

---

# INTRODUCTION

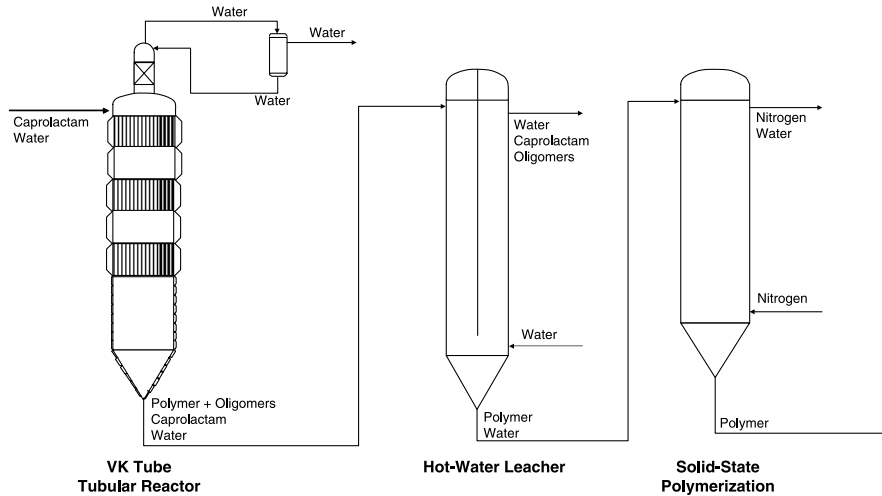
---

## 1.1 CASE STUDIES

In each of the case studies below, we present typical scenarios that challenge those who manufacture polymers. To face these challenges, this book introduces polymerization process modeling and product design. We develop process models to optimize the conversion of raw materials into polymer products. We do this by quantifying how operating conditions in each processing vessel impact conversion and product purity. In addition, we focus on product design because polymers are not a uniform chemical product, such as benzene or chlorine. Rather, they have a distribution of molecular weights and widely varying end-use properties.

### 1.1.1 Nylon-6 Polymerization

Figure 1.1 shows a multistage process for manufacturing nylon-6. Caprolactam monomer and water enter the top of the VK (Vereinfacht Kontinuierliches or simplified continuous) tube, which operates at about 250°C and 1 atm. Some monomer and water are flashed into the packed column, which separates the caprolactam and water and returns unreacted monomer and some water back into the column.



**Figure 1.1.** VK tube process for manufacturing nylon-6. The VK tube is followed by a hot-water leacher to remove unreacted monomer and oligomers. Afterward, the solid-state polymerization reactor dries the polymer and increases its molecular weight.

A mixture of polymer, unreacted monomer, water, and oligomers exits the bottom of the VK tube. This mixture enters a pelletizer, and the unwashed pellets enter the top of a hot-water leacher. Water flows in a countercurrent fashion to remove caprolactam and oligomers from the polymer pellets.

At the end of the process, polymer pellets laden with water enter the top of a solid-state polymerization reactor. Dry gas enters the bottom of the reactor and flows countercurrently with respect to the polymer phase. As the polymer travels down the reactor, it is dried and increases in temperature. Drying the polymer at high temperature drives the reaction equilibrium toward a higher polymer molecular weight.

Consider the following scenarios:

- Your manager has given you a directive to increase the amount of conversion of caprolactam monomer in the VK tube. You accomplish this by increasing the pressure in the VK tube. This reduces the residual caprolactam left in the polymer stream by 2%, yet causes a 5% reduction in the polymer molecular weight. To compensate downstream in the process, you decide to: (a) decrease the freshwater feed rate in the leacher and (b) increase the dry gas flow rate. By how much can you decrease the freshwater feed and still sufficiently wash the polymer, and by how much do you have to increase the dry gas flow rate to ensure sufficient molecular weight build? This is an example of process and product design, where we make changes in the process operating conditions to better manufacture the current product with the desired molecular weight and end-use properties.
- To meet new customer demand, management would like to produce a new nylon-6 polymer using your VK tube process. They would like to use an acid in the process, terminating some of the free amine ends in the nylon-6

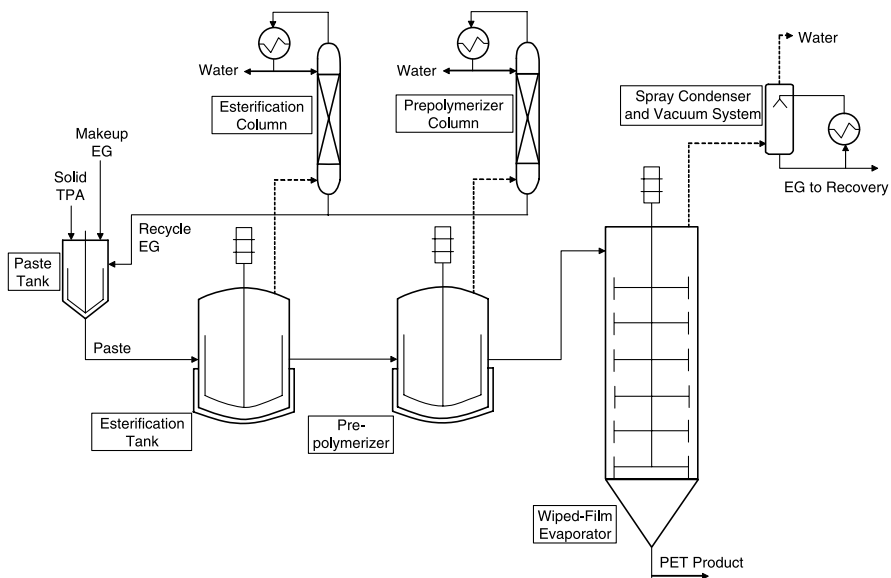
polymer. Determine what reactor/leacher/solid-state polymerization conditions are needed to make the new product.

- In order to more fully integrate the plant, management would like to use a water stream containing some oligomers instead of freshwater in the leacher. Is it possible to do so, while maintaining the desired product purity and quality?
- With increasing/decreasing demand, management would like to run the process at an unprecedented high/low rate. Is this possible, and, if so, what temperatures/pressures/flow rates are needed at these new rates?

Your goal is to meet the objectives of each challenge using a combination of plant experimentation, historical operating data, and intellect, while wasting the minimum amount of time and raw materials.

### 1.1.2 Poly(Ethylene Terephthalate) Polymerization

Figure 1.2 shows a train of reactors used to produce poly(ethylene terephthalate) (PET). Ethylene glycol (EG) is mixed with solid terephthalic acid (TPA) in a paste tank and fed to a stirred-tank reactor that operates at high pressure and temperature. Poly(ethylene terephthalate) oligomer exits the esterification tank and enters a second stirred tank



**Figure 1.2.** PET melt process—ethylene glycol and solid terephthalic acid enter a mix tank to form a paste. This paste enters the esterifier, and then the prepolymerizer to form PET oligomer. Afterward, the oligomers are passed through a wiped-film evaporator to form a high-molecular-weight polymer. Ethylene glycol that is devolatilized from the esterifier and prepolymerizer is purified in a distillation column, then condensed and recycled back to the paste tank.

that operates at low pressure and high temperature. This vessel removes residual ethylene glycol and water and increases the oligomer molecular weight. Last, the low-molecular-weight polymer enters a wiped-film evaporator, which operates under high vacuum, and wipes a polymer film on the sides of the vessel to facilitate removal of EG and water. This drives the polymer molecular weight up, and the finished polymer melt exits the evaporator and is pelletized.

Each reactor has a vapor outlet stream containing EG and water. Ethylene glycol is recovered using distillation or a spray condenser and is usually recycled back to the beginning of the process.

Consider the following scenarios:

- You are interested in optimizing train performance by varying the feed ratio of EG to TPA. What effect does varying the EG/TPA ratio have on the final polymer molecular weight and conversion?
- Management would like to reduce the amount of acetaldehyde, a reaction by-product, in the final polymer melt. Use product design to determine what adjustments in temperature and pressure need to be made in the three reactors in order to minimize the acetaldehyde concentration in the product.
- The prepolymerizer vacuum system is sometimes plagued by a fouling problem that results in a loss of vacuum in the prepolymerizer. What is the best way to react to a loss in vacuum in order to minimize the amount of off-specification (“off-spec”) polymer produced?

As in the nylon-6 case study, your goal is to meet the objective of each challenge using a combination of experimentation, data, and intellect, while wasting the minimum amount of time and raw materials.

## 1.2 NEED FOR PROCESS MODELING

### 1.2.1 Approaches to Process and Product Engineering

The most straightforward way of answering the questions above is by manually making changes in the plant and observing the results. This is the *trial-and-error approach*. If we improve the process and are able to make the desired product, then we stick with the change. If not, we try another change.

The trial-and-error approach has the advantage that if a real improvement is realized in the plant, then we know for sure that a proposed solution does indeed work. Likewise, if a proposed solution fails, we know for sure that the proposed solution does not work. However, it can be wasteful because polymerization processes have a long residence time. Therefore, a trial-and-error approach may last for weeks, all the while producing off-spec product.

To minimize the waste of the trial-and-error approach, an intelligent chemical engineer uses his or her brain power, that is, an *intelligent approach*. They think and act with

varying levels of complexity. Some intelligent approaches, ranked in order of complexity, follow:

- *Use historical plant data to qualitatively infer better operating conditions* This approach works when there is a large amount of historical operating data that covers the range of operating conditions in which one is interested.
- *Use statistical analysis to develop a regression model, and use this model to predict better operating conditions* This approach is essentially a quantitative version of the first approach. Since it is empirical, that is, not based on fundamentals, it should not be used to extrapolate outside of the range covered by the historical data.
- *Use chemical engineering fundamentals to develop a process model, and use this model to predict better operating conditions* This approach leverages the achievements of great researchers of the past and present to create a fundamental process model. This model should be able to extrapolate better than a regression model. In addition, we require less plant data to develop a fundamental model, compared to a regression model.

There are advantages and disadvantages of each intelligent approach. The first approach, qualitatively inferring the necessary process conditions using historical data, is the easiest and quickest way of getting an answer. However, the answer can only be qualitative and is limited to the amount and range of the process data available. If little or no data is available, we cannot use this approach. Important situations where there is little or no data include designing a new process or product.

The second approach can be viewed as a systemization of the first approach. Like the first approach, we can develop a regression model rather quickly. However, the resulting model suffers from the same limitations as the qualitative approach. Importantly, we should never use a regression model to extrapolate outside of the data range on which the model was developed. This means that again, we cannot use a regression model for critical applications such as designing a new process or product.

The third approach, developing a fundamental model, is more time-consuming. It requires a substantial body of knowledge regarding, for example, the polymerization mechanism and kinetics. This body of knowledge should either be available internally or in the open literature. However, once we have quantitatively characterized the fundamentals, building process models should be fast. The number of uncharacterized free parameters in the process model should be small and, hence, would require only a small amount of plant data to characterize. The resulting models are extremely flexible and can be used to extrapolate. We use them to investigate changes in equipment configuration and changes in product chemistry and properties. This approach is a long-term solution to the modeling problem; though it requires significant up-front investment of time, it is the approach that promises the most benefits.

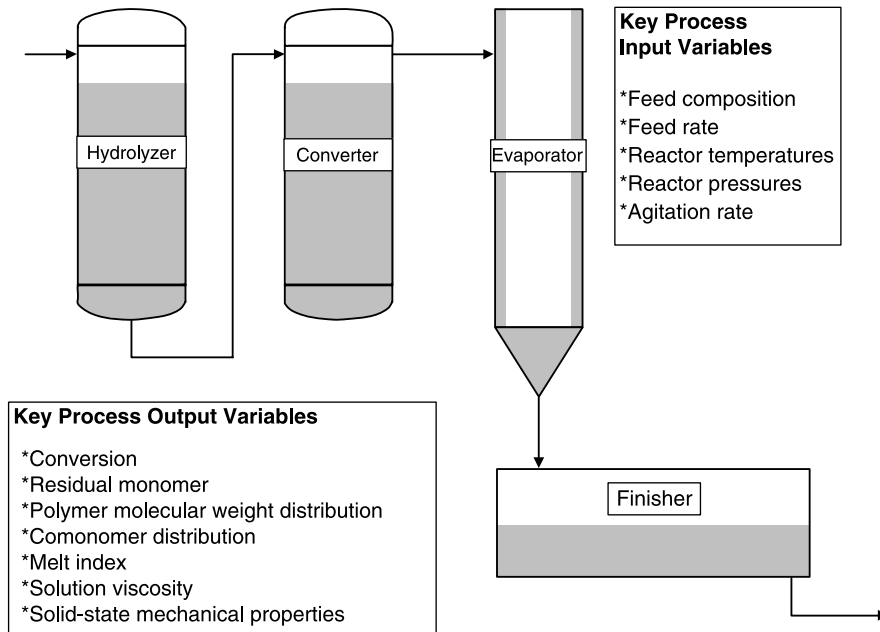
## 1.2.2 Fundamentals of Polymerization Processes

Since fundamental models employ basic polymer science and engineering knowledge, such as reaction kinetics, they can unify our view of different but related processes. For example, we may attempt to use the same polymerization kinetics fundamentals to describe different manufacturing technologies. In contrast, empirical models have to be redeveloped or at least reevaluated for every separate process and should never be used to extrapolate outside of the bounds of experience.

The fundamentals of polymerization processes are generally more complex than standard chemical processes for the following reasons:

- *Reaction Kinetics* A polymer is not a homogeneous chemical product but rather a mixture of individual chemical species with different chemical compositions, topologies, and/or molecular weights. Multiple, concurrent reactions contribute to this complexity, and quantifying parameters associated with these reaction sets, sometimes numbering 50 or more, is a challenge.
- *Phase Behavior* Polymerizations can be multiphase, with extreme cases being emulsion polymerization (four phases—separate monomer and polymer droplets dispersed in a liquid, with vapor), slurry polymerization (three phases—solid particles dispersed in a liquid, with vapor), and gas-phase polymerization (two phases—solid particles dispersed in vapor). These multiple phases usually behave and interact in complex ways, for example, dispersed phases and particles can grow, agglomerate, and break apart. The phase behavior can also depend on the polymer chemical composition and molecular weight distribution.
- *Transport Limitations* Polymers have low heat- and mass-transfer coefficients and high viscosities. These cause strong nonidealities within unit operations such as imperfect mixing, imperfect heat transfer, and mass-transfer limitations (for example, the mass-transfer-limited devolatilization of polymer melts).
- *Product Properties (Particularly End-Use Properties)* Predicting the properties of polymer products is challenging and is often frustrated by the complex nature of standardized property testing itself. For example, the melt index measures some combination of shear and extensional viscosities that depend in complex ways on chemical composition, molecular weight distribution, and topology.

Because of seemingly endless complexity, developing fundamental polymerization process models is an *iterative* process. We build complexity layer by layer, until a single, unified model is capable of describing multiple phenomena adequately. In the first iteration, we consider only the reaction kinetics. In the second iteration, we add fundamentals describing phase behavior and physical properties such as liquid and vapor densities. In the third iteration, we attempt to describe transport limitations. Last, we attempt to fundamentally predict end-use properties. Parallel development also takes place, for example, we develop better descriptions of reaction kinetics together with improved representations of transport limitations.



**Figure 1.3.** Polymerization train—key process input variables are those important variables that we directly control, and key process output variables are the important results of the manufacturing process. These results define the profitability of the process.

### 1.2.3 Integrated Modeling of Industrial Polymerization Processes

Developing fundamental models of industrial polymerization processes is usually *integrated* because it focuses on the modeling of *an entire polymer manufacturing train* (including reactors, separators, recycle coolers/condensers, etc.), not merely reactors alone. Integrated modeling is necessary because, in one model, it quantitatively captures the relationship between key process input variables (KPIVs) and key process output variables (KPOVs). Figure 1.3 illustrates a polymerization train with KPIVs and KPOVs.

There is no way to predict the final product properties by considering, in isolation, any one of the reactors in Figure 1.3. All of them must be considered together to represent seamlessly the conversion of monomer to polymer as to predict product properties.

## 1.3 BOOK OVERVIEW

In this book, we show the reader how to systematically develop integrated polymerization process models for step-growth polymers, using chemical engineering

fundamentals. We can use the resulting models for process design and to analyze the steady-state and dynamic operation of a production train. We can also use the models for product design, to study the impact of process conditions on the properties of the polymer product. This will enable the polymer production engineer to find out which potential solutions to the above case studies have a high probability of succeeding and which potential solutions are most likely not worth trying.

To build our models, we use a standard, step-by-step approach. We develop the fundamentals to model:

1. Physical properties such as vapor pressure and liquid molar volume
2. Phase equilibrium and mass-transfer limitations
3. Reaction mechanisms and kinetics
4. Enthalpy
5. Multiphase stirred tanks (usually stirred-tank reactors)
6. Multiphase plug-flow reactors
7. Flowsheets consisting of multiple reactors and associated unit operations

Our chapter listing is nearly identical to this approach. We now outline the title and content of the upcoming chapters:

2. Fundamentals of Simulating Stirred Tanks and Plug-Flow Reactors: We illustrate the basic approach that we use to develop conservation equations for stirred tanks and plug-flow reactors (PFRs). We then give an overview of the numerical methods and techniques that we use to solve the resulting equations. In particular, we use an ordinary differential equation integrator to solve the material balances for a stirred tank, and the method of lines to solve the partial differential equations representing the material balance equations for PFRs. These equations give a context within which we develop more fundamentals, and latter chapters further develop these equations for more complex reactors.
3. Physical Properties: We show how to model basic physical properties to make design calculations. For example, we require the liquid molar volume to translate any given amount of moles into a concentration. Furthermore, we need the liquid molar volume to compute a volumetric flow rate, which is important in accurately computing the residence time in a reactor. Additional physical properties that we model include vapor pressure, vapor molar volume, molecular diffusivity, critical properties, thermal conductivity, and viscosity.
4. Phase Equilibrium and Mass Transfer: We first show how to quantify the chemical potential of a phase using the activity coefficient approach. We assume an ideal vapor phase. We then show how to use these concepts to develop equations that quantify mass-transfer rates. The mass-transfer rate is

proportional to a concentration driving force, which is an expression for the difference in chemical potential between two phases.

5. **Reaction Kinetics:** We outline a fundamental description for the reaction mechanism for nylon-6 and PET polymerizations. We then teach the reader how to develop kinetic rate expressions that quantify the rate of change of all chemical species due to reaction. We also give some basic methods for computing polymer product properties, such as number-average molecular weight, relative viscosity, intrinsic viscosity, and also heat of reaction. These properties are useful in product design.
6. **Enthalpy Calculations:** We show how to compute the absolute enthalpy of any given mixture, as well as how to compute the difference in enthalpy that results in reaction and phase change.
7. **Stirred Tanks:** We develop the master set of material and energy balance equations that quantify a dynamic stirred tank. We consider up to three phases—solid, liquid, and vapor—with all phases exchanging material at some finite rate given by the mass-transfer equations developed in Chapter 4.
8. **Plug-Flow Reactors:** We develop multiple plug-flow reactor models to handle liquid-only plug-flow reactors, those with a plug-flow liquid phase and a well-mixed vapor phase, and those with countercurrent liquid–liquid or liquid–vapor plug-flow phases. For each of these dynamic models, we develop both the material and energy balances.
9. **Flowsheet Simulation:** We pull together our basic stirred-tank and plug-flow reactor models to simulate entire manufacturing trains. We develop our calculation engine in FORTRAN and interface it with an MS Excel spreadsheet using Visual Basic for Applications (VBA) to enhance the usability of the models. This chapter introduces the concept of the open simulation environment (OSE), where practicing engineers can easily enter the desired operating conditions into the Excel spreadsheet to activate a simulation of the polymer process and observe the simulation results, without having to know the details of the process model behind the spreadsheet.
10. **Nylon-6 VK Tube Simulation in Polymers Plus:** We introduce the leading polymerization process modeling software Polymers Plus, from Aspen Technology. We use it to develop a model of the VK tube reactor for manufacturing nylon-6.
11. **Nylon-6 Leacher and Solid-State Polymerization Simulation in Aspen Custom Modeler:** We extend the Polymers Plus steady-state model and turn it into a dynamic model. We then develop custom unit operations for a leacher and a solid-state polymerization reactor using the customization capabilities available in Aspen Tech’s Custom Modeler.
12. **PET Melt Process Modeling in Polymers Plus:** We use Polymers Plus to develop a flowsheet simulation of the PET melt process. In particular, we

illustrate how we quantify mass-transfer limitations using an external FORTRAN subroutine.

13. Nylon-6 Bubble-Gas Polymerization Process Simulation in Polymers Plus: We use Polymers Plus to develop a flowsheet simulation of the nylon-6 bubble-gas process, including mass-transfer limitations.
14. Poly(Caprolactone) and Polyurethane Polymerization Process Simulation in Polymers Plus: We apply our model-building techniques to two polymers not encountered in the previous chapters.
15. Polylactide and Nylon-6,6 Polymerization Processes Simulation in Polymers Plus: We discuss how to apply our modeling techniques to two additional polymers.
16. Fine-Tuning Models: We teach the reader how to fine-tune models using process data. We develop a systematic, step-by-step methodology for diagnosing model discrepancies. This methodology is particularly useful given the complexity of modern process modeling models.
17. Multiscale Modeling of a Nylon-6 Leacher: We use molecular simulation methods to characterize phase equilibrium and solubility parameters and apply computational fluid dynamics (CFD) to predict the turbulent diffusivity of a fluid flowing over a packed bed. We need both sets of thermodynamic and transport properties to model a nylon-6 leacher. We show that a lack of data may be overcome using multiscale modeling techniques.
18. Recent Achievements and Future Challenges of Polymerization Process Modeling and Product Design: We finish our discussion with some perspectives on how the field of polymerization process modeling has evolved and might continue to evolve.

We begin the next chapter by introducing methods needed to simulate simple stirred tanks and plug-flow reactors.