Crystallization and Melting Behavior of Zenite Thermotropic Liquid Crystalline Polymers

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The crystallization and melting behavior of a DuPont Zenite™ series, namely, Z 6000 and Z 8000B, thermotropic liquid crystalline polymer (TLCP) have been investigated by differential scanning calorimetry (DSC). Both, non-isothermal and isothermal crystallizations were carried out. From the non-isothermal experiments, the crystallization temperature was found to be 234°C for a cooling rate of 10°C/min whereas it was only 228°C for 40°C/min for Z 8000B, and was found to be 296°C and 290°C, respectively, for Z 6000. In the isothermal experiment both the thermal and crystallization behaviors were studied as a function of the annealing temperature and annealing time. Two types of transition processes were evidenced in the low temperature region of the isothermal crystallization. One is fast transition, which may be regarded as liquid crystal transition, and is characterized by the enthalpy, which is independent of annealing time. The other is slow process, related to crystal perfection, and it shows increases in the transition temperature and enthalpy, which is dependent on annealing time.

INTRODUCTION

A study of the crystallization process provides a deeper insight into the effect of process parameters on structure development and, ultimately, on the properties of the end product. Crystallization of polymers is emerging as an important field of study from a fundamental as well as an application point of view. The process of crystallization can be studied at a constant temperature, i.e., isothermal crystallization, or at a constant cooling rate, i.e., non-isothermal crystallization. The isothermal crystallization studies are useful in elucidating the crystallizability of polymers. This information, however, is not relevant for the actual processing of polymers, as the crystallization of polymers takes place non-isothermally in the entire polymer processing operation. Thus, it is advantageous to study the crystallization process under both isothermal and non-isothermal crystallization conditions before deriving any conclusion about the crystallization of polymers.

Crystallization of molecules of thermotropic liquid crystalline polymers (TLCP) is considerably different from that of other conventional polymers such as polyethylene or polyethylene terephthalate (1). TLCPs have lesser flexibility compared to the latter, which implies that larger translations of their (TLCP) molecules are required for recrystallization (2-5). In general, the degree of crystallinity in such TLCPs is expected to be low. Crystallization occurs so rapidly on cooling that the process of quenching from the nematic to the glassy state inevitably results in some crystallization (6). Cheng et al. (7) showed the presence of two transition processes for different molar ratios of hydroxybenzoic acid (HBA)/hydroxy-naphthoic acid (HNA) copolymers for the transition from nematic to solid state: (a) fast transition due to aggregation of rigid chains, and (b) slow transition during heat treatment. These two processes result in different crystal structures. The fast process leads to hexagonal packing with cylindrical symmetry along the chain direction while the slow process gives rise to orthorhombic packing (8-13). The origin of these two transition mechanisms is not yet determined.

Similar crystallization processes were observed for Xydar and other Hoechst Celanese LCPs by Cheng...
et al. (14). Blackwell et al. (15) suggested the presence of some additional crystalline structure for some nematic LCPs depending on the preparation and heat treatment of the materials. Lin and Winter (16, 17) reported that the rate of crystallization increases with supercooling, i.e., the interval between its melting point, \( T_m \), and the desired experimental temperature, \( T \). Moreover, they found that quenching immediately after deformation at a high temperature could lower the degree of crystallinity. Their data indicates that low cooling rates and large elongation lead to the highest crystallinity, and the rate of crystallization depends on annealing temperature, and mechanical and thermal history of the materials (18, 19). In addition, a higher annealing temperature leads to a slower crystallization. Chung et al. (20, 21) re-examined the crystallization mechanism of LCPs using commercial grades such as Vectra A-900 or A-950 (which is made of 73/27 HBA/HNA), in contrast with previous works based on experimental grades.

Recently, studies of crystallization, melting and the effects of annealing on the commercial TLCP materials have received much attention because of the changes observed in the melting temperature, crystal structure and physical properties. Though there is an extensive literature on Vectra and Xydar LCPs, none is available on Zenite LCPs, namely Zenite 6000 and Zenite 8000B. Hereafter we refer them as Z 6000 and Z 8000B, respectively. These are wholly aromatic polyester resins, and are easily melt processed because of the presence of comonomers such as HBA, TA, and HQ. Hence, these materials find applications requiring high-temperature performance, retention of properties over a wide temperature range, dimensional stability, chemical resistance, and excellent electrical properties. Zenite resins are found to be well suited for use in automotive, electrical/electronic, fiber, optics, telecommunications, and aerospace industries.

When a crystallizable homopolymer is modified by random incorporation of comonomers, crystallinity and melting temperature are lowered, and related properties are modified. So, it is very important to control their transitions, which play a key role in the processing and use conditions of these materials. Generally, DSC is often associated with optical microscopy to identify the nature of the mesophase, and can be successfully used to determine phase transitions in TLCPs (22-24). Therefore, we investigate in this paper the effect of thermal post-treatment on the crystallization behavior of Z 6000 and Z 8000B using a differential scanning calorimeter (DSC).

### 2. EXPERIMENTAL SECTION

**Materials**

Two semicrystalline TLCP resins were studied, namely, Zenite 6000 and Zenite 8000B of DuPont. These resins are composed of varying ratios of terephthalic acid (TA), 4-hydroxybenzoic acid (HBA), hydroquinone (HQ), 2,6-naphthalenedicarboxylic acid (NDC), and other aromatic diols, aromatic dicarboxylic acids (25, 26). Structures of monomers along with their chemical names are given in Table 1. Therefore, they can be categorized as wholly aromatic polyester resins.

**TGA**

A thermogravimetric analyzer PE TGA-7 was used to investigate the thermal stability of the material, using a scanning rate of 20°C/min.

**Polarized Light Microscope (PLM)**

Photographic observation was carried out by using a cross-polarized light microscope (PLM) with a heating stage and an automatic camera. The heating rate was controlled at about 20°C/min. The sample was sandwiched between two thin glass slides and placed on the heating stage, under PLM to observe the liquid crystalline texture under crossed polarizers.

**DSC**

A Perkin-Elmer Pyris 1 DSC was used. The instrument was calibrated with high-purity melting standards (indium and zinc). All the measurements were run under dried nitrogen. During the measurement, the samples were kept under a nitrogen environment of 20 psi with an online subtraction of baseline. Samples were heated from 50°C to 400°C at a rate of 20°C/min and treated isothermally by holding the sample at 400°C for 3 minutes, and then cooled to 50°C and kept isothermal for 2 minutes. Further, the second and third heating cycles were carried out following the same procedure as earlier.

For non-isothermal crystallization, samples were heated to 400°C and held at that temperature for 3 minutes. The samples were then cooled to 50°C at different cooling rates and the DSC cooling traces were recorded.

### Table 1. Chemical Structures and Names of the Monomers Used in Zenite™ TLCPs.

<table>
<thead>
<tr>
<th>Monomer Structure</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Structure Image]</td>
<td>Hydroquinone (HQ)</td>
</tr>
<tr>
<td>[Structure Image]</td>
<td>4,4'-dihydroxybiphenyl (BP)</td>
</tr>
<tr>
<td>[Structure Image]</td>
<td>Terephthalic acid (TA)</td>
</tr>
<tr>
<td>[Structure Image]</td>
<td>2,6-naphthalenedicarboxylic acid (NDA)</td>
</tr>
<tr>
<td>[Structure Image]</td>
<td>4-hydroxybenzoic acid (HBA)</td>
</tr>
</tbody>
</table>
For isothermal crystallization, samples were heated to 400°C and held at that temperature for 3 minutes. The samples were then cooled to a prechosen crystallization temperature, $T_c$, as rapidly as possible, and maintained there for different periods of times, $t_c$. Samples were then heated again to 400°C at a standard heating rate of 20°C/min and the DSC heating traces were recorded as a function of time ($t_h$) and temperature ($T_h$).

The sample weights were controlled in a range of 5–10 mg for both non-isothermal and isothermal experiments. The transition temperatures correspond to the maxima or minima of the peaks and their uncertainty is ± 0.3°C. The heats of transition have been evaluated using a program for computing the partial areas, and their uncertainty is ± 0.05 J/g.

### 3. RESULTS AND DISCUSSION

Figure 1 represents a set of thermal analysis curves for Z 8000B TLCP, during the heating and cooling process from 50°C to 400°C with a heating and cooling rate of 20°C/min. In the case of Z 8000B, very weak endothermic peaks appeared at 240°C and 270°C, respectively, in the second and third heating curves. However, an exothermic peak was found at 230°C for each cooling curve. Similarly for Z 6000, weak endothermic peaks appeared at 290°C and 330°C, respectively, in the second heating curve with an exothermic peak at 294°C for each cooling curve.

Further investigations of the weak endothermic peaks were carried out through non-isothermal and isothermal experiments.

### Non-isothermal

In the case of non-isothermal crystallization, the samples were heated to 400°C and held at that temperature for 3 minutes, and then cooled to 50°C at different cooling rates. In the present case, for both Z 6000 and Z 8000B, cooling rates of 10, 15, 20, 30 and 40 °C/min were used. It was seen that (see Fig. 2) the faster the cooling rate, the broader the exothermic peak. In addition, the crystallization temperature, referred to as the peak temperature, was found to shift to a higher temperature as the cooling rate was decreased. This observation may be explained by the fact that transition kinetics is slow relative to the experimental cooling rate [26]. The estimated values for peak temperature for both Z 6000 and Z 8000B are tabulated in Table 2. The crystallization temperature was found to be 234°C for a cooling rate of 10°C/min, whereas it was only 228°C for 40°C/min in the case of Z 8000B, and was found to be 296°C and 290°C, respectively, for Z 6000.

### Isothermal

The isothermal study was carried out for Z 8000B and Z 6000 resins both as a function of annealing time and annealing temperature. To investigate the
different crystallization processes, in the case of Z 8000B the temperature range was split into two regions: the lower temperature region of 200–220°C for the slow crystallization test, and the high temperature region of 230–250°C for the fast crystallization test. In the present case the annealing temperatures chosen were 210, 220, 230, 240, and 250°C and the annealing times were 10, 30, 60, 120, 240, and 480 minutes for Z 8000B. Similarly, for Z 6000, the annealing temperatures chosen were 260, 270, 280, 290, and 300°C and the annealing times were 10, 30, 60, 120, 240, and 480 minutes.

**Low-Temperature Region**

Figure 3 shows the DSC thermograms for Z 8000B annealed at 220°C for various periods of annealing time. In the melting process of the TLCP Z 8000B three peaks are identified: a large endothermic peak at 233°C and a smaller endothermic peak at around 270°C, and another very weak endothermic peak at about 226°C. It is clear that the endothermic peak at 233°C is found to shift to a higher temperature along with an increase in the enthalpy, depending on the annealing time. The endothermic peak at 270°C is found to remain unchanged. The DSC heating traces for Z 8000B crystallized at 225°C after different periods of annealing time are shown in Fig. 4. Again, one can see that there are two distinct endothermic melting peaks (T_m(l) = 250°C and T_m(h) = 272°C), along with a very weak endothermic peak (T = 216°C). The high melting peak remained at the same temperature, which is independent of the annealing time. The low melting peak shifted to a higher temperature with increasing annealing time and the enthalpy increased as well (as tabulated in Table 3).

A very similar observation was found for Z 6000 TLCP while annealing the sample at 270°C. Figure 5 shows clearly two melting endothermic peaks. However, the samples crystallized at 280°C show two endothermic peaks only for the initial short annealing time. As the annealing time increases the two peaks coalesce and the peak shifts to a higher temperature. The DSC heating traces for the sample annealed at 290°C, which is very close to the crystallization peak

![Graph](image-url)
Crystallization and Melting Behavior of Zenite

**Fig. 3.** DSC thermograms of Z 8000B annealed at 220°C at different annealing times.

**Fig. 4.** DSC thermograms of Z 8000B annealed at 225°C at different annealing times.
Table 3. Transition Properties of Z 8000B as a Function of Isothermal Annealing at 225°C.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>$T_d(l)$ (°C)</th>
<th>$\Delta H_d(l)$ (J/g)</th>
<th>$T_d(h)$ (°C)</th>
<th>$\Delta H_d(h)$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>245.9</td>
<td>0.79</td>
<td>272.2</td>
<td>0.48</td>
</tr>
<tr>
<td>30</td>
<td>250.9</td>
<td>1.15</td>
<td>272.2</td>
<td>0.36</td>
</tr>
<tr>
<td>60</td>
<td>254.5</td>
<td>1.60</td>
<td>272.5</td>
<td>0.26</td>
</tr>
<tr>
<td>120</td>
<td>259.5</td>
<td>1.42</td>
<td>271.2</td>
<td>0.19</td>
</tr>
<tr>
<td>240</td>
<td>264.5</td>
<td>2.65</td>
<td>271.0</td>
<td>0.12</td>
</tr>
<tr>
<td>480</td>
<td>269.5</td>
<td>5.20</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Temperature shown in Fig. 6. In the initial stage of annealing, only one strong endothermic peak appears; but as the annealing time increases, the peak becomes broader and broader, and a shoulder peak is found to appear on the higher temperature side for $t = 240$ and 480 minutes.

The trends are similar to that of copolymer of 73/27 HBA/HNA and 60/20/20 HNA/AP/TA, both LCPs. The presence of two distinct endothermic melting peaks represents the two different transition processes that were described by Cheng (10, 27). One is referred to as the high melting peak, which is independent of annealing time. The other is referred to as the low melting peak that is dependent on the annealing time. The peak temperature shifted to a higher temperature as the annealing time increased along with an increase in the enthalpy.

In the present case, the two endothermic melting peaks observed during heating are labelled as $T_d(h)$ for high melting peak and $T_d(l)$ for the low melting peak. The corresponding heats of transition for the peaks are $\Delta H_d(h)$ and $\Delta H_d(l)$, respectively. In the low temperature regions of isothermal experiments, the crystals formed by solidification were provided with a chance for crystal annealing by the following isothermal condition. It has been found that the heat of transition for the crystals obeys a linear relationship with logarithmic time, $\log t_c$ (annealing time $t_c$), as described by the following equation:

$$\Delta H_d(h, T_c, t_c) = A(T_c) \log t_c + B(T_c)$$  \hspace{1cm} (1)

The parameter $A(T_c)$ is related to the rate of the transition. The relationships between the heat of transition, $\Delta H_d$, and logarithmic time, $\log t_c$, for both high and low melting peaks are illustrated in Fig. 7a. From Fig. 7a, it is clear that the enthalpy of the fast transition process is almost independent of annealing time, (since the slope of $\Delta H_d$ vs. $\log t_c$ is very small and almost equal to zero). This indicates that there exists a frozen liquid crystalline structure while quenching Z 6000 TLCP from 400°C to the room temperature. In other words, the formation of liquid crystals may be very rapid from its isotropic phase. At the same time, crystal growth is very slow for these frozen liquid crystals. Moreover, it implies that the crystallization
temperature plays a more important role in crystal growth than the crystallization time. However, a different situation was observed for the low melting peaks (see Fig. 7a). The heat of transition, \( \Delta H_l(1) \), increases rapidly with time. This implies that the rigid LCP chains at elevated temperatures may have a tendency to perform a translational or rotational motion with respect to the chain direction to have better intermolecular packing and to reduce the Gibbs free energy. Similar behavior has been observed in the case of other polyester-based TLCPs (20-22).

The relationships between transition temperature, \( T_d \), and logarithmic time, \( \log t_c \), for both high and low melting peaks are shown in Fig. 7b for Z6000 TLCP that has been crystallized at 270°C. It is clear that \( T_d(h) \) does not change much with time. This phenomenon is quite similar to that of \( \Delta H_l \) vs. \( \log t_c \), and thus it reveals that liquid crystal phases quenched from isotropic phase are difficult to further perfect with annealing at 270°C. However, \( T_d(l) \) increases linearly with \( \log t_c \) for \( T_c \):

\[
T_d(l,T_c,t_c) = C(T_c) \log t_c + D(T_c) \tag{2}
\]

where \( C(T_c) \) is related to the change in crystalline perfection. Thus the linear relationship refers to the perfection processes that take place during the crystal growth for Z6000 TLCP.

**High-Temperature Region**

A single transition was discovered while carrying out isothermal experiments in the temperature region at and above 230°C for Z8000B. Figure 8 shows a set of DSC traces for Z8000B at a higher annealing temperature of 240°C. From this figure, we can see that only one endothermic peak appears regardless of the annealing time. Also, there exists a weak endothermic peak at 220°C regardless of the annealing time. The presence of only one endothermic melting peak in each of the DSC heating scans indicates a simple transition process. The peak temperature is found to shift to higher temperatures, and also its corresponding enthalpy increases as the annealing time increases. The same trend was found for an annealing temperature of 250°C. Changes of the heat of transition with respect to logarithmic time are plotted in Fig. 9a for two chosen temperatures (240°C and 250°C). It is seen that such changes slow down with an increase of temperature. The transition temperature increases linearly with \( \log t_c \) (as illustrated in Fig. 9b for 240°C and 250°C); this implies that the rate of increase in crystalline perfection is essentially constant over the annealing process.

When the isothermal experiments were done in the temperature region above 290°C for the Z6000 TLCP, the transition behavior changes. Figure 10 illustrates
Fig. 7. (a) Relationship between $\Delta H_d$ and $\log t_c$ of Z 6000 @ $T_i = 270^\circ C$ and (b) relationship between $T_d$ and $\log t_c$ of Z 6000 @ $T_i = 270^\circ C$. 
the DSC heating scans for the Z 6000 TLCP crystal-
ized at 300°C for various annealing times. Only one
strong endothermic melting peak was observed with a
very weak endothermic peak at around 260°C ir-
spective of the annealing time. It is clear that the in-
tense endothermic melting peak broadens up and also
the peak temperature was found to shift to the higher
temperature along with increasing annealing time.
The enthalpy values (see Table 4) of this peak are
found to increase as the annealing time increases
from 10 to 480 minutes.

Figure 11 shows the DSC thermograms for Z 8000B
annealed for 120 minutes at various annealing tem-
peratures (210°C, 220°C, 230°C and 240°C). It is clear
that the two transition peaks approach each other and
gradually merge into a single transition peak (when
the annealing temperature is 230°C) as the annealing
temperature increases from 210°C to 240°C (27).

Multi-melting behavior seems to be a common fea-
ture in many TLCPs (7, 10, 14). In general, the lower
melting peak corresponds to less perfect crystals
formed in the isothermal crystallization process dur-
ing annealing. During the DSC heating scan, these
less perfect crystals reorganize into more perfect crys-
tals, and melt partially and recrystallize to form more
perfect crystals, which melt at higher temperature.

Based on the classical theory of polymer crystalliza-
tion, the overall crystallization rate is measured both
as the rate of nucleation and growth (2). However, ac-
cording to Liu et al. (28), it is believed that LCPs do
not require nucleating agents: small aggregates of
local oriented rod-like segments in nematic phase
could act as primary nuclei as well as the secondary
nuclei. The improvement in the molecular motion is
the major requirement for fast crystallization of LCPs.
It is known that the p-linked aromatic units impart
the liquid crystal nature; on the other hand, the non-
p-linked units or other comonomers could promote
the molecular motion of the segments, i.e., they re-
duce the anisotropy by disrupting the rigid chain
structure and thereby depress the melting point.
These Zenite series TLCPs are believed to consist of
HBA, HQ, TA and HQ derivatives, the presence of
which could also enhance the molecular motion by re-
ducing the rigid chain sequence of HBA. A similar ob-
ervation was made by Cantrell et al. (29) in their
work on the insertion of HQ/TA into HBA chains.
They concluded that either longer HBA sequence at
higher HBA mole fraction or a longer HQ/TA sequence
at higher HQ/TA mole fraction could inhibit molecu-
lar motion. Equimolar combinations of HBA and
HQ/TA units would be the best case for the accelera-
tion of crystallization rate. However, the presence of
comonomer units will usually reduce the crystallinity
of polymers, although it may accelerate the crystal-
lization rate.
Fig. 9. (a) Analysis of $\Delta H_d$ Vs. $\log t_c$ relationships in isothermal experiments for Z 8000B @ $T_c = 240^\circ$C & 250$^\circ$C and (b) analysis of $T_d$ Vs. $\log t_c$ relationships in isothermal experiments for Z 8000B @ $T_c = 240^\circ$C & 250$^\circ$C.
The presence of two crystallization processes is not restricted to the TLCPs based on HBA/HNA. Similar phenomena have been reported for a TLCP consisting of HBA, HQ and carbonyl units and another TLCP based on phenylhydroquinone terephthalate and HBA and for the TLCP PSHQ10 (30). According to Han and Kim (11), this may indicate that the underlying mechanisms are independent of the chemical structure and may be an intrinsic property of TLCPs. The existence of slow and fast crystallization processes, however, is also reported for the random copolymers of polyethylene terephthalate-co-adipate, which are not LCPs. The random copolymer character may therefore be the origin of the two different crystallization processes.

Table 4. Transition Properties of Z 6000 as a Function of Isothermal Annealing at 300°C.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>T_d (°C)</th>
<th>ΔH_d (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>337.1</td>
<td>0.49</td>
</tr>
<tr>
<td>30</td>
<td>341.8</td>
<td>1.03</td>
</tr>
<tr>
<td>120</td>
<td>349.8</td>
<td>1.44</td>
</tr>
<tr>
<td>240</td>
<td>355.4</td>
<td>1.63</td>
</tr>
<tr>
<td>480</td>
<td>363.1</td>
<td>2.56</td>
</tr>
</tbody>
</table>

**CONCLUSION**

From these experimental results, we can see that there is a variation in thermal behavior with varying annealing temperatures and times. This indicates that a variety of crystalline structures could be generated.
Fig. 11. DSC thermograms of Z 8000B annealed for 120 min at various annealing temperatures.

Fig. 12. PLM micrograph of Z 8000B at 500x.
in this polymer. There is conclusive evidence that when annealing temperature is low, two distinct transitions can be found. One is a function of annealing temperature and time, while the other is independent of them. As the annealing temperature increases, these two transition processes merge into a single transition process, which is also a function of annealing temperature and time. Linear relationships between \( T_d \) and log \( t_c \) in the low-temperature regions indicate perfection processes during the crystal growth for the copolymers. Further investigations on these polymers are still in progress.

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REFERENCES

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