

# Solid-State Polymerization and Bulk Crystallization Behavior of Poly(ethylene terephthalate) (PET)

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**ABSTRACT:** The main variables involved in solid-state polymerization of PET homopolymers, originally with molecular weight within the commercial range, were sequentially studied to determine their influence in polymerized products. These variables were precursor crystallinity, catalyst, and time and reaction temperature. An increasing molecular weight sequence was then used to study the bulk crystallization behavior with Avrami analyses. It was determined that thermal conditions at dissolution affect the prereaction morphology. This was important in the polymerization process because it was found that high crystallinity levels in precursors result in higher molecular weights. In agreement with other reports, typical catalysts used in melt polymerizations enhance postpolycondensation processes in the solid state. High reaction times and temperatures were also required to obtain high molecular weights. As the molecular weight increased, there was a decrease in nucleation density and Avrami analyses, applied to the isothermal bulk crystallization, indicating that the nucleation process changed from instantaneous to spontaneous with the increase in molecular weight. The consequences and relative importance of the observed results is discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 78–86, 2000

**Key words:** solid-state polymerization; bulk crystallization; PET

## INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the few thermoplastic semicrystalline polymers capable of being physically and chemically recycled down to low-grade resins and even to the departure monomers. This makes PET one of the most attractive polymeric materials in the manufacture of high technology engineering parts. These types of applications are, however, limited by the molecular weight obtained from the molten state synthesis. Limitations are mainly due to the na-

ture of melt polymerization where the high viscosity impedes the diffusion of by-products and, as a consequence, dictates chemical reaction limits to the molecular weight. One option to increase the molecular weight of PET, even up to levels of ultrahigh molecular weight, is the solid-state polymerization (SSP) method.<sup>1–5</sup> This, however, requires polymeric precursors with high surface area and also high reaction times and temperatures. In one of the earliest works on the topic, Chen et al.<sup>6</sup> studied the solid-state polymerization mechanism and determined that the controlling step was chemical reaction rather than internal or external diffusion of by-products. Several control models were then proposed, which were reviewed and criticized by Ravindranath and Mashelkar.<sup>7</sup> These authors developed a corrected mathematical model to simulate the SSP of PET

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and proposed that the reaction mechanism could either be controlled by diffusion or chemical reaction (or both), depending on the process and operating conditions. Karayannidis et al.<sup>2</sup> performed solid-state polymerization of as-received and reprocessed (i.e., dissolved) PET from soft-drink bottles. In as-received samples, both esterification and transesterification took place. However, in dissolved samples transesterification was present only at high reaction temperatures. In a subsequent work, Karayannidis et al.<sup>3</sup> studied the thermal behavior of samples immediately after dissolution and did not observe glass transition temperatures. This was taken as an indication of a high crystallinity in polymeric precursors and as the cause of a decrease in polycondensation reactions during solid-state polymerization. More recently, Kokkalas et al.<sup>8</sup> studied the effect of  $\text{Sb}_2\text{O}_3$  as a catalyst in SSP, and determined that this chemical compound, normally used in melt polymerization, also affected ester interchange reactions during SSP.

Even though the general characteristics of SSP of PET are technically well known, there has not been a morphological analysis of the main variables involved in the process of polymerization or of the isothermal bulk crystallization behavior of polymerized products. Understanding the morphology–property relationship is important both for scientific and practical reasons. Understanding bulk crystallization kinetics is important to give insight into the overall changes occurring during the crystallization process for engineering purposes.

## EXPERIMENTAL

### Materials

Commercial PET was obtained from Eastman Chemical Co., TN, as grade 10388. The number-average molecular weight of the as-received PET was 22,600 g/g-mol for a weight-average molecular weight of 72,800 g/g-mol and a polydispersity index of 3.2 (both determined at Eastman). The viscosity-average molecular weight was 56,400 g/g-mol, and the intrinsic viscosity 0.884. The DEG content was lower than 2%.

### Experimental Methods

Solid-state polymerizations were carried out in a fixed-bed glass reactor with a constant and dry

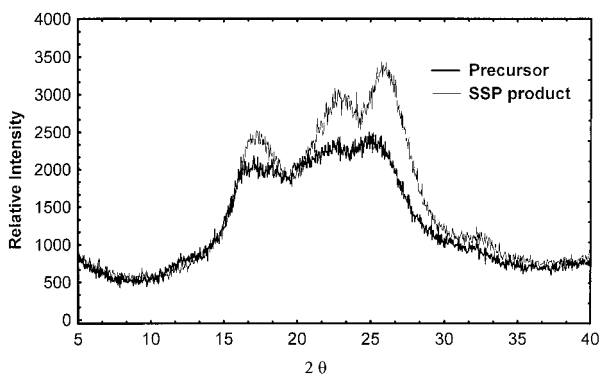
inert gas flow rate. A mixture of potassium nitrate and sodium nitrate was used in a thermal bath to control the polymerization temperature inside the reactor. A very thin thermocouple was positioned close to the fixed bed, and in this way, changes in temperature were continuously monitored. Variations in molecular weight were determined through gel permeation chromatography (GPC). In this case, a Shimadzu Liquid Chromatograph LC-10AD, with two progel-TSK columns at 35°C, was the experimental equipment. Dual detection was carried out in the GPC measurements using ultraviolet and refractive index detectors. With the purpose of determining molecular weights, samples were dissolved in pure 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and diluted with chloroform up to a ratio 98 : 2<sup>9</sup> for a final concentration of 0.1% w/v. For the mobile phase, pure chloroform was used with a constant flux of 1 mL/min. The relative molecular weights of samples were obtained after calibrations with polydisperse PET. With the purpose of quantification of residual catalyst, atomic absorption measurements were made on a spectrophotometer (Varian Spectra AA). The thermal behavior of the polymerized products was characterized in a differential scanning calorimeter (DSC) Perkin-Elmer DSC-7 working under a constant and dry flux of nitrogen. Transmitted polarized light intensity was measured with a Mettler photomonitor ZUFP82 adapted to an Olympus BMX 60 polarizing optical microscope. Two HT82 Mettler hot stages and the fast transfer method were used for isothermal crystallization experiments. X-ray diffraction patterns in the reflection mode were obtained for precursors and polymerized products along the  $2\theta$  range of 5–60°. In this case, a Rigaku diffractometer DMAX-2000, with an accelerating voltage of 40 kV and a filament intensity of 30 mA, was the experimental equipment.

## RESULTS AND DISCUSSION

### Solid-State Polymerization

#### *Precursor Crystallinity*

High molecular weight PET is mainly produced through ester interchange reactions (transesterification) in the solid state with the parallel liberation of ethylene glycol (EG).<sup>2,8</sup> In the solid state, the process takes place more rapidly with high surface area particles, allowing better diffusion of the EG by-product. One option to prepare precu-



**Figure 1** WAXD patterns of precursor (dissolution temperature 25°C) and the corresponding SSP product polymerized at 238°C.

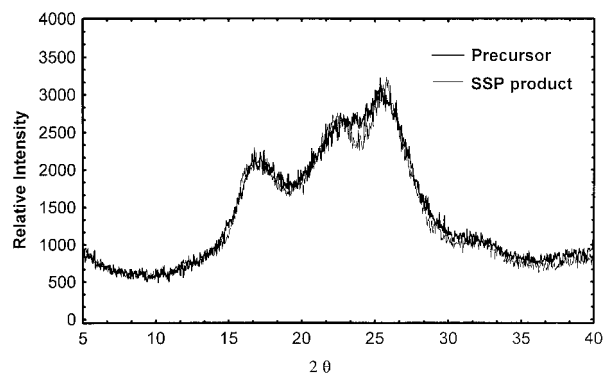
sors with a high surface area is to dilute the as-received polymer in a solvent and then slowly cast it into a nonsolvent. This precipitates a precursor that is filtered, dried, and recovered in the form of high surface flakes, fibrous-like material, or powder. The recovered product is then polymerized in the solid state using high reaction times and temperatures and an inert gas carrier for by-products. There is, however, a wide variety of solvents for PET, the selection of which gives rise to different physical forms, depending on solubility and, as a consequence, on concentration.<sup>2,4</sup> After trying several solvents in this work, a mixture of trifluoroacetic acid/dichloromethane (TFA/DCM) (50/50%, v/v)<sup>2</sup> and phenol were selected to analyze the effect of polymerization variables in the polymerized product and the main characteristics of the bulk crystallization process.

In a first set of samples and after TFA/DCM dissolution, methanol was used as nonsolvent, and no catalyst was added to the system. In this particular case, as-received samples were first dissolved (12.5%, w/v)<sup>3</sup> at the temperatures of 25 and 85°C, and then cast into methanol at 25°C. These preparations were boiled at 65°C to evaporate the remaining methanol and filtered to recover the respective fibrillar precursor. Fibrils were then dried in a vacuum oven at 75°C for 2 h before polymerization.

A brief note is in order, concerning the type of gas and the gas flow rate used in our experiments. Lichen<sup>10</sup> reported that the molecular weight of PET increases with the gas flow rate up to a constant value of approximately 2 L/min. It has also been observed that the SSP process depends on the type of by-product carrier gas used. Some gases that have been used are nitrogen, carbon

dioxide, helium, argon, neon, krypton, xenon, several industrial waste gases, and mixtures.<sup>5</sup> Nitrogen is, however, the gas most frequently used,<sup>2</sup> as in the present study. An argument supporting the use of nitrogen can be as follows. It is known that the mass transfer coefficient of gases increases with flux and diffusivity. At constant flux, this coefficient will only be affected by diffusivity—in our case of EG in different gases. Based in the Fuller-Schettler-Giddings equation<sup>14</sup> we calculated the diffusivities of DEG in N<sub>2</sub>, CO<sub>2</sub>, He, Ar, and other gases. It was determined that the diffusivity of DEG in N<sub>2</sub> is the highest and equal to 0.278 cm<sup>2</sup>/s. Therefore, nitrogen was used in our studies. Based also in the work by Lichen<sup>10</sup> we selected two different gas flow rates (1 and 2 L/h). There was not, however, any important difference between polymerized products after 6 h of polymerization at 238°C using 1 or 2 L/h. As a consequence, considering the low density of the packed bed and with the purpose of decreasing fluidization we decided to use nitrogen with a flow rate of 1 L/min.

The glass transition temperature of PET is 80°C; therefore, the TFA/DCM mixture together with dissolution temperatures of 25 and 85°C were selected with the specific purpose of obtaining amorphous and crystalline precursors. This was expected to determine the influence of crystallinity on polymerized products. Figures 1 and 2 show the WAXD patterns of both types of precursors and their corresponding polymerized products. From these results it is observed that, as expected, precursors prepared from dissolution at 25°C are rather amorphous, and those prepared from dissolution at 85°C are crystalline. Table I shows, on the other hand, the molecular weights



**Figure 2** WAXD patterns of precursor (dissolution temperature 85°C) and the corresponding SSP product polymerized at 238°C.

**Table I** Effect of Dissolution Temperature on Molecular Weights of Precursors and SSP Products

Sample Characteristics		$M_w$	% $X_c$
As received		72,800	—
Precursor	$T_d = 25^\circ\text{C}$	67,800	16.87
SSP Product	$T_d = 25^\circ\text{C}$	73,000	27.40
Precursor	$T_d = 80^\circ\text{C}$	60,800	22.02
SSP Product	$T_d = 80^\circ\text{C}$	74,900	26.60

$T_d$ : Dissolution temperature;  $M_w$ : weight-average molecular weight; % $X_c$ : crystallinity content.

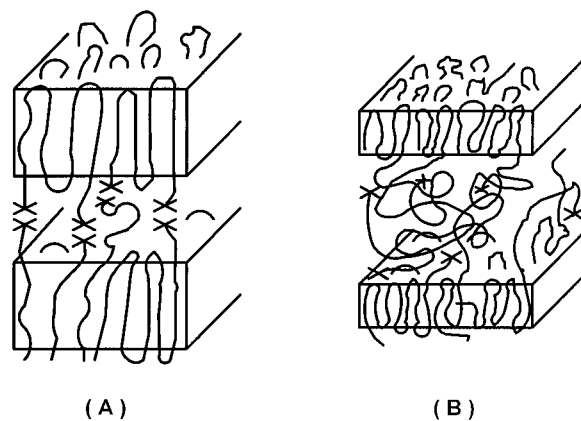
for each sample before and after solid-state polymerization together with as-received PET. The corresponding crystallinities are also shown for each sample.

The main characteristic of these results is the well-known degradation process following solvent treatments.<sup>3</sup> For example, there was a 7% decrease in molecular weight after dissolution at 25°C, and the corresponding thermal treatments, compared with a 16% decrease after dissolution at 85°C. Another important characteristic of the results in Table I is that even though the starting polymer had a higher average molecular weight after dissolution at 25°, it only increased in about 8% after SSP. However, in the case of dissolution at 85°C, there was an increase of 23%. The SSP process demands that molecular ends reach each other before reacting together. Therefore, and considering the lack of molecular mobility associated with the polymerization process itself, the only way to promote this interaction is through a morphological variable of the precursors such as crystallinity. The previous results were, therefore, correlated with a morphological variable (crystallinity) to explain the observed results. WAXD crystallinities are shown in Table I, indicating that the crystallinity content for samples dissolved at 25°C increased 63% after SSP. However, for dissolution at 85°C it only increased in about 21%. These results, were taken as an indication that, for the purpose of obtaining a large increase in molecular weight, high crystallinities in precursors were required. This is contrary to a suggestion given by Karayannidis et al.,<sup>3</sup> who did not observe glass transition temperatures in precursors and concluded that because of the high crystallinity present, there would not be a high increase in molecular weight after SSP. Understanding these effects is complicated because of

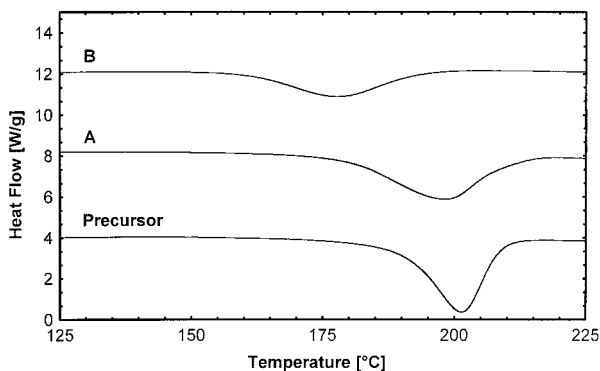
the thermal treatments involved. However, one attempt to explain them is shown in Figure 3. In this schematic, it is considered that the macromolecular chain ends have to meet first before getting bound together. As a consequence, any source of molecular orientation will help the process. This can be found in a lamellar-stacked system such as the one shown in Figure 3. The drawing is based on the experimental fact that low average molecular weights develop either thicker or more perfect crystals (i.e., those with a higher melting point). Thick crystals originate as a consequence of a higher probability of segmental orientation in the thin amorphous portion of the lamellar-stacked system. On the contrary, high molecular weights give rise to thinner or more imperfect crystals or to a stacked system with thicker amorphous portions that overall decreases the average orientation of chain ends. In this last case, a lower increase in molecular weight could be expected in agreement with the results mentioned before.

#### Catalyst Effect

Antimony trioxide,  $\text{Sb}_2\text{O}_3$ , is a well-known transesterification reaction promoter in the synthesis of PET. It has also been determined that it promotes SSP of PET<sup>8</sup> and that the catalytic effect increases with the content of  $\text{Sb}_2\text{O}_3$  up to 2000 ppm. In the present work, calibration solutions of acetone/ $\text{Sb}_2\text{O}_3$  were first prepared with the purpose of determining a reference atomic absorption curve to quantify the amount of catalyst introduced in precursors. The as-received PET was first dissolved in phenol (10% w/v) together with 2000 ppm of  $\text{Sb}_2\text{O}_3$ , and the preparation was



**Figure 3** Morphological effect of crystallinity in precursors in the solid-state polymerization of PET.

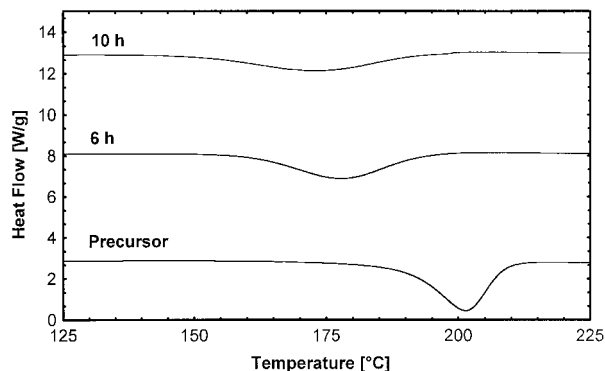


**Figure 4** DSC cooling traces from the melt ( $T_m^c = 280^\circ\text{C}$ ; 3 min) of precursor and polymerized samples: (A) without catalyst, and (B) with catalyst.

added to the nonsolvent-precipitating acetone. The remaining solutions were then measured and compared with the calibration curve. It was determined that on average 100 ppm (5%) of  $\text{Sb}_2\text{O}_3$  were present in the remaining solutions. The catalyst effect in the polymerized product was then determined after solid-state polymerization at the relatively low temperature of  $238^\circ\text{C}$ , rendering on average an increase of 10% in the original molecular weight. It was also observed that cooling the melt at a controlled rate in nonisothermal form had a pronounced effect in polymerized products. For example, the use of  $\text{Sb}_2\text{O}_3$  decreased the overall crystallization temperature by approximately  $20^\circ\text{C}$  and also the crystallization enthalpy by about 47%, as shown in Figure 4.

#### Reaction Time and Temperature

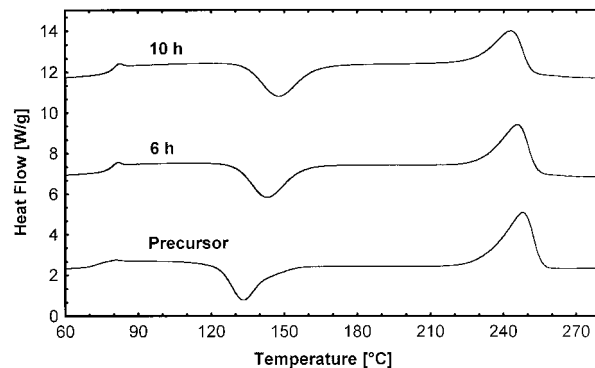
Reaction time and temperature are important variables in the SSP process of PET. Their effects are well documented in the work by Jabarin and Lofgren,<sup>1</sup> who even generated an empirical relationship between time–temperature and molecular weight for a series of solid-state polymerized samples. Therefore, in the present study we concentrated our discussion on the main nonisothermal thermal characteristics of polymerized samples prepared from phenol after different reaction times (6 and 10 h) and temperatures ( $238$ ,  $240$ , and  $243^\circ\text{C}$ ). Figure 5 shows the DSC cooling traces from the melt of samples polymerized at different times (for an SSP temperature of  $243^\circ\text{C}$ ), and Figure 6 the corresponding traces after heating the amorphous state. As mentioned before, long polymerization times produce high molecular weights which, as shown in the DSC



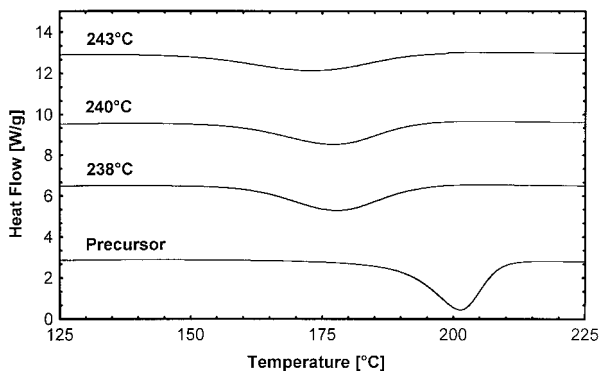
**Figure 5** DSC traces after cooling ( $10^\circ\text{C}/\text{min}$ ) from the melt ( $280^\circ\text{C}$ ; 3 min) of PET samples SSP at the indicated times.

traces of Figure 5, retard the induction time for crystallization and also decrease the crystallization enthalpy (area under the crystallization curve). When the amorphous state is heated, as a consequence of the increase in molecular weight, the DSC traces display an expected increase in the glass transition temperature,<sup>11</sup> a higher overall crystallization temperature, a lower crystallization enthalpy, and a corresponding lower melting point and melting enthalpy as shown in Figure 6. This is a common indication that as the molecular weight increases, thinner and/or less perfect crystals are formed. It also needs to be mentioned that in the time range studied there was an increase of 40% in molecular weight.

The effect of polymerization temperature was studied for the highest polymerization time (10 h). Figure 7 shows the DSC traces of polymerized products after cooling the melt at a controlled rate, and Figure 8 the corresponding experiments



**Figure 6** DSC heating traces ( $10^\circ/\text{min}$ ) from the amorphous state of SSP samples of PET at the indicated times.



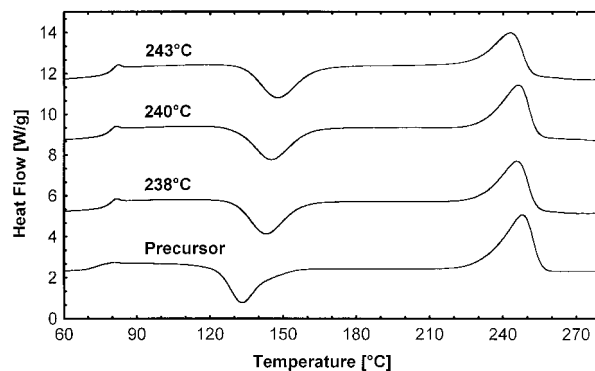
**Figure 7** DSC traces after nonisothermal cooling (10°C/min) from the melt (280°C; 3 min) of PET samples SSP at the indicated temperatures.

after heating the amorphous state. In these results it is observed that the effect of temperature is equivalent to the effect of time. However, in terms of temperature there is a limit corresponding to the so-called sticking temperature, and in terms of time there also seems to be a limit (close to 10 h), after which the molecular weight increases only slightly.<sup>3</sup> We determined an overall increase of 28% in molecular weight in the temperature range studied.

From the previous results emerges the relative importance of every variable. For example, a catalyst effect seems less important with the lowest relative contribution to the molecular weight. However, crystallinity content in precursors, and time and reaction temperature were relatively equivalent. It is usually considered in the literature that reaction time and temperature are the most important variables. However, in accordance with the results in the present work, more studies along the lines of precursors morphology should be made to determine their exact impact in SSP of PET.

## BULK CRYSTALLIZATION

Understanding the bulk crystallization behavior of polymers is mostly important for engineering applications where nonisothermal transformations are most frequent. However, an adequate study should begin with isothermal bulk analyses before getting into a more complicated nonisothermal case. In the present work, we have studied the isothermal bulk crystallization of SSP/PET with the purpose of determining changes in the overall nucleation and growth patterns. The



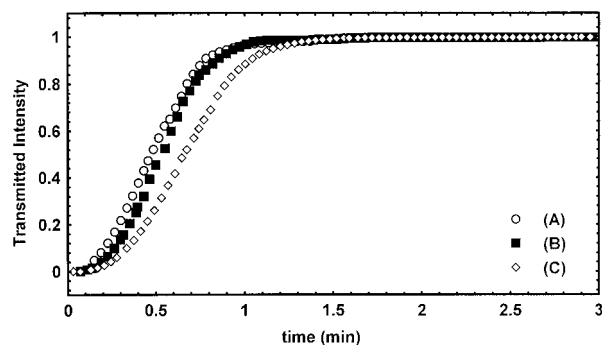
**Figure 8** DSC heating traces (10°C/min) from the amorphous state of SSP samples of PET at the indicated temperatures.

main focus was the study of the important engineering variables of polymerization time and temperature. Therefore, to obtain the corresponding Avrami curves, the intensity of light transmitted was taken to be proportional to the crystallization process. The emerging data were first normalized then reprocessed into an Avrami type of analysis using a simple two-phase method.<sup>12</sup>

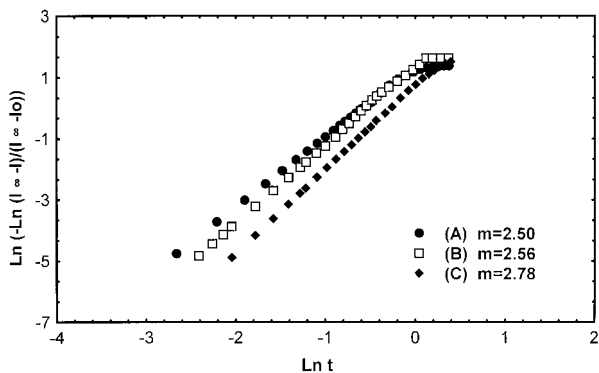
In terms of this model, the quiescent process of growth is given by

$$X(t) = 1 - \exp(-kt^m) \quad (1)$$

where  $k$  is a constant for a given material and  $m$  is a function of the geometry of the growth process. This equation has to be modified for polymers because in this case spherulites are partly crystalline and partly amorphous. Therefore, considering  $X_0$ , the mass fraction of spherulites, eq. (1) can be rewritten



**Figure 9** Isothermal Avrami curves as a function of polymerization temperature after 6 h of polymerization. Polymerization temperatures are shown.



**Figure 10** Avrami analyses for low polymerization times (6 h) as a function of polymerization temperature.

$$X_o(t) = 1 - \exp(k't^m) \quad (2)$$

In terms of our experimental device, the intensity  $I_o$  was that of a purely amorphous polymer. When the entire view became filled with crystals, the intensity  $I_\infty$  was the intensity of the fully spherulitic material,  $I_t$  was the intensity at time  $t$ , and in these terms, eq. (2) can be written as

$$1 - I_o = [(I_\infty - I)/(I_\infty - I_o)] = \exp(-k't^m) \quad (3)$$

This simplified model assumes constant growth rate, constant nucleation density and geometry, a single type of nucleation, and no effects of secondary crystallization in early stages of the process of growth. All these are, however, rough simplifications for polymers where a mixture of effects is often observed.<sup>13</sup> Nonetheless, based on our experimental observations, we considered this technique as a good approach for SSP polymerized PET. For example, we did not observe changes in nucleation density in the same exper-

iment or strong effects associated with secondary crystallization. Equation (3) was, therefore, adapted to the experimentally measured intensity of transmitted polarized light and rearranged to give a straight line from where the Avrami index was calculated.

$$\text{Ln}(-\text{Ln})[(I_\infty - I)/(I_\infty - I_o)] = m \text{Ln } t + \text{Ln } k' \quad (4)$$

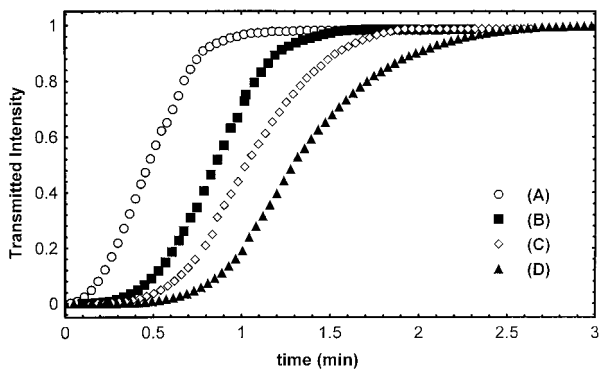
Figure 9 shows typical isothermal bulk crystallization curves corresponding to relatively low polymerization times (6 h) (precursors obtained from phenol preparations) as a function of the polymerization temperature, and Figure 10 the corresponding Avrami plots. Table II, on the other hand, shows the calculated and reported Avrami indices. The main characteristic of the results, after 6 h of polymerization, is an apparent increase in Avrami indices with molecular weight (i.e., with the polymerization temperature). Assuming (as is apparent in the micrographs shown later) that there is not a change in the geometry of the overall morphology as the molecular weight increases, then the increase in Avrami indices can be taken as an indication of changes in the primary nucleation process. It is important to mention that in isothermal bulk crystallization experiments, the crystallization temperature was selected above the maximum in radial growth of 180°C<sup>14</sup> as for having a single type of growth control (i.e., interface control); otherwise, there would be a mixture of Avrami indices related to the type of growth control.

To better elucidate the effect of molecular weight on the crystallization characteristics, the same types of experiments were carried out after 10 h of polymerization. Figure 11 shows the sigmoidal crystallization curves where a clear increase in induction time is observed as the polymerization time (i.e., the molecular weight) in-

**Table II** Avrami Indices for Polymerized Products

Sample	Avrami Coefficient Measured (Expected)	Nucleation Type	Growth Geometry	Growth Control
Precursor	2.50 (2.5)	—	—	—
$T_{\text{SSP}} = 240^\circ\text{C}$ (6 h)	2.56 (2.5)	—	—	—
$T_{\text{SSP}} = 243^\circ\text{C}$ (6 h)	2.78 (3.0)	Instantaneous	Sphere	Interface
$T_{\text{SSP}} = 238^\circ\text{C}$ (10 h)	2.98 (3.0)	Instantaneous	Sphere	Interface
$T_{\text{SSP}} = 240^\circ\text{C}$ (10 h)	3.30 (3.5)	—	—	—
$T_{\text{SSP}} = 243^\circ\text{C}$ (10 h)	3.99 (4.0)	Homogeneous	Sphere	Interface

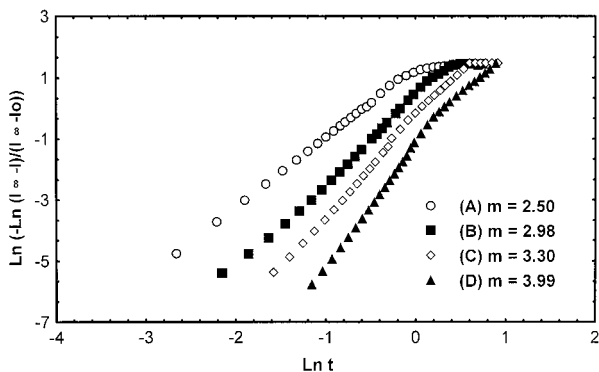
$T_{\text{SSP}}$ : Solid-state polymerization temperature.



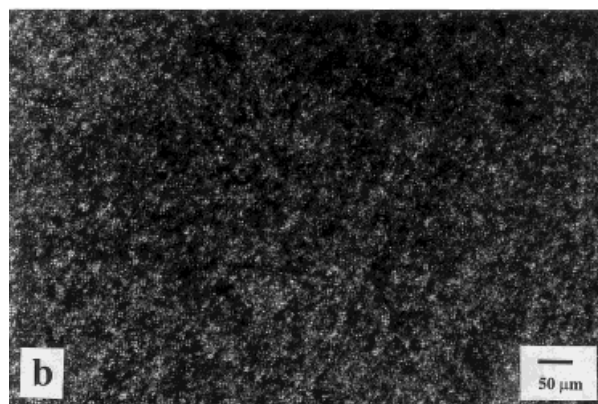
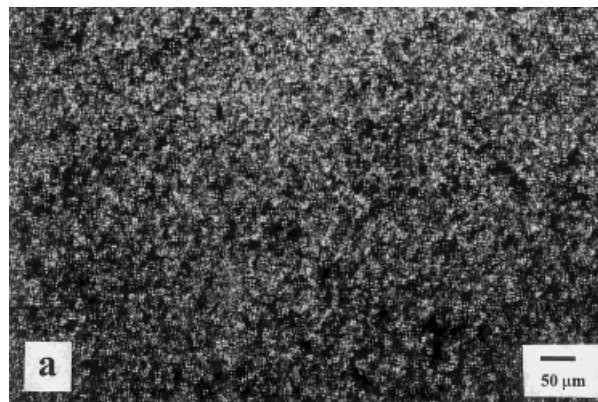
**Figure 11** Isothermal Avrami curves as a function of polymerization temperature after 10 h of polymerization. Polymerization temperatures are shown.

creases. Figure 12 shows the corresponding Avrami plots for these high polymerization times. Table II summarizes the relationship between Avrami indices and growth characteristics for this polymerization sequence. From here a clear increase can be seen in the Avrami index, which in this case changes from 3 to 4, which confirms that the nucleation patterns change as the molecular weight increases.

Several attempts were made to verify optically the previous results at low and high polymerization time; however, in both cases, the nucleation density was too high to permit the direct observation of the detailed morphology. Nevertheless, several extra attempts were made, but now using polymerized samples for which no catalyst was added. This was expected to decrease heterogeneities, and as a consequence, to better define the overall nucleation patterns. The results are shown in Figure 13, from where the overall char-



**Figure 12** Avrami analyses for high polymerization times (10 h) as a function of polymerization temperature.



**Figure 13** Polarized Optical Microscopy micrographs showing overall nucleation characteristics along isothermal crystallization ( $T_c = 200^\circ\text{C}$ ) after (a) SSP temperature of  $238^\circ\text{C}$  and  $t_c = 1.0$  min; (b) SSP temperature of  $243^\circ\text{C}$  and  $t_c = 1.1$  min.

acteristics indicate that indeed, as the molecular weight increases, there is a corresponding decrease in nucleation density. From the processing engineering point of view, the increase in induction time for crystallization is an advantage to obtain oriented products. However, the decrease in nucleation density, as the molecular weight increases, is against the need of high crystallinity of precursors if they are going to be precursors of sequential repolymerizations.<sup>5</sup> Here then, emerges the need of optimizing morphology of the initial precursor to obtain ultra-high molecular weights through the sequential repolymerizations method.

## CONCLUSIONS

Solid-state polymerization of PET is a method that mainly depends on catalyst presence, pre-



cursor morphology and time, and reaction temperature. Even though these effects are documented in the literature, it was determined that, contrary to a previous proposition, high crystallinity levels in precursors are necessary to obtain high molecular weights. In this form, crystallinity becomes an important variable in SSP of PET. The isothermal bulk crystallization behavior of solid-state polymerized PET has indicated that as the molecular weight increases, together with an increase in induction time for crystallization, the Avrami indices also increase. This last was an indication of a change in the nucleation patterns from instantaneous to sporadic. It was then concluded that solid-state polymerized PET can be useful for oriented applications. However, from these results the need of optimizing crystallinity of polymerized products also emerged if they are going to be precursors of sequential repolymerizations.

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