be solved simultaneously with those for chemical reactions in a rational model for these complex situations.

In the finishing stage of nylon 6, nylon 66, and PETP polymerizations, higher molecular mass polymers may be obtained by solid-state polymerization in which polymerization occurs by heating chips or flakes of a material below its melting point in a stream of hot gases in a fluidized bed or in a drier operated under vacuum [3.21]–[3.25]. The monomer, condensation products, and various byproducts diffuse out, and further reaction takes place inside the solid. The progress of these types of reaction is affected significantly by the diffusion of the condensation products and the morphology of the solid.

Although step-growth polymerization has a very long history, a systematic kinetic treatment

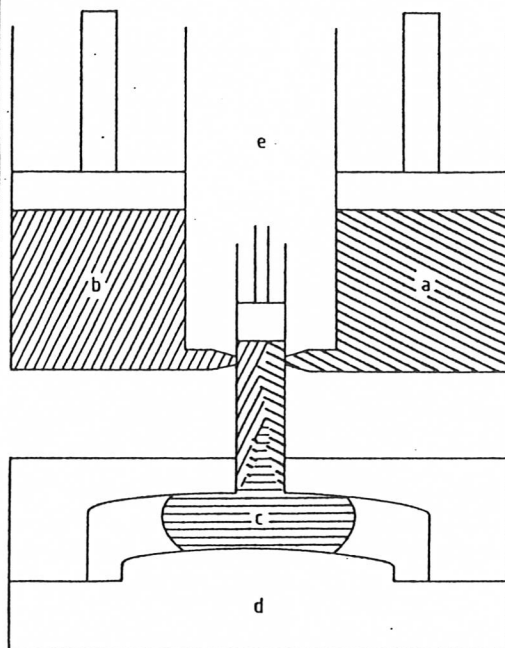


Figure 22. Schematic drawing of the RIM process
a) Monomer A; b) Monomer B; c) Polymerizing mixture;
d) Mold; e) Mixer

like that available for free-radical polymerization does not exist because of limitations due to system-specific side reactions and the scarcity of reliable kinetic data. However, this synthetic route is becoming more important due to the recent development of new and important materials synthesized by step-growth polymerization such as aramides, PPS, PEK, and PES. The production technology of step-growth polymers seems to have revived as an attractive research area and is enjoying a Renaissance period.

3.2.2. Specific Processes

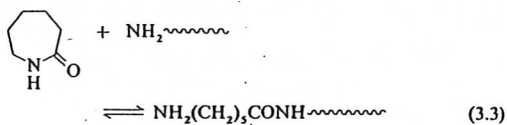
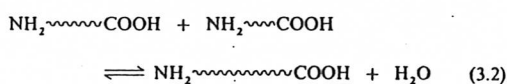
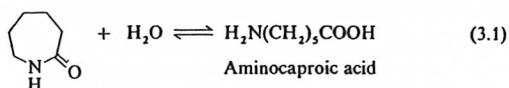
Polyamides (see also → Polyamides) are manufactured by two basic routes. One of these is synthesis from cyclic monomers such as lactams. Polymerization of these substances requires ring opening and subsequent chain growth. Another class of synthetic polyamides is formed from diamines and diacids.

The most common types of polyamides are nylon 6 and nylon 66. The term nylon is often used for synthetic aliphatic polyamides. One number indicates that the product was prepared from a single monomer and represents the number of carbon atoms in the repeating unit. Two

numbers refer to the number of carbon atoms in the diamine and that in the diacid, respectively.

Nylon 6 is typically produced by the hydrolytic polymerization of ϵ -caprolactam [3.26]–[3.30], although polymers with higher molecular mass can be produced by ionic polymerization [3.26], [3.28], [3.31]. The major reactions in the hydrolytic polymerization are

- 1) Ring opening of ϵ -caprolactam by water (Eq. 3.1), which produces aminocaproic acid (ACA)
- 2) Polycondensation of ACA (Eq. 3.2)
- 3) Acid-catalyzed polyaddition (ring-opening polymerization) by nucleophilic attack of the amine nitrogen on the lactam (Eq. 3.3)

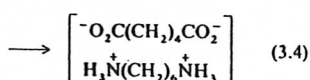
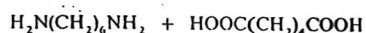


Step-growth polymerization of the amino acid (Eq. 3.2) accounts for only a few percent of total polymerization of ϵ -caprolactam. However, step-growth polymerization is important since it usually determines the final degree of polymerization at equilibrium. The molecular mass distribution is essentially the most probable distribution, except for the presence of monomer and cyclic oligomers. Since low molecular mass substances lower the polymer quality, they are usually removed by leaching or vacuum treatment of the polymer melt. The formation of cyclic oligomers is an important side reaction [3.32]–[3.34]. For the simulation and optimization of polymerization reactors, only small ring formation or overall ring formation is considered to make the analysis easier [3.35]–[3.38].

Various types of polymerization reactors have been proposed both for batch and continuous processes. A commonly used industrial reactor for a continuous process is a tubular reactor such as the conventional VK column (Vereinfaht Kontinuierliches Rohr) [3.26], [3.27], [3.39], which consists of a vertical tube operating at atmospheric pressure. The feed enters the top of the

column and is heated to ca. 220–270°C. The simplest model for this type of reactor is a PFR. However, according to impulse response experiments, the flow is approximately laminar rather than plug flow [3.27], [3.40], and the reactor should be modeled as a CSTR followed by a tubular reactor when a large quantity of water is used since a significant convection current and mixing is provided by the evaporating water [3.27].

Nylon 66 is manufactured by polycondensation of hexamethylenediamine and adipic acid [3.41], usually in a multistage process. First, nylon salt (hexamethylenediammonium adipate) is prepared from stoichiometric quantities of hexamethylenediamine and adipic acid in water. The salt can easily be separated by precipitation with methanol.

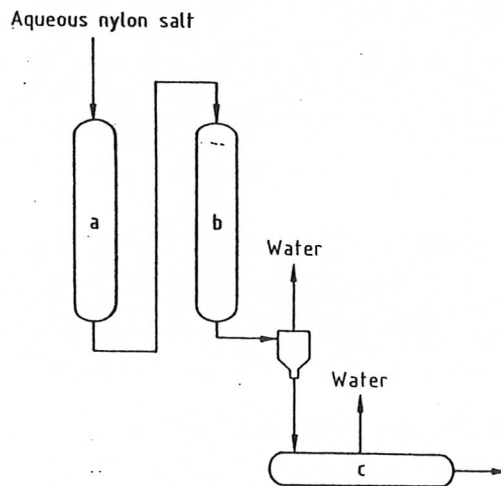


The use of nylon salt guarantees the presence of equimolar amounts of $-\text{NH}_2$ and $-\text{COOH}$ groups. Close control of diamine–diacid balance is important to control the final polymer molecular mass and reactive end groups.

Nylon 66 is fairly unstable at high temperatures in the presence of oxygen. Not only degradation but also cross-linking may occur. Because of this instability, polymerization used to be carried out solely in batch processes. However, complete elimination of oxygen has made it possible to carry out continuous polymerization. An example of a continuous melt polymerization process is shown in Figure 23. The aqueous nylon salt solution is heated to above 200°C at > 17 bar in an oxygen-free atmosphere. Thereafter, the pressure is reduced to atmospheric and vapor is separated from polymer to promote polymerization to the desired high molecular mass. It has also become possible to polymerize molten hexamethylenediamine and adipic acid directly [3.35], [3.41]. Polymerization can also be completed in the solid state.

Several kinetic studies on the synthesis of nylon 66 have been published [3.42]–[3.46]. However, more information is necessary for detailed simulation and optimization of nylon 66 reactors.

Polyesters (see also → Polyesters). The production of high molecular mass polyesters differs



	a	b	c
Hold-up time, min	15–30	15–30	60
Temperature, °C	200–235	270–290	270–290
Pressure, 10 ⁵ Pa	17–24	17–24	atmospheric

Figure 23. Continuous melt polymerization of nylon 66

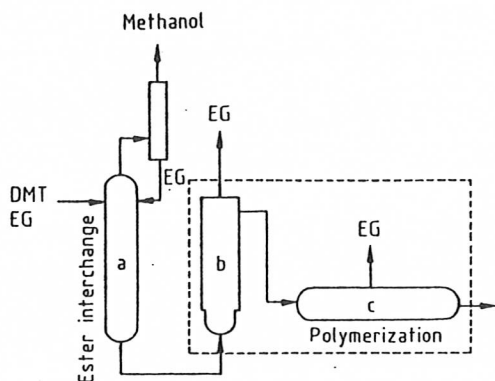
somewhat from that of polyamides. In the case of nylons, the chemical equilibrium favors the polyamide under polymerization conditions. With polyester formation, however, the equilibrium is much less favorable. In order to drive the reaction in the forward direction, the condensation product must be removed continuously, usually by application of high vacuum. For polyester reactors, a high vacuum, a high temperature, and a high interfacial area with sufficient surface renewal are required, especially at high conversions.

Both saturated and unsaturated polyesters are produced. Among the saturated polyesters, poly(ethylene terephthalate), PETP, is produced in the largest quantity, and is used for production of fibers, films, molding plastics, and beverage containers. In this section, the engineering aspects of PETP formation are illustrated as an example of a polyester production process.

There are two major routes to synthesize PETP industrially, although the objective in each case is to obtain an intermediate product—i.e., bis(hydroxyethyl)terephthalate (BHET).

Two major routes to synthesize BHET are ester interchange of dimethyl terephthalate (DMT) and direct esterification of terephthalic acid.

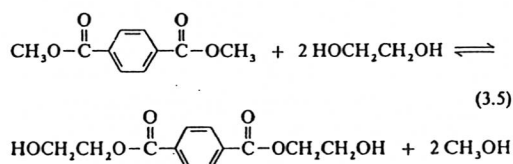
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	a	b	c
Hold-up time, h	4-6	2-3	2-3
Temperature, °C	150-210	265-285	265-285
Pressure, 10 ² Pa	atmospheric	13-133	<< 6

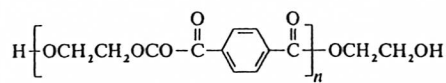
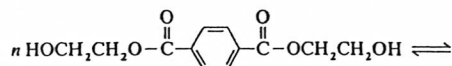
Figure 24. Continuous polymerization process of PETP via ester interchange route

Figure 24 shows an example of the PETP production process via the ester interchange route. The ester interchange reaction



is operated in the temperature range 150–210°C at atmospheric pressure. The use of a catalyst is common [3.47], [3.48]. The methanol and ethylene glycol (EG) emerging from the reactor are passed through a rectifying column and EG is fed back to the reactor. It is very difficult to force the ester interchange reaction to completion, and therefore after a particular conversion (usually 90–95%), the reaction mixture is passed on to the polycondensation stage. The reaction mixture consists of oligomers of various types. Oligomers with degrees of polymerization as high as three may be formed [3.47], [3.49], [3.50]. Several reactor models for both batch and continuous processes have been proposed [3.47]–[3.55]. An optimization study showed that the ester interchange reactor should be operated initially at high temperature to obtain high conversion; the temperature should be lowered to reduce side reactions [3.48], [3.53].

In the polycondensation stage, the reaction temperature is raised to 265–285°C to keep the reaction mixture molten and polymerization fast.

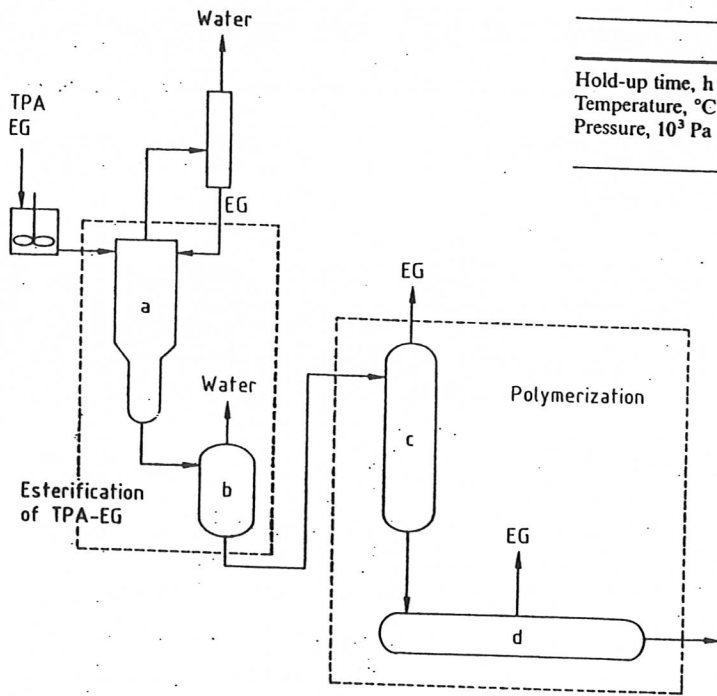


For PETP production, a dual catalyst system in which one component is specially active for ester interchange and the other for polymerization is quite often used [3.56]. The production of high molecular mass polymer requires the complete removal of ethylene glycol due to the unfavorable equilibrium, and therefore a vacuum is applied. Especially in the final stage of the polycondensation reaction, a very high vacuum is required since the reaction system becomes highly viscous. Consideration of the limitations of mass and heat transfer is very important. Various types of reactors such as rotating disc contactors, wiped film reactors, partially filled screw extruders have been developed as finishers for the polycondensation reaction [3.47], [3.48], [3.55]. Details of fluid mechanics, mixing, and mass and heat transfer characteristics are required for a rational analysis and design of such high-viscosity reactors. In addition to polycondensation reactions, various side reactions must also be considered since a very high temperature is used.

Melt polycondensation of PETP is not generally carried out beyond a particular extent of polymerization since the degradation reactions dominate the process and the product quality may suffer from various undesirable byproducts. To attain higher molecular masses, the products may be subjected to solid-state polymerization [3.21]–[3.25]. Newer processes, especially for beverage and food containers, prefer to stop melt polymerization at lower conversion, and solid-state polymerization is extensively applied.

Direct esterification of terephthalic acid (TPA) and ethylene glycol was generally not preferred earlier because of the difficulties in the purification of TPA due to its low solubility and high melting point. However, with improvements in technology, the direct esterification method has been gaining in importance. The process is claimed to give polyesters with superior quality due to their low content of carboxyl

conveyor belt reactor!



	a	b	c	d
Hold-up time, h	3-5	1-3	2-3	2-3
Temperature, °C	240-260	240-260	265-285	265-285
Pressure, 10 ³ Pa	100-300	atmospheric	1-10	<< 0.6

Figure 25. Continuous polymerization process of PETP via direct esterification route

end groups and diglycol linkages [3.56]. In the modeling of this process, aside from the difficulties caused by the various reactions and mass balances involved, it is necessary to take account of the heterogeneity of the reactions due to the low solubility of TPA in EG. Simulation and control of the direct esterification reactors is reported in [3.48], [3.55], [3.57]–[3.59]. Figure 25 shows a flow diagram of a continuous process for PETP production by direct esterification.

emulsion, suspension, dispersion, and gas-phase processes) may be found elsewhere [3.60]. Special cases where spatial variations in temperature and concentrations are important (e.g., in tubular reactors or packed beds) are also considered.

Bulk, solution, and suspension polymerization systems are characterized by the fact that all of the reactions proceed in a single phase with no spatial variations in temperature and concentration. A model for a reactor carrying out such polymerizations would consist of a set of material balances giving the rates of accumulation, inflow, outflow and a reaction source (sink) term for the various monomers, initiators, chain-transfer agents, and polymer in the reactor. These balance equations are now given in general form

Monomer balances:

$$dN_i/dt = F_{i,in} - (N_i/V)V_{out} - R_{pi}V \quad (3.7)$$

where

N_i is the number of moles of monomer i in the reactor

$F_{i,in}$ are molar flow rate of monomer i into the reactor

V is the reaction volume in the reactor

3.3. Processes and Reactor Modeling for Chain-Growth Polymerization

3.3.1. Material Balance Equations for Batch, Semi-Batch, and Continuous Reactors

The following material balance equations apply for multicomponent polymerization, accommodate operation of a well-stirred reactor (no spatial variations in temperature and concentrations), and may be used to simulate different comonomer systems under a variety of operating conditions. Bulk (suspension) and solution polymerizations are considered first; extensions required for multiphase systems (emulsion, inverse