

Solid-State Polymerization of Poly(ethylene 2,6-naphthalate)

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Received 12 June 2006; accepted 22 August 2006

DOI 10.1002/app.25341

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The solid-state polymerization (SSP) of poly(ethylene 2,6-naphthalate) (PEN) was studied and compared with that of poly(ethylene terephthalate) (PET). The SSP of PEN, like that of PET, could be satisfactorily described with a modified second-order kinetic model, which was based on the assumptions that part of the end groups were inactive during SSP and that the overall SSP followed second-order kinetics with respect to the active end-group concentration. The proposed rate equation fit the data of the SSP of PEN quite well under various conditions. PEN prepolymers in pellet and cube forms with intrinsic viscosities (IVs) ranging from 0.375 to 0.515 dL/g, various particle sizes, and various carboxyl concentrations were solid-state polymerized at temperatures ranging from 240 to 260°C to study the effects of

various factors. The SSP data obtained in this study could be readily applied to the design of commercial PEN SSP processes. Because PEN and PET share the same SSP mechanism, in general, the SSP behaviors of PEN are similar to those of PET. Thus, the SSP rate of PEN increased with increasing temperature, increasing prepolymer IV, and decreasing prepolymer particle size. However, because of the much higher barrier properties of PEN, the prepolymer particle size and carboxyl concentration had much greater effects on the SSP of PEN than on the SSP of PET. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1075–1084, 2007

Key words: kinetics (polym.); polyesters; solid-state polymerization

INTRODUCTION

With similar but superior properties, poly(ethylene 2,6-naphthalene dicarboxylate) or poly(ethylene 2,6-naphthalate) (PEN) is the high-performance brethren of widely known poly(ethylene terephthalate) (PET). With much higher barrier properties, dimensional stability, mechanical strength, and thermal, chemical, and radiation resistance, PEN is suitable for numerous demanding applications for which PET is not, such as beer bottles, baby food jars, hot-fill bottles, returnable/refillable soft-drink containers, pharmaceutical/cosmetic packaging, miniature video and data-storage tapes, industrial fibers, electrical insulation and capacitor films, and industrial plastic.^{1–4} Furthermore, relatively small amounts of PEN can be blended with PET to produce copolymers with substantially improved properties over the PET homopolymer. For example, 92/8 mol % PET/PEN can be used to produce hot-fill bottles, and PET modified with 1–2 mol % PEN has greatly enhanced chemical and UV resistance. In fact, because of the high price of PEN, more PEN resins are used to blend with PET for copolymer applications than are used alone for homopolymer applications.

In general, the manufacturing processes for PEN are similar to those for PET. PEN can be synthesized from dimethyl-2,6-naphthalene dicarboxylate (NDC) and ethylene glycol (EG) or from 2,6-naphthalene dicarboxylic acid (NDA) and EG. Because crude NDA is very difficult to purify, purified NDA is much more expensive than NDC. Therefore, practically all current commercial PEN resins are produced from NDC and EG.

Like PET, PEN is crystallizable with a high melting temperature (T_m) and can be polymerized in the solid state. Because the melt viscosity of PEN is several times higher than that of PET at the same intrinsic viscosity (IV) and temperature,⁵ the melt polymerization of PEN is usually terminated at a relatively low IV (e.g., <0.55 dL/g). If the melt polymerization is continued further, the polymer melt becomes prohibitively difficult to handle, and the polymerization rate decreases, whereas the degradation (notably, color formation) rate increases because of the poor efficiency of byproduct removal. For many applications that require higher IVs, PEN resins can be more advantageously produced by a combination of melt and solid-state polymerization (SSP) processes.

Descriptions of various aspects of the SSP of PEN and the preparation of PEN prepolymers for use in SSP can be found in a number of U.S. patents^{6–11} and a research article.¹² Earlier, I⁶ proposed an SSP process for PEN, which includes a devolatilization step before the crystallization step to prevent the

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puffing (often referred to as *popcorning*) or expansion of PEN pellets during the crystallization step (more discussion on devolatilization follows). Tung and I⁶⁻¹⁰ also described the apparatus and procedure for use in the experiments of the SSP of PEN, provided experimental data for the SSP of PEN in the temperature range of 240–260°C, and disclosed various prepolymer particle forms with reduced diffusion resistance and, therefore, higher SSP rates. Stouffer et al.¹¹ disclosed a novel crystalline form of the PEN prepolymer produced from molten or glassy low-molecular-weight PEN material by means of rapid heat transfer to or from the material. The PEN prepolymer thus produced can be solid-state polymerized without having to go through the devolatilization step that I⁶ proposed.

In a more recent article, Sun and Shieh¹² presented the kinetics of the SSP of PEN, the effects of prepolymer IV and particle size on the SSP of PEN, and the melting behaviors of various solid-stated PEN samples. No doubt this article provides valuable data related to the SSP of PEN. However, its applicability to commercial SSP processes for PEN is limited mainly because the SSP experimental procedure, prepolymer IVs and particle sizes, and reaction temperatures used in their study were very different from those used in commercial SSP processes for PEN. Therefore, I decided to present an article to provide more useful data that could be readily applied in the design of commercial SSP processes for PEN. Another purpose of this article is to present a simple SSP rate equation that is capable of describing and explaining the observed SSP behaviors and fitting the experimental data.

SSP of PEN

Like the SSP of PET, the SSP of PEN involves two types of polycondensation reactions, namely, transesterification and esterification. Transesterification is the reaction between two hydroxyl (more accurately, 2-hydroxyethyl) end groups with EG as the reaction byproduct. Esterification is the reaction between a hydroxyl end group and a carboxyl end group with water as the reaction byproduct.

Although the SSP processes for PEN and PET are similar in general, there are two major differences between the two, mainly because of their differences in glass-transition temperature (T_g) and T_m values. PEN has much a higher T_g and T_m than PET, about 120 and 270°C, respectively, for PEN versus about 80 and 255°C, respectively, for PET.

The first major difference is in the crystallization procedure. Unlike PET, which can be directly exposed to its crystallization temperature (150–180°C) without problems, if PEN is directly exposed to its crystallization temperature (180–200°C), the pellets will puff or expand, as mentioned earlier. The puff-

ing or expansion of PEN pellets takes place because, as the pellet temperature is rapidly raised to near the temperature just before significant crystallization starts (ca. 20°C above the T_g), the pellets soften, while the internal vapor pressure of the pellets is increased to above the external pressure (i.e., near atmospheric pressure). Puffing or expansion of the pellets not only causes pellet-sticking problems but also results in popcornlike or distorted pellets. Therefore, it is necessary to heat the PEN prepolymer at temperatures below the softening temperature (usually between 100 and 120°C) to reduce its volatile contents (mainly moisture) sufficiently (i.e., for 1 to several hours to lower the moisture content to below 0.07%) to prevent these problems. The reduction of the volatile contents before crystallization is referred to as *devolatilization* to distinguish it from drying, which reduces the volatile contents to a greater extent and is usually conducted at the crystallization temperature or higher temperatures. The pellet puffing problems can also be prevented by crystallization of the prepolymer at 25 psig or a higher pressure in gas or liquid phase as I illustrated in two U.S. patents.^{13,14} PET does not have puffing or expansion problems during crystallization at atmospheric pressure because of its much lower softening and crystallization temperatures and much lower internal vapor pressure at the softening temperature. However, according to my experience, puffing can occur if PET pellets with a sufficiently low IV (e.g., lower than about 0.45 dL/g) are dried or crystallized *in vacuo* because of the combination of the low melt strength of the low-IV PET and the low external pressure. Sun and Shieh¹² did not observe PEN puffing problems in their PEN SSP experiments because they predried the prepolymers at 120°C, which was below the softening temperature of PEN, overnight before their SSP runs.

Another major difference between the PEN and PET SSP processes is in the SSP temperature range. The maximum allowable or safe SSP temperature is determined by the maximum temperature at which pellet sticking or agglomeration does not occur. The maximum safe SSP temperature for unmodified PET is about 230°C for the batch process (conducted in tumble dryers *in vacuo*) and about 220°C for the continuous moving-bed process with a mechanical discharger. The SSP temperature range used in the commercial production of solid-stated PET is 200–230°C. Probably due to the higher rigidity of PEN molecular chain, PEN can be solid-stated in a tumble dryer at 260°C, which is no more than 10°C below its T_m . The commercial SSP temperature range for PEN is from about 240 to about 260°C. Sun and Shieh¹² conducted their PEN SSP experiments within the temperature range of 200–245°C, which is substantially lower than that used in commercial SSP

processes for PEN. Because they used ground PEN prepolymers, the SSP rates were reasonably fast even at the low end of this temperature range. Had they used prepolymers in pellet form, the SSP rate near the lower end of this temperature range would have been extremely slow.

Rate equation for the SSP of PEN

Sun and Shieh¹² used a power-of-the-time rate equation to fit their PEN SSP data. Although this equation fit their data satisfactorily, it has two shortcomings. First, it does not have any physical meaning. Second, it predicts infinite molecular weight at an infinite solid-state polymerization time (t), whereas in reality, the molecular weight always levels off after prolonged SSP.

Because PEN and PET share the same SSP mechanism, the following semiempirical rate equation that I¹⁵ proposed for the SSP of PET should also be adequate for the SSP of PEN:

$$-\frac{dC}{dt} = 2k(C - C_i)^2 \quad (1)$$

where C is the total end-group concentration, t is the SSP time, C_i is the apparent inactive end-group concentration, and k is the apparent reaction rate constant.

This equation is based on the concept of the existence of inactive end groups during SSP. The inactive end groups are those trapped inside the crystals and chemically dead end groups. C_i includes the contributions of the true inactive end groups and is affected by many factors, including the temperature, particle size, prepolymer IV, and prepolymer carboxyl concentration, just as k . This equation represents the net SSP rate without a distinction between the types of end groups or polycondensation reactions. It is capable of adequately describing and explaining the observed SSP behaviors. The presence of the inactive end groups agrees with the observation that in each prolonged SSP run, the SSP ceases once an ultimate number-average molecular weight (M_n) or ultimate IV is reached. In fact, the maximum achievable M_n and IV can be predicted by the value of C_i . According to eq. (1), the SSP rate increases with increasing k and decreasing C_i . Because k and C_i are fitting parameters, factors that increase the SSP rate tend to increase the value of k and/or decrease the value of C_i and vice versa.

After one integrates eq. (1) and solves for the integration constant with the initial conditions $C = C_0$ at $t = 0$, where C_0 is the initial total end-group concentration, the resulting equation can be rearranged into the following form:

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

where

$$a = 2k(C_0 - C_i)$$

and

$$b = 2k(C_0 - C_i)C_i$$

Therefore, if $(C_0 - C)/t$ is plotted against C with experimental data, a straight line with slope a and intercept $-b$ can be obtained with the assumption that the rate equation is adequate. It is obvious that $C_i = b/a$. Once C_i is determined, k can be calculated from either a or b . The four parameters, a , b , k , and C_i are referred to as the *kinetic parameters*.

Solving eq. (2) for C yields

$$C = \frac{C_0 + bt}{1 + at} \quad (3)$$

In the polyester industry, C is more conveniently expressed in the units of micromoles per gram. Thus, C is related to M_n by the following equation:

$$C = \frac{2 \times 10^6}{M_n} \quad (4)$$

M_n is, in turn, related to IV by the following equation, which is based on 60/40 phenol/tetrachloroethane IV solvent at 25°C, developed by the Polyester R&D Division of Goodyear Tire & Rubber Co., Akron, Ohio:

$$IV = 4.97 \times 10^{-4} M_n^{0.68} \quad (5)$$

With eqs. (3)–(5), the solution for IV is obtained:

$$IV = 9.5732 \left[\frac{1}{C} \right]^{0.68} = 9.5732 \left[\frac{1 + at}{C_0 + bt} \right]^{0.68} \quad (6)$$

EXPERIMENTAL

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

Prepolymers used in the experiments

All of the prepolymers used in the experiments for this study were in pellet or cube form and were produced in the Polyester Pilot Plant or Polyester Resin Plant of Goodyear Tire & Rubber Company. All of the prepolymers contained 80 ppm manganese (as an ester-interchange catalyst), 40 ppm phosphorus (as a stabilizer), and 200 ppm antimony (as a polycondensation catalyst). Typical T_g and T_m values of

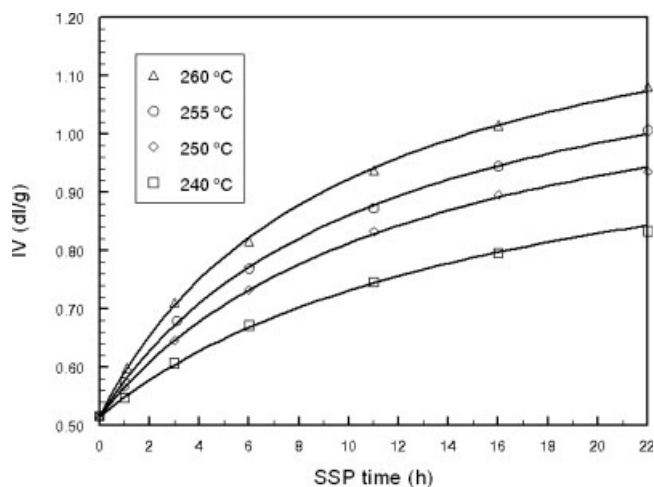


Figure 1 IV buildup curves for the SSP of PEN at 240, 250, 255, and 260°C.

these prepolymers were 120 and 268°C, respectively. The prepolymers with different pellet sizes used in the experiments for the study of the pellet-size effect were prepared by the repelleting of a melt PEN resin from a typical batch to ensure that all properties other than the pellet size were the same. The melt resin was first devolatilized at 120°C in a vacuum oven for 4 h and then dried at 180°C overnight. The dried resin was extruded with a small extruder into a melt strand, which was quenched and solidified in a water trough and then chopped into pellets of the desired pellet size with a small pelletizer. The pellet size was controlled by the variation of the screw rotating speed and/or the strand speed.

Experimental apparatus

The reactor used to conduct the SSP experiments was constructed of a 50 cm long glass column with a diameter of 28 mm. The reactor had a cone-shaped bottom, which was connected to a nitrogen (purge gas) supply tube that had a diameter of 4 mm and a length of 150 cm, 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 30 cm deep thermostated oil bath, whose temperature was controlled to within $\pm 0.1^\circ\text{C}$. The nitrogen supply tube also served as a heat exchanger, which heated the incoming nitrogen to the desired experimental temperatures. During the experimental runs, the polymer bed temperature was monitored with a thermocouple.

Experimental procedures

For each SSP run, 80 mL of PEN prepolymer was charged into the reactor. The prepolymer was first devolatilized at 120°C for 3 h with nitrogen passing

through the polymer bed at a flow rate of 8 L/min. Then, the oil-bath temperature was raised to 190°C and held there for 1 h to crystallize and dry the polymer. During the first 10 min of this crystallization/drying step, the nitrogen flow rate was momentarily increased to 90–120 L/min, depending on the polymer particle size, to fluidize the polymer bed and heat up the polymer bed quickly. Meanwhile, a metal rod was used to stir the polymer bed to help prevent polymer agglomeration. After the crystallization/drying step, the oil-bath temperature was raised to the desired SSP temperature, which ranged from 240 to 260°C, over 10–15 min. Again, the nitrogen flow rate was momentarily increased to 90–120 L/min to fluidize the polymer bed, and the polymer bed was stirred with a metal rod to help prevent polymer sticking during the heating period. Once the bed temperature reached the desired SSP temperature, the nitrogen flow rate was returned to 8 L/min to maintain a static bed and to start the SSP step, which lasted 20–24 h. Samples (ca. 10 mL each) were taken at various intervals throughout the SSP step. All of the samples were tested for IV.

RESULTS AND DISCUSSION

Effect of temperature on the SSP rate

The prepolymer chosen to study the temperature effect on the SSP rate had an IV of 0.515 dL/g with a pellet size of 0.027 g. The prepolymer pellets were solid-state polymerized at 240, 250, 255, and 260°C for 22 h. The IV data for these SSP runs are shown in Figure 1. These IV data were used to prepare the $(C_0 - C)/t$ versus C plots shown in Figure 2. Four straight lines were obtained in Figure 2; this indicated that the proposed rate equation fit the SSP data well for all four SSP runs. From the values of a

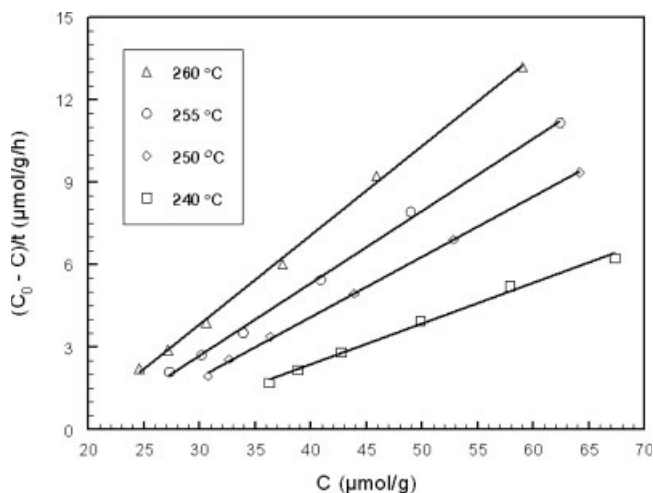


Figure 2 $(C_0 - C)/t$ versus C plots for the SSP of PEN at 240, 250, 255, and 260°C.

TABLE I
Values of the Kinetic Parameters for the SSP of PEN at Four Temperatures

SSP temperature (°C)	a (h ⁻¹)	b (μmol/g) h ⁻¹	$k \times 10^3$ (μmol/g) ⁻¹ h ⁻¹	C_i (μmol/g)
240	0.1486	3.5723	3.0022	24.04
250	0.2186	4.6404	4.1790	21.23
255	0.2640	5.2369	4.9162	19.84
260	0.3241	5.8933	5.8555	18.18

and $-b$, the values of k and C_i could be calculated for each SSP temperature. Table I lists the values of a , b , k , and C_i for the SSP of PEN at the four temperatures. The values of a and b or k and C_i listed in Table I can be inserted into eq. (6) to express the IV as a function of t for each SSP temperature. The IV equations thus obtained are plotted in Figure 1 for the four SSP runs. All curves fit the SSP data satisfactorily.

As expected, k increased with increasing temperature. This was readily understood because the SSP rate should increase with increasing temperature. As the temperature was increased, the mobility and activity of the chain ends also increased, resulting in increased rates of polycondensation reactions. Furthermore, the diffusion rates of the reaction byproducts also increased with increasing temperature. This also increased k . C_i decreased with increasing temperature mainly because the numbers of inactive end groups decreased with increasing temperature. As the temperature increased, part of the inactive end groups trapped inside the crystals at lower temperatures were rejected into the amorphous phase, where polycondensation took place, as a result of morphological transformation. Of course, the increases in the byproduct diffusivity could also result in a lower C_i and a higher k .

Figure 3 shows the Arrhenius plot for k with the k values listed in Table I. The temperature dependence of k can be expressed by the Arrhenius equation

$$k = A \exp \left\{ \frac{-E_a}{RT} \right\}$$

where A is the frequency factor, E_a is the apparent activation energy, T is the absolute temperature (K), and R is the universal gas constant. From the slope and intercept of the straight line in Figure 3, the values of A and E_a could be determined. Thus, $A = 147,488$ (μmol/g)⁻¹ h⁻¹ and $E_a = 18,056$ cal/mol.

E_a for the SSP of PEN pellets in the temperature range of 240–260°C was comparable with that for the SSP of PET pellets in the temperature range of 190–220°C that I¹⁵ determined.

In Figure 4, C_i is plotted against the absolute solid-state polymerization temperature [T (K)]. C_i is approximately a linear function of SSP temperature and can be represented by the following equation:

$$C_i = -0.2903T + 173.0347$$

Because the SSP rate is influenced by k and C_i , which is also a function of temperature, E_a alone is insufficient for comparing rates at different temperatures. There are two ways to compare the SSP rates at two different temperatures. Most people are more interested in the average rates (in terms of IV increase per hour) over an IV range of interest. For example, the reaction times required to achieve a product IV of 0.80 dL/g were 16.4, 9.3, and 5.3 h at 240, 250, and 260°C, respectively (Fig. 1). Within the tem-

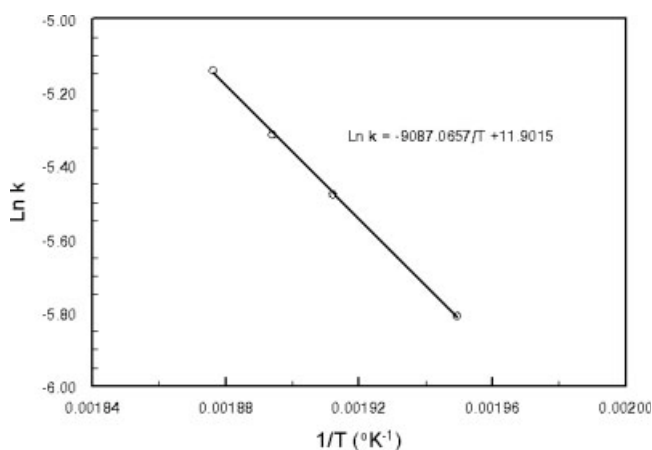


Figure 3 Arrhenius plot for k for the SSP of PEN.

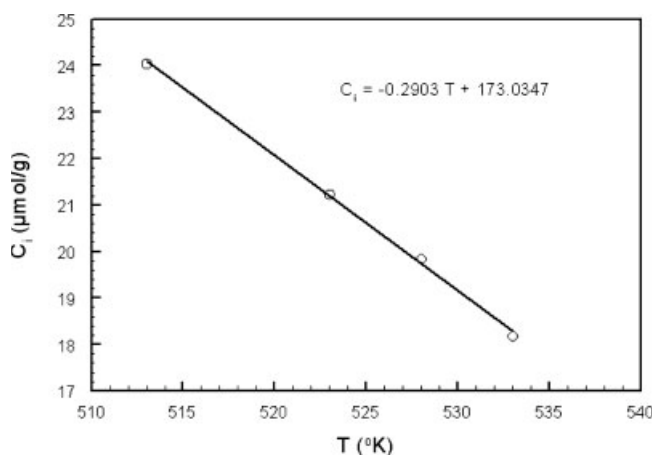


Figure 4 C_i versus temperature plot for the SSP of PEN.

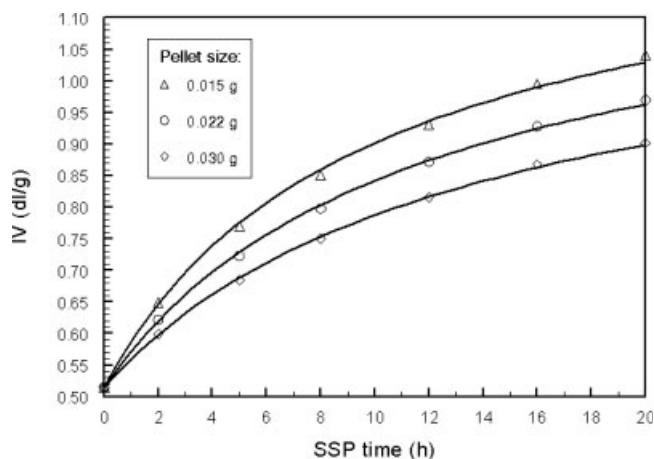


Figure 5 IV buildup curves for the SSP of PEN prepolymers with different pellet sizes at 250°C.

perature range 240–260°C, the average SSP rate for the product with an IV of 0.80 dL/g increased by about 76% with each 10°C increase in temperature. Similarly, the average SSP rate increase with every 10°C temperature increase was determined to be about 66% over the IV range of 0.515–0.70 dL/g. For comparison, for the SSP of PET pellets within the temperature range 210–220°C over the IV range of 0.574–0.780 dL/g, the average SSP rate increased by about 77% with each 10°C in temperature as I^{15} determined. Alternatively, the SSP rates at a specific IV could be calculated for different temperatures with eq. (1). For example, at 0.80 dL/g, the SSP rates were 1.25, 2.49, and 4.82 ($\mu\text{mol/g}$) h^{-1} at 240, 250, and 260°C, respectively. The rate almost doubled for each 10°C increase in temperature. Similarly, it could be readily determined that at 0.70 dL/g, the SSP rate increased by about 76% for each 10°C increase in temperature.

Effect of particle size on the SSP rate

Because SSP involves the diffusion of reaction by-products from within to outside the polymer particles and the diffusion resistance decreases with decreasing pellet size, the SSP rate of PEN was expected to increase with decreasing pellet size. Figure 5 shows the IV buildup curves, and Table II lists the values of a , b , k , and C_i for the SSP of three prepolymers

with an equal IV of 0.515 dL/g but different pellet sizes of 0.015, 0.022, and 0.030 g at 250°C. As expected, the SSP rate and k increased, whereas C_i decreased with decreasing pellet size.

From Figure 5, I estimated that within the pellet-size range of 0.015–0.030 g, the average SSP rate of PEN increased by about 50% for the product with an IV of 0.80 dL/g if the pellet size was reduced by 0.01 g. For the production of a lower IV product, the average rate increase would be lower. For example, for the product with an IV of 0.70 dL/g, the rate increase was about 45% with the same pellet-size reduction. This was because, in the early stage, more reactions took place near the pellet surface and the effect of pellet size on the diffusion resistance was smaller. As the SSP progressed further, the end groups near the surface were depleted, and more reactions took place deeper inside the pellets, which resulted in a greater pellet-size effect.

For comparison, for the product with an IV of 0.82 dL/g from prepolymer with an IV of 0.60 dL/g IV, the average SSP rate of PET increased about 15% if the pellet size was reduced by 0.01 g. Obviously, the prepolymer pellet size had a much greater effect on the SSP of PEN than on the SSP of PET. This is mainly due to the much higher barrier properties (or higher byproduct diffusion resistance) of PEN. For example, the water vapor transmission rate within PEN was less than one-third that within PET. Another reason is that the PEN prepolymers used had lower relative carboxyl contents than the PET prepolymers. As a result, the SSP byproducts of the PEN prepolymers had higher proportions of EG, which has a lower diffusivity than water.

Although the SSP rate of PEN can be substantially increased by the reduction of the pellet size, there are several factors to consider. First, as mentioned earlier, more PEN resins are used in blends with PET resins than used alone. It will be easier to ensure uniform blends if the two component resins have similar pellet sizes. Second, the sticking temperature of PEN pellets in the SSP reactor decreased with decreasing pellet size. Third, some polyester processors prefer bigger pellets because pellets that are too small tend to cause more handling problems (e.g., they may plug the screens of some handling equipment). Fourth, reducing the pellet size means reducing productivity and increasing pelletizing time, which

TABLE II
Values of the Kinetic Parameters for the SSP of the PEN Prepolymers with Different Pellet Sizes at 250°C

Pellet size (g)	a (h^{-1})	b ($\mu\text{mol/g}$) h^{-1}	$k \times 10^3$ ($\mu\text{mol/g}$) $^{-1}$ h^{-1}	C_i ($\mu\text{mol/g}$)
0.015	0.3125	5.9538	5.7355	19.05
0.022	0.2469	5.0271	4.6430	20.36
0.030	0.1952	4.2720	3.7791	21.88

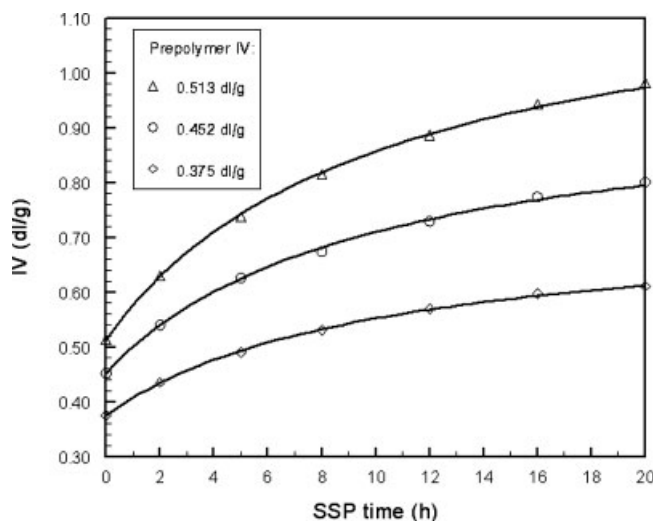


Figure 6 IV buildup curves for the SSP of PEN with different prepolymer IVs at 250°C.

may significantly increase polymer degradation because it will take longer to empty the melt reactor in a batch process. Therefore, the pellet sizes of most commercial PEN resins are between 0.015 and 0.030 g, similar to those of PET resins.

Two ways to reduce the diffusion resistance within PEN particles without changing the particle outer dimension have been claimed in four U.S. patents.^{7–10} Tung and I^{7,8} proposed a method to prepare pellets, each with an open-ended cavity (hollow pellets, each with an O-shaped cross-section). One example showed that PEN hollow pellets with a 9% void fraction solid-state polymerized 78% faster than solid pellets with identical outer dimension between 0.48 and 0.75 dL/g at 250°C. I^{9,10} proposed the use of foamed PEN chips to increase the SSP rate. In one example, nitrogen was whipped into the polymer melt inside the melt reactor. The polymer melt was then extruded and diced into 1/8 in. cubes. These foamed cubes had an IV of 0.50 dL/g and a void fraction of 21%. These foamed cubes and solid cubes with the same IV were solid-state polymerized at 250°C to compare their SSP rates. Surprisingly, over the IV range of 0.50–0.80 dL/g, the foamed cubes solid-state polymerized 4.5 times as fast as the solid cubes. The dra-

matic SSP rate advantage of the foamed cubes over the solid cubes still cannot be satisfactorily explained.

Effect of the prepolymer IV on the SSP rate

Several researchers^{15–18} have determined that the SSP rate of PET increases with increasing prepolymer IV. It was expected that the prepolymer IV should have a similar effect on the SSP rate of PEN.

Figure 6 shows the IV buildup curves for the SSP of three PEN prepolymers with different IVs at 250°C. These prepolymers had similar pellet sizes (0.0199–0.0202 g) and carboxyl concentrations (17–19 $\mu\text{mol/g}$). Indeed, Figure 6 shows the SSP rate of PEN also increased with increasing prepolymer IV. Table III lists some properties of these prepolymers and the values of a , b , k , and C_i for the SSP of these prepolymers at 250°C. k increased, whereas C_i decreased, with increasing prepolymer IV. The SSP rates of the prepolymers with different IVs at each fixed IV can be compared with eq. (1). For instance, at IV = 0.55 dL/g, the SSP rates were 3.26, 12.17, and 22.23 ($\mu\text{mol/g}$) h^{-1} (in terms of rate of decrease of C) for the prepolymer IVs of 0.375, 0.452, and 0.513 dL/g, respectively. In terms of rate of IV increase, these were equivalent to 0.018, 0.068, and 0.125 (dL/g) h^{-1} , respectively. The rate improvement with increasing prepolymer IV increased at a higher product IV. Furthermore, because C_i decreased with increasing prepolymer IV, the maximum achievable IV increased with increasing prepolymer IV.

Wu et al.¹⁷ and Kim and Jabarin¹⁸ attributed the effect of the prepolymer IV to the fact that the crystallinity during SSP increases with decreasing prepolymer IV. They reasoned that the higher crystallinity resulted in higher byproduct diffusion resistance and lower end-group mobility. However, a recent study of mine¹⁹ indicated that the SSP rate can actually increase with increasing crystallinity, mainly because higher crystallinity results in higher end-group concentrations in the amorphous regions where polycondensation reactions take place. The negative effects of the higher crystallinity are outweighed by the positive effects.

The concept of the existence of inactive end groups during SSP may explain the prepolymer IV effect

TABLE III
Some Properties of PEN Prepolymers with Different IVs and Values of the Kinetic Parameters for the SSP of These Prepolymers at 250°C

Prepolymer IV (dL/g)	Pellet size (g)	COOH concentration ($\mu\text{mol/g}$)	a (h^{-1})	b ($\mu\text{mol/g}$) h^{-1}	$k \times 10^3$ ($\mu\text{mol/g})^{-1} \text{h}^{-1}$	C_i ($\mu\text{mol/g}$)
0.375	0.0199	17	0.2232	9.7279	3.0298	43.58
0.452	0.0200	19	0.2573	7.4831	4.2876	29.08
0.513	0.0202	18	0.2794	5.7965	5.2506	20.75

TABLE IV
Some Properties of PEN Prepolymers with Different Carboxyl Concentrations and Values of the Kinetic Parameters for the SSP of These Prepolymers at 250°C

Prepolymer IV (dL/g)	COOH concentration ($\mu\text{mol/g}$)	a (h^{-1})	b ($\mu\text{mol/g h}^{-1}$)	$k \times 10^3$ ($\mu\text{mol/g}^{-1} \text{h}^{-1}$)	C_i ($\mu\text{mol/g}$)
0.497	11	0.1058	3.0996	2.1955	29.30
0.501	16	0.1360	3.5433	2.6917	26.05
0.501	25	0.2021	4.5429	3.7356	22.48
0.425	52	0.2939	5.5971	3.7442	19.04

more satisfactorily. Because a lower IV prepolymer has a greater number of end groups per unit mass, when the prepolymer crystallizes, statistically the concentration of the end groups trapped inside the crystals will be higher. This leads to a higher C_i . The differences in the crystallization rate and the average length of the chain ends that stick out of the crystals between two prepolymers with different IVs may also contribute to the prepolymer IV effect. A lower IV prepolymer crystallizes faster, and more hastily formed crystals tend to trap more end groups. Statistically, the chain ends that dangle outside the crystals should be shorter on average in a lower IV prepolymer and should result in lower end-group flexibility and mobility and, therefore, lower reaction rates.

Effect of carboxyl concentration on the SSP rate

^{16,20} have discussed in detail the effect of the prepolymer carboxyl concentration on the SSP rate of PET. According to those studies, the combined chemical reaction rate (the sum of the rates of the two polycondensation reactions, transesterification and esterification) is highest when the carboxyl concentration is zero. This was demonstrated by the fact that in the absence of diffusion resistance or in the presence of low diffusion resistance (e.g., within powdered prepolymer with a particle size no greater than 35 mesh), the SSP rate was highest with a prepolymer carboxyl concentration of zero. As the prepolymer particle size and the diffusion resistance increase, esterification is favored more and more because its reaction byproduct, water, has a higher diffusivity and is removed more quickly than that of transesterification, EG. Therefore, there exists an optimal prepolymer carboxyl concentration (ca. 1/3 of the C) for the SSP of pelletized or diced PET. Because the SSP of PEN involves the same polycondensation reactions and the diffusion of the same byproducts, the prepolymer carboxyl concentration should have a similar effect on the SSP of PEN. Also, because PEN has much higher barrier properties, the effect is expected to be much greater.

In NDC-based PEN, as well as in dimethyl terephthalate (DMT)-based PET, all carboxyl ends are

formed by degradation and side reactions, which take place throughout the melt polymerization process even in the presence of a stabilizer. Two major degradation reactions are responsible for the generation of carboxyl ends and acetaldehyde: (1) the degradation of hydroxyl ends, which forms carboxyl ends and generates acetaldehyde, and (2) chain scission at diester links, which creates carboxyl and vinyl ends. The vinyl ends can react with hydroxyl ends to reform diester links and generate acetaldehyde. If the acetaldehyde generated is not removed immediately, color bodies will be formed. These two degradations are most severe during the later part of the polycondensation stage when the melt temperature is the highest. Some side reactions also generate carboxyl ends, but they are minor contributors of carboxyl ends. Although degradation and side reactions may be good in that they create carboxyl ends, which may increase the SSP rate, they are bad because they may lead to inferior polymer quality (notably, high color). NDC-based PEN prepolymers usually have carboxyl concentrations within a relatively narrow range (typically between 15 and 25 $\mu\text{mol/g}$). Prepolymers with far higher than normal carboxyl concentrations are usually produced as a result of some process upsets that cause excessive degradation and unacceptable polymer quality.

All of the prepolymers used in the study of the carboxyl concentration effect were in the form of 1/8-in. cubes with a particle size of about 0.06 g. The IVs and carboxyl concentrations of these prepolymers are listed in Table IV. The first three prepolymers had similar IVs (ca. 0.50 dL/g), with carboxyl concentrations ranging from 11 to 25 $\mu\text{mol/g}$ (equivalent to 14 to 33% of the Cs). The fourth prepolymer, with a much higher carboxyl concentration (52 $\mu\text{mol/g}$, equivalent to 53% of the C) and a substantially lower IV (0.425 dL/g), was unintentionally produced as a result of a long hold inside the finishing reactor due to dicer problems.

Figure 7 shows the IV buildup curves for the SSP of these four prepolymers at 250°C. The t values required for the first three prepolymers with IVs near 0.50 dL/g and carboxyl concentrations of 25, 16, and 11 $\mu\text{mol/g}$ to polymerize from 0.50 to 0.70 dL/g were estimated to be 6, 10.5, and 16 h, respectively. If the prepolymer carboxyl concentrations were in-

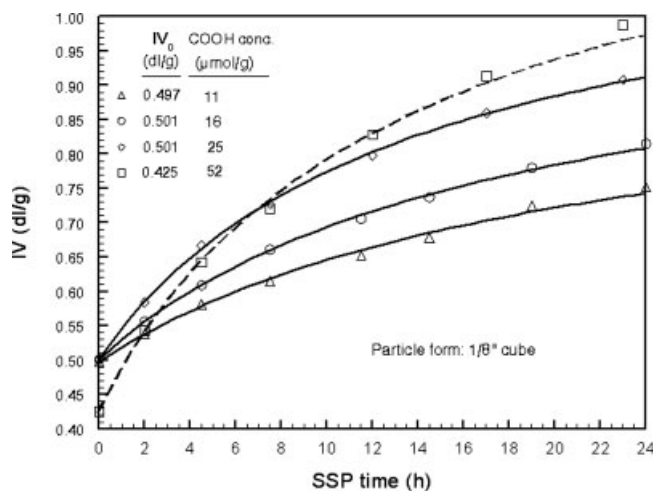


Figure 7 IV buildup curves for the SSP of PEN prepolymers with different carboxyl concentrations at 250°C.

creased by 10 from 11 to 21 $\mu\text{mol/g}$ and from 15 to 25 $\mu\text{mol/g}$, the average SSP rate within this IV range increased by about 108 and 88%, respectively. It appeared that the SSP rate improvement for NDC-based PEN with a 10 $\mu\text{mol/g}$ increase in prepolymer carboxyl concentration could be greater than that with a 10°C increase in SSP temperature. The fact that the SSP rate increased with increasing prepolymer carboxyl concentration within this carboxyl range indicated that the optimum prepolymer carboxyl concentration for the SSP of PEN must have been higher than 33% of the C.

What was more amazing was the high SSP rate of the fourth prepolymer, with a carboxyl concentration of 52 $\mu\text{mol/g}$. Despite its substantially lower IV, it solid-state polymerized much faster than all three of the other prepolymers with much lower relative carboxyl concentrations (expressed as a percentage of C). It is not clear whether the relative carboxyl concentration of this prepolymer, 53%, was below or above the optimum value. However, it is certain that the optimum relative carboxyl concentration for PEN was much higher than that for PET (ca. 33%). Obviously, the prepolymer carboxyl concentration had a more pronounced effect on the SSP of PEN than on the SSP of PET because of the much higher barrier properties of PEN.

The values for the kinetic parameters for the SSP of the PEN prepolymers with different carboxyl concentrations at 250°C are included in Table IV. For the three prepolymers with IVs near 0.50 dL/g, k increased, whereas C_i decreased with increasing carboxyl concentration, indicating that the SSP rate and the ultimate IV increased with increasing carboxyl concentration within the range 11–25 $\mu\text{mol/g}$. Although the fourth prepolymer had a substantially lower IV (0.425 dL/g), it had a higher k value and a

lower C_i value than all of the other prepolymers because of its high carboxyl concentration.

On the basis of the previous observations, it was obvious that the SSP rate of NDC-based PEN could be drastically improved by an increase in its carboxyl concentration. In a U.S. patent, I²¹ proposed a method to increase the carboxyl concentration of DMT-based PET. A similar method could be used to increase the carboxyl concentration of NDC-based PEN. In the melt-phase polycondensation process, a small amount of NDA could be added to the melt reactor after the completion of the ester interchange stage. This would effectively increase the carboxyl concentration in the resulting prepolymer without excessive degradation. With some experimentation, the amount of NDA required to obtain the optimal prepolymer carboxyl concentration could be determined.

CONCLUSIONS

Various aspects of the SSP of PEN were investigated. A modified second-order rate equation based on a kinetic model, which assumed that there were two types of end groups, active and inactive, during SSP, and the SSP followed second-order kinetics with respect to the active end-group concentration. The rate equation contains two fitting parameters, k and C_i . The SSP rate was influenced by both k and C_i , and the maximum IV achievable with the SSP could be predicted by C_i . This kinetic model fit the SSP data well and was capable of describing and explaining the observed SSP behaviors of PEN under various conditions.

One peculiar behavior of PEN not observed with PET is that PEN particles tend to puff or expand if directly exposed to the crystallization temperature. Therefore, a devolatilization step, in which the volatile contents were sufficiently reduced at temperature below the T_g , was required before the crystallization step for PEN.

Because PEN and PET share the same SSP mechanism with the same reactant end groups, hydroxyl and carboxyl end groups, and reaction byproducts, EG and water, the SSP behaviors of PEN are, in general, quite similar to that of PET. Thus, the SSP rate increased with increasing temperature, increasing prepolymer IV, and decreasing particle size. However, because the barrier properties of PEN were much higher than those of PET, the effects of the prepolymer particle size and carboxyl concentration were much greater on the SSP of PEN than on the SSP of PET. PEN prepolymer produced from NDC and EG tended to have a carboxyl concentration far lower than optimum. The carboxyl concentration could be optimized by the addition of a small amount of NDA into the melt polycondensation reactor in the manufacture process of the prepolymer. This is

particularly advantageous if the prepolymer is to be used to produce a very high-IV solid-stated product.

The author thanks Goodyear Tire & Rubber Co. for providing the materials for the study and for characterizing the samples.

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