

Effects of Crystallinity on Solid-State Polymerization of Poly(ethylene terephthalate)

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ABSTRACT: There has been a widely held assumption that the solid-state polymerization (SSP) rate of poly(ethylene terephthalate) (PET) decreases with increasing crystallinity. Several published articles that purported to prove this assumption were based on faulty experiments. Therefore, a proper experimental procedure has been used to study the true effects of crystallinity on the SSP of PET. The results show that, for PET in pellet and powder forms, the SSP rate increases with increasing crystallinity. This is because an increase in the crystallinity results in increased end-group concentration in the amorphous phase, where SSP reactions take place, and decreased concentrations of inactive end groups trapped inside the crystals, thereby increasing the

rates of end-group collision and reactions. These positive effects outweigh the negative effect of the increased byproduct-diffusion resistance because of the increase in crystallinity. As the particle size of PET is increased beyond a critical value of about 7 mm, the SSP rate actually decreases with increasing crystallinity because of the excessively increased byproduct-diffusion resistance within the PET particles. However, this critical particle size is far greater than the pellet sizes of commercial PET resins. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 623–632, 2006

Key words: polyesters; solid-state polymerization; crystallization

INTRODUCTION

Solid-state polymerization (SSP) of a condensation polymer is the polycondensation that takes place in the solid particles of the polymer at temperatures between the glass transition temperature and the melting point of the polymer. It is an important process step for the production of poly(ethylene terephthalate) (PET) resins with very high molecular weights and/or very low acetaldehyde contents for soft drink bottle, frozen food tray, and tire cord applications, etc. First, a prepolymer with a moderately high molecular weight is produced by melt polycondensation. The prepolymer is then further solid-state polymerized to the molecular weight required for the desired end application.

Two types of polycondensation reactions take place during the SSP of PET: transesterification and esterification. Transesterification is the reaction between two hydroxyl (more accurately β -hydroxyethyl) end groups, with ethylene glycol as the reaction byproduct. Esterification is the reaction between a hydroxyl end group and a carboxyl end group, with water as the reaction byproduct. Because both polycondensation reactions are reversible, it is necessary to effectively remove the reaction byproducts, by vacuum or

by a stream of nitrogen, to promote the forward reactions.

The SSP of PET has been investigated by many researchers.^{1–14} Because SSP involves the diffusion of the reaction byproducts, ethylene glycol and water, and the crystallinity of the polymer impedes diffusion, there has been a widely held assumption that the SSP rate of PET decreases with increasing crystallinity. However, only a few researchers^{1–3} have conducted experiments to prove the assumption and published their results.

Review of prior works

Bamford and Wayne¹ first attempted to determine the effects of crystallinity on the SSP of PET. They believed that, since the end groups are concentrated in the amorphous phase, crystallinity should increase the SSP rate. They held 72-mesh PET powder with an intrinsic viscosity (IV) of 0.24 dL/g under nitrogen at a pressure just below atmospheric pressure, heated it to 230°C, and allowed it to cool overnight to prepare a highly crystallized prepolymer. They then solid-state polymerized heat-treated as well as untreated prepolymers at 180°C under vacuum. They did not check the IV of the prepolymer after the heat treatment, nor did they provide experimental data other than the rate constants they determined. The rate constants were found to be 7.7×10^{-4} and 8.7×10^{-4} L/mol/s for two SSP experiments with the heat-treated prepoly-

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mer, compared with 7.1×10^{-4} L/mol/s for the untreated prepolymer. One might think these experiments proved that the SSP rate increases with increasing crystallinity, until one reviews how they determined the rate constant. They assumed that the SSP of PET followed simple second-order kinetics just as the melt polycondensation of PET. However, as demonstrated by Duh,^{4,5} the second-order rate equation does not satisfactorily fit the experimental data. When this rate equation is used to fit the experimental data, the rate constant appears to change with time, and does not remain constant as assumed. Therefore, the rate constant thus determined is not accurate. Bamford and Wayne¹ admitted in the discussion of another SSP experiment that the rate constant appeared to decrease with the SSP time. Therefore, they concluded that the use of highly crystallized starting polymer has virtually no effect on the rate constant. But they did not think that this argued against the conception that crystallinity increases end-group concentrations in the amorphous phase. They defended their conclusion by saying that, since PET crystallizes rapidly at the SSP temperature, all the prepolymers used were equally highly crystallized. However, this is not true, because heat treatment at a temperature higher than the SSP temperature does increase the crystallinity substantially.

Heighton and Most² preheated 60–80 mesh PET powders with an IV of 0.40 dL/g under nitrogen in closed glass tubes, at 160, 218, and 235°C, etc. for 15 min, and then solid-state polymerized the preheated powders at 218°C under vacuum. The results showed that the SSP rate decreased with increasing preheating temperature of the powdered prepolymers. They theorized that the increased crystallinity due to the preheating led to increased byproduct-diffusion resistance, thereby retarding the SSP rate. However, in reality, they missed some points. First, according to Duh,⁴ with a particle size this small, the byproduct-diffusion resistance is practically negligible regardless of the crystallinity and the SSP is reaction-controlled. Therefore, the SSP rate should not be significantly affected by the crystallinity. Furthermore, because preheating PET at a temperature below the SSP temperature does not significantly increase its average crystallinity during SSP, at the SSP temperature of 218°C, the average crystallinities of the powders preheated at 160 and 218°C should be practically the same during SSP. Therefore, the reason for the difference in the SSP rate must lie elsewhere.

The main reason for the lower SSP rates for the powders preheated at 218 and 235°C is believed to be the hydrolytic degradation of the polymer during the preheating. The degradation led to substantially higher carboxyl concentration. Amorphous PET generally has a moisture content of about 0.3%. During the heat-up in the preheating step, the rate of moisture

removal was very slowly in a closed tube. Consequently, substantial hydrolytic degradation, which lowered the IV and increased the carboxyl concentration, took place. The severity of the degradation increased with increasing preheating temperature. According to Duh's studies,^{4,6} for PET powders with particle sizes below 600 μm (equivalent to 30-mesh size), the SSP rate decreases rapidly with increasing carboxyl concentration, because the byproduct-diffusion resistance is small and the total rate of polycondensation reactions is the highest at zero carboxyl concentration. Heighton and Most² erroneously assumed that the IV at the beginning of the SSP was equal to the IV before the preheating in each case. However, they contradicted themselves by showing that the IV of the powder that was preheated at 235°C was still 0.40 dL/g after 1 h of SSP. By extrapolation of the SSP curve to 0 SSP time, it is estimated that the IV dropped to about 0.30 dL/g after the preheating at 235°C, increasing the carboxyl concentration by about 51 $\mu\text{mol/g}$. This large increase in the carboxyl concentration severely decreased the SSP rate of the powdered prepolymer preheated at 235°C.

Another reason may be the increase in the inactive end-group concentration as a result of the degradation. Because of the very slow rate of moisture removal, the remaining moisture within the crystalline phase could split the polymer chains (by means of reverse reactions) without destroying the crystals, creating end groups that were trapped inside the crystals.

Chang³ heat-treated 1/8" (3.175 mm) PET cubes with an IV of 0.6 dL/g, at temperatures ranging from 170 to 250°C for 15–60 min under nitrogen, in a close system (unvented oven), to prepare prepolymers with various initial crystallinities for SSP. He ground the heat-treated as well as untreated cubes into 35–48 mesh powders, and then solid-state polymerized these powders at 230°C in a fluid-bed reactor. He also found that the more severe the heat-treatment conditions, the slower the SSP rate, and concluded that the SSP rate decreased with increasing crystallinity. He attributed the slower SSP rates of the more severely heat-treated prepolymers to the lower byproduct diffusivity, which he assumed to be proportional to the amorphous fraction, which in turn decreases with increasing crystallinity. His data clearly indicated that there were substantial IV drops during the heat treatments—the more severe the treatment conditions, the greater the IV drop. For example, after the 60-min heat treatment at 250°C, the IV dropped to 0.47 dL/g, resulting in a carboxyl-concentration increase of about 23 $\mu\text{mol/g}$. Clearly Chang's study³ suffered from the same pitfalls as the study of Heighton and Most²

In view of the faulty experiments and questionable conclusions of the aforementioned researchers, it was decided to present a proper experimental procedure to

determine the true effects of crystallinity on the SSP of PET and to offer an opposing view.

Theoretical development

To gain some insight into the effects of crystallinity on the SSP of PET, it will be helpful to examine the mechanism of the SSP of PET, the end-group distribution within the polymer mass, and the morphological transformation of PET during heat treatment and annealing.

Mechanism of the SSP of PET

It is generally believed that the SSP of PET consists of the following four steps:

1. diffusion and collision of end groups,
2. reaction of end groups,
3. diffusion of reaction byproducts from the interiors to the surfaces of the polymer particles, and
4. diffusion of reaction byproducts from the surfaces of the polymer particles into the bulk of the gas phase.

For convenience, the first step is referred to as the end-group diffusion or collision step, combination of the first and second steps, the reaction step, and combination of the third and the fourth steps, the byproduct diffusion step (or simply the diffusion step.) In a fluid-bed or fixed-bed reactor, if a sufficiently high nitrogen flow rate is used, the interfacial diffusion resistance is negligible and Step 4 can be considered to be instantaneous.^{4,5} If, in addition, the polymer particle size is fine enough (e.g., smaller than 60-mesh size), the byproduct diffusion resistance in Step 3 is negligible, Step 3 can be considered to be instantaneous, and the SSP can be considered to be reaction-controlled.⁴

The preconception about the effect of crystallinity on the SSP rate of PET is based on the effect of crystallinity on the byproduct-diffusion resistance within the polymer particles. If the crystallinity could be changed without changing the other polymer properties, it would be easy to predict that increasing the crystallinity would decrease the SSP rate of PET pellets, but would not have a significant effect on the SSP rate of very fine PET powder (with negligible byproduct-diffusion resistance). In reality, it is impossible to change the crystallinity without also changing the other polymer properties, which may have opposing (positive) effects on the SSP rate of PET.

End-group distribution

In the amorphous state, the end groups of PET are uniformly distributed throughout the polymer mass. Because end groups are structurally different from the

repeating units, they cannot fit into the crystal lattice. Therefore, in partially crystalline PET particles, most of the end groups reside in the amorphous regions. However, there will always be small parts of the end groups that are embedded or trapped inside the imperfect crystals, which are formed hastily when the amorphous PET is first heated to crystallization temperature. These trapped end groups can be considered as defects of the crystals. During annealing or heat treatment, PET undergoes a morphological transformation,^{15,16} and some of the trapped end groups will be rejected into the amorphous regions as the degree of perfection of the crystalline structure increases.

Because most of the end groups are located in the amorphous regions and because the mobility of the embedded end groups are severely restricted by the crystalline structure, practically, all the SSP reactions take place in the amorphous regions. The concentration of the end groups in the amorphous phase has a positive effect on the SSP rate, because it is generally considered that the polycondensation reactions are of second order with respect to the end-group concentrations. If all the end groups reside in the amorphous phase, the SSP rate will be proportional to the square of the factor f , which is defined as $f = 1/(1 - X_c)$, X_c being the fraction of the crystalline phase. After averaging for the whole polymer mass, the overall rate is still greater, than if the end groups were uniformly distributed throughout the entire polymer mass by a factor of f .

It should be emphasized that the distribution of end groups in the amorphous regions is not uniform. Normally, when a polymer chain folds its segments and crystallizes, its two chain ends will stick out into the amorphous phase. Therefore, it is expected that the end-group concentrations are the highest near the boundaries of the crystallites. Because of the chain entanglement and the relative low chain mobility in the amorphous phase, the collision and the possible reaction of end groups depend largely on the diffusion of the chain ends, and not on the transportation of the whole chains. The disproportionately high concentrations and proximity of the end groups near the surfaces of the crystallites are particularly favorable to the SSP.

Some researchers⁷⁻¹⁰ suggested that the presence of crystallinity reduces the mobility of polymer chains, thereby impeding end-group collision. But this negative effect should be somewhat mitigated by the high end-group concentrations near the surfaces of the crystallites.

Morphological transformation of PET during heat treatment and annealing

Heat treatment is the most effective and the only practical way to increase the crystallinity of PET. It is

well known that, during heat treatment or annealing, PET undergoes morphological transformation, in which the crystallinity, density, melting point, and average crystallite size increase, more defects of the crystals (including the embedded end groups) are rejected into the amorphous regions, and the crystalline structure becomes more orderly.^{15,16} Therefore, the morphological transformation is the crystal perfection process. For the purpose of this study, it is important to note that, as the crystallinity is increased in the process of morphological transformation, the total number of the inactive end groups trapped inside the crystals decreases.

The rate of the morphological transformation of PET is very sensitive to the treatment temperature—it increases drastically with increasing temperature. If PET is treated at a temperature for a short time and then annealed at a higher temperature, the effects of the lower-temperature heat treatment will be overshadowed or masked by the effects of the subsequent higher-temperature annealing. Therefore, to obtain a significantly higher average crystallinity during SSP, the PET prepolymer must be heat-treated at a temperature higher than the SSP temperature.

The volume fraction crystallinity of a polymer sample, X_v , is related to the density of sample, ρ , by

$$X_v = \frac{\rho - \rho_a}{\rho_c - \rho_a} \quad (1)$$

where ρ_c and ρ_a are, respectively, the ideal values of the density of the crystalline and amorphous phases of PET. The values,^{17,18} $\rho_c = 1.455 \text{ g/cm}^3$ and $\rho_a = 1.335 \text{ g/cm}^3$, are widely adopted in the PET industry.

In summary, an increase in the crystallinity has positive effects as well as negative effects on the SSP rate. Negative effects include increased byproduct-diffusion resistance and decreased polymer-chain mobility. The increase in the byproduct-diffusion resistance is the most detrimental to the SSP, because it not only retards byproduct diffusion, but also increases byproduct concentrations within the polymer particles and promotes reverse reactions. Positive effects include increased end-group concentrations in the amorphous regions, especially at the vicinity of the crystallites, and decreased inactive end-group concentrations. Whether an increase in the crystallinity increases or decreases the SSP rate depends on whether the combined positive effect outweighs the combined negative effect or the other way around.

SSP rate equation

A rate equation that satisfactorily fits the experimental SSP data will be convenient for us to draw the SSP curves and to calculate the SSP rate at any time during

the SSP. The simple empirical rate equation proposed by Duh^{4,5} should be adequate for the purpose. This is based on the concept of the existence of inactive end groups. The inactive end groups are those that are trapped inside the crystals as well as chemically dead end groups. Thus the rate equation can be expressed as follows:

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

where C is the total end-group concentration, C_i , the apparent inactive end-group concentration, t , the SSP time, and k , the apparent reaction rate constant. Note that C and C_i are composite quantities for the whole polymer particle, and not point quantities. Although actual inactive end-group concentration changes during SSP, C_i is considered to be constant in this equation. This equation represents the net SSP rate, without making distinction between the types of end groups or polycondensation reactions. It is capable of adequately describing the observed SSP behaviors, but not the true SSP mechanism. The presence of the inactive end groups agrees with the observation that, in each prolonged SSP run, the reaction ceases once an ultimate number-average molecular weight or IV is reached. According to eq. (2), the SSP rate increases with increasing k and decreasing C_i . Because k and C_i are fitting parameters, factors that increase the SSP rate tend to increase the value of k and/or decrease the value of C_i .

After integrating eq. (2) and solving for the integration constant using the initial condition $C = C_0$ at $t = 0$, the resulting equation can be rearranged into the following form:

$$\frac{C_0 - C}{t} = aC - b \quad (3)$$

where $a = 2k(C_0 - C_i)$ and $b = 2k(C_0 - C_i)C_i$. Therefore, if $(C_0 - C)/t$ is plotted against C using the experimental data, a straight line with slope a and intercept $-b$ can be obtained. It is obvious that $C_i = b/a$. Once C_i is determined, k can be determined either from a or b .

Solving eq. (3) for C yields

$$C = \frac{C_0 + bt}{1 + at} \quad (4)$$

In the polyester industry, C is more conveniently expressed in the unit of $[\mu\text{mol/g}]$. Thus C is related to the number-average molecular weight M_n by the following equation:

$$C = \frac{2 \times 10^6}{M_n} \quad (5)$$

The number-average molecular weight is in turn related to the IV, which is measured in 60/40 phenol/tetrachloroethane solvent at 25°C, by the Moore equation¹⁹ as follows:

$$IV = 7.50 \times 10^4 M_n^{0.68} \quad (6)$$

Using eqs. (4)–(6) the solution for the IV is obtained:

$$IV = \left[\frac{50.7569}{C} \right]^{0.68} = 14.4456 \left[\frac{1 + at}{C_0 + bt} \right]^{0.68} \quad (7)$$

EXPERIMENTAL

All the experimental works for this study were conducted in the Polyester R & D Lab of Goodyear Tire and Rubber Company, Akron, Ohio.

Prepolymer used in the experiments

The prepolymer used in the experiments for this study was unmodified PET produced in the Goodyear Polyester Resin Plant at Point Pleasant, WV. It had an IV of 0.544 dL/g, a DSC melting point of 256°C, a carboxyl content of 36 $\mu\text{mol/g}$, and a pellet weight of 0.0223 g. The pellets had approximately a cylindrical shape with a major axis of 3.16 mm, a minor axis of 2.42 mm, and a length of 3.0 mm, based on the averages of 10 pellets. For convenience, the nominal particle size of the pellets is taken to be 3.0 mm as an approximation. Two forms of the prepolymer, as-is pellet and 80–100 mesh-size (particle size = 0.15 mm) powder, were used to conduct two series of SSP experiments, to study the crystallinity effects. In addition, another series of SSP experiments using the pellets and classified powders with various particle sizes were performed, to determine the maximum particle size for which the SSP is reaction-controlled.

Experimental apparatus

Each of the reactors used to conduct the experiments was constructed of a 50-cm-long glass column with a diameter of 28 mm. The reactor had a cone-shaped bottom, which was connected to a 4-mm-diameter, 150-cm-long nitrogen (purge gas) supply tube, which was coiled up around the lower half of the reactor column. Two types of reactors were constructed for the experiments with the pellets and the powder. For the powder only, each of the reactors was fitted with a porous glass filter at the base of the column (just above the cone-shaped bottom), to distribute the nitrogen as well as to support the powder. During the experimen-

tal runs, the reactor with its nitrogen supply tube was immersed in a 30-cm deep oil bath, whose temperature was controlled to within $\pm 0.1^\circ\text{C}$. The nitrogen supply tube also served as a heat exchanger, which heated the incoming nitrogen to the desired experimental temperatures. During the experimental runs, the polymer bed temperature was monitored with a thermocouple.

Experimental procedures

To prevent or minimize the hydrolytic degradation during SSP or higher-temperature heat treatment, the powder and the pellet prepolymers were dried (and precrystallized) in a nitrogen stream in the reactor at 170°C for 0.5 and 1.0 h, respectively, to reduce the prepolymer moisture content to below 50 ppm. This drying step is the main feature that sets this study apart from earlier studies of the effects of crystallinity on the SSP of PET.^{1–3}

The drying step did not change the IV of the pellets, but increased the IV of the powder slightly. The SSP temperature of 220°C was chosen, because it was near the maximum safe temperature that can be used in a commercial-scale SSP reactor equipped with a Hosokawa-Bepex mechanical discharger.

For each run in the series of SSP experiments to study the particle size effect, 2 g of powdered prepolymer was charged into the reactor, whose oil-bath temperature had been controlled at 170°C, with nitrogen passing the reactor at a flow rate of 3–5 L/min to fluidize the polymer. The bath temperature was held there for 30 min to crystallize and dry the polymer. Then the bath temperature was raised to 220°C over about 10 min to start the SSP. After 3 h of SSP, the product was removed and tested for IV.

Four SSP runs were conducted for each series of the SSP for the crystallinity-effect study, using pellet or powder prepolymers. Each control run consisted of two steps, precrystallization (drying) at 170°C (30 min for the powder and 1 h for the pellets) and SSP at 220°C (8 h for the powder and 20 h for the pellets). An additional 15-min higher-temperature heat treatment step at 230, 240 or 250°C was included in each of the other SSP runs. This additional step, which imparted higher polymer crystallinity during SSP, is referred to as “over preheating.”

Two sets of reactors each, with its dedicated hot oil bath, were used to conduct an SSP run for the crystallinity-effect study. This greatly shortened the polymer heat-up times at the beginnings of the over-preheating step and the SSP step. The amount of the prepolymer charged for each run was 10 g powder or 80 mL pellets.

For the runs with the powder, a nitrogen flow rate of 3 L/min was used at all time, to maintain a stable fluid bed. For the runs with pellets, a nitrogen flow

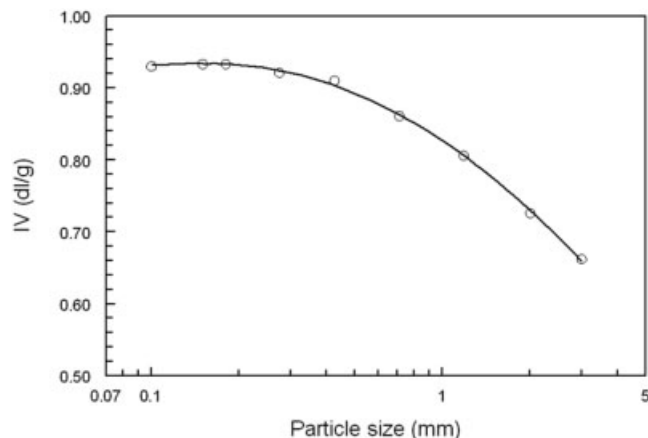


Figure 1 IVs of PET with various particle sizes after 3 h of SSP at 220°C.

rate of 8 L/min was used to maintain a static bed during the drying step and the bulk of the SSP step. During the over-preheating step and the first 3 min of the SSP step, a nitrogen flow rate of 90 L/min was used to fluidize the pellet bed, to prevent or reduce agglomeration of the pellets and to bring the bed to the desired temperatures quickly (within 3 min).

Considerable clumping of powder and lumping of pellets occurred during over preheating at 240 and 250°C. Therefore, it was necessary to break up the clumps and lumps in a bowl with a pestle before the SSP step.

The experimental procedure for a typical SSP run (other than the control run) can be summarized as follows: (1) Charge the desired amount of the prepolymer into the first reactor, whose oil-bath temperature had been stabilized at 170°C to dry and precrystallize the prepolymer for the required time. (2) Transfer the dried prepolymer into the second reactor, whose oil-bath temperature had been stabilized at 230, 240, or 250°C to over preheat the prepolymer for 15 min. (3) Transfer the over-preheated prepolymer back into the first reactor, whose oil-bath temperature had been reset and stabilized at 220 °C to start the SSP, which lasted 8 h for powder and 20 h for the pellets.

For each run for the study of crystallinity effects, the samples were taken at various intervals during the SSP. All samples were tested for IV. In addition, all pellet samples were tested for density. The density measurements were performed using a density gradient tube. It is reasonable to assume that the density values of a pellet sample and a powder sample are the same if they have been subjected to the same thermal history.

RESULTS AND DISCUSSION

Effect of particle size on the SSP rate

Figure 1 shows the IVs of powdered PET samples with various particle sizes and pellet sample after 3 h of SSP

at 220°C. It can be seen that the IV increases as the particle size is decreased until it reaches about 0.18 mm (80-mesh size). When the particle size is further decreased, the IV remains unchanged. This means that with particle size equal to 0.18 mm or smaller, the reaction byproducts can be removed immediately and the SSP is reaction-controlled. This agrees with the finding in a previous SSP study with low-IV prepolymers.⁴

Effects of over preheating on the density and crystallinity of PET during SSP

The density of each sample taken during the four SSP runs with the pellets was converted into volume fraction crystallinity, using eq. (1). Figure 2 shows the volume % crystallinity versus SSP time plots for PET pellets, with and without over preheating at various temperatures. It can be seen that over preheating substantially increases the density and crystallinity during SSP and the higher the over-preheating temperature, the greater the effects.

Effect of crystallinity on the SSP rate

The IV data for the SSP of the PET powder and the pellets are plotted in Figures 3 and 4, respectively. These data were used to determine the two parameters, k and C_i , for the rate equation for each of the SSP runs by linear regression. The results are listed in Table I. As expected, for both polymer forms, k increases while C_i decreases, with increasing over-preheating temperature and crystallinity. The k values for the powder are greater than their respective counterparts for the pellets, while C_i values for the powder are

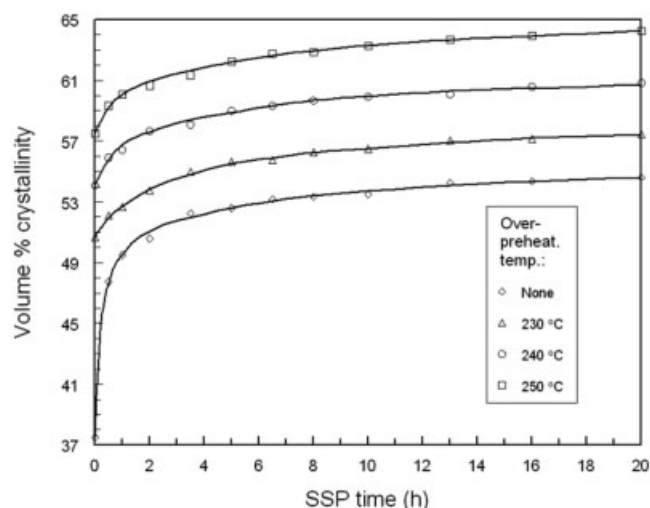


Figure 2 Volume % crystallinity versus SSP time plots for the SSP of PET without over preheating and with over preheating at various temperatures.

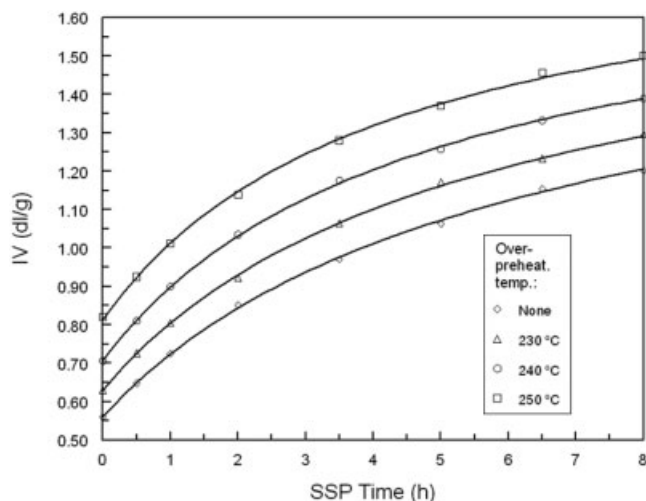


Figure 3 IV build-up curves for the SSP of PET powder without over preheating and with over preheating at various temperatures.

smaller than their respective counterparts for the pellets. This is because of the negligible byproduct-diffusion resistance within the fine powder particles. Since the crystallinity during the SSP increases with the over-preheating temperature and since the SSP rate increases with increasing k and decreasing C_i , the SSP rate increases with increasing crystallinity for both the powder and the pellets.

There were considerable IV increase and significant inactive end-group decrease during each over preheating. However, it should be noted that the inactive end-group decrease was not due to the polycondensation reactions because the polycondensation reactions took place within the amorphous phase. Rather, the inactive end-group decrease was a result of the

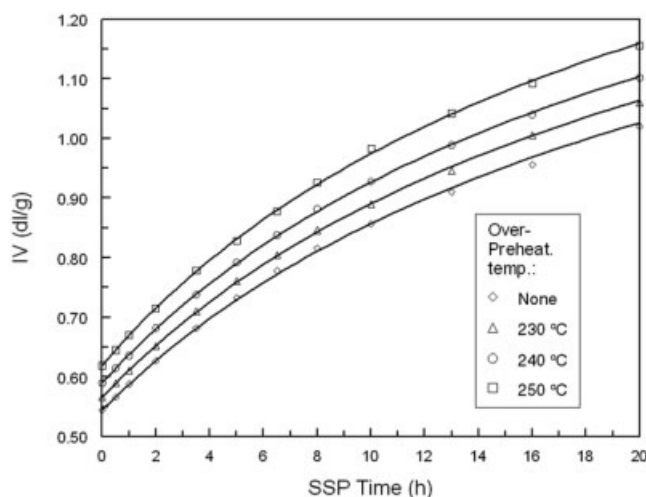


Figure 4 IV build-up curves for the SSP of PET pellets without over preheating and with over preheating at various temperatures.

TABLE I
Calculated Values of k and C_i for SSP of PET Powder and Pellets Without Over Preheating and with Over Preheating at Various Temperatures

Over-preheating temperature (°C)	IV_0 (dL/g)	$k \times 10^3$ (g/ μ mol/h)	C_i (μ mol/g)
Powder form			
NA (control)	0.560	3.2892	22.69
230	0.629	4.0724	22.02
240	0.706	5.2100	21.23
250	0.821	6.6756	20.33
Pellet form			
NA (control)	0.544	0.7740	24.45
230	0.566	0.8383	23.70
240	0.590	0.9004	22.76
250	0.619	0.9879	21.53

morphological transformation or the crystallinity increase during the over preheating.

The values for k and C_i can be plugged into eq. (7) to draw the IV versus SSP time plots. As shown in Figures 3 and 4, the curves fit the data quite well for all the SSP runs.

There are two ways to quantitatively compare the SSP rates of the SSP runs for the powder and the pellets: first, by the average rates over an IV range, and second, by the rates at a specific IV. As an example, the average SSP rate, $\Delta IV/\Delta t$, for each run over the common IV range of 0.82–1.02 dL/g can be determined using Figures 3 and 4. The SSP rate, $-dC/dt$, for each SSP run at a specific IV (e.g., the mid-point of the above range, 0.92 dL/g) can be calculated using eq. (2), with the values of k and C_i listed in Table I. The value for $-dC/dt$ is then converted to the value for $d(IV)/dt$ using eq. (7). The average SSP rates over the IV range of 0.82–1.02 dL/g and the SSP rates at 0.92 dL/g thus determined are listed in Table II. For reference, the corresponding volume % crystallinity values are also determined using Figure 2 and included in this table. Furthermore, the rate ratio, which is defined as the SSP rate of an SSP run divided by the SSP rate of the control SSP run (the run without over preheating) in the same series, is also calculated for each SSP run. The rate ratios give good indications of relative rate increases due to the crystallinity increases.

It can be seen from Table II that the SSP rates for both the PET powder and the pellets increase with increasing over-preheating temperature and hence increasing crystallinity. This is because the increase in the crystallinity results in a decrease in the amorphous phase and an increase in the degree of crystal perfection. A decrease in the amorphous phase means an increase in the concentration of end groups within the amorphous phase, especially near the surfaces of the crystallites. This effectively shortens the average diffusion path length required for an end group to collide

TABLE II
Comparison of SSP Rates of PET Powder and Pellets Without Over Preheating and with Over Preheating at Various Temperatures

Over-preheating temperature (°C)	Over IV range of 0.82–1.02 dL/g			At IV = 0.92 dL/g		
	Volume % crystallinity	Average SSP rate (dL/g/h)	Rate ratio	Volume % crystallinity	SSP rate (dL/g/h)	Rate ratio
Powder form						
NA (control)	50.5–52.5	0.084	1.00	51.6	0.086	1.00
230	52.9–54.5	0.109	1.30	53.7	0.111	1.29
240	56.0–57.6	0.148	1.76	56.8	0.148	1.72
250	57.9–60.1	0.190	2.26	59.8	0.200	2.33
Pellet form						
NA (control)	53.6–54.9	0.018	1.00	54.2	0.018	1.00
230	56.0–57.2	0.020	1.11	56.7	0.021	1.15
240	59.2–60.4	0.023	1.29	59.7	0.024	1.31
250	62.0–63.6	0.027	1.49	62.7	0.028	1.56

with another end group and, hence, increases the rate of the end-group collision step. As the degree of crystal perfection is increased, more originally imbedded end groups (inactive end groups) are rejected into the amorphous phase and become active. This also favors end-group collision and reaction. In the SSP of the powder, the increase in the crystallinity does not have a significant effect on the end-group diffusion resistance, because of the fine particle size, and the combined positive effect easily outweighs the negative effect of lower polymer-chain mobility. In the SSP of the pellets, although the increase in the crystallinity results in greater byproduct-diffusion resistance and lower polymer-chain mobility, the decrease in the rate of the byproduct diffusion step is outweighed by the increase in the rates of the end-group collision and reaction steps.

Critical particle size at which crystallinity has no effect on the SSP rate

It is also obvious from Table II that, for each over-preheating temperature, the rate ratio for the powder is greater than that for the pellets and the difference between the ratios for the powder and the pellets increases with increasing over-preheating temperature and increasing crystallinity. This confirms that the byproduct-diffusion resistance within the pellets increases with increasing crystallinity. At any fixed crystallinity, no matter how high it is, as the particle size is increased, the byproduct-diffusion resistance is increased, but the end-group concentrations in the amorphous phase and the inactive end-group concentrations remain unchanged. Therefore, it is conceivable that there exists a critical particle size at which a change in the crystallinity has no effect on the SSP rate, because the combined positive effect is cancelled out by the combined negative effect, namely rate ratio = 1. Once the particle size exceeds the critical particle

size, the SSP rate will decrease with increasing crystallinity (rate ratio < 1).

To determine the critical particle size, rate-ratio data for at least three particle sizes are needed. Table II provides data for two particle sizes. The rate-ratio data for the third particle size can be conveniently obtained by assuming that, for each over-preheating temperature, the rate ratio for a finer powder (e.g., with a particle size = 0.10 mm) is equal to that for the powder used in the experiments (with particle size = 0.15 mm). This is reasonable because the byproduct-diffusion resistance inside the particles of either powder is negligible. The rate ratios over the IV range of 0.82–1.02 dL/g should be used to determine the critical particle size, because they are more representative than the rate ratios at any single IV for the overall SSP. Figure 5 is a semilogarithmic chart that shows the effects of particle size on the rate ratio, with over-preheating temperature as a parameter. The three

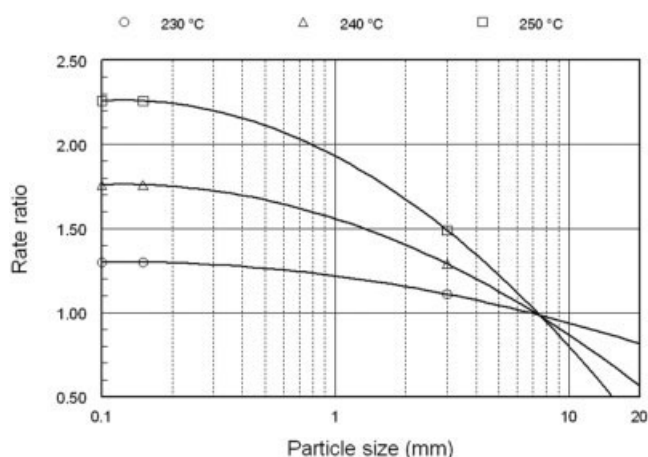


Figure 5 Effects of particle size on the SSP rate ratio for the SSP of PET with over-preheating temperature as a parameter.

curves are obtained by curve fitting using second-order polynomial functions, with logarithmic scaling for the x -axis. These curves intercept the straight line, rate ratio = 1, at 6.8, 7.1, and 7.3 mm for over-preheating temperatures of 230, 240, and 250°C, respectively. These values are fairly close. In view of the fact that approximation and extrapolation are used in the determination of these values, for the sake of simplicity, it is reasonable to consider the critical particle sizes are practically the same and equal to 7 mm for all cases. This means that, with particle size greater than 7 mm, the SSP rate of PET actually decreases with increasing crystallinity as predicted by the conventional wisdom. However, this critical particle size is much bigger than the pellet sizes of the commercial PET resins. The biggest PET chips ever produced are 1/8" cubes, which are becoming very rare nowadays. Since no PET chips as big as 7 mm will ever be produced for SSP, it is safe to say that the SSP rate increases with increasing crystallinity.

Deficiencies of existing comprehensive SSP models in treating the crystallinity effects

Many ambitious, comprehensive models have been proposed in an attempt to simulate the mechanism of the SSP of PET.^{3,7-14} Despite their complexity, they all can use some refinements in dealing with the effects of crystallinity on the SSP. Some of these models disregard the crystallinity effects.¹¹⁻¹³ Many of these models incorporate the negative effects, such as decreased byproduct diffusivities and/or reduced polymer-chain mobility, and predict that the SSP rate decreases with increasing crystallinity.^{3,7-10} Only a few of these models account for the increased end-group concentrations in the amorphous phase (by multiplying the end-group concentrations with the factor f , for example), but still do not give enough credit to the beneficial effects of crystallinity.^{8,14} None of these models take into account the particularly high end-group concentrations near the boundaries of the crystallites and the presence of the inactive end groups. It is hoped that some future models will take into account all the positive effects of crystallinity to predict the right trends.

Possible applications in the PET SSP process

It has been well known that the sticking tendency of PET pellets inside the SSP reactor decreases with increasing crystallinity and over preheating can achieve higher crystallinity. However, this concept has not been well received by the designers of PET SSP processes, partly because of the engineering difficulties, and partly because of the concern that an increase in the crystallinity could lead to a lower SSP rate, based on the conventional wisdom. Now that it has been

proven that the SSP rate increases with increasing crystallinity, there are even more incentives to pursue the technology. Not only can an increase in the crystallinity by itself increase the SSP rate, but it also allows for a higher reactor temperature, which further increases the SSP rate. These double advantages can be achieved by increasing the capacity and the agitation efficiency of the preheater, to enable over preheating without causing pellet sticking, and incorporating a cooling section into the preheater or adding a separate intercooler to cool the over-preheated pellets to the desired reactor temperature. The obvious advantage of this enhanced process is its ability to substantially increase the productivity in the production of regular IV products (e.g., 0.82–0.84 dL/g for bottle applications) using regular IV (0.55–0.65 dL/g) feed polymers. But its unique strength lies in its ability to achieve what the conventional SSP process cannot achieve or has difficulties to achieve, namely the production of exceptionally high IV products (e.g., >1.0 dL/g for tire cord applications) using regular IV feed polymers or production of regular IV products using very low IV feed polymers. Thus, the incorporation of the over-preheating feature will greatly increase the flexibility in the design of the overall process (an integrated melt/solid-state polycondensation process) for the manufacture of PET resins.

CONCLUSIONS

1. A satisfactory experimental procedure for the SSP of PET has been used to generate data that show the true effects of crystallinity on the SSP rate of PET.
2. With PET pellets or powder, the SSP rate increases with increasing crystallinity as a result of the increased end-group concentrations in the amorphous phase, particularly near the boundaries of the crystallites, and the decreased numbers of the inactive end groups trapped inside the crystals. Although an increase in the crystallinity also increases the byproduct-diffusion resistance and possibly decreases the mobility of the polymer chains, the rate of decrease in the byproduct-diffusion step is outweighed by the rate increases in the end-group collision and reaction steps.
3. An increase in the PET particle size at any crystallinity results in increased byproduct-diffusion resistance and increased rates of reverse reactions (because of increased byproduct concentrations within the polymer mass), but has no direct effects on end-group collision and rates of forward reactions. Therefore, there exists a critical particle size, at which the combined positive effect due to the increased crystallinity is exactly offset by the combined negative effect and,

hence, the SSP rate is not affected by the crystallinity. The critical particle size is determined to be about 7 μm .

4. With particle size greater than the critical particle size, the SSP rate of PET decreases with increasing crystallinity as commonly believed.

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