Thermal Analysis of Poly(bisphenoxyphosphazene); Single Crystals and Melt Crystallized Samples

S. J. KOZMISKI and IAN R. HARRISON, *Polymer Science Section, Material Science and Engineering Department, The Pennsylvania State University, University Park, Pennsylvania 16802*

Synopsis

High-molecular-weight polyphosphazenes are of considerable interest because of their potential use as relatively high temperature materials that also possess low glass temperature. A number of authors have examined the thermal properties of a wide range of polyphosphazenes. These studies, however, have usually been limited to compression-molded samples or to samples where the morphology or thermal history are poorly understood or highly complex. This article reports the thermal behavior of a single polymer, poly(bisphenoxyphosphazene) starting with the simplest morphological entity—the single crystal. The result of crystallization from the mesomorphic state [above $T(1)$] and from the melt were also examined, together with the influence of thermal cycling and heating rate. The effects of a variety of parameters on $T(1)$ are reported. This work clearly demonstrates the importance of morphology–crystallization conditions in determining $T(1)$ and suggests the presence of two crystal forms for this polymer.

INTRODUCTION

High-molecular-weight, linear polyphosphazenes have been extensively synthesized in the past fifteen years. The incipient impetus for this development came from the fact that the phosphorous–nitrogen bond in cyclic trimeric and tetrameric organophosphazenes, $[NP(OR)_2]_{3 \text{ or } 4}$, showed evidence of high thermal and chemical stability. The first synthesis of a fully substituted poly(organophosphazene) was reported in 1965 by H. R. Allcock.[1] Linear homopolymer organophosphazenes are known to be highly crystalline;[2] research on the thermal and particularly the morphological[3] properties of these polymers, however, has been somewhat limited.

Previous thermal analysis[2,4] of crystalline poly(organophosphazenes) has revealed that several of these polymers display two widely separated first-order thermal transitions: a lower transition designated $T(1)$ which involves a large enthalpy change, and an upper transition designated T_m with very little enthalpy change. At $T(1)$ the polymer softens, but some degree of order is retained. The upper temperature transition represents passage to the isotropic liquid; hence it is the true melting temperature. X-ray examinations[2] showed that the $T(1)$ transition corresponds to a transition from a crystalline to a mesomorphic state. This mesomorphic state has a pseudohexagonal structure which possesses ordered packing of parallel chains in two dimensions and disorder in the third dimension. A thorough description of mesomorphic order in poly(organophosphazenes) has been given by Desper.[5]

DSC analysis of films of poly(bisphenoxyphosphazene), (PBPP) which were compression molded at 373–433K and 100 atm have been reported.[4] These films

CCC 0021-8995/82/051783-12$02.20

yielded thermograms showing two endotherms in the $T(1)$ range; the temperature of the higher endothermic peak was ~433K.

Schneider and Desper[6] have reported a T_m for PBPP of 663K obtained by a TMA system when used in the penetrometer mode. Other polyaryloxphosphazenes were also examined, and the recorded values of T_m occurred in a relatively narrow range and appeared to be almost insensitive to structure. It should be pointed out, however, that these T_m values were very close to, and in several cases higher than, the indicated temperatures of decomposition determined as the onset of weight loss by TGA. Thus, in some cases, T_m merely indicated the maximum temperature at which structure persisted and supported the analyzer probe.

In an initial study of crystalline polymers it is desirable to work with the simplest structure possible, normally single crystals. This simplest entity is obtained when polymers are crystallized from dilute solution and many organic polymers are known to form single crystals.[3] Since single crystals are used as models to develop an understanding of the properties of bulk organic polymers, it was proposed that a similar approach be attempted for polyphosphazenes having an inorganic backbone. This article reports our initial attempts to grow single crystals of poly(bisphenoxyphosphazene), PBPP, and some preliminary thermal data on these crystals. Solution-grown crystals were also melt recrystallized and used to perform a more thorough thermal analysis of melt-crystallized PBPP.

EXPERIMENTAL

The polymers used in this study were prepared by the bulk ring-opening polymerization of hexachlorocyclotriphosphazene, followed by the conversion of the resulting poly(dichlorophosphazene) to the polyorganosphosphazene. The procedure has been described in detail elsewhere.[7] Two samples of PBPP were obtained. Sample I was prepared by H. R. Allcock's laboratory at the Pennsylvania State University (PSU) while sample II was received from The Army Materials & Mechanics Research Center (AMMRC), Watertown, Mass. The repeat unit for the polymer is given by:

$$\left[-N=P-\left(O-\bigcirc \right)_{\!\!/2} \right]_n$$
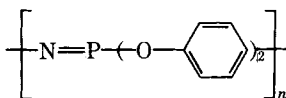
Both samples are believed to be of high molecular weight and completely substituted. Sample II has been characterized by the AMMRC, who kindly provided the information shown in Table I; intrinsic viscosity $[\eta]$, $\overline{M}_n$, $\overline{M}_w$, z-average radius of gyration $S^2_z{}^{1/2}$, and second virial coefficient A_2.

An attempt to grow single crystals of PBPP was made by dissolving the polymer in boiling xylene under nitrogen. Five 0.05% solutions were prepared and placed in constant temperature baths for isothermal crystallization at crystallization temperatures (T_c) of either 45°C, 50°C, or 55°C. (Three solutions

TABLE I
Dilute Solution Parameters for Sample II

$[\eta]$, dl/g = 1.227	$\overline{M}_w/\overline{M}_n$ = 6.0
$\overline{M}_n$ = 4.04 × 10⁵	$S^2_z{}^{1/2}$ = 643Å
$\overline{M}_w$ = 2.43 × 10⁶	A_2, ml-mole/g₂ = 6.14 × 10⁻⁵ in THF

of sample I at all three T_c's and of sample II at $T_c = 50°C, 55°C$). The polymer precipitated out of solution within 45–90 min depending on T_c. After removal of the mother liquor, the crystals were washed three times with fresh xylene at the crystallization temperature. Each suspension was held at the specific crystallization temperature for 25 h. The resulting polymer suspensions were examined on a Philips transmission electron microscope (TEM). Each suspension was viewed by placing a few drops on a carbon-coated grid which was then allowed to dry at room temperature. Thermal analysis was carried out using a Perkin-Elmer DSC 2. Unless otherwise stated, sample sizes were typically 1 mg and heating rate was 20K/min. T_c values are reported in degrees centigrade; all transition temperatures, however, will be given in degrees Kelvin.

RESULTS AND DISCUSSION

Morphology

Structures believed to be single crystals were seen in the TEM. These are lathelike in shape with lengths varying from 3 to 12 μm and widths ranging from 0.4 to 1.0 μm. TEM photographs are shown in Figure 1. All five suspensions produced crystals that appeared the same in shape, size, and structure.
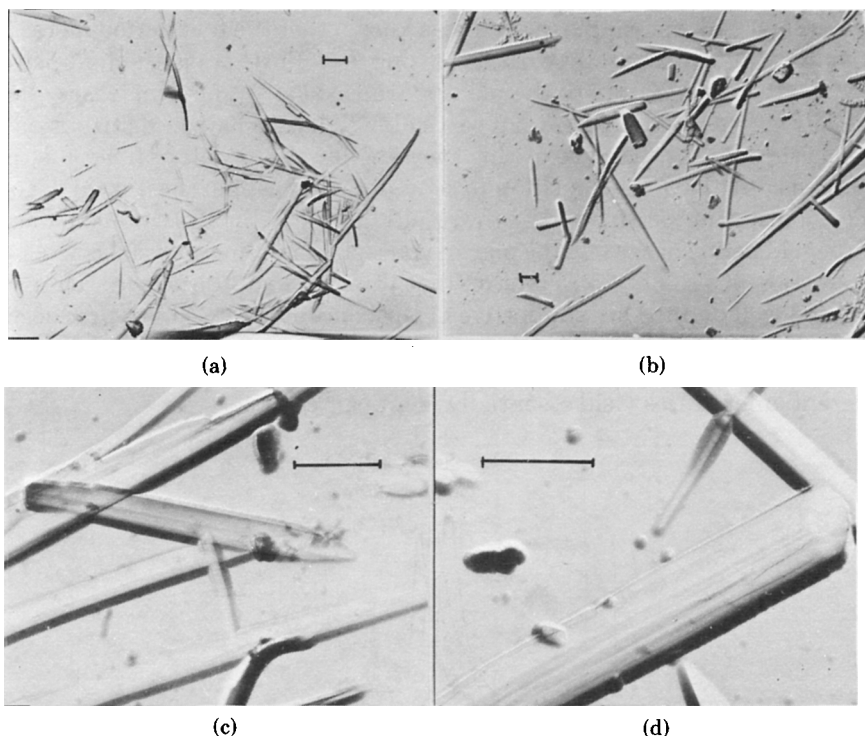

(a) (b)

(c) (d)

Fig. 1. Electronmicrograph of PBPP crystal. Micron markers are shown on the figures. (a) PBPP-I, $T_c = 55°C$; (b) PBPP-II, $T_c = 50°C$; (c) PBPP-I, $T_c = 45°C$; (d) PBPP-I, $T_c = 45°C$.

TABLE II

DSC Analysis of $T(1)$ in Poly(bisphenoxyphosphazene) Single Crystals

	Sample			
	I	I	I	II	II
T_c (°C)	45	50	55	50	55
$T(1)$ (K)	395.7	397.8	399.7	397.7	399.6

DSC Analysis of Single Crystals

The first part of our thermal study consisted of an examination of the "as formed" crystals. Thermal analysis was performed on dried crystals of each of the five single crystal preparations. The $T(1)$ transition was examined and the results are given in Table II. The $T(1)$ transition temperature is taken as the position of the peak maximum. Thermograms for the three preparations of sample II are shown in Figure 2. The results indicate, for both polymer samples, that as T_c increased the temperature at which the $T(1)$ transition occurred also increased.

In a search for T_m, samples of I and II were scanned at temperatures up to 700K without revealing any trace of the expected melting peak. Since the scans were made at a heating rate of 40K/min, a sensitivity of 0.5 m cal/s, and a sample size of 10 mg, it should have been possible to detect an endotherm with about 1% of the enthalpy change at $T(1)$; however, no upper transition was observed. On the basis of additional work (to be discussed later) the true melting transition of PBPP is believed to be at, or slightly above, 650K.

For organic polymer single crystals it is known that the fold period increases approximately exponentially with increasing T_c. Further, as the fold period increases, the temperature of the melting transition, T_m, also increases. Isothermally grown single crystals at a particular T_c have a narrow distribution of lamellar thicknesses; because of this they exhibit sharp well-defined melting transitions. If the $T(1)$ transition in poly(organophosphazenes) is analogous to the T_m in organic polymers, then the results of the DSC analysis would indicate that the fold period of the poly(bisphenoxyphosphazene) single crystals increased as a function of T_c. The observation that the $T(1)$ endotherms are relatively sharp and well defined are supportive of the concept that we have produced a uniform morphological structure, as anticipated for isothermally grown single crystals. It should also be noted that the two polymer samples produced by different laboratories yield essentially identical results.
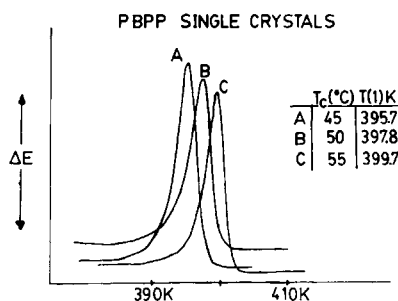

PBPP SINGLE CRYSTALS

	T_c(°C)	$T(1)$K
A	45	395.7
B	50	397.8
C	55	399.7

Fig. 2. $T(1)$ transitions of PBPP single crystals grown at different crystallization temperatures, T_c.

Thermal analysis has been performed on poly[bis(p-chlorophenoxyphos-phazene)][8] PBCPP which is quite similar to PBPP. Allen and co-workers[2] have reported a true melting transition for PBCPP at temperatures exceeding 625K, observed by optical microscopy, and at 680K, observed by differential thermal analysis (DTA). DSC analysis by Schneider, Desper, and Singler[8] on PBCPP revealed no trace of the T_m transition although it should have been possible to detect an endotherm with about 2% of the enthalpy change at $T(1)$. The latter's observation is very similar to the one reported in this article concerning the T_m of PBPP.

Melt-Crystallized PBPP

In an attempt to distinguish between the thermal behavior of crystals grown from solution and those produced from the melt, the following scheme was used for the production of melt-crystallized samples.

PBPP single crystals were heated to temperatures that were believed to be above T_m and cooled to room temperature. The crystals were heated to 650K (or higher) at 160K/min, held at that temperature for a short time (15 s), and cooled. The cooling process was done in two phases: the polymer was cooled from 650 to 440K at 160K/min and then subsequently from 440 to 300K at 20°C/min. The fast cooling and heating rates were used to limit any degradation that might occur at high temperatures. The lower cooling rate at low temperatures was used to allow for controlled crystallization from the melt or mesomorphic state. A characteristic crystallization exotherm is shown in Figure 3.

When cooled from 650K, sample I showed a large exotherm at 377K. Cooling from a higher temperature (700K) gave an exotherm at approximately the same temperature (379K). Single crystals of sample II cooled from 650K and 700K show large exotherms at 385 and 388K, respectively. The ability which II has to recrystallize at temperatures some eight or nine degrees higher than I is probably due to factors such as degree of branching or molecular weight distribution.
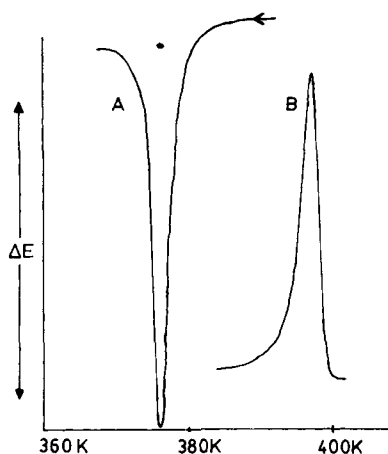

Fig. 3. (A) Crystallization exotherm of PBPP cooled from 650K. (B) $T(1)$ endotherm of PBPP single crystals, $T_c = 55°C$.

DSC Analysis of Melt-Crystallized PBPP

DSC analysis was performed on the two melt-crystallized samples in the range 300–440K, i.e., from below $T(1)$ to some temperature above $T(1)$ but below T_m. By melt crystallized we simply PBPP that was initially cooled from 650K or higher prior to any subsequent heating cycle. Both samples exhibited two endotherms when scanned through the designated range. Characteristic thermograms are shown in Figure 4. Both endotherms were present whether the polymer was cooled from 650 or 700K, or repeatedly cycled between 300 and 440K. For I the first peak appeared within a temperature range of ~399–404K and the second peak within a range of ~419–423K. For II, the first and second peaks appeared within a temperature range of ~406–410K and 424–427K, respectively.

The peak height and area of each endotherm for both polymer samples were usually equal. Exceptions to this observation, however, were noted. Many DSC scans were performed, and the results indicated that the peak size of each endotherm was not readily predictable for samples cooled from 650K or higher.

Detailed thermal analysis by Schneider et al.[8] on PBCPP revealed that the organization in the mesomorphic state, as influenced by thermal history, has a profound effect on the peak position, area and sharpness of the endotherm at $T(1)$. As noted, DSC analysis[4] has also been performed on films of PBPP which were compression molded at 373–433K at 100 atm. The resulting thermograms showed two endotherms with the higher temperature peak at 433K. (The observation of two endotherms is similar to that reported here for melt-crystallized PBPP). Although this temperature is some 35K higher than the temperature reported for single crystals, it is only a few degrees above the higher $T(1)$ endotherm of melt-crystallized PBPP. These results are indicative of the different morphologies that can be obtained in the preparation of PBPP and of their influence on thermal properties.

As stated, on heating melt-recrystallized samples, two endotherms are observed that are about 20K apart. Repeated cycling between 300 and 440K did not shift the peak positions of the two endotherms and had little effect on the peak size. This can be contrasted with the strong influence of cycling shown by compression-molded samples.[4,8] Compression-molded samples of PBCPP were not heated to temperatures of 650K or higher where the transition to an isotropic liquid takes place. Therefore, the morphology that resulted when PBCPP was
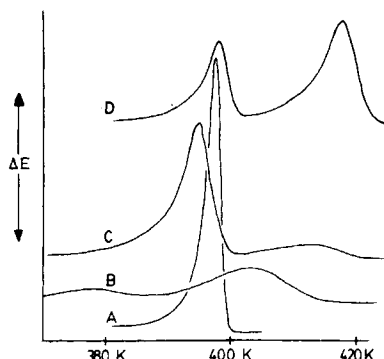

Fig. 4. (A) $T(1)$ transition of PBPP single crystals, $T_c = 55°C$. (B)–(D) Thermogram of PBPP single crystals cooled from 500, 600, and 650K, respectively.

compression molded above $T(1)$ was retained to some extent by the partial ordering that exists in the mesomorphic state. Perhaps chain-folded crystallites (with a wide distribution of lamellar thicknesses) were formed on cooling of the compression-molded sample from above $T(1)$. When heated above $T(1)$, the partial ordering of the mesomorphic state limits the structural rearrangements of the chain-folded crystallites by prohibiting massive motion of the polymer chain. Hence, the structure of the crystal bears a relation to that of the mesomorphic state. On each cycle above $T(1)$, however, some reorganization does occur leading to the observed changes in the $T(1)$ endotherm.

In contrast, when PBPP is heated above T_m an isotropic liquid forms and all remnants of the crystallite structure disappear. Cooling from above T_m allows the mesophase to form its own novel (equilibrium?) structure. This is followed by a mesomorphic-to-crystal transformation at about 380K. Crystal structures are formed within the restricted chain movement imposed by the partial ordering within the mesomorphic structure. Presumably, this represents some sort of equilibrium structure as it is observed that the peak positions of the resulting endotherms do not shift appreciably with repeated cycling above $T(1)$.

Origin of Multiple Endotherms in Melt-Crystallized PBPP

The phenomenon of multiple endotherms seems to exist with most polymers, and various explanations have been proposed.[9] Often an understanding of this behavior can be obtained by varying heating rate of the thermal analysis. Upon heating it is possible for a polymer sample to melt partially or completely, recrystallize in a more stable form (longer fold period), and melt again. This phenomenon will depend on the time the sample spends in the annealing region ($\sim$40K below its T_m). On slow heating the sample will spend enough time in this region so that fold period changes can occur. The observed T_m will correspond to the melting point of the annealed sample. On fast heating, however, the sample will spend a relatively short time in this annealing region. In this case the observed melting point will be that of the original sample. At intermediate rates two melting endotherms may be seen where the low and high temperature peaks correspond to the melting of the original and annealed material, respectively.

Thermal analysis in which the heating rate was varied was performed on melt-crystallized samples of sample I to obtain an insight into the origin of the two observed endotherms. The resulting thermograms are shown in Figure 5. The polymer was cycled between 300 and 440K (cooled at 20K/min). Fast (20K/min), intermediate (10K/min, 5K/min), and slow (2.5K/min) heating rates were used. There was little change in the relative area of the peaks, the second increased marginally as the heating rate was increased, and the peak positions were not affected. The results of the heating rate test indicate that the observance of the two endotherms is not due to fold period changes (structural rearrangements) in the "annealing" region.

When melt-crystallized samples of either I or II were heated to a temperature between the two endotherms, cooled to 300K at 10K/min, a small crystallization exotherm was observed at 388K for I and 396K for II. This exotherm is much smaller (approximately one-tenth the area) and occurs at a temperature about 10K higher than the exotherm observed when melt-crystallized samples are
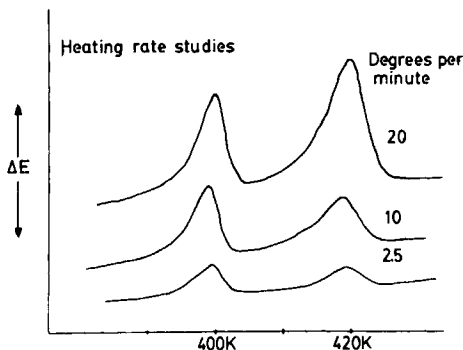
Fig. 5. Heating rate study of melt-crystallized PBPP.

heated to 440K and cooled at room temperature. On a subsequent scan through the heat cycle, the first peak had disappeared and the second had become much larger (Fig. 6).

The results of the DSC analysis suggest that melt-crystallized PBPP crystallizes into two different lattice structures. On heating to a temperature between the two endotherms, the higher melting crystal form remains; on cooling, more polymer crystallizes into the higher melting form. PBPP single crystals show a large well-defined endotherm at about 400K, i.e., approximately the same temperature as the lower of the two endotherms above. Perhaps the lattice structure of the single crystals is the same as the lattice structure responsible for the low-temperature-melting endotherm of melt-crystallized PBPP. To test the above hypothesis, it should be possible to obtain x-ray diffraction patterns of melt-crystallized PBPP containing both crystal phases and the high temperature phase by itself. X-ray analysis of the single crystals should yield a diffraction pattern that corresponds to that of the low-melting crystal form of melt-crystallized PBPP. This study is now in progress at PSU.

Thermal Cycling of Single Crystals of PBPP

Earlier we contrasted the behavior of melt-crystallized and compression-molded samples exposed to temperature cycling. Single crystals of I and II were also subjected to repeated cycling to temperatures above $T(1)$ and back to 300K.
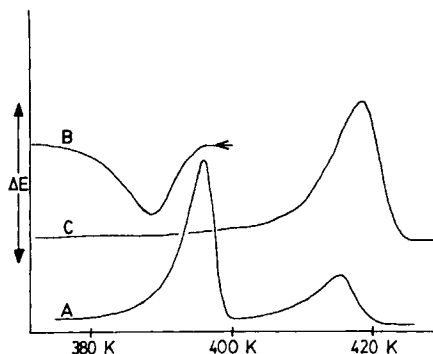

Fig. 6. (A) Thermogram of melt-crystallized PBPP. (B) Thermogram of melt-crystallized PBPP heated to 406K and cooled to 300K. (C) Melting endotherm obtained when melt-crystallized PBPP is heated to 406K, cooled to 300K, and scanned from 300 to 440K.

TABLE III
DSC Analysis: Thermal Cycling of PBPP Single Crystals in Sample I

Cycle	Sample Pretreatment Crystallized from	XL_{exo}	Peak I	Peak II
1	Single crystals (55°C)	—	399.7	—
2	Cooled from 440K	346.1	376.3	400.2
3	Cooled from 500K	350.9	378.8	403.4
4	Cooled from 550K	359.9	392.4	407.6
5	Cooled from 550K	363.0	393.1	409.1
6	Cooled from 600K	370.6	396.0	414.2
7	Cooled from 600K	372.4	397.0	415.0
8	Cooled from 650K	377.2	398.6	418.9
9	Cooled from 680K	379.1	400.3	420.3
10	Cooled from 440K	377.0	399.6	419.1

The temperature to which the samples were heated increased on each cycle. For each cycle the recrystallization exotherm and melting endotherms were recorded, and these are given in Tables III and IV. After cooling from 440K, single crystals of I and II on reheating showed endotherms approximately 20K apart. These were observed for both samples in the $T(1)$ range. As the samples were heated to higher temperatures and cooled, the temperature at which recrystallization took place and the area of the exotherms increased. In addition the two endotherms shifted to higher temperatures and became larger and more defined for each sample (see Fig. 4). At no time, however, were they larger or better defined than the endotherm obtained from the original crystals. Cooling from above 650K (melt crystallizing) only slightly increased the temperature at which the recrystallization exotherm and melting endotherms appeared relative to that obtained at 650K.

Single crystals cooled from 440K exhibited a smaller exotherm and endotherms with peak positions 20K–30K lower than melt-crystallized samples cooled from 440K. This appears to indicate that melt-crystallized PBPP when heated to a temperature slightly above $T(1)$ and cooled retains a greater degree of crystalline order than PBPP single crystals treated in the same manner.

Further, when single crystals of II were heated to 400K three times and cooled, the temperature at which recrystallization took place increased and the two

TABLE IV
DSC Analysis: Thermal Cycling of PBPP Single Crystals in Sample II

Cycle	Sample Pretreatment Crystallized from	XL_{exo}	Peak I	Peak II
1	Single crystals (50°C)	—	397.7	—
2	Cooled from 440K	365.0	395.4	412.0
3	Cooled from 440K	371.5	399.2	416.0
4	Cooled from 440K	373.5	401.5	417.2
5	Cooled from 500K	376.3	401.2	420.0
6	Cooled from 550K	379.1	404.4	421.5
7	Cooled from 600K	382.0	406.8	423.5
8	Cooled from 650K	384.8	408.0	425.3
9	Cooled from 680K	386.3	408.8	426.6
10	Cooled from 700K	387.6	409.0	427.3
11	Cooled from 440K	383.9	406.1	424.2

endotherms shifted to higher temperatures on each cycle. When melt-crystallized samples were similarly cycled between 300 and 440K, there was no shift in the crystallization exotherms or the two melt endotherms. Presumably, morphological differences between single crystals and melt-crystallized PBPP accounts for the different behavior that occurs when these samples are cooled from temperatures slightly above $T(1)$. These differences will be considered in the next paragraphs.

Isothermally grown polymer single crystals are proposed to be chain-folded structures with a narrow distribution of lamellar thicknesses. The polymer molecule passes through a crystalline core, folds, and reenters. Therefore the crystalline core is bound by an amorphous fold surface on top and bottom. On heating above T_m, fusion of the crystalline core occurs and a polymer melt is formed in which the polymer molecules take on random conformations; the single crystal entity no longer exists. In contrast, on heating above $T(1)$ to 440K, the crystalline core of the PBPP single crystal does not become a random arrangement of polymer chains but now consists of a mesomorphic core bound on top and bottom by an amorphous fold surface. On cooling, the limited chain movement allowed by the mesomorphic state permits recrystallization into two different lattice structures.

On heating single crystals above $T(1)$, the amorphous fold surface presumably experiences a driving force to take on mesomorphic order. Perhaps this driving force is strong enough to cause structural rearrangements of the mesomorphic core to accommodate some of the material that was in the fold surface. Cooling from 440K and subsequent heating yields a thermogram (with two broad endotherms) that is quite different from the thermogram of the original single crystals, i.e., a structural change has occurred. Cooling the single crystals again from 400 or 500K (or higher) shifts the two endotherms upward in temperature and increases the peak area, i.e., the resulting thermograms appear similar to the thermogram of melt-crystallized PBPP. This indicates that structural rearrangements due to molecular interaction between the amorphous fold and the mesomorphic core increase as the samples are heated to higher temperatures. This rearrangement brings about a structure similar to the mesomorphic structure obtained when PBPP is cooled from the isotropic liquid (melt). This is entirely analogous to annealing in organic polymers, where thin lamellar crystals reorganize to thicker more perfect crystals at temperature below T_m. Cooling PBPP from above its T_m allows the mesophase to form it own inherent structure. The behavior of the melt-crystallized samples discussed above indicates that the crystal structures formed on cooling from the melt are readily developed from the inherent mesomorphic structure. On melting these crystal structures, the inherent mesomorphic structure again results. Therefore subsequent cooling from 440K allows the melt-crystallized PBPP to recrystallize at higher temperatures than the single crystals.

Melting Point of PBPP

T_m for PBPP has been reported to occur at 663K as determined by TMA.[4] This transition has not been detected by DSC, although results from the thermal cycling experiments indicate that T_m is near this temperature. As PBPP single crystals are recrystallized from successively higher temperature above their

original $T(1)$, subsequent $T(1)$ endotherms become larger, better defined, and shift to higher temperatures. Upon being cooled from 650K, two well-defined $T(1)$ endotherms are observed that do not become larger or better defined when cooled from 680 or 700K, although they shift to slightly higher temperatures (see Tables III and IV). This suggests that cooling from this temperature (650K) allows the mesophase to form its own inherent "equilibrium" structure. If this were not the case, one would anticipate that the two $T(1)$ endotherms would become larger or better defined when samples are cooled from 680 or 700K.

The slight shift in temperature of the endotherms when samples were cooled from 680 to 700K could be attributed to a longer interaction between the mesomorphic and amorphous states. Occasionally, samples cooled from 680 or 700K exhibited a much smaller exotherm than expected. On the subsequent heat cycle, the two endotherms obtained were much smaller (or disappeared) and shifted to lower temperatures. This behavior is attributed to degradation of the polymer.

CONCLUSIONS

(1)   We have been able to grow single crystals of PBPP. These exhibit $T(1)$ transitions that are a function of T_c.

(2)   Recrystallization from the mesomorphic state [above $T(1)$ but below T_m] leads to structures that are highly sensitive to the number and upper temperature limit of the thermal cycle(s), provided the samples have never experienced T_m.

(3)   Apparently two different crystal structures are formed on crystallization from the mesomorphic state.

(4)   Crystallization from the melt leads to an equilibrium morphology that is insensitive to additional thermal cycling above and below $T(1)$.

(5)   In many respects, the $T(1)$ transition is similar to a critical annealing temperature found in organic polymers. Above $T(1)$, the sample will "anneal," "reorganize" to a more stable form unless it has already experienced a higher temperature.

References

1. H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, **87**, 4216 (1965).

2. G. Allen, C. J. Lewis, and S. M. Todd, *Polymer*, **11**, 44 (1970).

3. P. H. Geil, *Polymer Single Crystals*, Wiley, New York, 1963.

4. R. E. Singler, G. L. Hagnauer, N. S. Schneider, B. E. Laliberte, R. E. Sacher, and R. W. Matton, *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 433 (1974).

5. C. R. Desper, N. S. Schneider, and E. Higginbotham, *J. Polym. Sci. Polym. Lett. Ed.*, **15**, 457 (1977).

6. N. S. Schneider and C. R. Desper, "Liquid Crystalline Order in Polymers," in *Mesomorphic Structure in Polyphosphazenes*, Alexandre Blumstein, Ed., Academic, New York, 1978, chap. 9.

7. R. E. Singler, N. S. Schneider and G. L. Hagnauer, *Polym. Sci. Eng.*, **15**, 322 (1975).

8. N. S. Schneider, C. R. Desper, and R. E. Singler, *J. Appl. Polym. Sci.*, **20**, 3087 (1976).

9. J. P. Runt and I. R. Harrison, *"Methods of Experimental Physics-Polymer Physics"*, in *Thermal Analysis*, Ron Fava, Ed., Academic, New York, 1980, chap. 9.