Revisit the Crystallization Mechanism of Vectra,™ a Liquid Crystal Polymer

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ABSTRACT: We have studied isothermal transition kinetics and crystallization mechanisms of the Hoechst Celanese liquid crystal polymer Vectra™ A-950 using a differential scanning calorimetry. This material is a random copolymer with a composition made of 73 mol %/27 mol % of HBA (1,4-dihydroxybenzoic acid)/HNA (2,6-dihydroxynaphthoic acid). When comparing our results to previous work on 75/25 HBA/HNA, we found some similarities as well as dissimilarities. In the case of similarities, both polymers show two types of transition processes in the low-temperature region (below 495 K). One is a fast process, which can be regarded as liquid crystal transition, and is characterized by a heat of fusion that does not vary significantly with annealing time. The other transition is a slow process related to crystal perfection and shows increases in the heat of transition and the transition temperature with increasing annealing time. However, the apparently slight difference in polymer composition also leads to a few surprising results. For example, previous work on 75/25 HBA/HNA two transition peaks (slow and fast processes) were observed after annealing it at 505 K, while in the current work only one transition peak in the case of 73/27 HBA/HNA was observed. In addition, based on the relationship between heat of fusion and annealing time, the LCP made from 73/27 HBA/HNA may perfect faster (in the time scale we study); hence, its posttreatment processes may be accomplished more efficiently than that of 75/25 HBA/HNA. This result also suggests that the former may have a better sequence or a better matching of molecular dimensions for crystallization than that of the latter. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1139–1150, 1999

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INTRODUCTION

Thermotropic liquid crystal polymers (LCPs) have received a great deal of attention from both academia and industry in the last 2 decades. Several review articles have described the historical progress on this subject.[1–6] In addition to the synthesis of new LCP materials, emphasis has been placed on the fundamental understanding of the origins and modification of physical and thermal properties, and the analysis of the corresponding structure and property relationship during posttreatments. This is due to the fact that often as-spun LCP fibers need further heat treat-

ment to improve its performance and market values. In general, annealing near T_m leads to an increase in molecular weight as well as to an increase in the degree of perfection in crystallinity.[1,3–5] For example, in a typical heat treatment, the fiber is subjected to a high temperature (typically 10–20°C below the melting temperature) in an inert environment for a prolonged time (10 min to several hours). As a result of heat treatment, the tenacity shows a dramatic increase from about 10 g/day for as-spun fibers to values in excess of 20 g/day, occasionally reaching values as high as 40 g/day. In addition, chemical resistance, melting point, elongation, thermal retention of tensile properties, and end-use temperature also increase. Although many thermotropic copolyester fibers do not show significant increases in fiber moduli (typically about 500–650 g/day) with heat treatment (possibly due to the absence of orientational changes during this process), this is not true for all copolyesters. Some may more than double their modulus on heat treatment.

Solid-state polymerization of as-synthesized LCPs has also been demonstrated under a reduced pressure or in a nitrogen environment in order to yield higher molecular-weight products. Experiments suggest that a multiple step change in temperature profile can facilitate the molecular weight enhancement, but the final temperature is recommended to be about 10–30°C below the original melting point.[1,3–5] These two examples clearly demonstrate the importance of a fundamental understanding of LCP crystallization mechanisms.

Early investigations of the phase transitions of LCPs indicated that the transition enthalpies and entropies of LCPs were very low compared to conventional random coil polymers.[1,3–5] This was due to the fact that LCPs possess a unique condition in which their long-range molecular orientational order persists in the absence of various types of short-range translational order. As a result, chain rigidity prevents molecules from chain folding, and mesophase transitions usually occur through aggregation of rigid chain molecules. Cheng[7] found that two transition processes exist for 75/25, 58/42, 30/70 molar ratios of HBA/HNA (4-hydroxybenzioc acid/4-hydroxy-2-naphthoic acid) LCPs during the transition from nematic to solid state; one is a fast transition process, ascribed to the aggregation of rigid chains, and the other is a slow transition process developing gradually during the later heat-treatment stage. These two processes also manifest in different crystal structures, as suggested by Biswas, Black-

well, and Cheng and his co-workers:[8,9] the fast process yields hexagonal packing with a cylindrical symmetry along the chain direction, while the slow process leads to an orthorhombic packing. However, the detailed origins of these two transition mechanisms are still unsolved.

Cheng and his co-workers[9,10] also studied Amoco's Xydar and other Hoechst Celanese LCP variants observing similar crystallization processes to the HBA/HNA thermotropic system. However, X-ray data, based on Blackwell et al.[11] and Field et al.,[12] suggested that more than two possible crystalline packings for some nematic LCPs depending on sample preparation and annealing history.

Other researchers also investigated Hoechst Celanese's Vectra A and B type LCPs. For example, Lin and Winter[13] reported that when Vectra A-950 was in a supercooled liquid state and underwent gradual crystallization, the rate of crystallization increased significantly with increasing supercooling, i.e., the interval between its melting point, T_m, and the desired experimental temperature level, T. In addition, they found that quenching immediately after deformation at a high temperature could lower the degree of crystallinity. Their data indicated that low cooling rates and large elongation (extensions) lead to the highest crystallinity, and the rate of the crystallization depends on annealing temperature as well as on mechanical and thermal histories of the samples.[14,15] A higher annealing temperature leads to a slower crystallization. Calundann[16,17] and Roggero et al.[18] revealed that thermal and mechanical treatments on LCPs could alter local order and changed the ability of subsequent crystallization of LCPs.

Geil and his co-workers[19,20] investigated LCP formation and crystal structure using an innovative approach. They conducted thin-film solution polymerizations and found lamellar single crystals from poly(2,6-oxynapththoate/m-oxybenzoate) and from poly(p-oxybenzoate). Han et al.[21] also studied the effect of thermal history on a main-chain thermotropic liquid-crystalline polyester with flexible units. Nakai et al.[22] investigated phase-separation processes and self-organization of textures in the biphase region of a thermotropic liquid crystalline polyester using a polarizing light microscopy. They reported and quantitatively analyzed morphological changes during the heating from a fully anisotropic phase to a biphase region and during the cooling from a isotropic phase to a biphase region. They concluded that phase-separation occurred as a con-

sequence of chain segregation according to the chain length, while self-organization of textures was strongly depend on the thermal history. The effects of thermal treatment on LCPs have also been reviewed by Economy and Goranov,[23] and Jaffe et al.[24]

In this article, we revisit the crystallization mechanism of liquid crystalline polyesters. This is because much of the previous work on Vectra A type polymers was based on experimental variants with a variety of compositions, i.e., 75/25, 58/42, and 30/70 molar ratios of 4-hydroxybenzioc acid (HBA) to 6-hydroxy-2-naphthoic acid (HNA), and most of them were experimental grade materials. Because the most popular commercial grade LCP is Vectra A-900 or A-950 polymer, which is made of 73/27 HBA/HNA, it is worthwhile to investigate the crystallization kinetics of this composition.

Figure 2   A set of DSC heating traces during isothermal experiments of Vectra A-950 in the low-temperature region ($T_c = 485$ K).

THEORY

The crystallization behavior of macromolecules has been extensively studied during the last 4 decades. It is well known that the crystallization of flexible polymers can be quite rapid because two neighbour moieties or molecular chains can readily adjust their sequences into a growing crystalline structure.[24−26] For many linear, flexible, random-coil macromolecules, crystallization from a melt initiates from heterogeneous nucleus and proceeds by chain-folded lamellar crystal growth with spherulitic morphologies. The Avrami equation has been used to express the macroscopic, overall crystallization process:[27,28]

$$1 - V^c = \exp(-Kt^n) \qquad (1)$$

where V^c is the volume-fraction crystallinity, K is a temperature-dependent constant (also depen-

dent upon nucleation and growth rates which, in the present case, are presumed to be constant throughout the course of phase transition[29]), t is time, and n is the Avrami parameter. For a time-dependent three-dimensional homogeneous crystallization growth, n is theoretically equal to 4. For n to be equal to 3, either the nucleation is homogenous and growth is two-dimensional or the nucleation is heterogeneous (nonsporadic in time) and the growth is three-dimensional.[29] For LCPs, low n values have been reported.[7,30] A microscopic mechanism of polymer crystal growth was proposed after the discovery of chain-folded lamellar crystals.[25] Modern theories to describe this crystal growth are based on activated state theory and assume surface free energy is the main limiting effect preventing large three-dimensional crystal growth. Additional concepts have been proposed by Cheng and Wunderlich,[31] and Sadler[32] based on molecular segregation and continuous crystal surfaces.

A convenient method to measure the Avrami n is to obtain volume-fraction crystallinity, V^c, by utilizing a differential scanning calorimetry. Equation (1) can be written as the following form

$$1 - \Delta H_d(T_c, t_c)/\Delta H_d^\circ = \exp\{-K(T_c)t_c^n\} \qquad (2)$$

where ΔH_d (T_c, t_c) is the heat of fusion in J/g or J/mol as measured experimentally, and ΔH_d° is the ideal heat of fusion of the perfect crystal, which can be estimated from the extrapolation of the relationship between ΔH_d and $(\text{Log } t_c)^{-1}$ by

Figure 1   Scheme to calculate $\Delta H_d(h)$ and $\Delta H_d(l)$ in overlapping DSC curves.

Figure 3 A set of DSC heating traces during isothermal experiments of Vectra A-950 in the low-temperature region (T_c = 495 K).

considering that ΔH_d° is the heat of fusion after polymeric chains experiencing infinite crystallization time.[7–10] T_c is the crystallization temperature, and t_c is the crystallization time.

Once ΔH_d° and T_d° were obtained, one can easily estimate the entropy change during the transition based on the following equation:

$$\Delta S_d^\circ = \Delta H_d^\circ / T_d^\circ \tag{3}$$

EXPERIMENTS

Hoechst Celanese Vectra A-950 was used in this investigation. This polymer is comprised of 73 mol % 4-hydroxybenzioc acid (HBA) and 27 mol % 6-hydroxy-2-naphthoic acid (HNA), and has been studied extensively.[1–6,7–9,11,23,24] Based on X-ray diffraction study, Vectra A is a random copolymer.[33] The molar mass of the average repeating units is 133.5 g/mol. The preparation of the copolymers has been described in details elsewhere.[16,17] To avoid any influence of previous thermal history, every sample was used only once.

A Perkin-Elmer Pyris 1 DSC was used for scanning calorimetry. Both temperature and heat flow scales were calibrated with high-purity melting standards (indium and zinc) in the certain heating rate range. All thermal analyses were run under dried nitrogen.

The isothermal crystallization samples were heated to 673 K (400°C), which was above the metastable equilibrium crystal to nematic transition temperature, T_d° (see below), and held there for 1.5 min. The samples were then cooled to prechosen crystallization temperatures, T_c, as rapidly as possible, and maintained there for different periods of time, t_c. Samples were then reheated again to T_d° with a standard heating rate of 10 K/min, and the DSC heating traces were recorded as a function of time and temperature. The sample weights were controlled in a range of 5–10 mg. All pan weights were within a deviation of ±0.02 mg or less.

In this article, the peak temperatures for the heating trace were used to characterize transitions. To compare our data to that of Cheng, we

Figure 4 Relationship between ΔH_d and log t_c of Vectra A-950 at T_c = 485 K (open symbol) and 495 K (solid symbol) (square symbols represent the fast transition process, triangular symbols represent the slow transition process and circular symbols represent the overall change of ΔH_d).

Figure 5 Relationships between T_d and log t_c of Vectra A-950 at T_c = 485 K (open symbol) and 495 K (solid symbol) (square symbols represent the fast transition process and triangular symbols represent the slow transition process).

followed his specifications and techniques. For example, when two melting peaks were observed during heating, their temperatures were determined to be $T_d(h)$ for the high melting peak and $T_d(l)$ for the low melting peak. The corresponding heats of transition for the peaks were $\Delta H_d(h)$ and $\Delta H_d(l)$, respectively.

In the case of multiple peaks in the DSC curves, we employed the following approach to split the overlapping peaks and calculate $\Delta H_d(h)$ and $\Delta H_d(l)$. As illustrated in Figure 1, the over-lapping curve consists of $\Delta H_d(l)$ for the low-transition process and $\Delta H_d(h)$ for the fast-transition process. Because the heat of fusion and the transition temperature of the fast-transition process are almost constant, this transition is considered to be a liquid crystal transition. It is, therefore, reasonable to assume that $\Delta H_d(h)$ has a symmetric bell-shape profile. Because one can easily measure one-half (the later one-half) of the peak area during the fast-transition process, the whole value of the $\Delta H_d(h)$ [in Fig. 1, $S_{GOIDE} = \Delta H_d(h)$]

Table 1 Isothermal Transition Properties of Vectra™ A-950 (Low Temperature Region)

Annealing Time (min)	T_d (l) (K)	T_d (h) (K)	ΔH_d (l) (kJ/mol)	ΔH_d (h) (kJ/mol)
	T_c = 485 K, heating rate = 10 K/min			
10	510.709	552.539	0.1349	0.1148
30	516.382	554.035	0.1642	0.1138
60	525.057	553.375	0.4024	0.1254
120	528.876	553.03	0.4281	0.1263
240	533.715	553.207	0.5911	0.1268
480	539.708	553.708	0.6944	0.1274
720	540.714	553.048	0.7147	0.1287
	T_c = 495 K, heating rate = 10 K/min			
10	535.187	553.527	0.2346	0.1955
30	536.692	552.521	0.4427	0.2014
60	538.546	553.040	0.5747	0.1965
120	544.560	553.854	0.6007	0.1864
240	548.278	552.181	0.6427	0.1872
480	550.855	553.853	0.7580	0.1934

Table II   Isothermal Transition Properties of Vectra™ A-950 (High Temperature Region)

Annealing Time (min)	T_d (K)	ΔH_d (kJ/mol)
$T_c = 505$ K, heating rate = 10 K/min		
5	552.543	0.3595
15	552.200	0.3774
30	552.196	0.5181
60	552.711	0.4891
120	553.377	0.6643
200	555.175	0.7021
300	557.041	0.6751
480	558.373	0.8322
720	559.041	0.9354
$T_c = 515$ K, heating rate = 10 K/min		
10	554.339	0.2311
30	555.507	0.2541
60	558.332	0.3786
120	560.845	0.5258
240	563.001	0.6353
480	566.156	0.7585
$T_c = 530$ K, heating rate = 10 K/min		
10	561.203	0.2590
30	563.628	0.3012
60	565.374	0.3256
120	568.054	0.4853
240	574.213	0.5494
480	575.855	0.7666

can be calculated. Then, by integrating the over-lapping peak area [S_{ABCDE}] and using the following relation:

$$S_{ABHF} = S_{ABCDE} - S_{GOIDE} = \Delta H_d(l) \qquad (4)$$

the value of $\Delta H_d(l)$ is thus obtained.

RESULTS AND DISCUSSION

Isothermal Experiments in Low-Temperature Regions

Figures 2 and 3 show two sets of DSC heating traces for the copolymer of 73/27 HBA/HNA crystallized at 485 and 495 K for various periods of time, t_c. Consistent with earlier results on the 75/25 HBA/HNA LCP,[7] there were two resolved endothermic melting peaks (K→N), suggesting two separate transition processes. One is identified as the high melting peak (square symbols in

Figs. 4 and 5), which is essentially invariant as a function of annealing time. The second peak is identified as the low melting peak (triangle symbols in Figs. 4 and 5), which has melting points dependent on the annealing time.

The heat of transitions, $\Delta H_d(h)$, in high melting peaks could be expressed by the following relationship with logarithmic crystallization time, $\log t_c$:

$$\Delta H_d(h, T_c, t_c) = A(T_c)\log t_c + B(T_c) \qquad (5)$$

where $A(T_c)$ is the parameter related to the rate of the transition. Because the slopes of $\Delta H_d(h, T_c, t_c)$ vs. $\log t_c$ are very small (approximate to zero) as illustrated in Figure 4 and Tables I and II, this information indicates that $\Delta H_d(h, T_c, t_c)$ is almost independent of t_c. This result implies that there is always a frozen liquid crystalline phase when quenching this polymer from 673 K to room temperature. In order words, the formation of liquid crystals from the isotropic phase can proceed very rapidly. Similar conclusions have been reported for a polyimide LCP quenched from 350°C in air and exhibiting a fine frozen liquid crystalline texture under polarized light microscopy.[34,35] On the other hand, the low slope value of the $\Delta H_d(h, T_c, t_c)$ vs. $\log t_c$ also implies that the crystal growth from this frozen liquid crystal is very slow, and that the crystallization temperature plays a more important role in crystal growth than crystallization time.

The situation changes in the case of the lower transitional (melting) peaks (triangle symbols in Fig. 4). The heat of transition, $\Delta H_d(l)$, increases rapidly with time. This indicates that rigid LCPs chains at elevated temperatures may have a tendency to perform translational motion along the chain direction motion or/and rotational motion with respect to chain axis to have a better intermolecular packing and to reduce the Gibbs free energy. Figure 4 also plots the overall changes (circle symbols) of ΔH_d with respect to the time ($\log t_c$).

Relationships between transition temperature, T_d, and time, $\log t_c$, for both high and low melting peaks are also shown in Figure 5 and Table I. One can see that $T_d(h)$ does not change much (within 2 K) with increasing time, $\log t_c$. This phenomenon coincides with that of $\Delta H_d(h, T_c, t_c)$ vs. $\log t_c$, and clearly reveals that liquid crystal phases quenched from the isotropic phase are difficult to further perfect with annealing at 485 and 495 K. However, $T_d(l)$ in low-temperature regions increases linearly with $\log t_c$ at different T_c:

Figure 6 A comparison of ΔH_d vs. $\log t_c$ relationships at $T_c = 485$ K between the present work and Cheng's data[7] (open symbol is the experimental result, while solid symbol is Cheng's data) (square symbols represent the fast transition process, triangular symbols represent the slow transition process, and circular symbols represent the overall change of ΔH_d).

$$T_d(l, T_c, t_c) = C(T_c)\log t_c + D(T_c) \qquad (6)$$

where $C(T_c)$ can be related to a rate of change in crystalline perfection. This linear relationship indicates perfection processes occurring during the crystal growth for Vectra A-950.

Figures 6 and 7 give comparisons between this work and Cheng's experimental data[7] at 485 K. Both data set the same trends between ΔH_d and $\log t_c$ and between T_d and $\log t_c$. However, $\Delta H_d(h)$ in the present work has a lower value than

Cheng's, while $\Delta H_d(l)$ and overall ΔH_d in the present work have higher values than Cheng's. Because our LCP is 73/27 HBA/HNA, while his is 75/25 HBA/HNA, these DSC results suggest that the 2% difference in HNA or HBA composition changes their end group sequence and crystallization kinetics.

In practice, the annealing time for conventional LCP fibers may last from 30 min to 4–7 h. Based on the slopes of $\Delta H_d(l)$ or overall ΔH_d vs. $\log t_c$ in this period (as shown in Fig. 6), 73/27

Figure 7 A comparison of T_d vs. $\log t_c$ relationships at $T_c = 485$ K between the present work and Cheng's data[7] (square symbols represent the fast transition process, triangular symbols represent the slow transition process. (Open symbol is the current work, while solid symbol is Cheng's data.)

(a)

(b)

(c)

Figure 9 A set of DSC heating traces on isothermal experiments at T_c = 515 K for Vectra A-950.

Figure 10 A set of DSC heating traces on isothermal experiments at T_c = 530 K for Vectra A-950.

HBA/HNA has a higher slope. Therefore, LCP made from 73/27 HBA/HNA may have a faster annealing or solid state polymerization process in this time scale, and its posttreatment process can be accomplished more economically than that of 75/25 HBA/HNA.

However, the major difference in crystallization kinetics between the recent commercial 73/27 HBA/HNA and the earlier 75/25 HBA/HNA occurs at an annealing temperature of 505 K. Cheng's results still show two transition processes; a low and a fast transition processes, while the current work shows only one transition process (Fig. 8A–C). For readers' information, Cheng's observed one transition process occurring at 512 K. Clearly, the slight difference in HBA/HNA composition ratio leads to different thermal properties and molecular sequence. Because the overall kinetics of the transition is a combination of molecular translation, rotation, and nucleation (aggregation), and is strongly dependent on the crystallization condition and chemical structure of the counits, and because 2,6-naphthalene groups cannot rotate as easily as phenylene

groups in the copolymer 75/25, the 7 K reduction in this critical temperature (from two to one transition process) is a surprise. The only possible answer is that the LCP made of 73/27 HBA/HNA may have a better sequence or a better matching of molecular dimensions for crystallization than that of 75/25 HBA/HNA.

Isothermal Experiments in High-Temperature Regions

When carrying out isothermal annealing experiments in the temperature region at or above 505 K for the 73/27 HBA/HNA, the transition behavior changes. Figures 8A, 9, and 10 exhibit some typical DSC results. There is only one endothermic melting peak in each DSC run, indicating a simple transition process. The melting peak also broadens with increasing annealing time, and the entire peak moves to higher temperatures, listed in Table II. Figures 11 and 12 are plots of the transition temperature and the heat of transition with respect to logarithmic time at three chosen temperatures (505, 515, and 530 K), respectively. Because the

Figure 8 Isothermal experiments at T_c = 505 K. (A) A set of DSC heating traces for Vectra A-950. (B) A comparison of ΔH_d vs. log t_c relationships between the present work (cross symbols with a solid line) and Cheng's data[7] (broken lines, square symbols represent the fast transition process, triangular symbols represent the slow transition process, and circular symbols represent the overall change of ΔH_d). (C) A comparison of T_d vs. log t_c relationships between the present work (cross symbol in solid line) and Cheng's data[7] (broken lines, square symbols represent the fast transition process and triangular symbols represent the slow transition process).

Figure 11 Analysis of ΔH_d vs. log t_c relationships in isothermal experiments for Vectra A-950 at T_c = 505, 515, and 530 K.

transition temperature increases linearly with logarithmic time (Fig. 11), this indicates the rate of increase in crystalline perfection is essentially constant over the annealing process (in the time scale we study). In addition, the slope of $dT_d/d(\log t_c)$ steepens with an increase in annealing temperature [$C(T_c)$ = 5.455, 7.246, and 9.280 at 505, 515, and 530 K, respectively], showing the sensitivity of crystalline perfection to annealing temperature and the rate of crystalline perfection increasing rapidly with the annealing temperature in the experimental range we study. These results are in agreement with previous experimental work that reported the recommended heat treatment condition for Vectra-

type LCPs should be at a temperature 10–20°C below the as-spun fiber melting point.[1–3] Because the melting point of Vectra A-950 is about 550 K, our data suggest annealing at 530 K is more desirable than that at 515 K.

ΔH_d° and T_d° at Metastable Equilibrium and Avrami Parameter *n*

Adopting an approach similar to Cheng,[7] the reciprocal heats of transition and the transition temperatures for Vectra A-950 were plotted against (log $t_c)^{-1}$ and extrapolations were made to infinite crystallization time to estimate their thermodynamic

Figure 12 Analysis results of T_d vs. log t_c relationships in isothermal experiments for Vectra A-950 at T_c = 505, 515, and 530 K.

Figure 13 Extrapolation of ΔH_d° at different temperatures based on the relationships of $(\Delta H_d)^{-1}$ vs. $(\log t_c)^{-1}$ for Vectra A-950.

properties, ΔH_d° and T_d°, at metastable equilibrium. Figure 13 shows the extrapolation of $(\Delta H_d^{\circ})^{-1}$ with respect to $(\log t_c)^{-1}$ at different temperatures, T_c. The extrapolated value at $(\log t_c)^{-1} = 0$ indicates the heat of transition, ΔH_d°, for Vectra A-950 at metastable equilibrium is 2.532 kJ/mol. Figure 14 illustrates the extrapolation of T_d with respect to $(\log t_c)^{-1}$ and leads to an extrapolated value of T_d° (607.5 K) at metastable equilibrium. Because ΔH_d° and T_d° have been obtained, the entropy changes during the transition can be calculated following the equation:

$$\Delta S_d^{\circ} = H_d^{\circ}/T_d^{\circ}.$$

For Vectra A-950, $\Delta S_d^{\circ} = 4.168$ J/(K mol). The ΔH_d°, T_d°, and ΔS_d° of the 75/25 HBA/HNA polymer have been reported by Cheng;[7] they are 3.68 kJ/mol, 610 K, and 6.03 J/(K mol), respectively. Probably because both 73/27 HBA/HNA and 75/25 HBA/HNA have similar compositions, their T_d° are close (607.5 vs. 610 K). The higher value of ΔH_d° for 75/25 HBA/HNA may be due to the fact that this composition can eventually form bigger crystals than that of 73/27 HBA/HNA. The slopes of ΔH_d vs. $\log t_c$, shown in Figure 6, support our explanation. Although 73/27 HBA/HNA has a greater slope in the early stage of annealing [between 31.6 ($\log t = 1.5$) and 316 min ($\log t = 2.5$)],

Figure 14 Extrapolation of T_d° at different temperatures based on the relationships of T_d vs. $(\log t_c)^{-1}$ for Vectra A-950.

Table III Avrami Parameters of the Transition Kinetics of Vectra™ A-950

Vectra™ A-950 (73/23 HBA/HNA)			Cheng's Data (75/25 HBA/HNA)		
T_c, K	n	log K	T_c, K	n	log K
485	0.46	−1.71	485	0.67	−2.69
495	0.31	−1.23	495	0.54	−2.31
505	0.23	−1.01	505	0.49	−1.95
515	0.37	−1.44	515	0.34	−1.37
530	0.32	−1.34	530	0.45	−1.70

75/25 HBA/HNA has a greater slope in the later stage [between 316 and 1000 min (log t = 3)]. The lower value of ΔS_d° for 73/27 HBA/HNA reinforces our previous hypothesis that the LCP made of 73/27 HBA/HNA may have a better sequence or a better matching of molecular dimensions for crystallization than that of 75/25 HBA/HNA.

Table III summarizes the calculated Avrami parameter n as a function of temperature for the present and previous work.[7] In short, all ns are in the range of 0.2 to 0.5 for the present case, while in the range of 0.3 to 0.7 for Cheng's case. As explained by Cheng's, these low n values may be due to the fact that each crystal does not grow with a constant radial growth rate.

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