Reaction Kinetics for Solid-State Polymerization of Poly(ethylene terephthalate)

BEN DUH

Polyester Technical Center, Shell Chemical Company, 130 Johns Avenue, Akron, OH 44305

ABSTRACT: A simple kinetic model capable of describing the behaviors of solid-state polymerization (SSP) of poly(ethylene terephthalate) (PET) has been developed. According to this model, there are two types of end groups, namely active end groups and inactive end groups, and the solid-state polycondensation reaction is a second-order reaction with respect to the active end group concentration. The inactive end groups include chemically dead end groups and functional end groups that are immobilized by the crystalline structure. The inactive end group concentration determines the ultimate intrinsic viscosity (IV) or molecular weight achievable in the SSP—the lower the inactive end group concentration, the higher the ultimate IV. Four pulverized PET prepolymers with IV values ranging from 0.20 to 0.35 dL/g were solid-state polymerized in a fluid-bed reactor at temperatures between 200 and 230°C to generate data to test the model. The experimental results fit the proposed rate equations very well, confirming the adequacy of the proposed kinetic model. Under these SSP conditions, the activation energy is about 23.6 kcal/mol and the average SSP rate about doubles with each 10°C increase in temperature. The rate constant increases, while the inactive end group concentration decreases, with increasing temperature and prepolymer IV. This explains why the reaction rate and the ultimate IV increase with increasing prepolymer IV as well as temperature in the SSP of PET. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1748–1761, 2001

Key words: poly(ethylene terephthalate); solid-state polymerization; kinetics; inactive end groups; activation energy

INTRODUCTION

Solid-state polymerization (SSP) has been widely used to produce very-high-molecular-weight (>24,000) poly(ethylene terephthalate) (PET) for bottle, frozen food tray, and tire-cord applications. PET resins produced via a solid-state polymerization process are commonly referred to as "solid-state PET." Today, solid-state PET accounts for more than one-third of world production of PET. The remaining world PET production is used predominantly in textile fiber applications with a number average molecular weight of 17,000–21,000. In practice, number average molecular weight is more conveniently expressed in terms of intrinsic viscosity (IV). Thus textile-fiber-grade resins have IV values within the range of 0.57–0.65 dL/g; bottle-grade resins, 0.72–0.85 dL/g; tray resins, 0.85–0.95 dL/g; and tire-cord resins, 0.95–1.05 dL/g.

SSP in itself is not a complete manufacturing process. Rather, it is an extension of the melt phase polymerization process (or simply melt process). First, a prepolymer with an intermediate IV is produced from dimethyl terephthalate (DMT)
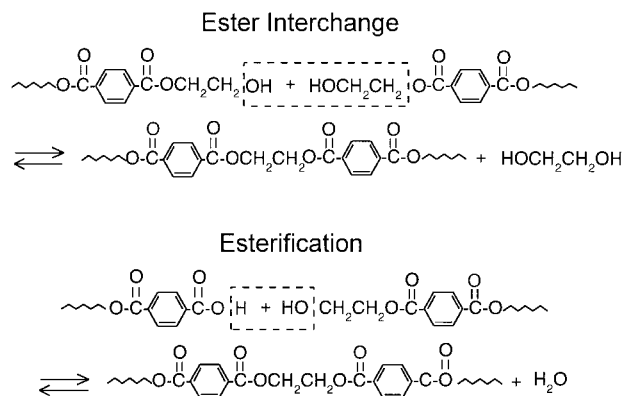
Ester Interchange

Esterification

Figure 1 Two types of polycondensation reaction for solid-state polymerization (SSP) of poly(ethylene terephthalate) (PET).

and ethylene glycol (EG) or from terephthalic acid (TPA) and ethylene glycol by a melt process. The prepolymer thus produced is then further polymerized in the solid phase at a temperature substantially above the glass transition temperature but below the crystalline melting point in the presence of a stream of an inert gas (usually nitrogen) or under a vacuum. Within the SSP temperature range, the functional end groups of the polymer chains are sufficiently activated to collide and react with one another to increase the molecular weight.

SSP of a commercially produced PET prepolymer is a very complex process. It involves two types of polycondensation reactions and diffusion of the reaction byproducts. Commercially produced PET prepolymers are usually in pellet form with IV values of 0.55–0.65 dL/g. This is because most of the solid-state PET producers started as fiber producers or as suppliers of fiber-grade resins. Naturally, they are more comfortable with the melt process designed to produce PET resins with IV values within this range. These prepolymers contain carboxyl ends as well as glycolic ends. Typically 10–35% of the total end groups of commercially produced prepolymers are carboxyl end groups. At least part of the carboxyl end groups are formed during later stages of polycondensation in the melt process as a result of thermal degradation, which also generates acetaldehyde. Therefore, during SSP, two types of chemical reaction, namely ester interchange and esterification, take place as shown in Figure 1. Although glycolic ends can function as hydroxyl ends and as 2-hydroxyethyl ends in polycondensation reactions, for convenience, they are usually

referred to as hydroxyl ends. Because the prepolymer is in pellet form, diffusion of reaction byproducts, EG and water, plays an important part in the overall SSP rate. This further complicates the kinetics of SSP.

It should be noted that the prepolymer does not have to be in pellet form with an IV within the aforementioned range. In fact, U.S. Patent 4,165,420 to Rinehart[1] and U.S. Patent 4,205,157 to Duh[2] suggest the use of a finely divided prepolymer with a substantially lower IV (e.g., 0.20–0.35 dL/g) in a fluid-bed SSP process can yield products with better color (because of shorter exposure to high temperatures in the melt polymerization process used to prepare the prepolymer) and higher purity (with lower catalyst and acetaldehyde contents). Because a viable fluid-bed SSP process requires prepolymer powder with a narrow particle size distribution, preparation of such prepolymer powder by a conventional size reduction method, such as grinding, may be uneconomical. Rinehart[1] solved the problem by proposing a spray-congealing process, which is capable of producing low IV PET powder of particle size 100–150 μm. Duh[2] discovered that, in the absence of diffusion resistance, maximum SSP rate is achieved with zero carboxyl content of the prepolymer and, with zero carboxyl content, maximum SSP rate is achieved with the lowest catalyst concentration (e.g., ~150 ppm Sb or ~5 ppm Ti). He further provided methods for the production of low IV PET prepolymers with minimal carboxyl contents. With such a finely divided PET prepolymer, esterification reaction and diffusion resistance within the prepolymer particle can be ignored. This offers a convenient way to study the reaction kinetics of the most fundamental solid-state polycondensation of PET, which is the subject of this article.

Characteristics of SSP of PET

The kinetics of SSP of PET is quite different from that of melt polymerization of PET. Regardless of the particle size and the carboxyl content of the prepolymer used, the SSP of PET is characterized by the following distinct features:

1. There exists an ultimate (or limiting) IV for each prepolymer IV at each SSP temperature. Once this ultimate IV is reached, PET ceases to polymerize even if the SSP is continued further. The ultimate IV in-

creases with increasing prepolymer IV and SSP temperature.

2. The SSP rates within the same IV range are not equal for prepolymers with different IV values. The higher the prepolymer IV, the higher the SSP rate.

Although numerous papers dealing with the SSP of PET have been published, none of the authors has offered a kinetic model that can satisfactorily describe the above observations.

Review of Previous Related Works

The reaction kinetics of melt phase ester interchange during the early stage of polycondensation, where the melt viscosity is still low and the diffusion resistance is negligible, has been investigated by Challa[3] and by Hovenkamp.[4] Both researchers found that polycondensation is a second-order reaction with respect to the concentration of the hydroxyl ends, $[OH]$. Thus the forward rate constant of polycondensation, k_f, can be expressed as

$$-\frac{d[OH]}{dt} = 2k_f[OH]^2 \qquad (1)$$

where t is the reaction time. Obviously, equation (1) cannot adequately describe the SSP of PET because it does not predict a limiting molecular weight or IV. In most published works on the SSP of PET, the prepolymers used invariably had a substantial carboxyl end group concentration and/or the experimental conditions were such that SSP is jointly controlled by reaction and diffusion.

Bamford and Wayne[5] studied the SSP of bis(2-hydroxyethyl)terephthate (BHET) and PET. Based on the experimental data for the SSP of powdered PET, they suggested that the rate of ester interchange reaction in the solid phase was also a second-order reaction with respect to the end group concentration. They fitted their SSP data with a rate equation similar to equation (1) despite the fact that they were aware of the existence of the limiting IV and the fact that moisture was observed during the experimental runs. In the same article, they further noted that the rate constant increases with increasing prepolymer IV and that the rate constant decreases as the SSP proceeds, but were not able to come up with a satisfactory explanation. Since the apparent rate constant changes with time

and the rate equation they proposed does not predict the existence of a limiting IV, it is obvious that the SSP of PET does not follow the second-order kinetics.

Gaymans et al.[6] investigated the SSP of Nylon 6 with various starting molecular weights. According to their description of the SSP behaviors of Nylons, there are striking similarities between the solid-state polyamidation and solid-state polycondensation. For example, in the SSP of Nylon 6, the starting (or prepolymer) molecular weight also has a strong effect on the reaction rate and the apparent rate constant also decreases with increasing SSP time. They explained the decreasing apparent rate constant in terms of the diffusion of the reacting end groups. They reasoned that the diffusion of the reacting end groups is the rate limiting process, and, as the SSP proceeds, the distribution of the end group-to-end group distance changes in such a way that the average rate of collision of the end groups is substantially reduced. The paper does not mention the existence of the limiting molecular weight, nor does the proposed model predict a limiting molecular weight, although some of the molecular weight vs. SSP time curves prepared with the SSP data appear to level off toward the end of the experiments.

Chen et al.[7] solid-state polymerized PET prepolymers with 8–20-mesh particle size at temperatures of 160–200°C and concluded that the SSP rate of PET under these conditions was controlled by the reaction step. However, they proceeded to describe the SSP of PET by a diffusion model. Chang[8] studied the SSP of powdered and granulated PET in both fluid-bed and fixed-bed reactors in the temperature range of 210–250°C. He concluded that diffusion was the rate-limiting step when the temperature was higher than 210°C and the particle size was no smaller than 100 mesh, although no proof was offered to support the conclusion.

Chen and Chen[9] analyzed the SSP process of PET taking into account the effect of the diffusion of end groups on the reaction rate as suggested by Gaymans et al.[6] They determined that the SSP of PET with a particle size of <70–80 mesh at temperature <200°C is an end-group diffusion limited process, and with a particle size of >16–18 mesh at temperatures of >210°C is a byproduct diffusion-limited process. The incorporation of the end-group diffusion effect term in the rate constant can describe the decreasing apparent rate constant during the course of the SSP but still

cannot explain other characteristics of the SSP of PET.

Therefore, it is the purpose of this article to provide a simple kinetic model for the most fundamental SSP reaction that can satisfactorily describe the aforementioned general SSP characteristics of PET.

Development of Kinetic Model

It will be helpful to define the term "prepolymer" formally at this point. For the purpose of this paper, a prepolymer is a polymer, usually of low or moderate IV, prepared by melt polymerization, and intended for further polymerization in solid state. In some special cases, a solid-stated polymer can be remelted to be used as a prepolymer for a second SSP to achieve a very high IV, which is not attainable with one single SSP run.

As mentioned earlier, PET prepolymers can be prepared via either the DMT process or the TPA process. The precursors used are DMT and EG in the DMT process and TPA and EG in the TPA process. In the DMT process, it is difficult to completely react all the methyl end groups of the precursor DMT. Because most of the unreacted methyl end groups will become dead end groups in the subsequent SSP step, PET prepolymers prepared via the DMT process generally have lower SSP rates. Therefore, the TPA process is preferred for the production of PET prepolymers.

As a general practice, in both melt processes, during the later stages of polycondensation, a relatively high reactor temperature (e.g., 280°C or higher) is used to overcome the high melt viscosity and to facilitate efficient agitation to maintain an acceptable polymerization rate. This invariably causes thermal degradation, which forms carboxyl end groups and generates acetaldehyde. Therefore, commercially produced PET prepolymers generally contain 10–35% carboxyl end groups and 30–150 ppm acetaldehyde. The carboxyl content of the prepolymer can be minimized by maintaining a relatively low melt polymerization temperature (e.g., no higher than 275°C), delaying the catalyst addition, adding makeup EG, and discharging the melt at a relatively low IV as described in U.S. Patent 4,205,157.[2]

If carboxyl end groups are present in a significant concentration, both ester interchange and esterification reactions will take place during SSP as shown in Figure 1. If the carboxyl end group concentration in the prepolymer is negligibly small, as in the case of this work, we are only concerned with ester interchange and the kinetics of SSP is simplified.

Major Steps of SSP

The SSP of PET involves the following steps:

1. Diffusion of end groups within the polymer particles
2. Collision and reaction of end groups
3. Diffusion of reaction byproducts from the interior of the polymer particle to the particle surface
4. Diffusion of reaction by-products from the particle surface into the bulk of the gas phase

In the classical theory of reaction kinetics, steps 1 and 2 are considered as one single step, namely the reaction step, and their effects are taken into account in the determination of the reaction rate constant. Steps 3 and 4 can also be conveniently considered as one single step, namely the diffusion step. If the particle size is small enough and the gas flow rate is high enough (as in a fluidized bed), diffusion resistances in steps 3 and 4 will be negligible and the overall SSP becomes reaction controlled.

Proposed Kinetic Model for SSP of PET

The kinetic model proposed in this study employs two major assumptions:

1. There are two types of end groups, namely active end groups and inactive end groups. Only the active end groups participate in reaction and the inactive end group concentration remains constant throughout the course of SSP.
2. The reaction of the active end groups follows the second-order kinetics, namely, the SSP reaction is a second-order reaction with respect to the concentration of active end groups.

Thus, the proposed kinetic model for the SSP of PET is a "modified second-order kinetic model."

To simplify the treatment, the following measures were taken:

1. Special attention was taken in the preparation of the prepolymer so that the concentration of the carboxyl end groups is

negligibly small. Thus the SSP is caused by ester interchange only.

2. A sufficiently small prepolymer particle size and a sufficiently high gas velocity were used in the SSP experiments so that the reaction byproduct is removed as soon as it is produced. In other words, the SSP is reaction controlled and there is no reverse reaction.

With the above assumptions and simplifying measures, the rate of SSP can be expressed in terms of the rate of disappearance of the active end groups. Thus,

$$-\frac{d(C - C_i)}{dt} = 2k(C - C_i)^2 \quad (2)$$

where C is the total end group concentration (or simply the end group concentration), C_i, the inactive end group concentration, t, the reaction time, and k, the rate constant. In this study, the unit of end group concentration is mole per million grams of polymer ($mol/10^6$ g). This is a convenient concentration unit widely used in the industries for solid polymer and often expressed as $eq/10^6$ g or meq/kg. Since the density of PET changes very little during SSP, the use of this concentration unit is reasonable. Note that equation (2) is a modified form of the second-order reaction rate equation, equation (1). When $C_i = 0$, equations (2) and (1) are identical.

Equation (2) can be integrated to give

$$\frac{1}{C - C_i} - \frac{1}{C_0 - C_i} = 2kt \quad (3)$$

where C_0 is the initial total end group concentration or the prepolymer total end group concentration.

Solving for C yields

$$C = \frac{C_0 + 2k(C_0 - C_i)C_i t}{1 + 2k(C_0 - C_i)t} \quad (4)$$

According to this equation, as time approaches infinity, C approaches C_i (i.e., all active end groups will be consumed). Therefore, the highest attainable IV or number average molecular weight can be calculated from C_i.

Equation (3) can also be rearranged to give the following form:

$$\frac{C_0 - C}{t} = 2k(C_0 - C_i)C - 2k(C_0 - C_i)C_i \quad (5)$$

Therefore, if the assumed modified second-order kinetics fits the experimental data, the $(C_0 - C)/t$ vs. C plot should be a straight line with

$$\text{Slope} = 2k(C_0 - C_i) \quad (6)$$

$$\text{Intercept} = -2k(C_0 - C_i)C_i \quad (7)$$

However, equation (7) does not have a physical meaning because C will never be equal to zero according to the model. Instead of equation (7), the following relationship can be used to solve for C_i:

$$\text{At} \quad (C_0 - C)/t = 0 \quad \text{or} \quad t = \infty, \quad C = C_i \quad (8)$$

Thus, the intercept of the C axis is equal to C_i. With the value of C_i determined, k can be calculated from equation (6). With C_i and k known, the total end group concentration C at any time during the SSP can be calculated from equation (4).

EXPERIMENTAL

The PET prepolymers used in the experiments were prepared by reacting high-purity TPA from Amoco and polymer grade EG from Union Carbide in a bench scale reactor. Necessary measures mentioned earlier were taken to minimize side reactions and to ensure that the carboxyl end groups of all prepolymers did not exceed 1% of the total end groups, so that esterification polycondensation during the SSP could be ignored. Four prepolymers with IV values of 0.20, 0.26, 0.305, and 0.35 dL/g, were selected. These IV values approximately cover the most practical IV range of PET prepolymers for the fluidized bed SSP process, as indicated in the Rinehart and Duh patents.[1,2] All the prepolymers contained 210 ppm Sb catalyst. The prepolymers were ground and classified. The particle sizes of the prepolymers used to determine the particle size effect on the SSP rate ranged from 12 to 200 mesh. The particle size of the prepolymers used in the SSP kinetic study was 100–150 mesh.

The reactor used to conduct the SSP experiments was constructed of a 20-inch-long glass column, 1.25 inches in diameter. The bottom of the column was fitted with a porous filter for

supporting the polymer and distributing the purge gas (nitrogen). Below the filter, the column was necked down and connected to a $\frac{1}{4}$-inch diameter, 60-inch-long glass tube, which was coiled upward around the lower half of the column. This small glass tube served to supply nitrogen to the reactor. During the experimental runs, the reactor with its nitrogen supply tube was immersed in a transparent constant temperature oil bath about 12 inches deep. The nitrogen supply tube also served as the heat exchanger which heated the incoming nitrogen to the desired experimental temperatures.

The nitrogen superficial velocity through the reactor was normally 5 feet per minute (FPM), about 5 times the minimum fluidizing velocity, except for the series of runs designed to evaluate the effect of the purge gas flow rate on the SSP. For this particular series of runs, nitrogen superficial velocities ranging from 0.25 to 10 FPM were used. Four SSP temperatures—200, 210, 220, and 230°C—were used to generate SSP rate data.

For each normal SSP run, 10 g of powdered prepolymer was charged into the reactor. High-purity nitrogen was introduced to the bottom of the reactor through the coiled tube at a suitable flow rate (e.g., 5 FPM) to maintain a stable fluidized bed. The bath temperature was first maintained at 140°C for 1 h to dry the prepolymer to a moisture content below 0.005% to prevent hydrolytic degradation during the subsequent SSP step. During this drying period, no significant IV change took place. Then the reactor with its nitrogen supply tube was transferred to another oil bath whose temperature had been controlled at the desired SSP temperature. By using another oil bath, it was possible to heat the dried prepolymer to the reaction temperature within 2 minutes. The reaction was allowed to proceed at the constant SSP temperature for 20 h. Throughout the SSP period, samples were taken at various intervals to monitor the IV buildup.

The IV of each sample was determined with a Cannon-Ubbelohde viscometer at 25°C using 60/40 phenol/tetrachloroethane mixture as the IV solvent. The IV is related to the number average molecular weight by the Moore equation[10]:

$$IV = 7.50 \times 10^{-4} \bar{M}_n^{0.68} \tag{9}$$

According to the definition, end group concentration is related to the number average molecular weight by the following equation:

$$C = \frac{2 \times 10^6}{\bar{M}_n} \tag{10}$$

Once the IV is determined, the number average molecular weight and the total end group concentration can be readily calculated using equations (9) and (10).

RESULTS AND DISCUSSION

Effects of Particle Size on SSP Rates

Since the main purpose of this work is to study the reaction kinetics of the SSP of PET, the experimental conditions under which the reaction is the rate-controlling step (or the diffusion resistance is negligible on either the solid side or the gas side) must be established first. The solid side diffusion resistance is influenced by the particle size, while the gas side diffusion resistance is determined by the velocity of the purge gas.

A decrease in the particle size shortens the diffusion path of the reaction byproduct (i.e., EG) inside the particles and increases the total surface area for the diffusion into the gas phase. Therefore, it is expected that the SSP rate increases with decreasing particle size within a certain particle size range. The SSP rate should approach the highest value as the diffusion resistance become negligible compared with the reaction resistance. It can be seen in Figure 2 that the IV buildup rate increased as the particle size was decreased from 12 mesh (1,700 μm) and reached its highest value when the particle size was between 80 mesh (180 μm) and 150 mesh (106 μm). Further decrease in the particle size to <200 mesh (75 μm) resulted in particle agglomeration and an apparent drop of SSP rate. Therefore, the particle size for the samples used in all the remaining SSP runs was 100–150 mesh.

Effects of Nitrogen Flow Rate on SSP Rate

The role of the nitrogen flow is to agitate the particles, provide heat to the particles, and remove reaction by-products from the particle surface. An increase in the nitrogen flow rate not only increases the heat and mass transfer rates in the gas–solid system, but also reduces the byproduct concentration in the gas phase and decreases the resistance to the diffusion of the byproduct from the particle surface into the bulk of the gas phase. Figure 3 shows the effect of nitrogen ve-
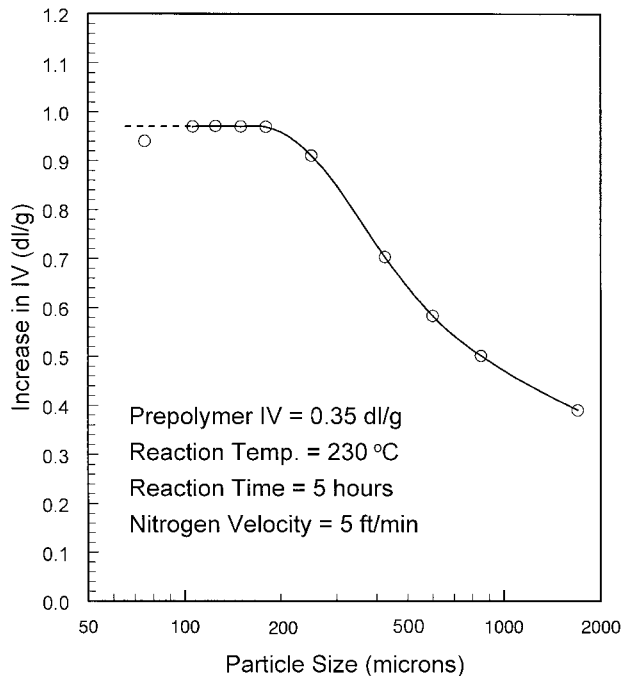
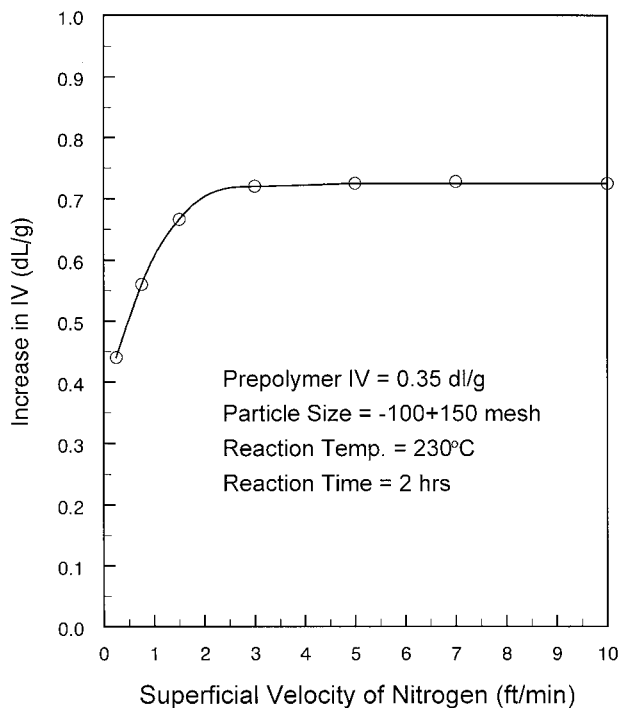**Figure 2** Effect of particle size on solid-state polymerization (SSP) rate of poly(ethylene terephthalate) (PET).

Figure 3 Effect of nitrogen velocity on solid-state polymerization (SSP) rate of poly(ethylene terephthalate) (PET).
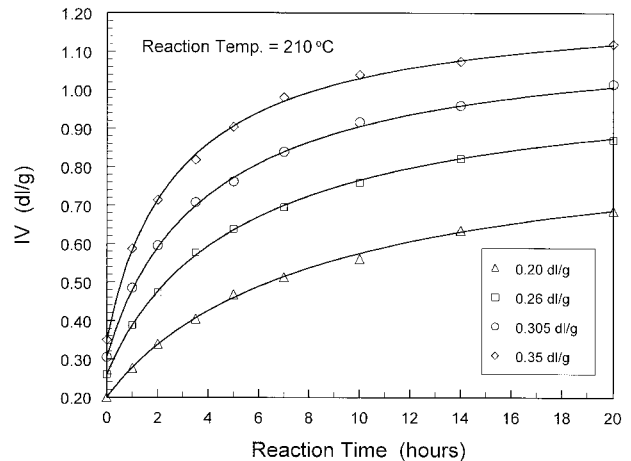

Figure 4 Intrinsic viscosity (IV) buildup curves for solid-state polymerization (SSP) of poly(ethylene terephthalate) (PET) prepolymers with various IV values at 210°C. Curve fittings are based on the proposed model.

locity on the SSP rate of PET with a particle size of 100–150 mesh. The SSP rate reached the highest value at the superficial nitrogen velocity of about 3 FPM.

From Figures 2 and 3, it can be concluded that when the particle size is 80–150 mesh, and the superficial nitrogen velocity is >3 FPM, the diffusion resistance is negligible compared with the reaction resistance, and the SSP of PET is reaction controlled.

Determination of Inactive End Group Concentrations and Rate Constants

PET prepolymers with IV values of 0.20, 0.26, 0.305, and 0.35 dL/g and particle size of 100–150 mesh were solid-state polymerized at 200, 210, 220, and 230°C in the fluid-bed reactor with a nitrogen flow at a superficial velocity of 5 FPM to obtain kinetic data.

Figure 4 shows the IV buildup curve for the SSP of PET prepolymers with various IV values at 210°C. It can be seen that the SSP rate increases with increasing prepolymer IV (e.g., compare slopes within an IV range of 0.40–0.50 dL/g). Each of the four curves appears to level off and approach an ultimate IV, which increases with increasing prepolymer IV.

Figure 5 shows the IV buildup curves for the SSP of the 0.26 dL/g IV prepolymer at the four reaction temperatures. It can be seen that the SSP rate and the ultimate IV increase pronouncedly with increasing reaction temperature.
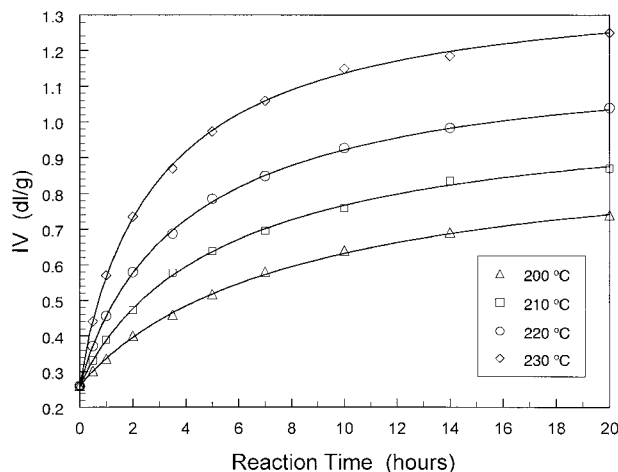
Figure 5 Intrinsic viscosity (IV) buildup curves for solid-state polymerization (SSP) of poly(ethylene terephthalate) (PET) prepolymer with IV of 0.26 dL/g at various temperatures.

The SSP data in Figure 5 can be used to prepare the $(C_0-C)/t$ vs. C plots in Figure 6 for the 0.26-dL/g IV prepolymer. A straight line is obtained for each reaction temperature indicating that the proposed reaction kinetics model fits the SSP experimental data. The equations for the four straight lines can be obtained by linear regression. Thus, for the prepolymer with $IV_0 = 0.26$ dL/g or $C_0 = 368.02$ mol/10^6 g,

$$\frac{C_0 - C}{t} = 0.5917C - 32.1314 \qquad \text{at 200°C}$$

$$\frac{C_0 - C}{t} = 1.0420C - 48.9755 \qquad \text{at 210°C}$$

$$\frac{C_0 - C}{t} = 1.6906C - 65.2565 \qquad \text{at 220°C}$$

$$\frac{C_0 - C}{t} = 2.8967C - 89.2190 \qquad \text{at 230°C}$$

The inactive end group concentration C_i for each temperature can be calculated first by setting $C = C_i$ at $(C_0-C)/t = 0$. With the value of C_i known, the reaction rate constant k for the same temperature is readily determined using equation (6).

Similarly, the $(C_0-C)/t$ vs. C plots for the other three prepolymers can be prepared using their respective SSP data. In all cases, straight lines are obtained. Therefore, it can be con-

cluded that the polycondensation reaction of the SSP of PET follows the proposed modified second-order kinetics.

The values of the inactive end group concentrations and the reaction rate constants thus determined for the four prepolymers are listed in Table I. With C_i and k known for each prepolymer IV and SSP temperature, the end group concentration C, number average molecular weight $\bar{M}_n$ and IV at any time during the SSP can be calculated using equations (4) and (9) and (10) for each case. The curves in Figures 4 and 5 are obtained by using these equations. It can be seen that the curves fit the data very well.

Effects of Temperature and Prepolymer IV on Reaction Rate Constant

Figure 7 shows the Arrhenius plots for the reaction rate constants for the four prepolymers using the k values in Table I. Straight lines with near-constant slopes are obtained. Therefore the temperature dependence of the rate constant can be conveniently represented by the Arrhenius equation:

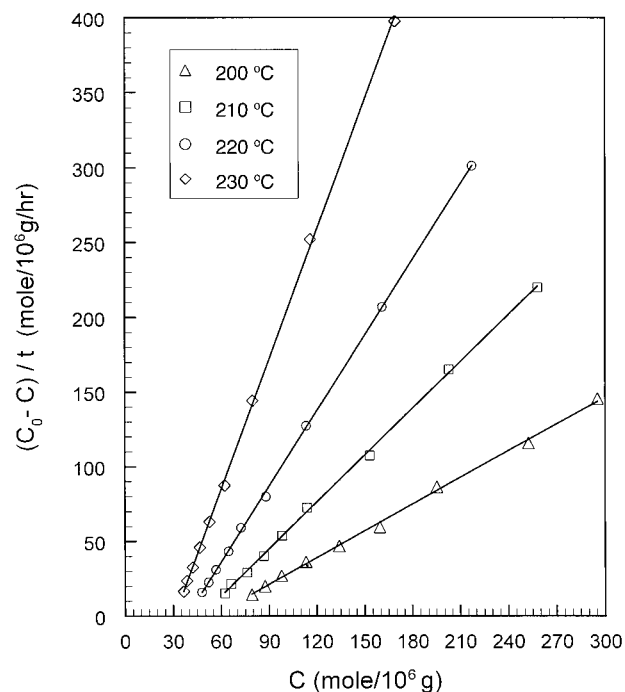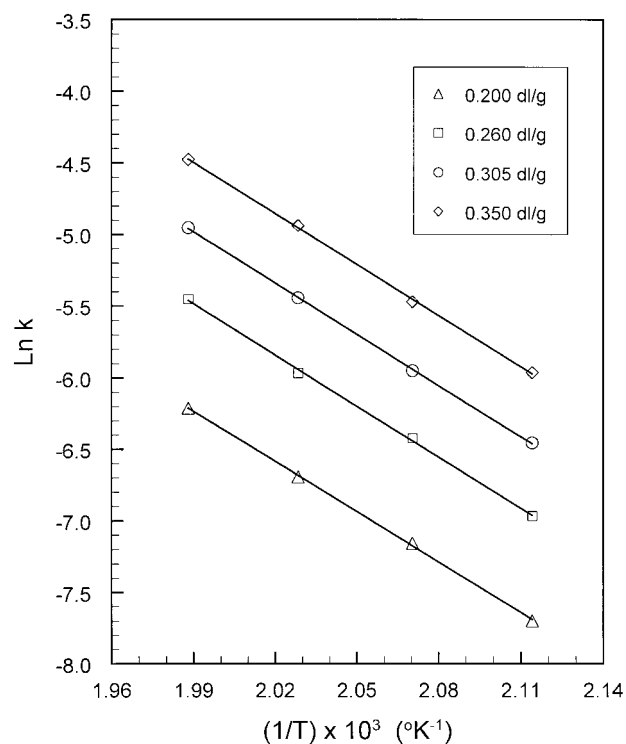$$k = A \exp\left\{\frac{-E}{RT}\right\} \qquad (11)$$

Figure 6 $(C_0 - C)/t$ vs. C plot for solid-state polymerization (SSP) of poly(ethylene terephthalate) (PET) prepolymer with IV of 0.26 dL/g.

Table I   Inactive End Group Concentrations and Reaction Rate Constants for SSP of PET

Prepolymer IV (dL/g)	C_0 (mol/10^6 g)	C_i (mol/10^6 g) and k (10^6 g/mol/h)	Reaction Temperature (°C)			
			200	210	220	230
0.20	541.30	C_i	70.0	58.5	46.9	34.6
		$k \times 10^3$	0.4538	0.7797	1.2377	2.0070
0.26	368.02	C_i	54.3	47.0	38.6	30.8
		$k \times 10^3$	0.9431	1.6230	2.5660	4.2950
0.305	291.02	C_i	48.1	40.6	34.3	28.2
		$k \times 10^3$	1.5718	2.6056	4.3256	7.0671
0.35	237.70	C_i	42.2	37.4	32.1	25.8
		$k \times 10^3$	2.5712	4.2066	7.1739	11.373

Figure 7   Arrhenius plot for solid-state polymerization (SSP) of poly(ethylene terephthalate) (PET).

where A is the frequency factor, E, the activation energy, T, the absolute temperature, and R, the universal gas constant. The values of A and E for each prepolymer can be determined from the intercept and the slope, respectively, of the corresponding straight line and are listed in Table II.

It can be seen that the activation energy is approximately constant within the prepolymer IV range of 0.20–0.35 dL/g. Taking the average of the four values, the activation energy is determined to be 23.5645 kcal/mol. This is close to that for the solid-state ester interchange as determined by Chen and Chen,[8] 24.0 kcal/mol, and that for the melt phase ester interchange as determined by Challa,[3] 23 kcal/mol.

The frequency factor A appears to increase with increasing prepolymer IV. In Figure 8, the natural logarithm of A is plotted against C_0. The plot is approximately a straight line. Therefore, A can be expressed as an exponential function of C_0,

$$A = 1.0287 \times 10^9 \exp(-0.0068C_0) \quad (12)$$

Combining equations (11) and (12), the rate constant k can be expressed as a function of prepoly-

Table II   Values of Frequency Factor and Activation Energy for the Four Prepolymer IV Values

Prepolymer IV (dL/g)	Frequency Factor A (10^6 g/mol-h)	Activation Energy E (kcal/mol)
0.20	2.6026×10^7	23.2735
0.26	8.1515×10^7	23.6642
0.305	14.1452×10^7	23.7105
0.35	20.7262×10^7	23.6097

Figure 8 Ln A vs. C_0 plot for solid-state polymerization (SSP) of poly(ethylene terephthalate) (PET).
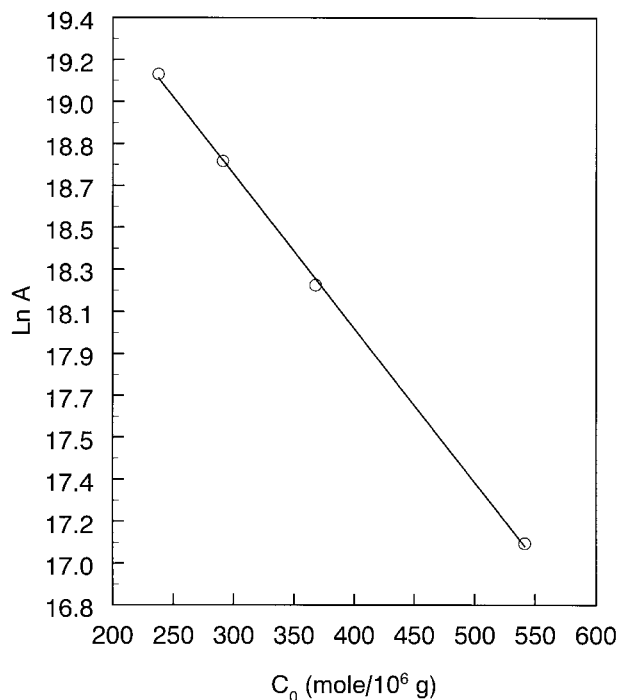

Figure 9 C_i vs. C_0 plot for solid-state polymerization (SSP) of poly(ethylene terephthalate) (PET).

mer end group concentration and SSP temperature:

$$k = 1.0287 \times 10^9$$

$$\times \exp \left\{ -0.0068C_0 - \frac{23{,}565}{RT} \right\} \quad (13)$$

This equation indicates that the rate constant is influenced by the prepolymer IV or molecular weight, as well as by the SSP temperature. Challa[3] noted that the forward rate constant for the ester interchange reaction in the melt phase also increases with increasing molecular weight.

Effects of Temperature and Prepolymer IV on Inactive End Group Concentration

Another factor that influences the SSP rate is the inactive end group concentration, C_i. In Figures 9 and 10, C_i is plotted, respectively, against the prepolymer end group concentration C_0 and against the absolute SSP temperature T using the values of C_i listed in Table I. In both Figures 9 and 10, straight lines are obtained. Thus, the C_i increases approximately linearly with prepolymer end group concentration and decreases approximately linearly with absolute temperature.
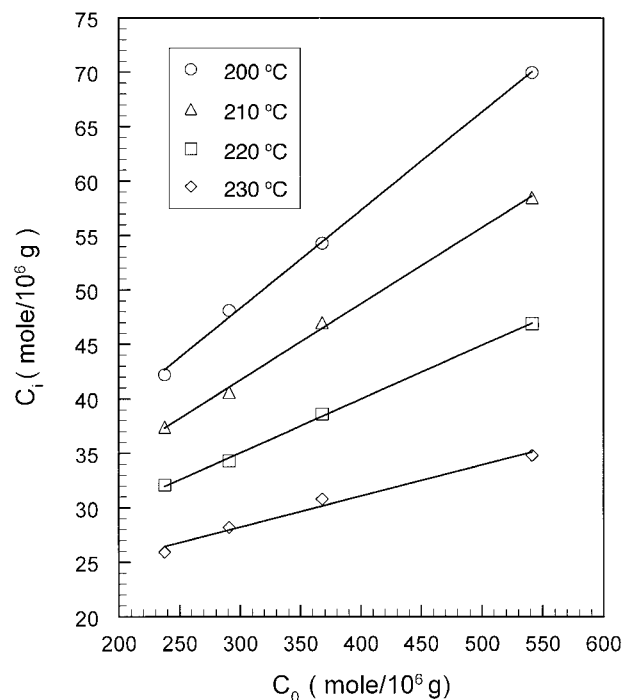
Since the end group concentration decreases with increasing prepolymer IV or molecular weight, the inactive end group concentration increases
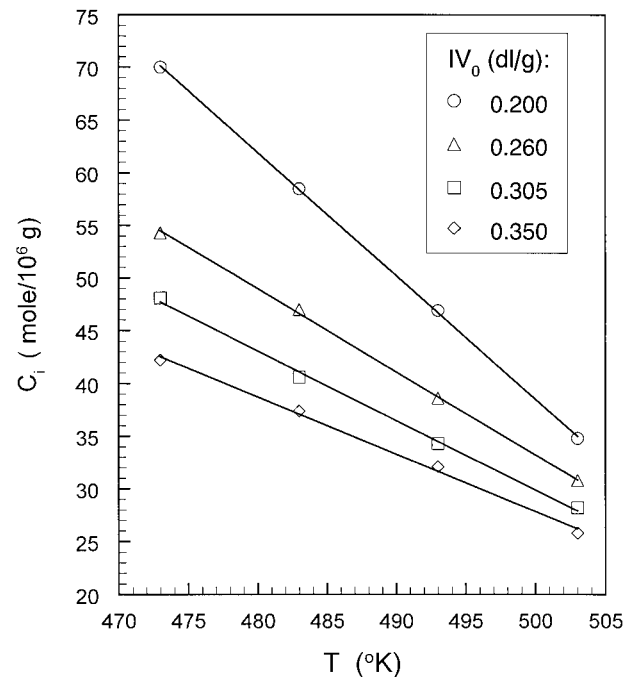

Figure 10 C_i vs. T plot for solid-state polymerization (SSP) of poly(ethylene terephthalate) (PET).

with decreasing prepolymer IV or molecular weight. The C_i values can be fitted reasonably well with the following equation:

$$C_i = 43.31 + 1.0723C_0 - 4.6830 \times 10^{-2}T$$
$$- 2.0755 \times 10^{-3}C_0T \quad (14)$$

With k and C_i available as functions of prepolymer end group concentration and reaction temperature [equations (13) and (14)], the end group concentration, C, the IV, and the number average molecular weight, $\bar{M}_n$, at any time during SSP can be readily estimated using equations (4), (9), and (10), respectively.

Effect of Temperature on SSP Rate

With a simple kinetic model, the rate constant or the activation energy alone is sufficient to compare the relative reaction rates at various temperatures. However, this is not possible with the proposed kinetic model because the SSP rate is also influenced by the inactive end group concentration, which in turn is influenced by the temperature [referring to equation (2)]. The SSP rate of each prepolymer at each temperature and each end group concentration or IV can be calculated using equation (2). However, in practice, we are more interested in the effect of the temperature on the average SSP rate over a certain IV range. This can be estimated with the IV-vs-time curves. For example, from Figure 5, the SSP times required for the 0.26 dL/g IV prepolymer to attain 0.70 dL/g IV are estimated to be 15, 7, 3.5, and 1.8 h at 200, 210, 220, and 230°C, respectively. Thus the average SSP rate about doubles with each 10°C increase in temperature. This simple relationship is, in general, also true for the other three prepolymers.

Justification of the Proposed Kinetic Model

In science and engineering, a model does not necessarily represent the truth. Rather it is a set of assumptions that can explain, through a straightforward logical derivation, some existing phenomena. Since solid-state polycondensation via ester interchange involves two hydroxyl end groups, it is natural to assume the second-order kinetics as the first approach. However, as has been found by many researchers, the simple second-order reaction rate equation [in the form of equation (1)] cannot fit the isothermal SSP data over a sufficiently long period of reaction time—the apparent

rate constant appears to decrease with increasing reaction time. One way to fix the problem is by using a variable rate constant that decreases as the reaction proceeds. Thus, Chen and Chen[9] proposed an "effective rate constant" that varies with the end group concentration to account for the so-called "end-group diffusion limiting reaction." Although they were able to determine the effective rate constant, their model leaves something to be desired. First, the reaction rate constant does not remain "constant" throughout an isothermal reaction, as it should according to the classic kinetics theory. Second, the rate equation does not yield an analytical solution. A more satisfactory model would use a rate constant that is independent of the reaction time or the end group concentration and try to obtain a better fit of the SSP data by modifying the end group concentration term in the rate equation. This consideration plus the fact that an ultimate or limiting IV exists in the SSP of PET lead to the modified second-order kinetic model proposed in this study. As it turns out, this model fits the SSP data very well and can satisfactorily explain or describe the SSP behaviors of PET, including the existence of the limiting IV and the fact that the rate and the limiting IV increase with increasing prepolymer IV. Furthermore, the model itself is simple and offers a rate equation that has a simple solution .

The rate equation and its solution contain kinetic parameters, rate constant k, and inactive end group concentration C_i, which are functions of reaction temperature T and prepolymer end group concentration C_0 [equations (13) and (14)]. The existence of C_i implies the existence of a limiting $\bar{M}_n$ or IV in the SSP of PET. Since C_i decreases with decreasing C_0 (or increasing prepolymer IV or $\bar{M}_n$) and increasing T, while k increases with decreasing C_0 and increasing T, according to equation (2), the reaction rate and the limiting IV increase with increasing prepolymer IV and reaction temperature. Unlike the rate constant in the simple second-order kinetics proposed by Bamford and Wayne,[5] the rate constant k in rate equation (2) does not change with SSP time.

At this point, it would be helpful to discuss the physical meaning of the inactive end groups and how they come about. There are two types of inactive end groups during the SSP: chemically inactive end groups and hydroxyl (and carboxyl if present) end groups that do not participate in polycondensation during SSP.

The first type of inactive end groups (chemically inactive end groups or dead end groups) may originate from the impurities in the precursor EG and DMT or TPA and may be formed by degradation and side reactions during melt phase polycondensation. With the high purity precursors available nowadays and with the relatively mild conditions and relatively short melt phase polycondensation times used to prepare the prepolymers used in this study, the concentration of dead end groups should be no more than a few mol/10^6 g in each of these prepolymers. In general, a DMT-based PET prepolymer may contain up to several mol/10^6 g methyl end groups as a result of incomplete trans-esterification between DMT and EG in the early stage of the melt polymerization process used to prepare the prepolymer. Most of the methyl end groups will behave as dead end groups during SSP. This is part of the reason why a DMT-based polyester prepolymer generally solid-state polymerizes slower than a TPA-based polyester prepolymer with equal IV.

The second type of inactive end groups, which account for the major part of the total inactive end groups, are the functional end groups that are firmly trapped in or severely restrained by the crystalline structure. These end groups do not have sufficient mobilities to participate in the reaction during SSP at a certain temperature. As indicated earlier, the kinetic data indicate that the inactive end group concentration, C_i, increases with decreasing IV but decreases with increasing temperature. This can be explained readily. The shorter molecular chains associated with a lower IV prepolymer fit into the crystal lattices more readily to form more "perfect" crystals and achieve a higher crystallinity. Therefore, more end groups will be immobilized and rendered inactive. Also, statistically, the higher total end group concentration, C_0, in a lower IV prepolymer should also lead to a higher inactive end group concentration, C_i. It is well known that the mobilities or the reactivities of the end groups increase with increasing temperature. As the temperature is increased, part of the end groups that are inactive at lower temperatures will be activated or mobilized to the extent that they become active. Therefore, the inactive end group concentration decreases as the reaction temperature is increased. As the reaction temperature is increased to above the melting point, all the crystallinity will be destroyed and the inactive end group concentration is expected to diminish or approach the chemically dead end group concen-

tration. The C_i vs. T plots for the four prepolymers (Fig. 10) show this general trend.

The prepolymer IV or end group concentration, C_0, also affects the rate constant k through the frequency factor A. As can be seen from Figure 8, the logarithm of the frequency factor decreases approximately linearly with the prepolymer end group concentration. This indicates that the rate constant k increases with increasing prepolymer IV. This can be explained in terms of the flexibility of the molecular chains and the mobility of the end groups. As the chain length increases with increasing prepolymer IV, it becomes more difficult for the molecular chains to fit into the crystal lattices, less "perfect" crystals will be formed, and a lower crystallinity will be attained at a fixed temperature. This leads to greater chain flexibility and end group mobility, resulting in a higher frequency factor.

In the commercial production of solid-state PET, pelletized prepolymer with a substantial carboxyl content is used, and the overall SSP is jointly controlled by chemical reaction and by-product diffusion. Even in this much more complex SSP process, the ultimate IV still exists and the overall SSP rate still increases with increasing prepolymer IV as predicted by the proposed kinetic model. It is believed that solid-state esterification also follows the proposed modified second-order kinetics. Thus, this work should provide a sound basis for development of a treatise capable of satisfactorily describing the commercial PET SSP process.

Ways to Increase the SSP Rate and the Ultimate Product IV

Based on the above discussion, it is evident that both the SSP rate and the highest attainable IV can be increased by increasing either the SSP temperature or the prepolymer IV. However, in practice, it is not always as straightforward as it appears. In the commercial production of solid-state PET, the maximum reaction temperature is constrained by the sticking tendency of the polymer, which also increases with increasing temperature. To ensure smooth production, a safe SSP reactor temperature, which is somewhat below the polymer sticking temperature, has to be used. The other alternative is to increase the prepolymer IV. But this may partially defeat the purposes of SSP. Two important purposes of SSP are to do away with the handling of the extremely high viscosity of high IV polymer melt and to

improve the product color. During the later stage of polycondensation in the melt phase polymerization process, the melt viscosity increases rapidly with the increasing polymer IV. To facilitate effective agitation, reactor temperatures as high as 330°C have to be used to lower the melt viscosity. Prolonged polycondensation at such a high temperature invariably results in discoloration due to polymer degradation. Besides, extra residence time in the finishing melt polycondensation reactor (e.g., a disk ring type reactor) is usually by far more expensive than extra residence time in the solid-state reactor. Therefore, depending on the solid-stated product IV desired, there exists an optimal prepolymer IV.

Another approach involves remelting a solid-stated product and solid stating the resultant new prepolymer again to maintain a reasonably high average SSP rate and to achieve a high IV not attainable with one single SSP operation. Bamford and Wayne[5] suggested this approach in 1969 and Moore et al. of Eastman Kodak Company in 1979 received a patent[11] for a process for the production of high molecular weight polyesters based on the same principle. It is evident in Figure 4, in the SSP of a prepolymer, as the polymer IV approaches the ultimate IV, the reaction rate diminishes. Before this happens, the solid-stated product is remelted, resolidified, and repelletized to be used as a new prepolymer for another SSP. The new prepolymer with a higher IV than the original prepolymer will solid-state polymerize at a much faster rate. Thus a solid-stated product with a very high IV can be produced in a shorter total SSP time. Furthermore, a product IV much higher than the ultimate IV of the original prepolymer can be achieved. This approach, although simple in theory, has not been practiced in the commercial production because the required remelting and repelletizing steps, etc., make the process uneconomical.

CONCLUSIONS

Solid-state polycondensation of PET has two distinct features: (1) there exists an ultimate IV that increases with increasing prepolymer IV and reaction temperature; and (2) the reaction rate increases with increasing prepolymer IV as well as reaction temperature. A kinetic model that aptly describes the behaviors of the SSP of PET has been developed.

According to the proposed kinetic model, in SSP, there are two types of end groups, active and inactive end groups, and the solid-state polycondensation is a second-order reaction with respect to the active end group concentration. The kinetic model provides a simple equation for the end group concentration or IV of PET during SSP as a function of prepolymer end group concentration and reaction temperature. This equation satisfactorily fits the experimental data for the fluid-bed SSP of powdered PET prepolymers with IV values within the range of 0.20–0.35 dL/g over the temperature range of 200–230°C. The activation energy for the SSP of these prepolymers is approximately 23.6 kcal/mol and the average SSP rate about doubles with each 10°C increase in temperature.

The inactive end groups include chemically dead end groups and functional end groups that are immobilized by the crystalline structure of PET. Because the inactive end group concentration remains unchanged throughout the course of SSP, it determines the ultimate IV attainable by SSP.

The inactive end group concentration decreases with increasing prepolymer IV and SSP temperature while the reaction rate constant increases with increasing prepolymer IV and SSP temperature. This explains why the ultimate IV and the SSP rate increase with increasing prepolymer IV and SSP temperature.

NOMENCLATURE

A frequency factor (10^6 g/mol-h)

C end group concentration (mol/10^6 g)

C_0 prepolymer end group concentration (mol/10^6 g)

C_i inactive end group concentration (mol/10^6 g)

E activation energy (cal/mol-°K)

IV intrinsic viscosity (dL/g)

IV_0 prepolymer intrinsic viscosity (dL/g)

k reaction rate constant of polycondensation during SSP (10^6 g/mol-h)

k_f forward rate constant of ester interchange reaction during melt phase polycondensation (1/mol-h)

$\bar{M}_n$ number average molecular weight

$\bar{M}_{n0}$ number average molecular weight of prepolymer

$[OH]$ concentration of hydroxyl end groups during melt phase polycondensation (mol/L)

R universal gas constant (= 1.987 cal/ mol-°K)

T reaction temperature (°K)

t reaction time (h)

REFERENCES

1. Rienehart, V. R. U.S. Pat. 4,165,420, Aug. 21, 1979.
2. Duh, B. U.S. Pat. 4,205,157, May 27, 1980.
3. Challa, G. Makromol. Chem 1960, 38, 105-137.
4. Hovenkamp, S. G. J Polym Sci. A-1, 1971, 9, 3617.
5. Bamford, C. H.; Wayne, R. P. Polymer 1969, 10, 661.
6. Gaymans, R. J.; Amirtharaj, J.; Kamp, H. J Appl Polym Sci 1982, 27, 2513.
7. Chen, F. C.; Griskey, R. G.; Beyer, G. H. AICHE J 1969, 15, 680.
8. Chang, T. M. Polym Eng Sci 1970, 10, 364.
9. Chen, S. ; Chen, F. J Polym Sci: Part A: Polym Chem 1987, 25, 533.
10. Moore, L. D., Jr. ACS Meeting, Cleveland, April, 1960, 1, No 1, 234.
11. Moore, L. D.; Rule, M.; Wicker, T. H. U.S. Pat. 4,446,303, May 1, 1984.