

Solid-State Polymerization of Poly(trimethylene terephthalate)

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ABSTRACT: The solid-state polymerization (SSP) of poly(trimethylene terephthalate) (PTT) has been studied and compared with that of poly(ethylene terephthalate) (PET). Because PTT and PET share the same SSP mechanism, the modified second-order kinetic model, which has successfully been used to describe the SSP behaviors of PET, also fits the SSP data of PTT prepolymers with intrinsic viscosities (IVs) ranging from 0.445 to 0.660 dL/g. According to this model, the overall SSP rate is $-dC/dt = 2k_a(C - C_{ai})^2$, where C is the total end group concentration, t is the SSP time, k_a is the apparent reaction rate constant, and C_{ai} is the apparent inactive end group concentration. With this equation, the effects of all factors that influence the SSP rate are implicitly and conveniently incorporated into two parameters, k_a and C_{ai} . k_a increases, whereas C_{ai} decreases, with increasing SSP temperature, increasing prepolymer IV, and decreasing pel-

let size, just as for the SSP of PET. Therefore, the SSP rate increases with increasing prepolymer IV and increasing SSP temperature. The apparent activation energy is about 26 kcal/mol, and the average SSP rate about doubles with each 10°C increase in temperature within the temperature range of 200–225°C. The SSP rate increases by about 30% when the pellet size is decreased from 0.025 to 0.015 g/pellet. Compared with PET, PTT has a much lower sticking tendency and a much higher SSP rate (more than twice as high). Therefore, the SSP process for PTT can be made much simpler and more efficient than that for PET. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3188–3200, 2003

Key words: solid-state polymerization; activation energy; polyesters

INTRODUCTION

Poly(trimethylene terephthalate) (PTT) is a newly commercialized polyester. With a unique combination of properties, PTT is particularly suited for use in textile and carpet fiber applications.^{1,2} PTT fibers have the resiliency and softness of nylon fibers and the chemical stability and stain resistance of poly(ethylene terephthalate) (PET) fibers. They will undoubtedly become an important new family of fibers. Currently, fiber-grade PTT resins are being marketed by Shell Chemical Co. and DuPont under the trade names of Corterra and Sorona, respectively. The number-average molecular weight (M_n) of PTT required for fiber applications is between 18,000 and 22,000, which is equivalent to an intrinsic viscosity (IV) between 0.80 and 0.94 dL/g, as measured in 60/40 phenol/tetrachloroethane at 30°C.

Manufacturing processes for PTT

Descriptions of the manufacturing processes for PTT can be found in the patent literature.^{3–5} Because PTT, in general, has properties similar to those of PET, its

manufacturing processes are similar to those used to produce PET. Nevertheless, there are sufficient differences in the properties between PTT and PET to result in substantial differences in the process requirements and process economies for the production of these two polyesters.

The melt-polymerization process for PTT, like that for PET, has two steps. The first step is the esterification of terephthalic acid (TPA) with 1,3-propanediol (PDO) or the transesterification of dimethyl terephthalate (DMT) with PDO. The second step is the polycondensation of the esterification or transesterification product, which is mainly a mixture of bis(3-hydroxy propyl) terephthalate and oligomers, *in vacuo*, which removes the polycondensation byproducts, PDO and water, until the desired molecular weight is reached. Lurgi Zimmer⁶ developed and is marketing a continuous process for the production of fiber-grade PTT resins (with an IV of 0.92 dL/g) with PDO and TPA as the precursors. In 2000, DuPont successfully started up a small continuous PTT polycondensation plant, which produces DMT-based PTT.⁷

The first step of the manufacturing process for PTT is basically the same as that for PET, except that PDO is used in place of ethylene glycol (EG). However, there are two major differences between the PTT and PET polycondensation steps. First, a titanium catalyst (usually a titanium alkanoate) is generally required for

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the polycondensation of PTT because the antimony catalyst commonly used in the polycondensation of PET is relatively inefficient. Second, because the thermal stability of PTT is much lower than that of PET and the chain scission of PTT produces dead ends, a maximum polycondensation temperature for PTT much lower than that for PET has to be used to prevent excessive degradation. This has a great impact on the process economy of the melt-polymerization process for PTT.

As the polycondensation proceeds, the melt viscosity increases dramatically. For the rapidly increasing melt viscosity to be countered, it is desirable to increase the reactor temperature in the polycondensation process. The use of a higher polycondensation temperature increases not only the diffusion rates of the reaction byproducts (PDO and water) but also the reaction rates. In the PET polycondensation, a reaction temperature in excess of 280°C can be used without excessive degradation reactions of the polymer being caused. With this high polycondensation temperature, the molecular weight of fiber-grade PET (ca. 20,000) can readily be achieved in a stirred-tank reactor, which is not very efficient in surface generation even if it is equipped with a helix or spiral agitator, and in a disk-ring (or basket) reactor, which is very efficient in surface generation. Because of the temperature constraint, if a stirred-tank reactor (as that used in a batch process) is used to conduct PTT polycondensation, the allowable temperature is too low to achieve the efficient removal of reaction byproducts by diffusion. Consequently, the IV required for fiber applications cannot be attained in a stirred-tank reactor. At some point before the required IV is reached, polymerization reactions are offset or even overwhelmed by degradation reactions. Many early researchers who tried to prepare fiber-grade PTT in a stirred-tank reactor were frustrated by this perplexing experience. Fiber-grade PTT can be produced by melt polymerization in a disk-ring reactor, which provides a high surface renewal rate to effect rapid byproduct removal. However, the reaction time required will be much longer than for PET because of the much lower polycondensation temperature. This means that a reactor volume much larger than that for PET will be required for the same production capacity. Because disk-ring reactors are very expensive, it is understood that a melt polycondensation process for fiber-grade PTT costs much more than that for fiber-grade PET. For example, according to Deiss,⁶ Zimmer's continuous melt-polymerization process for the production of fiber-grade PTT requires two disc-ring reactors (only one is required for the production of fiber-grade PET) and costs about two-thirds more than that for the production of fiber-grade PET for the same capacity.

Furthermore, because the solid-state polymerization (SSP) process for PTT can be much simpler and more

efficient than that for PET (to be explained later), a combination of a melt-polymerization process and an SSP process could be more economical than an all-melt-polymerization process for the production of fiber-grade PTT. In fact, Shell Chemical Co. has been producing fiber-grade PTT for years with such a combination of processes. First, a low-IV prepolymer is produced by a melt-polymerization process. The prepolymer is then further polymerized by an SSP process to an IV suitable for the desired application.

The SSP of PTT has been described in several U.S. patents.⁸⁻¹⁰ Stouffer et al.⁸ disclosed methods for preparing crystalline low-IV PTT prepolymer particles with large crystallite sizes. They claimed that these specially prepared PTT prepolymer particles do not require a lengthy annealing step before SSP and can be solid-state-polymerized at a higher temperature without sticking or agglomeration. Duh and Corey⁹ discovered that PTT pellets can safely be solid-state-polymerized at temperatures as high as a few degrees below the natural crystalline melting point (T_m) without a pretreatment and at temperatures above T_m after a few hours of SSP at a temperature below T_m . Duh¹⁰ disclosed a simplified continuous PTT SSP process in which the crystallization, drying, and preheating steps are combined into one single step, taking advantage of the fast crystallization rate and the low sticking tendency of PTT.

Rate equation for the SSP of PTT

SSP is the polycondensation that takes place at temperatures below T_m but above the glass-transition temperature (T_g) of the polymer. At these temperatures, the functional end groups are activated enough to collide and react with one another.

The SSP of a polyester has the following four steps: (1) the diffusion of functional end groups, (2) the collision and reaction of end groups, (3) the diffusion of reaction byproducts inside the polymer particle, and (4) the diffusion of reaction byproducts from the particle surface into the bulk of the gas phase.

There are two types of functional end groups in PTT, 3-hydroxy propyl and carboxyl (COOH). For convenience, the predominant end groups, the 3-hydroxy propyl end groups, are commonly called hydroxyl (OH) end groups. In DMT-based PTT, the COOH end groups are largely generated during the melt polycondensation stage as the result of chain scission degradation. In TPA-based PTT, some of the COOH end groups may be the remnants of the end groups of the precursor TPA. There are two types of polycondensation reactions in SSP, transesterification and esterification. Transesterification is the reaction between two OH ends with PDO as the reaction byproduct, and esterification is the reaction between a COOH end and an OH end with water as the reaction

byproduct. Because both polycondensation reactions are reversible reactions, unless the reaction byproducts are removed as soon as they are formed, backward transesterification and esterification reactions will take place. Backward polycondensation reactions can be prevented only if the polymer particle size is small enough (e.g., <60 mesh) and the purge gas flow around the polymer particles is fast enough as in the fluid-bed SSP of finely divided polyester.

Bamford and Wayne¹¹ first reported the two distinct characteristics of the SSP of PET. First, there exists a limiting IV. Once the limiting IV is reached, PET ceases to polymerize. Second, the SSP rate varies with the prepolymer IV: the higher the prepolymer IV is, the higher the SSP rate is. Many models with various degrees of complexity and sophistication have been proposed to describe the SSP of PET.^{11–20} Among them, the simple modified second-order kinetic model proposed by Duh^{19,20} appears to be quite adequate for the SSP of PET in most cases, ranging from the simplest fluid-bed SSP of a finely divided prepolymer with a zero carboxyl content to the most commonly practiced fixed-bed or moving-bed SSP of a pelletized prepolymer with both OH and COOH end groups. Because the behaviors of the SSP of PTT and PET are quite similar, this model is used to analyze the PTT SSP data in this article.

Therefore, for pelletized PTT, the SSP rate is expressed by the following equation:

$$-\frac{dC}{dt} = 2k_a(C - C_{ai})^2 \quad (1)$$

where C is the total end group concentration, t is the reaction time, k_a is the apparent reaction rate constant, and C_{ai} is the apparent inactive end group concentration.

This equation expresses the net solid-state polycondensation rate without making distinctions between hydroxyl ends and carboxyl ends. The effects of all factors, such as the catalyst concentration, temperature, prepolymer IV and COOH concentration, particle size, diffusion resistance, morphology, backward reactions, and degradation reactions, are lumped into two parameters, k_a and C_{ai} . Note that C and C_{ai} in eq. (1) are composite values based on the whole pellet and not point values.

By the integration of eq. (1) and with the initial condition $C = C_0$ at $t = 0$, the resulting equation can be rearranged into the following form:

$$\frac{C_0 - C}{t} = aC - b \quad (2)$$

where

$$a = 2k_a(C_0 - C_{ai}) \quad (3)$$

$$b = 2k_a(C_0 - C_{ai})C_{ai} \quad (4)$$

If eq. (1) fits the SSP data well, then the $(C_0 - C)/t$ versus C plot will be a straight line with slope a and intercept $-b$. From eqs. (3) and (4), C_{ai} is equal to b/a . Once the value of C_{ai} is known, k_a can readily be calculated with eq. (3).

Solving for C in eq. (2), we find

$$C = \frac{C_0 + bt}{1 + at} \quad (5)$$

According to this equation, as t approaches infinity, C approaches C_{ai} , which determines the limiting IV, IV_∞ .

In the polyester industries, C is often given in the unit of $\mu\text{mol/g}$. Therefore, C can be related to M_n by

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

In U.S. Patent 6,403,762,¹⁰ M_n values are given for five IVs (ranging from 0.25 to 0.94 dL/g) of PTT as measured in a 60/40 phenol/tetrachloroethane solvent at 30°C. From these data, the following Mark–Houwink equation is obtained to correlate the IV ($[\eta]$) and M_n of PTT:

$$[\eta] = 3.13 \times 10^{-4} M_n^{0.80} \quad (7)$$

With eqs. (5)–(7), the IV at any time during the SSP can be predicted by the following equation:

$$[\eta] = 34.3849 \left(\frac{1 + at}{C_0 + bt} \right)^{0.80} \quad (8)$$

EXPERIMENTAL

Prepolymers used in this study

Five PTT prepolymers were used in the experiments for this study. All of these prepolymers were produced from PDO and TPA in the pilot plant at the Polyester Technical Center of Shell Chemical Co. (Akron, OH). All the prepolymers contained 60 ppm Ti catalyst. Because the pellet sizes of these prepolymers as produced were not uniform, each was dried at 140°C in a vacuum oven overnight and then repelletized with a small extruder and a small pelletizer to obtain uniform pellets of desired sizes (commonly measured in grams per 100 pellets) for the experiments. The IV and COOH content did not change significantly before and after the repelletizing. Table I shows the IVs, COOH concentrations, and pellet sizes of these prepolymers after repelletizing. Prepolymers A, B, and C, with different IVs but approximately equal pellet sizes (≈ 1.90 g/100), were used to study

TABLE I
Selected Properties of the Prepolymers Used in
the SSP Experiments

Polymer	IV (dL/g)	COOH concentration ($\mu\text{mol/g}$)	Pellet size (g/100)
A	0.540	10	1.92
B	0.660	15	1.89
C	0.445	22	1.91
D	0.560	12	1.22
E	0.561	12	2.50
F	0.560	13	4.10

the effects of the temperature and prepolymer IV, IV_0 , on the SSP of PTT. Prepolymers D, E, and F, which were repelletized from the same melt polymer and had different pellet sizes, were used to study the effect of the pellet size on the SSP of PTT. All of these prepolymers had approximately equal T_g (45°C) and T_m (228°C) values. The true T_g should be lower than 45°C because all the repelletized prepolymers had degrees of crystallinity between 12 and 18%. DuPont researchers⁸ reported the T_g of PTT to be 35°C.

SSP experiments

The reactor used to conduct the SSP runs was constructed of a 50-cm-long glass column with a diameter of 37 mm. The reactor had a cone-shaped bottom, which was connected to a 7-mm-diameter, 150-cm-long nitrogen supply tube, which was coiled up around the lower half of the reactor column. During the experimental runs, the reactor with its nitrogen supply tube was immersed in a thermostated oil bath about 30 cm deep. The nitrogen supply tube also served as a heat exchanger, which heated the incoming nitrogen to the desired experimental temperature.

About 100 g of the prepolymer was used for each SSP run. The prepolymer was first crystallized and dried at 160°C for 1 h with a nitrogen stream passing through the polymer bed in the reactor at a flow rate of 7 standard liters per minute (SLPM). At this nitrogen flow rate, the polymer bed remained static. During the hour-long drying time, the polymer IV did not change significantly. Then, the oil temperature was raised to the desired SSP temperature, which ranged from 190 to 225°C. Meanwhile, the nitrogen flow rate was temporarily raised to 45–50 SLPM to fluidize the polymer bed to increase the heat-up rate of the polymer. It took about 10 min for the polymer to reach the desired SSP temperature. Then, the nitrogen flow rate was reduced to 7 SLPM to maintain a fixed bed during the SSP step, which lasted 18–22 h.

Samples were taken with a suction tube at various intervals throughout the SSP. The IV of each sample was measured.

It was surprising to note that, even at the highest SSP temperature used (225°C), the PTT samples could easily be sucked up without the need for chiseling the polymer bed with a pointed metal rod, as is necessary when PET samples are taken during SSP (usually conducted at about 210°C). This indicates that PTT has a much lower sticking tendency and can be solid-state-polymerized at higher temperatures than PET without sticking, even though PET has much higher T_g (ca. 74°C) and T_m (ca. 256°C) values.

RESULTS AND DISCUSSION

Testing of the adequacy of the rate equation

The IV data for the samples taken during the SSP of prepolymer A at various temperatures are presented in U.S. Patent 6,441,129.⁹ The IV data are plotted in Figure 1. With these IV data, $(C_0 - C)/t$ can be plotted against C for each SSP temperature, as shown in Figure 2. Five straight lines are obtained for the five SSP temperatures. With slope a and intercept $-b$ of each straight line known, the IV at any time during the SSP at each temperature can be predicted with eq. (8). Therefore, the curves of the IV versus the SSP time in Figure 1 are obtained for the five SSP temperatures with eq. (8). In the same fashion, curve fittings of the IV data for the SSP of prepolymers B and C with the proposed rate equation can be done, as shown in Figures 3 and 4. It can be seen in Figures 1, 3, and 4 that the curves fit the IV data quite well. Therefore, the proposed rate equation is adequate for the SSP of PTT.

The values of C_{ai} and k_a for the SSP of prepolymers A, B, and C can readily be calculated from the corresponding values of a and b and are listed in Table II.

Effects of the temperature and prepolymer IV on SSP

The IV buildup curves in Figures 1, 3, and 4 show that the SSP rate of PTT increases pronouncedly with the temperature. In each of these figures, the IV buildup curves appear to level off at different IVs as the SSP time approaches infinity; this indicates that the limiting IV attainable by SSP increases with the SSP temperature.

Because the SSP rate as expressed by eq. (1) is affected by C_{ai} as well as k_a , k_a alone is not sufficient for comparing the relative SSP rates at different temperatures. There are two ways of comparing the SSP rates at different temperatures. One way is to compare the actual SSP rate at a particular IV or C value with eq. (1). For example, the SSP rates of prepolymer A (with $IV_0 = 0.54$ dL/g) at 0.70 dL/g ($C = 130$ $\mu\text{mol/g}$) are 2.57, 6.25, 11.91, 24.78, and 37.65 $\mu\text{mol/g/h}$ at 190, 200, 210, 220, and 225°C, respectively. Between 200 and 225°C, the SSP rate at 0.70 dL/g about doubles with

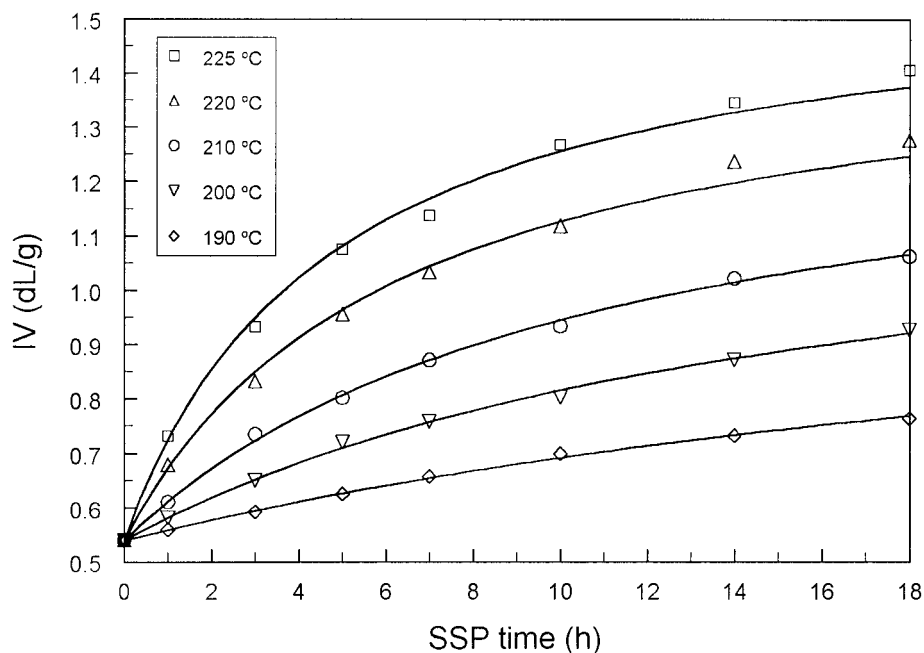


Figure 1 IV buildup curves for SSP of prepolymer A with an IV of 0.54 dL/g at various temperatures.

each 10°C increase in temperature. However, between 190 and 200°C, the temperature effect is substantially greater. Note that at different IVs, the temperature effects are usually different. For example, at 0.80 dL/g and between 200 and 225°C, the SSP rate increases by about 115% if the temperature is raised by 10°C. Alternately, the average SSP rate over a particular IV range may be compared. This is actually more useful in practice. For example, the average SSP rates between IVs of 0.54 and 0.92 dL/g at various tempera-

tures may be estimated by the determination of the SSP time requirements with Figure 1 or eq. (9). Therefore, the SSP times required for prepolymer A to achieve the product IV of 0.92 dL/g are 49.0, 18.0, 8.9, 4.12, and 2.65 h at 190, 200, 210, 220, and 225°C, respectively. The average SSP rate within the IV range of 0.54–0.92 and the temperature range of 200–225°C about doubles with each 10°C increase in temperature. The effects of the temperature on the SSP rates of PTT and PET are quite similar.

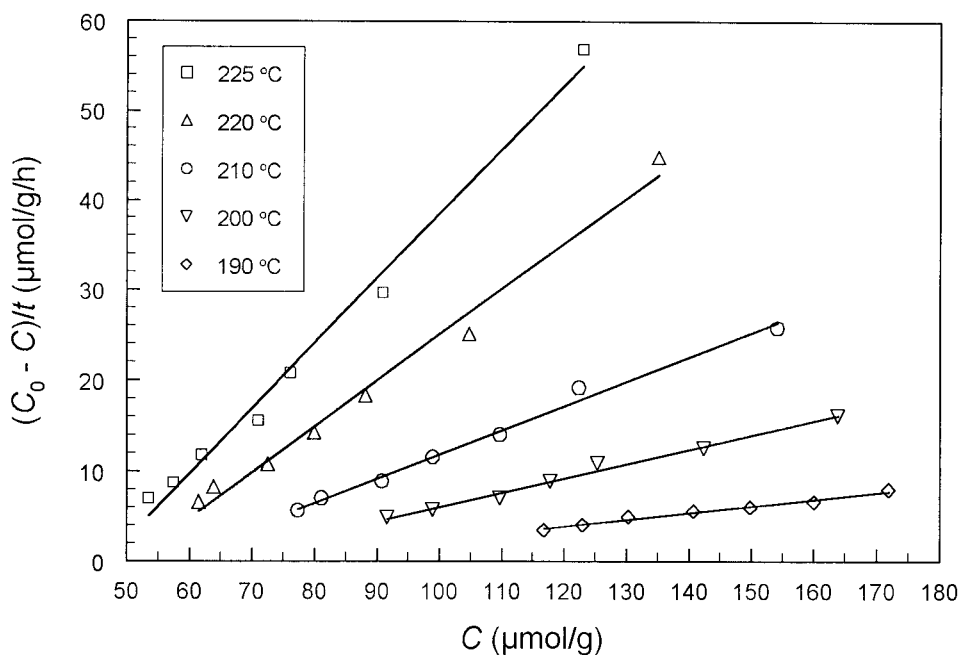


Figure 2 $(C_0 - C)/t$ versus C plots for SSP of prepolymer A with an IV of 0.54 dL/g at various temperatures.

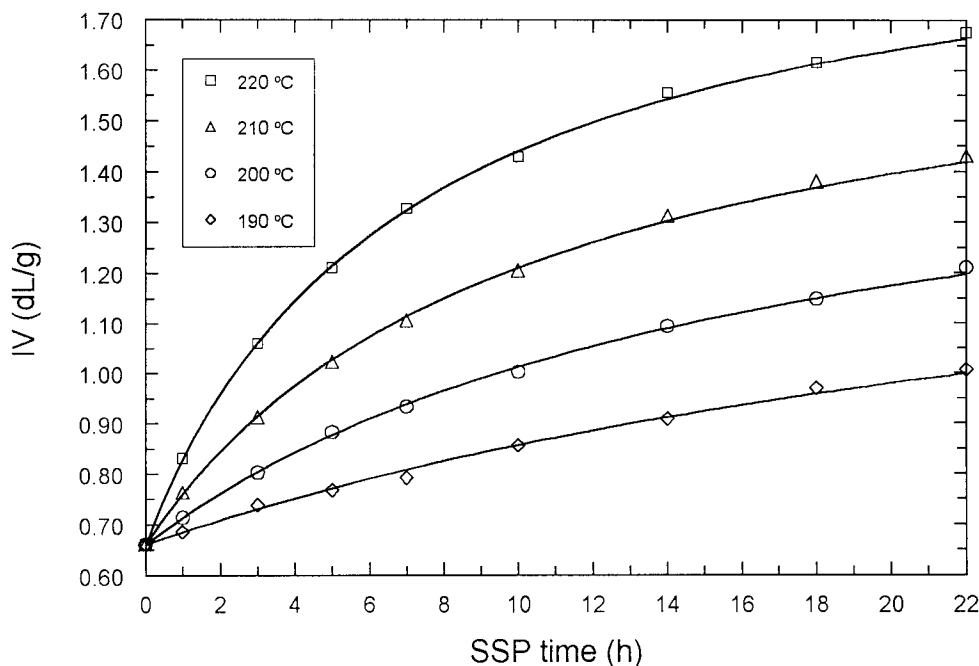


Figure 3 IV buildup curves for SSP of prepolymer B with an IV of 0.66 dL/g at various temperatures.

Figure 5 compares the curves of the IV versus the SSP time for the SSP of prepolymers A, B, and C at 210°C. These three prepolymers have practically equal pellet sizes (ca. 1.90 g/100) but different IVs. The SSP rate and the limiting IV also increase with increasing prepolymer IV.

The effects of the SSP temperature and the prepolymer IV on the SSP rate and the limiting IV can be explained in terms of C_{ai} and k_a . From Table II, it is

obvious that C_{ai} decreases and k_a increases with increasing SSP temperature and prepolymer IV. Therefore, according to eq. (1), the SSP rate increases with increasing prepolymer IV as well as increasing SSP temperature.

The apparent rate constant k_a increases with increasing temperature simply because the reactivities of the end groups, the mobilities of the chain segments, and the diffusivities of the reaction byproducts increase

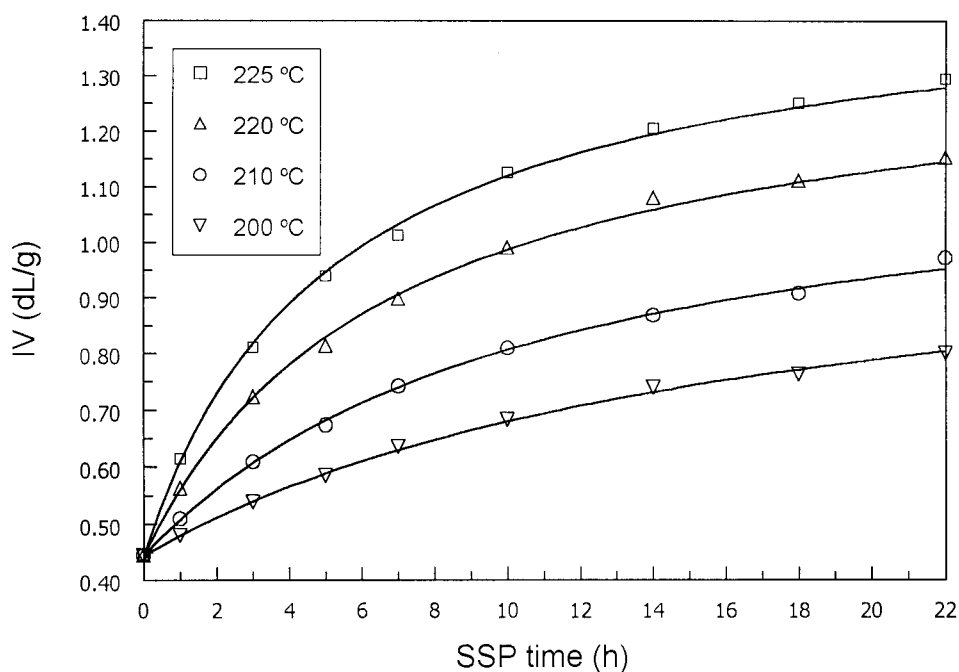


Figure 4 IV buildup curves for SSP of prepolymer C with an IV of 0.445 dL/g at various temperatures.

TABLE II
Values of a , b , C_{ai} and k_a for SSP of Prepolymers A, B, and C at Various Temperatures

Prepolymer		Temperature (°C)	a (h) ⁻¹	b [(μmol/g) (h) ⁻¹]	C_{ai} (μmol/g)	$k_a \times 10^3$ [(μmol/g) ⁻¹ (h) ⁻¹]
ID	IV (dL/g)					
C	0.445	200	0.1581	11.8762	75.12	0.5134
		210	0.2777	18.2324	65.65	0.8496
		220	0.5062	28.4274	56.16	1.4636
		225	0.7292	37.0252	50.78	2.0447
A	0.540	190	0.0756	5.1828	68.55	0.3396
		200	0.1579	9.7294	61.62	0.6676
		210	0.2665	14.7892	55.49	1.0713
		220	0.5060	25.5096	50.41	1.9543
		225	0.7176	33.2441	46.33	2.6867
B	0.660	190	0.0753	3.7050	49.20	0.4148
		200	0.1603	7.3234	45.69	0.8501
		210	0.3002	12.2364	40.76	1.5130
		220	0.5002	17.6816	35.35	2.3906

with increasing temperature. Note that the faster the reaction byproducts diffuse out of the pellets, the lesser the accumulations are of the reaction byproducts within the pellets and the slower the backward reactions are, and therefore, the greater the apparent rate constant is and the higher the net SSP rate is.

Some of the apparent inactive end groups are truly inactive end groups. These include chemically dead end groups (a small fraction) and end groups that are firmly trapped in the crystalline structure and unable to participate in the polycondensation reactions. As the temperature is increased, some of the end groups that are inactive at lower temperatures become sufficiently activated to participate in the reactions (in

other words, some of the previously trapped end groups are released into the amorphous phase). Therefore, C_{ai} decreases with increasing temperature.

There are two reasons why C_{ai} decreases with increasing prepolymer IV. First, as the molecular weight increases, it becomes more difficult for the polymer chains to fit into the crystal lattices, and the mobility of the chain segments is increased. Consequently, fewer end groups will be trapped and rendered inactive. Second, because there are fewer end groups in a higher IV prepolymer, statistically, less end groups are trapped and rendered inactive.

Figure 6 shows Arrhenius plots for the SSP of prepolymers A, B, and C with the k_a values listed in Table

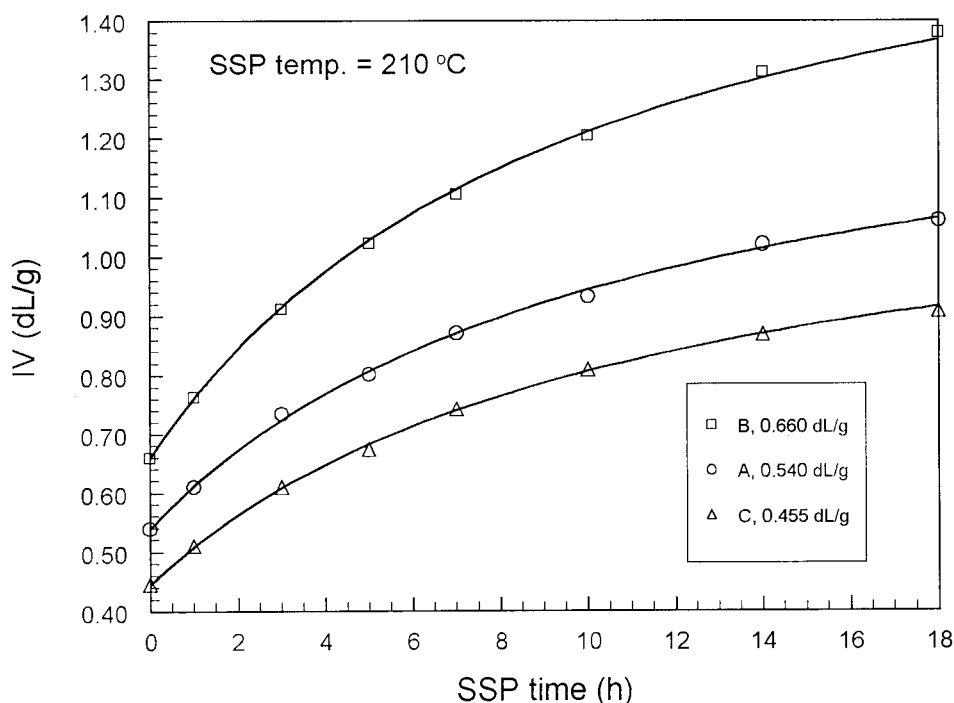


Figure 5 Comparison of IV buildup curves for SSP of prepolymers A–C with different IVs at 210°C.

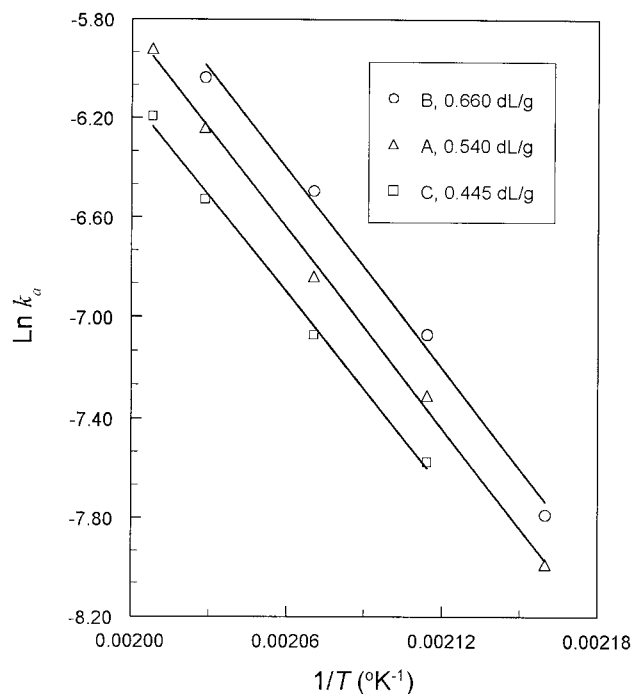


Figure 6 Arrhenius plots for SSP of prepolymers A–C with different IVs.

II. Three nearly parallel straight lines are obtained for these three prepolymers with different IVs. Therefore, the temperature dependence of the apparent rate constant for the SSP of each of these three prepolymer can be represented by an Arrhenius equation:

$$k_a = A_a \exp\left(\frac{-E_a}{RT}\right) \quad (9)$$

where A_a is the apparent frequency factor, E_a is the apparent activation energy, T is the absolute temperature, and R is the universal gas constant. The values of A_a and E_a for each prepolymer can be determined from the intercepts and slopes, respectively, of each corresponding straight line and are listed in Table III.

E_a appears to be quite constant ($\cong 26$ kcal/mol) within the prepolymer IV range of 0.445–0.66 dL/g. This is slightly greater than the activation energy (23.6 kcal/mol) for the fluid-bed SSP of powdered, low-IV (0.20–0.35 dL/g) PET with a zero COOH content and substantially greater than E_a (19.5 kcal/mol) for the fixed-bed SSP of 0.57 dL/g IV, pelletized PET as reported by Duh.^{19,20}

In Figure 7, C_{ai} is plotted against T for the SSP of each of the three prepolymers with the C_{ai} data in Table II. For each prepolymer, C_{ai} is approximately a linear function of T . Therefore,

$$C_{ai} = -0.9677T + 532.972$$

for prepolymer C with 0.445 dL/g IV (10)

$$C_{ai} = -0.617T + 353.876$$

for prepolymer A with 0.54 dL/g IV (11)

$$C_{ai} = -0.4648T + 264.9244$$

for prepolymer B with 0.66 dL/g IV (12)

On the basis of the slopes of these straight lines, the effect of temperature on C_{ai} decreases with increasing prepolymer IV.

With eqs. (3), (4), and (8)–(12), the IV at any time during the SSP of any of these three PTT prepolymers at any temperature between 190 and 225°C can be estimated.

Effect of the particle size

Prepolymers D, E, and F with the same IV (0.56 dL/g) and COOH concentrations (ca. 12 $\mu\text{mol/g}$) but different pellet sizes (1.22, 2.50, and 4.10 g/100, respectively) were used to study the effect of the pellet size on the SSP of PTT. Figure 8 shows the IV buildup curves for the SSP of these three prepolymers at 210°C. As expected, the SSP rate decreases with increasing pellet size because the average diffusion resistance increases with increasing pellet size. Table IV lists the values of C_{ai} and k_a for the SSP of these three prepolymers at 210°C.

It is obvious that C_{ai} increases and k_a decreases with increasing pellet size. An increase in the particle size not only increases the diffusion resistances to the reaction byproducts, PDO and water, but also increases the byproduct concentrations within the polymer particles; this, in turn, increases the backward reaction rates of transesterification and esterification. These effects are reflected by the increased C_{ai} values and the decreased k_a values.

Additional data showing the effect of the pellet size on the SSP rate of PTT have been presented in U.S. Patent 6,441,129⁹ in terms of the SSP times required for the prepolymer to achieve a product IV of 0.92 dL/g. Selected data useful in the commercial SSP process are listed in Table V.

The SSP time requirement data in Table V can be converted into relative average SSP rates (R_{rn}). Because both series of prepolymers include a common pellet size of 2.50 g/100, we may set $R_{rn} = 1$ for the 2.50 g/100 pellet size for

TABLE III
Values of A_a and E_a for SSP of Prepolymers A, B, and C with Different IVs.

Prepolymer ID	Prepolymer IV (dL/g)	A_a [$(\mu\text{mol/g})^{-1}(\text{h})^{-1}$]	E_a (cal/mol)
B	0.66	1.3974×10^9	26,490
A	0.54	1.1212×10^9	26,510
C	0.445	3.4484×10^8	25,620

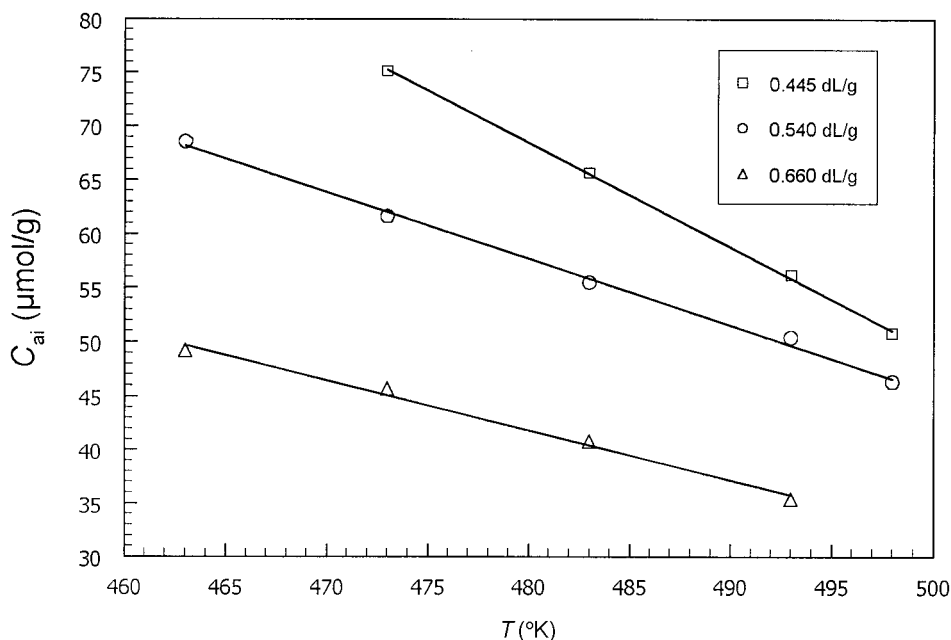


Figure 7 Effects of the temperature and prepolymer IV on C_{ai} for SSP of PTT.

each of the two series of prepolymers. R_{ra} for a particular pellet size is defined as follows:

$$R_{ra} = \frac{\text{SSP time requirement for 2.50/100 g pellet size}}{\text{SSP time requirement for the particular pellet size}}$$

Therefore, the R_{ra} values are obtained for each of the pellet sizes for each of the two series of prepolymers.

In Figure 9, R_{ra} is plotted against the pellet size. All the data points fall approximately on a straight line obtained by a linear regression of the average values of R_{ra} at various pellet sizes. The straight line is represented by the following equation:

$$R_{ra} = -0.31S_p + 1.775 \quad (13)$$

where S_p is the pellet size (g/100). This means that, within the prepolymer IV range of 0.56–0.666 dL/g,

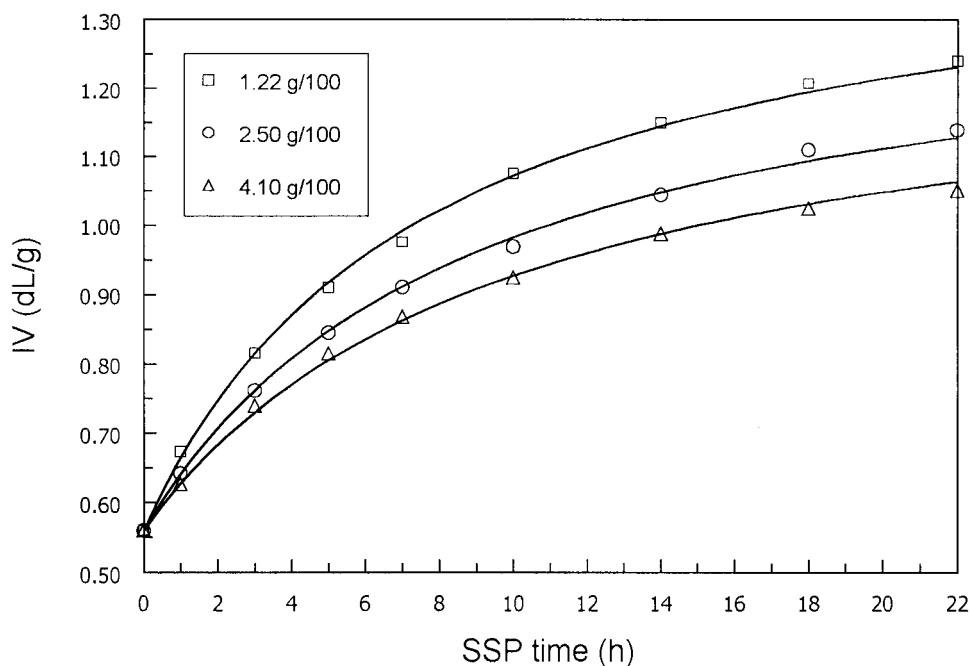


Figure 8 Effect of the pellet size on the SSP rate of the PTT prepolymer with an IV of 0.56 dL/g at 210°C.

TABLE IV
Values of C_{ai} and k_a for the SSP of Prepolymers
D, E, and F at 210°C

Prepolymer ID	Prepolymer pellet size (g/100)	C_{ai} ($\mu\text{mol/g}$)	$k_a \times 10^3$ ($\mu\text{mol/g}$) ⁻¹ (h) ⁻¹
D	1.22	50.33	1.5907
E	2.50	56.64	1.3207
F	4.10	60.34	1.1543

temperature range of 200–220°C, and pellet size range of 1.44–2.90 g/100, the SSP rate of PTT increases by 31% for each 1.0 g/100 decrease in pellet size. For comparison, the SSP rate of PET with a near-optimal COOH concentration increases by about 15% for each 1.0 g/100 decrease in pellet size according to heretofore unpublished data generated by the author. Therefore, the effect of the pellet size on the SSP rate of PTT is about twice that on the SSP rate of PET. There are two reasons. First, the major polycondensation byproduct of PTT, PDO, has a lower diffusivity than the major polycondensation byproduct of PET, EG. Second, because the PTT prepolymers tested had low [COOH]/[OH] ratios (<0.12), whereas the PET prepolymers tested had near optimal [COOH]/[OH] ratios (ca. 0.50), the SSP byproduct ratio of the PTT prepolymers, PDO/water, was much higher than that of the PET prepolymer, EG/water.

Equation (13) is very useful for estimating the SSP time requirements for various pellet sizes from a known SSP time requirement for a particular pellet size. In fact, with eqs. (3), (4), and (8)–(13), it is also possible to estimate the SSP time requirement of a PTT prepolymer with any IV between 0.56 and 0.66 dL/g and any pellet size between 1.44 and 2.90 g/100 at any temperature between 200 and 220°C without SSP experiments being conducted. For example, suppose we need to know the approximate SSP time required for a PTT prepolymer with an IV of 0.60 dL/g and a pellet size of 2.20 g/100 to solid-state-polymerize at 215°C to a product IV of 0.92 dL/g. This can be done in three steps. First, calculate the SSP time requirements for prepolymers with IVs of 0.445, 0.54, and 0.66 dL/g and a pellet size of 1.90 g/100 with k_a and C_{ai} values calculated with eqs. (9)–(12). Second, estimate the SSP time requirement for a prepolymer with an IV of 0.60 dL/g and a pellet size of 1.90 g/100 by interpolation with the SSP time requirements obtained for the three prepolymers in the first step. Third, calculate the R_{ra} values for prepolymers with pellet sizes of 1.90 and 2.20 g/100 and then calculate the desired SSP time requirement with the two R_{ra} values and the SSP time requirement value obtained in the second step.

Effects of the prepolymer carboxyl concentration

The concentration of the carboxyl end groups in the prepolymer has a great effect on the SSP rate of PET. It has been demonstrated that in the SSP of powdered PET, in which the diffusion resistance is small or negligible, the highest SSP rate is achieved with a zero carboxyl concentration and the SSP rate decreases monotonously with increasing prepolymer carboxyl concentration.^{19,20} However, in the presence of substantial diffusion resistance (as in the SSP of pelletized PET), there exists an optimal prepolymer carboxyl concentration for the fastest overall SSP rate.²⁰ This is because the presence of diffusion resistance favors esterification, which generates a byproduct (water) with a higher diffusivity than the byproduct of transesterification (EG). In most cases, the optimal COOH concentration for the SSP of pelletized PET is about one-third of the total end group concentration.

Because the byproduct of PTT transesterification, PDO, is a bigger molecule with a lower diffusivity than EG, it is expected that the COOH concentration should have an even greater effect on the SSP of PTT. However, a cursory study yielded seemingly contradictory results.

Prepolymers with IVs of about 0.65 dL/g and COOH concentrations ranging from 10 to 45 $\mu\text{mol/g}$ (accounting for 7.0–31.5% of the total end group concentration) produced in a batch polycondensation plant of Shell Chemical Co. were tested. In normal production, most prepolymers have COOH concentrations within the range of 10–20 $\mu\text{mol/g}$. Higher COOH concentrations are results of excessively long hold times during pelletizing or process upsets. Needless to say, the preparation of the prepolymers was not rigorous. Therefore, only qualitative conclusions can be drawn from the experimental observations.

The test results showed that the SSP rates for prepolymers with 10–20 $\mu\text{mol/g}$ COOH concentrations (typical prepolymers in normal production) were approximately equal, but the SSP rates for prepolymers with COOH concentrations higher than 25 $\mu\text{mol/g}$ decreased markedly with increasing COOH concen-

TABLE V
SSP Times (h) Required for PTT Prepolymers with
Various Pellet Sizes to Solid-State-Polymerize to
0.92 dL/g, IV at Various Temperatures

IV (dL/g)	Prepolymer Pellet size (g/100)	SSP temperature (°C)		
		200	210	220
0.560	1.50	11.3	5.7	2.9
	2.04	13.3	6.6	3.4
	2.50	15.0	7.5	3.5
	2.90	17.0	8.3	4.3
0.666	1.44	5.4	2.7	1.4
	1.90	6.2	3.1	1.6
	2.50	7.2	3.6	1.9

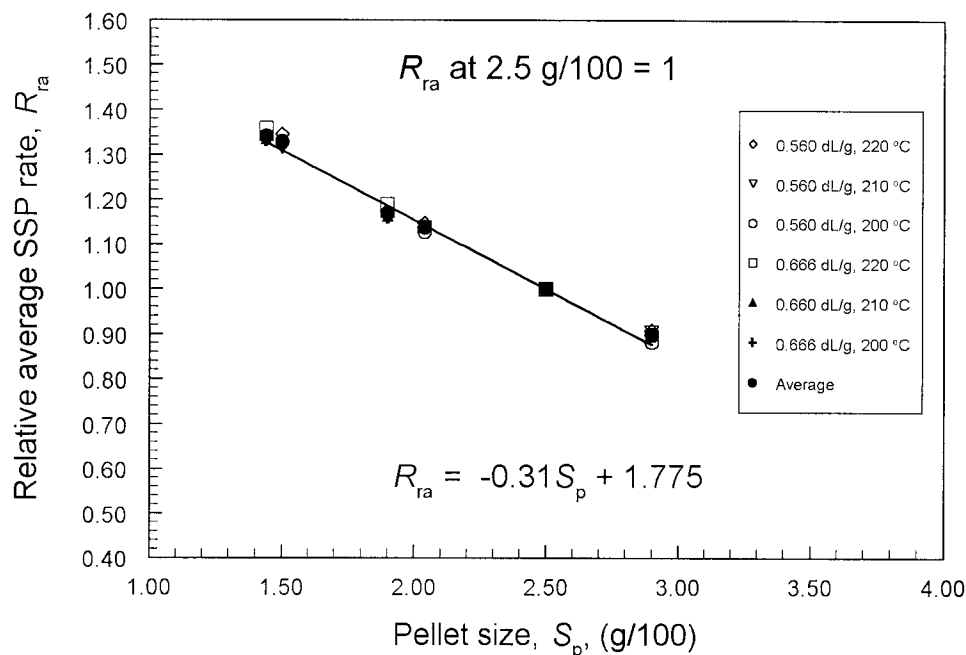


Figure 9 Effect of S_p on R_{ra} for PTT prepolymers with two different IVs at three different temperatures.

trations, contrary to expectation. Subsequent tests revealed that prepolymers with higher COOH concentrations also had higher allyl end group concentrations, which did not change significantly after the SSP. This finding not only can explain the unexpected SSP results of the prepolymers with various COOH concentrations but also provides another reason why the melt polycondensation of PTT must be conducted at temperatures substantially lower than the melt polycondensation temperatures for PET.

The allyl ends are mainly created by chain scission, which also creates COOH ends at the same time during the melt polycondensation of PTT. Because allyl ends behave as dead ends, the formation of allyl ends must be restrained with milder melt polycondensation temperatures. This is an important difference between the melt polycondensations of PTT and PET. Unlike allyl ends, the vinyl ends created by chain scission during the melt polycondensation of PET readily react with OH ends (2-hydroxy ethyl ends) to reform diester links and generate acetaldehyde. Therefore, the creation of COOH ends and acetaldehyde can be considered as the end results of chain scission during the melt polycondensation of PET, which is not always undesirable. For example, without chain scission, a DMT-based PET prepolymer will have a very low COOH concentration and, therefore, a low SSP rate. The COOH concentration of the PET prepolymer and its SSP rate can be pronouncedly increased with a higher temperature to promote chain scission during melt polycondensation.

For the SSP of the PTT prepolymers with COOH concentrations within the range of 10–20 $\mu\text{mol/g}$, the

effect of a higher average byproduct diffusion rate due to a higher COOH concentration is just about offset by the effect of a lower reaction rate due to the higher dead end group (allyl end group) concentration. For the SSP of the PTT prepolymers with COOH concentrations higher than 25 $\mu\text{mol/g}$, the effect of a lower reaction rate due to a higher dead end group concentration is greater than the effect of a higher average byproduct diffusion rate due to a higher COOH concentration.

Obviously, the effect of the COOH concentration on the SSP of PTT merits a rigorous study. So that the true effect can be observed, prepolymers with nearly equal IVs, various COOH concentrations, and minimal allyl end group concentrations must be carefully prepared. Because most of the COOH end groups in DMT-based PTT are created by chain scission, which also creates allyl end groups, PTT prepolymers to be used for a study must be prepared from PDO and TPA. For minimal allyl end group formation, the polycondensation should preferably be conducted in a disk-ring type reactor (or another type of reactor that provides a very high surface generation rate) at a relatively low temperature (e.g., $\leq 260^\circ\text{C}$). Admittedly, this will not be an easy task.

Comparison of the SSP rates of PTT and PET

Because the SSP rate increases with the increasing molecular weight of the prepolymer, for a fair comparison of the SSP rates of PTT and PET, prepolymers with approximately equal molecular weights must be

TABLE VI
Comparison of Average SSP Rates of PTT and PET at 220°C

Type	Prepolymer			Pellet size (g/100)	SSP time required to reach M_n of 21,600	Average SSP rate ($\mu\text{mol/g/h}$)
	IV (dL/g)	M_n	% COOH ends ^a			
PTT	0.445	8,700	9.6	1.6	6.86	19.9
PET	0.36	8,800	35.5	1.6	15.50	8.7
PTT	0.54	11,100	5.6	2.5	4.84	18.0
PET	0.42	11,000	28.2	2.5	10.72	8.3
PTT	0.66	14,300	10.7	2.3	1.90	24.9
PET	0.5	14,200	31.4	2.3	4.4	10.9

^a % COOH ends is the percentage of total ends that are COOH ends.

used. In practice, the average SSP rate between two particular molecular weights is more useful than any SSP rate at a particular molecular weight. Therefore, the average SSP rates of PTT and PET between a product M_n of 21,600 (equivalent to an IV of 0.92 dL/g for PTT and 0.665 dL/g for PET measured in the same IV solvent at the same temperature) and three prepolymer M_n 's at 220°C are listed in Table VI for comparison. The average SSP rate values for PET are estimated from heretofore unpublished data compiled by the author. The average SSP rate values for PTT are estimated with Figures 1, 3, and 4 and eq. (13).

It can be seen in Table VI that, for the three sets of prepolymers with similar molecular weights, PTT solid-state-polymerizes about 2.2 times as quickly as PET. Note that all the PET prepolymers have close to optimal COOH concentrations (ca. one-third of the total end group concentrations), whereas all the PTT prepolymers have far below optimal COOH concentrations (expected to be greater than one-third of the total end group concentrations). Therefore, the SSP rates of these PTT prepolymers can potentially be increased substantially by the optimization of their COOH concentrations.

Feasibility of combining melt-polymerization and SSP processes for the production of fiber-grade PTT

Although SSP has widely been used to produce PET for bottle, tire cord, and food tray applications, which require very low acetaldehyde contents and/or very high IVs, it has never been used commercially in the production of fiber-grade PET, mainly because fiber-grade PET can easily and economically be produced by a melt-polymerization process alone. As mentioned earlier, an all-melt-polymerization process for the production of fiber-grade PTT is very costly. Furthermore, the SSP process for PTT is much more efficient than that for PET. Therefore, the production of fiber-grade PTT by a melt-polymerization process followed by SSP appears economically viable.

Besides the fact that PTT solid-state-polymerizes more than twice as fast as PET, the PTT SSP process

can be much simpler and more trouble-free than the PET SSP process, and the PTT SSP reactor can safely be operated (without polymer sticking) at higher temperatures to achieve even greater SSP rates. Therefore, the PTT SSP process should be more efficient and economical than the PET SSP process with equal molecular-weight upgrading and throughput rate.

The standard continuous PET SSP process consists of crystallization, drying/annealing, preheating, reaction, and product cooling steps. Because of the high sticking tendency of PET during crystallization and preheating, vigorous agitation must be provided for the crystallizer and the preheater. The capital and operating costs for the crystallizer and preheater account for the major parts of the total production cost of the PET SSP process.

Taking advantage of the low sticking tendency of PTT due to its lower crystallization temperature, faster crystallization, higher crystallinity, and faster morphological transformation, Duh¹⁰ proposed a simplified PTT SSP process, in which the crystallization, annealing, and preheating steps are combined into one single step. Because only mild agitation is required to prevent the sticking of PTT, the operation cost and the capital cost of such a simplified SSP process can greatly be reduced.

As demonstrated by Duh and Corey,⁹ PTT can be solid-state-polymerized at a temperature as high as 225°C in a continuous SSP process without polymer sticking. This is only about 3°C below the natural T_m of PTT. For comparison, the maximum safe temperature for unmodified PET in the continuous SSP process is about 215°C, about 40°C below the natural T_m of PET.

Currently, there are many smaller PET melt-polymerization and SSP plants that are idle because they are no longer competitive. It is believed that some of these plants can advantageously be revamped to produce fiber-grade PTT with a combination of melt and SSP processes that can be economically attractive. This could be an especially prudent way of manufacturing fiber-grade PTT before the market is well developed.

CONCLUSIONS

The shapes of the IV buildup curves for the SSP of PTT are similar to those of the SSP of PET because PTT and PET share the same SSP mechanism. Therefore, it is not surprising that an empirical rate equation proposed for the SSP of PET also fits the SSP data of PTT very well. This rate equation is based on a model that assumes that there are two apparent categories of end groups in the PTT during SSP, apparent active and apparent inactive, and that the overall SSP rate is second-order with respect to the apparent active end group concentration. Therefore, the proposed rate equation contains two parameters, k_a and C_{ai} . With this model, it is not necessary to explicitly distinguish the two kinds of functional end groups, hydroxyl and carboxyl, and the two types of polycondensation reactions, transesterification and esterification, with their respective byproducts, PDO and water. With this model, it is also not necessary to explicitly break down the SSP process into different steps. Instead, the effects of all the factors that influence the SSP rate are implicitly and conveniently accounted for by the two parameters. For example, k_a increases and C_{ai} decreases with increasing SSP temperature and prepolymer IV and decreasing pellet size.

Within the prepolymer IV range of 0.445–0.660 dL/g, E_a for the SSP of pelletized PTT is approximately 26 kcal/mol, and the average SSP rate about doubles with each 10°C increase in temperature between 200 and 225°C. On the basis of the change in M_n or the end group concentration, PTT solid-state-polymerizes more than twice as quickly as PET. The effect of the pellet size on the SSP of PTT is more than twice as great as that on the SSP of PET: within the pellet size range of 1.5–2.9 g/100, the SSP rate of PTT increases by about 31% for each 1.0 g/100 decrease in the pellet size.

It has been discovered that the allyl ends created by chain scission during the melt polycondensation of PTT behave as dead ends during melt polymerization and SSP, unlike the vinyl ends in PET, which can

participate in polycondensation with OH ends. Therefore, the formation of allyl ends during the production of PTT prepolymers must be strictly limited.

Because of the substantially lower thermal stability of PTT relative to PET, the melt polycondensation of PTT has to be conducted at much lower temperatures than for PET. This makes an all-melt-polymerization process for the production of fiber-grade PTT much more complicated and expensive than that for the production of fiber-grade PET. Furthermore, because of the lower sticking tendency, higher safe SSP temperature, and much faster SSP rate of PTT relative to PET, the PTT SSP process is much more efficient and economical than the PET SSP process. Consequently, the production of fiber-grade PTT by a combination of a melt-polymerization process and an SSP process can be more economically attractive than an all-melt-polymerization process.

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