The Nature of the Thermal Transitions in Poly(*p*-oxybenzoate)

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ABSTRACT: The high-temperature transition at 340 °C for the homopolymer of *p*-hydroxybenzoic acid (PHBA) has been shown to display characteristics typical of a plastic crystal or a highly ordered smectic phase transition. For low molecular weight samples of the homopolymer a nematic texture can be induced above this phase transition by modest external shear. However, for high molecular weight samples the material is intractable in this temperature regime. A much higher transition at 445 °C has been identified and characterized by DSC, TMA, and polarized light microscopy, indicating the presence of a nematic mesophase. Processing of the homopolymer above this transition results in fusion of the material.

Introduction

This paper is concerned with elucidating the nature of the reversible, high-temperature transition observed in poly(*p*-hydroxybenzoic acid) (PHBA). This transition which occurs at about 340 °C has already been characterized in some depth by differential thermal analysis, high-temperature X-ray diffraction, thermal expansion coefficient determination, dielectric constant measurements, and electron diffraction.[1,2] From these results it is clear that there is significant loss in order above the transition and possibly some increase in molecular motions. On the other hand, the polymer could only be fabricated by compression sintering well above this transition at a temperature in excess of 400 °C. Also, high-energy rate forging of sintered specimens preheated to 300 °C has been shown to yield fused specimens with a high degree of orientation in the plane.[3] From these observations it has not been possible to characterize definitely whether the transition is a crystal–crystal transition (topotactic), a liquid–crystal transition, or even a plastic–crystal transition.[1]

Clearly, it is important to understand the nature of this transition, since the homopolymer is available as a commercial material under the tradename of Ekonol.[3] Furthermore, the monomer of PHBA is a major constituent in several liquid-crystalline aromatic copolyesters which are available either commercially or in developmental quantities.[4–6] The melting characteristics of these copolymers are determined by several factors including the melting points of the respective homopolymers, sequence distribution (blockiness), and ease with which the rodlike units can pack. Of concern is the fact that the melting point of the 2/1 copolymer of PHBA with biphenol terephthalate (BPT) is 421 °C, which is much higher than the 340 °C transition of the homopolymer.[7] Hence, this study was directed not only at elucidating the nature of the PHBA transition at 340 °C but also at examining the possible existence of a much higher transition for the homopolymer that is more consistent with the melting behavior of the PHBA/BPT = 2/1 copolymer. In fact, there was a report in the literature by Jackson suggesting a higher melting transition above 600 °C for the homopolymer.[8]

Preparing and evaluating the thermal behavior of a series of lower molecular weight homopolymer samples made it possible to arrive at a clearer picture of the reversible transition at 340 °C. Additional insight into the nature of the transition was made possible by examining the thermal behavior of single-crystal samples of the homopolymer and characterizing possible morphological changes by cycling samples through this transition. Finally, by use of very rapid heating rates in DSC experiments and by optical microscopy it was possible to identify a new and previously unreported nematic transition at 445 °C which appears to be consistent with the ability to fuse the polymer by forging and also with the melting behavior of the copolyesters.

Experimental Section

***p*-Acetoxybenzoic Acid Dimer and Tetramer.** The above compounds were prepared according to the procedures reported by Fischer[10] and Fischer and Freudenberg.[11] However, the synthesis was slightly modified by incorporating *p*-acetoxybenzoic acid into one of the reaction steps, enabling the coupling reaction of *p*-acetoxybenzoyl chloride with *p*-hydroxybenzoic acid and *p*-acetoxy(*p*-benzoyloxy)benzoyl chloride with *p*-hydroxy(*p*-benzoyloxy)benzoic acid to yield the dimer and tetramer, respectively.

Preparation of Poly(*p*-hydroxybenzoic acid). PHBA oligomers and polymers were prepared in similar fashion by simply varying the polymerization temperature. In a typical preparation, *p*-acetoxybenzoic acid was suspended in Therminol 66 in a ratio of 1/4 (wt/vol) in a flask equipped with a mechanical stirrer and an inlet and outlet for nitrogen. The polymerization was performed in a Wood's Alloy metal bath which was maintained at ±2 °C throughout the course of the polymerization. In all cases, polymerization time at a specific temperature was fixed at 20 h, after which the product was separated by suction filtration, Soxhlet extracted for 16 h with acetone, and vacuum dried at 100 °C for 24 h.

Thermal Analysis. Differential scanning calorimetry curves were obtained on a Perkin-Elmer DSC-2 equipped with a 3600 data station. Samples weighing from 3 to 20 mg were heated under nitrogen at rates ranging from 5 to 320 °C/min. Temperature calibration over the entire range of heating rates was obtained by using the melting point of zinc. Samples were weighed before and after each run to determine the extent of decomposition as evidenced by excessive weight loss (> 5 wt %). All temperatures cited are peak temperatuires. Thermomechanical analysis was performed on a Du Pont 943 TMA coupled with a 1090 controller using a 1.1-mm-diameter flat probe on prefused samples of approximately 2 mm thickness.

Molecular Weight Analysis. In general, 0.50 g of the homopolymer was refluxed in 5 mL of concentrated aqueous KOH ($\simeq$ 50 wt %) until the solution turned clear; reflux was then continued for another 3 h, and the cooled solution was acidified with 6 mL of concentrated H_3PO_4. A final dilution to 50 mL with deionized water provided the stock solution.

Stock solutions were analyzed with respect to acetic acid by employing a Varian Aerograph Series 1800 gas chromatograph with FID in conjunction with a Porapak Q (80–100 mesh)$^1/_4$-in. glass column conditioned with H_3PO_4 at 200 °C for several days. Thus, 5-μL samples were injected with an injector temperature of 220 °C, a column temperature of 200 °C, a detector temperature of 225 °C, and a helium flow rate of 30 cm^3/min. Propionic acid (250 ppm) was used as an internal standard. Assuming one acetoxy end group per chain, number average molecular weights were then calculated according to the following formula:

$$\bar{M}_n = \frac{(60 \times 10^6)(\text{g of polymer})}{(\text{ppm AcOH})(\text{mL of stock soln})}$$

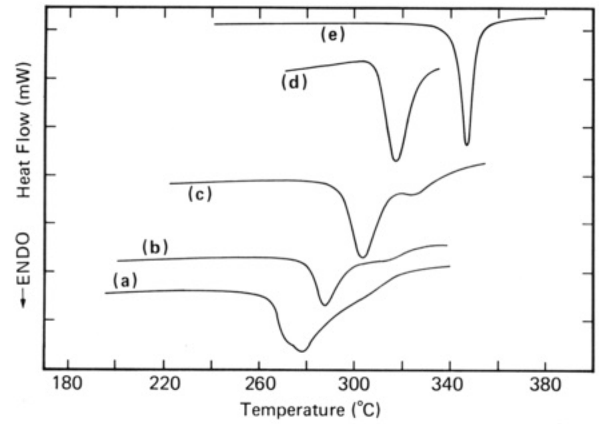

Figure 1. DSC thermograms at 10 °C/min of the homopolymer of PHBA as a function of molecular weight: (a) $\overline{DP} = 13$, (b) $\overline{DP} = 15$, (c) $\overline{DP} = 28$, (d) $\overline{DP} = 92$, (e) $\overline{DP} > 100$.

Table I
Transition Enthalpies and Entropies of PHBA as a Function of Increasing Molecular Weight

material	$\overline{DP}$	T_x, K	ΔH^a	ΔS^b
dimer		503	2530	5.03
tetramer		535	2300	4.31
polymer 200	13	551	1520	2.75
polymer 250	29	576	1180	2.04
polymer 300	92	591	1000	1.69
polymer 350	>166	621	1250	2.02

[a] cal/mol, oxybenzoyl unit. [b] cal/(K·mol), oxybenzoyl unit.

Electron Diffraction Analysis. TEM samples were prepared by impact fracturing the specimens at liquid nitrogen temperatures, ultrasonically dispersing the fragments in alcohol, and collecting them on carbon-coated grids. Small area electron diffraction was obtained by using a Philips 301 S(TEM) operating in the condenser/objective mode.

Transmitted Polarized Light Microscopy. Specimens were observed microscopically as a function of temperature, using a Zeiss (Jena) Amplival polarizing microscope and a Linkam THM600 hot stage and PR600 controller. Specimens were held between thin microscope cover slips, which have a small thermal mass compared to that of the hot stage. To minimize in situ specimen polymerization, the hot stage was preheated to the desired temperature, before the specimen was placed on it. Textures characteristic of a given temperature were water-quenched to room temperature, to allow microscopy with high-resolution objectives that necessarily provide only a short working distance. All micrographs shown below were obtained at room temperature. The preservation of textures in similar materials by quenching has been demonstrated previously.[12]

Specimens that did not flow spontaneously when heated to above their transition temperatures were subjected to shear by pressing on the upper cover slip with a dissecting needle. The sequence of heating, shearing, and quenching a specimen was always accomplished in under 15 s.

Results and Discussion

Nature of the Transition at 340 °C. The earlier confusion as to the nature of this transition was somewhat clarified from an examination of the high-temperature behavior of the low $\bar{M}_n$ samples of PHBA. Thus, as shown in Figure 1, all of the specimens showed an endotherm which tended to occur at higher temperatures with increasing $\bar{M}_n$, as reported earlier.[9,13] Calculation of the transition enthalpies for these endotherms (see Table I) showed that all of the values were very similar, although the dimer and tetramer were significantly higher. More significantly, several lower $\bar{M}_n$ polymers with $\overline{DP}$ of 15, 27, and 39 which were examined under a polarizing microscope tended to flow under modest shear above their transition and displayed a well-defined nematic texture containing disclinations of $\pm^1/_2$ and ± 1 (Figure 2a). After several minutes, these samples tended to solidify due to further polymerization, freezing the existing nematic texture. The courseness of the nematic texture was dependent on molecular weight with the sample of $\overline{DP} = 15$ exhibiting a coarse texture and the sample of $\overline{DP} = 39$ showing a much finer texture (Figure 2b). The higher molecular weight samples did not show any tendency to flow above this transition even when placed under somewhat higher localized shear.

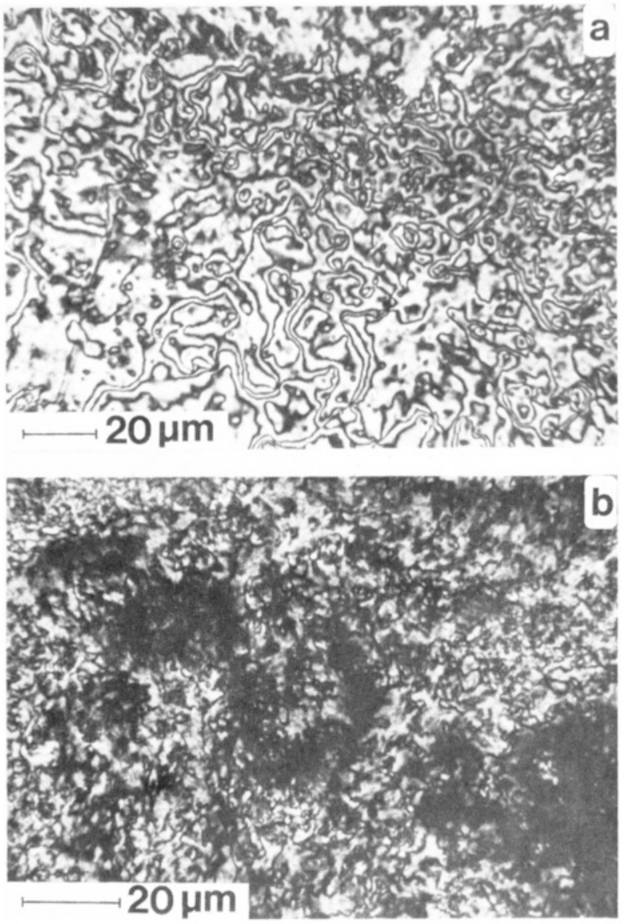

Figure 2. Nematic texture induced by moderate external shear in lower $\bar{M}_n$ samples: (a) $\overline{DP} = 15$, specimen quenched from 300 °C; (b) $\overline{DP} = 39$, specimen quenched from 330 °C. Polarizer and analyzer orientations were E-W and N-S, respectively.

To further characterize the nature of the high-temperature phase, an attempt was made to examine samples with electron diffraction techniques at temperatures slightly in excess of 340 °C. This study was complicated by the inability to accurately measure the temperature of the heated sample during the electron diffraction study since the temperature probe is not in direct contact with the heated sample. Presumably, the sample is at least 10–20 °C below the measured temperature. With single crystals of the high $\bar{M}_n$ polymer, it was possible to obtain an electron diffraction pattern of the high-temperature phase at an apparent temperature of 375 °C (see Figure 3). The fact that a number of the diffraction maxima retain the sharp definition of the room temperature pattern combined with the streaking of the 006 line suggests both vertical and horizontal displacement of the chains. The horizontal displacement probably is sufficient to permit free rotation of the phenylene units, while the vertical displacement still permits three-dimensional order through interchain dipole interactions. The absence of the 200 reflection in the high-temperature form is consistent with

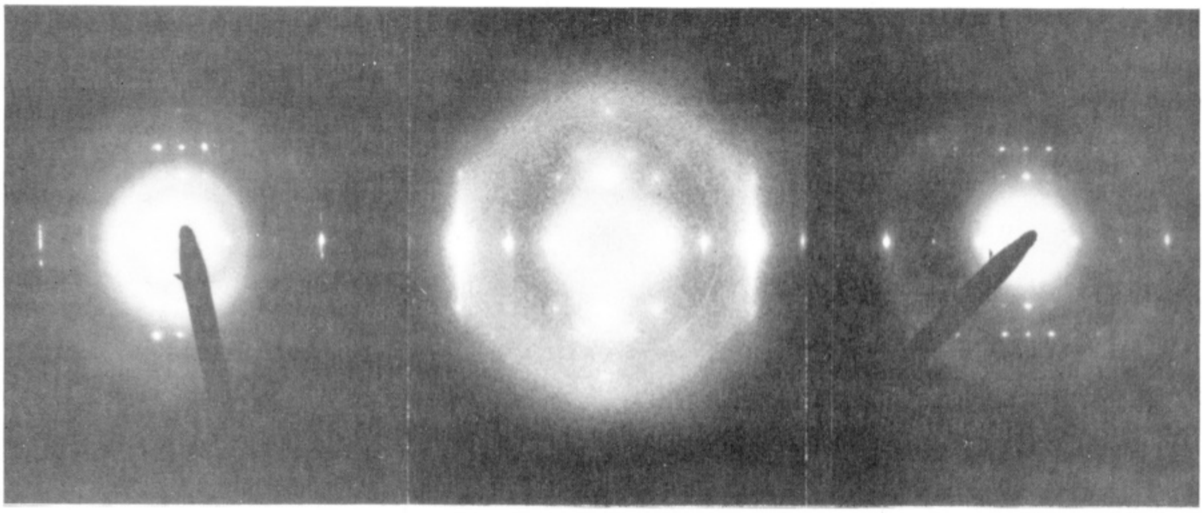

Figure 3. Electron diffraction pattern of PHBA sample ($\bar{DP} > 100$), *c*-axis diffraction.

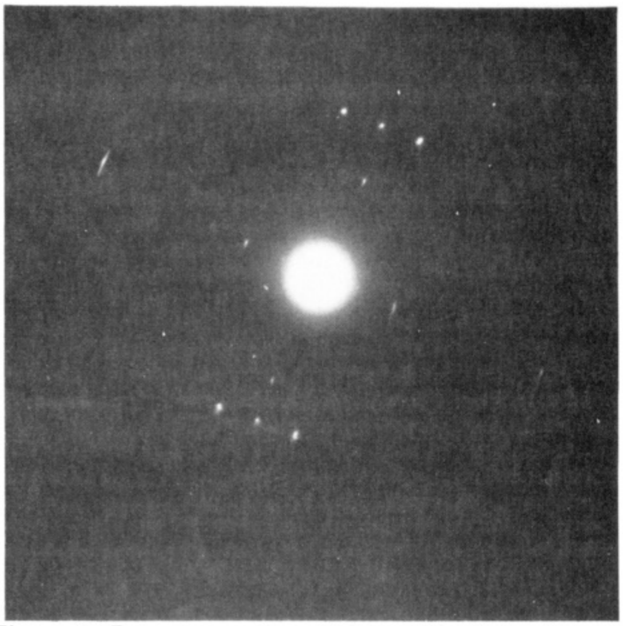

Figure 4. Room temperature electron diffraction pattern of PHBA sample ($\bar{DP} = 15$) heated to 300 °C and rapidly air cooled.

the pseudohexagonal phase suggested by Lieser.[14] The fact that the *d* values along the *c*-axis are unchanged and that many of the diffraction maxima are identical with the low-temperature phase argues for a three-dimensional packing closely related to the orthorhombic phase.[15]

Additional insights into the nature of the ordering in the high-temperature phase were obtained by heating single-crystal specimens of various molecular weights to just above the transition in the DSC, cooling and reexamining the specimens by electron diffraction.[2] It was found that with the high molecular weight samples a well-defined single-crystal pattern identical with that of the starting material was obtained, indicating that the high-temperature phase reverted to a three-dimensional, single-crystal structure (see Figure 3). The low $\bar{M}_n$ sample, which tended to flow under applied stress above its characteristic transition, was also examined in the same manner by heating to just above the transition, followed by rapid air cooling. A single-crystal pattern could be observed at room temperature by electron diffraction analysis (see Figure 4). Since the possibility exists for a slow, time-dependent diffusion process above the transition, the low $\bar{M}_n$ sample was heated for 100 min at a temperature just above the original transition and then rapidly air cooled. Again, a single-crystal pattern could be identified (see Figure 5), although one could justifiably argue that the sample increased in molecular weight and solidified within a few minutes. One can therefore conclude from this latter experiment that polymerization proceeds within the crystalline phase without disrupting the three-dimensional crystal morphology. There are some differences between Figure 4 and Figure 5 (the 200 spot is absent in Figure 5). This can be interpreted either as a quenched pseudohexagonal phase or more likely that this diffraction pattern

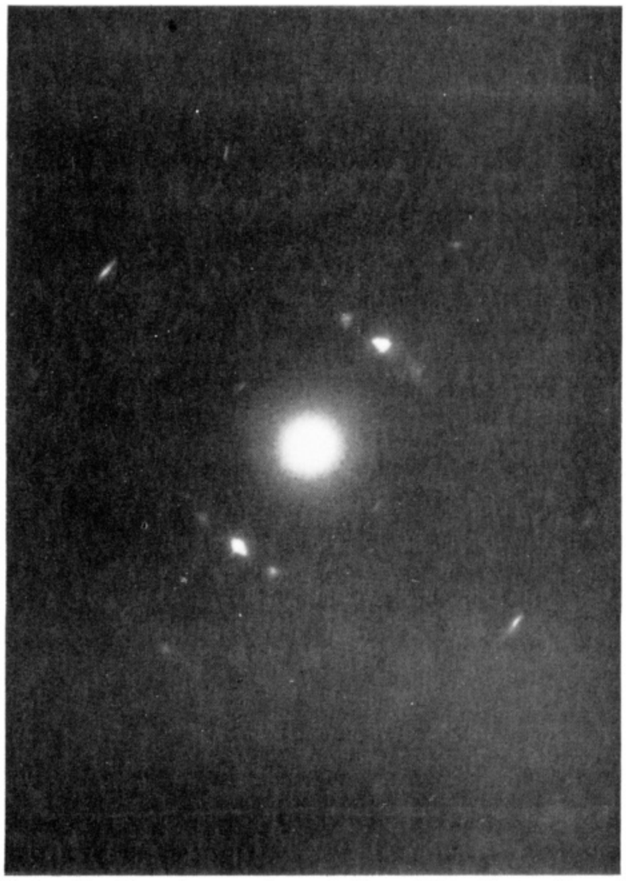

Figure 5. Room temperature electron diffraction pattern of PHBA sample ($\bar{DP} = 15$) heated to 310 °C, held for 100 min at 310 °C, and rapidly air cooled.

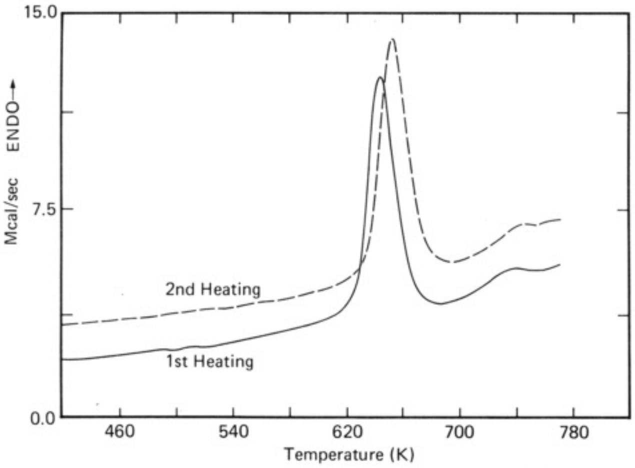

Figure 6. DSC thermogram of the homopolymer ($\bar{D}\bar{P} > 100$). Sample weight = 3.54 mg, scan rate = 320 °C/min, $T_1 = 370$ °C, $\Delta H_1 = 11.4$ cal/g, $T_2 = 461$ °C, $\Delta H_2 = 0.70$ cal/g.

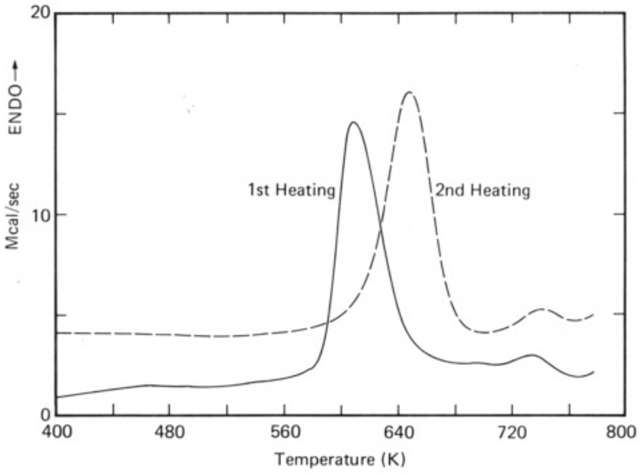

Figure 7. DSC thermogram of the homopolymer ($\bar{D}\bar{P} = 15$). Sample weight = 20.7 mg, scan rate = 160 °C/min $T_1 = 374$ °C, $\Delta H_1 = 9.0$ cal/g, $T_2 = 460$ °C, $\Delta H_2 = 0.50$ cal/g.

was taken at a different orientation of the observed crystal.

Interpreting the data on the low $\bar{M}_n$ samples is complicated by two seemingly contradictory observations: the low $\bar{M}_n$ polymer just above the transition can display a well-defined nematic texture when sheared under the polarizing microscope, and the same material in the absence of shear undergoes a reversible transition from a single crystal and back to the same single-crystal structure. Presumably, the reversible transition is accompanied by a change in packing of the chain, but the chain-to-chain registration and the external crystal habit are retained. Since a significant increase in thermal expansion coefficient accompanies the transition, it is reasonable to anticipate some freedom for localized molecular motion. The formation of a nematic phase observed as a result of shear requires that sufficient force be applied to overcome the dipolar interactions between chains. With the low molecular weight material ($\bar{D}\bar{P} = 15$) there are on the average only 15 ester units contributing to the stabilization of the structure and the applied shear is sufficient to overcome these dipolar interactions. The shear sensitivity is undoubtedly facilitated by the presence of lower molecular weight species. As the molecular weight increases and the preence of the oligomeric species becomes insignificant, the shearing process becomes increasingly difficult in direct relation with the increasing number of dipolar interactions until finally the polymer becomes intractable.

Evidence for the Existence of a Higher Temperature Transition in PHBA. The various techniques reported earlier for processing the homopolymer[3] such as compression sintering (400 °C), plasma spraying, and high-energy rate forging (HERF), suggest the possibility of a higher transition temperature where significant flow might occur. Since the high-energy rate forging generates a very large kinetic energy in a very short time cycle (used to form tungsten or titanium), it could very well be that a melting transition was masked by the decomposition of the polymer. Consequently, DSC experiments were carried out at an extremely fast heating rate of 320 °C/min, and indeed it was found that an endotherm could be detected at a temperature of 461 °C. This transition was reversible and on reheating appeared with the same intensity and at approximately the same temperature (see Figure 6). Using slower heating rates of 80, 40, or even 20 °C/min, one could still observe this transition but at a lower temperature of 445 °C. The high temperature of 461 °C is due to the thermal conductivity lag associated with the extremely rapid heating at 320 °C/min. Samples with $\bar{M}_n$ values of 1200 also showed this second endotherm but at a temperature at least 10–20 °C lower. On a second reheat of the low $\bar{M}_n$ samples, the endotherm shifted to the higher temperature of 460 °C, indicating that significant polymerization had occurred during the first heating (see Figure 7). Both the low and high $\bar{M}_n$ samples were examined under the polarizing microscope at temperatures of 450–470 °C, and nematic textures were observed at these

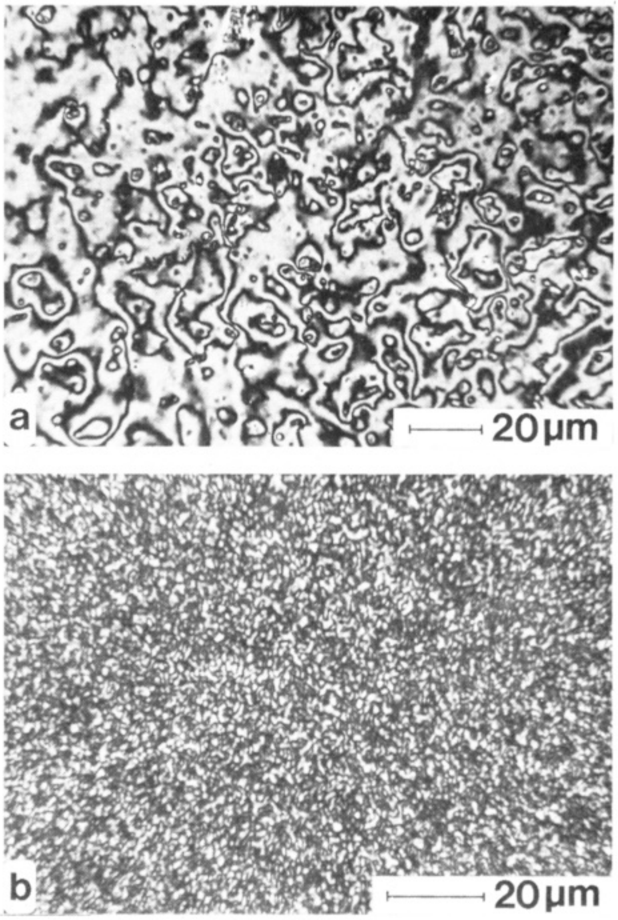

Figure 8. Nematic textures of specimens quenched from above the higher of the two transitions under discussion: (a) $\bar{D}\bar{P} = 15$, specimen quenched from 440 °C, no external shear applied; (b) $\bar{D}\bar{P} > 100$, specimen quenched from 480 °C, external shear was applied to increase the rate at which the fluid specimen spread between the glass surfaces above 480 °C. Polarizer and analyzer orientations were E-W and N-S, respectively.

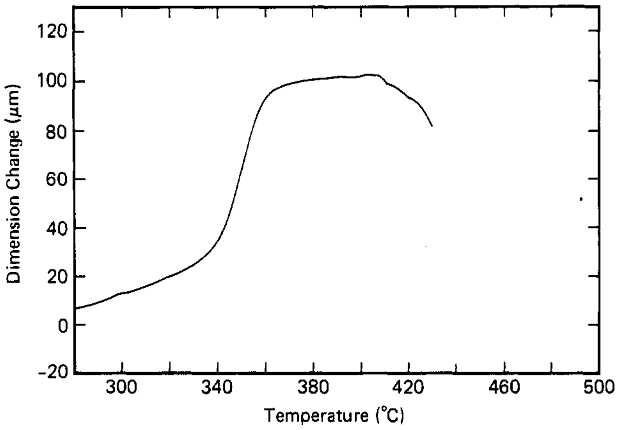

Figure 9. TMA analysis (penetration mode) of the homopolymer ($\bar{DP} > 100$). Scan rate = 10 °C/min, loading = 5 g.

temperatures even in the absence of externally applied shear. However, the samples were water-quenched to room temperature to allow microscopy with high-resolution objectives that necessarily provide only a short working distance (Figure 8).

From the above results, the following conclusions can be drawn concerning the two high-temperature transitions of the various molecular weight samples of PHBA. The first transition can be described as either a reversible plastic crystal transition or a highly ordered smectic transition. The two terms overlap sufficiently to be used interchangeably in this case. The term "plastic crystal" is applicable if one includes within its broad context those materials that have uniaxial, rotational freedom in a three-dimensional crystal. The term "highly ordered smectic" phase requires that the smectic phase displays three-dimensional order with the symmetry necessary to yield the original three-dimensional crystal structure on cooling. The shear-induced nematic texture observed for the low $\bar{M}_n$ samples is similar to that observed by heating the sample to 430 °C although the latter is somewhat coarser. At the lower temperature, the applied shear is sufficient to break down the dipolar interactions that hold the structure in a three dimensional state.

The possible existence of an even higher transition at 620 °C, reported earlier by Jackson,[7] was also examined. The high $\bar{M}_n$ sample was heated at 320 °C/min to just below the endotherm at 610 °C and then quenched to determine whether extensive degradation had already occurred. It was found that the sample degraded to such an extent that the endotherms at 340 and at 445 °C had completely disappeared. Hence, it seems reasonable that the high-temperature endotherm at 610 °C is only associated with degradation of the homopolymer.

To further characterize the transition at 445 °C, a high molecular weight sample ($\bar{DP} > 100$) was examined by thermomechanical analysis. As can be seen in Figure 9, the specimen showed an expansion at 340 °C, but at 430 °C and a pressure of 100 psi the probe easily penetrated the sample. Preliminary compression-molding studies indicate that the material is fused under these conditions. More detailed thermal analysis suggests that high molecular weight samples ($\bar{M}_n > 10\,000$) are stable at 450 °C for at least several minutes. This suggests the possibility for fabricating the homopolymer by using traditional plastic-forming techniques. A sample heated briefly above the 445 °C transition was examined with electron diffraction after cooling, but no single-crystal structure could be detected. The sample appeared far tougher in impact-fracturing experiments at liquid nitrogen temperatures, also suggesting some local sintering.

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Registry No. PHBA (homopolymer), 30729-36-3; PHBA (SRU), 26099-71-8; PHBA (dimer), 114943-43-0; PHBA (tetramer), 105450-50-8.

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