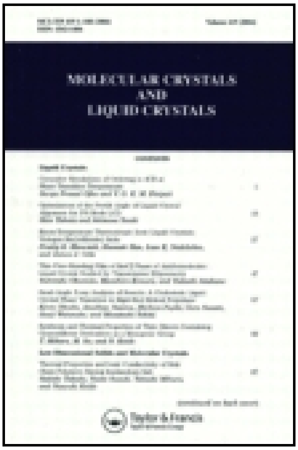

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Liquid Crystal Polymers. XI. Liquid Crystal Aromatic Polyesters: Early History and Future Trends

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Liquid Crystal Polymers. XI. Liquid Crystal Aromatic Polyesters: Early History and Future Trends

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This brief history and review of liquid crystalline polyesters (LCPs) is limited to all-aromatic LCPs except for a description of the discovery of the first thermotropic polymer to be injection molded or melt spun and characterized as being liquid crystalline: an Eastman PET/PHB (*p*-hydroxybenzoic acid) copolyester (first reported as being liquid crystalline in 1974). In the same year a Carborundum terephthalic acid/4,4'-biphenol/PHB all-aromatic copolyester was reported to be injection moldable, and later this polymer was shown to be liquid crystalline. In 1975 various Du Pont LCPs prepared with substituted hydroquinones were disclosed, and in early 1978 the first Celanese LCPs based on 2,6-oriented naphthalene monomers were disclosed. The development and characterization of all-aromatic LCPs up to 1987 are described, with the LCP classification based on the following monomers: 4,4'-biphenol; asymmetrically substituted monomers; 2,6-oriented naphthalene monomers; 3,4'-oriented benzophenone and diphenyl ether monomers; and kinking monomers. The commercial LCPs are also briefly described and future trends are discussed.

Keywords: liquid crystal, thermotropic, polyester, properties, fiber, plastic

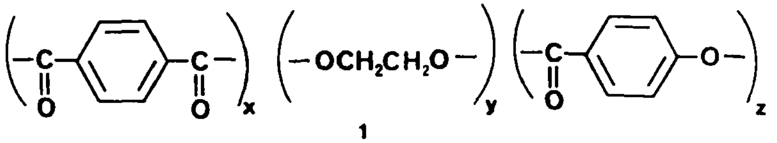
INTRODUCTION

The first thermotropic liquid crystalline polymer to be injection molded or melt spun and also characterized as actually being liquid crystalline was a copolyester of poly(ethylene terephthalate) (PET) and *p*-hydroxybenzoic acid (PHB). Because the events which lead to new scientific developments are of interest, the journal editor requested that the background leading to this discovery be described and that a history be given of aromatic liquid crystalline polyesters (LCPs). With the exception of the PET/PHB copolyesters, this history was to be limited to all-aromatic LCPs because they have the highest overall properties of the LCPs (including superior strength and stiffness in plastics and fibers, superior thermal and oxidative stability, and greater resistance to burning than LCPs containing aliphatic spacer units). These all-aromatic LCPs, therefore, exclude LCPs containing flexible spacers or cycloalkylene groups in the polyester backbone but include LCPs containing aliphatic substituents attached to aromatic rings in the backbone. Emphasis is given to the effects of composition on the melt processability and properties of LCP fibers and plastics. Procedures for preparing the polyesters and the test methods used for measuring the various polymer, plastic, and fiber properties are given in the references. In general, the all-aromatic LCPs were prepared from aromatic dicarboxylic acids and acetates of aromatic diols and hydroxy acids.

PET/PHB COPOLYESTERS

The research that led to the PET/PHB LCPs was initiated because of a desire to increase the mechanical properties, heat resistance, and fire resistance of PET fibers and plastics by increasing the aromatic content of the polymer. Before the 1972 publication of a paper[1] by F. L. Hamb of the Eastman Kodak Research Laboratories, we were aware of Hamb's modification of PET by reaction with 4,4′-isopropylidenediphenol diacetate and an equimolar amount of terephthalic acid. Since the properties of these copolyesters were of limited interest for our intended applications, we attempted to modify PET by reaction with equimolar amounts of hydroquinone diacetate and terephthalic acid. Very low molecular weight polymers having inherent viscosities (I.V.s) of only 0.1 to 0.2 were obtained after melt polymerization at 275°C to 280°C, and the polymers solidified during the polymerization when the hydroquinone terephthalate content was 25 mol% or more (75 mol% PET or less). Solid-state polymerization of these prepolymers gave I.V.s greater than about 0.4 only when the hydroquinone terephthalate content was less than 25 mol%.

It was then decided that an acyl ester of *p*-hydroxybenzoic acid might give better results. Microfilm records of research notebooks show that the first reaction was carried out in 1971 with 25 mol% of the propionate of PHB and 75 mol% of PET. A polymer with an I.V. of 0.31 was obtained, solid-state polymerization increased the I.V. to 0.39, and a heat-pressed film was clear and tough (creasable). Therefore, higher amounts of the PHB propionate were used. It was noted that at PHB levels of 35 mol% and higher the reaction mixture turned from clear to turbid as the polymerization progressed and shear opalescence was observed. Of course these effects were due to the liquid crystal nature of the polymers, but this was not suspected at the time. The copolyester contained the following repeating units:



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After it was found that a copolymer containing 60 mol% of the PHB component (x and y = 0.4 and z = 0.6 in Structure 1) could easily be prepared, two 100-gram batches were made and combined (I.V. = 0.58) in order to have enough to injection mold in a small 1-oz. injection-molding machine. To our amazement, the tensile bars had a tensile strength of 32,400 psi, and the flexural bars gave a flexural modulus of 14.4×10^5 psi, values far higher than had ever been observed with an unreinforced plastic. (Injection-molded PET bars have a tensile strength of about 8000 psi and flexural modulus of about 3.3×10^5 psi.)

Two additional 100-gram batches of the same PET/60 PHB copolyester were also prepared, combined, and melt spun with a 10-hole spinneret. The as-spun fibers had a tenacity of 3.3 g/den., elastic modulus of 196 g/den., and zero shrinkage in boiling water. Similarly spun PET fibers have a tenacity of about 2 g/den., elastic modulus of 30 g/den., and 30% shrinkage in boiling water.

Thus, by the end of 1971, it was apparent that some highly unusual polymers had been discovered. Patent applications covering the polymerization process[2] and the polymer compositions[3] were filed in 1972, and efforts were made to determine why, in the direction of polymer orientation, the tensile and flexural properties were so high and the coefficient of linear thermal expansion was essentially zero.

Table I shows some of these properties for injection-molded bars of PET and three of the PET/PHB copolyesters.[4] Note that PET/30 PHB, which is not liquid crystalline, has twice the tensile strength and 75% greater flexural modulus (stiffness) than PET, whereas PET/60 PHB has over four times the tensile strength and almost six times the flexural modulus of PET. The heat-deflection temperature (HDT, determined with a 264-psi load) is not increased because of a lack of crystallinity, but PET/80 PHB is crystalline and does have an appreciably higher HDT; the addition of 20 wt% of glass fibers to the polymer further increases the HDT to 200°C. Because the coefficients of linear thermal expansion of the LCPs are almost zero in the LCP bars, the bars did not shrink on cooling in the molds, and the mold shrinkage values are zero. As expected and desired, the oxygen index values increased with the PHB content, and PET/80 PHB is self-extinguishing in 1/8-in. thick bars (and also in 1/16-in. thick bars if 2 wt% triphenyl phosphate also is present[5]).

F. E. McFarlane in the Eastman laboratories thought that these polyesters might be liquid crystalline and, if so, should be orientable in a magnetic field. In a

TABLE I

Properties of injection-molded PET and PET/PHB copolyesters[4]

	PHB content, mol%			
	0	30	60	80
Cylinder temperature, °C	275	250	260	340
Inherent viscosity[a]				
Before molding	0.76	0.59	0.67	Insol.
After molding	0.62	0.54	0.62	Insol.[a]
Tensile strength, 10^3 psi	8.0	17.0	33.7	34.8
Elongation to break, %	24	12	20	24
Flexural modulus, 10^5 psi	3.3	5.8	18.1	14.0
Izod impact strength				
Notched, ft-lb/in.	0.3	1.0	7.8	2.2
Unnotched, ft-lb/in.	9.5	18.0	27.7	14.1
Rockwell hardness, L	73	82	42	65
Heat-deflection temp. (264 psi), °C	66	73	64	154
Mold shrinkage, %	0.6	0.1	0.0	0.0
Oxygen index	21[b]	–	30	39

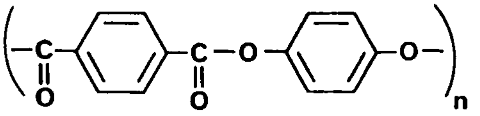
[a] Melt flow 28 g/10 min. at 325°C (0.04-in. capillary).

[b] Bar reinforced with 20 wt % glass fibers to avoid abnormally high value because of dripping.

cooperative effort with an NMR expert, V. A. Nicely, he demonstrated in 1973 that the proton wide-line NMR spectra of melts of PET/60 PHB and similar polyesters had the shape characteristics uniquely indicative of liquid crystalline melts. The first public report of this work took place when McFarlane gave a lecture in July 1974 in New Hampshire at the Gordon Research Conference on Polymers. Later this information, which included the effects of composition on liquid crystallinity of other PET copolyesters, was published as the second paper in this LCP series.[6] The first paper[4] discussed a number of the unique properties of thermotropic LCPs: very low melt viscosities; very high tensile and flexural properties of injection-molded bars; anisotropic physical properties of injection-molded plaques, depending upon the direction and degree of orientation of the polymer chains; and an essentially zero coefficient of linear thermal expansion in the direction of polymer orientation. The process and composition patents[2,3] also indicated that the copolyesters can be used as reinforcing agents to increase the strength and stiffness of other plastics, and one of the patents[3] pointed out that the copolyesters can be blended with other polymers, such as polyesters of aromatic diols and aromatic dicarboxylic acids, to reduce their melt viscosity and improve processability.

EARLY LCP-TYPE AROMATIC POLYESTERS

In an early review[7] of Eastman all-aromatic LCP results it was noted that the basic structures in liquid crystalline polyesters are benzene rings interlinked at *para* positions through ester groups:



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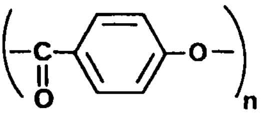

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The benzene rings can be replaced with other aromatic rings, such as biphenyl attached at *para* positions or naphthalene attached at 1,4-, 1,5-, or 2,6-positions to the linking ester groups, but the above structures can be considered to be the basic LCP structures. Structure 2 is derived from terephthalic acid (T) and hydroquinone (HQ) and Structure 3 from PHB.

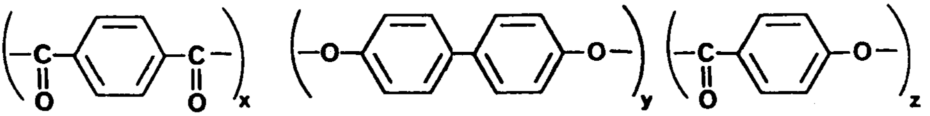
In 1959 Eareckson[8] reported poly(1,4-phenylene terephthalate) (2) to be infusible, and the next year Korshak[9] reported the melting point to be above 500°C. We prepared a prepolymer from T and HQ diacetate, further polymerized the granulated prepolymer in the solid state under reduced pressure, and obtained a melting point of 600°C with a differential scanning calorimeter (DSC) at a scan rate of 80°C/min to minimize thermal degradation.[7] For a liquid crystalline mesophase to be observed, a lower melting composition is required in order to avoid excessive thermal decomposition. Lower melting polymers can be obtained by the introduction of disorder into the symmetrical all-aromatic structure.

One method of introducing disorder is by the addition of a substituent to either or both of the aromatic rings in Structure 2. In two British patents which were issued in 1965, Goodman, McIntyre, and coworkers described aromatic polyesters prepared at ICI by heating substituted hydroquinones with terephthaloyl chloride[10] or substituted terephthaloyl chlorides[11] in an inert solvent (such as a chlorinated biphenyl) at 200°C to 300°C. Hydrogen chloride was evolved, and the polymers separated from solution. The all-aromatic compositions melted above 350°C (the actual values above 350°C were not determined), and these polymers were insoluble in all the solvents tested. The substituents were CH_3, CH_3O, Cl and Br. When asked recently about the objectives which led to this work, Goodman said that he had been interested in studying the effect of substituents on the crystallinity of the polymers, and if the polymers had melted below 300°C, he would have melt spun them.[12] [In a paper published in 1983 Majnusz, Catala, and Lenz showed that poly(2-*n*-alkyl-1,4-phenylene terephthalates) were liquid crystalline and had melting temperatures between 217°C and 300°C when the alkyl substituent attached to the hydroquinone moiety ranged from hexyl to dodecyl.[13]] Thus, the ICI workers had been close to discovering the benefits of liquid crystallinity in polyesters.

The next development in aromatic polyesters having LCP-type structures was preparation of the PHB homopolyester (3) to high molecular weight. This was reported in 1970 at the spring ACS meeting by Economy, Nowak, and Cottis.[14] These scientists found no melting point for the polyester, even at 900–1000°F (482–538°C), where the polymer decomposes rapidly.[15] (A number of years later we prepared the polyester from *p*-acetoxybenzoic acid and obtained a melting point of 610°C at a DSC scan rate of 80°C/min to minimize thermal degradation.[7]) Even though the polymer had a very high melting point, shaped objects could be prepared by compression sintering at 800°F (427°C),[15,16] however, and in a later paper Economy and coworkers[17] noted that the polyester has a reversible, high-temperature (325°C to 360°C) crystalline transition which allows compression molding below the melting point. This polymer was commercialized with the trademark Ekonol by Carborundum. Economy[18] does not consider the polymer to be liquid crystalline because it retains three-dimensional order even when compression molded.

In a 1972 Carborundum patent[19] Cottis, Economy, and Nowak disclosed copolyesters based on T, HQ, and PHB (a combination of Structures 2 and 3). Also the use of 4,4′-biphenol instead of HQ was shown in one example.[19] Since all the copolyesters cited in the patent examples with these symmetrically oriented components softened above 800°F (427°C), melt spinning and injection molding would have been difficult, but compression molding at 900°F (482°C) was disclosed for a T/HQ/PHB composition.

A copolyester based on T, 4,4′-biphenol, and PHB with the trademark Ekkcel C-1000 was offered by Carborundum for compression molding and, according to a later paper[20] by Economy and coworkers, the components of this polymer in Structure 4 were present in *x*/*y*/*z* molar proportions of 2/2/1.



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Numerous properties of compression molded test specimens were listed by Cottis[21] in 1974, and a few of these of particular interest are tensile strength 10,000 psi at 73°F and 3000 psi at 500°F (260°C), tensile elongation 7–9%, and heat-deflection temperature (260 psi load) 572°F (300°C). In the same 1974 reference[21] Cottis also reported that an injection moldable grade of the copolyester was currently being evaluated. The few "preliminary" properties of the injection molded copolyester which he listed were tensile strength 12,000 psi at 73°F and 3000 psi at 500°F (260°C), tensile elongation 6–8%, heat-deflection temperature (264 psi load) >500°F (260°C), and notched Izod impact strength 1.0 ft-lb/in. This polymer was marketed under the trademark Ekkcel I2000 by Carborundum. According to a later paper[20] by Economy and coworkers, the polymer had Structure 4 with *x*/*y*/*z* molar proportions of 1/1/2.

A technical data sheet[22] for the copolyester listed a tensile strength of 14,000 psi and flexural modulus of 700,000 psi. These values appeared to be much too low for a polymer having a chemical structure which should be liquid crystalline, so we prepared the polymer from T, 4,4′-biphenol diacetate, and *p*-acetoxybenzoic acid. The copolyester, which melted at 380°C, was injection molded at 400°C. Table II compares our results with those in the data sheet.

Our use of 1/16-in. thick tensile bars is partly responsible for the higher tensile strength (1/8-in. thick bars used for the data sheet properties) because of the higher orientation obtained in the thinner bars, but we used the same 1/8-in. thick bars to measure the flexural modulus and obtained a value twice as high. Also we obtained zero shrinkage on molding, as with other LCPs. Thus, the injection-molded plastic properties were not anomalous after all, because the expected high tensile and flexural properties and zero mold shrinkage could be obtained.[7] When asked about this later, Economy explained that the Carborundum polymer was deliberately molded under conditions (low shear) to minimize the anisotropic properties so that the molded parts could be used in applications requiring isotropic properties.[18] The polymer had not been recognized as being liquid crystalline. As Economy noted in a review[23] of their work, the report on the thermotropic character of the PET/PHB copolyesters[4] provided more definitive evidence of the nature of their materials. Later they characterized both of the T/biphenol/PHB Ekkcel compositions in greater detail and demonstrated that these copolyesters exhibit highly viscous mesomorphic melt phases.[20]

TABLE II

Properties of injection-molded 4,4′-biphenol copolyester

	Data sheet[22]	Eastman results[7]
Tensile strength, psi	14,000	22,700
Elongation to break, %	8	9
Flexural modulus, 10^5 psi	7.0	15.2
Notched Izod impact strength ft-lb/in.	1.0	0.5
Heat-deflection temp. (264 psi), °C	293	>265[a]
Mold shrinkage, %	1.2	0.0

[a] Temperature limit of oil bath used in test.

Melt-spun fibers having higher moduli than the 196 g/den. reported for as-spun PET/60 PHB fibers[2,3] were obtained by Cottis, Economy, and Wohrer with copolyesters of T, isophthalic acid (I), 4,4'-biphenol, and PHB.[24] (The I was added to reduce the melting point sufficiently to permit melt spinning.) In the first example of their 1976 patent the fibers were spun at 350°C to 400°C and then heated in air at 320°C to increase the molecular weight by chain extension and crosslinking. The resulting fibers had a tenacity of 95,000 psi (~6 g/den.) and tensile modulus of 7×10^6 psi (~420 g/den.). After the fibers were drafted about 10% in air at 400°C, the tenacity was increased to 213,000 psi (~13 g/den.) and modulus to 14×10^6 psi (~840 g/den.). The Japanese patent application,[25] which was published April 18, 1975, is the first report of polyester fibers having such high tensile properties and the first report of LCP fibers to be heat-treated to attain increased tensile properties.

DEVELOPMENT OF LCP STRUCTURE/PROPERTY UNDERSTANDING

This section deals with the further developments, approximately in the order in which they were reported, of the understanding of the structure/property relationships of all-aromatic LCPs. The discussion is based primarily on published journal and patent literature in the critical years of 1975 through 1980. (A later section will briefly discuss subsequent developments.) When appropriate, interpretations are made and unpublished results given.

Asymmetrically substituted hydroquinone monomers

The next reports on LCP-type compositions, after the early work at Eastman and at Carborundum, were Du Pont Belgian,[26] Dutch, German,[27] Swedish, and Japanese patent applications published in 1975 (and in other countries in 1976). The Belgian and German applications, which disclose data from a combination of three U.S. patent applications, are referenced above instead of the U.S. patents to show the date that this information first became public (November 1975); the corresponding U.S. patents did not issue until up to three years later.[28-30] Most of the examples in these patents involved the use of asymmetrically substituted HQ monomers, and the polyesters were shown to be liquid crystalline because they gave optically anisotropic melts.

The contributions of the individual scientists are shown in the separate U.S. patents (applications filed May 10, 1974). Pletcher[28] disclosed LCPs of chloro-, bromo-, or methylhydroquinone, a symmetrical aromatic dicarboxylic acid (preferably T), and 4,4'-(ethylenedioxy)dibenzoic acid (which prevents the polymers from being literally all-aromatic but was needed to reduce the polymer melting points to a melt-processable range). Melt-spun fibers had tenacities up to 18 g/den. after heat treatment. Kleinschuster[29] disclosed LCPs of chloro-, bromo-, or methylhydroquinone, and 4,4'-oxydibenzoic acid. Schaefgen[30] disclosed and gave numerous examples of LCPs of chloro-, dichloro-, bromo-, methyl-, dimethyl-, or ethylhydroquinone, and symmetrical aromatic dicarboxylic acids (preferably T,-

2,6-naphthalenedicarboxylic, or 4,4′-biphenyldicarboxylic). When only all-aromatic dicarboxylic acids were used with one substituted HQ, two acids were selected so that the polymer melting or softening points would be below 375°C to permit good processability. Melt-spun fibers had tenacities up to 30 g/den. after heat treatment. Schaefgen pointed out the importance of the chain-extending bonds attached to the aromatic rings being either coaxial (as in 1,4-phenylene and 4,4′-biphenylene) or parallel and oppositely directed (as in 2,6-naphthylene).[30]

When asked how he became initially involved in this work, Shaefgen[31] said that he had been in the liquid crystal polyamides program at Du Pont, knew the effect of polyamide composition on liquid crystallinity, and tried various modifications of aromatic polyesters until he succeeded in reducing the high melting points to a range which permitted melt processability of the polymers. Thus, John Schaefgen deliberately set out to produce thermotropic LCPs and succeeded.

The early Du Pont patents[26-30] disclose heat treatment of the LCP fibers in an inert atmosphere to increase their tensile properties. Robert Luise was the inventor of the fiber heat-treatment process used by the other Du Pont inventors, but his U.S. patent[32] did not issue until 1980. It is obvious, however, that Luise's discovery of the heat-treatment process was independent of the discovery by Cottis, Economy, and Wohrer[24] at Carborundum because the Du Pont U.S. patent applications were filed (May 10, 1974) before the first Carborundum foreign patent application[25] was published (April 18, 1975). Since the Carborundum filing date was August 20, 1973, patent applications which disclosed heat treatment of aromatic polyester fibers to increase fiber tensile properties were filed by two companies within nine months of each other.

When asked how he discovered the heat-treatment process, Luise[33] said that because of the concern about the low fiber properties of the early LCP fibers spun at Du Pont, he was studying the effect of temperature on the loss tangent of Sephanie Kwolek's *trans*-hexahydroterephthalic acid/chlorohydroquinone LCP fibers. He noticed that a fiber which had been heated several hours felt stronger,

TABLE III

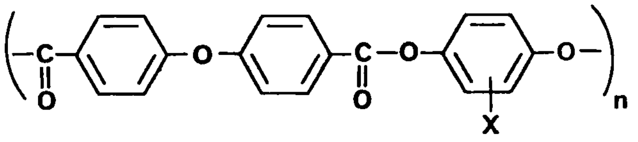
Fiber properties of polyesters of substituted hydroquinones

	R		
	Cl	CH_3	C_2H_5
Polymer I.V.	2.6	2.8	2.0
Polymer flow temp, °C	302	301	292
Properties, as-spun			
Tenacity, g/den.	6.6	5.5	3.2
Elongation, %	1.8	1.6	0.8
Initial modulus, g/den.	547	430	470
Heat-treatment, °C/hr	290/13	295–300/4.5	270–280/5.5
	260–280/2.5		300/7.5
Properties, heat-treated			
Tenacity, g/den.	30	20	12
Elongation, %	4.7	4.4	3.9
Initial modulus, g/den.	527	355	366

so he heated a sufficient amount of fiber in an oven to obtain fiber properties and discovered that the tenacity had greatly increased.

Table III illustrates three of Schaefgen's fiber compositions and the effect of Luise's heat-treatment process on the fiber tensile properties.[26,27,30,32] The LCPs were prepared from 70 mol% T, 30 mol% 2,6-naphthalenedicarboxylic acid, and the diacetates of chloro-, methyl-, and ethylhydroquinone. Our data indicate that if HQ had been used instead of a substituted HQ, the polymer melting points and flow temperatures would have been too high for the copolyesters to have been melt spun without thermal decomposition. Thus, Schaefgen's use of an asymmetrically substituted HQ and the 2,6-naphthalenedicarboxylic acid "crankshaft" type monomer were both necessary for reducing the high melting point of the basic LCP structure (2).

Kleinschuster obtained melt-processable liquid crystalline homopolyesters by the reaction of a "kinked" monomer, 4,4'-oxydibenzoic acid, with the diacetates of chloro- and methylhydroquinone[29] (5, X = Cl or CH_3).



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The tenacities of the heat-treated fibers (10 to 16 g/den.) were lower than those of the chloro- and methylhydroquinone LCPs in Table III (20 to 30 g/den.), however, because of the presence of the oxydibenzoic acid kinking component. In contrast to this composition, the homopolyester of 4,4'-oxydiphenol and chloroterephthalic acid (carbonyls and oxygens of ester group in 5 reversed) is not liquid crystalline,[7] and it is necessary to replace part of the 4,4'-oxydiphenol diacetate kinking monomer with a monomer such as chloro- or methylhydroquinone diacetate to obtain LCPs.[34]

Meta-oriented modifiers also can be used to reduce polyester melting points by the introduction of rigid kinks into the structures. Cottis, Economy, and Nowak[19] plotted the effect of PHB content on the softening and melting points of T/HQ/PHB copolyesters and I/HQ/PHB copolyesters and showed that the minimum value of the latter compositions was about 300°F (149°C) lower than that of the T copolyesters. Schaefgen[30] indicated that up to 25 mol% of aromatic polymer-forming units could have *meta* orientation, such as in I and *m*-hydroxybenzoic acid, but the preferred amount was no more than 5 mol%. Schaefgen was primarily interested in LCP fibers, and he would have observed reduced fiber properties at higher levels of modification. Also the higher modification levels reduce the polymer crystallinity, and fibers are more prone to stick together during the heat-treatment step to increase the tensile properties.

We were interested in LCPs for both plastics and fibers and, consequently, could tolerate higher levels of kinking components in LCPs for plastic applications than was possible in LCPs for fibers. McFarlane and Davis at Eastman studied the effect of I content on the preparative process and melt viscosity of polyesters prepared

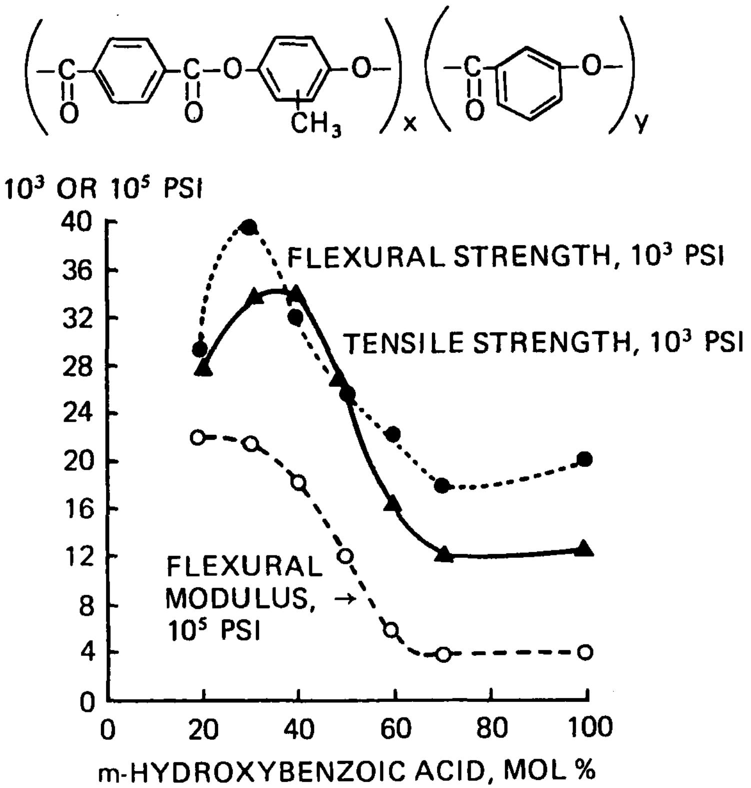


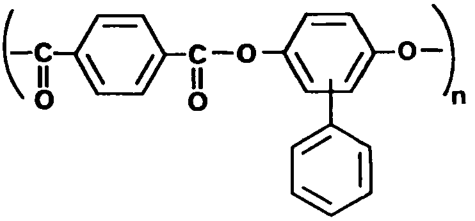
FIGURE 1 Effect of *m*-hydroxybenzoic acid content on properties of injection-molded copolyesters.

from T, I, and diacetates of substituted HQ's such as MeHQ, and in a 1977 patent[35] showed minima in plots of melt viscosity versus temperature for the compositions which were liquid crystalline. The increase in melt viscosity with increasing temperature after the minimum viscosity was reached was due to the decrease in liquid crystallinity because of the presence of the I kinking component.

LCPs of T or 2,6-naphthalenedicarboxylic acid, substituted HQs, and resorcinol are disclosed in an Eastment patent,[36] and plots[7] of the effects of resorcinol content in copolyesters with T and ClHQ or MeHQ show a decrease of tensile strength and flexural modulus in injection-molded plastics as the resorcinol content increases. Figure 1[7,37] is very instructive in showing the effect of a kinking component, *m*-hydroxybenzoic acid, on the tensile strength and flexural properties of injection-molded polyesters of T/MeHQ (*x* and *y* components in structure total 100 mol%). The lower tensile and flexural strengths obtained with 20 mol% *m*-hydroxybenzoic acid, rather than 30 mol%, may be due to the higher molding temperature (375°C) required for the 20 mol% composition (owing to its higher melting point) than for the 30 mol% composition (350°C molding temperature); more relaxation may have occurred at the higher temperature. At 60 mol% modification the melt was clear (isotropic) rather than turbid, as is characteristic of liquid crystalline melts, and almost all the high property values had been lost. (If the T and MeHQ units are counted separately rather than together as in the structure in Figure 1, a *y* component of 60 mol% calculates to be 43 mol%; that is, 43 mol% of the repeating units are kinked.)

Although kinked structures such as those just described and similar compounds are effective in reducing melting points of LCPs so they can be thermally processed,[7,38,39] these structures also reduce the extended chain orientation and the degree of liquid crystallinity of the polymers. Consequently, the tensile properties which can be attained in melt-spun fibers and injection-molded plastics are reduced.

When a small substituent (halogen or an alkyl group containing up to four carbon atoms) was attached to the HQ aromatic ring, the polyterephthalate homopolyesters melted above 400°C[7] and, as has been discussed, could not be melt processed without thermal decomposition. The next significant development in substituted HQ LCPs was the discovery at both Du Pont and Eastman that poly(phenyl-1,4-phenylene terephthalate) (6), prepared from terephthalic acid and the diacetate of phenylhydroquinone (PhHQ), melted at 340°C and was liquid crystalline.



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Payet at Du Pont made the discovery first, however, and was granted a patent[40] covering this composition; Eastman received a patent[41] disclosing similar polyesters in which a halogen or alkyl group was attached to the phenyl group. Both patents were issued in 1979.

Payet's patent[40] gives procedures for preparing 6 and a number of copolyesters and then melt spinning fibers. In spite of the bulky phenyl group attached to the hydroquinone moiety, the fibers had tenacities up to almost 30 g/den. after heat treatment for a number of hours in a nitrogen atmosphere at temperatures up to 325°C. In our work we found that the fibers could be heated in an argon atmosphere at 125°C for 1 hr and then heated directly to 340°C and held at this temperature for only 0.5 hr to obtain a tenacity of 27 g/den. (32 g/den. after 1 hr at 340°C).[7] The relatively short heat-treatment time at a temperature just below the crystalline melting point was possible because the high degree of crystallinity of the fibers prevented them from sticking together.[5] Also because of this high crystallinity, the fibers retain their tenacity at high temperatures, and Payet[40] showed that 70% of the fiber tenacity at 21°C was retained at 200°C.

Similar in this respect to the fibers, injection-molded T/PhHQ also had high tensile and flexural properties in spite of the presence of the bulky phenyl group (tensile strength 26,000 psi, flexural strength 31,000 psi, and flexural modulus 19 × 10^5 psi).[7]

Copolyesters of T and PhHQ with either *t*-butyl HQ[42] or PHB[43] or HQ[44] were disclosed in three patents, and a later paper[45] in this LCP series showed the effect of composition on the melting points and properties of these copolyesters as well as other LCPs prepared with substituted HQs. Injection-molded plastics of the various copolyesters had high tensile and flexural properties, and heat-treated, melt-spun fibers had high tensile properties.[45]

The polyesters of the substituted hydroquinone monomers discussed in this section were all prepared from aromatic carboxylic acids and acetates of aromatic hydroxy compounds. In a series of patents which issued in 1962[46–48] and 1964[49–52] Kantor and Holub at General Electric disclosed all-aromatic polyesters prepared by heating terephthaloyl, isophthaloyl, and chloroisophthaloyl chlorides with hydroquinone, chloro- or dichlorohydroquinone, 4,4′-biphenol, resorcinol, or catechol in a chlorinated aromatic hydrocarbon, such as a chlorinated biphenyl, and eliminating hydrogen chloride. So that melt-processable compositions could be obtained, it was necessary to use high levels of *meta*-oriented monomers. Films were melt pressed at 400–425°C, and fibers were melt spun. According to our present understanding of LCPs, none of the compositions of interest was liquid crystalline because of the large amount of kinking component present. It is of interest that PhHQ was used in one of the examples (Example 18 in U.S. Patent 3,160,602), and a copolyester was prepared from isophthaloyl chloride, 75 mol% HQ, and 25 mol% PhHQ. Tough, clear films were obtained by pressing samples at 400–415°C. If terephthaloyl chloride had been used instead of isophthaloyl chloride and the HQ level had not been over 40 mol% (so the melting point would not have been too high), a melt-processable LCP would have been obtained. Many years later we used this process to prepare an LCP from terephthaloyl chloride and PhHQ; we obtained a polymer with an I.V. of 2.1, melt spun it and obtained a tenacity of 6 g/den., and even then obtained fibers with a tenacity of 18 g/den. after heat treatment in argon for 1 hr at 125°C and 1 hr at 340°C.[5]

2,6-Oriented naphthalene monomers

An important development in the study of the effect of composition on the melting points and properties of all-aromatic LCPs was the discovery that 2,6-naphthalenedicarboxylic acid (N) was very effective in reducing the melting point of the basic LCP Structures 2 and 3 without the necessity of using either a substituted HQ comonomer or a kinking comonomer. This discovery was made at both Celanese and Eastman, but Celanese received a patent[53] in 1978 (patent filed in 1976) which claimed N/HQ/PHB copolyesters (because Gordon Calundann of Celanese made the discovery first), and Eastman received a patent[54] in 1979 (filed in 1977) which claimed N/T/HQ/PHB copolyesters. Figure 2[7] compares melting points (peak values of our DSC endotherms) of N/HQ/PHB LCPs (lower curve) with the DTA melting points reported by Cottis, Economy, and Nowak for their T/HQ/PHB copolyesters.[19] (The lower values plotted in their patent[19] are softening points.) Our melting points for the T/HQ and PHB homopolyesters are also added to the figure. The minimum melting points of both the N/HQ/PHB LCPs and the N/T/HQ/PHB LCPs are similar: about 325°C.[7] When Calundann replaced the HQ moiety of T/HQ/PHB with 2,6-naphthalenediol,[55] melting points somewhat lower

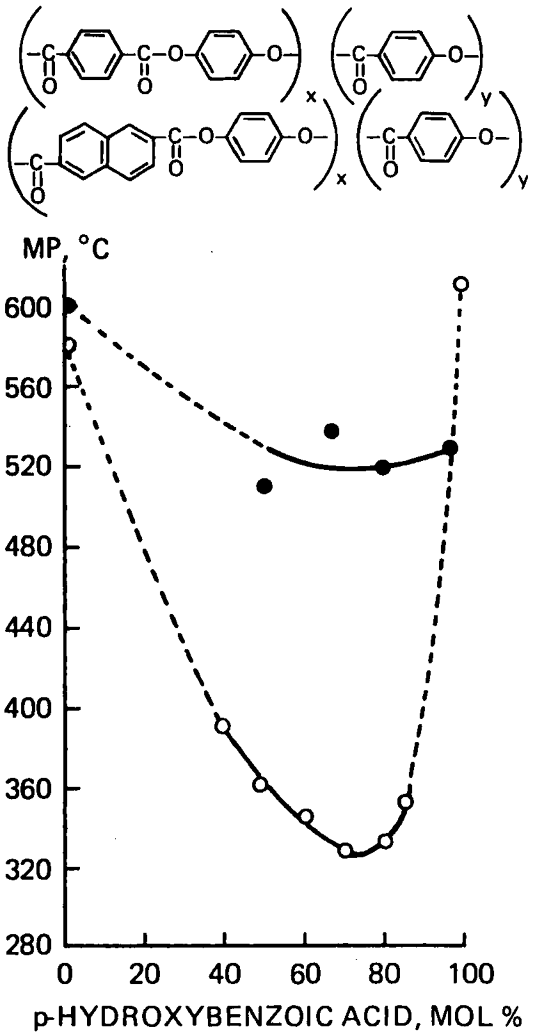


FIGURE 2 Melting points of *p*-hydroxybenzoic acid copolyesters.

than those in Figure 2 were obtained (minimum at about 280°C), and 6-hydroxy-2-naphthoic acid/PHB copolyesters had even lower melting points (minimum value at 245°C[56]). The minimum melting point of the T/4,4′-biphenol/PHB (4) copolyesters was reported by Cottis to be about 730°F (388°C).[21] Thus the "crankshaft" structure of the 2,6-oriented naphthalene monomers is particularly effective in reducing the high T/HQ/PHB melting points (minimum value about 520°C in Figure 2) to a range which permits easy melt processing of the polymers.

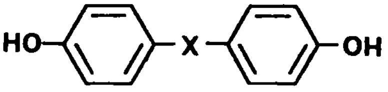
As Calundann has shown in the patents[53,55,56] disclosing the use of the three 2,6-oriented naphthalene monomers and in patents[57–59] of similar copolyesters prepared with additional comonomers, high fiber properties (tenacities over 20 g/den.) can be obtained by heat treating melt-spun fibers. In addition to the above patents, other patents which disclose all-aromatic LCPs prepared with 2,6-oriented naphthalene monomers (but not also a substituted HQ) issued during this time frame (1978–1980) to Du Pont[60] and Eastman.[61,62] The Du Pont patent[60] disclosed Irwin's LCPs from T, PHB, 2,6-naphthalenediol, and resorcinol or *m*-hydroxybenzoic acid; high-tenacity fibers were obtained after heat treatment. The Eastman LCPs were based on T, N, I, and HQ[61] and on T, N, HQ, and resorcinol.[62] Fiber and plastic properties of the latter two composition series were included in a later review[63] of Eastman work on LCPs containing naphthalene rings. Celanese work on LCPs containing naphthalene rings was also later reviewed by Calundann and Jaffe.[64]

As was noted in the preceding section, the earliest use of the "crankshaft" 2,6-oriented naphthalene monomers to help give melt-processable all-aromatic LCPs was by Schaefgen,[26,27,30] who prepared copolyesters from T, halogen and alkyl substituted HQs, and either N or 2,6-naphthalenediol. However, halogen (chlorine and bromine) and alkyl substituents on aromatic rings limit the thermal and oxidative stability of LCPs[45] and, therefore, limit use in applications requiring long exposure to air at high temperatures. Thus, the discovery that chlorine, bromine, or alkyl substituents can be avoided and all-aromatic LCPs prepared with 2,6-oriented naphthalene monomers to give high performance fibers and plastics was an important technology advance.

Classification of LCP compositions

At the Liquid Crystal Polymers Symposium at the University of Leeds in Great Britain in July 1980 it is noteworthy that the first four lectures referred to the high crystalline melting point of poly(1,4-phenylene terephthalate) (2) and methods that had been used to modify this composition to reduce the melting point without destroying thermotropic behavior. Lenz noted that three approaches had been used: "(1) the use of asymmetrically substituted hydroquinones and terephthalic acids; (2) the preparation of copolymers containing non-linear comonomers; and (3) the inclusion of soft aliphatic segments into the main chain."[38] Griffin and Cox[39] from ICI noted that the patent literature indicated three approaches which they classified as (1) "frustrated chain packing," which included unsymmetrically substituted aromatic rings and 2,6-oriented naphthalene monomers; (2) "flexible (aliphatic) links"; and (3) "non-linear (rigid) links." Our classification involved four approaches[7] for modifying the basic aromatic polyester structure: (1) flexible aliphatic units; (2) substituents on aromatic rings; (3) certain unsubstituted, rod-like components (4,4′-biphenylene ring or 2,6-naphthylene ring); and (4) rigid kinks. McIntyre and Milburn[65] cited literature references showing copolymers containing (1) rigid-rod segments only; (2) rigid-rod segments plus rigid angular elements; (3) rigid-rod segments plus flexible or semi-flexible elements; and (4) rigid units unsymmetrically substituted with groups such as chloro, bromo, methyl, or methoxy. Thus the classifications from four different laboratories recognized the same compositional elements. (Lenz's "non-linear comonomers" would have included 2,6-oriented naphthalene monomers and kinking components.)

At the conference Lenz reviewed the types of structures which had been reported in LCP patents and discussed his studies of LCPs with rigid or flexible spacer groups. In copolyesters of bisphenols (7) with ClHQ/T or MeHQ/T, he and his



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coworkers[38] noted that the bulkier *X* groups, particularly —$C(CH_3)_2$—, were more efficient in destroying thermotropic liquid crystallinity than smaller groups such as —O—. Griffin and Cox,[39] in a systematic study of replacing *para* units in a T/4,4′-oxydibenzoic acid/ClHQ LCP with various kinking monomers, observed the following "ascending order of disruptiveness towards the isotropic state":

para < *meta* < *ortho* < 4,4′-sulfonyldiphenol < bisphenol A.

Our review[7] of the effect of composition on the melting points and the plastic and fiber properties of Eastman LCPs also emphasized the importance of long relaxation times in order to attain high properties with injection-molded plastics and melt-spun fibers. Wissbrun[66] from Celanese also noted the long relaxation times, and he and Cogswell[67] (ICI) both discussed aspects of the unusual melt rheology of LCPs. McIntyre and Milburn[65] discussed the liquid crystallinity of polyesteramides they had prepared with *p*-*N*-methylaminophenol.

The history of LCPs from 1975 through 1980 has been considered in this section on structure/property relationships. During this period another type of monomer structure which gave a "crankshaft" mesogenic unit, 2,6-dihydroxyanthraquinone, was disclosed by both Du Pont and Celanese scientists, and LCP fibers having tenacities up to almost 20 g/den. were obtained after heat treatment.[60,68] A different type of liquid crystalline structure, polyestercarbonate, was prepared at Teijin from PHB, HQ, and diphenyl carbonate, and fibers having as-spun tenacities up to 10 g/den. were obtained.[69]

The liquid crystallinity in the LCPs which have been discussed so far has been primarily due to structures in which the bonds attached to aromatic rings were either opposite and coaxial or opposite and parallel. In 1980 Frazer[70] disclosed the use of diketoaromatic diols to prepare LCPs, and Irwin disclosed LCPs containing units from 4-hydroxy-3′-carboxybenzophenone.[71] These monomers would appear to give kinked structures and, therefore, reduce the liquid crystallinity and fiber properties. However, these and later patents discussed in the next section show that high tensile properties can be obtained with fibers of LCPs prepared from these monomers.

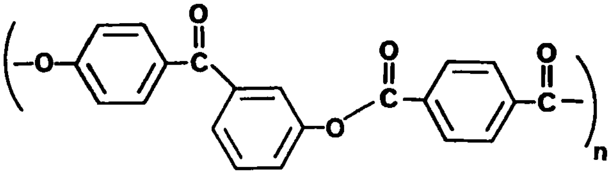
DEVELOPMENTS AFTER 1980

By 1980 scientists had a reasonably good idea of the LCP polymer structures needed in order to obtain high performance fibers and plastics, which were the most obvious high-volume applications for LCPs. Aliphatic components in the backbone of the polymers and aliphatic or halogen substituents on aromatic rings reduced the thermal and oxidative stability. Rigid kinks reduced the degree of liquid crystallinity and, as a result, increased the melt viscosity and decreased the tensile strength and modulus of fibers and plastics.

An unexpected type of structure, mentioned in the preceding section, which led to LCPs was 3,4'-oriented benzophenone monomers. Outside of this development, there have been no all-aromatic LCP structural surprises since 1980. Many patents and journal papers have been published, however, which give additional insight into details of the effects of polyester structure on melting point, liquid crystallinity, and various polymer properties. The following sections list representative patents and journal references; the list is incomplete because there have been such a large number published in the past few years. Numerous papers discuss various aspects of PET/PHB LCPs, but they are not included in the references because this history is limited to all-aromatic LCPs. For the same reason the large number of patents and papers related to LCPs containing aliphatic spacers and cycloaliphatic units are not cited, including those based on 4,4'(ethylenedioxy)dibenzoic acid, 4,4'-ethylenediphenol (bisphenol E), and *trans*-1,4-cyclohexanedicarboxylic acid.

3,4'-Oriented benzophenone and diphenyl ether LCP monomers

In a 1981 Du Pont patent[72] Irwin showed that the polyterephthalate of 3,4'-dihydroxybenzophenone (8) was liquid crystalline, and fiber tenacities of 5 g/den. as spun and almost 20 g/den. after heat treatment were obtained.



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This polyester was later described by Sweeny at a Society of Polymer Science of Japan International Polymer Conference[73] as being, to their knowledge, "the first truly helical, fully aromatic polyester" to be reported; a fiber tenacity of 31 g/den. was obtained after the fibers were heat treated at 280°C for 11 hr. The high tensile properties, which we would not have predicted, were due to the helical chain conformation of the polymer. Sweeny indicated in a conversation that they had not predicted these results either.[74] (Presumably, additional LCP structural surprises are waiting to be discovered.) Subsequent Du Pont patents disclose other LCPs prepared with 3,4'-oriented benzophenone[75-79] and diphenyl ether[75,79,80] monomers (diol,[75,78,81] hydroxy acid[76,77] and dicarboxylic acid[79,80]) and with diketoaromatic diols[75,78]; examples show heat-treated fibers with tenacities up to 20 g/den. Wunder and coworkers described the effects of temperature on the rheology and biphasic behavior of the polyterephthalate of 3,4'-dihydroxybenzophenone.[82]

Asymmetrically substituted aromatic LCP monomers

Numerous patents which disclose new LCPs prepared with asymmetrically substituted hydroquinones, terephthalic acids, or hydroxybenzoic acids have issued since 1980. The companies which have been involved in developing these compositions include Eastman (PhHQ),[44] Du Pont (phenylterephthalic acid[83,84]; *t*-butyl HQ[85]), ICI (unsubstituted and halogen- or alkyl-substituted salicylic acids[86]), Rhone-Poulenc (alkyl- or halogen-substituted HQs in polyestercarbonates[87]), Allied (Me or *t*-butyl HQs in polyestercarbonates[88,89]), Teijin (alkyl and aralkyl HQs[90]), Asahi (phenoxy HQs[91]), Bayer (3-chloro-4-hydroxybenzoic acid[92]), and Owens-Corning Fiberglas (1-phenylethyl HQ[93-95]). High fiber or plastic properties were generally reported in the examples.

In a Du Pont patent[96] which discloses a process for accelerating the heat-strengthening of LCP fibers by first coating the fibers with certain inorganic compounds (preferably potassium iodide or chloride), the examples illustrate the invention with PhHQ and ClHQ LCPs. In another Du Pont patent[97] Zimmerman disclosed a process for melt spinning LCPs and obtaining high as-spun tenacities (up to 15.6 g/den.) with certain PhHQ copolyesters.

Many journal papers which describe the syntheses and properties of LCPs prepared with asymmetrically substituted HQs or terephthalic acids have been published since 1980. The authors include Lenz and coworkers (higher alkyl-substituted HQs[13]; cycloalkyl and branched alkyl HQs[98]); Noel and coworkers[99] (MeHQ); Krigbaum and coworkers[100] (Cl, Br, Ph, hexyl HQs; Cl, Br, Ph Ts); Ballauff[101] (dialkoxy Ts); and Jin and coworkers[102] (Cl, Br, Me, Ph HQs; nitro, Br Ts). The LCP properties discussed in these papers were primarily DSC studies, X-ray studies, and liquid crystalline phase identifications. Our investigation of the effects of polymer composition on the rheological, plastic, and fiber properties of LCPs prepared with various substituted HQs also has been published,[45] and our latest paper describes the effect of heat-treatment temperature on the tenacity of T/PhHQ fibers heat treated in nitrogen and in air.[103]

The T/PhHQ homopolyester[40] (melting point 340°C) and T/PhHQ/HQ copolyesters[44,104] are of particular interest because they are easily melt-processable and because the phenyl substituent, unlike alkyl, alkoxy, or halogen substituents, does not reduce the polymer thermal or oxidative stability.[45] A comparison of the thermal-oxidative stabilities of films of LCPs prepared with various substituted HQs was made at 150°C and 300°C.[45] At 150°C the effect of the substituent on stability in air was as follows:

$$\text{phenyl} \gg \textit{tert}\text{-butyl} > \text{chlorine} > \text{methyl}$$

These observations were the basis for a process[105] for improving the chemical and solvent resistance of polyesters prepared with a chloro-, bromo-, alkyl-, or alkoxy-substituted aromatic diol by heating them in air (to crosslink the surface and thereby increase the solvent resistance).

In an earlier paper[7] our estimates of the T/PhHQ molecular weights determined by gel permeation chromatography were too low because we had assumed that the

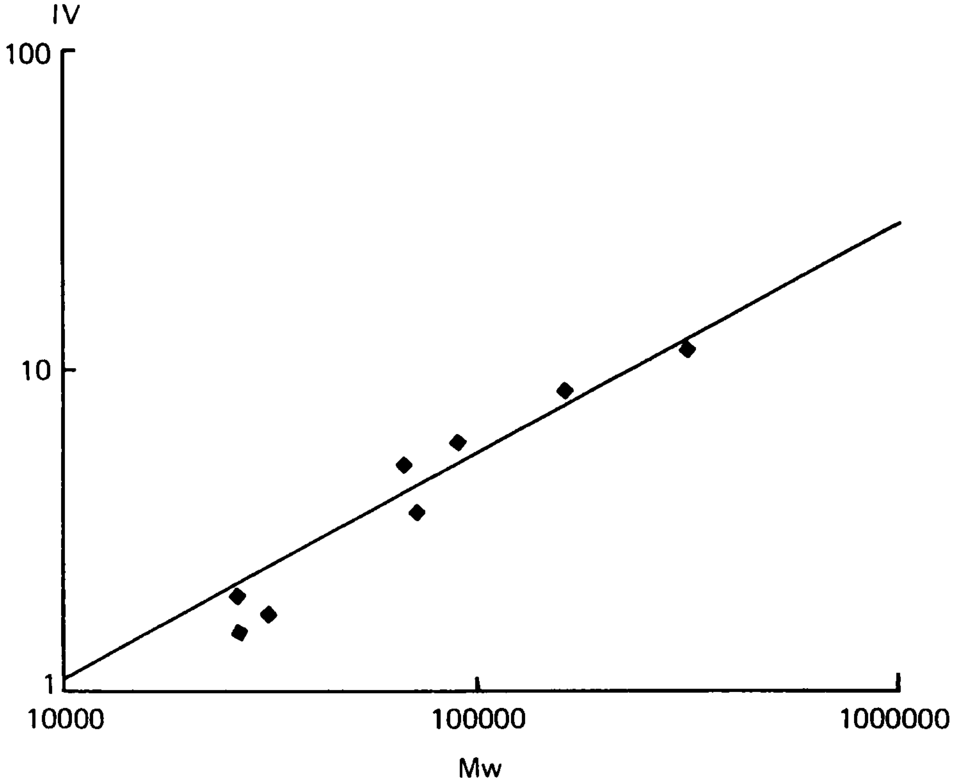

FIGURE 3 Correlation of inherent viscosity and molecular weight of poly(phenyl-1,4-phenylene terephthalate); inherent viscosities were determined in a 25/40/35 wt% mixture of phenol/*p*-chlorophenol/tetrachloroethane and molecular weights by LALLS in 1/1 by weight *o*-dichlorobenzene/*p*-chlorophenol.

universal calibration is applicable to rigid-rod molecules. The molecular weights were later determined by low-angle laser light scattering and, because of the widespread interest in this polymer, the results are shown in Figure 3.[106] With this information it was possible to correlate fiber tenacities and molecular weight, e.g., about 6 g/den. for 30,000 molecular weight and 20 g/den. for 300,000 molecular weight T/PhHQ fibers.[103]

4,4′-Biphenol LCP monomer

As discussed earlier, Cottis, Economy, and Nowak[19,21] at Carborundum found that T/4,4′-biphenol/PHB copolyesters melted low enough to be molded. Because the minimum melting point of these LCPs is reported to be about 388°C,[21] additional modification is required if lower melting polymers are desired. At Celanese[107] this was accomplished by adding a small amount of 6-hydroxy-2-naphthoic acid. At Bayer[108] the T component was replaced in part or completely by carbonate groups, and polyestercarbonates were obtained. At Du Pont[85] *t*-butyl HQ was added. The examples in the patents show high fiber tensile properties after heat treatment[107] or high injection-molded plastic properties.[85,108]

At Dart Industries[109] a flow modifier was added to the T/4,4'-biphenol/PHB LCP to permit lower molding temperatures; in the patent examples, the flow modifiers were copolyesters prepared from I, 4,4'-biphenol, and PHB.

At Sumitomo Chemical[110] I was added to reduce the melting point of T/4,4'-biphenol/PHB copolyesters, and a process was disclosed for treating and melt spinning the polymer and then heat treating the fibers. In one example fibers were obtained with a tenacity of 30.8 g/den. and an appreciably higher elastic modulus, 1420 g/den., than can be attained with most LCP fibers. This fiber is being commercialized by Sumitomo Chemical.[111]

At IBM, Economy and coworkers studied the two commercial T/4,4'-biphenol/PHB Carborundum copolyesters (which Economy helped to develop many years earlier[19]) and characterized their tendency to exhibit liquid crystalline behavior.[20] Approaches for achieving isotropic, uniaxial, and planar flow patterns were described in a subsequent paper.[112] Economy also reviewed the early development of these copolyesters.[23] While discussing these LCPs in a lecture at an IUPAC Symposium[113] in 1985, Economy commented that increasing the amount of the 4,4'-biphenol component decreased the liquid crystallinity and strength properties of the plastics because the two benzene rings in the diol are twisted with respect to each other.

The technology for producing the T/4,4'-biphenol/PHB copolyesters was purchased from Carborundum by Sumitomo Chemical[114] and by Dart and Kraft,[115] the production process was modified, and LCPs were offered under the trademarks Ekonol and Xydar.

2,6-Oriented naphthalene LCP monomers

As noted earlier, LCPs can be prepared with 2,6-oriented naphthalene monomers without also an alkyl- or halogen-substituted monomer or a kinking component and melt-processable polymers can be obtained which give high performance fibers and plastics.

A few of the additional Celanese patents which have issued since 1980 and disclose these LCPs are listed in the References[116-120]; fiber tenacities of 5 to 8 g/den. as spun and up to 23 g/den. after heat treatment were reported in the examples. Similarly, the use of these 2,6-oriented naphthalene monomers has been disclosed in LCP patents issued to other companies, e.g., Du Pont[78,80,121] and Fiber Industries.[122] Celanese patents[123-125] also disclose processes for extruding LCPs prepared from these monomers and the effects of processing conditions on the tensile properties of fibers or films. Other Celanese patents disclose blends of the LCPs with various polymers such as polyarylene sulfides,[126] polyalkylene terephthalates,[127-128] bisphenol polycarbonates,[129] and aromatic polyethersulfones.[130] Kiss[131] discussed the benefits of blending the Celanese LCPs with various isotropic polymers, such as an aromatic polyetherketone, polyethersulfone, polyetherimide, polyarylate, and polycarbonate.

Celanese patents also disclose polyesteramides prepared with the 2,6-oriented naphthalene monomers and *p*-aminophenol,[132-135] *p*-phenylenediamine,[132-135] and *p*-aminobenzoic acid[136]; melt-spun fibers in the examples had tenacities up to 12 g/den. as spun and up to 29 g/den. after heat treatment. A composition based on a 60/20/20 molar ratio of 6-hydroxy-2-naphthoic acid/T/*p*-aminophenol, for instance, gave as-spun fibers with a tenacity of 9.3 g/den. and heat-treated fibers with a tenacity of 29 g/den.; injection-molded test bars had a tensile strength of 36,000 psi, flexural modulus of 2.2 × 10^6 psi, and notched Izod impact strength of 5.8 ft-lb/in., all very impressive properties.[132]

In 1985 Celanese commercialized LCPs with the trademark Vectra for extrusion and high performance plastics applications.[137,138] One basic composition appears to be a copolyester based on PHB and 6-hydroxy-2-naphthoic acid and a second composition appears to be a polyesteramide of 6-hydroxy-2-naphthoic acid, T, and *p*-aminophenol. The polyesteramide reportedly has the higher retention of tensile strength and modulus at high temperatures. Some of the properties of the injection-molded plastics are compared with those of the Xydar LCPs in a later section.

The development of the Celanese LCPs has been described in reviews,[64,138] and numerous journal papers describe various properties of these polymers, particularly the PHB/6-hydroxy-2-naphthoic acid LCPs. Scientists who have conducted X-ray studies include Blackwell and coworkers (see References 139–142 for a few of their many papers); Stamatoff[143]; Mitchell and Windle[144]; Ward and coworkers[145]; Butzbach, Wendorff, and Zimmerman[146]; and Nakamae and coworkers.[147] Rheological and orientation studies were carried out by Ide and Ophir.[148,149] Sawyer and Jaffe[150] studied the morphologies of fiber and injection-molded specimens having a wide range of orientations. Thapar and Bevis[151] studied the micromorphology of injection-molded specimens after chemical etching. Donald and Windle[152–155] studied the banded structures of oriented LCPs by transmission electron microscopy. Cao and Wunderlich[156] studied the polymers by DSC and polarizing microscopy. Clements, Humphreys, and Ward[157] studied molecular motion by broad-line NMR. Muramatsu and Krigbaum[158] studied the effect of fiber spinning conditions and heat-treatment conditions on fiber properties.

Thus various aspects of these LCPs prepared with the 2,6-oriented naphthalene monomers have been studied at Celanese and at many universities. Our work with these monomers, particularly 2,6-naphthalenedicarboxylic acid, has been reviewed; melting point comparisons showed that copolyesters prepared with PHB and 1,4- and 1,5-oriented naphthalene monomers melt too high to be melt processable.[63] In addition, our last publication in this LCP series described the effects of spinning conditions (capillary *l*/*d* ratio, fiber take-up speed) and heat-treatment time on fiber tensile properties of one of these LCPs, and reasons were discussed why all-aromatic LCP fibers give 2 to 3 times higher tenacities after heat treatment than fibers of LCPs containing flexible spacers.[103]

Kinking monomers

In the preceding sections the primary means for reducing the high melting point of the basic LCP structure (2) to a melt-processable temperature was by the use of LCP monomers such as 3,4′-oriented benzophenone and diphenyl ether monomers, asymmetrically substituted hydroquinones and terephthalic acids, 4,4′-biphenol, and 2,6-oriented naphthalene intermediates. Sometimes a small amount of a kinking monomer, such as I, was also used; substantial amounts, however, decrease the liquid crystallinity and, therefore, increase the melt viscosity and decrease the tensile and modulus properties which can be attained in fibers and plastics.[7] In this section all-aromatic LCPs are described in which none of the above monomers was present and the kinking component, therefore, was required for reducing the polyester melting point to a melt-processable temperature range.

Deex at Monsanto disclosed LCPs prepared from I, HQ, PHB, and small amounts (0 to 6.7 mol%) of 4,4′-isopropylidenediphenol.[159,160] (When present, the latter component prevents the LCP from being literally all-aromatic because of the isopropylidene group.) At Bayer, LCPs were prepared from I, HQ, PHB, and 4,4′-dihydroxybenzophenone.[161] (In 1972 Cottis, Economy, and Nowak at Carborundum first disclosed I/HQ/PHB copolyesters[19]; the similar modified copolyesters disclosed by Monsanto and Bayer are described as having improved processability and improved properties on injection molding.) At Mitsubishi Chemical, LCPs were prepared from T, 1,4-naphthalenediol, PHB, and *m*-hydroxybenzoic acid[162]; the degree of anisotropy of the physical properties of injection-molded specimens could be controlled by the level of the *m*-hydroxybenzoic acid component in the polymer. (Because 1,4-naphthalenediol[63] gives higher melting LCPs than 2,6-naphthalenediol, the *m*-hydroxybenzoic acid is also needed to reduce the polyester melting point so that the polymer can be melt processed.)

Erdemir, Johnson, and Tomka carried out X-ray diffraction, TGA, and DSC studies with a series of I/HQ/PHB copolyesters and concluded that compositions containing 50 to 67 mol% PHB (50 to 33 mol% 1,4-phenylene isophthalate) were potentially useful thermotropic copolymers.[163] Kiss studied the rheology of a similar series of I/HQ/PHB LCPs and observed that in some compositions the melt viscosity increased with shear rate and with temperature.[164] Jin, Lee, and Park studied the thermal, optical, and rheological properties of a series of T/resorcinol/PHB copolyesters and observed that random copolyesters containing 50 and 60 mol% PHB (based on all repeating units) showed nematic optical textures under high shear, whereas blocked polymers were isotropic.[165]

Commercial LCPs

As noted earlier, in the 1970s Carborundum offered two T/4,4′-biphenol/PHB Ekkcel resins.[20,21] This technology was purchased by Sumitomo Chemical, and Ekonol resins were offered in Japan.[114] Also the technology was purchased by Dartco Manufacturing, a subsidiary of Dart & Kraft, and similar Xydar LCP resins were commercialized in 1984.[115,166] In 1985 Celanese commercialized Vectra LCP resins[137]; the resins are also marketed in Japan by Polyplastics, a joint venture of Daicel and Celanese.[167] One of the three Xydar grades contains a talc filler[166]; the Vectra grades contain particulate or mineral fillers, or graphite flake, glass fibers, or carbon fibers,[168] presumably to reduce the cost and the anisotropy of injection-molded parts and to impart certain desirable properties. Table IV compares some of the published property ranges of the injection-molded Xydar[166] and Vectra[169] resins. The most obvious difference in the property ranges is the higher heat-deflection temperatures of the Xydar resins. This is due to the very high crystalline

TABLE IV

Properties of injection-molded Xydar and Vectra LCPs

	Xydar[166]	Vectra[169]
Tensile strength, 10^3 psi	11.8–18.2	20–35
Tensile modulus, 10^6 psi	1.2–1.4	1.4–5.5
Break elongation, %	3.3–4.9	1.6–7.0
Flexural strength, 10^3 psi	16.2–19.0	22–43
Flexural modulus, 10^6 psi	1.6–1.9	1.3–5.0
Notched Izod impact strength, ft-lb/in.	1.4–3.9	1–10
Heat-deflection temp. (264 psi), °C	316–355	180–240
Limiting oxygen index, %	42–47	35–50

melting point, 421°C, of the basic LCP; consequently, a melt temperature of 400°C to 430°C is required for injection molding.[170] These Xydar and Vectra compositions also have excellent solvent resistance and electrical properties.

The high-melting Xydar resins are "expected to replace metals, ceramics, glass, composites, thermoset and thermoplastic resins, and other materials in such areas as telecommunications equipment, computers, aerospace, and automotive parts."[166] Expected market areas for the Vectra resins include electrical/electronic components, chemical processing, automotive, medical, aircraft, aerospace, consumerware, and fiber optics.[137,168]

Both Dartco and Celanese are reported to have joint ventures with a second company to develop high performance LCP fibers. Allied Fibers, a division of Allied-Signal, had plans to produce high tenacity, high modulus fibers under a joint development licensing agreement with Dartco.[171] These plans may be affected, however, by a report[172] in late 1987 that "an agreement in principle" has been reached for Amoco Chemical to purchase the commercial plastics operations of Dartco, which at the time was a unit of Premark International. The LCP melting point of the fiber composition is reported to be 720°F (382°C),[171] so apparently the T/4,4′-biphenol/PHB composition used by Dartco for molding applications has been modified to reduce the melting point (421°C) sufficiently to permit melt spinning. Similarly, Kuraray in Japan is reported to be developing a Vectran LCP fiber based on a Celanese composition.[173] Also, in a joint program Sumitomo Chemical and Japan Exlan, a subsidiary, have developed a high-tenacity, high-modulus fiber[111]; the composition is apparently similar to that of the Dartco/Allied fiber. The EKF fibers are reported to have a 30.8-g/den. tenacity, 1080-g/den. modulus, 2.9% elongation, and 0.0% water absorption.[174]

Three companies in Europe have developed LCPs. According to a recent report,[174] ICI is offering two new LCPs with heat-deflection temperatures of about 230°C, BASF has three developmental Ultrax LCPs, and Bayer has three trial LCPs.

A LCP which will compete with the above all-aromatic compositions in extrusion and plastics applications is Unitika's Rodrun LC-5000, a PET/PHB copolyester produced under a license from Eastman Kodak.[175–177] Even though not all-aromatic because of the presence of a small amount of a PET component, the polymer has excellent physical and electrical properties, a heat-deflection temperature (264 psi load) of 180°C, and excellent solvent resistance. Unitika also developed PET/PHBs for different applications, such as coatings for optical fibes (joint program with Nippon Telegraph and Telephone).[167] PET/PHB LCPs have a large advantage over other LCPs: a lower selling price because of the use of lower priced starting materials.

FUTURE TRENDS

An indication of the many scientists who have been involved in the development and study of all-aromatic LCPs can be obtained from the list of references at the end of this brief history (and the list is certainly incomplete). But one safe prediction can be made: Even more scientists will contribute to the development of these fascinating polymers which have such a unique combination of properties—melt viscosites lower than those of all other all-aromatic thermoplastic polymers; high solvent resistance; and orientability on extrusion or injection molding to give plastics, fibers, and films having high tensile strengths, high moduli, high heat resistance, and very low coefficients of linear thermal expansion.

Although the presence of halogen, alkyl, and alkoxy groups on aromatic rings (and alkylene or alkyleneoxy spacer groups between aromatic rings) does limit the thermal and oxidative stability of LCPs, for many applications the stability is quite adequate. The most important criterion is the price of the LCP: If the price is low, applications will be found, and if the price is high, the number of applications will be limited.

For this reason the use of diketoaromatic diols and of 3,4′-oriented benzophenone and diphenyl ether monomers is probably limited because the syntheses given for the diketo[70,75,78] and 3,4′-oriented[71,72,75,77] aromatic monomers in the LCP patents show that these intermediates are expensive to prepare. Of the substituted hydroquinones, the one of greatest interest is phenylhydroquinone, and an improved process for its preparation is being developed at Tennessee Eastman. LCPs prepared with substantial amounts of it, however, will still be relatively expensive. Lower cost syntheses for LCP monomers are needed, and it is believed that they will be developed.

Economy noted that "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 processability."[23] At IBM, rotational shear has been applied during injection molding, and specimens were obtained which contained both radial and circumferential orientation.[23,113] Even though injection-molded LCP plastics are noted for their very high tensile and flexural properties in the direction of orientation, it has been observed that for some applications two other properties, excellent processability and excellent solvent resistance, are of even greater importance.[178]

Celanese anticipates an LCP market breakdown in the mid-1990s to be 73% consumer/appliance, 8% industrial, 5% electrical/electronics, 5% telecommunications, 4% transportation, 3% aircraft/aerospace, and 2% other.[179] The growth of LCP usage is expected to take place partly by the replacement of metals, ceramics, thermosets, and other high performance thermoplastics by suitable design of LCPs into the next several generations of devices.[179]

As lower priced LCPs became available and more is learned about the control of the anisotropy of molded parts, numerous uses for LCPs will develop. In fact, the most important applications for LCPs probably have not yet been discovered, but these new applications will take advantage of the unique properties of LCPs.

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