p-Hydroxybenzoate/ethylene terephthalate copolyester: structure of high-melting crystals formed during partially molten state annealing

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A liquid crystalline poly(ethylene terephthalate)/4-hydroxybenzoic acid (PET/HBA) copolyester forms high-melting crystals (recrystallizes) when annealed in the partially molten state above its nominal melting temperature (d.s.c. peak). The dynamic mechanical moduli increase by one order of magnitude within 3 h. The new melting temperature appears ~20 K above the recrystallization temperature. An additional equatorial WAXS reflection appears at $d \sim 3.77$ Å and is typical for a HBA-rich ordered phase. During recrystallization, the long HBA sequences in the copolymer chains are believed to match the unmolten highly ordered HBA crystallites which act as nuclei, and thus, crystal growting is induced. Partial melting provides for the presence of residual highly ordered crystallites and molecular mobility and is a necessary condition for the formation of high-melting crystals. If residual crystallites are eliminated by preheating to a higher temperature, isothermal annealing at the same temperature does not lead to recrystallization. The formation of the high-melting crystals can be thermally reversed by temporarily heating the samples to 300°C for ~1 min. This suggests that the observed phenomena are of a physical nature, and if chemical changes did occur, they had no noticeable effect on rheology, WAXS or d.s.c.

(Keywords: liquid crystal polymer; copolyester; recrystallization)

INTRODUCTION

Thermotropic liquid crystalline polymers (TLCPs) with 4-hydroxybenzoic acid (HBA) as a major component seem to have many properties in common that need to be explored. Windle *et al.*[1,2] and Biswas and Blackwell[3–5] have reported that the solid-state structure of the copolymers of HBA and 6-hydroxy-2-naphthoic acid (HNA) has some three-dimensional order which is aperiodic in the direction of the chain axis. HBA and HNA units are able to cocrystallize into a single crystallite. Butzbach *et al.*[6] have observed that solid-state annealing of a polymer containing the same comonomers increases the size of these crystals which results in the sharpening of X-ray reflections and the increase of the d.s.c. melting temperature. Lin and Winter[7–9] have proposed from their study of a random copolymer containing 73% HBA and 27% HNA that partially molten state annealing leads to the formation of highly pure HBA crystallites which reinforce the HBA/HNA copolymer crystals and raise the melting temperature by 30–40 K. This structure could explain the observation of an additional equatorial X-ray reflection at $d \sim 3.8$ Å and the coincidence of the new melting temperature with the crystal/crystal transition temperature of pure poly(HBA). Residual high-melting crystallites and molecular mobility are necessary for the recrystallization process[9].

The universality of this phenomenon in the family of TLCPs containing HBA remains to be examined. For this reason, a random copolyester containing 40 mol% poly(ethylene terephthalate) and 60 mol% HBA (designated PET/60HBA) was selected to be investigated. Morphologically, PET/60HBA is very different from the HBA/HNA copolymer, since PET/60HBA is microphase-separated into dispersed PET-rich domains and a continuous HBA-rich matrix in both the solid and molten states[10–13]. In the HBA-rich phase, PET units cannot cocrystallize with HBA units but give rise to defects in the solid structure[14] and, hence, lower the melting temperature. Present work demonstrates that a fraction of HBA sequences can recrystallize into a more perfect solid structure of higher melting temperature during partially molten state annealing.

EXPERIMENTAL

Materials and sample preparation

The liquid crystalline polymer LCP3000 (Rodrun), supplied by the UNITIKA corporation, is a random copolymer containing 40 mol% PET and 60 mol% HBA (PET/60HBA). Its nominal melting temperature (peak temperature) of the d.s.c. heating scan at 20 K min^{-1} is ~200°C.

The received polymer pellets were dried under vacuum at 70°C for 20 h, moulded at 300°C into discs ($d = 25$ mm, $h = 1$ mm), and then quickly cooled to room temperature under blowing air.

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Apparatus

Rheological measurements were performed on a Rheometrics dynamic spectrometer (RDS-7700) using parallel plates. D.s.c. was carried out on a Perkin-Elmer calorimeter (DSC-4) at a heating rate of 20 K min^{-1}. WAXS pictures were taken at room temperature using Cu Kα radiation and a Ni-filtered statton camera with a sample to film distance of 53 mm.

RESULTS

Melting transitions

Melting of the two-phase morphology results in a notable decay in the dynamic mechanical moduli G' and G'' as measured in a temperature sweep experiment (*Figure 1*). The continuous phase, which consists of HBA-rich sequences, melts over a broad temperature range (175–265°C). The dispersed phase, rich in PET, exhibits a relatively narrow melting transition (between 230°C and 250°C) as shown by an accelerated modulus reduction. Above 265°C, G' and G'' level off to a plateau, indicating that the melting process is practically completed. The phase transitions are very similar to the ones of other PET/HBA copolymers of an earlier study[10].

Partially molten state annealing

Recrystallization was observed by placing a sample between the plates of the rheometer, heating it rapidly to the desired temperature (245, 250 or 255°C), holding the temperature for isothermal annealing, and measuring the dynamic moduli as they gradually increase with annealing time (*Figure 2*). In particular, G' increased by one order of magnitude within 3 h. In comparison, isothermal annealing in a completely molten state, i.e. above 265°C, does not result in any significant modulus growth within 3 h. This compares well with the recent study by Kalika *et al.* on a 20PET/80HBA copolyester[15].

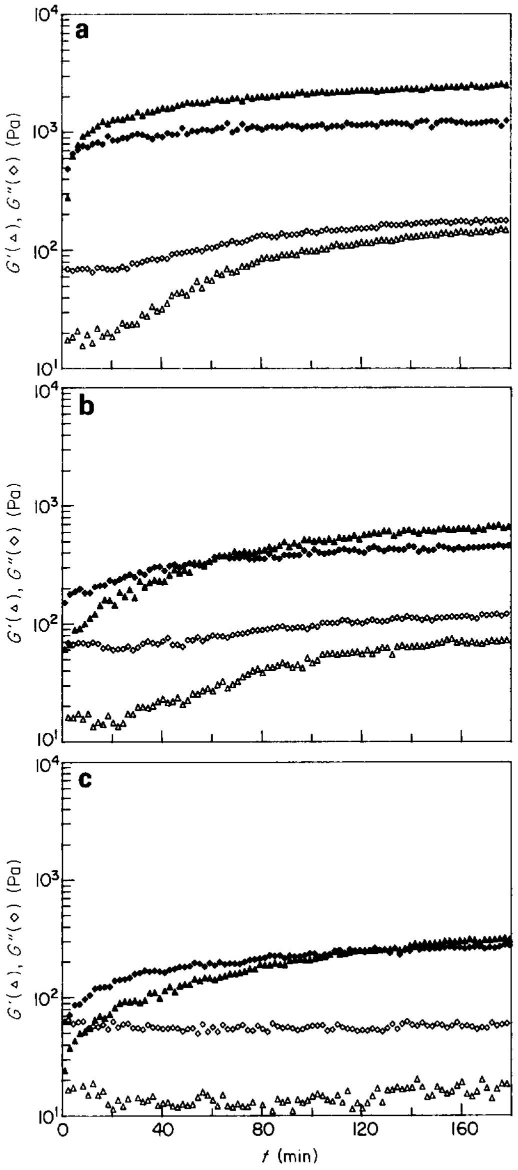

Figure 2 Modulus growth during isothermal annealing at (a) 245°C, (b) 250°C and (c) 255°C measured at 1 rad s^{-1}. Solid symbols represent samples that were not subjected to preheating and open symbols represent samples that were preheated to 300°C

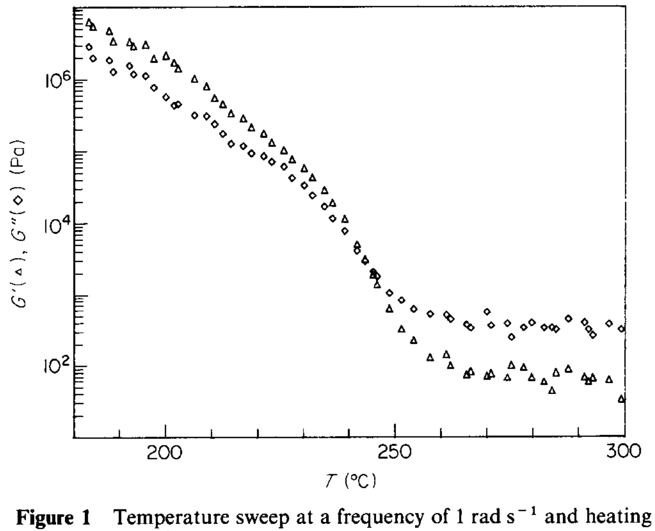

Figure 1 Temperature sweep at a frequency of 1 rad s^{-1} and heating rate of 5 K min^{-1}. Strain amplitude was limited to the linear viscoelastic region

Effect of high-temperature preheating

A sample which was first preheated to 300°C before annealing at 245, 250 or 255°C did not recrystallize (as shown by the open symbols in *Figure 2*). Initially, the preheated sample displays G' and G'' at the levels of the high-temperature modulus plateau. Then the moduli recover gradually to the level coinciding with the annealing temperature but do not show significant growth.

Melting transition of the recrystallized fraction

A temperature sweep experiment was conducted on a sample that had been partially molten state annealed at 245°C for 3 h (*Figure 3*). It is observed that the recrystallized fraction melts ~15 K above the recrystallization temperature. A comparison to the melting curve of a freshly moulded sample indicates that partially molten state annealing does not result in a shift of the entire melting curve but rather results in the appearance of a shoulder near the recrystallization temperature. At temperatures between 200°C and the annealing temperature, the dynamic moduli of the recrystallized sample are slightly lower than that of a fresh sample. However, below

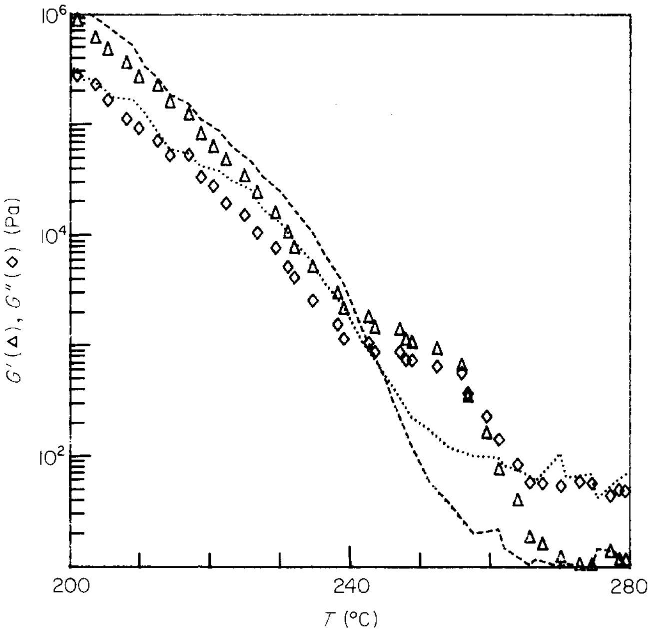

Figure 3 Temperature sweep of a sample annealed at 245°C for 3 h, with a frequency of 1 rad s^{-1} and a heating rate of 5 K min^{-1}. Broken lines indicate the moduli shown in *Figure 1* for a freshly moulded sample

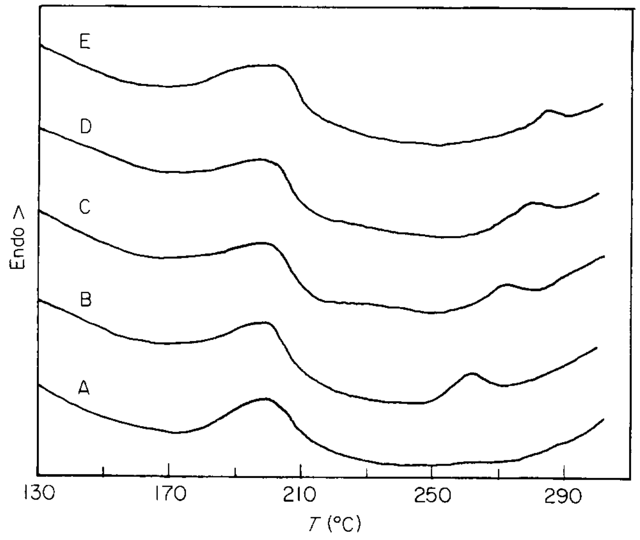

Figure 4 D.s.c. first heating scan at 20 K min^{-1} for the samples (A) freshly moulded, or after partially molten state annealing for 3 h at (b) 245°C, (C) 250°C, (D) 255°C, (E) 260°C. The second endotherm occurs at ~20 K above the annealing temperature

200°C the moduli of the recrystallized and fresh sample coincide. In d.s.c. analysis (*Figure 4*), a freshly moulded sample melts with only a single endothermic peak at ~200°C in the heating scan. By recrystallization for 3 h, samples gain a second endothermic peak at ~20 K above the recrystallization temperature. This second peak decreases in amplitude as the recrystallization temperature increases. The structural ordering is thermally reversible. This is evidenced by the fact that the second d.s.c. heating scan of recrystallized samples no longer shows the high melting peak, but only a single peak at 200°C as is observed in a freshly moulded sample.

It should be noted that the melting temperature of the recrystallized fraction is also time dependent. Dynamic mechanical measurements show that the sample recrystallized at 240 or 245°C for 3 h melts 15 K above the recrystallization temperature (*Figures 3* and *5*), but when recrystallized at 260°C for 1.5 h, the sample melts only 5 K above the recrystallization temperature (*Figure 5*). However, after the initial 3 h, the melting temperature of the recrystallized fraction increases quite slowly.

WAXS

Freshly moulded samples and the samples that have been annealed after preheating to 300°C, display five X-ray reflection rings at $d \sim 2.09$, 3.16, 3.45, 4.5 and 5.03 Å. After recrystallization in the partially molten state, the annealed samples display six X-ray reflections at $d \sim 2.09$, 3.16, 3.45, 3.77, 4.5 and 5.03 Å. WAXS analysis on a molecularly oriented sample that had been subjected to the same annealing procedure shows that $d \sim 3.77$ Å is an equatorial reflection.

DISCUSSION

The sample melts over a very broad temperature range, with a d.s.c. endotherm having its maximum at ~200°C and with the dynamic moduli dropping most severely at temperatures between 175°C and 265°C. HBA and PET seem to (crystallize and) melt separately[10,14]. This is suggested by the simple superposition of the WAXS patterns in which, compared to literature data[13,14], the reflections at $d \sim 2.09$, 3.16 and 4.5 Å result from the ordered region rich in HBA, while the reflections at $d \sim 3.45$ and 5.03 Å result from the ordered region rich in PET. The upper limit of the melting temperature of the ordered PET-rich region where some HBA units are present as defects[14] is given by the melting temperature of PET homopolymer ($T_m = 255°C$)[13].

Significant growth in the dynamic moduli during isothermal annealing and the appearance of a second d.s.c. endothermic peak at ~20 K above the annealing temperature indicates a recrystallization process. Since the recrystallized crystals melt above the T_m of PET homopolymer, it can be deduced that the formation of high-melting crystals results from the ordering of HBA sequences in the continuous HBA-rich phase. Further evidence for this deduction is the fact that the additional X-ray reflection at $d = 3.77$ Å matches one of the characteristic d-spacings of poly(HBA) low-temperature

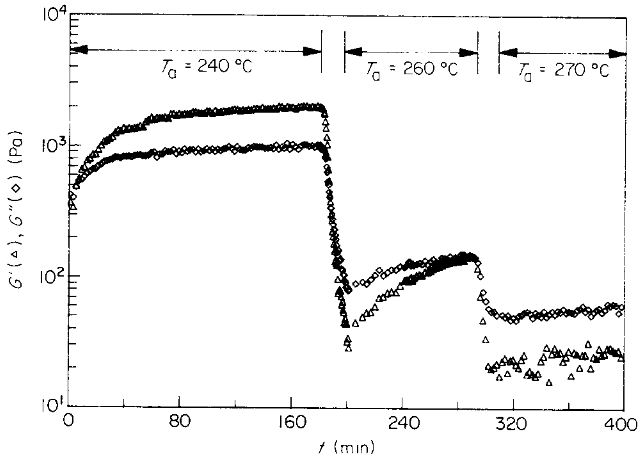

Figure 5 Moduli evolution of a sample that was partially molten state annealed at 240°C for 3 h, heated for annealing at 260°C for 1.5 h and heated for annealing at 270°C for 1.5 h

form crystallites[14]. The ordering of the HBA-rich phase involves lateral matching of HBA sequences in the adjacent copolymer chains. In a normal cooling process from the molten state, the short solidification time does not allow the copolymer chains to reach the longest match length. PET units that are present as defects in the ordered region decrease the structural order and prevent the HBA sequences from arranging into the relatively compact low-temperature form structure[14].

However, there is a distribution in the HBA match length or in the size of crystallites as shown by the broad temperature range of the melting transition (*Figure 1*). When the polymer is heated to a partially molten state, the ordered regions of long match length do not melt. These unmolten regions are assumed to act as nuclei during annealing and only long HBA sequences in the adjacent copolymer chains can match the local order to crystallize. The increased match length in the newly formed crystals enables the ordered HBA sequences to arrange into their more compact 'low-temperature form' which is responsible for the high-melting endothermic peak (*Figure 3*) and the X-ray reflection at $d \sim 3.77$ Å (*Figure 4B*). However, the fraction of HBA sequences that can recrystallize into the compact low-temperature form is small. This is shown by the fact that the appearance of the high-melting endothermic peak, which is small in comparison to the first melting peak, does not significantly change the amplitude or temperature of the first melting peak. The match length required for crystal growing depends on the annealing temperature. This is evidenced by the fact that the melting temperature of the newly formed crystals increases with recrystallization temperature (*Figure 3*). On the other hand, as the recrystallization temperature increases, the fraction of HBA sequences that are long enough to recrystallize decreases. This explains why the area of the second d.s.c. endothermic peak decreases with recrystallization temperature.

The recrystallization is thought to be due to a physical change rather than a chemical reaction. There are three observations in support of this model. First, the observation that isothermal annealing above 265°C does not lead to modulus growth suggests the presence of a physical change since if it were due to a chemical change, the moduli would grow faster as the annealing temperature increases. Second, thermal reversibility is shown by both d.s.c. analysis and dynamic mechanical measurements. After temporarily heating the high melting structure to 300°C, the second endothermic peak in the d.s.c. heating scan vanished, and the dynamic moduli G' and G'' are brought back to their initial value. Third, WAXS analysis shows no change in *d*-spacings except for the formation of a new ring. If chemical changes were involved, one would expect a difference in *d*-spacings.

Preheating experiments show that partial melting, which provides for the presence of residual crystallites that consist of long HBA sequences, is a necessary condition for recrystallization. Preheating to a high temperature results in the elimination of the residual high-melting crystallites[7–9], and thus, high-melting crystals cannot form due to the lack of nuclei[9]. This is responsible for the rather stable rheological behaviour of the preheated samples which exhibit moduli that show no growth but gradually recover from the high-temperature modulus plateau to the level corresponding to the annealing temperature. When comparing with the results from partially molten state annealing at the same temperatures, one can see the great destabilizing effect of residual crystallites on the LCP rheology.

Partial melting also provides a high molecular mobility which is necessary since the lateral matching of long HBA sequences requires a relatively large amplitude of the motion between the adjacent chains. In the solid state, the polymer chains are interlocked by the crystallites. The extremely low molecular mobility excludes the possibility for the lateral matching of long HBA sequences and, hence, also the possibility for recrystallization. As a matter of fact, the experiments in this study show that isothermal annealing below 170°C leads only to the sharpening of the X-ray reflections at $d \sim 2.09$, 3.16, 3.45, 4.5 and 5.03 Å, and not to the appearance of the X-ray reflection at $d \sim 3.77$ Å.

As compared with Vectra A900, a random copolymer containing 73% HBA and 27% HNA, LCP3000 displays much smaller changes in physical properties resulting from recrystallization in the partially molten state. This is most likely due to the fact that the PET sequences are unable to cocrystallize with HBA units but are always present as defects in the HBA-rich crystalline regions. This also explains the observation that recrystallization only gives rise to a shoulder (*Figure 3*) rather than to an overall shift in the melting transition zone.

CONCLUSIONS

Annealing in the partially molten state results in the formation of HBA 'low-temperature form' crystallites. This is shown to be a common phenomenon in the family of thermotropic copolyesters containing HBA as a major component. In this recrystallization process, sufficiently long HBA sequences match into highly ordered regions of high melting temperature. Partial melting for the presence of residual crystallites and molecular mobility is necessary for the formation of high-melting crystals[9]. Several different experiments suggest that the observed phenomenon is of a physical nature, unrelated to transesterification chemistry. The understanding of this solid-state structure and phase transition behaviour is needed for processing LCPs at low temperatures and for finding ways to increase their thermal resistance through thermal treatment.

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