

Effects of the Carboxyl Concentration on the Solid-State Polymerization of Poly(ethylene terephthalate)

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ABSTRACT: There are two types of polycondensation reactions in the solid-state polymerization (SSP) of poly(ethylene terephthalate) (PET), namely, transesterification and esterification. Transesterification is the reaction between two hydroxyl ends with ethylene glycol as the byproduct, and esterification is the reaction between a carboxyl end and a hydroxyl end with water as the byproduct. The SSP of powdered PET in a fluid bed is practically a reaction-controlled process because of negligible or very small diffusion resistance. It can be proved mathematically that an optimal carboxyl concentration for reaction-controlled SSP exists only if $k_2/k_1 > 2$, where k_2 and k_1 are the forward reaction rate constants of esterification and transesterification, respectively. Several interesting observations were made in fluid-bed SSP experiments of powdered PET: (1) the SSP rate increases monotonously with decreasing carboxyl concentration, (2) $k_2 < k_1$ in the presence of sufficient catalyst, (3) k_1 decreases with increasing carboxyl concentration if the catalyst concentration is insufficient, and (4) the minimum catalyst concentration required to achieve the highest SSP rate decreases with decreasing carboxyl concentration. In the SSP of pelletized PET, both reaction and diffusion are important, and there exists an optimal carboxyl concentration for the fastest SSP rate because esterification, which generates the faster diffusing byproduct, is retarded less than transesterification in the presence of substantial diffusion resistance. The optimal prepolymer carboxyl concentration, which ranges from 25 to 40% of the total end-group concentration in most commercial SSP processes, increases with increasing pellet size and product molecular weight. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1288–1304, 2002

Key words: poly(ethylene terephthalate) (PET); solid-state polymerization (SSP); diffusion; reaction rate constants; catalysts

INTRODUCTION

Solid-state polymerization (SSP) has been widely used to produce high molecular weight poly(ethylene terephthalate) (PET) resins for bottle, food-tray, and tire-cord applications. First, a prepolymer with an intermediate molecular weight or intrinsic viscosity (IV) is produced from dimethyl terephthalate (DMT) and ethylene glycol (EG) or

from terephthalic acid (TPA) and EG by a melt-phase polymerization 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 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 mobile and activated to collide and react with one another to further increase the molecular weight. The SSP product is commonly called solid-state PET.

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The SSP of PET is a very complex process. Major factors influencing the SSP rate include the catalyst (type and concentration), temperature, particle size, and concentration of carboxyl end groups or carboxyl content. The effects of the first three factors are readily understood. However, the effect of the carboxyl content, which is the subject matter of this article, has not been properly discussed. Although in theory it is possible to prepare zero-carboxyl PET prepolymers, most commercially produced PET prepolymers have substantial carboxyl contents, with 15–40% of the total end groups being carboxyl end groups. Therefore, the SSP of PET involves two types of polycondensation reactions, namely, transesterification and esterification. Transesterification is the reaction between two 2-hydroxyethyl ends with EG as the reaction byproduct, and esterification is the reaction between a carboxyl end and a 2-hydroxyethyl end with water as the reaction byproduct. For convenience, 2-hydroxyethyl ends are commonly called hydroxyl ends. Naturally, the presence of carboxyl ends in the prepolymer has an important effect on the overall SSP rate.

Review of Previous Related Works

Many articles on the SSP of PET have been published. However, only a few discuss the effect of the carboxyl content on the SSP. Chen et al.,¹ Chang,² Ravindranath and Mashelkar,³ and Cai et al.⁴ did not include esterification in their SSP models, totally ignoring the presence of carboxyl ends in the prepolymers. Devotta and Mashelkar,⁵ Tang et al.,⁶ Kang,⁷ and Mallon and Ray⁸ included esterification as well as transesterification in their SSP models to properly account for the contribution of esterification to the overall SSP. However, the reaction rate constants for transesterification and esterification used by these authors were extrapolated from melt polycondensation data without justifications. The adequacy of their reaction rate constants for SSP certainly leaves room for discussion. Chang et al.⁹ indicated that, in the SSP of powdered PET, a high hydroxyl concentration results in a faster reaction rate, whereas in the SSP of granulated PET, a high carboxyl concentration is preferred. However, they did not provide experimental data or cite references to support their statement. Jabarin¹⁰ and Wu and Li¹¹ reported that the maximum SSP rate of pelletized PET is achieved when the hydroxyl concentration is twice that of the carboxyl concentration.

More detailed data for the effects of the carboxyl concentration on the SSP of PET can be

found in patent literature. An earlier East German patent to Schaaf et al.¹² claims that the SSP rate of PET is increased by the adjustment of the ratio of COOH and OH end groups so that the [COOH]/[OH] ratio is 0.3/1 to 0.6/1. A recent Japanese patent to Ishidera et al.¹³ describes a process in which low-IV PET prepolymers in pellet form with the following [COOH]/[OH] ratio are solid-state polymerized to produce high-IV products:

$$0.3 \leq \frac{[\text{COOH}]}{[\text{OH}]} \leq 1 \quad (\text{for } 0.07 \leq \text{IV} \leq 0.16)$$

Naturally, fast SSP is among the claimed advantages.

Two U.S. patents to Duh^{14,15} discuss the optimal carboxyl contents for PET prepolymers in greater detail. The first Duh patent¹⁴ relates to the SSP of finely divided, low-IV PET prepolymer in the fluid bed. With this prepolymer, the SSP rate increases with decreasing carboxyl content. The second Duh patent¹⁵ relates to the SSP of granulated or pelletized PET prepolymer. It is demonstrated that, with a pelletized PET prepolymer, there exists an optimal carboxyl content for the highest SSP rate. Although these two patents may seem to contradict each other, they actually complement each other.

In this article, the experimental data presented in the two Duh patents^{14,15} plus additional related data are analyzed to elucidate the effects of the carboxyl concentration on the SSP of PET. In addition, the effect of the carboxyl concentration on the efficiency of antimony catalyst in the SSP of PET is examined, the forward reaction rate constants for transesterification and esterification are determined from actual SSP data to compare them with those used in various SSP models, and methods for preparing prepolymers with optimal carboxyl concentrations are recommended.

Origins of Carboxyl Ends in PET

PET prepolymers can be produced from DMT and EG or from TPA and EG. Therefore, depending on the precursors used, there are two melt-phase polymerization processes for the production of PET, namely, the DMT process (or ester-interchange process) and TPA process (or direct-esterification process).

In DMT-based PET, all carboxyl ends are formed by degradation or side reactions, which take place throughout the manufacturing process even in the presence of a stabilizer. In TPA-based PET, some of the carboxyl ends are holdovers from the direct-esterification stage, and the remaining carboxyl ends are created by degradation reactions during the polycondensation stage.

The degradation reactions as well as the polycondensation reactions of PET were reviewed, modeled, or simulated by Ranvindranath and Mashelkar,¹⁶ Devotta and Mashelkar,⁵ and Yokoyama et al.¹⁷ Two major degradation reactions are responsible for the generation of carboxyl ends and acetaldehyde: (1) degradation of hydroxyl ends that forms carboxyl ends and generates acetaldehyde and (2) chain scission at diester links that creates carboxyl ends and vinyl ends. These two degradation reactions are most severe during the later part of the polycondensation stage when the reaction temperature is the highest. Carboxyl and vinyl ends can react with hydroxyl ends to reform diester links and generate equivalent amounts of water and acetaldehyde, respectively. In the presence of sufficient carboxyl end groups, the esterification reaction is another important polycondensation reaction, although the transesterification reaction is the predominant polycondensation reaction.

Carboxyl ends can also be generated via other routes. A hydroxyl-terminated polyester can react with EG to form a carboxyl-terminated polyester and diethylene glycol (DEG); two hydroxyl-terminated polymer chains can react to form carboxyl-terminated and DEG-terminated polymer chains.

Thus, carboxyl ends are constantly created by degradation reactions and consumed by polycondensation (esterification) reactions during the melt polymerization process, and there will always be some carboxyl ends remaining at the end of the polycondensation stage in both DMT and TPA processes. In general, DMT-based PET has a low carboxyl concentration. For example, the carboxyl concentration in DMT-based textile-grade PET ($IV = 0.55\text{--}0.65$ dL/g) is usually between 10 and 20 mol/10⁶ g. The low carboxyl content coupled with the presence of methyl ends contributes to the low SSP rate of pelletized DMT-based PET. With the TPA process, it is much easier to manipulate process variables to produce a PET prepolymer with an optimal carboxyl concentration to maximize the SSP rate. Therefore, TPA-based PET prepolymers are the preferred prepolymers for SSP

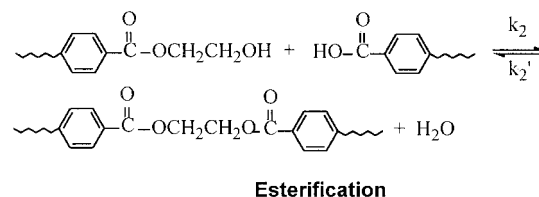
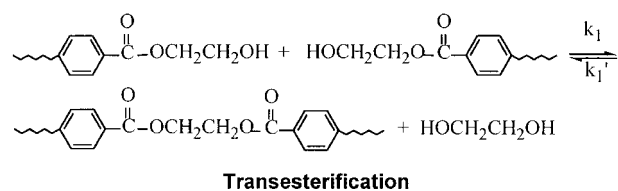
Kinetics of SSP of PET

For simplicity, the SSP process of PET can be broken down into the following steps:

1. Polycondensation reactions of end groups.
2. Diffusion of reaction byproducts from the interiors to the surfaces of polymer particles.
3. Diffusion of reaction byproducts from the surfaces of polymer particles to the bulk of the gas phase.

Although PET may contain other end groups besides hydroxyl and carboxyl end groups, their concentrations are usually very low. Therefore, for simplicity, it is reasonable to assume that the prepolymer contains only hydroxyl and carboxyl end groups. As in melt polymerization, there are two types of polycondensation reactions in SSP, namely, transesterification and esterification reactions. Theoretically, all the degradation reactions that take place in melt polymerization can also take place in SSP. However, because SSP is usually conducted at temperatures at least 50°C below the finishing melt polycondensation temperature, their rates are quite low, and for practical purposes, degradation reactions in SSP can be ignored.

Transesterification is the reaction between two hydroxyl ends with EG as the reaction byproduct, and esterification is the reaction between a carboxyl end and a hydroxyl end with water as the reaction byproduct. Both reactions are reversible. Therefore, the reaction byproducts must be removed to force the reactions to proceed toward the direction of increasing molecular weight:



If K_1 and K_2 are the equilibrium constants for transesterification and esterification, respectively, then

Table I Numerical Values of Rate Constants and Equilibrium Constants

Source	Temperature	k_1	k_2	k_2/k_1	K_1	K_2
Kang ⁷	230°C	1.326×10^{-3}	4.134×10^{-3}	3.12	0.5	1.25
Mallon et al. ⁸	230°C	0.907×10^{-3}	3.421×10^{-3}	3.77	0.5	1.25
Tang et al. ⁶	225°C	0.203×10^{-3}	0.783×10^{-3}	3.86	1.0	1.25
Parashar et al. ¹⁸	185°C	0.636×10^{-3}	0.312×10^{-3}	0.49		

Unit for k_1 and k_2 is $(\text{mol}/10^6 \text{ g})^{-1} \text{ h}^{-1}$. Values of k_1 and k_2 from Kang were converted from $(\text{mol}/\text{L})^{-1} \text{ h}^{-1}$ with a density value of 1300 g/L for PET at 230°C.

$$k'_1 = \frac{k_1}{K_1} \quad (1)$$

$$k'_2 = \frac{k_2}{K_2} \quad (2)$$

where k_1 and k'_1 are the forward and backward reaction rate constants, respectively, for transesterification and k_2 and k'_2 are the forward and backward reaction rate constants, respectively, for esterification.

Table I lists values of reaction rate constants and equilibrium constants for transesterification and esterification used in various PET SSP studies. The values from the first 3 sources are extrapolated from melt polycondensation data. The values given by Parashar et al.¹⁸ are determined from actual experimental data for reaction-controlled SSP.

Possible Optimal Prepolymer Carboxyl Concentration for Reaction-Controlled SSP

When the polymer particle size is sufficiently small and the inert gas flow rate around the polymer particle is sufficiently high, the diffusion resistances inside and outside the polymer particles are negligible, and the overall polycondensation reaction becomes the rate-controlling step. In this case, the reaction byproducts are removed as soon as they are created, and there are no backward reactions. This simplified SSP process offers an opportunity to study the relative rates of transesterification and esterification reactions. It will be interesting to know if there is an optimal carboxyl concentration for the fastest overall polycondensation for reaction-controlled SSP.

The total end-group concentration (C) can be calculated from the number-average molecular weight (M_n), which, in turn, can be calculated from the IV with Moore's equation¹⁹ for the IV

measured in 60/40 phenol/tetrachloroethane at 25°C:

$$\text{IV} = 7.50 \times 10^{-4} M_n^{0.68}$$

With $\text{mol}/10^6 \text{ g}$ as the unit for the end-group concentrations,

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

The carboxyl concentration (C_2) can be readily determined by a titration method. The carboxyl concentration in $\text{mol}/10^6 \text{ g}$ is often called the carboxyl number. Once C_2 is determined, the hydroxyl concentration (C_1) can be obtained by subtraction of C_2 from C .

The simple second-order rate equations for both transesterification and esterification reactions can be used to determine the optimal carboxyl concentration (if one exists) for the highest overall solid-state polycondensation rate at any fixed IV.

Expressed in terms of rates of disappearance of end groups, the transesterification rate (R_1), the esterification rate (R_2), and the overall solid-state polycondensation rate (R) are as follows:

$$R_1 = 2k_1 C_1^2 \quad (3)$$

$$R_2 = 2k_2 C_1 C_2 \quad (4)$$

$$R = -\frac{dC}{dt} = R_1 + R_2 = 2k_1 C_1^2 + 2k_2 C_1 C_2 \quad (5)$$

Because C is fixed at each fixed IV, an increase in C_2 means a corresponding decrease in C_1 . Therefore, it is easy to see that, unless k_2 is substantially greater than k_1 , the presence of carboxyl ends in the prepolymer always decreases R .

Substituting $(C - C_2)$ for C_1 in eq. (5) and differentiating R with respect to C_2 lead to

$$\frac{dR}{dC_2} = 2(k_2 - 2k_1)C - 4(k_2 - k_1)C_2 \quad (6)$$

Further differentiating both sides of eq. (6) with respect to C_2 yields

$$\frac{d^2R}{dC_2^2} = -4(k_2 - k_1) \quad (7)$$

Setting dR/dC_2 in eq. (6) to 0, we obtain the following relationship:

$$\frac{C_2}{C} = \frac{k_2 - 2k_1}{2(k_2 - k_1)} \quad (8)$$

If C_2 is not 0, the following relationship must be satisfied:

$$0 < \frac{C_2}{C} < 1$$

This means

$$k_2 > 2k_1 \quad (9)$$

and

$$k_2 > 0 \quad (10)$$

Relationship (10) is trivial. According to eq. (7), if $k_2 > 2k_1$, R has a maximum (the second derivative of R is negative) at

$$C_2 = \frac{(k_2 - 2k_1)C}{2(k_2 - k_1)} \quad (11)$$

For example, if $k_2 = 4k_1$, then at $C_2 = \frac{1}{3}C$, the overall SSP rate is the highest if the SSP is reaction-controlled.

EXPERIMENTAL

All experiments were conducted at the Polyester Division of Goodyear Tire and Rubber Co. The procedures for the SSP experiments and the preparation of the prepolymers used have been described in the two Duh patents.^{14,15} Two parts of the experiments are discussed. One involves SSP

of powdered PET in a fluid bed, and the other involves SSP of pelletized PET in a fixed bed. The first part of the experiments was designed to demonstrate that, in the fluid-bed SSP of powdered PET, the SSP rate increases, and the catalyst level required to achieve the highest SSP rate decreases with decreasing prepolymer carboxyl content. The second part of the experiments was designed to demonstrate that, in the fixed-bed SSP of pelletized PET, there exists an optimal prepolymer carboxyl content for the highest SSP rate.

All the prepolymers were prepared in a bench-scale reactor with EG and TPA as the precursors. For the first part of the SSP experiments, a number of nominal 0.25 dL/g IV prepolymers with Sb catalyst levels ranging from 0 to 300 ppm and carboxyl contents ranging from 4 to 130 mol/10⁶ g were prepared. No stabilizers were added to the prepolymers. Each of these prepolymers was ground and classified with the fraction that passed through a Tyler no. 28 mesh screen but remained on a Tyler no. 35 mesh screen retained for use in the SSP experiments. The SSP experiments were conducted in a 1-in.-diameter fluid-bed reactor with nitrogen as the fluidizing gas at a superficial velocity of about 30 feet/min (fpm). For each run, the prepolymer was first dried at 150°C for 1 h and then heated to 230°C to start the SSP reaction, which lasted 7–50 h depending on the catalyst and carboxyl concentrations of the prepolymer.

For the second part of the experiments, a number of nominal 0.45 dL/g IV prepolymers having carboxyl concentrations ranging from 10 to 89 mol/10⁶ g and containing 5 ppm Ti catalyst and no stabilizer were prepared. Each prepolymer was pelletized to obtain near cylindrical pellets, each weighing about 0.01 g, for use in the fixed-bed SSP experiments. The fixed-bed reactor used had a diameter of 1.25 in. The reactor was purged with nitrogen at a superficial velocity of 30 fpm, which is high enough to eliminate the gas side diffusion resistance but low enough to maintain a fixed bed. For each run, the prepolymer was predried at 160°C for 2 h before the bed temperature was raised to 230°C to effect the SSP, which lasted 24 h.

RESULTS AND DISCUSSION

Fluid-Bed SSP of Powdered PET

Each prepolymer used in this part of the SSP experiments had a particle size between 425 and

Table II Results of Fluid-Bed SSP of Powdered PET Prepolymers

Run Number	Catalyst Concentration (ppm Sb)	Carboxyl Concentrations at Various IVs (mol/10 ⁶ g)				Reaction Time Required to Achieve Various IVs		
		0.25 dL/g	0.4 dL/g	0.5 dL/g	0.6 dL/g	0.4 dL/g	0.5 dL/g	0.6 dL/g
1	0	13			3			23.4
2	0	72			16			31.0
3	0	130			32			38.0
4	20	12			6			6.3
5	20	35			17			11.5
6	20	58			26			13.7
7	20	94			40			18.4
8	100	7			4			2.4
9	100	39			22			5.3
10	100	70			39			7.4
11	100	102			51			10.4
12	210	4			1			2.4
13	210	39			21			3.1
14	210	43			27			2.8
15	210	90			45			5.0
16	210	110			55			7.0
17	300	9	7	6	5	0.70	1.40	2.5
18	300	46	37	32	26	0.90	1.70	3.1
19	300	76	60	50	40	1.10	2.30	4.5
20	300	115	84	68	57	1.60	3.60	7.1

600 μm . According to my data, the particle size needs to be reduced to below about 250 μm to practically eliminate diffusion resistances. However, at the particle size of 425–600 μm , the diffusion resistances are small, and the SSP is predominately reaction-controlled. Therefore, for simplicity of discussion, we may assume that the SSP is reaction-controlled without compromising the purpose of this article.

Table II lists the results of the fluid-bed SSP of powdered prepolymers. The data for runs 1–16 are from the first Duh patent,¹⁴ and the data for runs 17–20 are additional data provided by the author to expand the catalyst concentration range to 300 ppm. The data in Table II can be analyzed to illustrate the effects of the prepolymer carboxyl and catalyst concentrations on the overall polycondensation, esterification, and transesterification rates and the effect of the carboxyl content on the effectiveness of the catalyst. Furthermore, the reaction times required to achieve two intermediate IVs (0.40 and 0.50 dL/g) and the carboxyl concentrations at these two intermediate IVs for the prepolymers containing 300 ppm catalyst enable us to estimate the reaction rate constants, k_1 and k_2 , for this series of SSP runs.

In Figure 1, the reaction time required to achieve a 0.60 dL/g IV is plotted against the pre-

polymer carboxyl concentration for each of the prepolymers with various catalyst concentrations. It can be seen from this figure that the reaction time requirement decreases (or the average SSP rate increases) monotonously with decreasing prepolymer carboxyl content, regardless of the catalyst concentration. This means the SSP rate does not have a maximum: its value is the highest when the carboxyl concentration is zero. Therefore, k_2 is smaller than $2k_1$, indicating that the extrapolated values of k_1 and k_2 used by various authors^{6–8} in their SSP models are questionable. It can also be seen that the addition of a small amount of catalyst dramatically increases the average SSP rates, especially those of low-carboxyl prepolymers. For example, the addition of just 20 ppm Sb increases the average SSP rates between IVs of 0.25 and 0.60 dL/g by about 300% and about 75% for prepolymers with 10 and 100 mol/10⁶ g COOH concentrations, respectively. The SSP rate increases with increasing catalyst concentration until the catalyst concentration reaches a certain limit, above which a further increase in the catalyst concentration does not influence the SSP rate. This limit is no higher than 210 ppm. Also note that the highest SSP rate can be achieved with about 100 ppm Sb cat-

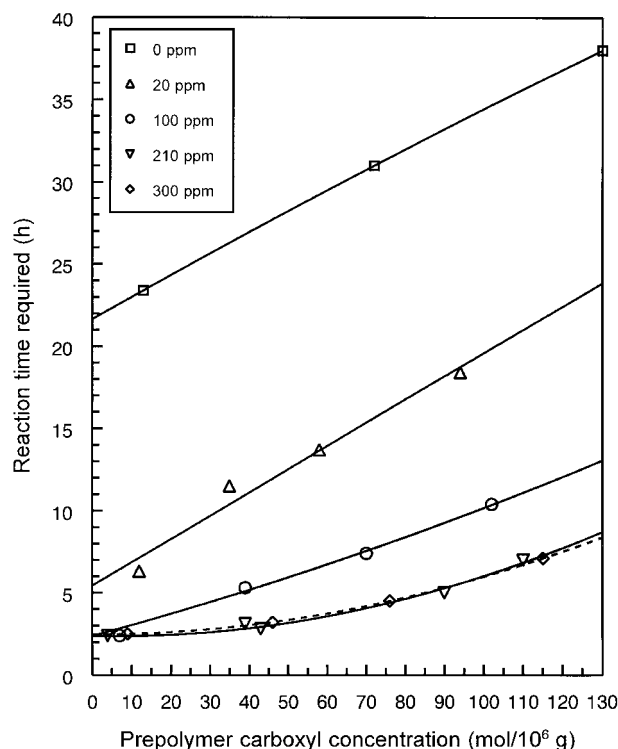


Figure 1 Effect of the prepolymer carboxyl concentration on the reaction times required to achieve a 0.60 dL/g IV for prepolymers with various catalyst concentrations.

alyst if the prepolymer has a zero carboxyl content.

In Figure 2, the carboxyl concentration of a 0.60 dL/g IV SSP product is plotted against the prepolymer carboxyl concentration for each of the prepolymers with various catalyst concentrations. As expected, at each fixed catalyst level, the product carboxyl concentration increases with increasing prepolymer carboxyl concentration. However, with the prepolymer carboxyl concentration fixed, the product carboxyl concentration increases with increasing Sb concentration until it reaches about 100 ppm. This indicates that the presence of the catalyst increases the transesterification rate more than the esterification rate. Therefore, if the lowest carboxyl concentration at a certain IV is the only goal, it is most achievable in the absence of a catalyst.

From these two figures, the reaction times required to achieve a 0.60 dL/g IV and the carboxyl concentrations at a 0.60 dL/g IV for prepolymers with 0, 10, 40, 70, and 100 mol/10⁶ g carboxyl concentrations and various catalyst concentrations were obtained, and they are listed in Table III.

Effects of the Prepolymer Carboxyl Concentration on SSP Rates of Powdered Prepolymers

The average overall polycondensation (or SSP), esterification, and transesterification rates within the IV range of 0.25–0.60 dL/g in terms of rates of disappearance of end groups for each of the prepolymers can be readily calculated with the data in Table III. The average overall polycondensation rate is equal to $-\Delta C/t_r$, where ΔC is the difference between the total end-group concentrations of the prepolymer and product and t_r is the reaction time required for the prepolymer to achieve the product IV. Because the reaction of each carboxyl end group causes a decrease of two end groups, the average esterification rate is $-2\Delta C_2/t_r$, where ΔC_2 is the change in the carboxyl concentration. The average transesterification rate is simply the difference between the average overall polycondensation rate and the average esterification rate. Thus, the data in Table III are used to prepare Figures 3–6.

Figure 3 shows the effects of prepolymer COOH and Sb concentrations on the average esterification rate. As expected, within the COOH concentration range of 0–100 mol/10⁶ g, the es-

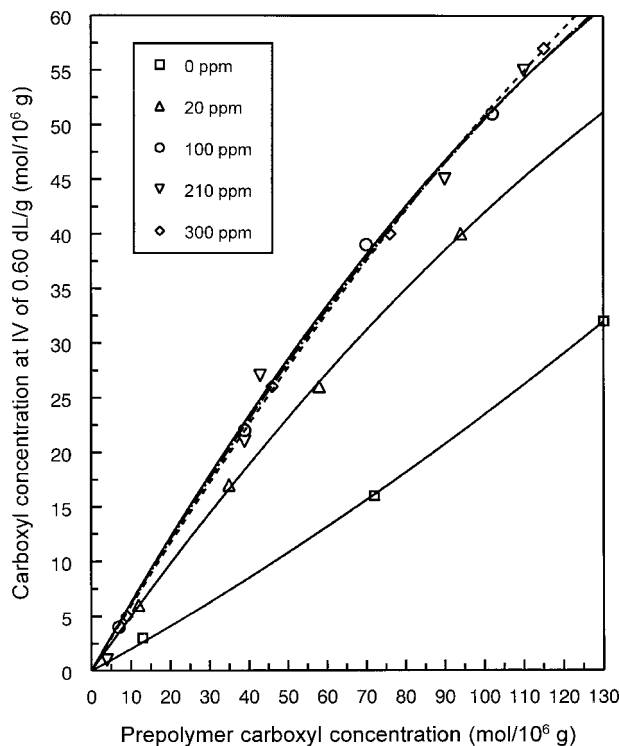


Figure 2 Effect of the prepolymer carboxyl concentration on the carboxyl concentrations of 0.60 dL/g IV SSP products with various catalyst concentrations.

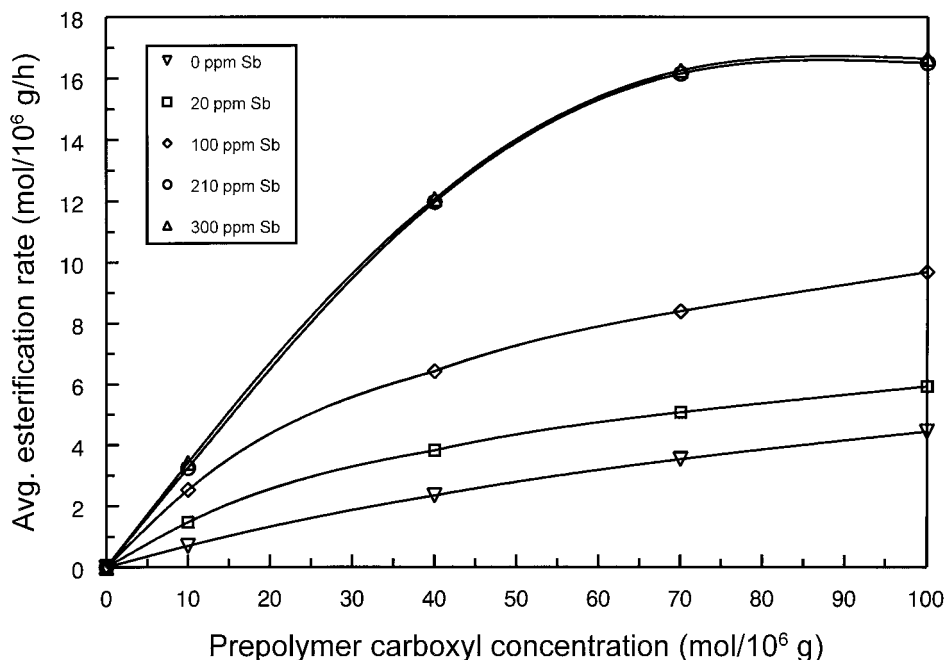
Table III Reaction Times Required to Achieve 0.60 dL/g IV and Carboxyl Concentrations at 0.60 dL/g IV for Prepolymers with Various Catalyst and Carboxyl Concentrations

Catalyst Concentration (ppm Sb)	Reaction Time Required to Achieve 0.60 dL/g IV (h) for Prepolymer with Carboxyl Concentration (mol/10 ⁶ g)					Carboxyl Concentration At 0.60 dL/g IV (mol/10 ⁶ g) for Prepolymer with Carboxyl Concentration (mol/10 ⁶ g)				
	0	10	40	70	100	0	10	40	70	100
0	21.7	23.0	26.9	30.8	34.4	0.0	2.0	8.5	15.6	23.5
20	5.4	6.8	11.1	15.3	19.6	0.0	5.0	18.8	31.2	41.9
100	2.4	3.0	5.2	7.6	10.2	0.0	6.2	23.3	38.1	50.6
210	2.4	2.4	2.8	4.0	6.0	0.0	6.1	23.0	37.7	50.5
300	2.4	2.4	2.9	4.0	5.9	0.0	5.9	22.5	37.5	50.9

terification rate increases with increasing prepolymer carboxyl concentration. It can be expected that, as the prepolymer COOH concentration reaches a certain level, the average esterification rate of each prepolymer will reach a maximum and then decrease as the COOH concentration is further increased as a result of diminishing OH concentration. Because each COOH end needs an OH end with which to react, if the COOH concentration exceeds the OH concentration, some of the COOH ends will eventually become dead ends as the OH ends are depleted. It is also obvious that the esterification

rate increases with increasing Sb concentration until it reaches a saturation level, which is no higher than 210 ppm. Because most commercially produced PET prepolymers contain at least 210 ppm Sb, it is reasonable to say that most commercially produced PET prepolymers contain more than enough catalyst for the maximum esterification rate (and SSP rate).

Figure 4 shows the effects of COOH and Sb concentrations on the average transesterification rate. It is obvious that the transesterification rate increases with decreasing COOH concentration and increasing Sb concentration. The catalyst ef-

**Figure 3** Plots of the average esterification rate versus the prepolymer carboxyl concentration for prepolymers with various catalyst concentrations.

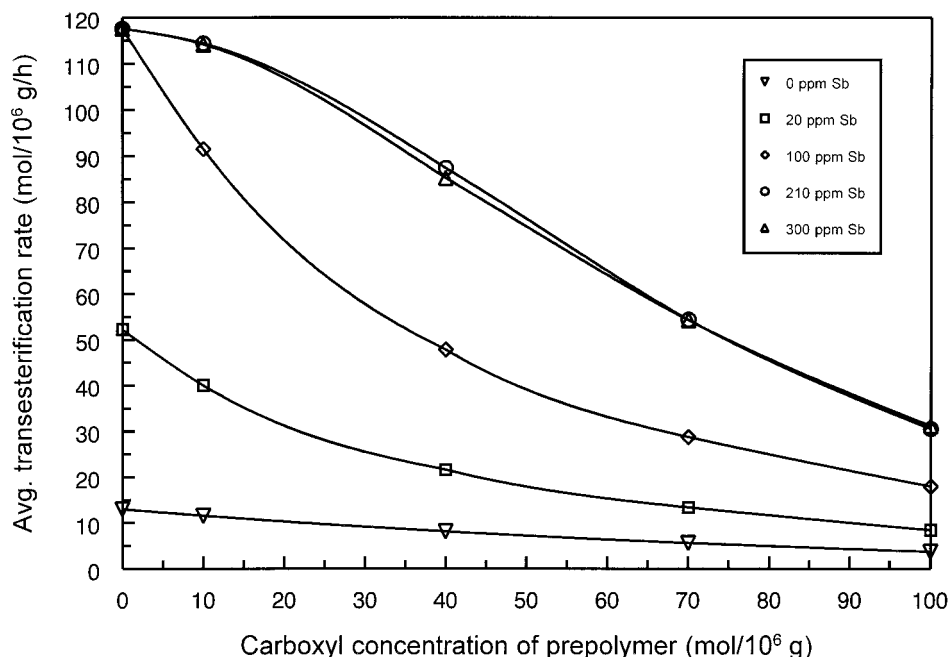


Figure 4 Plots of the average transesterification rate versus the prepolymer carboxyl concentration for prepolymers with various catalyst concentrations.

fect on the transesterification rate is more pronounced on prepolymers with lower COOH concentrations and less pronounced on prepolymers

with higher COOH concentrations. Similar to the esterification rate, the transesterification rate also attains the highest value when the Sb concentration reaches a certain value, which is no

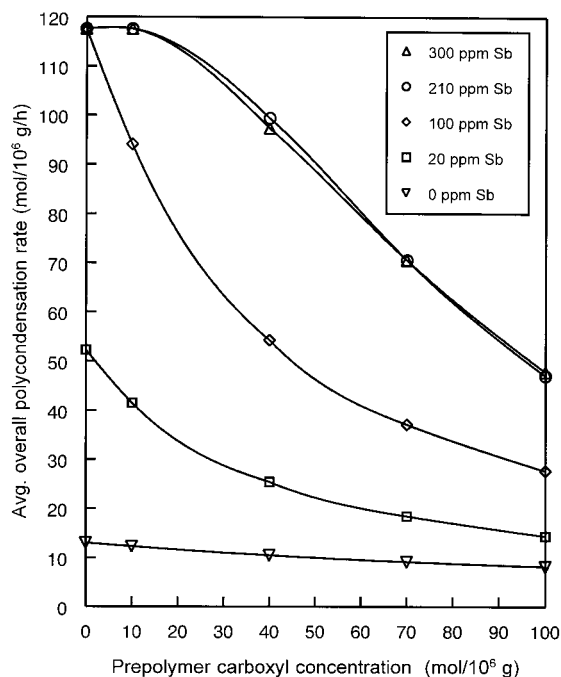


Figure 5 Plots of the average overall polycondensation rate versus the prepolymer carboxyl concentration for prepolymers with various catalyst concentrations.

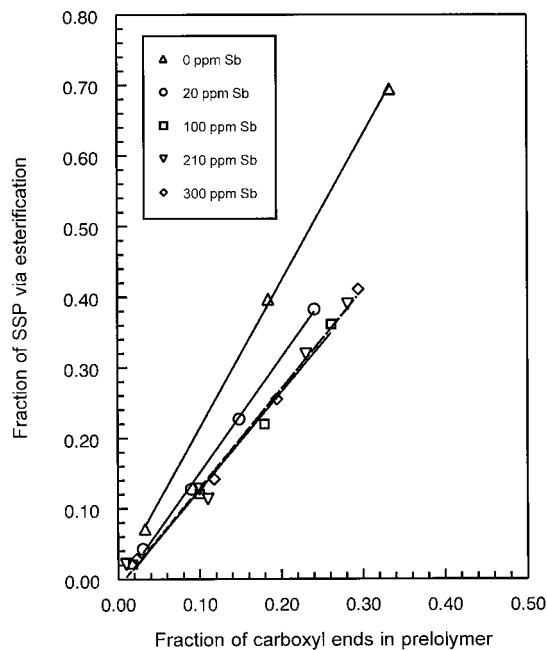


Figure 6 Effects of the fraction of carboxyl ends in the prepolymer and the catalyst concentration on the contribution of esterification to overall SSP.

higher than 210 ppm. It is particularly interesting to note the curve for the prepolymer containing 100 ppm Sb. At a zero COOH concentration, the transesterification rate of the prepolymer containing 100 ppm Sb achieves the highest possible level, which is as high as that of the prepolymer containing 210 ppm or more Sb. However, as the COOH concentration increases from 0, the transesterification rate of the prepolymer containing 100 ppm drops off markedly and becomes much lower than that of the prepolymer containing 210 ppm or more Sb. This indicates that, unless there is a sufficient amount of catalyst, COOH ends will compete with OH ends for catalyst and effectively decrease the amount of catalyst available for OH ends. Therefore, it is expected that if the catalyst concentration is insufficient (below the saturation level), the forward transesterification rate constant, k_1 , will decrease with increasing COOH concentration. However, when there is an excess of catalyst (e.g., the Sb concentration is 210 ppm or higher), k_1 should not be affected by the COOH concentration.

Figure 5 shows the effects of the COOH and Sb concentrations on the average overall polycondensation (or SSP) rate, which are quite similar to those on the average transesterification rate because transesterification is the predominant polycondensation reaction. The overall polycondensation rate always increases with decreasing prepolymer COOH concentration, and a prepolymer with a lower COOH concentration requires a lower catalyst concentration to achieve the highest possible SSP rate. This figure also shows that the SSP rates for prepolymers with various COOH concentrations remain unchanged when the Sb concentration is increased above 210 ppm.

Figure 6 shows the effects of the prepolymer COOH and Sb concentrations on the contribution of esterification to the overall SSP over an IV range of 0.25–0.60 dL/g. The fraction of SSP due to esterification increases with decreasing Sb concentration and is approximately proportional to the fraction of COOH ends in the prepolymer. This also indicates that the greatest reduction in the COOH concentration over a fixed IV range can be achieved with no catalyst added, although this will require the longest SSP time to reach the final IV.

Determination of Forward Reaction Rate Constants k_1 and k_2

The fact that the overall polycondensation rate increases monotonously with decreasing COOH

concentration indicates that the k_2/k_1 ratio must not be greater than 2. With the additional data for the reaction time requirements and the COOH concentrations at two intermediate IVs for each of the series of prepolymers containing 300 ppm Sb (runs 17–20, Table II), the forward transesterification and esterification rate constants, k_1 and k_2 , respectively, can be estimated for this series of prepolymers. Integrating eqs. (3) and (4) from 0 to t_r leads to the following two equations:

$$\int_0^{t_r} R_1 dt = 2k_1 \int_0^{t_r} C_1^2 dt = -(\Delta C - 2\Delta C_2) \quad (12)$$

$$\int_0^{t_r} R_2 dt = 2k_2 \int_0^{t_r} C_1 C_2 dt = -2\Delta C_2 \quad (13)$$

where t_r is the reaction time required for the prepolymer to attain a 0.60 dL/g IV. Because the values of C_1^2 and $C_1 C_2$ decrease rapidly in the early stages of SSP and level off toward the end of SSP, each is best fitted with the following exponential function of reaction time t within the IV range of 0.25–0.60 dL/g:

$$C_1^2 \quad \text{or} \quad C_1 C_2 = a_0 + a_1 \exp(-t/a_2)$$

where a_0 , a_1 , and a_2 are constants. Figure 7 shows that curve fittings for C_1^2 and $C_1 C_2$ for the prepolymers with various COOH concentrations are reasonably good in general. Thus, after integration, k_1 and k_2 are readily calculated for each of the prepolymers. The calculated values for k_1 and k_2 of the prepolymers containing 300 ppm Sb are listed in Table IV.

Because 300 ppm Sb is more than sufficient for the prepolymers, theoretically k_1 and k_2 should be independent of the prepolymer carboxyl concentration; in fact, the calculated values for k_1 and k_2 do not change much with the prepolymer COOH concentration if we consider the experimental errors and calculating errors involved. If we take the averages, $k_1 = 1.40$, $k_2 = 1.19$, and $k_2/k_1 = 0.85$. This estimated k_2/k_1 ratio value is much smaller than the extrapolated values for the ratio (between 3.0 and 4.0) used in the SSP models by various authors^{6–8} and is closer to that determined by Parashar et al.¹⁸ from actual experimental data for SSP of PET at 195°C. Because the particle size used is believed to be still not small enough to completely eliminate the diffusion re-

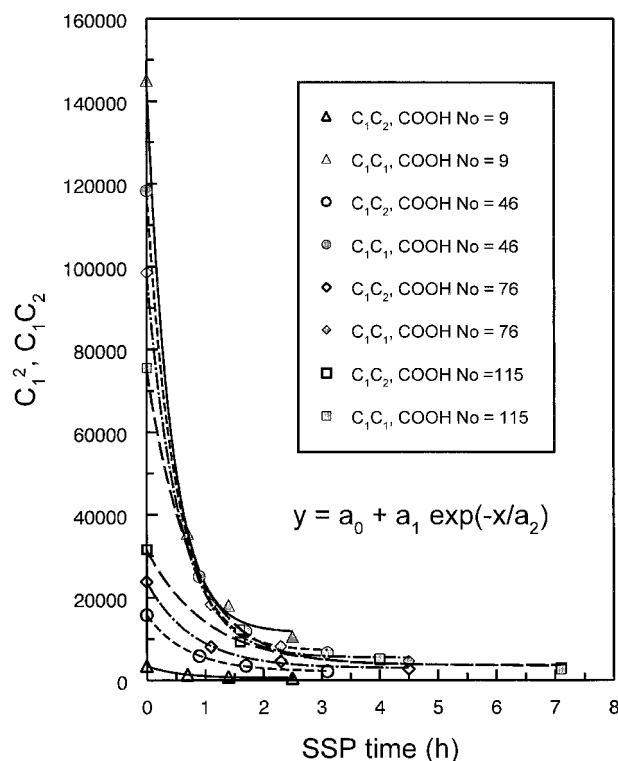


Figure 7 Curve fittings of C_1^2 and C_1C_2 with exponential functions for prepolymers with various COOH concentrations.

sistance, the actual values for both k_1 and k_2 should be somewhat greater. However, the actual value for the k_2/k_1 ratio should be even lower than 0.85 because esterification is retarded less than transesterification in the presence of some diffusion resistance. Therefore, there is a good reason to doubt the adequacy of the extrapolated values for k_1 and k_2 .

Possible Applications for Fluid-Bed SSP of Powdered Low-IV PET

High-purity PET with excellent color, clarity, and stability can be economically produced by SSP of a powdered low-IV (e.g., 0.20–0.45 dL/g) prepolymer with a low carboxyl content (e.g., <10 mol/10⁶ g). The catalyst concentration can be greatly reduced without the SSP time required to attain the desired product IV being unduly prolonged. Thus, the Sb level can be reduced from about 250 ppm in a typical PET formulation to 100 ppm with little loss in the SSP rate. The catalyst reduction can be even more dramatic if a more active catalyst is used. For example, my data show that a titanium (Ti) catalyst as low as 2–5

ppm can be as effective as 100 ppm Sb in catalyzing low-carboxyl PET. At this low level, the problems of polymer yellowing and crosslinking associated with PET catalyzed with a normal Ti catalyst level (≥ 20 ppm) can be avoided. Germanium (Ge) catalyst is well known for its use in the production of PET with excellent color and clarity, but it is much more expensive than the standard Sb catalyst. When the Ge catalyst is used in this process, the amount and cost required can be greatly reduced. Because a catalyst in PET catalyzes degradation reactions as well as polycondensation, a stabilizer (usually a phosphorous compound) is routinely included in the standard PET formulation. With a lower catalyst content, the need for a stabilizer is eliminated or drastically reduced. Another important advantage of this process is the very low product carboxyl content. The presence of COOH ends in PET has been known to reduce the stability of PET against thermal and hydrolytic degradations.²⁰ Various end-capping agents, including carbodiimides,²¹ epoxides,²² and benzoyl-lactams,²³ have been proposed to eliminate or reduce the carboxyl content of PET to improve its stability. Yet another advantage of this process is the ability to produce PET resins with extremely low acetaldehyde content because of the relatively low prepolymer acetaldehyde content and SSP temperature (compared with melt polycondensation temperatures), small polymer particle size, and large IV lift.

Possible applications for the products of this process include those that require high purity (e.g., medical devices and packaging), excellent color and clarity (e.g., photographic films and cosmetic packaging), very low acetaldehyde content (e.g., mineral water bottles), and very low carboxyl content (e.g., paper-making screens and conveyor belts).

Table IV Forward Reaction Rate Constants k_1 and k_2 for Transesterification and Esterification, Respectively, for Fluid-Bed SSP of Powdered Prepolymers Containing 300 ppm Sb

Prepolymer COOH Concentration (mol/10 ⁶ g)	$k_1 \times 10^3$ (mol/10 ⁶ g) ⁻¹ h ⁻¹	$k_2 \times 10^3$ (mol/10 ⁶ g) ⁻¹ h ⁻¹
9	1.63	1.38
46	1.57	1.25
76	1.37	1.07
115	1.03	1.07

Methods for Producing Low-Carboxyl Prepolymers

Low-IV prepolymers with uniform, small particle sizes are best prepared by spray congealing, as proposed by Rinehart.²⁴ Spherical particles with 100–250- μm diameters can be obtained with this method. The optimal IV of the prepolymer is between 0.20 and 0.35 dL/g. Below this range, the SSP rate is too slow. Above this range, spray congealing yields fibers instead of small particles. To ensure a low prepolymer COOH concentration, milder polycondensation temperatures, preferably no higher than 275°C, should be used to suppress degradation reactions. Preferably, the prepolymer IV should not exceed 0.45 dL/g, above which melt viscosity becomes too high for efficient agitation without the polycondensation temperature being raised, and it will require too much energy to grind the resulting prepolymer.

Although low-carboxyl prepolymers can be produced more easily by the DMT process, a DMT-based prepolymer is not desirable for three reasons. First, the DMT process is less economical than the TPA process. Second, in addition to the polycondensation catalyst, the DMT process requires an ester-interchange catalyst (e.g., manganese acetate) that has to be blocked by the addition of a phosphorous stabilizer to prevent it from catalyzing degradation during the polycondensation stage. The presence of the additional catalyst and stabilizer compromises the product purity. Third, it is difficult to completely react all the methyl ends during the ester-interchange stage, especially in a continuous process. With very low reactivity, the remaining methyl ends become dead ends during SSP, resulting in a lower SSP rate. Therefore, the TPA process is preferred for the production of the highest purity prepolymer. With the TPA process, the prepolymer carboxyl content can simply be reduced with a higher EG/TPA molar charge ratio (1.30 being optimal according to the first Duh patent¹⁴). However, this could increase DEG formation during the esterification stage. Other methods include the addition of 3–10% excess makeup EG after, for example, 95% completion of the esterification of the TPA, and delayed addition of catalyst. Normally, a polycondensation catalyst is added at the beginning of the polycondensation stage (or the vacuum stage). With catalyst addition delayed until, for example, 20–60 min after the vacuum stage is begun, more COOH ends will be consumed because, in the absence of a catalyst, transesterifi-

cation will be held back more than esterification in melt polymerization just as in SSP.

Fixed-Bed SSP of Pelletized PET

It is now evident that the average overall reaction rate of fluid-bed SSP of powdered PET increases monotonously with decreasing prepolymer COOH concentration. In this case, byproduct diffusion resistances are small or negligible. Because $k_2/k_1 < 2$ (in fact, $k_2 < k_1$), the presence of COOH ends decreases the overall SSP rate. In the SSP of pelletized or granulated PET, byproduct diffusions become important, and the effect of the prepolymer COOH concentration on the average overall reaction rate will be different, mainly because of different diffusivities of the reaction byproducts, EG and water. The diffusivities of EG and water in PET are 3.1×10^{-6} and 5.7×10^{-6} cm^2/s , respectively, at 230°C according to Kang⁷ and 2.6×10^{-6} and 5.8×10^{-6} cm^2/s , respectively, at 225°C according to Tang et al.⁶ With a molecule smaller than EG, the diffusivity of water is about twice that of EG within the SSP temperature range. In the presence of significant diffusion resistances, the reaction byproducts cannot be removed immediately, and backward reactions become important. The backward reaction rate constants of transesterification and esterification, k'_1 and k'_2 , respectively, are usually calculated with eqs. (1) and (2), respectively. The values of the equilibrium rate constants for transesterification, K_1 , and esterification, K_2 , widely used in PET SSP and melt polycondensation models are 0.5–1 and 1.25, respectively (referring to Table I). Because of the lower diffusivity of EG, the transesterification byproduct EG tends to accumulate inside the pellet to a higher average concentration than the esterification byproduct, water. Furthermore, k'_1 is greater than or equal to k_1 (if $K_1 = 0.5$ –1), whereas k'_2 is smaller than k_2 (if $K_2 = 1.25$). The combination of a higher EG concentration and a higher backward reaction rate constant results in a higher backward reaction rate of transesterification. Therefore, inside a PET pellet, transesterification is retarded much more than esterification.

The experimental results of the SSP runs with the pelletized 0.45 dL/g IV PET prepolymers with various COOH concentrations are shown in Figure 8. During the early stage of SSP, the IV buildup rate increases with decreasing prepolymer COOH concentration. As the SSP is further continued, the SSP rates of lower carboxyl pre-

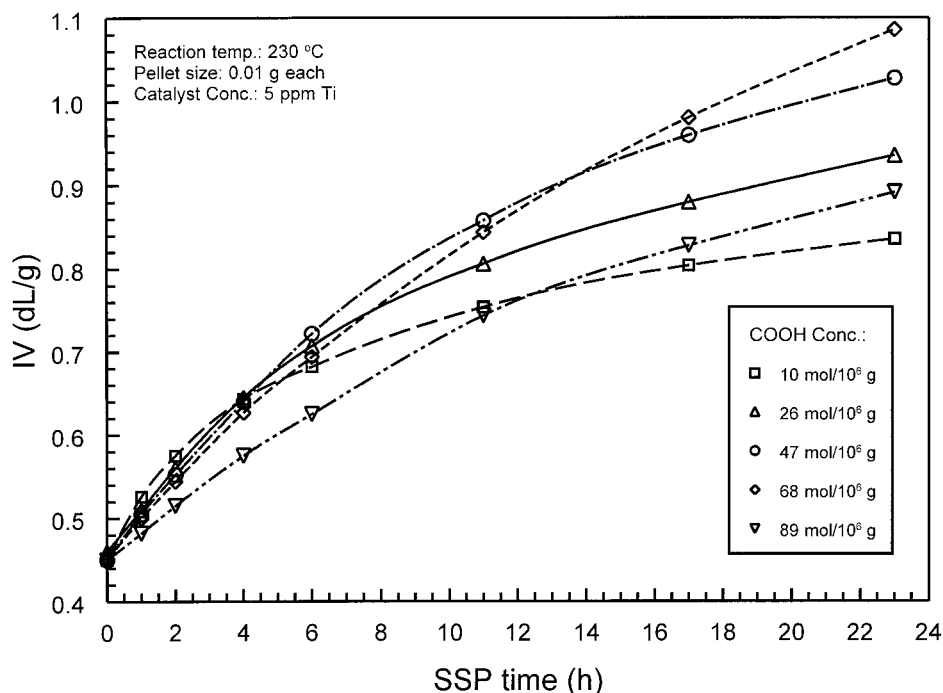


Figure 8 IV buildup curves for SSP of pelletized PET prepolymers with various carboxyl concentrations.

polymers slow down more than that of higher carboxyl prepolymers. Thus, after certain periods of SSP time, the SSP rates of IVs of lower carboxyl prepolymers are overtaken by the SSP rates of some higher carboxyl prepolymers. These observations can be explained in terms of byproduct diffusivities or diffusion resistances. In the early stage of SSP, the bulk of SSP takes place near the pellet surfaces, where byproduct diffusion resistances are small and the effect of the COOH concentration is similar to that in the SSP of powdered PET; that is, the average SSP rate increases with decreasing COOH concentration. As the SSP proceeds, the end-group concentrations near the pellet surfaces decrease, and more and more reactions take place deeper inside the pellets where diffusion resistances are greater. As a result, esterification, which generates the faster diffusing smaller molecule byproduct (water), is favored.

Optimal Carboxyl Content for SSP of Pelletized PET

On the basis of the aforementioned observations, the optimal prepolymer COOH concentration for the fastest average SSP rate or the shortest SSP time required to achieve the desired product IV is

expected to depend on the desired product IV or IV lift (ΔIV). The SSP times required to achieve product IVs of 0.62, 0.72, and 0.82 dL/g for prepolymers with various COOH concentrations can be determined from Figure 8. The results are plotted in Figure 9. Note that 0.62 dL/g is the IV required for textile fiber, 0.72 dL/g is required for unpressurized water bottles, and 0.82 dL/g is required for carbonated soft drink bottles. If the ΔIV is small enough, a prepolymer with zero COOH concentration will achieve the product IV in the shortest SSP time, and if the ΔIV is large enough, there exists an optimal prepolymer COOH concentration that yields the shortest SSP time requirement. It is obvious that the effect of the prepolymer COOH concentration on the average SSP rate for the production of a higher IV product can be quite dramatic. Table V lists the optimal prepolymer COOH concentrations, the corresponding fractions of total ends that are COOH ends, and the shortest SSP time requirements for the three products of different IVs. Because the optimal COOH concentration varies greatly with the prepolymer IV, the optimal fraction of COOH ends or the $[COOH]/[OH]$ ratio, which varies only mildly with the prepolymer IV, is more commonly used.

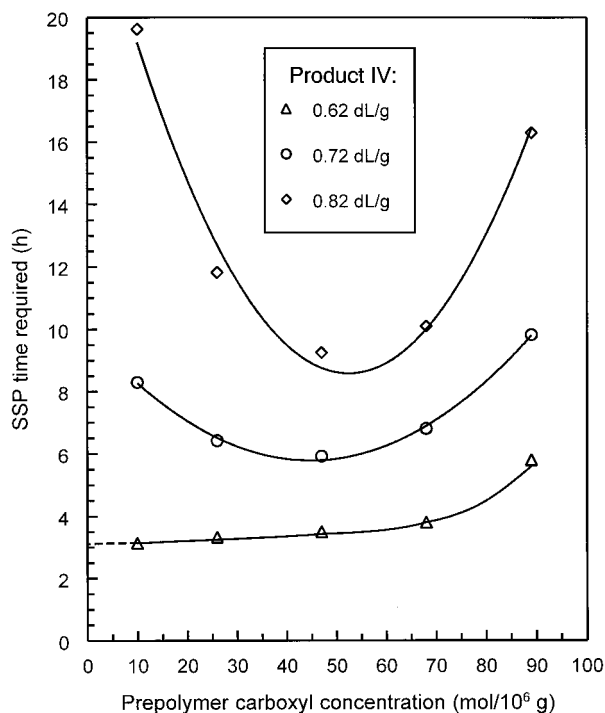


Figure 9 Effects of the prepolymer carboxyl concentration on SSP times required to achieve various product IVs.

Factors Affecting the Optimal Carboxyl Concentration for SSP of Pelletized PET

It is understood that the optimal prepolymer COOH concentration depends on the relative rates of transesterification and esterification reactions and the relative diffusivities of the reaction byproducts, EG and water. Therefore, it is conceivable that the optimal prepolymer COOH concentration can be affected by the catalyst (type and concentration), pellet size, prepolymer and product IVs, and so forth.

Depending on its effectiveness for transesterification and esterification, the type of catalyst can influence the optimal prepolymer COOH concentration. If the catalyst favors esterification, the optimal COOH concentration will be higher, and vice versa. As indicated earlier, if the Sb concentration is insufficient (e.g., far below about 200 ppm), the forward reaction rate constant for transesterification, k_1 , decreases with increasing COOH concentration. Therefore, the optimal COOH concentration is expected to decrease with decreasing catalyst concentration below the saturation level as a result of the decreasing overall polycondensation rate.

Because the average diffusion resistance increases with pellet size, the optimal COOH con-

centration should increase with increasing pellet size. This is obvious from observations of the effects of the COOH concentration on the SSP rates of powdered PET and pelletized PET. Because the average diffusion resistance also increases with increasing ΔIV , the optimal prepolymer carboxyl fraction should also increase with increasing ΔIV . With a fixed prepolymer IV, the optimal prepolymer carboxyl fraction should increase with increasing product IV. Conversely, with a fixed product IV, the optimal prepolymer carboxyl fraction should increase with decreasing prepolymer IV. However, there is a limit to the optimal prepolymer carboxyl fraction. Regardless of how big the pellet size is or how large ΔIV is, it is quite unlikely that the optimal prepolymer carboxyl fraction exceeds 0.45 (hydroxyl fraction < 0.55). This is because, above this prepolymer carboxyl fraction, there will not be sufficient hydroxyl ends to maintain the highest average combined rate of transesterification and esterification over the SSP time required to achieve the desired product IV.

The prepolymers used in the experiments had a nominal IV of 0.45 dL/g and a nominal pellet size of 0.01 g and contained 5 ppm Ti catalyst. It is well known that a Ti catalyst concentration of about 20 ppm is required to achieve the highest melt polymerization rate, although this high Ti level tends to yellow the polymer and form gel. Therefore, increasing the Ti catalyst concentration from 5 ppm and increasing the pellet size from 0.01 g will significantly increase the optimal COOH concentrations. In the production of bottle resins (the bulk of solid-state PET resins with IVs between 0.72 and 0.84 dL/g), most of the prepolymers used have IVs between 0.55 and 0.65 dL/g and pellet sizes between 0.015 and 0.03 g and contain 200–300 ppm Sb catalyst. The optimal carboxyl fraction of about 0.33 reported by Jarbarin¹⁰ for the production of bottle resins appears to

Table V Optimal Prepolymer Carboxyl Concentrations for SSP Products of Various IVs

Product IV (dL/g)	0.62	0.72	0.82
ΔIV (dL/g)	0.17	0.27	0.37
COOH concentration (mol/10 ⁶ g)	0	45	53
Fraction of COOH ends	0	0.27	0.32
SSP time required (h)	3.1	5.8	8.6

Prepolymer IV = 0.45 dL/g; pellet size = 0.01 g; catalyst concentration = 5 ppm Ti; SSP temperature = 230°C.

be in line with the previous discussion. As a rule of thumb, the optimal prepolymer COOH concentration for the production of solid-state PET resin in pellet form is between 25–40% of the total end-group concentration, depending on pellet size, prepolymer IV, product IV, and so forth. If the activation energies of transesterification and esterification reactions or the activation energies of diffusivities of EG and water differ substantially, the SSP temperature will have a significant effect on the optimal COOH concentration. My data indicate that the temperature effect is small within the SSP temperature range normally used in the commercial production of solid-state PET.

Incidentally, optimal COOH concentrations for the most efficient combinations of esterification and transesterification reactions also exist during melt polycondensation because, as the molecular weight increases, the melt viscosity also increases and the byproduct diffusion resistance becomes important. Berkau and Hocutt²⁵ specified the following preferred COOH concentration region for ease of polymerization during melt polycondensation within the M_n range of 980–10,000 (or IV range of 0.08–0.39 dL/g):

$$1.6 \times 10^5 M_n^{-0.98} \leq [\text{COOH}] \leq 6.7 \times 10^6 M_n^{-1.35}$$

According to this relationship, the preferred ranges of carboxyl fractions are 0.092–0.301 and 0.096–0.134 at M_n 's of 980 and 10,000, respectively. Note that the preferred COOH concentration at a 0.39 dL/g IV for melt polymerization is much lower than that for SSP of pelletized PET. They suggested that the preferred COOH concentrations could be obtained by adjustments of the residence time, temperature, pressure, and EG/TPA molar ratio. It is expected that the optimal COOH concentration for the most efficient melt polycondensation at each IV varies with the design of the melt reactor. For example, in a melt reactor that provides more efficient agitation or creates thin films more effectively, the optimal COOH concentration range should be lower.

Methods for Producing Pelletized PET Prepolymers with Optimal Carboxyl Concentrations

In most production processes, optimal prepolymer carboxyl concentrations do not happen automatically. Rather, they are usually obtained by design.

Because all the COOH ends in a DMT-based PET prepolymer are generated by degradation reactions, the carboxyl fraction of the total ends in

a DMT-based prepolymer is usually far below the optimal value. There have been attempts to increase the carboxyl contents of DMT-based prepolymers with very high polycondensation temperatures (e.g., >300°C) to promote side reactions that generate carboxyl ends. However, this invariably results in high product color and acetaldehyde content. A better way to increase the prepolymer carboxyl content is the addition of TPA to the reaction mixture after the completion of the ester-interchange stage but before the partial vacuum stage of the melt polymerization process. The addition of TPA during the ester-interchange stage is not recommended because TPA can deactivate the ester-interchange catalyst. Preferably, TPA is added with a stabilizer and a polycondensation catalyst (e.g., Sb_2O_3) after the completion of ester interchange and is allowed to dissolve and react for 15–30 min before the precondensation stage begins. The amount of TPA required is 0.1–0.3 mol/mol of DMT according to the second Duh patent.¹⁵

It is much easier and more efficient to control the COOH concentration of a TPA-based prepolymer. In a TPA process, an overall EG/TPA molar charge ratio of 1.03–1.10 is required to produce a prepolymer with an optimal COOH concentration according to the second Duh patent.¹⁵ However, in the standard TPA processes, 1.2 or higher charge ratios are used for reasons of material handling. In a batch process, an EG/TPA charge ratio lower than 1.2 will make the batch difficult to agitate initially. In a standard continuous TPA process, EG and TPA are charged together into the direct-esterification reactor (esterifier) in paste form. To make an easily pumpable paste, a charge ratio of 1.2 or higher is often required. Without some process modifications, this higher than optimal charge ratio usually yields prepolymers with lower than optimal COOH concentrations. One way to correct the problem is to add makeup TPA to the reaction mixture after 90–95% completion of direct esterification to bring the overall EG/TPA charge ratio within the optimal range. However, there are better ways.

In an improved batch process called the heel process,²⁶ a proper charge ratio can be used without difficulties. This improved batch process requires at least two reactors, one for direct esterification and the other for polycondensation, and the esterifier should have a capacity at least twice that of a standard esterifier. In each production series, a heel whose size is about 20% larger than a normal batch size (based on polymer formed) is first built in the

esterifier with a 1.2/1.0 EG/TPA molar charge ratio. The heel is completed after 90–95% of the COOH ends are consumed, as determined by the amount of water distilled. Then, a batch of an EG–TPA mixture of normal batch size is charged on top of the heel in the esterifier. The EG/TPA ratio of this first batch charge should be appropriately lower to bring the overall EG/TPA charge ratio to the desired optimal value. After the completion of the direct-esterification stage of the first batch, only a fraction of the esterifier content (equaling the normal batch size) is transferred to the polycondensation reactor, leaving the heel inside the esterifier. For each of the subsequent batches, the desired optimal charge ratio can be used. A heel is a mixture of esterification products, including bis(2-hydroxyethyl) terephthalate, oligomers, and a small amount of dissolved TPA. It speeds up the dissolution of TPA added in each subsequent batch and increases the heat-transfer rate, thereby greatly shortening the direct-esterification time of each normal batch. Therefore, a batch process using a heel not only allows for an optimal EG/TPA charge ratio to obtain an optimal prepolymer COOH concentration without agitation difficulties but also substantially reduces the batch cycle time.

In some continuous TPA processes,²⁷ dry TPA is charged separately by pneumatic conveying, and an optimal EG/TPA charge ratio can be maintained without agitation problems because the esterifier of a continuous process always contains a heel. However, these processes require large amounts of nitrogen to convey TPA into the esterifiers.

In a standard continuous TPA process, a paste with an EG/TPA molar ratio of 1.2 or higher is charged into the esterifier by pumping. In this case, an effective EG/TPA ratio in the esterifier can be controlled to the optimal value by the diversion of part of the overhead EG reflux away from the esterifier.

Because SSP is only a part of the overall manufacturing process for the production of solid-state PET resins, in pursuit of the optimal COOH concentration for the fastest SSP, one should not lose sight of the overall process economy. As pointed out earlier, the most efficient melt polycondensation process may not yield a prepolymer with an exactly optimal COOH concentration for SSP. Therefore, fixating on achieving the optimal prepolymer COOH concentration may not be a good idea; it may even be counterproductive. A case in point is the production of a prepolymer with a high optimal COOH concentration (e.g.,

near 40% of the total end-group concentration). To obtain such a prepolymer may require a dangerously low EG/TPA ratio, and a small undercharge of EG or overcharge of TPA can lead to process instability during melt polycondensation, producing a prepolymer with a substantially lower than target IV and/or an excessively high COOH concentration. In this case, it would be preferable to shoot for a prepolymer COOH concentration somewhat lower than the exactly optimal value to ensure stable operations of melt polymerization.

CONCLUSIONS

The presence of COOH ends has profoundly different effects on the SSP of PET depending on the byproduct diffusion resistance, which is determined mainly by the particle size and the flow rate of the purge gas. Several conclusions can be drawn from the experimental data for the SSP of powdered PET in a fluid bed and the SSP of pelletized PET in a fixed bed.

For reaction-controlled SSP,

1. The SSP rate increases monotonously with decreasing COOH concentration.
2. Sb catalyst increases the transesterification rate more than the esterification rate.
3. The presence of COOH ends can reduce the catalyst efficiency of Sb on transesterification. Thus, the minimum Sb concentration required for the highest SSP rate decreases with decreasing COOH concentration, and if the Sb concentration is insufficient (e.g., no higher than 100 ppm), k_1 decreases with increasing COOH concentration.
4. Within the COOH concentration range of 0–130 mol/10⁶ g, a Sb concentration of 210 ppm is more than sufficient to achieve the highest transesterification, esterification, and overall SSP rates.
5. In the presence of a sufficient Sb concentration, $k_2/k_1 < 1$, in contrast to $k_2/k_1 = 3$ –4, which was used in several published studies.

For SSP jointly controlled by reaction and diffusion:

1. With a substantially large ΔIV , as in most cases, there exists an optimal COOH con-

centration or COOH end fraction for the fastest SSP rate.

2. The optimal COOH end fraction is influenced by the ΔIV as well as the pellet size, and in most cases, it is between 0.25 and 0.40.

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