Liquid Crystalline Aromatic Polyesters

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ABSTRACT

The background to development of liquid crystalline aromatic poly-
esters is reviewed. Specific programs directed at the development
of the homopolymer of p-hydroxybenzoic acid and copolymer with
biphenol terephthalate are described. Work on novel processing
techniques is highlighted in this paper while questions of synthesis,
structure, and properties are considered somewhat more briefly.

INTRODUCTION AND BACKGROUND

The commercial development of high performance liquid crystal-
line polymers can easily be traced back to the early 1970s, with the
announced availability of Ekonol (1970), Kevlar (1971-2), and Ekkcel
(1972-3). (Tradenames for poly-p-hydroxybenzoic acid, poly-p-
phenylene terephthalamide, and the copolymer of p-hydroxybenzoic
acid/terephthalic acid/biphenol, respectively.) These developments
undoubtedly had their roots in a much earlier quest by DOD and the
aerospace industries for structural, high temperature polymers. It
is in this earlier phase, starting in the mid-1950s, that Speed Marvel
made a number of key contributions to define promising directions
that were pursued in the development of more thermally stable poly-
mers. In particular, his pioneering studies on inorganic and hetero-

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cyclic polymers provided much of the early impetus to this field and helped lay the groundwork for what followed.

Subsequently, in the early 1960s, one of the important thrusts was the search for polymers with the highest possible thermal oxidative stability. The ladder polymers, developed in the mid-1960s, were a result of this research, and again Speed Marvel was one of the major contributors in this area [1]. However, much of the momentum toward developing polymers with ultrahigh thermal stabilities began to disappear with the realization that the intrinsic thermal stability of polymers in air was limited to about 350-400°C. For example, carbon and graphite are attacked by air between 350 and 400°C, and since graphite can be looked upon as the ultimate ladder polymer, there appeared to be little likelihood for further improvements in the thermooxidative stability of polymers [2].

Also in the mid-1960s, work began to shift, particularly in the industrial laboratories, toward development of more processible polymers. One of the important directions was the goal of developing polymers which could be injection molded directly into shapes and retained some mechanical integrity up to 300°C. It was in this period where work on aromatic polysulfones and ketones was intensively pursued and when our own program on the aromatic polyesters of PHBA began to take some direction.

Our study on the aromatic polyesters of p-hydroxybenzoic acid (PHBA) was initially prompted by a report in the literature that the homopolymer of PHBA did not melt and, in fact, decomposed at 350°C [3]. This latter point appeared unreasonable, since the structure consisted of relatively thermally stable groups, i.e., phenylene and ester units. At the time, the report that the polymer was nonmelting did not appear to be a major obstacle as long as the material could be sintered. Sintering techniques were used routinely in the ceramics and metal industries to fabricate refractory shapes, and it appeared that such approaches might be essential to achieve shapes which retained their properties to temperatures in excess of 300°C. With the successful synthesis of the homopolymer of PHBA, we began to understand some of the opportunities and limitations of this novel sinterable material [4, 5]. It also became clear that a melt processible system with a use temperature of 300°C would have a far wider market potential not only as an injection molding-grade material but possibly as a fiber or film former. The earlier reports on copolymers of PHBA with m-hydroxybenzoic acid did not appear particularly encouraging because of the reported intractability of the 60/40 system [3]. Similarly, other aromatic copolymers based on terephthalic and isophthalic acids with the appropriate dihydroxy group (e.g., hydroquinone) yielded semicrystalline materials with high melting points but their use temperatures were limited by the relatively low glass transition temperatures [6, 7]. Initially, our approach was to design a copolymer of all-para aromatic polyesters in the hope that a melt eutectic would be obtained low enough for processing on standard equipment. In addition, we hoped that the linear nature of the chains would yield a continuous ordered phase and a dis-

continuous glassy phase so that going above T_g would not result in a disastrous loss in properties. In our initial studies it was found that certain aromatic copolyesters could be melt processed at temperatures of 400°C and yet showed very high heat deflection temperatures approaching 300°C [8]. The ease with which the melt tended to fibrillate under shear and the anisotropy in properties suggested that we were dealing with a material significantly different than had been anticipated. Initially, our work was directed not at maximizing the anisotropic properties but rather to minimize them during injection molding to yield a more isotropic character. On the other hand, the ease with which the material oriented under shear would be highly desirable for fibers or films. Shortly after the announcement of the Aramid fibers in 1971 [9], we were able to produce melt spun fibers of the copolymer of biphenol terephthalate (BPT) with PHBA which approached the key mechanical properties of Kevlar [10]. In the ensuing years other workers have reported on the liquid crystal character of the aromatic polyesters and shown the potential of producing injection-molded shapes with much higher modulus values in one direction [11, 12]. More recently in a study carried out at IBM, we have demonstrated that injection-molded shapes with much higher planar mechanical properties can be obtained by applying a shear rotational deformation during molding [13].

To summarize, a large amount of work has been carried out, starting in the late 1960s and continuing through the 1970s, to develop synthetic routes to these aromatic polyesters. These studies have been carried out primarily in industry where the goal has been to prepare low cost, melt processible systems that retain properties to temperatures approaching 300°C and do not discolor during high temperature processing. The data obtained to date indicates that the PHBA/BPT copolymer is the only system which uniquely satisfies these requirements. At present, work on the liquid crystalline aromatic polyesters is shifting toward development of new and innovative processing techniques with the goal of achieving shapes which take advantage of the unique mechanical properties and melt processibility. Hence, in this paper attention is focused primarily on the novel processing techniques devised for fabricating both the homopolymer and copolymers of PHBA. Questions of synthesis and structure of the homopolymer and copolymer are dealt with somewhat more briefly in the next section, since the information is available in earlier reports.

SYNTHESIS AND STRUCTURE OF THE AROMATIC POLYESTERS

Homopolymer

Studies to prepare the homopolymer of PHBA go back to over 100 years ago [3, 14, 15]; however, these approaches, which include ther-

mal polymerization of p-hydroxybenzoic acid or p-acetoxybenzoic acid, did not yield the desired product. In both cases the polymerization was carried out initially in the melt, but the oligomers solidified too quickly so that the reaction was actually run in the solid state. In these experiments it appears that the temperature must have gotten out of control so that degradation reactions began to compete with polymerization. One degradation product that is observed with both of these starting materials is the formation of the phenyl ester of p-phenoxybenzoic acid [16]. The source of such a by-product is not particularly obvious but must be related to the acid catalyzed, thermal condensation of the hydroxyl or acetoxy units to yield the diphenyl ether unit. The observed by-product could be formed by the etherification of a dimer and a monomer followed by decarboxylation at elevated temperatures.

The PHBA polymer can be prepared unequivocally by the polymerization of the phenyl ester of p-hydroxybenzoic acid or p-acetoxy benzoic acid in an appropriate heat exchange medium [16]. These approaches differ significantly with respect to the relative rates of polymerization, M_n values, and morphology. Thus, the polymerization of the phenyl ester proceeds slowly at temperatures of 275–325°C yielding a product with an M_n of 6,000–8,000. With the p-acetoxy ester the polymerization is very rapid at these temperatures, and M_n of 12,000–20,000 can be obtained; however, the polymer is isolated in the form of small single crystals. From a more practical view, the PHBA from the phenyl ester is more readily processible and hence is the monomer used in preparing the commercial product. The polymer from the p-acetoxy monomer as typically prepared displays a highly ordered single crystal morphology. In fact, fracturing under cryogenic conditions of the slablike superstructures (Fig. 1) yields very small single crystal fragments measuring a few hundred Å in thickness which can be studied by electron diffraction techniques (see Fig. 2). Depending on the time, temperature, and degree of polymerization, one can isolate a rich array of ordered morphologies which are either single crystal or are derived directly from these single crystals [17]. Thus, ordered morphologies can vary from very thin to large slablike structures and accordionlike morphologies (see Fig. 3) to needlelike shapes. The interrelationships between these morphologies has been studied and a logical etiology developed showing the effect of the synthetic variables. For example, in the SEM shown in Fig. 3, one can detect the earlier presence of a slablike morphology, which is breaking up into thin lamella, which in turn appear to be breaking up further into thin needles. The fracture planes are across the basal plane of the crystal, and may even occur uniquely along the a and b axes where the polymer chains are held together by van der Waal and dipole forces.

Because of the single crystal nature of the polymer prepared from acetoxybenzoic acid, it was possible to carry out a reasonably com-
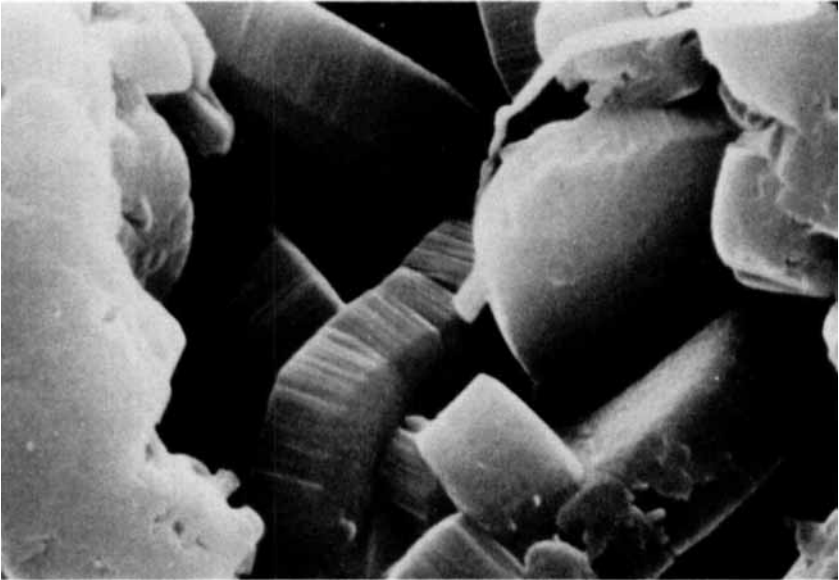
FIG. 1. PHBA slablike superstructure.

FIG. 2. Single crystal fragment of PHBA from cryogenic fracturing.

FIG. 3. PHBA accordionlike superstructure.

plete crystal structure determination using electron diffraction tech-
niques [18]. Single crystal lamella of a sample with $M_n \sim 20,000$
could be isolated by impact fracturing at liquid N_2 temperatures. Two
distinct electron diffraction patterns were obtained, one perpendicular
to the plane of the lamella and the other along the edge (which was
showing tendencies to break up into a microfibrillar structure). The
pattern taken along the edge showed a twofold symmetry (see Fig. 4)
while the pattern taken perpendicular to the lamella defined the "c"
axis. The unit cell dimensions are indicated in Table 1. From this
analysis, one can conclude that the chain axis lies in the plane of the

FIG. 4. Single crystal PHBA electron diffraction pattern showing twofold symmetry.

TABLE 1. Unit Cell Dimensions for PHBA Homopolymer

a = 7.68 Å
b = 5.80 Å
c = 12.64 Å

Orthohombic Symmetry

Volume = 563 $Å^{-3}$/unit cell

Density = 1.42 g/cm^3 (calculated)

= 1.43 g/cm^3 (measured)

lamella and more specifically along the axis of the microfibrils which are distinguishable in Fig. 3. With respect to the slablike structure, the the chain axis is perpendicular to the larger surface of the slab. At the molecular level the aromatic polyester can be described as an extended chain with a cis configuration and an angle of 57° between ester units. The chain has four nearest neighbors, and adjacent chains display a reverse head-to-tail configuration. Based on this study, it is possible to dismiss the earlier report of a double helix structure for the homopolymer [16], a structure that was suggested from earlier electron diffraction patterns indicating a threefold symmetry.

Copolymer of PHBA/BPT

As noted earlier, work on the copolymer of PHBA had its origin in the perceived need for a melt processible polymer which retained properties to 300°C. Earlier results reported on copolymerization of the acetoxy esters p-hydroxybenzoic acid and m-hydroxybenzoic acid were not encouraging since the 60/40 mixture yielded an intractable and presumably blocky polymer. On the other hand, when we prepared the copolymer from the dimer (P-HBA-m-HBA), an amrophous polymer was obtained which flowed at ~140°C [19]. One might consider preparing the trimer (p-HBA-m-HBA-p-HBA) to increase the melting point; however, this approach was unattractive both from the view of the expense of preparing such a starting material as well as the relative unavailability of the meta isomer. We also repeated some of the earlier work [6, 7] on aromatic copolyesters using m-isophthalic acid to reduce the melting point; however, such systems were semicrystalline and displayed glass transitions at relatively low temperatures.

Another approach that was pursued consisted of preparing a linear copolyester derived from two nonmelting homopolymers. As noted earlier, our goal was to obtain a eutectic which melted at ~400°C. Furthermore, if there was sufficient ordering, we might achieve a continuous polycrystalline phase with a discontinuous amorphous phase so that the high temperature properties would be dominated by crystalline phase as opposed to T_g. A large number of comonomers were tested with PHBA, and from this relatively empirical screening it was concluded that a linear copolymer based on biphenol, terephthalic acid, and PHBA appeared to satisfy most of our goals [20]. Thus, the BPT/PHBA copolymer was derived from relatively low cost monomers, was melt processible and, most important, displayed some retention of properties between 250-300°C. In fact, the 2/1 copolymer of PHBA/BPT could be melt processed at 400°C by injection molding and showed a heat distortion temperature at about 300°C. The report of Jackson [12] on the thermotropic character of their aromatic polyester provided more definitive evidence on the nature of our materials. To summarize with respect to the background, one cannot help but note the close similarity between the liquid crystalline polymers that were obtained and the relatively crude concept driving our initial work, i.e., to achieve an eutectic of a random or blocky linear copolyester in which there was sufficient order to give a continuous crystalline phase (albeit somewhat disordered).

The PHBA/BPT copolymers could be prepared from a slurry of the acetoxybenzoic acid, diacetoxy biphenol, and terephthalic acid (initially the terephthalic acid was not in solution). The reaction was continued in an appropriate heat exchange medium up to temperatures of 300-325°C. Further reaction from 325-350°C could be carried out by directly heating the free flowing powder. A number of variations
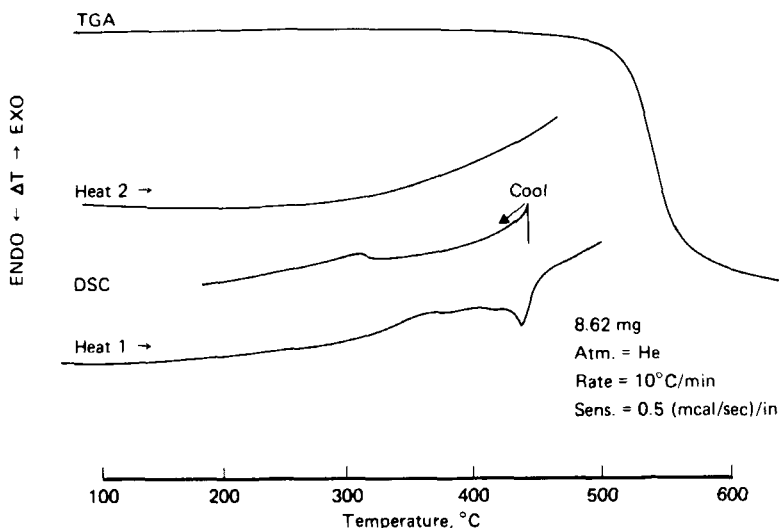
FIG. 5. DSC of 2/1 copolymer of PHBA/PBT.

were explored, including melt polymerization to oligomers, followed by grinding and advancement of the powder. The preferred synthetic route would, to a considerable extent, be dictated by the scale of manufacture.

The copolymer as prepared was insoluble in all solvents and therefore not amenable to characterization by solution techniques. Hence, approaches to analyze the degree of polymerization and the nature of the copolymer structure were not immediately obvious. Some insight on the molecular weight could be obtained from melt flow studies at different shear rates. Also, the degree of polymerization can be tracked roughly by measuring the initial melting point by DSC. Thus, at completion of polymerization, this value is approximately 425°C (see Fig. 5) while much lower values of 325-350°C are observed at earlier stages of polymerization. Approaches to studying the degree of blockiness in the copolymer were equally difficult. This was considered a problem since most of the polymerization reaction is carried out under heterogeneous conditions so that one would not expect to obtain a random copolymer typical of a homogeneous polymerization reaction. In fact, the propensity for the PHBA monomer to react with itself to yield ordered single crystals described in the previous section represented a major concern. On the other hand, the fact that this PHBA homopolymer could only be sintered and the BPT homopolymer was intractable, while those copolymers within a PHBA/BPT

ratio of 2/1 to 1/2 all melted, provided atrong evidence that copolymerization was indeed taking place.

There are two approaches for clarifying the sequence distribution of monomer units in the copolymer, namely use of C-13 solid NMR and by actually synthesizing the copolymer under conditions which would tend to yield long blocks or short blocks of PHBA. With NMR the resolution was inadequate to provide useful information on sequence distribution, but use of C-13 spectra taken as a function of cross-polarization (CP) times gave some insight into relative amounts of PHBA units in ordered versus disordered regions [21]. Typically, the carbon resonance in the ordered region cross-polarizes more rapidly because of the greater dipolar interaction in the crystalline region. Examination of a series of CP spectra for a copolymer of PHBA/BPT 2/1 showed that approximately 50% of the PHBA existed in more ordered regions. This could be readily detected from the two-step growth of the PHBA peak where ~50% cross-polarized before emergence of the BPT peak. Hence, we can infer from these results that approximately 50% of the PHBA is in ordered regions. On melting and cooling the 2/1 copolymer, one can no longer detect the two-step growth in the CP spectra, suggesting that the crystalline phase has now converted to a more homogeneous mesomorphic phase. From these results we can also conclude that the slurry polymerization reaction does not yield a mesomorphic product directly but results in a more ordered polycrystalline phase.

In another set of experiments designed to further characterize sequence distribution [21], polymerization of the PHBA monomer was first carried out to 20 and 50% completion respectively, based on acetic acid evolution. Analysis of the polymer showed that in the former case the M_n of the polymer was ~800 (6-7 units), while in the latter case the M_n was approximately 1600 (~15 units). The biphenol and terephthalic acid were added then to bring the reaction mixture to a 2/1 PHBA/BPT ratio. In the first case, continued polymerization yielded a product very similar to the 2/1 copolymer as described earlier, while in the latter case a material was obtained that showed many of the characteristics of the homopolymer of PHBA, i.e., a reversible endotherm at ~330°C and a powder x-ray diffraction more similar to that of the homopolymer. The material did not melt and flow, suggesting that the long blocks of PHBA result in a polymer with most of the characteristics of the homopolymer. Although rather crude in their design, these experiments when combined with the results from the cross-polarization spectra and the heterogeneous nature of the polymerization reaction, indicate that the copolymer has sequences of PHBA units probably between 5-10 units. Preparation of a highly ordered 2/1 PHBA/BPT where the monomer consisted of a sequence of $+$PHBA-BP-PHBA-T$+_x$ yielded a more crystalline material that was intractable and showed no transition in a DSC scan [22].

PROPERTIES AND FABRICATION OF THE
AROMATIC COPOLYESTERS OF PHBA

The excellent properties of both the homopolymer and copolymers of PHBA prompted us to explore a number of novel techniques for fabricating these materials into useful shapes. In the case of the homopolymer, the relative intractability of the material led us to examine forming techniques which are normally reserved for the more refractory metals. In the case of the melt processible copolyester of PHBA/BPT, our initial focus was directed at developing conditions for injection molding which yielded relatively isotropic character and minimized the tendency for producing sharply differing thermal expansion coefficients (TEC) at seams arising from the high shear sensitivity of these copolymers. The tendency for fibrillation during melt processing even under moderate shear was considered a serious shortcoming and hence molding conditions which minimized this characteristic were sought. The potential for molecular composites consisting of fibrils in a matrix of the same composition was recognized as an important opportunity, especially for fabricating simple shapes, but as noted above, applicability to molding complex shapes remained a deterrent. In some very recent work [13] at IBM we have been able to achieve high strength and modulus in a more planar configuration by combining injection molding with a shear rotational deformation.

In the following sections the properties of the homopolymer are reviewed and then several techniques for fabricating shapes and coatings described. The properties of the melt processible copolymers are then considered with particular emphasis on processing to generate a variety of high strength/modulus shapes.

HOMOPOLYMER OF PHBA

As noted earlier, we were not particularly deterred by the relative intractability of the homopolymer of PHBA, since capabilities were available to us to evaluate high temperature sintering processes normally reserved for forming ceramics. In fact, the material did show some flow under high pressures of 5,000-10,000 psi at temperatures of about 400°C. The reason for this flow was undoubtedly due to a loss in some of the crystalline order at about 350°C (see Fig. 6) where a very sharp reversible endotherm was observed. Thermal expansion coefficient measurements also showed a sharp increase in this temperature range as shown in Fig. 7. In addition, powder could be coalesced into brittle films by use of an electrically heated two-roll mill at a temperature of 380°C. More important, the excellent properties observed with compression sintered pieces (see Table 2) suggested an important potential for the material as a high performance engineering resin.
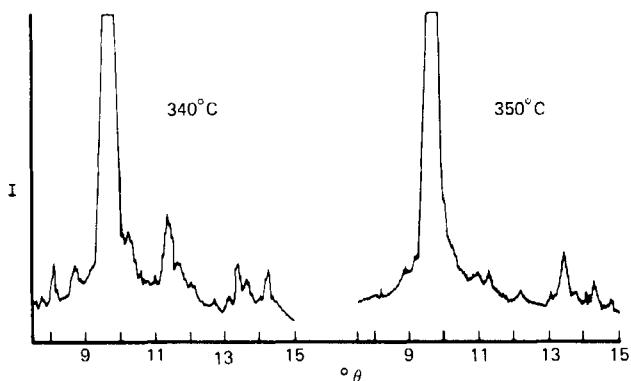
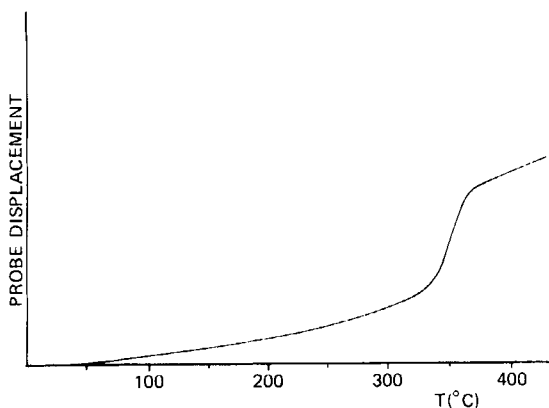FIG. 6.   Comparison of x-ray diffraction patterns of PHBA at 340 and 350°C.

FIG. 7.   Thermal expansion coefficient scan of PHBA.   Heating rate: 10°C/min.

The high temperature flexural modulus properties of the homo-
polymer compared to other engineering plastics is illustrated in Fig. 8.
The sintered specimens show a flexural strength of only 10,000 psi with
an elongation in the range of 1-2%.   The brittleness of these specimens
very likely arises from the relatively low $M_n \sim$ 6000-8000 and very

high degree of crystallinity.   The unusually high thermal conductivity
noted in Table 2 most likely arises from the high degree of crystal-
linity of the homopolymer.   The low coefficient of friction is most un-

TABLE 2. Properties of Compression Sintered PHBA

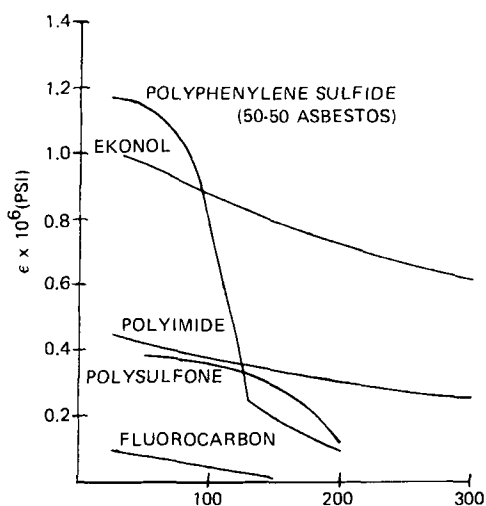|	
Density (g/cm^3)	1.44
Flexural strength (psi)	10,700
Flexural modulus (psi)	1.00×10^6
Thermal conductivity (10^{-4}/cal/s/cm$^2 \cdot °$C·cm)	18
Thermal expansion coefficient (10^{-5} in./in./$°$ F)	2.8
Coefficient of friction	0.10-0.16

FIG. 8. Comparison of flexural modulus of various engineering plastics at elevated temperatures ($°$C).

usual considering the high bulk modulus of the polymer. This property can be further enhanced by the addition of small amounts of fluorocarbon polymer. In fact, such specimen displays limiting PV values far in excess of high performance bearings such as oil-filled bronze. To better understand the mechanism by which the PHBA homopolymer responds to high surface shear, samples of the polymer that transferred to the metal work piece were examined by x-ray diffraction. As can be seen in Fig. 9, much of the crystallinity has disappeared. In fact, the x-ray pattern resembles more closely the x-ray patterns observed with PHBA/BPT copolymers which have melted and converted to a meso-morphic state. Hence, this process is not the same as the reversible
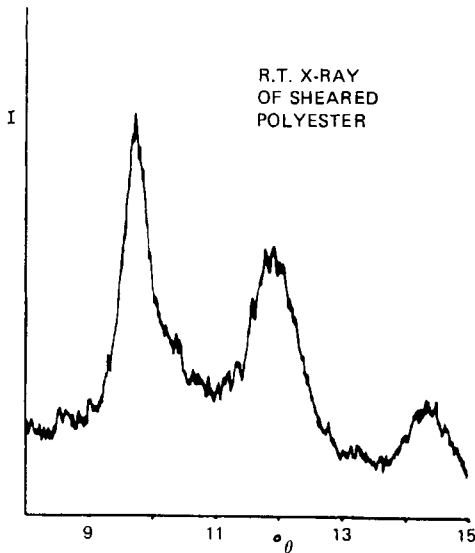
FIG. 9. X-ray diffraction pattern of thin coatings of sheared PHBA.

transition observed at about 330-350°C which is best looked upon as a
reversible topotactic transition. This irreversible transition to a less
ordered state could be interpreted as a degradative oxidation reaction.
Alternatively, one might argue that the surface shear is sufficient to
destroy the registration necessary for achieving the reversible topo-
tactic transition and that the increase in surface temperatures is suf-
ficient to induce a transition to a liquid crystalline self-lubricating
state.
    Turning to methods for processing the homopolymer, one of the
most intriguing features of this program was the ability to apply metal-
forming techniques such as forging and spray coating. Because of the
relative intractability of the homopolymer, it was necessary to use
high energy rate forging (HERF) and plasma spraying to obtain suffi-
cient flow of the polymer. The use of these techniques has been de-
scribed earlier [14], and a brief review is provided here for purposes
of continuity. The HERF technique is used to fabricate metals such as
tungsten and titanium. Typically, a force of 10,000-100,000 ft-lb is pro-
duced in such a way that most of the kinetic energy is transferred to
the work piece. To fabricate PHBA, it was necessary to use preformed
shapes which were first heated to 325°C and then forged between
15,000-20,000 ft-lb. A cycle of 6-10 s was required for inserting,
forging, and ejecting the work piece. Samples produced in this fashion
were completely fused and showed a significant degree of orientation
with the chain axis perpendicular to the direction of applied pressure.
In fact, the flexural modulus in the plane was measured at 2.3×10^6 psi

or over 2 times the modulus of the sintered piece. The fact that the forged specimens were fused and that x-ray diffraction showed strong orientation effects as well as some loss in order further suggests that we are observing some form of mesomorphic flow during the forging cycle. The need for such high temperatures and pressures associated with HERF indicates a very high viscosity normally observed with highly ordered liquid crystal structures.

The technique currently in use commercially for producing coatings is plasma spraying. The powder of the homopolymer is fed into an extremely high temperature plasma of helium. The plasma is formed by passing the helium through a carbon arc and the temperature is then maintained by induction heating. Although temperatures in the plasma may be as high as several thousand degrees C, little or no degradation is observed in the polymer coating since the contact time is so short. Depending on the condition of the plasma, one can obtain coatings which range from granular to relatively smooth coherent films. Pinholes in the coating can be eliminated by applying a surface burnishing. Coatings made in this manner can be used continuously at temperatures of 325°C. To minimize problems of stress associated with differences in thermal expansion coefficient between the polymer and metallic substrates, powders are available commercially which contain metal filler, e.g., Al powder. Interestingly, 50/50 v/o coatings of aluminum powder and the homopolymer may form what appears as two continuous phases, indicative of the fact that both materials melted and flowed during the plasma spraying process.

COPOLYMERS OF PHBA

Development of processes to fabricate liquid crystalline polymers of PHBA/BPT presents a number of challenges to exploit the potential of these materials effectively. On the one hand, the opportunity to injection mold a variety of complex shapes which retain properties to 300°C necessitates a more isotropic character in the flow patterns to minimize stresses at seams associated with differences in TEC. On the other hand, the tendency for these melts to orient under shear is exactly the feature desired in fibers, tape, and rods where high modulus and strength are required in one direction. A more complex problem is posed in the case where strength and modulus are desired in the planar direction. Obviously, to mold shapes or sheets with high mechanical properties in the planar direction requires development of new approaches. The potential for achieving more planar properties in films should be feasible using standard techniques such as bubble extrusion or biaxial orientation after extrusion.

Properties of Ekkcel copolymers as first made available in developmental quantities in 1972 are given in Table 3. The two materials differ in composition in that the compression molded grade material has a ratio of PHBA/BPT of 1/2 versus 2/1 for the injection molding grade

TABLE 3. Copolyester Properties

Properties	Ekkcel C-1000	Ekkcel C-2000
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 264 psi	300	293
Coefficient of thermal expansion (in./in./°F)	2.87×10^{-5}	1.60×10^{-5}
Specific gravity	1.35	1.40

material. This change in composition leads to significant changes in the melt flow characteristics under shear, i.e., the 2/1 system appears to flow far more easily under shear and has a strong tendency to fibrillate. Injection molding of the 2/1 copolymer at 400°C and under conditions designed to minimize shear leads to properties as shown in Table 3. On the other hand, by use of higher temperatures and a narrower gate, Jackson [23] recently has been able to prepare samples which display more anisotropic properties, e.g., flexural strength and modulus values of 2.27×10^{5} and 1.52×10^{6} psi, respectively. These results appear to be consistent with earlier data on similar polyesters [11, 12].

The development of high strength-modulus fiber based on the Aramids provides an important example of maximizing properties in one direction by exploiting the shear sensitive nature of these rodlike chains. The commercial success of this product over the past 12 years is sufficient testimony to the importance of this general class of rigid rodlike polymers. Additional advantages of the Aramid fibers included good resistance to heat and ease of processing into finished articles such as fabrics. Shortcomings are primarily associated with the manufacturing process, namely the cost of the raw materials and the need to spin filaments from a H_2SO_4 solution. In our initial studies

in 1971, we found that the aromatic polyesters based on PHBA/ BPT could yield continuous filament with modulus and strength values approaching those of the Aramid fibers [9]. Equally as important, these filaments could be spun directly from the melt, eliminating the need for use of a highly noxious solvent such as H_2SO_4. The polyester monomers were commercailly available, e.g., PHBA and terephthalic acid could be purchased directly and the biphenol was readily accessible from low cost starting materials. To achieve a nonmelting character in the fibers and enhance retention of properties at elevated temperatures, it was necessary to modify the composition of the PHBA/ BPT. By going to compositions with slightly more than 2/1 PHBA/BPT, it was possible to design copolymers which at higher MW's were intractable. Melt spinning of such material could be carried out at temperatures of 325°C by using a partially polymerized intermediate with a molecular weight of several thousand. The filament could then be advanced in molecular weight by heating at 325-350°C followed by drawing at 400°C. If one is willing to sacrifice dimensional stability to high temperature excursions such as observed in a flame, one could spin filaments directly from the 2/1 composition. This would have greatly simplify processing but have compromised some of the envisioned high temperature applications. It should be noted that formation of high strength/modulus ribbon or film oriented in one direction would be possible by a simple extension of the processes indicated above.

A goal on which we have placed a high priority was the development of molded shapes which display high strength and modulus in the plane of the specimen. As shown in Table 4, the kinds of properties that one would anticipate with a high degree of orientation in the plane would present a significant advantage in properties over fiber glass epoxy composite. Furthermore, use of injection molding techniques to achieve such shapes would greatly simplify composite lay-up techniques for achieving such shapes. During the last few years we have been exploring various techniques to achieve such a goal. We have found that by applying a rotational shear during injection molding, we can obtain a high degree of planar orientation by first injecting the polymer melt through a center port to obtain radial orientation and then by rotating one of the dies while cooling the mold to cool the specimen below its melting point or to a point where the viscosity is high enough to minimize problems of relaxation. In this way a curvilinear orientation is introduced into the specimen which provides both radial and circumferential orientation of the polymer. The flow profiles obtained in this type of molding are as illustrated in Fig. 10. To date, this technique has been used to fabricate linear polyethylene, polypropylene, and the PHBA/PET copolymer 80/20 obtained from Tennessee Eastman. Some typical modulus values are indicated in Table 5. PHBA/BPT has not as yet been processed by this technique because of the need for higher processing temperatures.

To conclude, engineering plastics have over the past 20 years found

TABLE 4

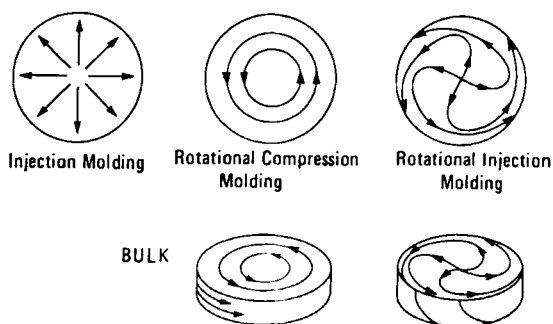|	Planar properties projected for aromatic polyesters	Reported for epoxy fiberglass
Modulus (msi)	9	2.5
Strength (ksi)	80	50
Density (g/cc)	1.4	1.9
Moisture absorbed (85% RH), %	<0.1	2
Dielectric constant	2.9	4.5
Thermal conductivity, $(10^{-4}$ cal/s/cm^2/1 ($^\circ$C))	~Steel	7
Thermal expansion coefficient $(10^{-5}$ in./in./$^\circ$C)	0	4
Continuous use temperature ($^\circ$C)	250	175

FIG. 10. Flow profiles in rotationally shear deformed specimen.

TABLE 5. Circumferential Modulus of Rotational Shear Deformed Specimens

Material	Modulus ($\times 10^6$ psi)[a]
Polyethylene	2.5
Polypropylene	0.8
PHBA/PET (80/20)	2.8

[a]Tensile modulus in the radial direction is approximately one-third the circumferential value.

extensive use in structural applications which in the past have been dominated by metals such as aluminum. Significant progress has been made in the past decade in use of new types of fiber reinforced composites as substitutes for metal for high performance, lightweight structures. With the development of liquid crystalline, aromatic polyesters, the potential now exists to fabricate high temperature, structural polymers at relatively modest costs into a myriad of forms including fibers, films, and injection-molded shapes with almost isotropic, unidirectional, or planar properties. Of the various polyester candidates, the copolymer of PHBA/BPT appears to provide the best combination of low cost, processibility (at an acceptable temperature range), high temperature stability, and mechanical properties. Techniques for fabricating these novel materials are still in their infancy, particularly for exploiting the unique mechanical properties that are potentially achievable with these liquid crystalline polymers.

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