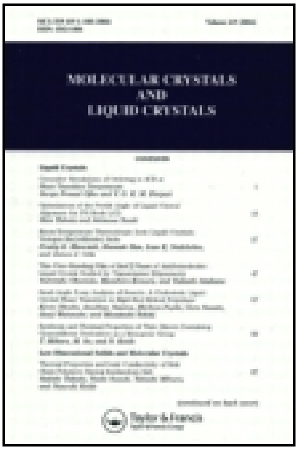

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Aromatic Polyesters of *p*-Hydroxybenzoic Acid

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Keywords: aromatic polyester, p-*hydroxybenzoic acid, fiber, processing*

INTRODUCTION

In this paper I would like to first review the background to the commercial development of the aromatic polyesters of *p*-hydroxybenzoic acid and then describe some of our recent work on 1) elucidating their structure–property relationships, 2) the effect of the synthetic route, and 3) the role of processing in optimizing properties.

BACKGROUND

It seems appropriate that as this field emerges today as a major commercial development that the history of work in this area be recorded more definitively. Approximately 25 years have passed since we first successfully prepared the homopolymer of *p*-hydroxybenzoic acid (PHBA) in the early spring of 1963 at the Carborundum Co. At the time, many scientists were actively working to develop new types of high temperature polymers based on heterocyclic units which might act to facilitate their processability in polar solvents. It was our feeling that such systems would always be expensive to prepare and the need to process from polar solvents would greatly limit their commercial potential. In 1962, I came across a reference describing the melt polymerization of PHBA which indicated that the polymer was intractable and tended to decompose at 350°C.[1] Because this report appeared inconsistent with the thermal stability one would have predicted, we decided to repeat the synthesis. From a commercial view this system was attractive since it could be synthesized from very low-cost starting materials and the experience and skills within the Carborundum Co. were well suited for sintering and processing of high temperature materials. On repeating the synthesis we did indeed observe the same reported instability at 350°C. However, during the synthesis, a significant amount of a sublimate, the phenyl ester of *p*-phenoxybenzoic acid, was isolated suggesting that the polymerization reaction was not proceeding as anticipated and more particularly that the reaction temperature had gone out of control as the melt solidified during the early stages of the polymerization.[2] We decided to carry out the polymerization using a heat exchange medium and also to start with the phenyl ester of PHBA to minimize the possibility for decarboxylaton through acid catalysis to yield the degradation product. With the first attempt, we successfully isolated a material which was very stable in air even up to 400°C and could be compression sintered at 400°C and 10,000 psi to yield specimens with flexural modulus values of over 1×10^6 psi.[3] The material displayed a sharp reversible endotherm at ~340°, however little or no flow could be detected above this temperature indicating that this was not a classical melting transition.[2] The fact that compression sintered specimens could be prepared at 400°C, encouraged us to look at other metal-forming processes such as forging and plasma spraying. In fact, by 1966, we had shown that fused specimens could be formed by high energy rate forging (HERF) of samples preheated to 300°C. These fused samples also showed a high degree of orientation based on X-ray diffraction analysis with flexural modulus values in the plane of 2.3×10^6 psi. Although this technique appeared very promising at the time, it was felt that fabricators would be unwilling to make the necessary capital investment to purchase HERF equipment. In the meantime, we were successfully pursuing other processing techniques such as plasma spraying and at the beginning of 1970, announced the commercial availability of the homopolymer of PHBA under the trade name Ekonol (See Table I for a listing of properties demonstrating the extremely high stiffness, self-lubricating character and high thermal conductivity). In Figure 1, a comparison of high temperature mechanicals for various engineering plastics is shown.

By the mid 1960s, the need for a melt processible (injection moldable) material which displayed a use temperature of 300°C had become clear to us. We therefore undertook to modify the PHBA homopolymer in such a way that it would melt at about 400°C, yet display a use temperature in excess of 300°C. We reasoned that a random copolyester of PHBA with another *p*-aromatic ester would yield rod-like chains which would pack to yield three dimensional order with sufficient defects to depress the melting point to well below 440°C which was the upper temperature limit for injection molding equipment. The high temperature use properties of such a system presumably would be controlled by the relatively high degree of crystalline order rather than by the glass transition. A large number of systems were prepared and evaluated and of these the biphenol terephthalate (BPT) comonomer with

TABLE I

Properties of compression sintered PHBA

Density (g/cm^3)	1.44
Flexural strength (psi)	10,700
Flexural modulus (psi)	1.00×10^6
Thermal conductivity (10^{-4}/cal/s/cm^2·°C·cm)	18
Thermal expansion coefficient (20^{-5} in./in./°F)	2.8
Coefficient of friction	0.10–0.16

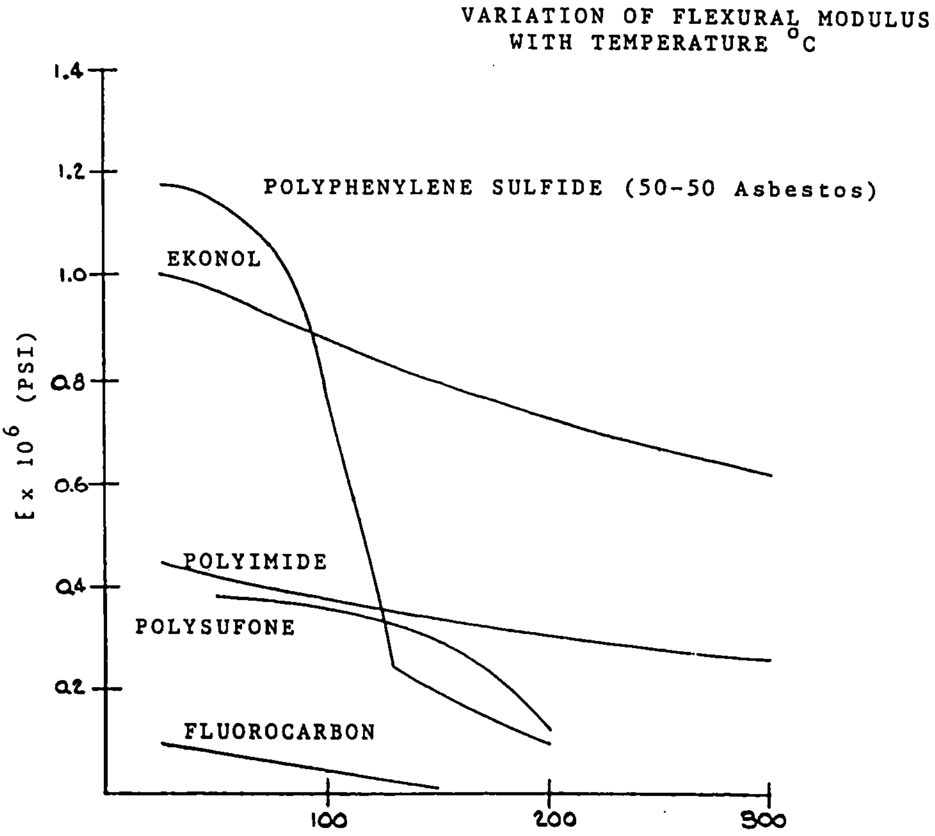


FIGURE 1 Modulus versus temperature from various engineering plastics.

PHBA appeared to provide the best combination of desired properties. Thus, the monomers were low cost or at least readily accessible and injection molded specimens showed practically no discoloration after injection molding. By 1968, we were in a position to begin to submit a series of patent applications to protect this development.[4] It is interesting to note that by designing a rod-like copolyester which melts, we had in effect defined the molecular structure of the first melt processible liquid crystalline polymer. By 1972, our work had progressed to the point where we were able to make two systems, namely the 2/1 and 1/2 PHBA/BPT copolymers available commercially as Ekkcel I-2000 and Ekkcel C-1000 (see Table II for a listing of properties). The I-2000 was designed as an injection molding grade and the C-1000 as a compression molding grade material. With the 2/1 composition, it was apparent early in the work that the material tended to orient and even fibrillate with modest shear during melt processing yielding significant anisotropy in the molded shapes. This was deemed undesirable especially for complex geometries where local variations in flow resulted in significant changes in thermal expansion coefficient and resultant localized stresses. We were not particularly concerned with this phenomena, since use of fillers tended to sharply reduce this problem.

TABLE II

Properties of PHBA/BPT copolyesters

Properties	Ekkcel C-1000	Ekkcel I-2000
PHBA/BPT	1/2	2/1
Tensile strength (psi)	10,000	14,000
Tensile modulus (psi)	190,000	350,000
Elongation (%)	7–9	8
Flexural strength (psi):		
at 23°C	15,000	17,000
at 260°C	5,000	4,000
Flexural modulus (psi):		
at 23°C	460,000	700,000
at 260°C	125,000	235,000
Heat distortion temperature (°C) at 265 psi	300	293
Coefficient of thermal expansion (in./in./°F)	2.87×10^{-5}	1.6×10^{-5}
Specific gravity	1.35	1.40

In 1970, rumors began to emerge of the development of the high strength/modulus benzamide fiber which was spun from anisotropic solution. At the time, we were in the process of developing a high modulus BN fiber[5] as an alternative to graphite fiber based on PAN. Hence the potential of high mechanical properties associated with ribbon or rod-like structures was clear and the advantages for a melt spun polyester fiber became immediately obvious. In addition, the anisotropic character of the melt seemed to represent a close parallel to that of the solution used in the benzamide spinning. Within several months, we were able to melt spin filaments of a modified version of Ekkcel I-2000 which displayed strength and modulus values approaching the values of the benzamide fiber.[6] The modification consisted of replacing ~50% of the terephthalic acid with isophthalic acid and melt spinning a low molecular weight material which could subsequently be advanced.

Today, practically all of the above products developed at Carborundum Co. are available commercially. In the USA, the Ekonol is a highly profitable specialty polymer used as a plasma spray coating and available from Carborundum (British Petroleum). The Ekkcel I-2000 was licensed to Dart Kraft, who in 1984 put a 20 million pound plant on stream and sells the material under the trade name of Xydar. The polyester fiber indicated above was recently announced in 1987 by Allied Signal with Dart Kraft. In Japan, Sumitomo Chemical originally under license from Carborundum, has been selling the Ekonol resin and the Ekkcel I-2000 since the early 1970s. In the fall of 1985, they introduced the above fiber to the market place as the Ekonol fiber. (See Table III for a comparison of properties with Kevlar).

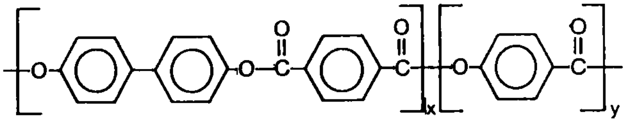
To complete the discussion on the commercial development of the aromatic polyesters, Tennessee Eastman workers reported,[7] in the mid 1970s, the development of a copolyester based on polyethylene terephthalate (PET) and PHBA while Celanese workers described in the late 1970s[8] their work on a copolyester of PHBA with 2,6-hydroxynaphthoic acid (HNA). Representative structures of the three copolyesters are shown in Figure 2.

TABLE III

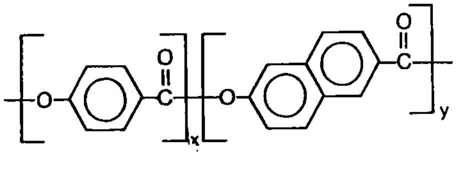
High strength/modulus organic fibers

	Kevlar 49	Ekonol Fiber
Density, g/cc	1.45	1.40
Tensile strength, psi	400,000	550,000
Tensile modulus, psi	20×10^6	24×10^6
Elongation, %	2.7	3.0
Moisture absorption, %	2.0	0.01

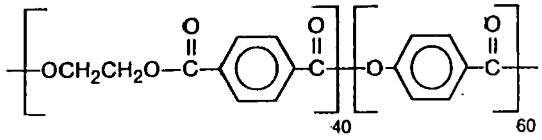
One question of possible historical value is, at what point did we first recognize the existence of the liquid crystalline character of these various materials? In the case of the homopolymer of PHBA, we have only recently shown that this system forms a nematic melt at a temperature of 445°C which provides a clear explanation for the orientation observed during forging. In the case of I-2000 (PHBA/PBT 2/1) all of the characteristics associated with a liquid crystalline melt were recognized in 1967, namely the high shear sensitivity, the tendency to form anisotropic melts which produced highly fibrillated extrudates, and of course the anisotropy in properties. The fact that these melts could also be described as liquid crystalline occurred to us with unpublished reports in 1970 of the successful preparation of the benzamide fiber from an anisotropic solution (first patent appeared in 1971[9]).



Dart-Kraft (Carborundum)



Celanese



Tennessee Eastman

FIGURE 2 Representation structures of the three commercial copolyesters.

To summarize, our work from 1962–1971 led to a new class of commercially available thermotropic polyesters based on PHBA. Today this field is one of the most active areas for advanced polymer R & D in industry as well as basic studies in universities. For the most part, these polymers are used primarily because of their exceptional retention of properties to well over 300°C and melt processibility at 410°C. In addition, there appears to be good potential for melt-spun filaments with high strength/modulus values. For the future, enormous opportunities lie ahead as techniques emerge for inducing controlled orientation into molded shapes which minimize skin core effects and local internal stresses associated with variable TEC.

Turning now to the present, it is surprising that most of the work leading up to the commercial development of this class of polymers was carried out from 10 to 25 years ago. Yet, today a number of basic questions remain concerning the nature of the high temperature transitions, the relationship between the synthetic routes and the microstructure and the effect of processing on properties?

In the following sections, I will describe some of our work aimed at elucidating these questions under the following three themes:

1. Synthesis and Structure of the aromatic polyesters,
2. Natue of the High Temperature Transitions, and
3. Processing and Properties of the Aromatic Polyesters.

SYNTHESIS AND STRUCTURE

The preparation of the homopolymer of PHBA has been described in the literature in some detail[3] and will only be reviewed briefly here. On the other hand, the synthesis of the copolyesters of PHBA/BPT, PHBA/PET, and PHBA/HNA are not well described undoubtedly because of the proprietary nature concerning their preparations. In fact there is a need for accurate structural data concerning sequence distribution, possible variations in composition and molecular weight which would not only permit meaningful insights into the polymerization process but are essential to understand and optimize properties. Relating these structual features to the synthetic route is complicated by the fact that the polymerization reactions are normally carried out in larger reactors designed to handle very viscous melts at elevated temperatures. The relative insolubility of the product polymers further hinders study of these materials by normal solvent techniques. Pertinent questions on which little or no information are available include 1) reactivity ratios, 2) tendency for transesterification during polymerization, and 3) effect of polymerizing in an isotropic melt, a nematic phase or the solid state. Another question that arises concerns the possible reactions during subsequent annealing processes in the solid state. It is well recognized that the degree of crystallinity can increase dramatically during solid state annealing. What is not clear in the annealing of copolyesters is the extent to which increased ordering is a result of slow diffusion processes leading to improved packing or transesterification leading directly to more ordered crystallizable units. Recently at IBM, we have undertaken to examine all of these factors to arrive at a comprehensive interpretation of the polymerization reactions in the copolyesters. Hence, in the following paragraphs I will include some of the progress made from these studies.

Let me begin with the work on the PHBA homopolymer. A detailed description of the polymerization of PHBA to the homopolymer was published 12 years ago.[2] The earlier problems associated with solidification during melt polymerization[1] were clarified and a mechanism was proposed describing formation of the major degradation product, i.e., the phenylester of *p*-phenoxybenzoic acid. Successful polymerization of both the phenylester and the acetoxyester of PHBA was described and shown to depend on the use of a heat exchange medium. It was also shown that the polymerization proceeded initially in solution, but that after the M_N exceeded several units precipitation occurred and in the case of the acetoxyester was found to form single crystals of the oligomers. Polymerization then continued at the surface of the single crystal and within the crystal indicating that the end groups within the single crystal are positioned to facilitate further reaction. A rich variety of single crystal morphologies have been identified and their etiology examined and shown to depend on M_N and on the conditions of polymerization.[10] As shown in Figure 3 the polymer precipitates as very thin single crystal flakes at the early stages of polymerization. In Figure 4 are shown single crystal morphologies typical of the later stages of polymerization. The distinguishing feature in this reaction as compared to that of the copolyesters is that practically the entire polymerization takes place in the ordered state with reactions occurring both at the surface and within the crystalline structure. The kinetics of this polymerization can best be described as zero order.[11]

Turning now to the copolyesters of PHBA, we have three somewhat different processes to consider. Thus in the case of the 60/40 PHBA/PET, the reaction is carried out by transesterification of *p*-acetoxybenzoic acid in a melt of PET.[7] Until recently, the copolymer was considered to have a composition of 60/40, display no thermal transitions in the DSC, have a random sequence distribution, and contain several percent of a microscopically observable second phase with unknown composition.[7,12] However, some confusion has emerged in the literature concerning the structure and morphology of this system particularly with the observation of multiple glass transitions and crystallization endotherms.[13-15] We undertook to more carefully analyze this material by solution fractionation with chloroform followed by C^{13} NMR studies of the various fractions.[16] What we have found is that there is a chloroform soluble fraction (17%) of a 44/56 (PHBA/PET) copolymer where the PHBA dyad content is twice that compared to the predicted random distribution (see Figure 5). The remaining 83% appears to be random. The DSC scan of the original unfractionated sample can be interpreted as a mixture of the two phases with approximate compositions of 44/56 PHBA/PET and 62/38 PHBA/PET (see Figure 6). The fact that the crystallization endotherm of the 17% fraction is almost equivalent in intensity to that of the major fraction indicates the importance of the blocky structure in crystallization. These results also explain the recent report by Denn[17] that the melt of the 60/40 copolymer displays isotropic and nematic phases. Presumably the presence of a PET rich fraction can explain the coexistence of an isotropic phase in the melt. It is likely that such compositions when placed

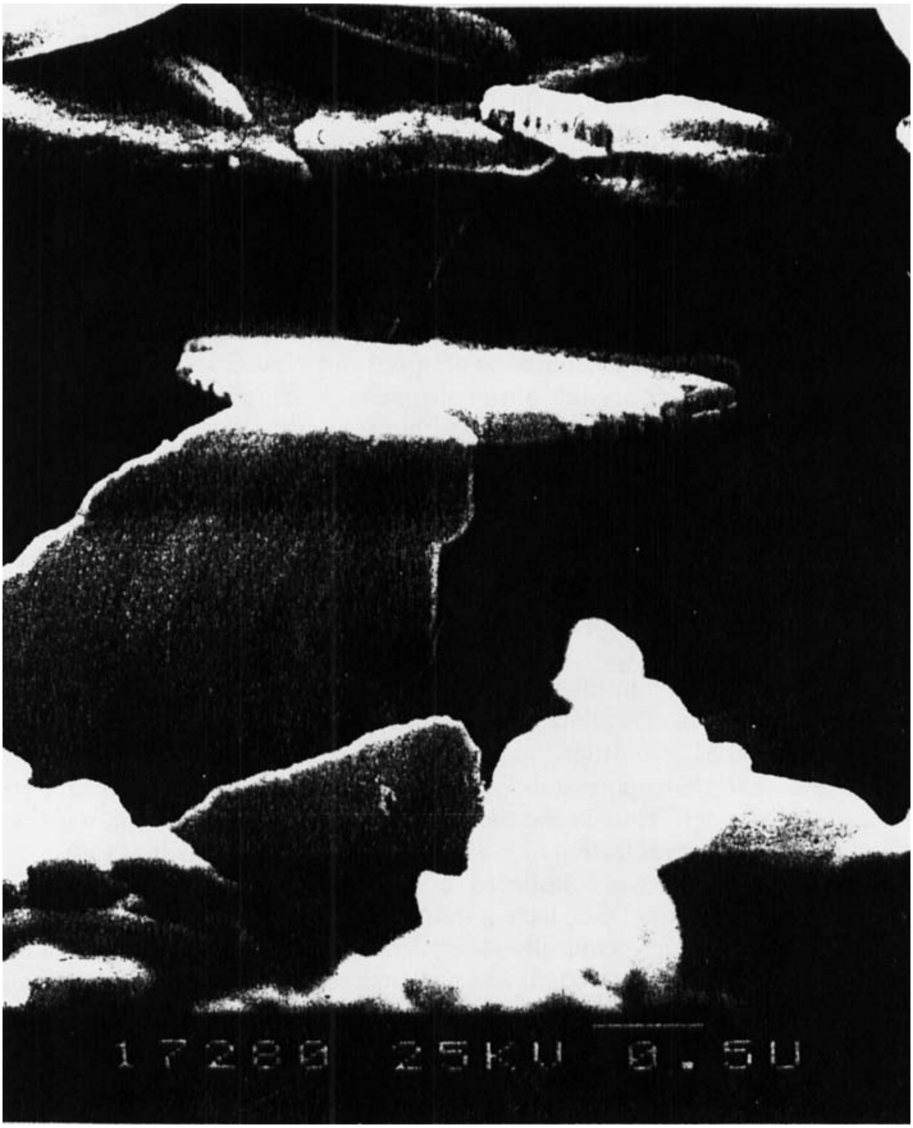


FIGURE 3 Precursor morphology M_N of 1,000.

under high shear in the melt could display shear sensitivity typical of liquid crystalline behavior.

From these results, one can conclude that the ester interchange between the *p*-acetoxybenzoic acid and PET proceeds rapidly in the melt resulting in a copolymer with an apparent 60/40 composition. The fact that the large majority of the 60/40 copolyester is random indicates that transesterification (or scrambling) occurs readily either in the isotropic or nematic melts. The presence of a discrete second phase with ~44/56 PHBA/PET is surprising since one might predict a continuous distri-

FIGURE 4 PHBA morphology M_N of 8,000.

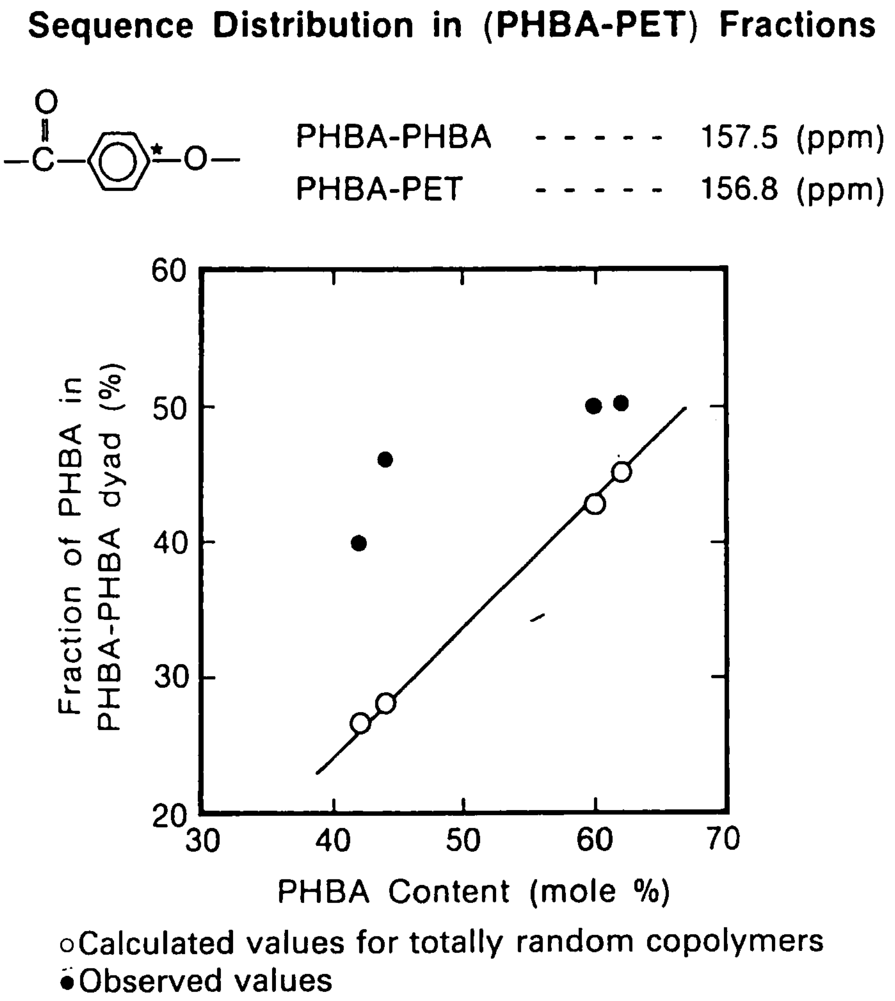
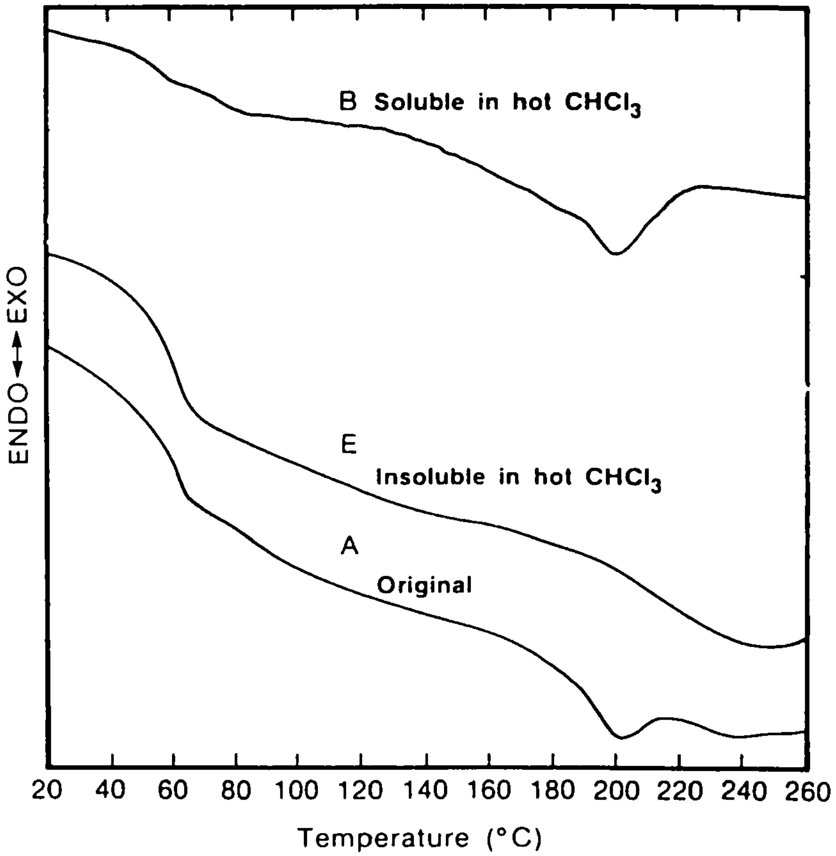


FIGURE 5

bution in composition rather than one which is bimodal. On the other hand, once phase separation occurs in the melt between the isotropic and nematic phases, then no mechanism is available to further enrich the isotropic phase with the richer PHBA fractions present in the nematic phase. Hence the 44/56 PHBA/PET persists as a vestigal composition unable to react further. The blockiness of the 44/56 PHBA/BPT composition remains inexplicable, and one is tempted to propose solidification of the blocky structure during polymerization. The presence of two glass transitions in the 44/56 composition suggests further phase separation between PET rich fractions where one is more random and the other more blocky.

The complexity of this type of polymerization process is demonstrated from an analysis of a different batch of 60/40 PHBA/PET which was obtained some years



Thermal Behavior of (PHBA-PET) Copolymer Fractions

DSC Thermograms at 20°C/min after cooling from 300°C at 5°C/min

FIGURE 6

earlier. In this case, it was found that extraction yielded 28% of a soluble fraction which analyzed 50/50 PHBA/PET and the remainder analyzed 68/32 PHBA/PET.[16] From all of the above results one can conclude that much of the confusion in the published literature arises from the inhomogeneous nature of the copolymer and that significant variations can occur from batch to batch. In the case of the 80/20 PHBA/PET, the compositional inhomogeneity is further complicated by the increased tendency of the PHBA to react with itself to form an insoluble highly crystalline polymer. In fact, examination of this crystalline phase with electron diffraction techniques shows the presence of a single crystal pattern identical to that of the homopolymer of PHBA.[18]

In the case of the 73/27 PHBA/HNA copolyester (LCP-2000) manufactured by Celanese, fibers have already been examined in some detail by x-ray diffraction techniques.[19] From these investigations, it has been inferred through modeling experiments that the sequence distribution in the copolymer is random. We are currently examining this system and have developed NMR methodologies to obtain a more quantitative assessment of sequence distribution along with accurate information on M_N and composition.[20] To briefly summarize, it is now possible to conclude that

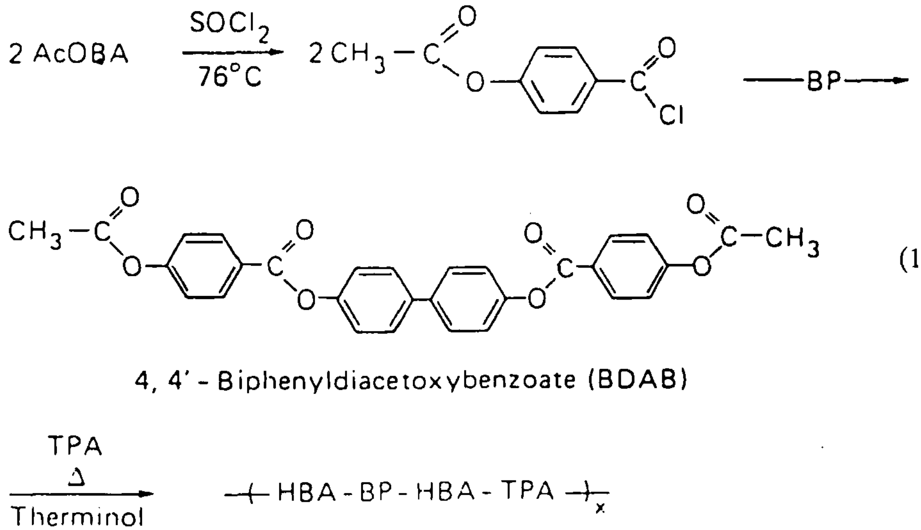
1. Melt polymerization of the 73/27 PHBA/HNA copolyester (LCP-2000) results in a random sequence distribution (within 2% error).
2. The composition of the copolymer is identical to that of the feedstock, and
3. The M_N of the LCP-2000 is approximately 10,000.

Studies on the affect of long term annealing of the LCP-2000 have shown that the degree of crystallinity increases from ~25% to 60%[21] while our work shows that M_N also increases sharply during much shorter term annealing.[22] At this point, it is not clear whether some interchange may occur during annealing to yield a more ordered structure and one that tends to crystallize more readily. This question will be resolved shortly in a set of definitive experiments now underway in our group. We have studied the kinetics of polymerization of the 50/50 PHBA/HNA mixture in Therminol solution as well as the homopolymerization of the HNA monomer.[23] Results of this work indicate that copolymerization proceeds by second order kinetics while the HNA reaction proceeds by zero order kinetics in a process remarkably similar to that of PHBA polymerization. The tendency for ester interchange (scrambling) during copolymerization has also been verified with NMR using C^{13} labeled PHBA copolymerized with the dimer of PHBA-HNA.[24]

The preparation of the PHBA/BPT 2/1 copolyester in some ways represents the greatest degee of complexity in that the reaction begins as a slurry where the acetylated PHBA and biphenol are soluble in the Therminol solvent, while the terephthalic acid (TA) is not. The slurry is heated to about 280°C at which point the reactants have formed a viscous homogeneous melt which separates from the solvent. The reaction is continued to the point where the low molecular weight polymer solidifies. The material is ground up and the polymerization is continued in a solid state slurry by heating at 350°C. At the early stages of the reaction, the PHBA tends to react with itself and with the biphenol due to the relative insolubility of the TA. At the point that the homogeneous melt is formed, presumably most of the TA has reacted. At this stage, there is potential opportunity for randomization; however, once the growing polymer solidifies, polymerization then is more likely to proceed with ordering as the major driving force. Analysis of the polymer is complicated by the lack of solubility of both the final material as well as the intermediate melt. The high degree of crystallinity of the as prepared polymer suggests a considerable degree of blockiness (see Figure 7 for a comparison of the X-ray diffraction pattern of the highly crystalline polymer as prepared versus the typical supercooled nematic formed after melting and quenching). In fact, cross polarization dynamics measurements of the polymerized material indicate that at least 50% of the PHBA units reside in a more ordered state.[25] Interestingly, synthesis of the regularly alternating [HBA-BP-HBA-TA] polyester indicated below yields an intractable product which shows no high temperature transition in the

DSC.[26] From the available data it appears likely that the copolymer formed during solid state polymerization is not random; however, on subsequent processing in the nematic melt it very likely tends to scramble towards a more random structure.

Alternating Copolyester

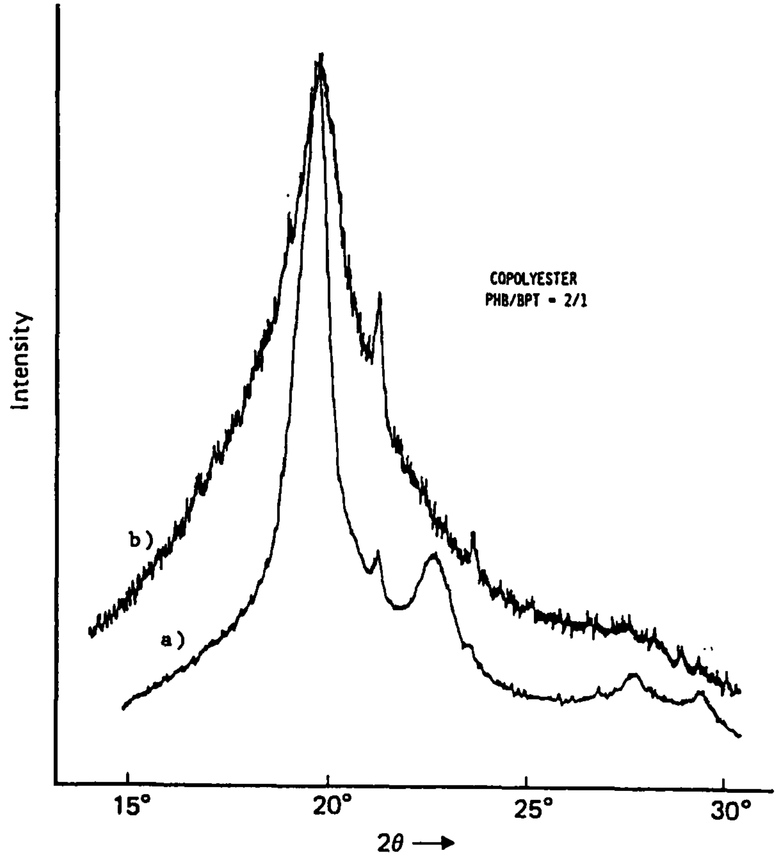


4, 4'-Biphenyldiacetoxybenzoate (BDAB)

(1

NATURE OF THE HIGH TEMPERATURE TRANSITIONS

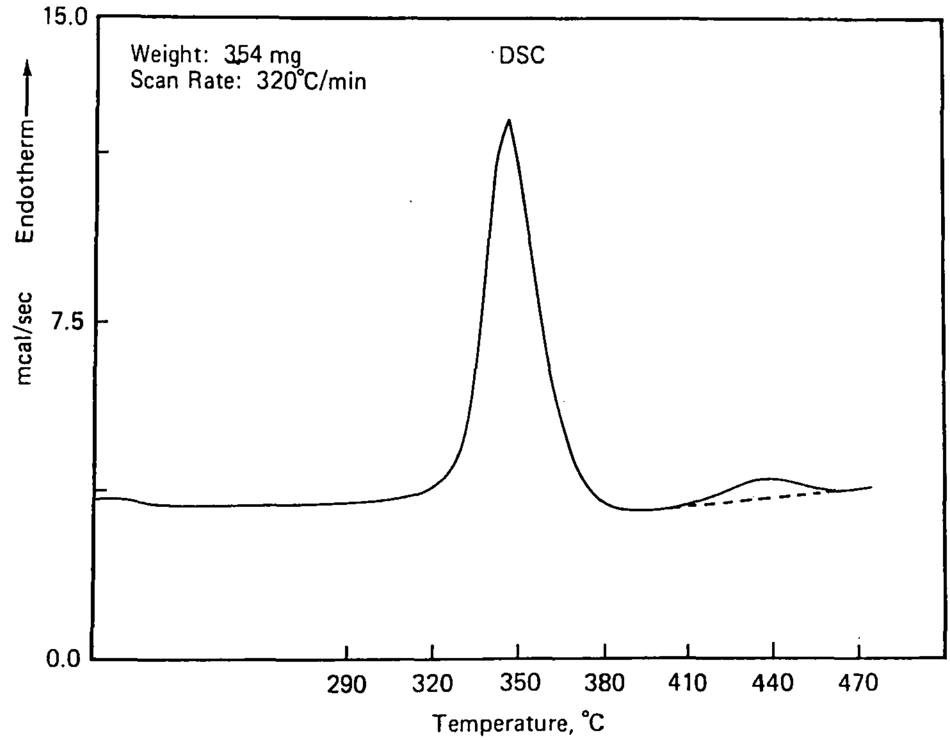
At present it is well accepted that the copolyesters of PHBA/BPT (2/1), PHBA/HNA (3/1), and PHBA/PET (60/40) display a crystal to nematic transition at 421°, 285° and somewhere above 240°C, respectively. Attempts to relate these transitions to those of the corresponding homopolymers is complicated by the fact that the PHBA shows a reversible endotherm at 340°C,[2] a temperature well below the value for PHBA/BPT copolyester at 421°. This problem has recently been resolved with the identification of a much higher transition for the PHBA homopolymer at 445°C.[27] From this study, it has been shown that poly PHBA undergoes a reversible crystal → nematic transition at 445° (see Figure 8). A previously reported endotherm at 610° appears to be associated only with rapid degradation of the polymer.[28] A reasonably good understanding now exists as to the nature of the 340°C transition, which can be interpreted either as a "plastic crystal" or a "highly ordered smectic" transition. The two terms appear to overlap sufficiently so that they can be used interchangeably in this particular case. Streaking in the electron diffraction pattern of the high temperature phase (>340°C) suggests some horizontal and vertical displacements of the chains (see Figure 9). The fact that most of the spots in the high temperature diffraction pattern are unchanged, indicates that the packing in the high temperature form is closely related to the orthorhombic structure of the low temperature phase[29] (see Figure 10). The close similarity between these two phases is demonstrated by the fact that the single crystal morphology is retained



(a) Virgin Material Scale 10,000 CFS
(b) Material after being Heated to Above its Melt Transition (scale = 2,000 CFS)

FIGURE 7

on heating and cooling through the transition. Hence, in this transformation registration between the chains as well as the external crystal morphology must persist. Interestingly, the large increase in thermal expansion coefficient which accompanies the transition does not appear to disrupt the crystal morphology. The expansion occurs almost completely in the *a,b* basal plane since no change in the *c* axis dimension can be detected between the low- and high-temperature electron diffraction patterns. Undoubtedly, in a high-temperature crystal phase, some molecular motion occurs, most likely in the form of phenylene rotation as would be expected in a plastic crystal with one degree of freedom. Lower M_N samples of the homopolymer also show the same endothermic transition, but at significantly lower temperatures (see Figure 11). In fact, samples with a degree of polymerization of ~13 not only retain the single crystal morphology on heating and cooling through the transition, but, with applied shear above the transition, display a well defined nematic texture. The same sample without shear also displays a crystal nematic transition at 415°C, somewhat lower than the 445° for the high M_N sample. Pre-



DSC Scan of Poly PHBA

FIGURE 8

sumably, the applied shear above the first transition is sufficient to break down the ester–ester dipoles which still persist and yield the nematic texture while at 415° no shear is required to produce the nematic state. With higher molecular weight, i.e., DP of >40 the aggregate of ester dipole interactions between chains is large enough to make the material behave more like an intractable solid at 350°C. Shown in Figure 12 is the nematic texture of the sheared materials with degrees of polymerization of 13 and 39, respectively. The dark areas with DP ~ 39 indicate the increasing intractability of the specimen. Also noteworthy, is the finer texture associated with increasing M_N.

We have carried out some studies on the homopolymer of HNA to better characterize this system, since the only data in the literature[30] indicates a possible melting transition at ~340°C. What we have found is that the HNA homopolymer shows the same kinds of transitions as the HBA homopolymer and amazingly almost at the same temperatures.[31] The HNA polymer also shows the same kinds of single crystal morphology as the PHBA system. Some work is now underway to better characterize the structure of the polymer by electron diffraction analysis.

We have carried out some preliminary studies on the nature of the nematic melts of the PHBA homopolymer and the copolymers of PHBA/BPT and PHBA/HNA using thermomechanical measurements.[32] Thus, the homopolymer at 430°C required a pressure of 100 psi for the probe to penetrate the sample. In the case of

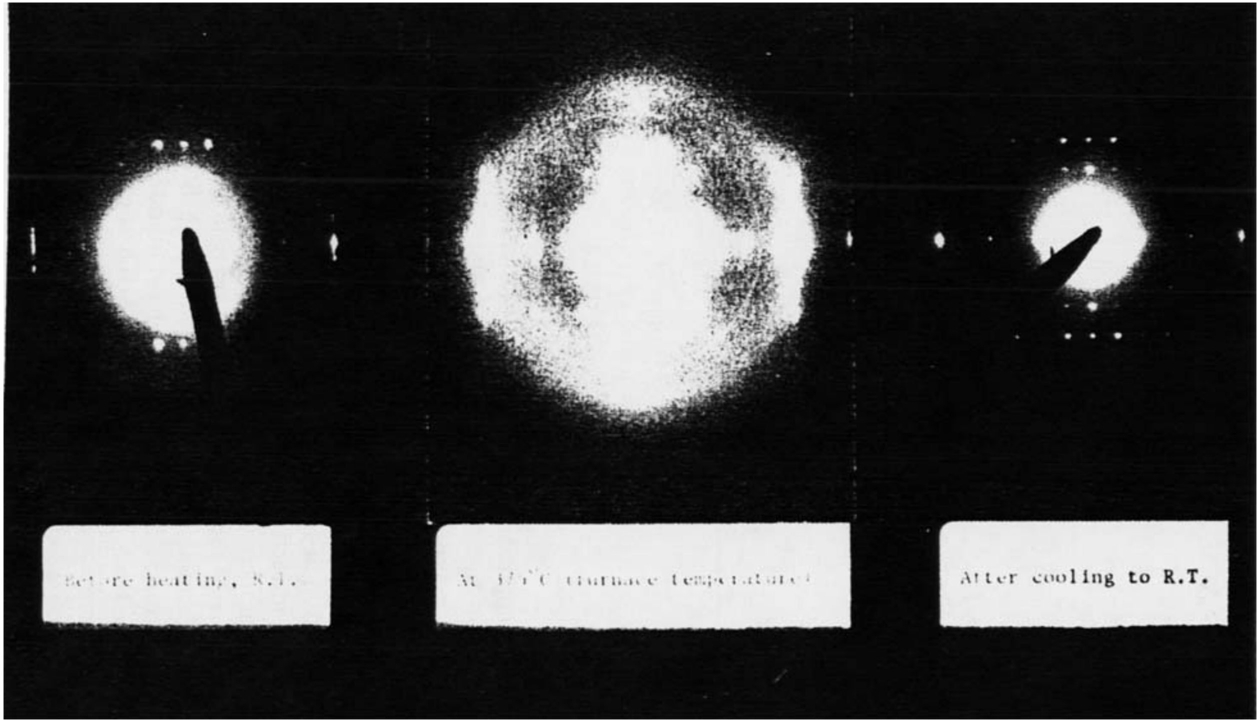
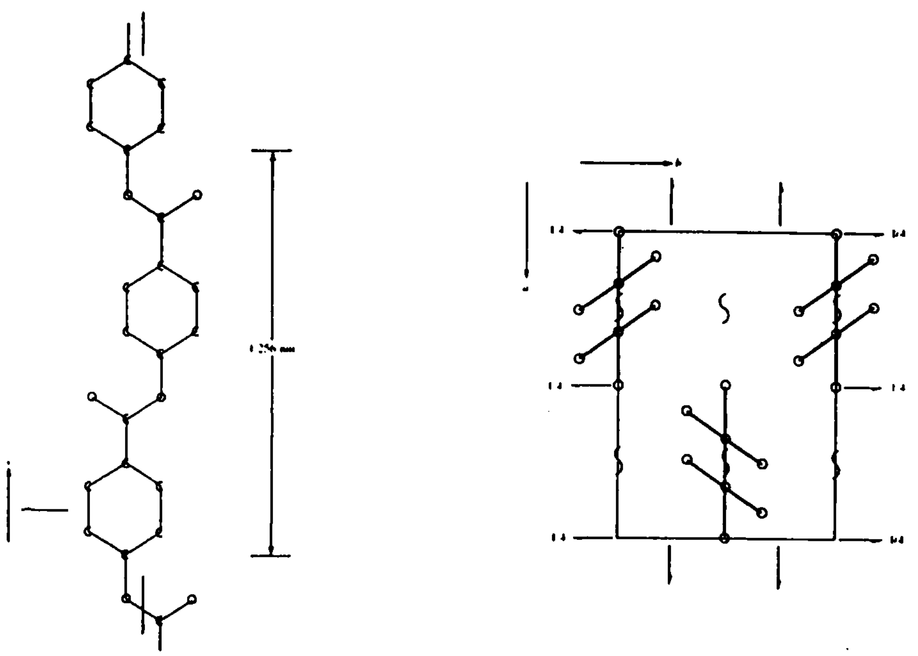


FIGURE 9 Electron diffraction pattern of the PHBA homopolymer.



a = 0.762 nm, b = 0.570 nm, and c = 1.256 nm

Orthorhombic Unit Cell, Space Group = $P2_12_12_1$

FIGURE 10 Proposed crystal structure of poly(*p*-oxybenzoate).

PHBA/HNA 75/25, the probe penetrated the sample with little applied pressure above the crystal nematic transition at 285° while with the PHBA/BPT 2/1 intermediate pressures were required to penetrate the specimen at temperatures of ~400°C. These preliminary results suggest that the nematic melts can display significant differences in stiffness which appear to depend not only on the molecular weight, but also on the order parameter.

Recently, we have initiated a program to better characterize the onset of molecular motions at elevated temperatures in these polyesters. The intent is to correlate the onset of motions such as rotation of the phenylene or naphthalene units with various high temperature transitions as well as long range mechanical properties such as creep. Preliminary results indicate that in the copolyester of PHBA/BPT, all the rings display significant rotation at temperatures of 140°C while at room temperature there is no detectable ring motion.[33] On the other hand, the homopolymer of PHBA displays no significant ring motion at temperatures of 140°C. In the case of PHBA/HNA copolyester the PHBA unit already displays ring flips at −50°C while the HNA unit shows motion near 100°C.[34,35]

To summarize, as a result of these recent insights into the high temperature transitions of poly PHBA a clear picture now exists as to the relationship between the crystal nematic transitions of the homopolymer and those of its copolymers

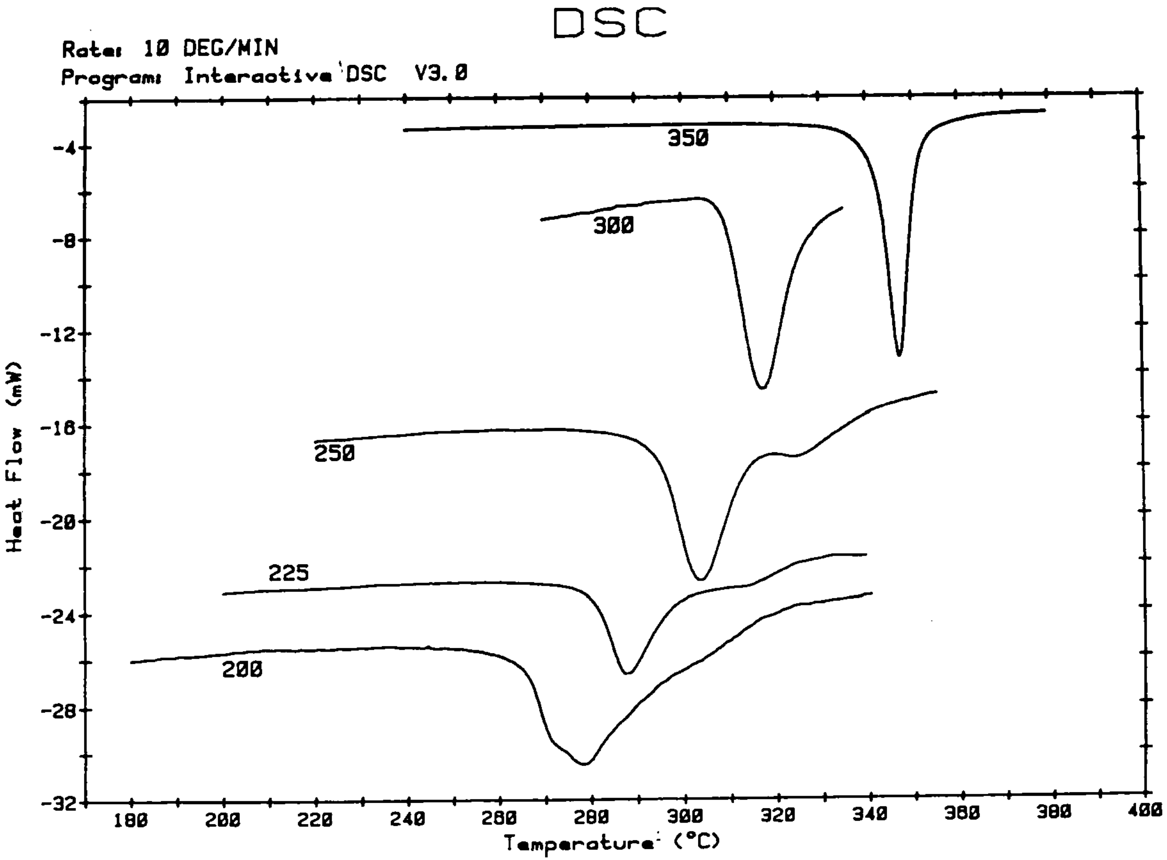


FIGURE 11 DSC traces of PHBA prepared at the indicated temperatures.

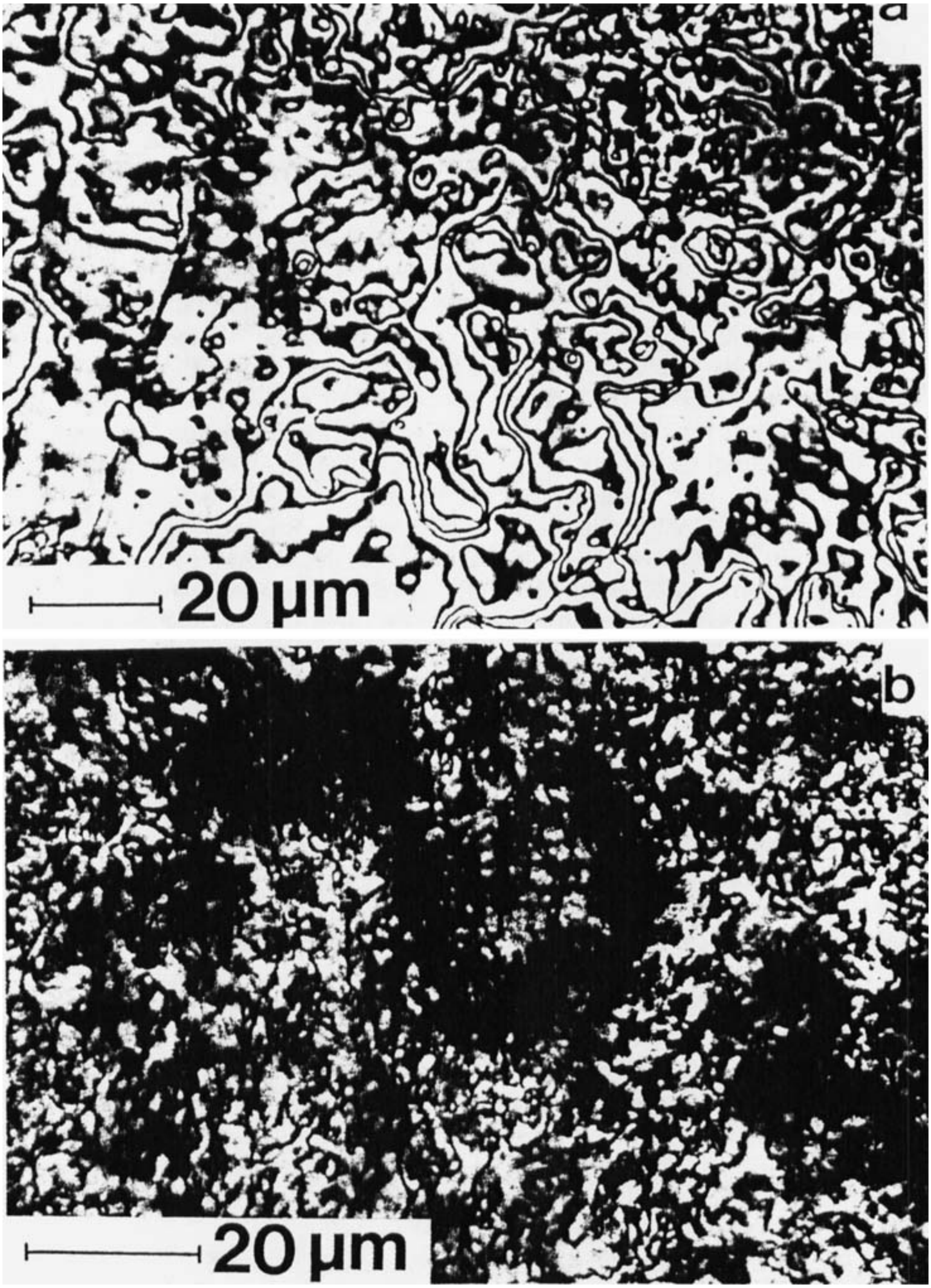


FIGURE 12 Nematic textures of sheared specimens with a) a DP of 13, b) a DP of 39.

with BPT, HNA and PET. The discovery of the crystal–nematic transition for the homopolymer also suggests potential commercial application for melt processing where the contact time at 450–460° is less than one minute.[36]

PROCESSING AND PROPERTIES OF THE AROMATIC POLYESTERS

In this section, I will review the present status in processing of these materials and also discuss what is required in order that this class of materials fulfill their potential. To begin with, the thermotropic polyesters provide several important advantages over the lyotropic aramids in that they can be processed directly from the melt into a wide variety of shapes including film, fiber and molded shapes. With the development of the PHBA/BPT copolyester and more recently with the observation of a nematic melt for the homopolymer it is now possible to use low cost, rapid fabrication techniques to form shapes which can retain mechanical properties to well over 300°C. This suggests that for the first time, engineering plastics can compete with high strength aluminum as well as steel. It is important to remember that aluminum at temperatures of 225°C begins to deform and recrystallize, while many steels begin to undergo rapid oxidation processes at temperatures over 300°C. The fact that the aromatic polyesters are, for the most part, derived from relatively low cost materials whose densities are 1/5 to 1/6 the value of steel, would suggest tremendous economic advantage in the use of these polymers. Finally, the potential exists to achieve directional mechanical properties in molded shapes which far exceed the values of aluminum and are comparable to those of steel. This anisotropic character also extends to properties such as thermal expansion coefficient and possibly to thermal conductivity (see Table I). Thus, it is very important to develop and optimize processing techniques which can effectively take advantage of these anisotropic properties. In particular, it is essential that processing techniques be devised which minimize problems of skin-core effects associated with differential sheer flow typical of melt processes involving liquid crystalline materials.

Shown in Table IV is a comparison of properties of these copolyesters which have been injection molded to produce test bars with orientation in the direction of flow.[37] As is apparent, the flexural modulus is almost an order of magnitude greater than typical engineering plastics and approximately 1/4 the value of alu-

TABLE IV

Properties of liquid crystalline copolyesters (oriented)

	Xydar (2/1)	LCP-2000	PHBA/PET (60/40)
Tensile strength, psi	20,000	24,000	15,500
Tensile modulus × 10^6 psi	2.4	1.4	1.5
Flexural strength, psi	19,000	24,500	15,900
Flexural modulus × 10^6 psi	2.0	1.3	1.3
Heat deflection 264 psi (°C)	355	180	70
Processing temperature °C	410	320	280

minum. The retention of properties at elevated temperatures is dramatically illustrated by the Xydar sample which displays a heat distortion temperature of 350°C. The effect of orientation and increased order is demonstrated by examining the heat distortion temperature of the Ekkcel I-2000 shown earlier in Table II. Although these materials are identical in composition, the heat distortion temperature is only 300° for the latter material which was molded under conditions designed to minimize orientation effects. The importance of the degree of three-dimensional crystalline order can also be seen from a comparison of the heat distortion values of the LCP-2000 and of the Tennessee Eastman copolymers versus Xydar. In these two cases, the heat distortion temperatures are controlled by the T_g which are approximately 140° and 70°C, respectively.

The potential for significantly higher mechanical properties in the aromatic polyesters is illustrated from a comparison of the properties for Kevlar 49 and Sumitomo Chemical's Ekonol fiber (a modified version of the Ekkcel I-2000)(See Table III). In the direction of draw, both fibers display stiffness and strength properties comparable to steel fibers with the obvious advantage of having 1/5 to 1/6 the weight. The polyester fiber also has excellent resistance to moisture uptake and can be melt spun over a range of deniers. One shortcoming of both the Aramid and polyester fibers is their poor compressive character. This is in part related to the clearly definable skin/core effect in these fibers which results from the higher shear condition generated at the interface between the spinneret hole and the polymer melt (or solution). The shearing is further exacerbated by the anisotropic nature of the melt or solution. The end result is a skin with a high degree of orientation compared to the core. The consequences of the skin-core effect and for that matter the microfibrillar structure which constitutes the core are even more critical in highly oriented molded shapes with complex geometrics.

Attempts to produce simple molded shapes with highly directional properties have been explored.[38] Disks were injection-molded through a center port and one of the dies rotated at 30–40 rpm. In such a process, one obtains initially a radial orientation with circumferential orientation superimposed on it. The tensile modulus values in the circumferential direction are very high while the radial properties are approximately 1/3 the circumferential value. As might be anticipated, examination of specimens made in this way, display the typical skin-core effect. It is noteworthy that this technique can yield extremely high modulus values for systems other than LC polymers, e.g., polyethylene and polypropylene.

Based on the problems associated with the high shear sensitivity of liquid crystalline melts leading to the skin core effect, it would appear highly desirable to reexamine solid state metal forming techniques such as HERF mentioned early in this Section. In such processes preformed specimens heated to 300°C can be forged rapidly with a cycle time of 10 seconds. Presumably heating to higher temperatures, e.g., 400°C would permit use of forging techniques which do not require the unusually high kinetic energy impulses associated with HERF.

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