High-Temperature Recrystallization and Rheology of a Thermotropic Liquid Crystalline Polymer

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ABSTRACT: The liquid crystalline melt of a random copolyester of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) recrystallizes above the nominal melting temperature. The recrystallized HBA/HNA (r-HBA/HNA) seems to contain periodic HBA crystals as evidenced by an additional equatorial reflection at d = 3.8 Å and by its increased melting temperature (about 325 °C). On the other hand, the d spacings in the WAXS pattern of the original low-melting crystals of this random copolyester are not suppressed by the recrystallization process. This suggests that the r-HBA/HNA consists of the original aperiodic crystal structure, however, reinforced by high-melting crystals with long HBA sequences. The r-HBA/HNA can be reversed by temporarily heating above 330 °C. Any effect of a possible transesterification reaction could not be detected here. Dynamic mechanical experiments show that the rate of recrystallization depends on thermal history prior to melting, preheating temperature, recrystallization temperature, and degree of molecular orientation. Molecular mobility and nuclei (residual high-melting crystallites) are two necessary conditions for forming high-melting crystals. The recrystallization behavior opens up new possibilities for processing of liquid crystalline polymers near their melting temperature and in the supercooled state (increasing mechanical properties and thermal resistance).

Introduction

The crystalline structure and crystallization behavior of liquid crystalline polymers (LCPs) have been the subject of many recent publications.[1–15] Rigid rodlike homopolymers, like the polycondensate of 4-hydroxybenzoic acid (HBA), usually have a very high melting temperature, which precludes melt processing. Several different modifications of molecular structure have been successfully used to lower the melting temperature. Most typically, the copolyester structure suppresses, at least initially, the formation of high-melting crystals and hence lowers the melting temperature. The extended chain character is maintained in copolyesters, although the molecular order is reduced. The melting temperature, at which the copolymer undergoes a transition from crystalline solid to the nematic state, varies with thermal and mechanical histories. It has been reported that melting temperatures of LCPs are significantly raised by annealing either in the solid state above the glass transition temperature[1,2] or in the molten state above the nominal melting temperature.[3,4,6,10,11,15]

The complex structure in the solid state results in a broad temperature range of melting and a large extent of supercooling during solidification. X-ray analyses on copolymers of HBA and 6-hydroxy-2-naphthoic acid (HNA) over the entire composition range show that the crystals of the copolyesters are aperiodic in the chain axis and have some three-dimensional order.[12–14] Several models have been proposed to describe the solid-state structure of LCPs. A most interesting model has been proposed by Windle and co-workers,[6,7] who suggest that short identical sequences in random copoly(HBA/HNA) chains match each other laterally, forming nonperiodic layer (NPL) crystals that have three-dimensional order. Recently, Biswas and Blackwell have proposed another possible model[12–14] which suggests that the development of three-dimensional crystallinity only requires that one monomer sequence on each chain lie about a register plane perpendicular to the chain axis; the lateral matching of identical copolymer sequences is not regarded as a necessary condition for forming aperiodic crystals. Butzbach et al.[1] have reported that solid-state annealing of a random copolymer containing 58 mol % of HBA and 42 mol % of HNA increases the crystallite size, as indicated by sharpened X-ray reflections and increased DSC melting temperature. Additionally, the phase-transition behavior of LCPs may be futher complicated by chemical reactions that change the sequence distribution and the molecular weight. Lenz et al. have reported that transesterification occurs in the nematic melts of random thermotropic poly(4-oxybenzoate-*co*-ethylene terephthalate) and poly(3-chloro-4-oxybenzoate-*co*-ethylene terephthalate), forming insoluble and infusible block copolymers irreversibly.[15]

In recent years, a commercial liquid crystalline aromatic polyester, Vectra A900 (Hoechst-Celanese Corp.), has been extensively studied in our laboratory.[8–11] One of the most interesting phenomena is the severe dependency of melt stability on the thermal treatment. After preheating to 320 °C, for example, the polymer shows a relatively stable nematic melt state at 290 °C, i.e., the dynamic moduli stay constant for several hours.[9] Without prior heating to an elevated temperature, however, the nematic melt at 290 °C recrystallizes and the melting temperature rises by 20–40 K. The effect of temperature on the rate of recrystallization has been studied previously.[10] In the present work, a structural model of high-temperature recrystallization is proposed, and a series of factors that affect the high-temperature recrystallization are separately investigated and discussed in the light of this model.

Experimental Section

Materials and Sample Preparation. The liquid crystalline polymer, Vectra A900 (Hoechst-Celanese Corp.), is a random copolyester containing 73 mol % 4-hydroxybenzoic acid (HBA) and 27 mol % 6-hydroxy-2-naphthoic acid (HNA). The nominal melting temperature (peak temperature of DSC heating scan at 20 K/min) is about 285 °C, above which the polymer is in a nematic state. The clearing temperature is well above the thermal decomposition temperature.

The received polymer pellets were ground into powder and then dried under vacuum at 120 °C for 20 h. The samples for rheological measurements were vacuum molded at 320 °C into disks (d = 25 mm, h = 1 mm).

Apparatus. Rheological measurements were performed on a Rheometrics Mechanical Spectrometer (RMS-800) using par-

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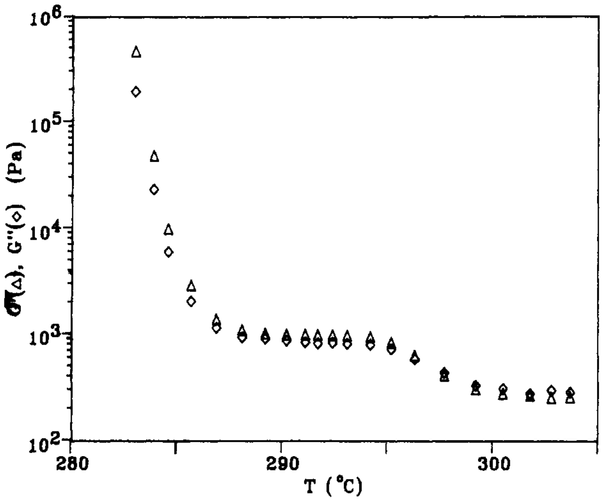

Figure 1. Temperature sweep at ω = 1 rad/s. The sample was heated at 2 K/min.

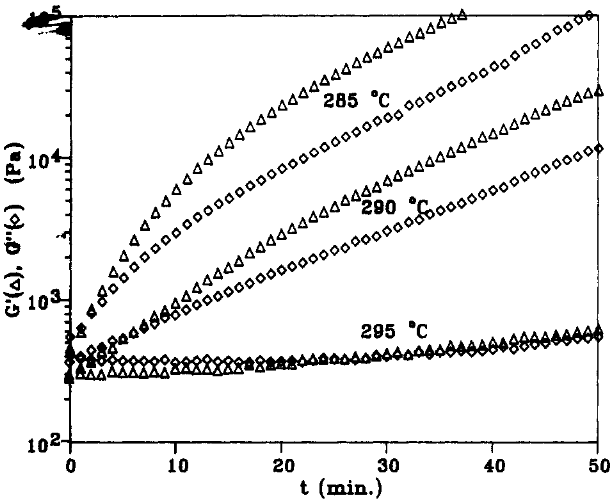

Figure 2. Modulus growth at indicated temperatures, ω = 1 rad/s.

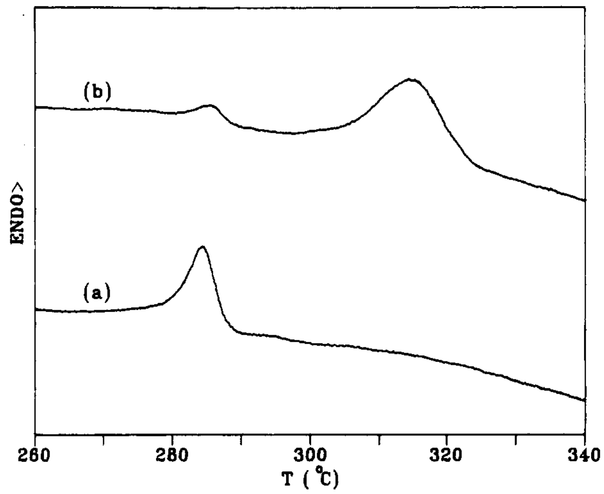

Figure 3. DSC first heating curves of the samples (a) freshly molded and (b) after high-temperature recrystallization at 285 °C for 50 min, at a heating rate of 20 K/min.

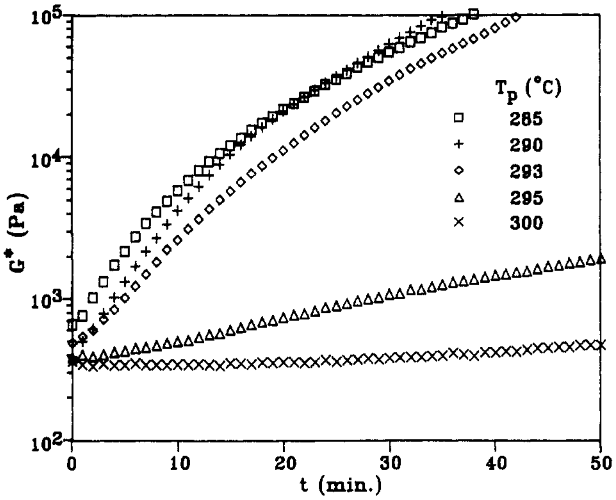

Figure 4. Modulus growth at 285 °C, ω = 1 rad/s. Sample had been preheated to indicated temperatures.

allel plates. Differential scanning calorimetry was carried out on a Perkin-Elmer calorimeter (DSC-4). Wide-angle X-ray scattering was made at room temperature using Cu Kα radiation and a Ni-filtered statton camera. The distance from sample to film was 53 mm. Mechanical properties were measured by a three-points bending test on a tensile machine (Instron Model TTBM).

Melting Transitions. During a temperature sweep on the RMS at a frequency of 1 rad/s and a heating rate of 2 K/min, the LCP displays first a major melting transition at about 285 °C and then a minor melting transition at about 297 °C (Figure 1). It is noted that the temperature of both melting transitions, especially the minor one, varies with the heating rate and the thermal history of the sample. The LCP already flows above the major melting transition temperature corresponding to the nominal T_m. The minor transition is attributed to the melting of highly ordered crystallites, which can persist above the major melting transition. The following experiments will show how the presence of these highly ordered crystallites severely influences the stability of the LCP melt in the temperature range between the major and the minor melting transitions.

Recrystallization above the Nominal Melting Temperature (T_m). When the LCP is heated to a temperature just above T_m, it melts into a nematic liquid only for a limited time since it recrystallizes gradually. The recrystallization process was monitored by dynamic mechanical measurements (Figure 2). At 285 °C, the initial melting results in low dynamic moduli (about 500 Pa). Within 50 min, however, the storage modulus G' and the loss modulus G'' increase by 3 and 2 orders of magnitude, respectively. The rate of recrystallization decreases with temperature and the phenomenon loses its strength above 295 °C, corresponding to the minor melting transition temperature. It seems that the LCP melt does not recrystallize significantly in the absence of the highly ordered crystallites.

The thermal treatment not only affects the molecular mobility as seen in the rheological experiment but also changes the DSC melting endotherm and the WAXS pattern. The freshly molded sample melts over a wide temperature range with a DSC peak at about 285 °C (Figure 3). The peak temperature is called the nominal melting temperature even if the crystalline structure is not yet completely molten at this temperature. The DSC measurement is not sensitive enough to show the minor melting transition. After heat treatment at 285 °C for 50 min, a second melting peak at 315 °C appears in the DSC first heating scan (Figure 3). As we reported earlier,[10] the high-temperature recrystallized samples (r-HBA/HNA) display a new reflection at d = 3.8 Å on the WAXS patterns, besides the ordinary reflections with d spacings at 6.8, 4.6, 3.3, and 2.1 Å. The structural changes are thermally reversible. After heating to 330 °C for a few seconds, the higher melting peak and the additional WAXS reflection at d = 3.8 Å disappear and the samples return to the DSC heating curve and WAXS pattern typical for freshly molded samples.

Effects of the preheating temperature (T_p) above T_m were examined by the following procedure. A sample was first heated to a defined T_p for 1 min, then cooled to 285 °C, and held there for G', G'' measurements during recrystallization (Figure 4). A high preheating temperature ($T_p \geq 295$ °C) slows down the recrystallization dramatically. This confirms that the LCP can have a relatively stable molten state after eliminating the highly ordered crystallites. With a T_p between 285 and 293 °C, the

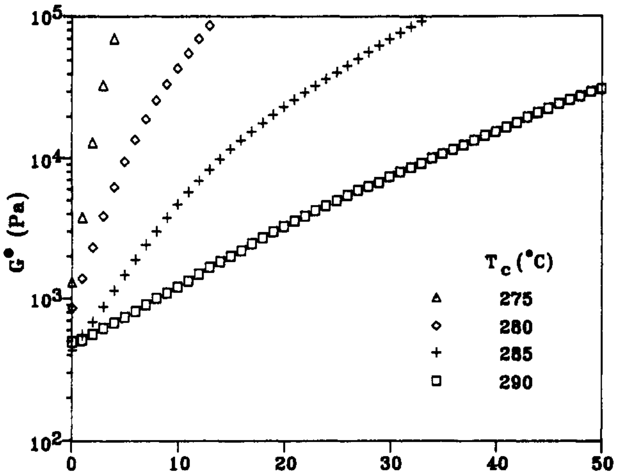

Figure 5. Modulus growth at indicated temperatures, ω = 1 rad/s. Samples had been preheated to 290 °C.

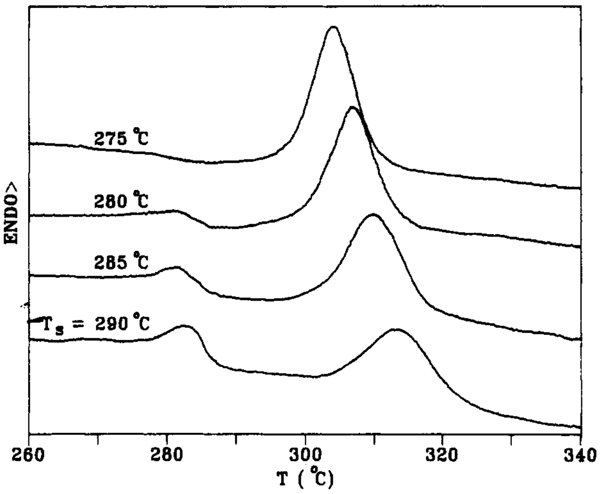

Figure 6. DSC first heating curves of the samples that had been preheated to 290 °C and then solidified at indicated temperatures for 50 min, heating rate = 20 K/min.

samples display a rapid increase in the complex modulus at 285 °C, indicating that such preheating has little effect on the rate of recrystallization. For achieving a high-melting structure, one has to keep both the preheating temperature and the solidification temperature below 293 °C.

Effect of Crystallization Temperature (T_c). The high-melting structure forms more rapidly at higher degrees of supercooling. This can be seen in the following experiment. After having been preheated to 290 °C for 1 min, a sample was cooled to a defined T_c for isothermal crystallization (Figure 5). The rate of modulus growth increases by a factor of about 2 for each 5 K of lowering T_c. It is interesting to note that the nominal melting temperature, T_m = 285 °C, no longer has any significance in this experiment. This implies that the degree of supercooling requires a new definition when the preheating temperature is between 285 and 295 °C, i.e., when some highly ordered crystallites remain as nuclei. The newly formed high-melting structure is very different from the solid-state structure of a freshly molded sample.

After 50 min of crystallization at T_c, samples were taken out for DSC analysis. The DSC first heating scan confirms the formation of a high-melting structure (Figure 6). Slow crystallization leads to a slightly higher melting temperature than rapid crystallization.

Effect of Solid-State Annealing Prior to Melting. The recrystallization process seems to depend on the residual solid fraction in the polymer after melting below 295 °C. This residual solid fraction of higher melting temperature and higher order may be increased by solid-state annealing prior to the apparent melting/solidification experiment. The important parameters are annealing temperature (T_a) and annealing time (t_a); the temperature of recrystallization was kept constant at 290 °C. With t_a = 10 min (Figure 7), annealing at 240 °C does not change the rate of recrystallization at 290 °C, annealing at 250 °C increases the rate by a factor of about 2. However, the rate of recrystallization does not increase monotonically with the T_a, it decreases when T_a was raised to 270 °C or above. With T_a = 260 °C (Figure 8), the rate of recrystallization at 290 °C increases with t_a and reaches a maximum at about 20 min. Worthy of note is that after having been annealed at higher T_a or for longer t_a, the samples melt very slowly and incompletely, as indicated by the relatively high value of the initial complex viscosity (Figure 7, T_a = 270 °C, and Figure 8, t_a = 30 min).

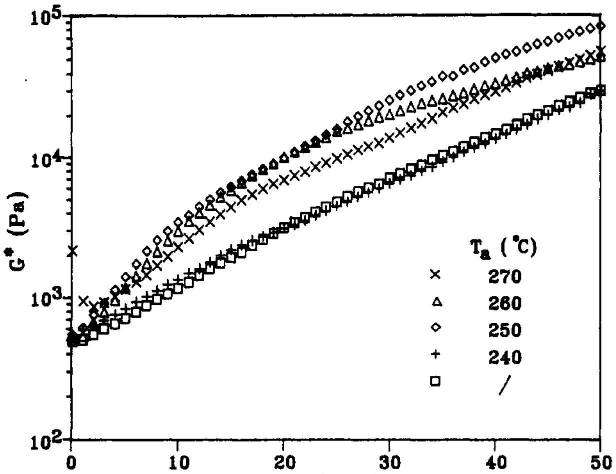

Figure 7. Modulus growth at 290 °C, ω = 1 rad/s. Samples had been annealed at indicated temperatures for 10 min.

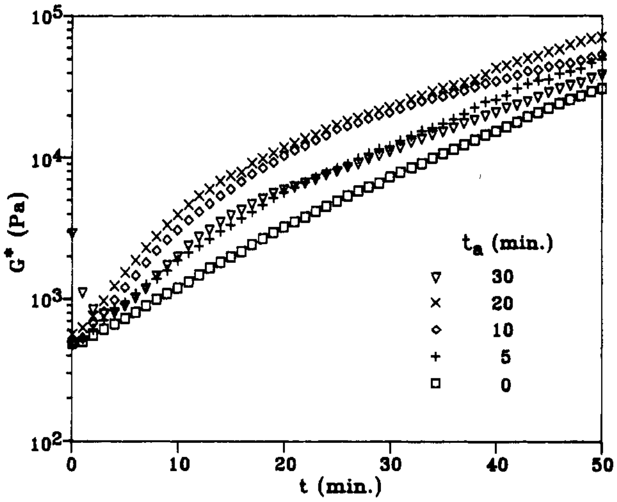

Figure 8. Modulus growth at 290 °C, ω = 1 rad/s. Samples had been annealed at 260 °C for indicated times.

Effect of Shear-Induced Molecular Orientation. Earlier experiments showed that extensional flow-induced molecular orientation accelerates crystallization of the LCP.[8,10] The effect of shear-induced molecular orientation is studied in the present work. Cone/plate geometry was used for achieving uniform strain throughout the samples. A sample was molded in the rheometer at 320 °C, cooled to 290 °C, and held there for 15 min to relax the molding effects and then cooled to room temperature at a rate of 30 K/min. The sample was reheated to 290 °C in the rheometer and a constant shear rate of 0, 0.008, 0.016, 0.032, 0.064, or 1.0 s^{-1} was applied for 62 s, yielding a final strain of 0, 0.5, 1.0, 2.0, 4.0, or 62 shear units. The applied shear strain was held during the following dynamic mechanical measurements. The ratio between the recrystallization rate of a sheared sample and that of an unsheared sample, K, is evaluated through fitting the modulus growth curves (Figure 9). In a wide range of strain, the sheared samples recrystallize about 1.6 times as fast as an unsheared sample does. Note that the recrystallization rate of

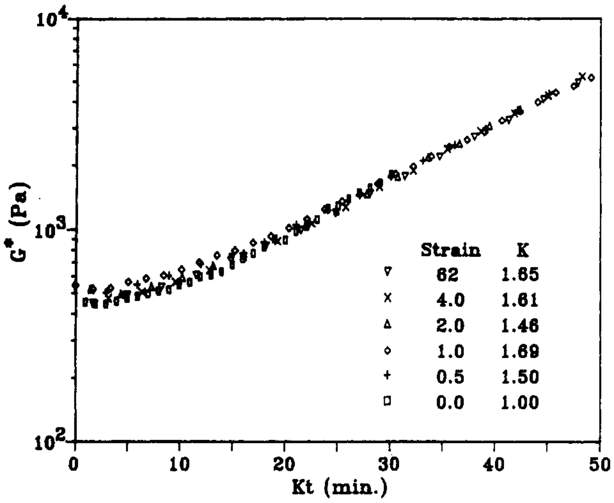

Figure 9. Modulus growth curves of sheared samples at 290 °C, $\omega = 1$ rad/s, which are shifted in the time scale by using a rate ratio K as the shift factor.

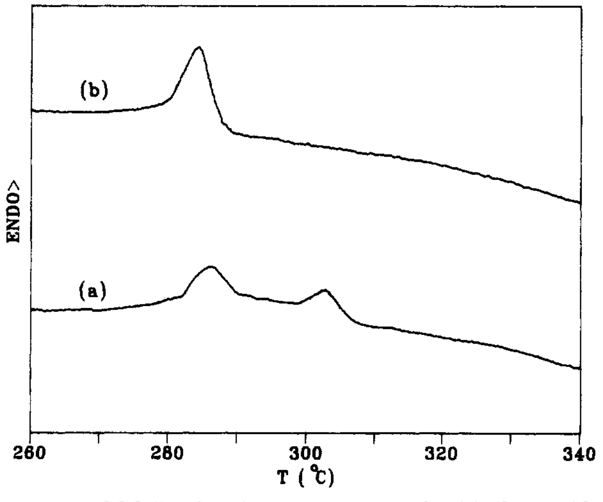

Figure 10. DSC first heating curves of samples (a) fiber molded at 290 °C without preheating and (b) fiber molded at 290 °C after preheating to 320 °C.

a cone/plate molded sample is lower than that of a parallel-plates molded sample (compare Figure 2, $T = 290$ °C, with Figure 9, $\gamma = 0$). This shows that different sample molding conditions (including different cooling rates after molding) can change the rate of recrystallization.

Fiber Molding above T_m. The purpose of this experiment is to (i) examine the effect of molecular orientation, which already exists prior to melting, on the rate of recrystallization and (ii), on the basis of the present knowledge of this phenomenon, develop a new processing technique for LCPs in order to get better mechanical and thermal performances for these materials.

After preheating to 320 °C, LCP fibers were drawn in the supercooled molten state to get a high degree of molecular orientation. Then the solidified fibers were cut to the length of 6 cm and unidirectionally aligned in a mold 1 cm wide. As soon as the mold was directly heated to 290 °C, a compression force of 1000 kg was applied and held there until the mold was cooled to room temperature. The fiber-molded specimen retains the fiber texture. The WAXS pattern shows a high degree of molecular orientation and an additional equatorial reflection at $d = 3.8$ Å. The DSC first heating curve of the sample (Figure 10) shows two separated melting peaks at 285 and 305 °C. These observations indicate that the high degree of molecular orientation in the LCP fibers results in a rapid recrystallization during a short time of molding at 290 °C. The rapid recrystallization in turn prevents a relaxation of the molecular orientation of the LCP fibers. However, if the fibers were first heated to 320 °C for 1 min, then cooled to 290 °C, and molded under the same compression force, they do not recrystallize at 290 °C. Such a preheated fiber-molded specimen loses the fiber texture and shows a low degree of molecular orientation in the WAXS pattern. It has only a single melting peak at about 285 °C in the DSC first heating scan (Figure 10).

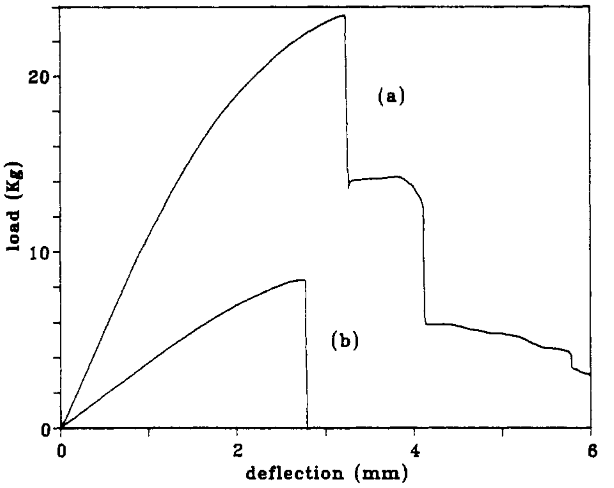

Figure 11. Stress growth curves of three-point bending, cross-head rate = 1 mm/min, distance between two supports = 42 mm. The samples have dimension of 60 × 10 × 3.4 mm^3. (a) Fiber molded at 290 °C without preheating; (b) fiber molded at 290 °C after preheating to 320 °C.

The mechanical properties of the fiber-molded specimens were tested by three-points bending with a distance between the two supports of 4.2 cm and a cross-head rate of 0.1 cm/min. Figure 11 shows the stress growth curves. The flexural strength and the flexural modulus of the preheated fiber-molded sample are 444 MPa and 17 GPa, respectively. These values are practically indistinguishable from the values of the specimens molded from randomly aligned and 320 °C preheated pellets. On the other hand, the unpreheated fiber-molded specimen displays a flexural strength of 1230 MPa and a flexural modulus of 50 GPa along the fiber axis, almost three times as high as the values of the preheated molded specimens. Futhermore, the unpreheated fiber-molded specimen shows progressive fracture (Figure 11), indicating that the fiber texture in the specimen hinders the propagation of failures. This result suggests that a rapid recrystallization is the key to high mechanical performance of the LCP through the fiber-molding technique.

Discussion

Structure and Formation of High-Melting Crystals. The previous experimental observations show that some kind of high-melting crystals form during high-temperature recrystallization. The melting temperature of the crystals increases with time until it reaches an upper limit of about 325 °C.[10] This upper limit of T_m coincides with the temperature range of the crystal–crystal phase transition of HBA homopolymer.[16] Furthermore, the high-melting crystals have a d spacing of 3.8 Å, which is identical with one of the characteristic d spacings of HBA homopolymer.[16,17] Worthy of note is that a random copolymer of 40 mol % poly(ethylene terephalate) and 60 mol % HBA displays the d spacing after a similar procedure of high-temperature recrystallization.[20] These observations suggest that some crystallites consist of sufficiently long HBA repeat sequences and the high degree of perfection of these crystallites is responsible for the increased melting temperature.

The aggregation of long HBA blocks does not seem to result from a possible transesterification in the present experiment, since the formation of high-melting crystals is thermally reversible. Both the high-melting peak and an additional reflection at $d = 3.8$ Å disappear after heating to 330 °C for a few seconds. Furthermore, the fiber-molded samples have similar meridional WAXS reflections as the samples in the absence of high-melting crystals, while it has been reported that the meridional WAXS profile would be a sensitive indicator of changes in monomer sequence distribution.[18,19] This suggests again that the monomer sequence distribution of the copolymer is not affected by high-temperature recrystallization.

Although the solid-state structure of random copoly(HBA/HNA) is not yet completely understood, two points seem to be generally accepted: (i) the copolymer crystals are aperiodic in the chain axis; (ii) the formation of the aperiodic crystals requires lateral matching in either sequence[6,7] or the register plane.[12-14] The present model of high-melting crystals is based on this physical picture. In a normal cooling process, fast cooling results in rapid crystallization, which does not allow the random sequences in adjacent chains to find the longest matching. Thus, formed aperiodic crystals shows "apparent" melting at the nominal T_m. At a temperature slightly above the nominal T_m, the nematic melt contains residual high-melting crystallites, which might consist of long HBA blocks (Figure 1). These residual crystallites act as nuclei, inducing crystallization only as the long HBA blocks in adjacent chains approach the crystallites. In the present study, where the random copolyester contains 73 mol % of HBA, statistical analysis supports the presence of long HBA blocks in the random chains. The volume fraction of long HBA blocks is small, but the interlocking of long HBA blocks has an effect of "physical cross-linking", which restricts the thermal motions of random blocks between the long HBA crystallites. This allows these random blocks to form aperiodic crystals at a temperature above the nominal T_m. As a consequence, the newly formed aperiodic crystals are locked between long HBA crystallties and do not melt until the long HBA crystallites melt.

It is well-known that a HBA homopolymer does not melt in the accessible temperature range, but the long HBA crystallites in a copolyester can melt due to the thermal disturbance of the chemically bonded copolymer chains. Economy et al.[16] have reported that the homopolymer of HBA has a crystal–crystal phase transition in the range 325–360 °C and suggested from dielectric measurement that above the transition the carboxyl groups have greater rotational freedom. In other words, the phase transition of HBA crystallites reduces restriction to molecular motions. In a HBA/HNA random copolymer, HBA crystallites in high-temperature form may no longer be strong enough to resist the thermal disturbance of the chemically bonded random chains. Therefore, the crystal–crystal phase transition of HBA crystallites results in the melting of long HBA crystallites themselves and the whole high-melting crystals. The upper limit of the melting temperature is the crystal–crystal phase transition temperature of HBA crystallites. DSC and WAXS results of our experiments and those reported by other researchers[4,6] support this model. Note that random chains that have no long HBA blocks locked into high-melting crystallites are not able to recrystallize at high temperatures but can crystallize when they are cooled below the nominal T_m. These later-formed aperiodic crystals always have a melting temperature identical with the nominal T_m (285 °C), as shown by the first melting peak in subsequent DSC analyses (Figures 3 and 10).

Effect of Residual Crystallites. Residual high-melting crystallites play a very important role in the nucleation of high-melting crystals. Residual crystallites might be melted by heating the sample temporarily to a higher temperature. Previous studies show that after preheating to T_p = 320 °C, the LCP melt displays almost constant dynamic moduli for several hours at a temperature just above the nominal T_m,[9,10] indicating that high-melting crystals cannot form in the absence of residual crystallites. Figure 4 shows that 295 °C is a material characteristic T_p, above which the rate of crystallization decreases dramatically. This indicates that most of the residual crystallites are starting to melt at 295 °C (Figure 1). It is important to point out that the characteristic T_p varies with the thermal history prior to melting. For instance, after solid-state annealing at 270 °C for 10 min, the LCP shows a characteristic T_p at 305 °C.[11] Besides raising the melting temperature of the residual crystallites, solid-state annealing increases also the volume fraction of high-melting crystallites. As shown in Figures 7 and 8, prior solid-state annealing increases the rate of high-temperature solidification. These observations imply that solid-state annealing leads to better ordered and larger high-melting crystallites.

In the supercooled molten state, the presence of residual crystallites not only leads to the formation of high-melting crystals (Figure 6) but also accelerates the crystallization. This is demonstrated by the rate of growth of the complex modulus: the supercooled melt at 275 °C attains 10 MPa in only 8 min (Figure 5), which is 30 times faster than the supercooled melt which had been preheated to 320 °C.[9] Preheating to 320 °C elminates residual crystallites and, hence, delays the recrystallization of the supercooled melt due to the lack of nuclei. The modulus starts to grow only after an initial nucleation stage.[9] The resulting aperiodic crystals have a relatively low melting temperature.

It is important to note that processing during faster crystallization retains a higher degree of flow-induced molecular orientation.[8,9] It can increase both mechanical properties and thermal resistance.

Effect of Molecular Mobility. The formation of high-melting crystals involves the matching of long HBA blocks to appropriate crystal growing locations. This requires large-amplitude translational motion. The required chain mobility is achieved at or above the nominal melting temperature T_m. One has to keep in mind, however, that T_m depends on thermal history.

In the solid state, the LCP chains are in a physically cross-linked state, which provides little probability for the formation of long HBA crystallites. Solid-state annealing can also raise the apparent melting temperature,[1,2] but it is essentially due to an increase in crystal size and takes much more time. For example, a sample of Vectra A900 was annealed at 270 °C, below the onset temperature of the nominal melting peak (Figure 3), to avoid "partial" melting. After 24 h, the sample shows apparent melting at 309 °C but does not show an additional WAXS reflection at d = 3.8 Å. This indicates that solid-state annealing does not form significant volume fraction of long HBA crystallites. Butzbach et al.[1] have reported the similar observations on a random copolymer containing 58% HBA and 42% HNA. Therefore, it can be concluded that "apparent" or at least "partial" melting is one of the necessary conditions for the formation of long HBA crystallite reinforced high-melting crystals.

As shown in Figures 7 and 8, the rate of crystallization at 290 °C does not increase monotonically with solid-state annealing temperature or time (T_a or t_a). This can be explained by the effect of molecular mobility. After annealing at high T_a or for long t_a, some aperiodic crystals do not melt at 290 °C due to increased size, as indicated by the relatively high values of the initial complex modulus (Figure 7 and 8). These unmolten crystals reduce the molecular mobility and also the probability of forming long HBA crystallites.

Effect of Molecular Orientation. The crystallization of the LCP involves some type of lateral matching. For rigid copolymer chains, lateral matching is essentially realized via relative longitudinal motion, which is hindered by the random polydomain structure. Flow-induced molecular orientation increases the molecular mobility (as expressed in a reduced viscosity) and facilitates molecular motion, therefore increasing the rate of crystallization. It is found that not only uniaxial molecular orientation but also equibiaxial molecular orientation[8,9] accelerate the crystallization.

When the LCP fibers are molded at 290 °C without preheating to an elevated temperature, the previously developed high degree of molecular orientation leads to a rapid crystallization, as shown by the second melting peak in later DSC analyses (Figure 10). The rapid crystallization has a cross-linking effect, which suppresses the relaxation of molecular orientation and, hence, maintains the fiber texture. However, if the fibers were first preheated to 320 °C, the melting of residual crystallites and the relaxation of molecular orientation prevent the formation of high-melting crystals.

Conclusions

After partial melting between 285 and 295 °C, the residual crystallites lead to the formation of high-melting crystals, increasing the thermal resistance of the LCP. The high-melting structure of r-HBA/HNA is proposed to consist of large HBA crystallites that reinforce the otherwise aperiodic crystals. The presence of residual crystallites and "apparent" or at least "partial" melting are two necessary conditions for the formation of high-melting crystals. Molecular orientation further accelerates the crystallization.

Accelerated crystallization helps to retain processing-induced molecular orientation. Possible applications are blow molding or film blowing in the supercooled state after preheating the Vectra A900 between 285 and 295 °C. The recrystallization behavior also suggests a new process, which we call "fiber molding". Similar to glass fiber reinforced composites, the fiber-molding technique allows one to make multiaxially oriented samples (films, 3-D objects) with enhanced mechanical properties. Molecular orientation is retained in the fibers, which are melted together at temperatures between 285 and 295 °C and then recrystallized into their high-melting form.

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