Analysis and Design of Melt and Solution Polycondensation Processes

Lance L. Jacobsen and W. Harmon Ray
Dept. of Chemical Engineering, University of Wisconsin, Madison, WI 53706

Polycondensation processes include up to three distinct process stages: prepolymerization, polymerization, and finishing. One or more of these stages often have serious reaction rate limitations due to chemical equilibrium and the need to remove a condensate product. The problems arising in each process stage and the methods of designing each stage are unique. This article discusses many of the problems inherent to each process stage and basic design tools useful in designing each process stage. Two process design tools discussed are the mass-transfer potential and pressure-chain length plots. The application of these tools is illustrated through two design examples: nylon-6,6 and poly(ethylene terephthalate) production.

Introduction

Polycondensation or step-growth polymerization processes are difficult to design. The polymerization is usually carried out under conditions such that the reactions are reversible and thus equilibrium-limited. One of the most pressing problems for polycondensation polymer processes is the removal of a condensate byproduct of the reaction in order to shift the reaction equilibrium to higher molecular weights. Without such condensate removal the production of high polymer may be impossible. The removal of the condensate, however, is difficult due to limited rates of diffusion of the condensate through the polymer and limited rates of interphase mass transfer. An understanding of the physical and kinetic processes occurring is important for developing and modifying polycondensation processes. By approaching these problems from the basics of fundamental modeling, it is possible to develop useful design tools for polycondensation processes.

A general kinetic modeling technique (Jacobsen and Ray, 1992) has been developed based on general kinetics mechanisms for polycondensation. This technique provides a unified approach to modeling polycondensation kinetics and can model a host of polycondensation polymers. The resulting modeling equations are described in detail by Jacobsen and Ray (1992) and are also used in the CAD package, POLYRED, from the University of Wisconsin. These equations will be used for the kinetic modeling in this article. The mechanisms included in this approach are given in Table 1.

The general mechanisms of Table 1 are applicable to a wide range of condensation polymers. Table 2 shows just a few examples with the important functional groups which participate in the kinetics. Modeling of these example systems, as well as comparisons to experimental data, is treated in Jacobsen and Ray (1992).

The extent to which equilibrium limits the main chain growth mechanism is illustrated in Figure 1 where the equilibrium chain length in the absence of condensate removal is plotted against the equilibrium constant (assuming only the polycondensation I mechanism in Table 1 occurs). The various types of condensation polymers shown as points on the figure indicate the severity of equilibrium limitations for different polymers. From this plot, one sees, for example, that nylons have much less severe equilibrium limitations than polyesters so that the extent of condensate removal necessary for high polymer production can vary considerably from polymer to polymer.

Many published papers deal with the modeling of polycondensation reactors, and the literature collection is quite diverse (cf. Jacobsen and Ray, 1992). Therefore, we will not try to be comprehensive here, but rather will discuss a selection of representative work. Most of the previous work deals with the modeling of mass transfer. This is a result of the reversible kinetics in polycondensation systems causing the condensate to be an interfering byproduct. This prior work presents useful techniques that may be of help in designing polymerization processes.

Diffusion of the condensate through a polymer film was studied by Ault and Mellichamp (1972a). They modeled the diffusion through stagnant liquid films. They also developed an efficiency factor that expresses the importance of diffu-

---

Correspondence concerning this article should be addressed to W. H. Ray.

Table 1. Polycondensation Reaction Mechanisms

	Chain Building Reactions
Polycondensation I:	$P_{m,a,b}+P_{n,e,f}\rightleftharpoons P_{m+n,a+e-\delta(i),b+f-\delta(j)}+C_{ij}$
Polycondensation II:	$P_{m,a,b}+P_{n,e,f}\rightleftharpoons P_{m+n,a+e-\delta(i)-\delta(j),b+f}+P_{\delta k,2\delta(l),0}$
End Group Transformation:	$P_{m,a,b}+P_{n,e,f}\rightleftharpoons P_{m+n,a'+e-\delta(i),d+f-\delta(j)}+C_{ij}$
Polymer Addition:	$P_{m,a,b}+P_{n,e,f}\rightleftharpoons P_{m+n,a+e-\delta(i),b+f-\delta(j)}$
Ring Addition:	$P_{m,a,b}+R_n\rightleftharpoons P_{m+n,a,b-\delta(i)+\delta(j)}$
	Side Reactions
Redistribution:	$P_{m,a,b}+P_{n,e,f}\rightarrow P_{m+n-r,a+e-s,b+f-t}+P_{r,s,t}$
Deactivation:	$P_{n,a,b}+Z\rightarrow P_{n,a-\delta(i),b}$
Two Chain Reformation:	$P_{m,a,b}+P_{n,e,f}\rightarrow P_{m-1,a-\delta,b+\delta}+P_{n',e',f'}$
Ultimate Monomer Degradation:	$P_{n,a,b}\rightarrow P_{n-1,a-\delta,b+\delta}+C$
Scission Degradation:	$P_{n,a,b}\rightarrow P_{n-r,a-s+\delta,b-t}+P_{r',s',t}$
	Precondensation Reactions
Ring Opening:	$R_m+C\rightleftharpoons P_{m,\delta,\delta}$
Salting:	$S_e+S_f\rightarrow P_{\delta(e)+\delta(f),\delta(i),\delta(j)}+C_{ij}$

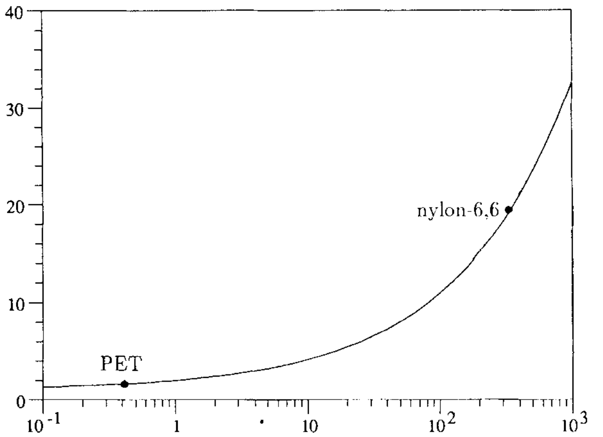


Figure 1. Polymer equilibrium chain length vs. polycondensation equilibrium constant for reactions without mass transfer.

sional resistance in the reactor. In another paper, Ault and Mellichamp (1972b) also investigated how to increase the condensate removal rate by periodically mixing the polymer film.

Amon and Denson (1980), who developed a general model for wiped film reactors, found that the best way to increase molecular weight was through condensate removal, not increased residence time. Their results showed that reaction rates tended to slow down in the presence of condensate and reversible reactions, thus giving an equilibrium conversion.

The technique of using orthogonal collocation for a wiped-film reactor producing poly(ethylene terephthalate) (PET) was presented by Kumar et al. (1984). They developed the modeling equations and compared results to those of finite difference methods. The collocation technique required only ten collocation points to give comparable results. The same technique was used by Gupta et al. (1984) for *A-B* type polymers.

The wiped-film reactor has advantages over the simple thin-film reactor because the increased mixing of the film produces greatly increased mass transfer. Other groups have studied similar reactors. For example, Gupta et al. (1983a) looked at wiped-film reactors for generalized *A-A B′-B″* kinetics.

Biener (1989) developed a model for reactive distillation columns. The model uses orthogonal collocation to reduce the computational requirements as compared to modeling each tray. The model developed uses *A-B* polycondensation kinetic modeling. The distillation column has the ability to separate the condensate from any volatile monomer and polymer. Any polymer in the distillation column is also subject to reaction.

Tai et al. (1983) studied the placement of heat exchangers on tubular reactors for nylon-6 and developed the model equations for this reactor configuration. Their results suggested that the temperature distribution affected the molecular weight distribution. Gupta et al. (1983b) also investigated the polymerization of nylon-6 in tubular reactors. They modeled the use of recycle to increase the rate of polymerization. Ravindranath and Mashelkar (1982a, b, 1984) investigated the design of poly(ethylene terephthalate) (PET) reactor stages by modeling each process stage from fundamental principles. Other recent work on finishing reactors includes: Steppan et al. (1989, 1990) on nylon-6,6 polymerization models for the finishing stage and Castres Saint Martin and Choi (1991) on the dynamic behavior of PET finishing stages.

Using an approach in design that is tightly coupled with the fundamental chemistry and physics will lead to well designed processes. The method of process design used in this paper is to use kinetic modeling based on the mechanisms occurring in a polymerization process. A full discussion of the kinetic model

Table 2. Some Types of Polycondensation Polymerization Polymers

Product	Nylons	Polyesters	Polyurethanes	Phenol-Formaldehyde	Polysiloxanes	Epoxy
Typical Functional Groups	—NH$_2$ —COOH	—OH —COOH	—NCO —OH	—OH —HCO	R′ | HO-Si-OH | R	—Cl —OH
Reactor Types	Batch CSTR Tubes	Batch CSTR Distillation Thin Film	Batch CSTR	Batch CSTR	Batch CSTR	Batch CSTR
Mass-Transfer Problems	Small	Large		Small		Small

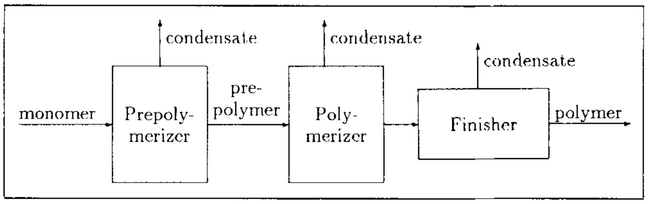


Figure 2. Three process stages common to condensation polymerization.

is presented in Jacobsen and Ray (1992). We use this model together with special analysis tools introduced in this paper to synthesize process designs for two example systems. These analysis tools are based on the characteristic equilibria, reaction kinetics, and mass-transfer rates arising from the complex kinetic model.

Two analysis tools are emphasized here. The concept of mass transfer potential (MTP) indicates whether polymer growth in a reactor is kinetically-limited or mass-transfer-limited. This tool will help focus on the exact reactor design needs and allow one to determine whether better mass transfer or increased reactor residence time is required to increase polymer molecular weight. The second tool is a pressure-chain length (PCL) plot, which indicates the minimum vapor-phase pressure reduction in a reactor required to make polymer of a given chain length.

In the next section, we will discuss the principal stages of polycondensation processes, the important design problems at each stage, and the typical reactor designs found from the patent literature. As part of this discussion, the mass-transfer potential and pressure-chain length plots are used to choose appropriate designs. The emphasis in this paper is on melt and solution reactors; a future paper will consider the case of solid-phase reactors. Finally, two detailed polycondensation process designs are carried out to illustrate the design procedures: nylon-6,6 and PET production in continuous reactors.

Process Analysis

For existing polycondensation processes, three distinct process stages exist (see Figure 2). The first process stage (prepolymerizer) is used to prepare a prepolymer from the monomers. The second stage (polymerizer) is used to polymerize the prepolymer to a moderate molecular weight. The final stage (finisher) is used to react the polymer up to the final, desired molecular weight.

Each process stage is inherently different due to kinetic, mass-transfer and heat-transfer problems. Different reactor designs are developed due to unique problems at each process stage.

Prepolymerization stage

The prepolymerization stage is used to prepare a short-chain prepolymer for polymerization. Three examples of polymer systems that use prepolymerizers are nylon-6, nylon-6,6, and PET. Nylon-6 uses this stage to initiate the reaction by opening the ring monomer (ϵ-caprolactam) so that polymerization may proceed. In making nylon-6,6, this stage is used to make a polymer salt from the two monomers (adipic acid and hexamethylene diamine). PET production uses this stage by producing a prepolymer called bishydroxy ethylene terephthalate (BHET). The reasons for using the prepolymerization stage for these systems become clearer when looking at problems involving this stage.

Problems. Several problems typical of polycondensation need to be considered when designing a polycondensation process that may include a prepolymerization stage.

Proper end group stoichiometry exists due to the structure of the monomers used in making the particular polymer. To make polymer of high molecular weight, the A and B end groups must be present in ratios close to 1:1. When making polymer (such as nylon-6,6) with an A-A and a B-B monomer, it is difficult to produce the one-to-one end group ratio. This may be solved by performing the reaction in a way that causes the polymer to form a salt.

The loss of volatile monomer removed with condensate can cause two problems: 1) the loss of product and 2) the disruption of the end group stoichiometry. This may be solved by the recovery and reuse of the volatile monomer. PET production typically involves the recovery of the volatile monomer ethylene glycol from the prepolymerization reactor through fractionation from the condensate in the reactor vapor.

The presence of a monomer that does not polymerize until it has been initiated poses *reaction initiation* problems. For example, ring monomers (such as ϵ-caprolactam) will not polymerize until a few rings have been opened. After the rings are opened, polycondensation or ring addition may occur. In addition, a catalyst often must be present to initiate the ring opening reaction.

Side reactions tend to cause a decrease in polymer quality either by the presence of some component or by temperatures causing the side reaction to occur. If a component in the reaction mass causes the side reaction, then it should be removed. If high or low temperatures can cause side reactions, the problem may be solved by operating the reactor at temperatures that do not promote the side reactions.

Design Analysis. The first step to take when developing a process design is to analyze the basic chemistry involved. In the case of the prepolymerization stage, this will immensely help the development of a successful design. The determining factor of whether or not a prepolymerization stage will help is based on the overall polymerization mechanism.

Three kinetic mechanisms from Table 1 should trigger the need for a prepolymerization stage. Two of the three mechanisms (ring opening and salting reactions) involve a monomer that must go through some prepolymerization reaction before normal polymerization proceeds. The other mechanism is the parallel existence of two chain building reactions, where one of the mechanisms is preferred. PET and PBT are examples of systems with parallel chain building reactions.

The existence of *ring opening* will require a prepolymerization stage if the monomer is a ring [for example, nylon-6 (ϵ-caprolactam)]. In this situation, ring-to-ring reactions do not exist. Therefore, a few rings must be opened before any chain growth may occur. The polycondensation I or ring addition reactions may proceed after the initial ring opening. Ring opening, however, will not occur without a catalyst present. For nylon-6, the catalyst is the condensate, thus it is required that the design include condensate initially in the reactor or inlet flow. The forced removal of condensate at this stage is not necessary. In fact, condensate removal may slow the overall polymer growth.

Table 3. Reactor Types Used as Prepolymerization Units

Reactor Types	Patent References
CSTR(s)	Kharkov et al. (1971) Griehl et al. (1972)
Cascading CSTRs	Fujimoto et al. (1971) Griehl et al. (1972) Yates et al. (1982)
Distillation Column	Busot (1969) Sauerbrunn (1983)

If a polymer system has multiple monomers, typically *A-A* and *B-B* monomers, it might be possible to utilize a *salting reaction*. The two monomers (*A-A* and *B-B*) will form a dimer that can be made to precipitate out of the reaction mixture. The advantage of this procedure is that the ratio of *A* end groups to *B* end groups for the precipitated dimer is 1:1. This process will insure proper end group stoichiometry, which allows high-molecular-weight polymer to be produced in later stages.

Some polymers exhibit *multiple reaction pathways* for chain building. An excellent example of this is PET polymer. The two pathways for PET are via the polycondensation I and II reactions. It may be possible to select either one of the pathways as the chain building reaction by judicious reaction design in the prepolymerization stage. For PET this is done by running one of the reaction pathways (polycondensation I) to completion without much reaction by the other pathway. There are two factors that allow this to be done for PET: (i) each pathway produces and therefore is inhibited by a different condensate; (ii) the catalyst favoring one of reaction pathways is selected over the other.

Therefore, for PET the condensate produced by the polycondensation I reaction (methanol) is completely removed, thus driving that reaction to completion. An excess amount of the condensate for the polycondensation II reaction (ethylene glycol) prevents its growth. As long as the condensate for the polycondensation I reaction is not reintroduced to the process later, that reaction pathway will play no role in the later polymerization stages. These points will be illustrated in detail below.

Reactors. Reactor types typically used in industry as prepolymerizing stages are listed in Table 3. The simplest continuous process unit for a prepolymerizer is the CSTR. The physical properties of the monomers may demand a more complicated design. For multiple monomer systems it may be possible for one or more monomers to be volatile along with the condensate. In these situations, if there is condensate removal occurring, recovery of the monomers will be enhanced by using a reactive distillation column.

Polymerization stage

The polymerization stage is used to polymerize prepolymer to a moderate molecular weight. All polymer systems require the polymerization stage. Condensate removal may be nonexistence to moderate depending on the polymer system. The stronger the reverse chain building reactions, the more necessary mass transfer becomes. If condensate removal is required, the polymerization stage is usually designed to operate until the point of relatively easy mass transfer ends.

Problems. Several problems occur and must be considered when designing this reaction stage.

Nonuniformity in viscosity or composition reduces polymer quality. This problem may be caused by incomplete mixing or nonuniform residence times in the reactor. It is critical to maintain uniform viscosity and composition at this stage because any nonuniformity present is transferred to the finishing stage where very high viscosity makes maintaining a uniform composition even more difficult. This problem may be minimized by periodically blending or mixing the polymer.

Condensate removal is essential in the polymerization stage because the concentration of condensate limits molecular weight due to the reversible nature of the polycondensation reaction. Mass transfer of the condensate may be governed by diffusion rates, heat-transfer rates, or surface mass-transfer rates. The removal of condensate may require the reactor to have a high surface-area-to-volume ratio.

The problem of *reactor heat transfer* has two aspects: (i) the reactor must provide enough energy to vaporize the condensate if mass transfer occurs; (ii) there must be sufficient heat transfer to prevent excessive temperatures from depolymerizing the polymer or accelerating side reactions.

A broad *residence time distribution* in the reactors can cause the polymer to have a broad molecular weight distribution and make grade changes more difficult. To solve this, reactors with more plug-flow-like qualities may be used. While maintaining narrow residence time distributions, it is important to maintain uniform composition in the polymer product.

Side reactions lead to the same problems that occur in the prepolymerization stage and the solutions are also the same.

Foaming is caused by the polymer bubbling when the condensate is removed. Problems related to foaming will occur when the vacuum space above the polymer is too small. A result may be the loss of polymer due to the evacuation of polymer (foam) with the condensate. As remedies, antifoaming agents may be added or the reactor may be designed to reduce foaming or to increase the vapor space above the foam.

Product reproducibility means making the same quality of product day after day. An important aspect of achieving this is through controlling parameters that affect the product viscosity. This may be accomplished through controlled mass transfer (pressure control) or by adjusting the end group stoichiometry to limit ultimate molecular weight. Such solutions to maintaining product quality are a challenging process control problem.

Design Analysis. Since reactors designed for mass transfer are more complicated and costly, the simplest reactors for a given task are typically the best. Therefore, knowledge of the mass-transfer requirements and performance will help in the design of the polymerization stage. Once again, an investigation based on the kinetics of the polymer system will help develop an effective design.

An analysis tool introduced in this work is the *mass transfer potential*. The MTP of a polymer system is a measure of the need for increased mass transfer and defined as:

$$\mathrm{MTP}(DP_n,T,P,\ldots) \equiv \frac{\left.\dfrac{dDP_n}{dt}\right|_{DP_n}^{\mathrm{irrev}} - \left.\dfrac{dDP_n}{dt}\right|_{DP_n}^{\mathrm{nominal}}}{\left.\dfrac{dDP_n}{dt}\right|_{DP_n}^{\mathrm{irrev}}} \qquad (1)$$

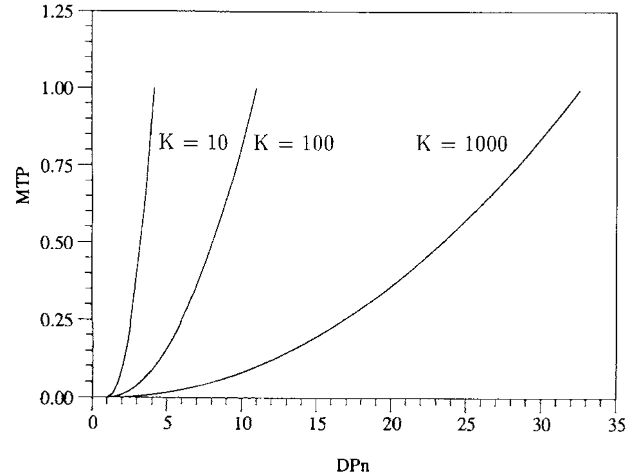


Figure 3. MTP for the simple polymerization of *A-B* monomer for different equilibrium constants.

It is the fractional difference between the rate of chain growth with complete removal of condensate (kinetics completely irreversible) and the rate of chain growth of the system at the same nominal conditions. Note from Eq. 1 that the MTP depends on chain length (DP_n), reactor temperature (T), reactor vapor-phase pressure (P), and overall heat- and mass-transfer rates. The irreversible kinetic term

$$\left.\frac{dDP_n}{dt}\right|_{DP_n}^{\text{irrev}}$$

can be obtained from the kinetic model assuming no reversible reactions and is essentially independent of system pressure and mass-transfer conditions. The physical equilibrium term

$$\left.\frac{dDP_n}{dt}\right|_{DP_n}^{\text{nominal}}$$

may depend only on temperature if the nominal condition is a closed reactor with no mass transfer. Alternatively, the nominal condition may be the current conditions of temperature, pressure and mass transfer. Figure 3 illustrates the MTP for a closed reactor at varying temperatures.

The MTP indicates whether the reaction is kinetically-limited or mass-transfer-limited at a given chain length or conversion. A MTP of zero means increased mass-transfer capabilities will not improve the rate of polymer growth. A MTP of unity means the process is totally limited by chemical equilibrium and improvements in mass-transfer rate will substantially increase the rate of chain growth.

Table 4. Mass-Transfer Design Schedule for Simple Polymerizations of *A-B* Monomer for Different Equilibrium Constants

K	DP_n to start Mass Transfer	DP_n to End Stage
10	3	20
100	8	20
1,000	—	23

Table 5. Reactor Types Used as Polymerization Units

Reactor Types	Patent by
CSTR	Dietze et al. (1969) Busot (1969) Buyalos et al. (1984)
Tank with Internals	Yokouchi et al. (1970)
Tubular	Markel et al. (1970) Rotzoll et al. (1982) Buyalos et al. (1984)
Screw	Wheeler et al. (1971)
Kneader	Fritsch (1986)
Wiped Film	Urgesi and Rothert (1972)

Kinetic modeling (for example, the model developed by Jacobsen and Ray, 1992) makes it possible to determine the two rates of change for the number-average chain length needed to calculate the MTP. The term *nominal* is obtained by modeling the process at the nominal design conditions being considered, and the term irrev is obtained by modeling the process with irreversible kinetics with respect to any chain building reaction involving condensate. The definition (Eq. 1) can be simplified to an analytical form for very simple kinetics; however, the real power of the concept is in analyzing real complex systems where the MTP can only be calculated numerically from the detailed kinetic model.

To illustrate the MTP on a simple polymer system, consider a polymer with only the polycondensation I reaction. The initial condition of the reactor is pure *A-B* monomer. Figure 3 shows the MTP for several polymer systems of this type. The only difference is that each system has a different equilibrium constant.

Based on the MTP plots in Figure 3 for the simple polymer systems, a design for each polymerization stage may be developed. The MTP plot may help determine if mass transfer is required by choosing a cutoff value of MTP. If the MTP is below the cutoff value, mass transfer is not necessary; above the cutoff value, mass transfer is required. For example, suppose the goal of the polymerization stage for the simple polymer systems in Figure 3 to be a DP_n of at least 20. This goal represents where the viscosity of the polymer begins to interfere with uniform mixing. This value of DP_n must be determined individually for each actual polymer system. The best value of MTP in each case can be decided by economic analysis; however, let us choose MTP = 0.5 as the cutoff value for this example. Table 4 shows the value of DP_n at which mass transfer should start and when the polymerization stage ends for each value of K of the simple polymer system. Note that one design goes beyond the goal DP_n of 20 due to the reduced mass-transfer requirements of that system. Above a DP_n of 20, a plug-flow-like reactor may be needed to suppress uneven mixing problems since the viscosity is so great.

Reactors. Reactor types typically used in industry as polymerizing stages are shown in Table 5. The simplest continuous process unit for a polymerizer is the CSTR. The physical properties of the monomers may demand a more complicated design. If the viscosity of the polymer becomes great enough to prevent uniform mixing, the reactor should have more of a plug-flow pattern. If mass transfer is used during the polymerization stage, it should only be used while the viscosity is low. Mass transfer with high viscosity should be done in the finishing stage. Low-viscosity conditions allow the use of simple tank reactors with internal surfaces (uniform mixing is possible) and falling-film reactors (lower viscosity allows the polymer to flow).

Finishing stage

The finishing stage is used to drive polymer to a higher molecular weight. Commonly, the polymer molecular weight is limited by the condensate in the reactor; therefore polymer growth is accomplished by intensive removal of condensate via mass transfer. This stage may be considered mass-transfer-limited due to the magnitude of the problem.

The polymer is also highly viscous at this stage of production. The viscosity requires major consideration in the design of the reactor. The viscosity of the polymer leads to several problems.

Problems. There are several important problems to be aware of when designing the finishing stage.

As in the polymerization stage, *nonuniform viscosity and composition* cause problems. In this stage, it is even more difficult to prevent since the polymer viscosity is higher. Due to uneven mixing, there may be multiple residence time paths through the reactor.

Condensate Removal. It poses the same basic problem as in the polymerization stage. The only difference is that here condensate removal is diffusion-limited, and a high mass-transfer-area-to-volume ratio and a small diffusion path are critical in reactor design.

Fluid transport from inlet to outlet due to the high viscosity of the polymer. The viscosity may require an extra driving force to push the polymer through the reactor by adding equipment (such as screws, fingers, and paddles) inside the reactor.

Reactor heat transport poses similar problems to those in the polymerization stage.

Temperature variations can produce hot and cold spots in the reactor; usually these are caused by the reactor design. Consider a thin film that has not been mixed. The temperature of the fluid contacting the reactor wall may differ from that near the mass-transfer surface, and these hot and cold spots may result in nonuniform composition of the product. Thus, each individual design must be analyzed to eliminate temperature variations.

Side reactions pose similar problems here as in the prepolymerization stage. The resulting solutions are also similar.

Splattering and fouling may be a serious problem in the finishing reactor. When the polymer enters the finisher, the condensate within the polymer begins to evaporate. If this evaporation occurs at high rates, the polymer will *bubble and splatter* onto the reactor surfaces. The polymer may stick and stagnate on the surface of the reactor. This stagnated polymer will continue to polymerize to a ultra high molecular weight. If the stagnated polymer breaks loose from the reactor wall, it may cause fouling of equipment and result in lost product. This may be reduced by removing as much condensate from the polymer as possible before starting the finishing stage. The inclusion of wiped and scraped surfaces inside the reactors help reduce this problem.

The problems associated with *product reproducibility* are similar to those in the polymerization stage. The resulting solutions are also similar.

Design Analysis. Even though the finishing stage is mass-transfer-limited, a look at the polymer chemistry will be quite helpful. Some finishing reactors are designed to have high shear mixing, but some polymers may be too fragile for these reactors. A basic understanding of the chemistry involved in making a specific polymer will also help determine how the mass transfer should be accomplished to produce the needed molecular weight.

Some polymer systems consist of quite *fragile monomers* that are sensitive to shear forces (forced mixing) causing chain scission. For example, the monomer unit of the polymer PBT, butylene glycol, is quite fragile compared to its cousin, ethylene glycol, in the polymer PET. The typical mixing action in many finishing reactors will degrade the PBT by breaking the butylene repeat unit. This problem has to be solved by using finishing reactors that use minimal amounts of shear mixing. The reactors of choice for PBT have been of the thin-film type.

The usual technique for *mass transfer* in the finishing stage is to operate the reactor under vacuum. This forces the condensate out of the reaction mixture and into the vapor space of the reactor. There is a limit, however, to the extent which vacuum can push the growth reactions forward. By considering the basic kinetics for a polymer system and applying a general concept for mass transfer (such as the technique discussed by Jacobsen and Ray, 1992) it is possible to see how much vacuum is required to obtain a certain molecular weight. For example, when there are no liquid-phase bulk diffusion limitations in the reactor, the rate of mass transfer for a volatile component in a reactor may be represented by Eq. 2. The rate of mass transfer is the difference between the liquid and gas activities of the volatile component multiplied by the mass-transfer coefficient, $k_{m,i}$, and the mass-transfer surface area, A_m. The volatile components may include condensate, monomer, solvent, or some other component.

$$\text{rate}_i = A_m k_{m,i}(a_{l,i} - a_{v,i}) \tag{2}$$

The activity of a given component in the vapor phase, $a_{v,i}$, may be estimated by assuming ideal gases. The vapor activity is then equal to the partial pressure of the given species and also the vapor mole fraction of the species multiplied by the total pressure.

$$a_{v,i} = P_i = y_i P \tag{3}$$

The activity of a volatile component in the liquid phase, $a_{l,i}$, may be expressed using the partition equation for vapor-liquid equilibrium (VLE), where the volatile component's vapor pressure is P_i^o, the liquid activity coefficient is $\gamma_{\phi,i}$, and the volatile species volume fraction is ϕ_i:

$$a_{l,i} = P_i^o \gamma_{\phi,i} \phi_i \tag{4}$$

The liquid activity coefficient may be derived from the Gibbs free energy using the Flory-Huggins theory and Van Laar theory of mixing, where the number average chain length is DP_n, the polymer volume fraction is ϕ_p, and the Flory-Huggins interaction parameter is χ_i:

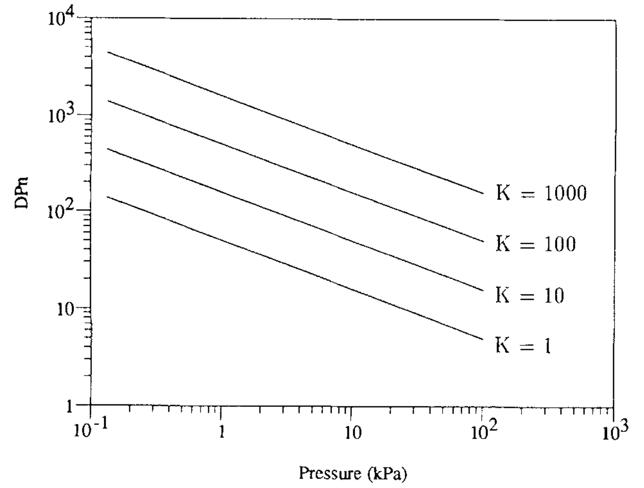


Figure 4. PCL plot for simple polycondensation I polymer systems with different equilibrium constants.

$$\gamma_{\phi,i} = \exp\left[\left(1-\frac{1}{DP_n}\right)\phi_p + \chi_i\phi_p^2\right] \tag{5}$$

If there is only one volatile component in the reactor, then the equations given above are sufficient for modeling the mass transfer in the reactor. The only operational parameter that has to be set is the partial pressure of the volatile component (P_i) in the reactor. The activity of the component in the vapor phase is directly found by using Eq. 3 with the partial pressure.

If more than one volatile component is in the reactor, then the vapor phase of the reactor must be included in the modeling. By assuming a pseudo-steady state for the vapor phase, a relation between the vapor and liquid phases evolves:

$$y_i = \frac{a_{v,i}}{\Sigma_j a_{v,j}} = \frac{a_{l,i}}{\Sigma_j a_{l,j}} \tag{6}$$

This means that the ratios of the activities for the components in the liquid and vapor phases are the same. The actual values of the vapor-phase activities are determined by the total pressure in the reactor (Eq. 3). The mass-transfer rate in Eq. 2 will be zero when the total pressure in the reactor equals the sum of the liquid activities for each component ($P = \Sigma_i a_{l,i}$) as well as the sum of vapor activities.

With the addition of the vapor-phase modeling it is possible to specify a total pressure in the reactor. Then, using Eq. 3 the vapor activities of each component may be calculated. If there are also bulk liquid-phase diffusion limitations, then more complex mass-transfer modeling must be carried out. In this situation, the rate of mass transfer in Eq. 2 is only an upper bound to the overall mass-transfer rate.

Table 6. Vacuum Pressure Designs for Simple Polycondensation I Polymer Systems with different Equilibrium Constants*

K	Vacuum Pressure (kPa)
1	0.065
10	0.65
100	6.5
1,000	65

*The given vacuum pressures will produce polymer chain lengths of 200.

Table 7. Reactor Types Used as Finishing Units

Reactor Types	Patent by
Tank with Internals	Albrecht et al. (1969) Leybourne et al. (1969) Schnock and Scheizer (1971)
Extruders	Dew et al. (1969) Crawford et al. (1970) Abbott et al. (1971)
Tubular	Markel et al. (1970) Rotzoll et al. (1982) Buyalos et al. (1984)
Thin Film	Perry (1969) Brignac (1970) Sasaki et al. (1986)
Wiped Film	Urgesi and Rothert (1972)

A valuable tool in analyzing reactors with mass transfer is the *pressure-chain length (PCL) plot*, which is the vapor-phase pressure (P) required to achieve a given chain length (DP_n) under conditions of physical equilibrium between the liquid and bulk vapor and uniform condensate composition in the liquid. For example, consider a simple polycondensation I polymer system with various equilibrium constants ($K = 1$, 10, 100 and 1,000). Simulations using the kinetic model for the simple system under conditions of infinitely high mass-transfer coefficients are developed for several pressures ($P = 0.5$, 1.0, 10.0 and 101.3 kPa). The simulation results in Figure 4 provide an equilibrium chain length for each reactor pressure.

Using the PCL plots in Figure 4 it is possible to develop the vacuum requirements for a finishing stage design assuming perfect mass transfer. If the desired number-average chain length is known, then the PCL plot may be used to determine the proper operating pressure of the reactor. Table 6 shows the vacuum pressures required to produce polymer with a chain length of 200 for the simple polymer system. The PCL plot is a general tool that may be used with polymer systems which have complex kinetic mechanisms. Note that in practice there still may be mass-transfer limitations so that vapor-liquid equilibrium is not achieved. Thus, the actual design may require improved mass-transfer coefficients or even lower operating pressures to reach the target DP_n value.

Reactors. Reactor types typically used in industry as finishing reactors are listed in Table 7. These reactors are designed for maximum surface areas and plug-like flows to decrease the reaction times needed. If fragile polymers are being used, then intensive mechanical mixing is avoided.

Process Examples

The design analysis and modeling techniques are illustrated by two complete process flowsheet examples: one for nylon-6,6 and the other for PET. Both polymers are industrially important condensation polymers.

All simulation results presented here were created using the POLYRED package. POLYRED is a CAD package for polymerization systems developed at the University of Wisconsin in Madison. POLYRED was developed to simulate many types of polymer processes including free radical, ionic, group trans-

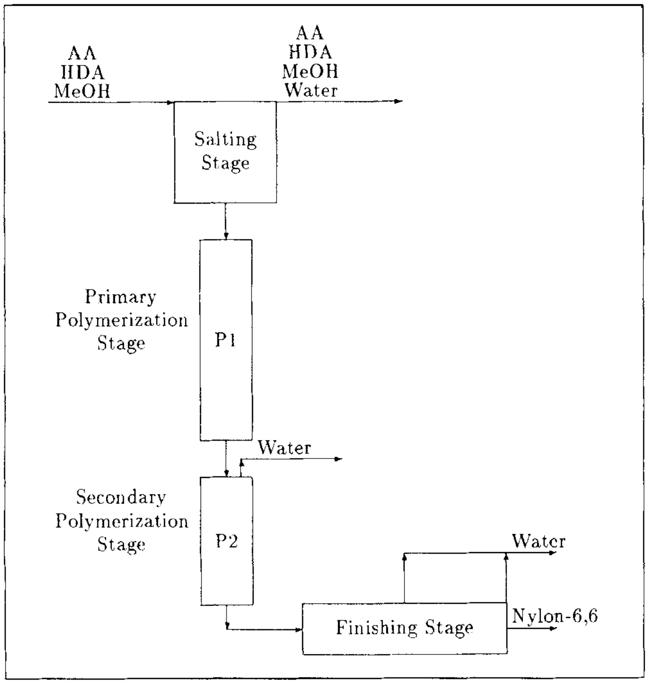


Figure 5. Constant temperature (280°C) melt process for production of nylon-6,6.

The prepolymerization stage consists of a salting CSTR. The feed into the salting CSTR contains adipic acid (AA) and hexamethylene diamine (HDA). The polymerization stage consists of two tubular reactors. The primary polycondensation reactor (P1) is operated as a closed tubular reactor. The secondary polycondensation reactor (P2) is operated as an open tubular reactor run at reduced pressure (1.7 MPa). Water is flashed out the P2 reactor. The finishing stage, an extruder, is operated at atmospheric pressure.

fer, Ziegler-Natta and condensation processes. The POLYRED program CPC incorporates the general modeling to simulate kinetics for copolymers and nonlinear polycondensation polymers. The general mechanisms in Table 1 are modeled by the program, but only a subset is used for each example.

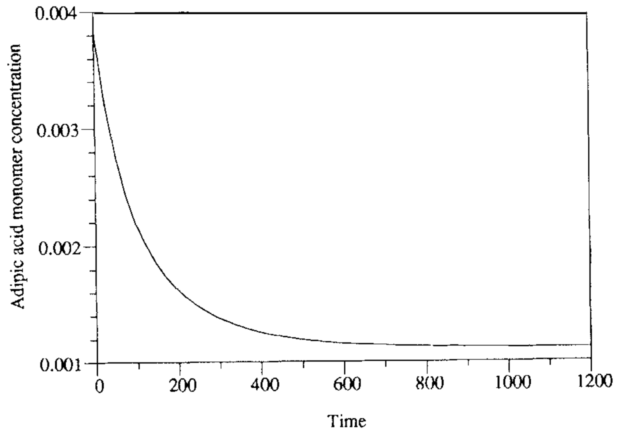


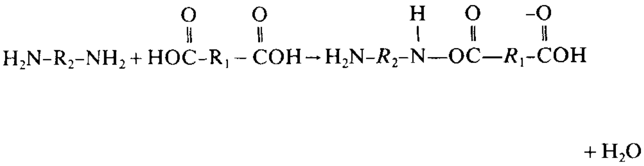
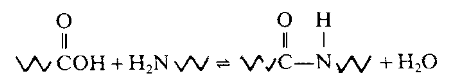
Figure 6. Adipic acid monomer concentration vs. time during startup with an initially full reactor.

Initial conditions are for equal molar quantities of the monomers hexamethylene diamine and adipic acid in a 50 wt. % solution of methanol.

Nylon-6,6

Nylon-6,6 is an industrial polymer processed by using all three of the stages discussed earlier. A melt polymerization process patented by DuPont (Taylor, 1944) is shown in Figure 5. The process consists of a salting reactor (prepolymerizer), a closed tubular reactor (primary polymerizer), an open tubular reactor at 1.7 MPa (secondary polymerizer), and an extruder operating at atmospheric pressure (finisher). The mechanisms used to model nylon-6,6 in this process are given in Table 8.

Table 8. Nylon-6,6 Kinetic Mechanism

Salting:	$S_{\delta(1)} + S_{\delta(2)} \rightarrow P_{\delta(1)+\delta(2),1,1} + C$
	 $H_2N\text{-}R_2\text{-}NH_2 + HO\overset{O}{\overset{\|}{C}}\text{-}R_1 - \overset{O}{\overset{\|}{C}}OH \rightarrow H_2N\text{-}R_2\text{-}\overset{H}{\overset{\mid}{N}}\text{—}O\overset{O}{\overset{\|}{C}}\text{—}R_1\text{-}\overset{-O}{\overset{\|}{C}}OH + H_2O$
Polycondensation 1:	$P_{m,a,b} + P_{n,e,f} \rightleftharpoons P_{m+n,a+e-1,b+f-1} + C$
	 $\sim\overset{O}{\overset{\|}{C}}OH + H_2N\sim \rightleftharpoons \sim\overset{O}{\overset{\|}{C}}\text{—}\overset{H}{\overset{\mid}{N}}\sim + H_2O$

$S_{\delta(1)} = P_{\delta(1),2,0} \equiv$ hexamethylene diamine
$S_{\delta(2)} = P_{\delta(2),0,2} \equiv$ adipic acid
$C \equiv$ water

The rate of polycondensation developed by Ogata (1961b) is shown in Eq. 7. The expression for the forward polycondensation rate is a function of the initial condensate concentration in the reactor. The units of $[C]_o$ are moles condensate per mole of polymer repeat unit; T is in kelvin; and k_1 is in kg/kmol·h. The reasons for Ogata's use of the condensate term are certainly not clear; however, we will use it in this example. The rate constant used for the salting reaction is $k = 15.6$ kg/kmol·h.

$$\log k_1 = \frac{13.1}{[C]_o^{0.025}} - \frac{4,830}{T} \tag{7}$$

The equilibrium constant from Ogata's work (1961a) is:

$$\log K = \frac{5,800}{T} - 8.32 \tag{8}$$

The vapor pressure of water (Eq. 9) is required by the model:

$$\log P_W^o(\text{kPa}) = 10.644 - \frac{2,100}{T(\text{K})} \tag{9}$$

Steppan et al. (1987) have developed an improved rate expression and equilibrium constant based on the instantaneous value of condensate in the reactor.

The technique of producing a salt in the prepolymerization stage is used for this example. The salting reactor is a two-phase CSTR. Reaction occurs in the liquid phase between the monomers adipic acid and hexamethylene diamine in a solution of methanol. The dimer product will then precipitate into a nonreactive solid phase. The salting reactor is used to insure

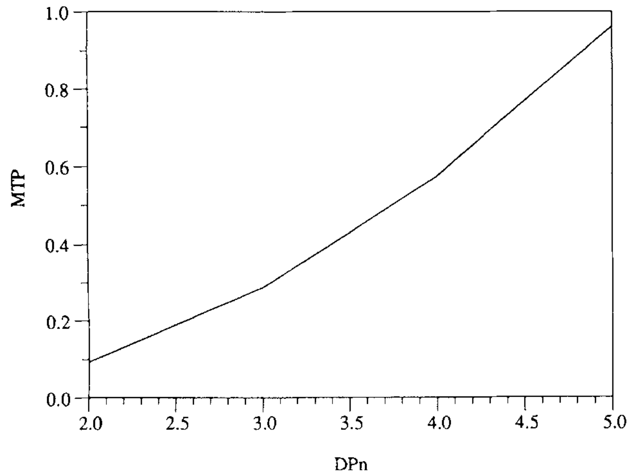


Figure 7. Mass-transfer potential for the primary polymerization stage.

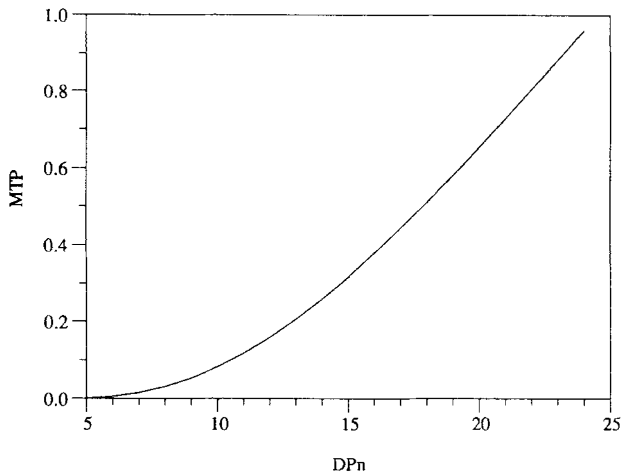


Figure 9. Mass-transfer potential for the secondary polymerization stage.

that the monomers are introduced to the reaction mixture at a ratio of 1:1. The residence time of the CSTR is 1,000 seconds.

Figure 6 shows the dynamic startup of the salting reactor if the reactor is initially full of equal molar quantities of the monomers hexamethylene diamine and adipic acid in a 50 wt. % solution of methanol. The concentrations given in the figure are based on the total reactor contents. The solid phase is actually pure dimer in the model. The solid phase is extracted from the reactor and washed with water. A 50% water and 50% dimer molten solution (based on weight) is made of the product from the salting reactor. This melt is then fed to the primary polymerization reactor.

The primary polymerization reactor is a closed tubular reactor operating at 280°C. The mass-transfer potential may be used to help design the reactor. The MTP plot for the primary polymerization stage is given in Figure 7. Based on the MTP plot, the maximum DP_n that can be produced in this present reactor is about 5. Since reaction times are short in this reactor, an MTP of 0.9 can be used to determine the target value for the polymer DP_n produced in the reactor. An MTP of 0.9 corresponds to a DP_n of 4.8, as shown in Figure 7.

Using the kinetic model for nylon-6,6, the time required to reach a DP_n of 4.8 is 250 s. Figure 8 shows the reactor profile for DP_n in a closed tubular reactor with a residence time of 250 seconds. The inlet to the reactor (time = 0) is the 50% dimer melt. The resulting prepolymer leaving this reactor has a DP_n of 4.8.

The secondary polymerization reactor is an open tubular reactor operating at 280°C and 1.7 MPa with a surface mass-transfer coefficient and area $(k_{m,i}A_m)$ of 0.18 kmol/h·kPa for each component. This reactor is actually a devolatilization reactor with the pressure reduced to 1.7 MPa to flash off as much water as possible. The mass-transfer potential may also be used to help design this reactor. The MTP plot for the secondary polymerization stage is given in Figure 9. Based on

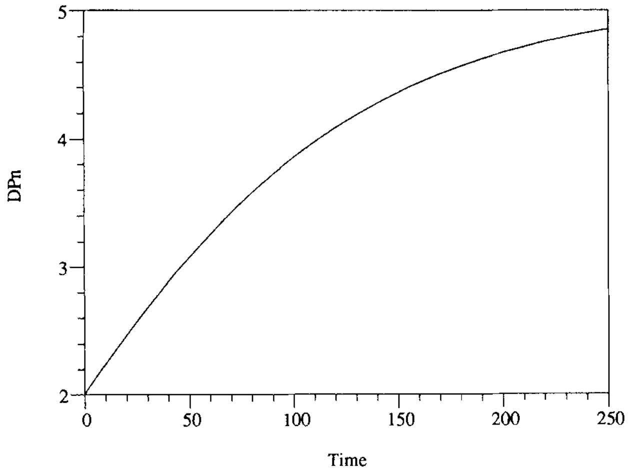


Figure 8. Number-average degree of polymerization profile in the primary polymerization stage.

The closed tubular reactor operating at a temperature of 280°C is designed to polymerize to a DP_n of 4.8 (MTP = 0.9). The resulting residence time in the reactor is 250 s.

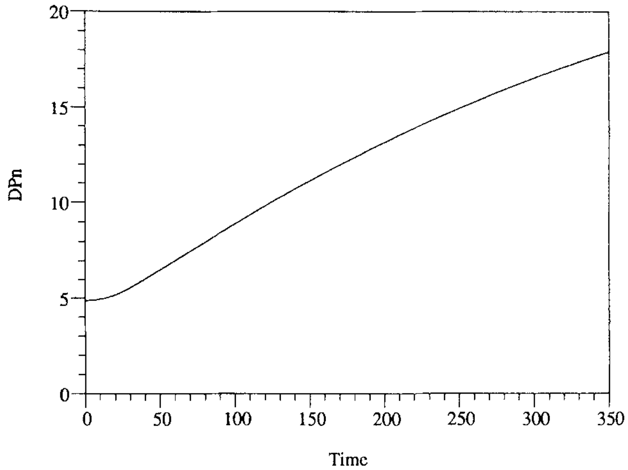


Figure 10. Number-average degree of polymerization profile in the secondary polymerization stage.

The open tubular reactor operating at a temperature of 280°C and a pressure of 1.7 MPa is designed to polymerize to a DP_n of 18 (MTP = 0.5). The resulting residence time in the reactor is 350 s.

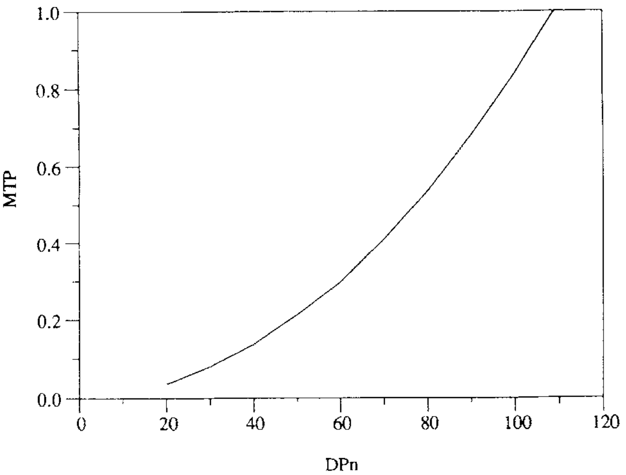


Figure 11. MTP for the finishing stage of the nylon-6,6 process.

the MTP plot, the maximum DP_n produced in this reactor is about 24. An MTP of 0.5 will be used to determine the target value for the polymer DP_n produced in the reactor. This MTP corresponds to a DP_n of 18, as shown in Figure 9.

Using the model for nylon-6,6, the time required to reach a DP_n of 18 is 350 s. Figure 10 shows the reactor profile for DP_n in an open tubular reactor with a residence time of 350 s. The inlet stream to the reactor (at time = 0) is prepolymer with $DP_n = 4.8$. The resulting polymer leaving this reactor has the design DP_n of 18.

The finishing reactor is an open extruder operating at 280°C and atmospheric pressure with a surface mass-transfer coefficient and area $(k_{m,i}A_m)$ of 0.18 kmol/h·kPa for each component. The polymer leaving this reactor is the end use polymer. Figure 11 shows the MTP plot for the finishing stage. Note that if we wish an exit DP_n of 104 the MTP will be about 0.95. This means that the exit polymerization rate is 20 times slower than what could be achieved if all the condensate could be removed by mass transfer. With the present design, to achieve a DP_n of 104, the polymerization at this stage is carried out nearly to an equilibrium value. Near this equilibrium, small fluctuations in the residence time of the reactor will not greatly affect polymer quality. To change the equilibrium value of polymer produced, the pressure in the reactor may be raised or lowered.

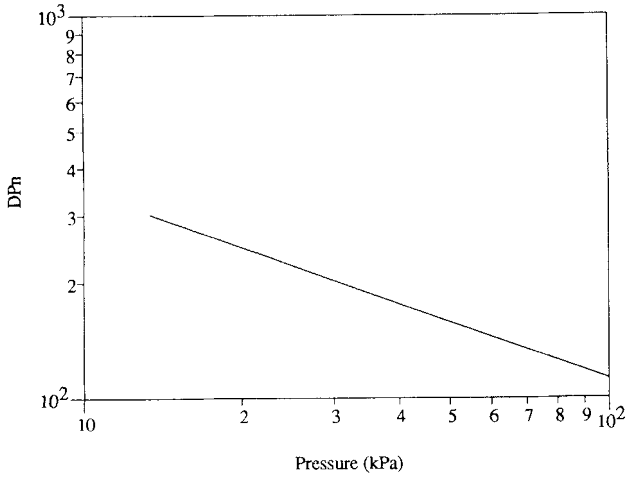


Figure 12. PCL plot for the nylon-6,6 process.

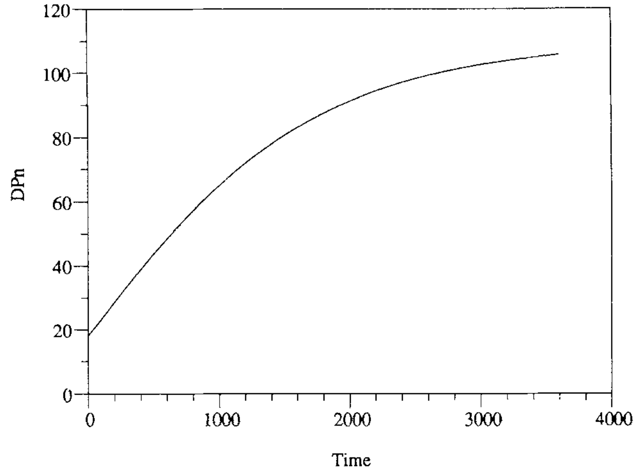


Figure 13. Number-average degree of polymerization profile in the finishing stage.

The open extruder operating at a temperature of 280°C and atmospheric pressure is designed to polymerize to a DP_n of 105. The residence time in the reactor is 3,600 s.

Figure 12 shows the PCL plot for reaching a given DP_n. By operating at atmospheric pressure, a DP_n of 109 may be obtained at vapor-liquid and chemical equilibrium. If we choose our target DP_n to be 104, the reactor will reach about 95% of equilibrium based on chain length.

Using the kinetic model for nylon-6,6, the time required to reach a DP_n of 104 is 3,600 s. Figure 13 shows the reactor profile for DP_n in an open extruder at atmospheric pressure with a residence time of 3,600 s. The inlet to the reactor (at time = 0) is polymer with $DP_n = 18$. The resulting polymer leaving this reactor has the design DP_n of 104. The polymer produced is used either for making polymer chips for later use in fiber spinning or for direct applications to molding.

Note that it would be possible to design this finishing process to operate with shorter residence times by further reducing the extruder pressure and improving the mass-transfer coefficients. In fact, the MTP plot in Figure 11 shows that improvements up to a factor of 20 are possible, thus greatly shortening the

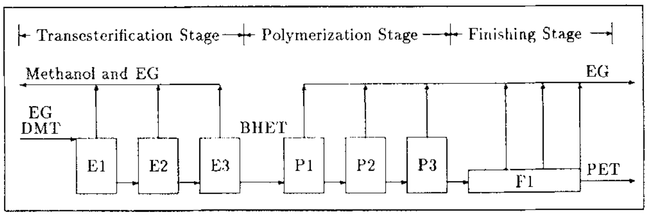
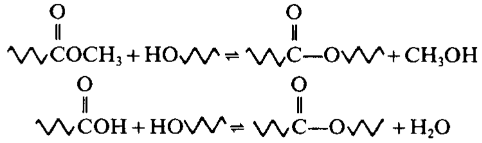


Figure 14. Three-stage continuous process for production of PET.

Feed to the process is ethylene glycol (EG) and dimethyl terephthalate (DMT). The first stage consists of three transesterification CSTRs (E1, E2, and E3). Methanol and ethylene glycol are evaporated from the transesterification stage. The second stage consists of three polymerization CSTRs (P1, P2, and P3). The final stage consists of an extruder (F1). The vapors removed from the final two stages consist mostly of ethylene glycol.

Table 9. PET Kinetic Mechanism

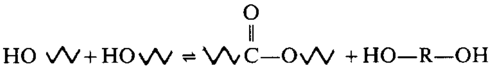
Polycondensation I: $P_{m,a,b} + P_{n,d,e} \rightleftharpoons P_{m+n,a+d-\delta(i),b+e-\delta(j)} + C_{ij}$



$$\sim\!\sim\overset{\overset{\displaystyle O}{\|}}{C}OCH_3 + HO\sim\!\sim \rightleftharpoons \sim\!\sim\overset{\overset{\displaystyle O}{\|}}{C}{-}O\sim\!\sim + CH_3OH$$

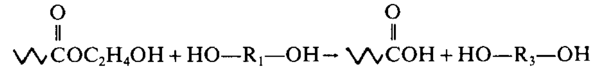
$$\sim\!\sim\overset{\overset{\displaystyle O}{\|}}{C}OH + HO\sim\!\sim \rightleftharpoons \sim\!\sim\overset{\overset{\displaystyle O}{\|}}{C}{-}O\sim\!\sim + H_2O$$

Polycondensation II: $P_{m,a,b} + P_{n,d,e} \rightleftharpoons P_{m+n-\delta(k),a+d-2\delta,b+e} + P_{\delta(k),2\delta,0}$



$$HO\sim\!\sim + HO\sim\!\sim \rightleftharpoons \sim\!\sim\overset{\overset{\displaystyle O}{\|}}{C}{-}O\sim\!\sim + HO{-}R{-}OH$$

Two chain reformation: $P_{n,a,b} + P_{m,x,y} \rightarrow P_{n-\delta(1),a-\delta(1),b+\delta(2)} + P_{m-\delta(1)+\delta(3),x-\delta(1)+\delta(2),y}$



$$\sim\!\sim\overset{\overset{\displaystyle O}{\|}}{C}OC_2H_4OH + HO{-}R_1{-}OH \rightarrow \sim\!\sim\overset{\overset{\displaystyle O}{\|}}{C}OH + HO{-}R_3{-}OH$$

$P_{\delta(1),2\delta(1),0} \equiv$ ethylene glycol
$P_{\delta(2),0,2\delta(1)} \equiv$ DMT
$P_{\delta(3),2\delta(2),0} \equiv$ diethylene glycol
$P_{n,a,\delta(2)} \equiv$ polymer with acid end groups
$P_{2\delta(1)+\delta(2),2\delta(1),0} \equiv$ BHET
$C_{11} = C_{21} \equiv$ methanol (condensate)
$C_{12} = C_{22} \equiv$ water (condensate)

reactor residence times. However, the present design at 95% of equilibrium has the advantage that the process is self-controlling at a DP_n close to 104. Variations in reactor residence time or rate constants will not affect DP_n very much so that the product DP_n is quite stable to process disturbances.

PET

Poly(ethylene terephthalate) is an industrial polymer processed using all three of the stages discussed earlier. A polymerization process discussed by Ravindranath and Mashelkar (1982a,b, 1984) is shown in Figure 14. The process consists of three transesterification CSTRs (prepolymerization stage) followed by three more polymerization CSTRs (polymerization stage) and then finally an extruder reactor (finishing stage). The mechanisms used to model PET in this process are given in Table 9. The rate parameters used for the simulations are given in Table 10. The vapor pressures of ethylene glycol, diethylene glycol, methanol and water are also needed and given in Eqs. 10 to 13.

$$\log P^o_{EG}(\text{kPa}) = 11.521 - \frac{3{,}066.5}{T(\text{K})} \qquad (10)$$

Table 10. DMT and Ethylene Glycol Kinetic Parameters

Parameter	PC I	PC II	Two Chain Reform.
Ao (1/kmol·min)	20.0	680	4.16×10^4
Eo (kJ/kmol)	62,800	77,400	125,000
K	0.15	1	—

$$\log P^o_{DEG}(\text{kPa}) = 11.125 - \frac{3{,}170.7}{T(\text{K})} \qquad (11)$$

$$\log P^o_{M}(\text{kPa}) = 10.541 - \frac{1{,}867.9}{T(\text{K})} \qquad (12)$$

$$\log P^o_{W}(\text{kPa}) = 10.644 - \frac{2{,}100}{T(\text{K})} \qquad (13)$$

Other specific parameters for the examples were assumed to take ideal solution values.

Because of the existence of both polycondensation I and II reactions in this process, the prepolymerization stage is used (see discussion on prepolymerization stage). The prepolymerization stage consists of three transesterification CSTRs. The prepolymerization stage is used to insure that the ethylene glycol monomer units are reacted before mass transfer may remove them from the reaction mixture. If too much ethylene glycol is removed from the mixture, the polymer molecular weight will be limited to an undesirably low level. In this example, excess ethylene glycol is fed to compensate for evaporation losses.

The feed into the first reactor is pure ethylene glycol and DMT monomers at a ratio of 3:1. The first reactor is operated at 180°C and 60.0 kPa. This temperature is well below the boiling point for ethylene glycol. The second reactor is operated at 200°C and 33.3 kPa. The third reactor is operated at 220°C and 13.3 kPa. The residence times of the CSTRs are one hour each.

Figure 15 shows the dynamic startup of the transesterifi-

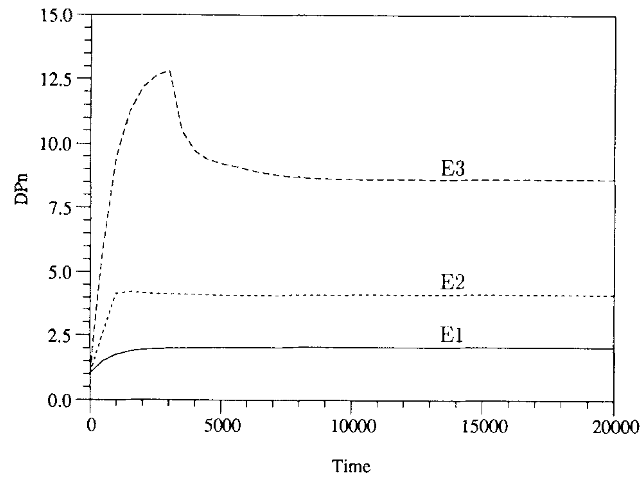


Figure 15. Number-average degree of polymerization vs. time during process start-up in the transesterification stage.

The open CSTRs are operating at temperatures and pressures of 180°C and 60.0 kPa, 200°C and 33.3 kPa, 220°C and 13.3 kPa. The residence times in the reactors are 1 h each.

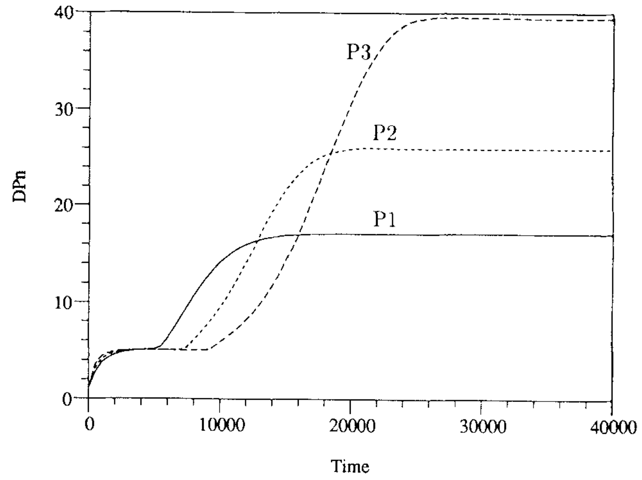


Figure 17. Number-average degree of polymerization vs. time during startup in the polymerization stage.

The open CSTRs are operating at temperatures and pressures of 260°C and 4.0 kPa, 270°C and 2.7 kPa, 280°C and 1.3 kPa. The residence times in the reactors are 1 h each.

cation reactors when the reactors are initially full of ethylene glycol and DMT monomer in the molar ratio of three to one. Even though the reactors each begin full, loss through the mass transfer of ethylene glycol slightly lowers the level in the reactors. The reactors are operated as overflow CSTRs, so initially there is no flow from one reactor to the next. The maximum value in the E3 reactor is due to the reactor acting as a batch reactor until the E1 and E2 reactors begin flowing into it continuously. The MTP plots for the transesterification reactors are given in Figure 16. The steady-state product out of the three reactors corresponds to MTPs of 0.6, 0.35, and 0.4. These numbers indicate that at this stage of the process the reaction rate is limited more by kinetic rates than by mass transfer. The prepolymer resulting from the third transesterification reactor is then fed to the polymerization stage of the PET process. This prepolymer has a 99% conversion of DMT end groups; therefore, the polycondensation I reaction is essentially complete.

The polymerization stage consists of three polymerization CSTRs. At this point in the process, enough ethylene glycol is contained in the prepolymer to increase the mass-transfer rate. Ethylene glycol monomer is now evacuated by mass transfer with lower vacuum pressures. This drives the polymerization forward since the main chain growth step is now the polycondensation II reaction.

The first polymerization reactor is operated at 260°C and 4.0 kPa. The second reactor is operated at 270°C and 2.7 kPa. The third reactor is operated at 280°C and 1.3 kPa. The residence times of the CSTRs are 1 h each.

The feed into the first polymerization reactor is the product of the transesterification stage (a prepolymer containing mostly

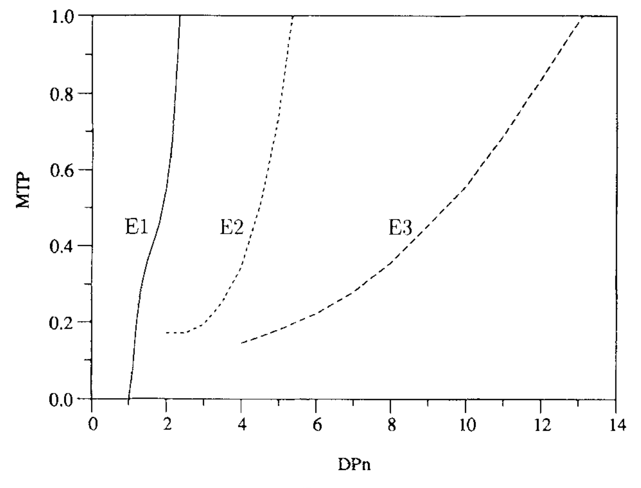


Figure 16. MTP for the PET transesterification stage at 180°C and 60.0 kPa, 200°C and 33.3 kPa, 220°C and 13.3 kPa.

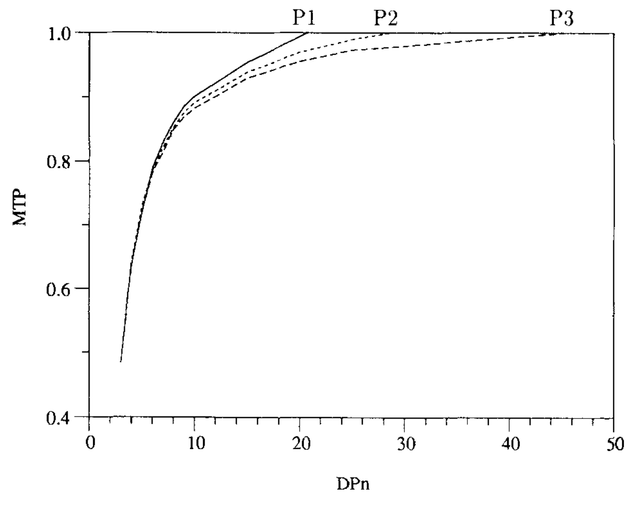


Figure 18. Mass-transfer potential for the PET polymerization stage at 260°C and 4.0 kPa, 270°C and 2.7 kPa, 280°C and 1.3 kPa.

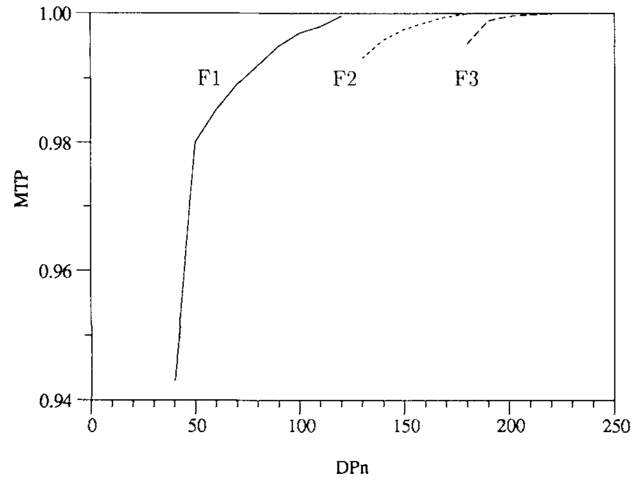


Figure 19. MTP for the finishing stage of the PET process.

BHET). Figure 17 shows the dynamic startup of the polymerization reactors, when the reactors are initially full of ethylene glycol and DMT monomers in the ratio of three to one. The MTP plots for the polymerization reactors are given in Figure 18. The steady-state product out of the three reactors corresponds to MTPs of 0.9, 0.95, and 0.98, which indicate that at this stage of the polymerization process, the reaction rate is greatly limited by mass transfer. In fact, the reactor rates (and required reactor residence times) could be improved by factors of 10 to 50 by increasing the mass transfer in these three reactors. Here, the MTP provides a clear picture of where to put process redesign effort.

The polymer resulting from the third polymerization reactor is then fed to the finishing stage of the PET process. The finishing reactor is an open extruder operating at 295°C and 0.067 kPa. The polymer leaving this reactor is the end use polymer. Figure 19 shows the MTP plot for the finishing stage. Note that for each reactor the MTP is greater than 0.99, indicating that chain growth rates could be increased by more than a factor of 100 by improved mass transfer in the finishing stage. Under the present design, the polymer in this stage is reacted nearly to an equilibrium value. To change the equilibrium value of polymer produced, the pressure in the reactor may be adjusted.

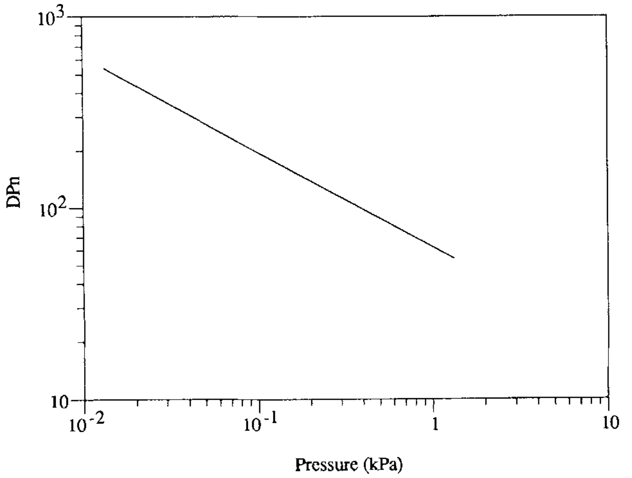


Figure 20. PCL plot for the PET finisher at 295°C.

Figure 20 shows the PCL plot for reaching a given DP_n. By operating at 0.067 kPa, a DP_n of 240 may be obtained at equilibrium. Running the actual reactor to 85% of the equilibrium DP_n value will give a design DP_n of 205.

Simulations using an equivalent three CSTRs in series were used to approximate the modeling of the open extruder. Figure 21 shows the dynamic startup of the finishing reactors (CSTRs), when the reactors are initially full of ethylene glycol and DMT monomers in the ratio of three to one. The residence times of the three CSTRs are each 1 h. The number-average molecular weight of the resulting polymer leaving the overall process during the startup is 20,000.

Here, the finishing stage produces the required polymer chain length with a 3-h reactor residence time. The MTP plot of Figure 19, however, shows that the reactor residence time could be reduced to a few minutes with good mass transfer in the finishing stage. This suggests that further design effort could profitably be made in this direction.

PET of this grade is usable for fiber spinning or film, but the existence of side reactions may cause polymer quality problems. Two of the side products in the PET process are diethylene glycol (DEG) and acid end groups. These two side products are created by the two chain reformation reaction, as shown in Table 9. The steady-state amount of these side products and operating conditions for each reactor is reported in Table 11. The acid end groups per repeat unit (A_r) was calculated as shown in Eq. 14. The quantity $[B_2]$ is the concentration of acid end groups, and $[R_2]$ is the concentration of terephthalate monomer units:

$$A_r = \frac{[B_2]}{[R_2]} \tag{14}$$

The weight percent DEG in polymer (Wp_{DEG}) was calculated as shown in Eq. 15. The quantities $[R_1]$, $[R_2]$ and $[R_3]$ refer to the concentrations of ethylene glycol, DMT and diethylene

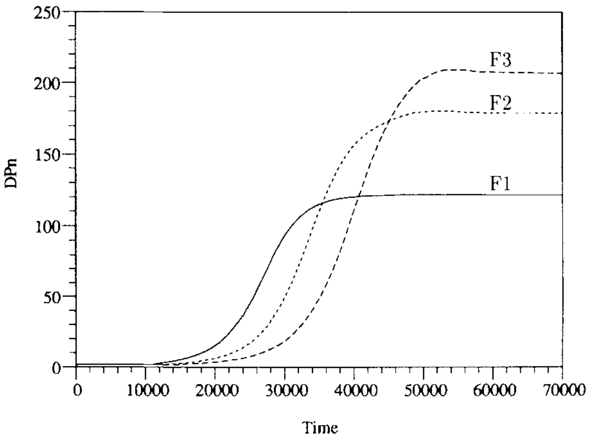


Figure 21. Number-average degree of polymerization vs. time during process startup in the finishing stage.

The open extruder operating at a temperature of 295°C and a pressure of 0.067 kPa is designed to polymerize to a DP_n of 190. The residence time in the reactor is 3 h. The extruder was approximated by three CSTRs in series.

Table 11. Operating Conditions and Resulting Impurity Levels in the PET Reactor Stages at Steady State*

Reactor	Temp. °C	Pres. kPa	$k_m A_m$ kmol/h·kPa	DP_n	Acid End Groups per Repeat Unit	DEG in polymer wt. %
E1	180	60.0	0.324	2.0	3.5×10^{-5}	0.012
E2	200	33.3	0.241	4.0	8.5×10^{-5}	0.040
E3	220	13.3	0.230	8.5	1.1×10^{-4}	0.072
P1	260	4.0	0.073	17	3.1×10^{-4}	0.078
P2	270	2.7	0.068	25	4.5×10^{-4}	0.084
P3	280	1.3	0.068	39	5.5×10^{-4}	0.088
F1	295	0.067	0.266	120	5.7×10^{-4}	0.088
F2	295	0.067	0.266	178	5.8×10^{-4}	0.089
F3	295	0.067	0.266	205	5.8×10^{-4}	0.089

*Reactor residence times for each stage is 1 h.

glycol monomer units; and $MW_{\rm EG}$, $MW_{\rm DMT}$ and $MW_{\rm DEG}$ refer to the corresponding molecular weights of the repeat units:

$$Wp_{\rm DEG}=\frac{MW_{\rm DEG}[R_3]}{MW_{\rm EG}[R_1]+MW_{\rm DMT}[R_2]+MW_{\rm DEG}[R_3]}\times 100 \qquad (15)$$

Other side reactions can be readily modeled from the mechanism in Table 1 using the approach of Jacobsen and Ray (1992).

Obviously, neither of these detailed process designs are optimal, but they are close to some current practice and serve to illustrate the use of the detailed kinetic models and the design tools, MTP plots and PCL plots, in creating such process designs. These tools have clearly indicated where effort could be applied to improve these initial designs. Economic optimization analysis should then be applied to tune such improved designs.

Conclusions

A general polycondensation process is divided into three process stages: prepolymerization, polymerization, and finishing. Each stage is physically unique due to the conditions present inside the reactor. The reactors used in each stage differ due to the unique problems inherent to the reaction conditions.

Studies based on kinetic modeling fundamentals are useful for design purposes. Two useful tools mentioned in this article are the mass-transfer potential and the pressure-chain length plot. Both of these tools are byproducts of using modeling based on fundamental chemistry. The mass-transfer potential indicates whether a reactor is kinetically- or mass-transfer-driven. The pressure-chain length plot shows the highest operating pressure required of a reactor to make polymer of a given chain length. These tools were illustrated for a PET process and a nylon-6,6 process. The use of kinetic modeling and the design tools also are of great value for a wide variety of other condensation polymers.

The computer makes it possible to simulate and design chemical processes with greater ease; however, the use of computers for design so far has been limited to specific systems, such as one specific polymer system. With increasing power available it is possible to develop a general CAD package for an entire class of step-growth polymers. A CAD package such as this requires a general modeling approach. The simulation package, POLYRED, from the University of Wisconsin is such a package.

Acknowledgment

This work was supported by the sponsors of the University of Wisconsin Polymerization Reaction Engineering Laboratory (UWPREL) and the National Science Foundation.

Notation

$a_{l,i}$ = activity of component i in the liquid phase
$a_{v,i}$ = activity of component i in the vapor phase
A_i = A end group number i
A_o = Arrhenius rate prefactor (noncatalyzed)
A_m = mass-transfer area
A_r = acid end groups per repeat unit
B_i = B end group number i
C_{ij} = condensate (ij identifies what type of Ai and Bj end groups created it)
DP_n = number-average chain length of polymer
E_o = energy of activation (noncatalyzed)
k_i = forward rate constant for reaction i
$k_{m,i}$ = mass-transfer coefficient for volatile component i
K = equilibrium constant
MW_i = molecular weight of monomer unit i
P = total pressure
P_i = partial pressure of component i
P_i^o = vapor pressure of component i
$P_{n,a,b}$ = polymer chain with n monomer units, a A end groups, and b B end groups
rate$_i$ = mass-transfer rate of volatile component i
R = ideal gas constant
R_i = monomer unit number i
R_n = ring polymer with n monomer units
S_n = salting compound with n monomer units
T = temperature
$Wp_{\rm DEG}$ = weight percent DEG in polymer
y_i = vapor-phase mole fraction of component i
Z = deactivation compound

Greek letters

$\delta(i)$ = unit vector [$\delta(i)_j=0$ for $i\neq j$ and $=1$ for $i=j$]
ΔH = change of enthalpy due to reaction
ΔS = change of entropy due to reaction
$\gamma_{\phi,i}$ = liquid activity coefficient for component i
ϕ_i = volume fraction of component i in the reactor
ϕ_p = volume fraction of polymer in the reactor
χ_i = Flory-Huggins molecular interaction parameter for component i

Literature Cited

Abbott, J. H., N. K. Harakas, and G. A. Latinen, "Continuous Condensation Polymerization Finisher," U.S. Pat. 3,595,627 (1971).

Albrecht, W., M. Dietze, W. Kraft, H. Scheller, and H. Ullrich, "Polycondensation Reactor," U.S. Pat. 3,440,019 (1969).

Amon, M., and C. D. Denson, "Simplified Analysis of the Performance of Wiped-Film Polycondensation Reactors," *Ind. Chem. Eng. Fund.*, **19**, 415 (1980).

Ault, J. W., and D. A. Mellichamp, "A Diffusion and Reaction Model for Simple Polycondensation," *Chem. Eng. Sci.*, **27**, 1441 (1972a).

Ault, J. W., and D. A. Mellichamp, "Complex Linear Polycondensation: II. Polymerization Rate Enhancement in Thick-Film Reactors," *Chem. Eng. Sci.*, **27**, 2233 (1972b).

Biener, R., "Polycondensation Processes in Distillation Tower Reactors," MS Diss., Univ. of Wisconsin, Madison (1989).

Brignac, E. P., "Process for Preparing a Polyamide," U.S. Pat. 3,501,441 (1970).

Busot, J. C., "Process for Producing Polyethylene Terephthalate," U.S. Pat. 3,487,049 (1969).

Buyalos, E. J., H. H. Rowan, A. Young, and D. Pendlebury, "Reactor," U.S. Pat. 4,432,940 (1984).

Castres Saint Martin, H., and K. Y. Choi, "Two-Phase Model for Continuous Final-Stage Melt Polycondensation of Poly(Ethylene Terephthalate): 2. Analysis of Dynamic Behavior," *Ind. Eng. Chem. Res.*, **30**, 1712 (1991).

Crawford, J. E., R. W. Edwards, E. D. Henze, and W. C. L. Wu, "Process and Apparatus for Polymerizing Liquids," U.S. Pat. 3,522,214 (1970).

Dew, Jr., W. F., B. T. Thompson Jr., and A. E. Leybourne, "Polymer Handling and Conveying Apparatus," U.S. Pat. 3,484,213 (1969).

Dietze, M., W. Kraft, H. Scheller, and H. Ullrich, "Polycondensation Reactor," U.S. Pat. 3,466,150 (1969).

Fritsch, R. P., "Method and Apparatus for the Continuous Production of High-Molecular Polymers," U.S. Pat. 4,591,487 (1986).

Fujimoto, Y., Y. Kimura, I. Terasaki, and T. Kitago, "Polyesterification Process and Apparatus," U.S. Pat. 3,609,125 (1971).

Gupta, S. K., A. Kumar, and A. K. Ghosh, "Simulation of Reversible $AA + B'B''$ Polycondensation in Wiped Film Reactors," *J. Appl. Polym. Sci.*, **28**, 1063 (1983a).

Gupta, S. K., D. Kunzru, A. Kumar, and K. K. Agarwal, "Simulation of Nylon 6 Polymerization in Tubular Reactors with Recycle," *J. Appl. Polym. Sci.*, **28**, 1625 (1983b).

Gupta, S. K., A. K. Ghosh, S. K. Gupta, and A. Kumar, "Analysis of Wiped Film Reactors Using the Orthogonal Collocation Technique," *J. Appl. Polym. Sci.*, **29**, 3217 (1984).

Griehl, W., W. D. Hahn, and J. Plenz, "Continuous Manufacture of Fiber-Forming Polyesters," U.S. Pat. 3,644,483 (1972).

Jacobsen, L. L., and W. H. Ray, "Unified Modeling of Polycondensation Processes," *J. Macrmol. Sci.—Rev. Macromol. Chem. Phys.*, in press (1992).

Kharkov, B. A., et al., "Apparatus for the Continuous Production of Polycaproamide," U.S. Pat. 3,607,102 (1971).

Kumar, A., S. K. Gupta, S. Madan, N. G. Shah, and S. K. Gupta, "Solution of Final Stages of Polyethylene Terephthalate Reactors Using Orthogonal Collocation Technique," *Polym. Eng. Sci.*, **24**, 194 (1984).

Leybourne, III, A. E., "Polymer Apparatus," U.S. Pat. 3,476,523 (1969).

Markel, K., E. Blumer, G. Kuazmann, J. Steinburg, and D. Stiller, "Apparatus for Continuously Polymerizing Lactams," U.S. Pat. 3,524,729 (1970).

Ogata, N., "Studies on Polycondensation Reactions of Nylon Salt: I. The Equilibrium in the System of Polyhexamethylene Adipamide and Water," *Makromol. Chem.*, **43**, 52 (1961a).

Ogata, N., "Studies on Polycondensation Reactions of Nylon Salt: II. The Rate of Polycondensation Reaction of Nylon 66 Salt in the Presence of Water," *Makromol. Chem.*, **43**, 117 (1961b).

Perry, E. S., "Method for Producing and Processing Viscous Materials Such as Polymers," U.S. Pat. 3,425,993 (1969).

Ravindranath, K., and R. A. Mashelkar, "Modeling of Poly(Ethylene Terephthalate) Reactors: 5. a Continuous Prepolymerization Process," *Polym. Eng. Sci.*, **22**, 619 (1982a).

Ravindranath, K., and R. A. Mashelkar, "Modeling of Poly(Ethylene Terephthalate) Reactors: 6. a Continuous Process for Final Stages of Polycondensation," *Polym. Eng. Sci.*, **22**, 628 (1982b).

Ravindranath, K., and R. A. Mashelkar, "Modeling of Poly(Ethylene Terephthalate) Reactors: 8. a Modified Continuous Transesterification Process," *J. Appl. Polym. Sci.*, **29**, 437 (1984).

Rotzoll, R. H., P. Matthies, G. Valentin, and W. Hoerauf, "Continuous Preparation of Polycaprolactam in Vertical Tubular Reactor," U.S. Pat. 4,354,020 (1982).

Sasaki, I., H. Mori, and M. Fujimoto, "Process for the Production of Polyester," U.S. Pat. 4,612,363 (1986).

Sauerbrunn, R. D., "Diamine Recovery Process," U.S. Pat. 4,380,615 (1983).

Steppan, D. D., M. F. Doherty, and M. F. Malone, "A Kinetic and Equilibrium Model for Nylon 6,6 Polymerization," *J. Appl. Poly. Sci.*, **33**, 2333 (1987).

Manuscript received Dec. 16, 1991, and revision received Apr. 17, 1992.