Solid State Polymerization (SSP) of Low Molecular Weight Poly(ethylene terephthalate) (PET) Copolyesters Compared to Conventional SSP of PET

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ABSTRACT: SSP, starting from very low molecular weight (MW) poly(ethylene terephthalate) (PET) precursors, is claimed to offer significant production cost advantages over conventional PET production. However, as the intrinsic viscosity (IV) of the PET precursor is reduced, there is a significant change in the crystallization behavior of PET and morphology that affects reactivity in SSP. Using small particle size PET to significantly reduce the effects of diffusion so that SSP is under chemical reaction control and using a kinetic model that describes an overall SSP rate, the effect of ethylene isophthalate substitution on the SSP rate from low MW PET precursor was determined. As the ethylene isophthalate comonomer content increases, the rate of SSP for low MW PET increases. The activation energy for SSP of low MW PET decreases with an increase in the ethylene isophthalate content. For the low MW PET copolyesters in this study, the SSP activation energy is comparable to conventional process when the comonomer content of the low MW polyester is around 7 mol % and the conventional precursor is around 3 mol %. However, even though the activation energy is reduced through the use of higher comonomer content, the overall rate of SSP for the low MW copolyesters studied is significantly slower than conventional SSP. This reduction in rate is explained by differences in crystallinity. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 230–238, 2002

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

INTRODUCTION

PET and its copolyesters are useful materials for fiber, film, and packaging applications. In the case of packaging and high tenacity fiber, PET polyesters are solid state polymerized (SSP) to higher molecular weights to provide the desired properties for these applications. In a typical SSP process, the polyester precursor for SSP is near a fiber grade molecular weight or intrinsic viscosity (IV) of 0.50 dL/g or higher. There are numerous patents that teach solid state polymerization processes for PET starting from a much lower molecular weight precursor with IVs in the range of 0.15–0.40.[1,2] The reasons for developing an SSP process that utilizes very low IV polyesters as its starting material are to reduce capital equipment expenditures and operation costs. The use of low IV polyester in SSP avoids expensive and sophisticated melt polymerization vessels in the manufacture of the PET precursor and the cost of operating this equipment. However, lowering the polyesters IV from the traditional melt phase precursor IV of 0.50–0.65 dL/g results in a significant change in the physical properties of the

polyester with respect to crystallization behavior. Low IV precursor in SSP results in faster crystallization rate, higher percent crystallinity, and an increase in the crystallite size. Also, the greater number of end groups in low molecular weight polyester creates more defects that change its melting behavior.

In addition to molecular weight differences, there are chemical composition effects on the morphology, thermal properties, and SSP rate of PET polyesters. Compositional effects are produced by the use of comonomer to modify the properties relative to homopolymer. Using a comonomer such as isophthalic acid changes, the properties of PET with respect to crystallization rate, morphology, crystallinity, and thermal properties. Isophthalic acid is typically used at a low level, 2–3 mol %, in PET packaging resins to improve the processing and performance of PET.[3]

This paper investigates the effect of ethylene isophthalate comonomer on the solid state polymerization of low IV PET and compares it to the SSP of the conventional PET precursor.

BACKGROUND

Polycondensation of PET polyester in a discrete particle below its melting point, also known as solid state polymerization or SSP, involves predominately two reversible reactions occurring simultaneously. One re-

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action is an ester interchange between two hydroxy-ethyl ester end groups, as shown in eq. (1):
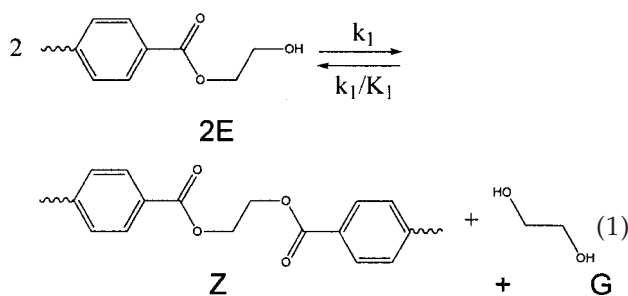
The other is an esterification reaction between a carboxylic acid end group and a hydroxyethyl ester end group as shown in eq. (2):
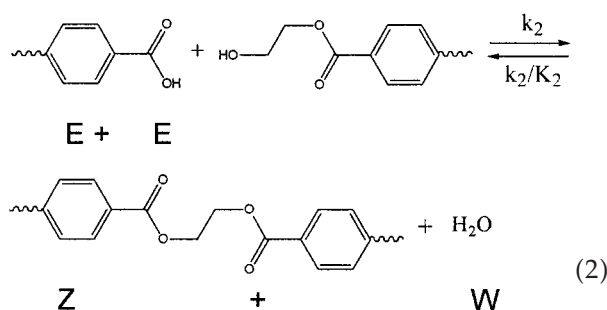
In solid state polymerization, it has been found that ester interchange or transesterification occurs at a faster rate than esterification. Because of this difference in reactivity and also the rate diffusion of volatile components, the ratio of end groups can have a significant effect on SSP reaction rates and the optimization of SSP.[4] However, to simplify the kinetic analysis of the SSP rate data, the model developed by Qui, Huang, Tang, and Gerking[5] was employed. This model describes an overall equilibrium reaction for SSP where G represents the volatile by-products.

$$2E \stackrel{k}{=} Z + G \qquad (3)$$

Also, as the size of the discrete particle is reduced and there is sufficient gas flow to remove the volatile products (water and glycol) from the surface of the particle, SSP becomes chemical reaction rate controlled. Since volatile components are removed as they are formed, the forward reaction can be described by a simple second-order reaction. This leads to eq. (4), which describes the change in the number average degree of polymerization, P_n, with time, t. Equation (4) was applied to the SSP results for low molecular weight copolyesters to determine the effect of composition on SSP and compare it to conventional molecular weight precursor.

$$P_n = P_{n0} + 4kt \qquad (4)$$

P_{n0} is the initial number average degree of polymerization and k is the overall reaction rate constant to produce diester. In this study, plots of P_n vs time give straight lines, indicating that SSP for these materials are under chemical reaction rate control.

EXPERIMENTAL

Synthesis of low molecular weight copolyesters

PET copolyesters with 3.0 mol % isophthalic acid

Terephthalic acid (838.28 g), ethylene glycol (378.03 g), isophthalic acid (25.93 g), antimony oxide (0.30 g), cobalt acetate tetrahydrate (0.101 g), and tetramethyl-ammonium hydroxide (0.50 g) were added to a batch polyester autoclave and mixed to form a paste. The autoclave was pressurized to 40 psi, and paste was agitated and heated to 262°C over 215 min to esterify terephthalic acid and isophthalic acid with ethylene glycol. The water produced during esterification was separated from ethylene glycol in an overhead column and the glycol was returned to the reactor. After the esterification, the pressure in the autoclave was brought to atmospheric pressure and 1.488 g of a 10% solution of phosphoric acid in ethylene glycol was added to the ester in the autoclave. The temperature of the ester was increased to 285°C and the pressure was reduced to 1.7 torr over 65 min. The autoclave was brought to atmospheric pressure and the polyester was dropped into an ice bath. The natural diethylene glycol (DEG) content was found to be 2.7 mol %. The intrinsic viscosity of the quenched, amorphous co-polyester was 0.180 and carboxylic acid end group concentration of 38.3 μeq/g.

PET copolyesters with 5.0 mol % isophthalic acid

Terephthalic acid (820.99 g), ethylene glycol (378.03 g), isophthalic acid (43.21 g), antimony oxide (0.30 g), cobalt acetate tetrahydrate (0.101 g), and tetramethyl-ammonium hydroxide (0.50 g) were added to a batch polyester autoclave and mixed to form a paste. The same reaction conditions described for PET copolyester with 3.0 mol % isophthalic acid were used. The intrinsic viscosity of the quenched, amorphous co-polyester was 0.188 and carboxylic acid end group concentration of 37.8μeq/g.

PET copolyesters with 7.0 mol % isophthalic acid

Terephthalic acid (803.71 g), ethylene glycol (378.03 g), isophthalic acid (60.49 g), antimony oxide (0.30 g), cobalt acetate tetrahydrate (0.101 g), and tetramethyl-ammonium hydroxide (0.50 g) were added to a batch

polyester autoclave and mixed to form a paste. The same reaction conditions described for PET copolyester with 3.0 mol % isophthalic acid were used. The intrinsic viscosity of the quenched, amorphous copolyester was 0.182 and carboxylic acid end group concentration of 37.7 μeq/g.

PET copolyesters with 9.0 mol % isophthalic acid

Terephthalic acid (786.43 g), ethylene glycol (378.03 g), isophthalic acid (77.78 g), antimony oxide (0.30 g), cobalt acetate tetrahydrate (0.101 g), and tetramethyl-ammonium hydroxide (0.50 g) were added to a batch polyester autoclave and mixed to form a paste. The same reaction conditions described for PET copolyester with 3.0 mol % isophthalic acid were used. The intrinsic viscosity of the quenched, amorphous copolyester was 0.191 and carboxylic acid end group concentration of 44.0 μeq/g.

Conventional PET

The conventional PET was produced in a commercial, continuous melt polymerization reactor train. This amorphous PET has an intrinsic viscosity of 0.635 dL/g, carboxylic acid end group concentration of 32 μeq/g, and ethylene isophthalate content of 2.8 mol % and a DEG content of 3.0 mol %. This resin has 250 ppm of antimony as a polycondensation catalyst, and 30 ppm of phosphorous as a stabilizer.

Solid state polymerization of crystallized, powdered PET copolyesters

The low molecular weight polyesters and the conventional polyester were milled under the same conditions in a Wiley laboratory mill using a 1-mm screen to give powders with the following particle size distribution.

Particle size (μ)	Weight%
1000 to 500	55
500 to 250	40
Less than 250	5

One hundred grams of powdered and crystallized copolyester was placed in a steel tube with the following dimensions: length of 9 in., outer diameter of 1 and 15/16 in., and inner diameter of 1 and 9/16 in. The steel tube was fitted with a retaining screen at the bottom of the tube and a nitrogen gas inlet tube with a ½ inch inner diameter. The steel tube containing the polyester was place in an oven set with temperatures ranging from 195 to 240°C and connected to a nitrogen supply heated to temperatures in the range of 195–240°C with a flow rate of 63 mL/min. The polyester

was held at these conditions for 2–36 h. Then the tube was removed from the oven and cooled.

Intrinsic viscosity measurement, IV and conversion to number average molecular weight

The IV was measured in *ortho*-chlorophenol at 25°C. The IV was converted to the number average degree of polymerization, P_n, using the following equation:

$$P_n = 205.28 * [\eta]^{1.47}$$

Carboxylic acid end group (CEG) determination

One to two grams of polyester were dissolved in 75 mL of a o-cresol/chloroform (70:30) mixture. The solution was placed in a potentiometric titrator and titrated with 0.1 N potassium hydroxide in methanol. The end point was determined and converted into carboxylic acid end group concentration in microequivalents per gram.

Differential scanning calorimetry (DSC)

The melting point and heat of fusion were determined using a Perkin-Elmer DSC7 at a scan rate of 10°C/min.

Density and volume percent crystallinity

The density was measured according to ASTM 1505-85, and the density was converted to volume percent crystallinity using the following equation:

$$V_c = (D_m - D_a)/(D_c - D_a) * 100$$

V_c is the volume percent crystallinity, D_m the measured density, D_a the amorphous polymer density, and D_c the crystalline polymer density (100%).

Powder x-ray diffraction

The apparent crystallite size was determined by X-ray powder diffactometry (XRD) using the procedure outlined in U.S. Patent No. 5,714,262 (ref. 1) with some minor modifications due to differences in instrumentation. The polymer was powdered in a mini-mill, and the powder was pressed into a disk 32 mm in diameter and approximately 1 mm thick. The disks were placed in a Scintag XDS 2000 diffractometer that unlike the Phillips instrument described in the reference is designed to detect reflected X-rays rather than transmitted X-rays. The initial experiments included runs with the underside of the sample coated with highly crystalline material (LaB6 or Si). There was no evidence of that any of the CuKα X-rays penetrated completely through the sample to the underlying adhesive. No corrections were needed for the adhesive layer. The

TABLE I
Intrinsic Viscosity of PET Copolyester with 3 mol %
Ethylene Isophthalate During SSP

SSP temp. (°C)	Time (h)					
	0	4	8	12	18	24
210	0.180			0.252	0.282	0.322
225	0.180			0.344	0.394	0.453
240	0.180	0.337	0.428			

TABLE III
Intrinsic Viscosity of PET Copolyester with 7 mol %
Ethylene Isophthalate During SSP

SSP temp. (°C)	Time (h)					
	0	4	8	12	18	24
210	0.182			0.328	0.351	0.388
225	0.182			0.421	0.493	0.587
240	0.182	0.397	0.486	0.607		

diffraction data was then collected from the rotated sample over the range of 15°–20° 2θ using a step scan at 0.05°/step, a 65 s/step acquisition time, and 1° slits. No curved beam monochrometer was used and the X-ray scan was run in step mode so a Lorenz-polarization correction was not necessary. The apparent crystallite size was calculated using the Sherrer equation on the 010 peak.

RESULTS AND DISCUSSION

The solid state polymerization of low molecular weight PET copolyesters was followed by the change in the IV with time. The IVs for the copolyesters with ethylene isophthalate of 3, 5, 7 and 9 mol % and solid state polymerized under various conditions are given in Tables I–IV.

The number average degree of polymerization, P_n, was calculated from the intrinsic viscosity for PET in o-chlorophenol at 25°C as describe in the experimental section. The degree of polymerization for each copolyester is plotted vs SSP time for each SSP temperature (see Figs. 1–4). The change in P_n with time at each temperature was found to be linear as shown in Figures 1–4. The small size of the discrete particles and the high gas flow rate minimizes the diffusion effect of condensation by-products on the rate of SSP. The linear relationship between P_n and SSP time indicate that SSP is under chemical reaction control.

The rate constant, k, for the overall polycondensation reaction can be determined from the slope of the line and the use of eq. 4. The rate constants in moles of diester per hour for each copolyester and SSP conditions are given in Table V.

The natural log of the rate constants in Table V was plotted vs $1/T$ (K) to give Arrhenius plots (Fig. 5) for each copolyester. From the slope of the Arrhenius plot, the activation energy for SSP can be calculated and the intercept gives an indication of the frequency factor for propagation.

Similar to the low molecular weight polyesters, the particle size of conventional polyester chip with an IV of 0.635 containing 2.8 mol % of ethylene isophthalate was reduced, and the chemical reaction rate constants for the overall SSP reaction was determined at 195, 210, and 225°C as described above (Table V). From the Arrhenius plot shown in Figure 5, the activation energy and the frequency factor for propagation was determined for SSP of the conventional polyester (Table VI).

Table VI compares the activation energy and frequency factors of these low molecular weight copolyesters with the conventional polyester. The SSP activation energy of comparable copolyester compositions is sixteen percent higher for this low IV precursor than the conventional precursor. The activation energy for solid state polymerization of low molecular weight co-PET with IVs ranging from 0.18 to 0.19 dL/g decreases with an increase in the ethylene isophthalate comonomer content (Fig. 6). The activation energy for SSP of these low IV copolyesters becomes equal to the activation energy for conventional PET with about 3 mol % comonomer when the comonomer content for the low IV co-PET reaches about 7 mol %. The activation energy for conventional SSP determined in this study is similar to SSP activation energy reported in the literature.[6] Even though the activation energy for these low IV PET prepolymers approaches the activation energy of conventional

TABLE II
Intrinsic Viscosity of PET Copolyester with 5 mol %
Ethylene Isophthalate During SSP

SSP temp. (°C)	Time (h)					
	0	4	8	12	18	24
210	0.188			0.288	0.335	0.377
225	0.188			0.376	0.457	0.552
240	0.188	0.352	0.467			

TABLE IV
Intrinsic Viscosity of PET Copolyester with 9 mol %
Ethylene Isophthalate During SSP

SSP temp. (°C)	Time (h)					
	0	4	8	12	18	24
210	0.191			0.354	0.370	0.429
225	0.191			0.434	0.537	0.623
240	0.191	0.388	0.508	0.608		
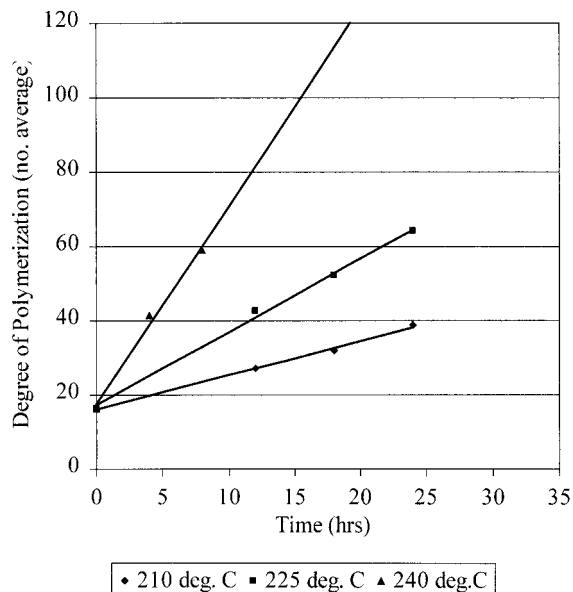
Figure 1 Degree of polymerization vs SSP time for PET copolyester with 3 mol % ethylene isophthalate.
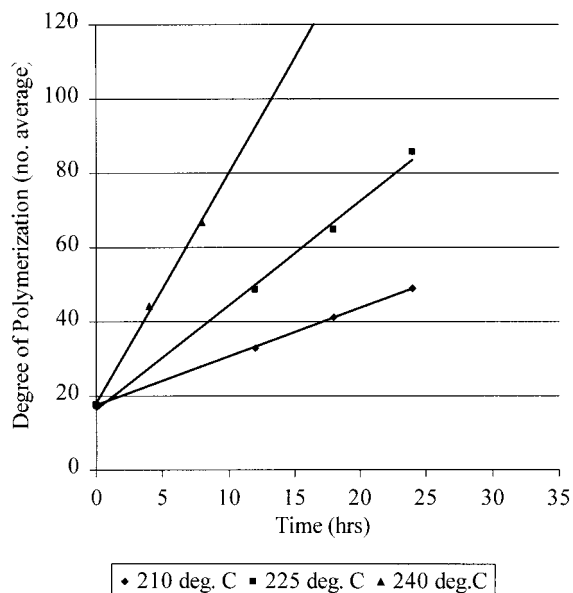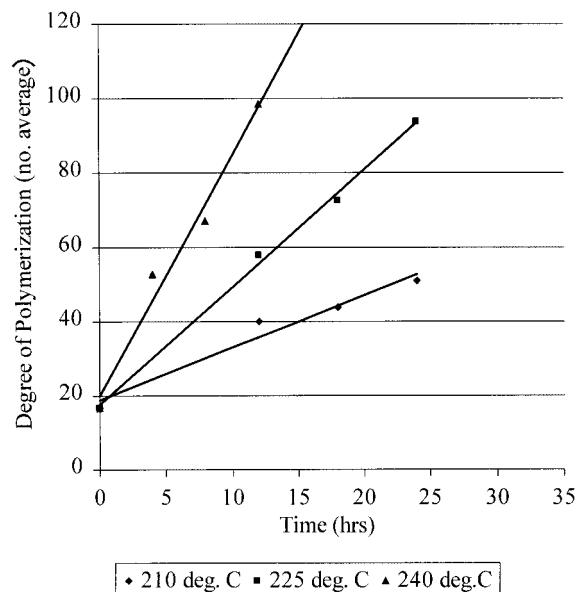

Figure 3 Degree of polymerization vs SSP time for PET copolyester with 7 mol % ethylene isophthalate.

SSP at higher comonomer content, the rate of SSP is significantly slower for these low IV PET precursors.

Low IV PET and conventional fiber grade PET have very different end group content by nature of the molecular weight differences between these polymers. The importance of end groups in the SSP of PET has been disclosed in several patents, and the relationship between IV, end groups ratio, and particle size was established.[4] Optimization of SSP for low IV PET requires the highest hydroxyethyl ester end group content and smaller particle size. For higher IV PET (fiber grade IV), the ratio of carboxylic acid content is opti-

mized from 18 to 40% due to the effects of diffusion. The conventional PET copolyester utilized in this work has been optimized for SSP and has a very different end group ratio than the low IV PET copolyester. However, these results show the differences and difficulties of SSP of low IV PET compared to high IV (fiber grade) PET.

Particle size, polymer end groups, catalysts, heat stabilizers, crystallinity, and comonomer content are all factors that affect the SSP rate of PET copolyesters. The particle size was reduced so that SSP was under chemical reaction rate control. The catalyst and heat

Figure 2 Degree of polymerization vs SSP time for PET copolyester with 5 mol % ethylene isophthalate.
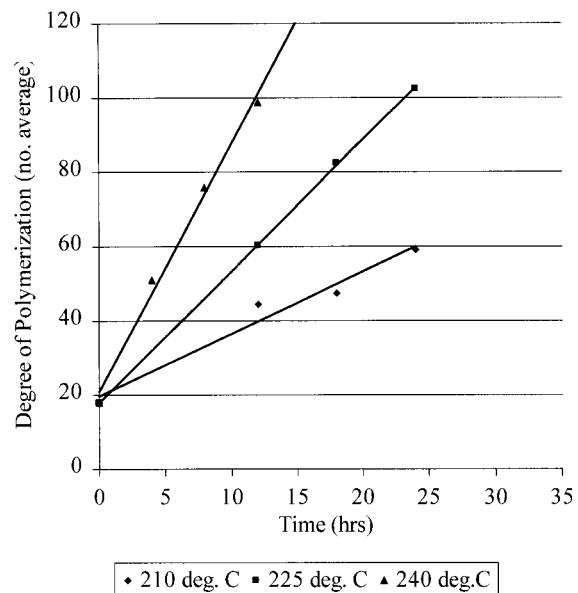
Figure 4 Degree of polymerization vs SSP time for PET copolyester with 9 mol % ethylene isophthalate.

TABLE V
Overall SSP Rate Constants, k, for co-PET from Figures 1–4

Temp. (°C)	k (moles/h) 3 mole % isophthalate	k (moles/h) 5 mole % isophthalate	k (moles/h) 7 mole % isophthalate	k (moles/h) 9 mole % isophthalate	k (mole/h) 2.8 mole % isophthalate (conventional)
195	—	—	—	—	0.65
210	0.23	0.33	0.36	0.42	1.33
225	0.49	0.70	0.79	0.88	2.61
240	1.33	1.54	1.62	1.67	—

stabilizer contents were the same for each polymer. As discussed previously, the end group ratio of hydroxyethyl ester groups to acid groups has a significant effect on the rate of SSP. In the current study, the end group ratio for the low molecular weight copolyester prepolymers is very similar. So, end group ratio is not a factor in the SSP rate for this set of low IV PET copolyesters. However, the conventional copolyester the end group ratio is quite different than low IV PET due to its molecular weight difference and optimization for SSP. This work illustrates the differences in SSP between low IV and higher IV PET some of which are due to morphology.

The slower SSP rate of these low IV PET prepolymers can be explained in part by the morphology of crystallized low molecular weight copolyester. Table VII shows how the crystallinity of low IV copolyester PET increases relative to conventional copolyester PET under various SSP conditions. Table IX shows that the SSP product from low IV PET precursor has thicker lamellar crystallites than conventional precursor. The higher crystallin-

ity and more perfect crystallites not only reduces the mobility of the end groups but also isolates them from reaction with other end groups. These effects result in diffusion limitation of end groups and volatile components. The negative effects of crystallinity on SSP have been documented in the literature.[7,8]

The quenched amorphous polymer is crystallized at a temperature about halfway between the T_g and T_m to produce a metastabilized crystalline state. Flexible polymer chains crystallize in folded lamellae that have dimensions much smaller than the extended end-to-end chain distances. On further heating (annealing), there is a thermodynamic driving force to reach a more stable state. During SSP, in addition to polymerization, there is melting of smaller less perfect crystallites and recrystallization to form more thermodynamically stable crystallites. This results in thicker lamellae crystallites (Table IX). A comparison of the effect of SSP conditions on these low IV precursors with the conventional SSP precursor shows there is a significant difference in the level of crystallinity and the type of crystallites present in the crystalline phase.

The crystallinity of low IV copolyester in the crystallized starting material and the final SSP product using different temperatures and times is given in Table VII, and is compared to conventional crystallized copolyester precursor and SSP product. While the crystalline low IV precursor and the crystalline conventional precursor start at about the same percent of crystallinity, the crystallinity in the solid state polymerized low IV copolyester increases to a much higher level than crystallinity observed during SSP of the higher molecular weight precursor. Since the low IV copolyester is less viscous and has less chain entanglement than high IV copolyester, higher percent crystallinity, and more perfect crystallites can be formed.

When the temperature becomes high enough, the density and the crystallinity of the solid state polymerized low IV copolyester begins to decrease. This can be seen beginning with the five mole percent ethylene isophthalate copolyester at 240°C (sample no. 8, Table VII). At higher temperatures and with greater crystalline defects due to increased comonomer level, chain folds can open and polymerize as tie molecules between crystalline lamellae[9].
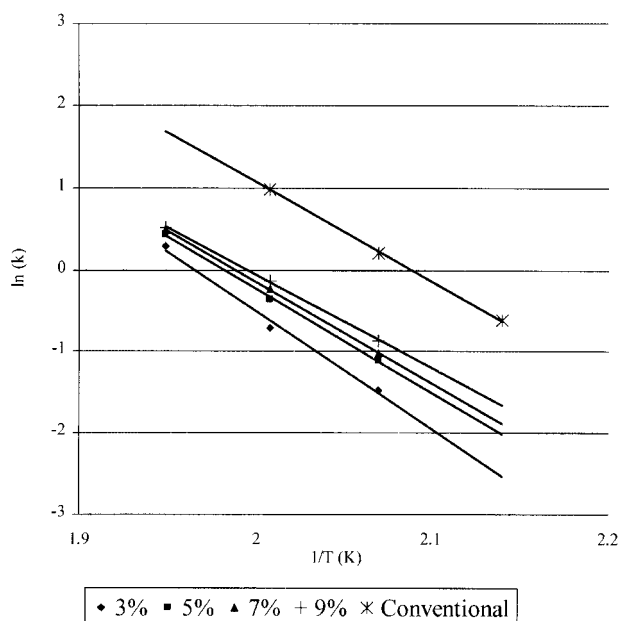

Figure 5 Ln(k) vs $1/T$ (K) for SSP of low IV PET copolyesters with 3, 5, 7 and 9 mol % ethylene isophthalate and for SSP of conventional PET precursor.

TABLE VI
Comparison of Activation Energy and Frequency Factors for Low IV Copolyester and Conventional Copolyester

Ethylene isophthalate (mole %)	3	5	7	9	2.8 (conventional)
Starting IV (dL/g)	0.180	0.188	0.182	0.191	0.635
Activation energy (kJ/mole)	120.6	106.6	104.3	95.3	103.5
Frequency factor	28.5	25.4	24.9	22.9	26.0

Inspection of the thermal properties in Table VIII shows that the crystallized and solid state polymerized low IV precursors with various compositions and molecular weights have different morphology than the conventional precursor. As a result of chain folding during polymer crystallization into lamellar crystallites, the melting points of the final SSP product from the low IV precursor at each SSP temperature are similar. However, the heat of fusion of the copolyester decreases as the comonomer content increases because of defects introduced by the comonomer. Also, the melt peak becomes narrower and the melting point increases as the SSP temperature increases. These effects are indicative of a thickening of the crystallites with SSP temperature and the exclusion of defects into the amorphous phase (see Table IX). At 210°C SSP temperatures, the SSP product for low IV, 3 and 5% ethylene isophthalate precursor has multiple melting peaks, indicating that melting and recrystallization was not complete leading to two different crystalline morphologies. In the case of the conventional SSP, there is some thickening of the crystallites during SSP (see Table IX), but it is a smaller effect than low IV polymer due to greater chain entanglements.

The SSP of these low IV copolyesters at 235°C for 36 h with 3, 5, and 7% ethylene isophthalate is shown in Table IX. Due to the high crystallinity and large crystallites, the polymerization stalls out and does not reach the predicted target IV. Increasing the comonomer content of the copolymer allows higher molecular weight to be obtained. This is due to an increase in the defect level with more comonomer that produces more melting and recrystallization that increases diffusion of chain ends. Also, higher crystallinity can slow the diffusion of volatile components, ethylene glycol and water, which results is slower SSP. So through lower crystallinity, condensation reactions more readily occur leading to reduced activation energy for SSP as the comonomer content increases, as shown in Figure 6.

CONCLUSION

While particle size, polymer end groups, catalysts, heat stabilizers content are factors that affect the SSP rate of PET copolyesters, morphology and comonomer can also play an important role in SSP. This work illustrates that differences in SSP between PET precursors are in part due to morphology that is affected by the comonomer content.

The morphology of crystallized and solid state polymerized PET copolyester depends on the molecular weight and comonomer content. There are significant differences in the nonequilibrium thermodynamic states of the crystallized and solid state polymerized copolyester that depends on composition and molecular weight. These differences affect solid state polymerization kinetics and the thermal properties of the product. The differences between low IV and conventional IV copolyester precursors are evident when comparing conventional SSP with SSP starting from a lower molecular weight.

The activation energy for SSP of these low molecular weight PET precursors is comparable to conventional SSP when the comonomer content of the low molecular weight polyester is around 7 mol % and the conventional precursor is around three mole percent. However, even though the activation energy is reduced through the use of higher comonomer content, the overall rate of SSP for the low MW copolyesters studied is three to five times slower than conventional SSP. This reduction in the rate is explained by reduced diffusion of end groups and volatile components in the discrete particle. This rate reduction can be par-

$$y = -3.91x + 130.16$$

Low IV SSP   Conventional
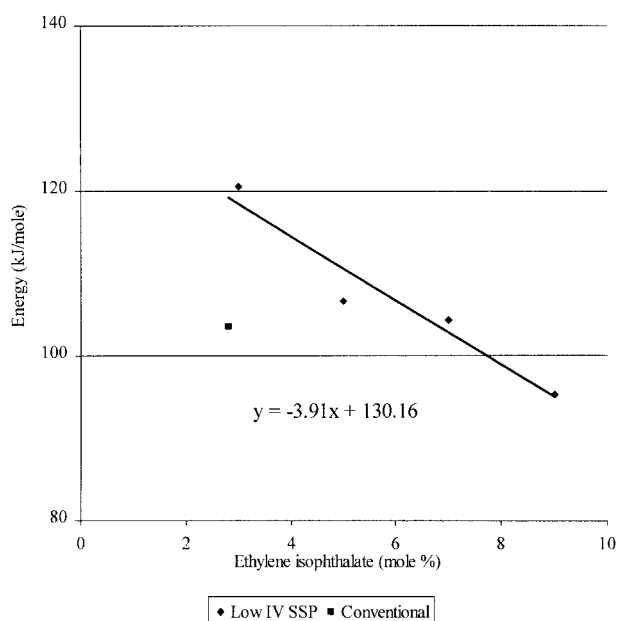
Figure 6 Activation energy for SSP of low IV copolyester vs ethylene isophthalate content compared to conventional SSP.

TABLE VII
Crystallized and Solid State Polymerized Low IV PET Compared to Conventional PET

Sample no.	Ethylene isophthalate (mole %)	Temp. (°C)	Time (h)	IV (dL/g)	Crystal. (vol. %)	Density (g/cc)
1	3.0	170	2	0.180	37.0	1.3763
2	3.0	210	24	0.322	65.3	1.4116
3	3.0	225	24	0.453	69.7	1.4172
4	3.0	240	12	—	72.3	1.4204
5	5.0	170	2	0.188	39.2	1.3790
6	5.0	210	24	0.377	66.1	1.4126
7	5.0	225	24	0.552	69.7	1.4171
8	5.0	240	12	—	67.9	1.4149
9	7.0	170	2	0.182	37.8	1.3772
10	7.0	210	24	0.388	65.4	1.4118
11	7.0	225	24	0.587	67.4	1.4142
12	7.0	240	12	0.607	61.2	1.4065
13	9.0	170	2	0.191	39.2	1.3789
14	9.0	210	24	0.429	65.7	1.4122
15	9.0	225	24	0.623	64.1	1.4101
16	9.0	240	12	0.608	53.3	1.3966
17	2.8	180	1	0.605	43.0	1.3838
18	2.8	205–220	20	0.860	57.0	1.4013

TABLE VIII
Thermal Properties of Crystallized and Solid State Polymerized Low IV Copolyester Compared with Conventional Copolyester

Sample no.	Ethylene isophthalate (mole %)	Temp. (°C)	Time (h)	T_m (onset) (°C)	T_m (peak) (°C)	Heat of fusion (J/g)
1	3.0	170	2	225.5	246.5	54.4
2	3.0	210	24	232.1	236.0	78.0
					249.4	
3	3.0	225	24	248.1	252.2	81.6
4	3.0	240	12	259.9	263.6	79.6
5	5.0	170	2	217.0	240.2	56.5
6	5.0	210	24	234.2	238.3	73.6
					245.3	
7	5.0	225	24	251.9	255.6	79.3
8	5.0	240	12	259.9	263.5	71.6
9	7.0	170	2	214.2	236.9	53.6
10	7.0	210	24	235.2	239.5	72.2
11	7.0	225	24	251.4	255.7	74.1
12	7.0	240	12	258.7	262.9	61.5
13	9.0	170	2	204.1	230.0	50.2
14	9.0	210	24	234.7	238.6	69.1
15	9.0	225	24	251.8	255.0	66.5
16	9.0	240	12	257.1	261.5	43.0
17	2.8	180	1	230.6[a]	243.7	36.5
18	2.8	205 to 220	20	237.0	240.4	61.5

[a]Conventional high molecular weight precursor is not completely crystallized under these conditions and in the DSC there is a crystallization transition with an onset at 127.3 °C and peak at 148.3 °C.

TABLE IX
SSP of Low MW Copolyester Crystallite Size Compared to Conventional Copolyester SSP

Ethylene isophthalate (mole %)	Starting IV (dL/g)	Final IV (dL/g)	Predicted IV (dL/g)	SSP iime/iemp. (h/°C)	ACS(010)[a] crystal. at 170 °C (nm)	ACS(010)[a] final SSP product (nm)
3	0.180	0.589	0.824	36/235	6.0	12.0
5	0.188	0.694	0.945	36/235	5.5	12.0
7	0.182	0.743	0.988	36/235	5.8	12.0
2.8	0.605	0.840	–	17/210	5.0	7.0

[a]Average crystallite size based on the X-ray diffraction peak from 010 reflection.

tially recovered by temperature and optimization of end groups, but the morphology and thermal properties of the final SSP polyester products are very different than the SSP polyester product produced from a conventional SSP process. This may lead to significant changes in the downstream processing of PET for conversion into packaging products.

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