



Technical Paper

LCP Introduction To Liquid Crystal Polymers



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ABSTRACT

Liquid crystal polymers (LCPs) present a special category of material which straddles the boundary between an ordinary solid and a liquid. From their first discovery in the laboratory to the realization that liquid crystals also exist in biology, these unique molecules are now omnipresent in a broad spectrum of modern-day applications. Different from typical thermoplastics such as polyesters and other aromatic polymers, LCPs have significant higher order structure particularly apparent in their liquid phase. This feature gives LCPs a host of particularly useful material properties such strength, dielectrics, chemical reactivity (resistance), and biocompatibility for medical applications. In this latter vein, Zeus has introduced LCP extruded as a monofilament fiber for use as vascular catheter reinforcement braiding. As a non-metallic braiding, catheters made with LCP monofilament can be used under magnetic resonance imaging (MRI). This imaging technique precludes the use of metals, and to date, no widely accepted MRI-compatible catheter has been achieved. Included here is an overview of LCPs, their unique chemical structure and orientation, and their relevance in industry as thermoplastics. We compare LCP monofilament to other catheter braiding materials including stainless steel and multifilament yarn. We show that LCP braiding rivals stainless steel in several areas and offers improved catheter construction. We present that catheters made with LCP monofilament braiding are poised to become the first fully MRI-compatible catheters both for performance and manufacturability.

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INTRODUCTION

Liquid crystal polymers are a unique class of material that only relatively recently has gained widespread interest. Liquid crystals, the building blocks of liquid crystal polymers, blur the boundary between properties of an ordinary liquid and a solid. These special molecules have even been found in biological molecules including DNA and micelles. Yet, appreciation of their significance almost did not happen. But where did these unique molecules come from? What is their origin? Once thought to be an unusual state of matter, liquid crystal polymers are now thoroughly embedded in our daily lives. Today, these special polymers are of greatest interest and utility in the area of thermoplastics. From food containers to mechanical parts to monofilament fibers, liquid crystal polymers have proven to be highly versatile – both in molecular design and properties.

LIQUID CRYSTALS: DISCOVERY

The origin of liquid crystal study is typically traced back to Austrian chemist and botanist Friedrich Reinitzer. In 1888, he observed and later wrote about the strange behavior of a solid after exposing it to changing temperatures. Using solid cholesteryl benzoate, Reinitzer noticed that at one temperature the solid became a hazy liquid, yet at a higher temperature, the hazy liquid became clear [1]. When cooling the clear liquid, again Reinitzer saw the liquid pass through two different color forms before returning to the original white solid with which he began [1]. Reinitzer had observed two different melting points for the same material – a phenomenon which should not exist. Perplexed by his discovery, Reinitzer forwarded the solid white material along with his findings to Otto Lehmann, a physicist working out of Aachen in what is now present day Germany.

Lehmann was better equipped to study the material than Reinitzer and expanded upon Reinitzer's work. Lehmann placed the material which he had received from Reinitzer on a microscope equipped with a heat stage and observed the material while heating it [2]. Lehmann observed the first (intermediate) hazy liquid as the white solid melted just as Reinitzer had. He described seeing crystallites – multiple small crystalline formations with irregular borders. Lehmann realized that this first intermediate *fluid* appeared to be crystalline in nature and that it must in fact be a new state of matter [2]. After further studying and refining his ideas, Lehmann named his discovery a *liquid crystal* [2]. Lehmann's (and Reinitzer's) observation received significant attention at the time, particularly after Lehmann published his findings in 1900. Indeed, by the early twentieth century nearly 200 other compounds were found to show liquid crystal behavior. However, after this initial attention, no practicable application for this new discovery was forthcoming, and interest in this new area of science soon waned.

While Reinitzer and Lehmann are routinely given note as the originators of liquid crystal science, they were also likely aware of earlier work by fellow German Wilhelm Heintz. This highly published and productive chemist had done significant work on fatty acids. By 1850, Heintz had noted that certain natural fats had two different melting points [3, 4]. His observations were nearly identical to Reinitzer's and Lehmann's: As Heintz raised the temperature of the fat substance he was analyzing, the substance first became cloudy, then fully opaque. Finally, the substance turned completely clear with continued heating [3, 4]. Just as Reinitzer's and Lehmann's official discovery in time garnered no real appreciation, so was the case with Heintz's observation on two melting points for a single substance. This observation of two melting points, however, would later become fundamental to identifying a liquid crystal.

THE NATURE OF THE LIQUID CRYSTAL

What Reinitzer, Lehmann, and others had found was a new state of matter somewhere between a true solid and a liquid. The liquid crystal contained small elements which appeared to be crystalline in nature but were suspended in a liquid phase. Also, unlike typical pure substances which

melt precisely at a given temperature, liquid crystals exhibited *two* melting points. This liquid crystal new in-between phase of matter was thus termed a *mesophase*. The individual molecules in the substance capable of forming a mesophase, or liquid crystal, are termed *mesogens*. These molecules are usually small to moderate size organic molecules and arrange themselves in varying degrees of organization or order. However, not all of these self-organizing molecules within the liquid crystal participate in the ordering thus giving the liquid crystal its unique behavior as neither a solid nor a liquid. As an example, gelatin is a substance which exhibits a mesophase.

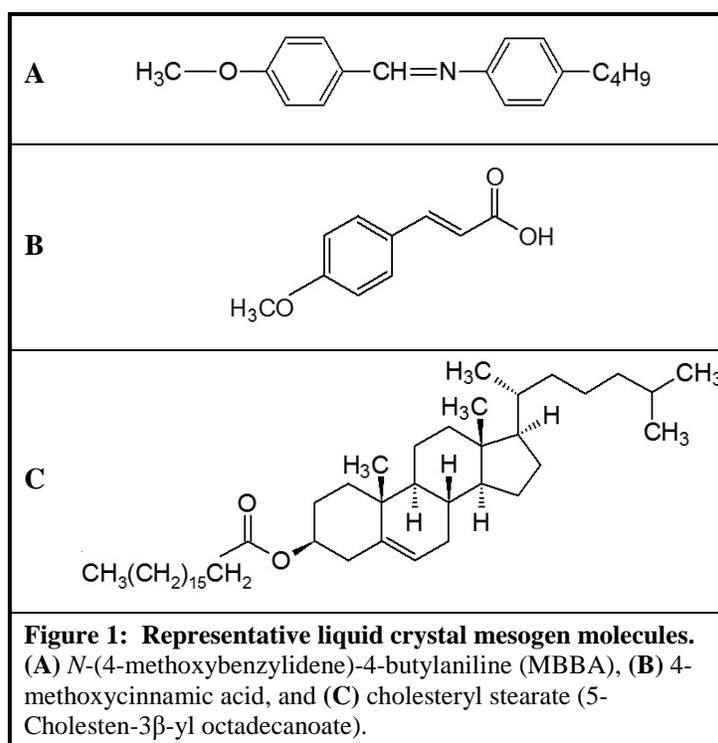
Further developments in the study of liquid crystals refined their natural character. Two general types of liquid crystal were determined: those that came about by heating a solid and those that resulted from addition of a solvent. Liquid crystals that could be brought about by solvation are called lyotropic; those of the type that Reinitzer and Lehmann discovered were the result of heating and are called thermotropic liquid crystals [5]. Thus, when considering mesophases (liquid crystals), it is perhaps more appropriate and for ease of understanding to view the changing states or *phases* of the mesophase substance as transitions from solid to liquid crystal to liquid. Both thermotropic and lyotropic mesophase types would have particular importance in industry and biology.

Making up the mesophase itself are the small organic molecules within it. While not all molecules are capable of forming mesophases, the possibilities for mesogenic molecule types are nearly limitless. Thus, mesogens usually have some degree of non-uniformity in their structure and connectivity of atoms; that is, they are not symmetrical. This non-symmetrical nature implies that the molecules have some degree of directionality and that certain of their qualities or properties vary according to this directionality. This directionality of properties is called *anisotropy*. As an example, *N*-(4-Methoxybenzylidene)-4-butylaniline (MBBA), the first synthetic liquid crystal molecule, is asymmetrical and exhibits anisotropic properties in its liquid crystal phase (**Fig. 1**). Conversely, molecules that are entirely symmetrical have properties that do not vary based upon any directionality; they are called *isotropic* [6]. These descriptors of isotropy and anisotropy can be extended to higher forms of matter to include solids, liquids, and gases. The degree of isotropic

and anisotropic character of the mesophase (liquid crystal) consequently dictates its behavior.

While liquid crystals exhibit unique behavior differing from solids and liquids, they also show myriad character even among themselves and other liquid crystals. At the root of the diversity of liquid crystals are the diverse arrangements of their mesophase molecules which contribute to their micro-crystalline formations. Among the first to organize and classify the different types of liquid crystals based on these arrangements was French mineralogists and crystallographer Georges Friedel.

Fundamentally, Friedel's mesophase classification focused on symmetry as a primary explanation for mesophase behavior [7, 8]. In 1922, Friedel proposed three classes based on the structure of the mesophase [7]. Since then, study has expanded the number and detail of liquid crystal structure descriptions, a full description of which is beyond the scope of this paper. This article, thus, will limit discussion of liquid crystal structures to isotropic (liquid), nematic, smectic A, smectic C, and crystalline (solid) forms.

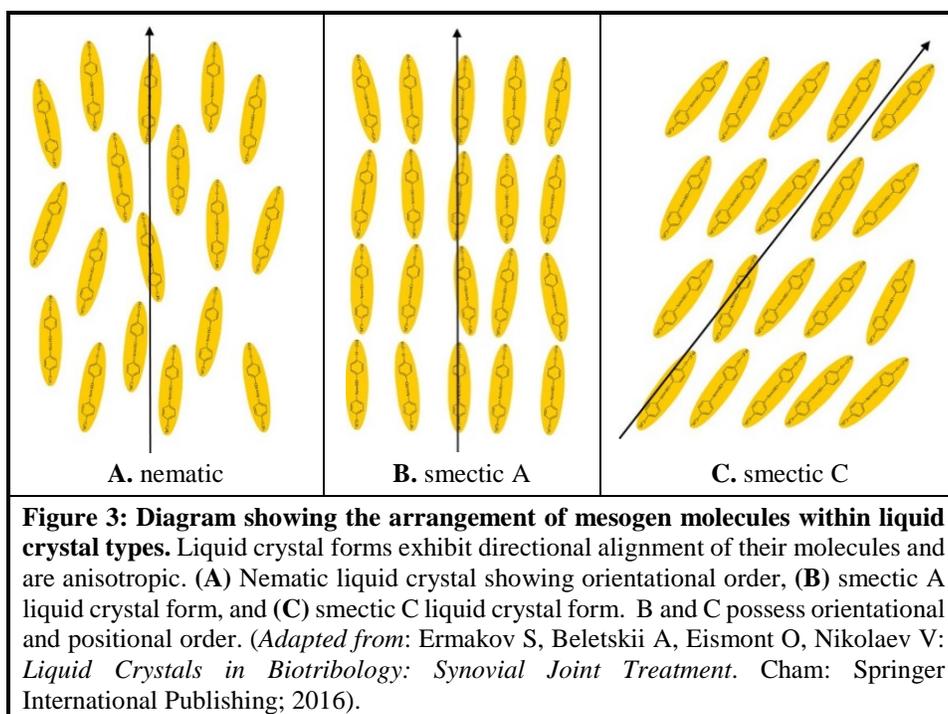
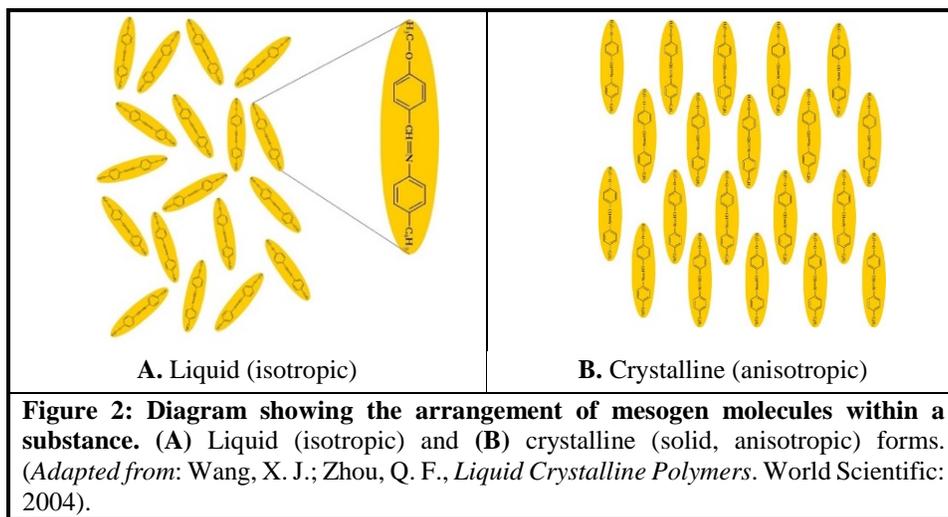


The orientation of the mesogen molecules lies at the heart of liquid crystal functionality. Recall that the liquid crystal lies in between the two fundamental states of liquid and solid. In a liquid, the mesogenic molecules become arbitrarily oriented with no directionality and form an isotropic fluid (**Fig. 2A**) [5]. These liquid state molecules have no fundamental order, and this liquid phase is isotropic in nature. Conversely, in their solid state, these same molecules are highly ordered and closely packed with almost no translational freedom (**Fig. 2B**). For liquid crystals, however, the distinguishing feature is that their

mesogenic molecules – which are non-symmetrical in nature – self-align along a definite axis; this axis is called the *director* (**Fig. 3**) [5]. This positional orientation along the director is the critical element for the formation of nematic and smectic liquid crystal structures as well as of the solid (crystalline) phase [9]. The longer range order of the liquid crystal is typified by the director. Nematic liquid crystal molecules, for example, maintain their directional orientation but do retain some freedom of movement within the liquid crystal (**Fig. 3A**) [6]. Smectic mesogenic molecules are arranged such that their principal axes are

parallel with their centers of mass in one plane; these liquid crystals exhibit positional as well as directional order (**Fig. 3B and C**) [5]. The material properties of liquid crystals such as optical activity, magnetic, and electrical properties are thus anisotropic. These properties aid in distinguishing liquid crystals and are largely the result of the degree of

mesogen directionality [10]. For a liquid, which is isotropic, these properties show no variation regardless of the direction from which they are measured. Apart from thermodynamics effects, the behavior of the liquid crystal is thus dictated by the pattern of mesogen alignment.

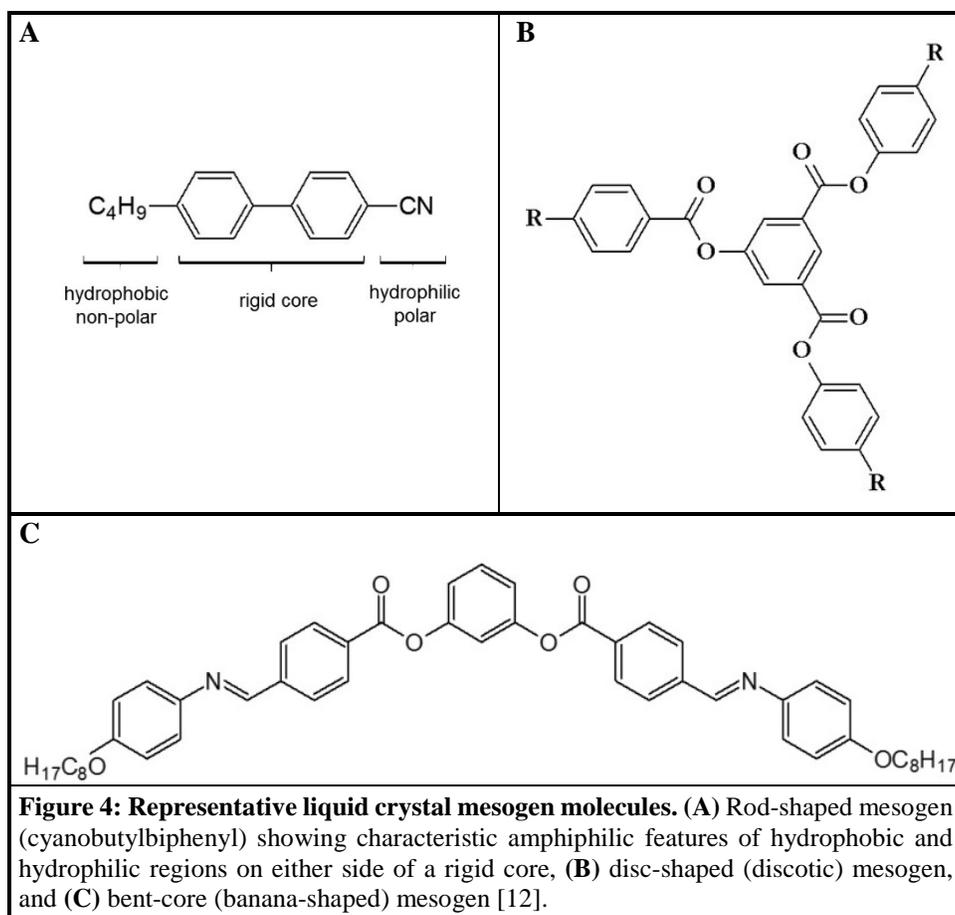


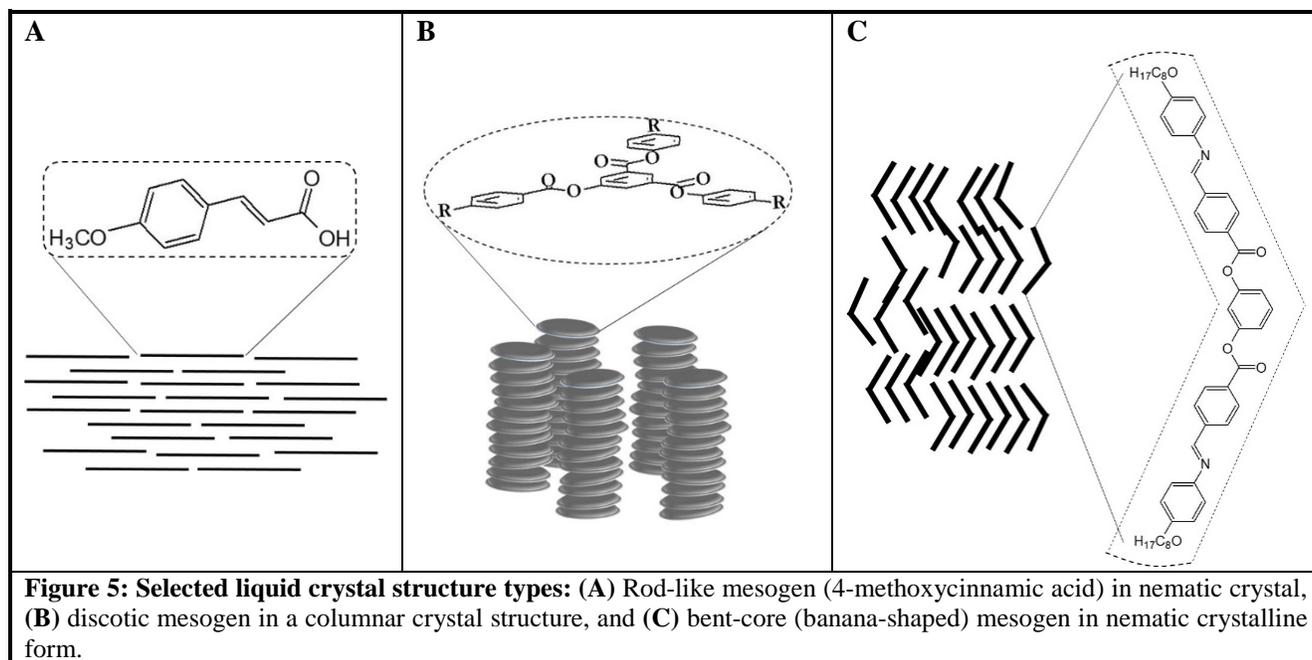
TYPES OF LIQUID CRYSTALS

Aside from their asymmetrical nature, liquid crystal materials generally exhibit several other characteristics in common. Like MBBA, mesogen features usually include rigidity along its longitudinal axis, a rod-like or ellipsoid molecular (monomer) structure, strong dipoles, and are easily polarized. These rod-like (calamitic) monomers possess a hydrophobic non-polar end and a polar hydrophilic opposite end – a characteristic called *amphiphilic* (**Fig. 4A**). Liquid crystals may also be composed of disc-shaped molecules and bent-core or banana-shaped molecules (**Fig. 4B and C**). Bent and disc-shaped mesogen molecules also have amphiphilic regions which facilitate their aggregation into liquid crystals just as rod-like mesogens [5].

Distinguished from their monomeric composition, liquid crystals may form many differing simple and

complex shapes when in their liquid crystalline states which effect their functional attributes. Rod-shaped (calamitic) liquid crystals can display a range of mesophases including nematic and varying smectic forms depending on the temperature (**Fig. 5A**) [6]. Disc-shaped (discotic) liquid crystals usually form nematic or column-like structure phases (**Fig. 5B**) [6]. Bent-core mesogens can display crystalline structures including nematic, smectic, and a range of their own unique banana liquid crystal phases (**Fig. 5C**) [11]. Liquid crystal phases may also be composed of rod-like and disc-like molecules combined into one complex structure [10]. This diversity among monomeric mesogen types and subsequent self-assembly results in a nearly limitless number of arrangement modes for these liquid crystalline structures. The concomitant properties of these liquid crystals have thus fostered a broad area of scientific research producing many significant innovations.

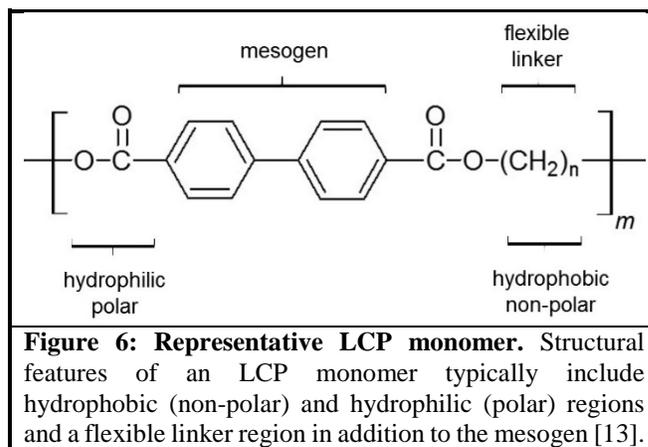




LIQUID CRYSTAL POLYMERS

The liquid crystals described heretofore represent the first generation of discovery and subsequent study of these unique molecules for utilitarian purposes. Later, investigators realized that liquid crystals also formed from more complex polymeric molecules. Rather than from just small-molecule individual mesogens, *liquid crystal polymers* (LCPs) consist of repeated monomer units but which are linked to form extended chain-like molecules. The primary units of the polymeric chain are attached to one another via a flexible linker which can be of varying lengths (**Fig. 6**). These polymeric chains aggregate to form LCPs just as single mesogen molecules do to form liquid crystals. The extended chain length of the polymeric units, however, affects enhanced intermolecular interactions

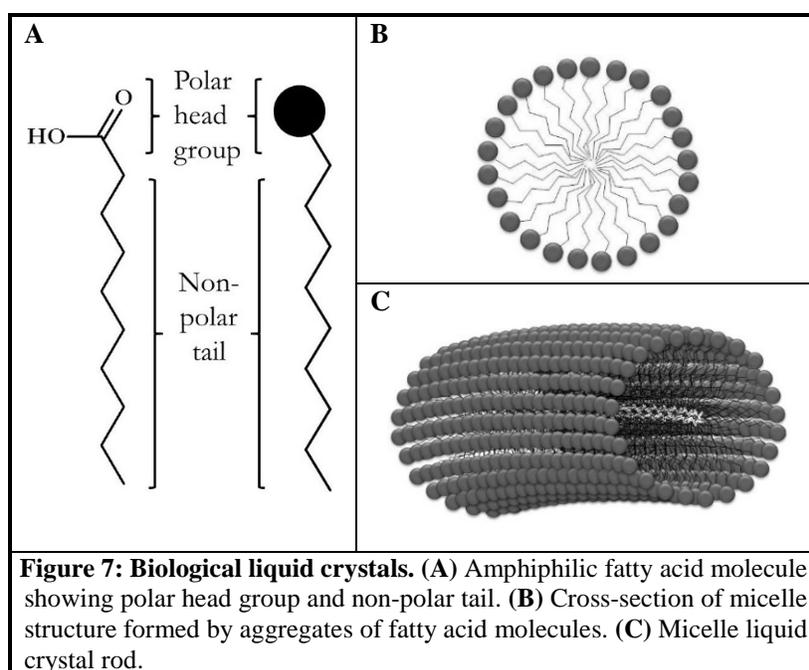
between the polymeric chains and thus has profound effects upon LCP behavior distinct from simple (non-polymeric) liquid crystals.



BIOLOGICAL LIQUID CRYSTAL POLYMERS

As suggested by Heintz and others, LCPs also exist in the biological realm, and these molecules bear many similarities with their non-biological counterparts. Biological LCPs are typically of a lyotropic nature but are likewise affected by temperature. Biological LCP monomers, too, are amphiphilic possessing a polar group at one end and a non-polar group at the other. Fatty acids,

for example, possess both a hydrophobic tail and hydrophilic head and aggregate into *micelles* which form liquid crystals [14] (**Fig. 7**). More complex amphiphilic lipid molecules, the primary component of cell membranes, and some viruses also possess liquid crystal phases [6]. DNA – the most important biological molecule – also has a liquid crystal state [15]. Each of these naturally occurring molecules has architectural or structural orders that are retained in their viscous state. Thus, despite their late arrival upon the scientific discovery frontier, LCPs are not nearly as uncommon as once believed.



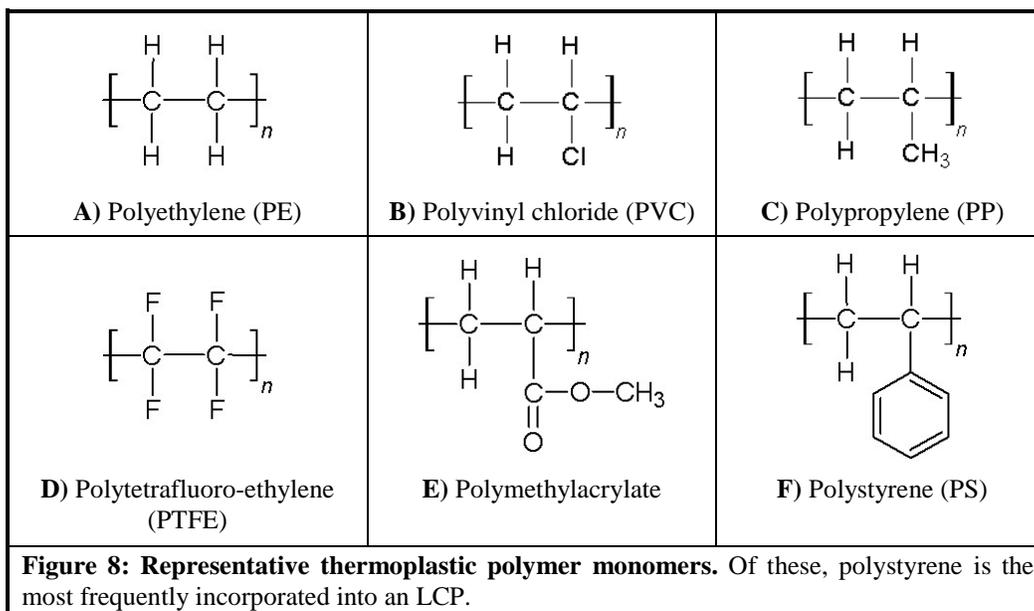
THERMOPLASTICS AND SYNTHETIC LIQUID CRYSTAL POLYMERS

The liquid crystal polymers generating much interest today are particularly those in the area of thermoplastics. Thermoplastic polymers, including LCPs, exist in everyday use and are known by such familiar names as polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polytetrafluoroethylene (PTFE), polystyrene (PS), and Kevlar® (**Fig. 8**). As thermoplastic

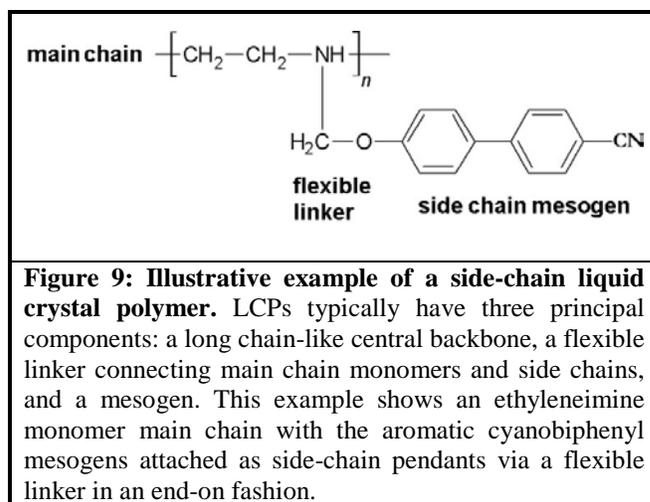
polymers, these materials become softer upon heating and can be remolded to form different shapes. While thermoplastics are made from a variety of polymers, not all are made from liquid crystal polymers. Typical plastic polymer chains maintain varying degrees of interaction between their chains when flowing, but LCPs distinguish themselves from these because LCPs retain significant crystallinity in their flow state. This partial crystalline structure also imparts properties that are unique to LCPs, and these properties can be manipulated to suit a broad

spectrum of applications. Since their initial development, innovations in LCP processing have produced plastics with exceptional strength, toughness, and high temperature and

chemical resistance. Today, LCP plastics are employed in diverse areas ranging from laser beam deflectors to automotive and aerospace parts to food containers.



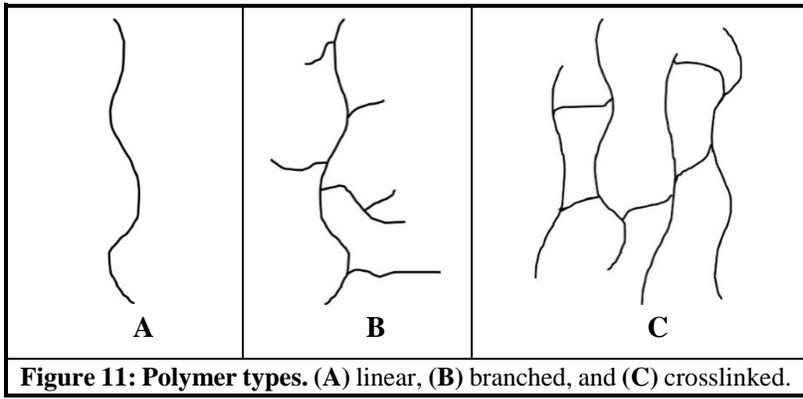
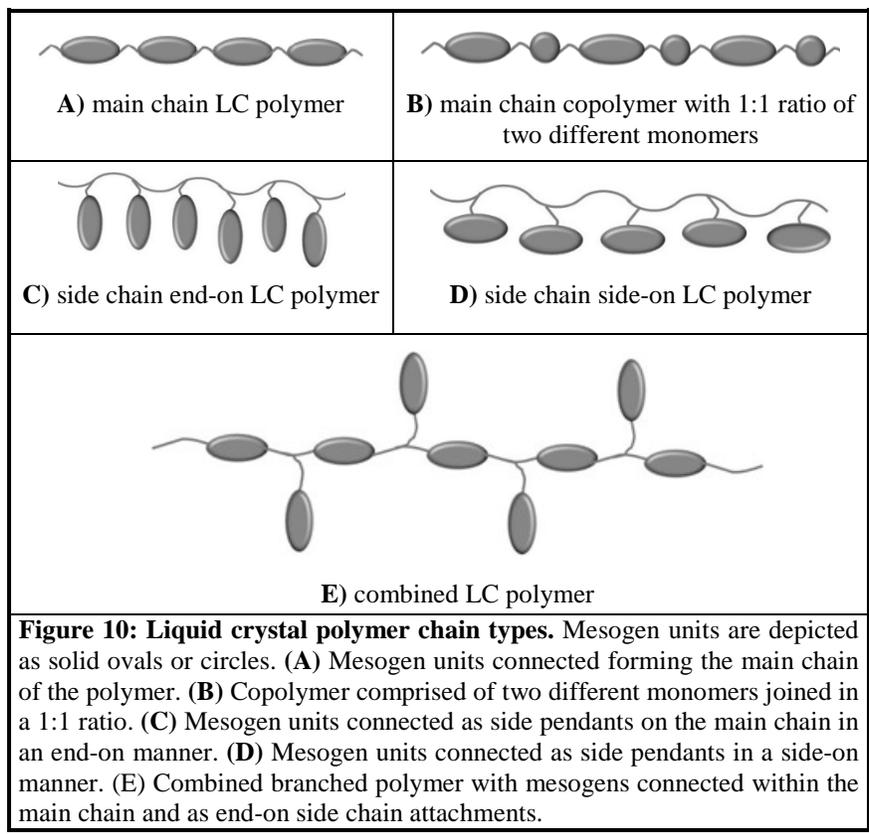
LCP thermoplastics specifically encompass a broad group of organic molecules primarily based upon polyesters and other aromatic polymers such as polystyrene. These polymers form a range of higher order structures beyond those of ordinary liquid crystals or typical polymer plastics. LCP structures are described based upon their connectivity and linkages. Like biological liquid crystal polymers, synthetic LCP structures contain repeated monomers in chains linked in a variety of ways but which form regular repeated structures. They typically contain a flexible central chain connecting the more rigid mesogen segments. When not joined within the main chain of the polymer, the mesogens are usually connected to the main chain via a flexible linker segment (**Fig. 9**). Each LCP unit thus features the characteristic amphiphilic polar and non-polar segments of the mesogen in addition to linker and non-mesogen chain components.



LCP chains can have varying linkages as well as varying monomer components. Main chain LCPs have mesogenic units connected in the central or primary molecular chain (**Fig. 10A and B**) [10]. LCPs can be

copolymers incorporating two or more different monomers (**Fig. 10B**). Side chain LCPs have their mesogenic units connected to the central chain or backbone as side pendants (**Fig. 10C and D**) [10]. LCPs may have mesogenic units connected both as side chains and as part of the backbone (**Fig. 10E**) [10]. The manner of attachment of side groups to the main chain or backbone of the polymer also affects their functionality. These groups may be joined to the main

chain via a lateral or side-on attachment, an end-on or terminal attachment, or via an off-center or shoulder attachment (**Fig. 9, 10C, and D**) [10]. LCP chains may also be crosslinked to one another forming networks that aid in preserving the liquid crystal itself (**Fig. 11**) [6]. These non-linear linkages and crosslinking likewise influence the final properties of the LCP [4].

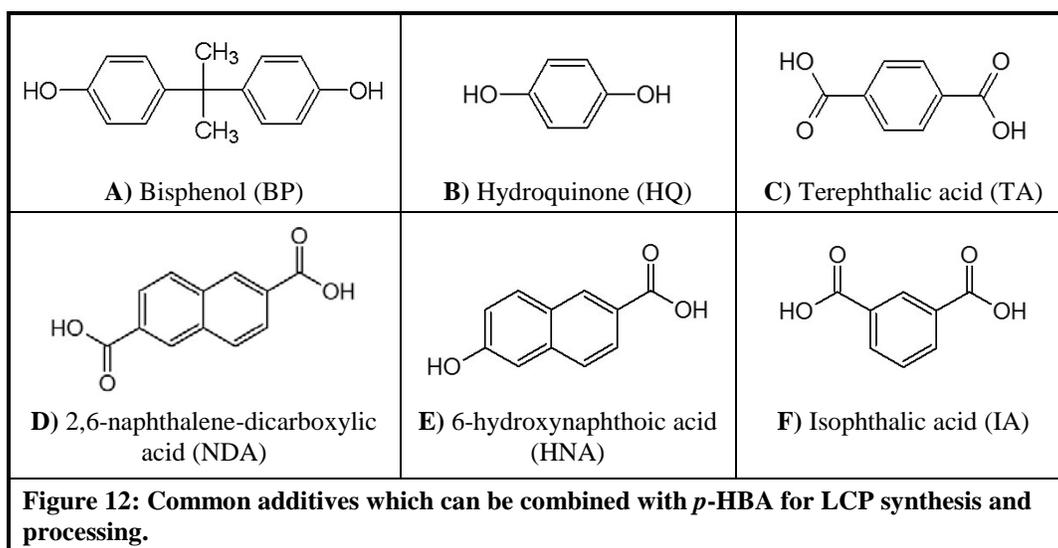


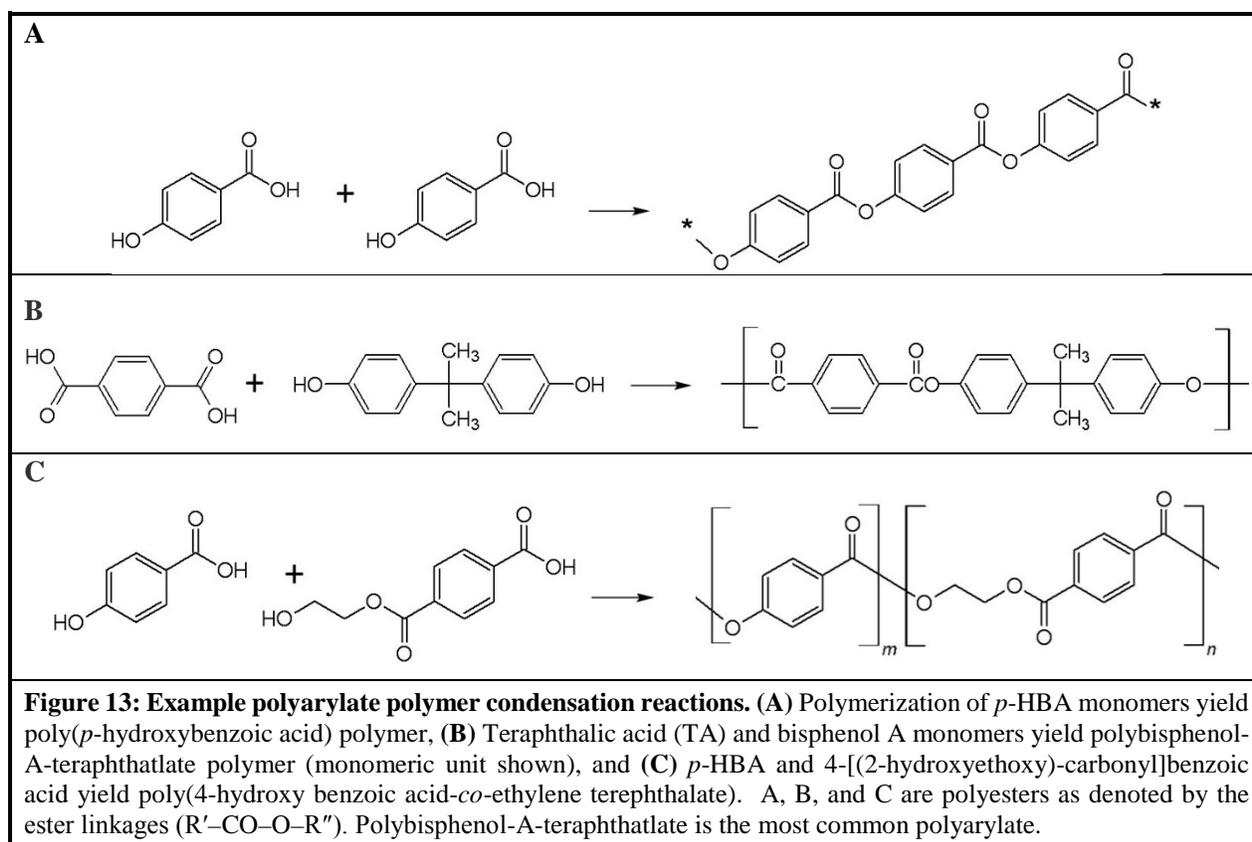
COMMERCIALIZATION OF LCPs AND THERMOPLASTICS

The multivariate linkage and connectivity possibilities of these polymers lend themselves to wide degrees of nuanced manipulation and synthesis. Thus, it is not surprising that LCPs have found favor in industry to bring out desired properties. Traits of polyester plastics such as elasticity, strength, hydrophobicity, shrinkage, flame resistance, and liquid crystallinity can be controlled through tailored synthesis methods including the incorporation of other monomers to create copolymers [16]. The resulting polymer structure thus governs the manner of crystalline formation and the properties stemming from the crystal and polymer. Furthermore, the incomplete crystalline nature of LCPs which results in their unique dual melting points provides a distinctive processing window during their flow state for manufacturing. These elements are particularly important in the commercialization of LCPs.

For manufacturability, nearly all commercially processed LCPs incorporate *p*-hydroxybenzoic acid

(*p*-HBA) as one of its monomers (**Fig. 13**) [17]. The polymers are typically derived from various condensation methods incorporating *p*-HBA and structurally similar monomers [18]. Homopolymers containing only *p*-HBA [poly(*p*-hydroxybenzoic acid)] form liquid crystals which do not flow at temperatures below 500 °C [17]. This processing temperature, however, can be significantly reduced through the introduction of other monomers such as bisphenol (BP), hydroquinone (HQ), terephthalic acid (TA), 2,6-naphthalenedicarboxylic acid (NDA), 6-hydroxy-2-naphthoic acid (HNA), isophthalic acid (IA), and others (**Fig. 12**) [17]. As an example, poly(4-hydroxybenzoic acid) – a high-melt polyester – is a polymer formed from the condensation of *p*-HBA monomers, while polybisphenol-A-terephthalate is produced from terephthalic acid (TA) and bisphenol A (BP), and poly(4-hydroxy benzoic acid-*co*-ethylene terephthalate) is a copolymer resulting from the condensation of *p*-HBA and 4-[(2-hydroxyethoxy)carbonyl]benzoic acid (**Fig. 13**). Indeed, LCPs are very amenable to blend processing with polycarbonate, polyolefins, or other polyester building blocks [16].



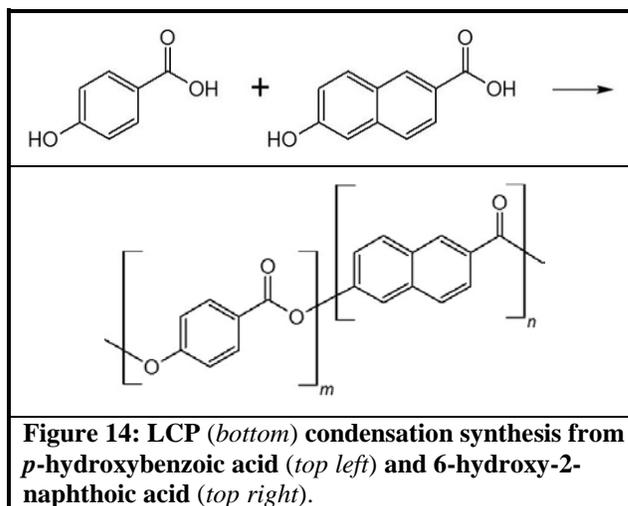


Besides the small molecule additives described above, other components, or fillers, can be added to the LCP resin to impart preferable traits. For example, addition of graphite confers resistance to chemicals and wear; carbon fiber and fiberglass add strength and rigidity; carbon black enhances electrical dissipation [16, 19, 20]; and pigments allow for different colors of the end product. These additions to the LCP resin provide another means to improve or otherwise alter performance of the LCP product and facilitate processing. This ability to vary LCP composition increases their range of properties and potential applications.

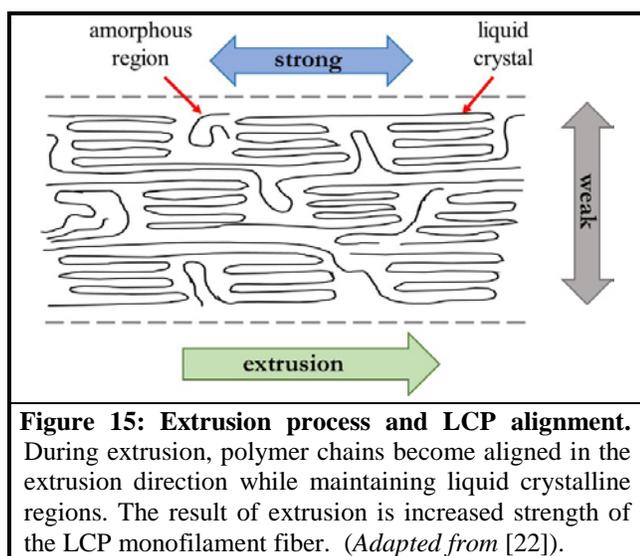
ZEUS LCP MONOFILAMENT

In light of the many distinct and desirable qualities achievable with LCPs, Zeus Industrial Products, Inc., has developed an LCP monofilament fiber with potentially broad applications. Zeus' LCP monofilament is made from a proprietary method subsequent to the condensation of *p*-HBA and 6-hydroxy-2-naphthoic acid (HNA). The result of the condensation is poly(4-hydroxybenzoic acid-*co*-6-

hydroxy-2-naphthoic acid) (**Fig. 14**). This copolymer polyester is comprised of high-continuity chains and forms a random melt-processable (thermotropic) material [19]. The LCP is formed in its melt phase typically at temperatures in the range of 220 °C to 280 °C and is extruded as a monofilament [16, 19].



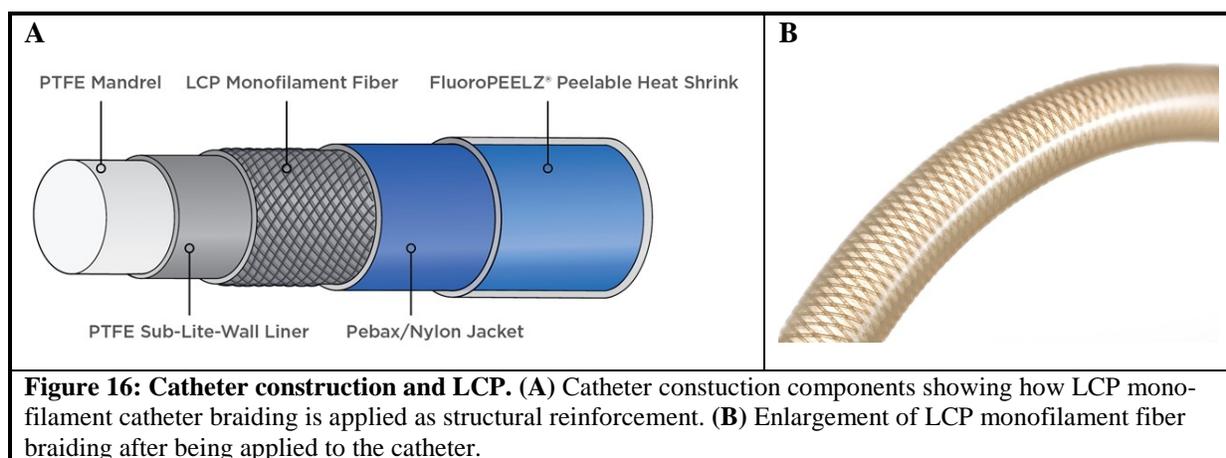
Structurally, the Zeus LCP monofilament fiber is comprised of rod-like mesogenic molecules. These molecules self-align during processing to form nematic liquid crystals. During processing and extrusion, the molecules become longitudinally arranged in the flow direction resulting in enhanced strengthening of the material (**Fig. 15**) [21]. In addition to their high chain continuity, there is a high degree of similarity between the liquid crystal and solid-state structures of these two phases of the LCP. The result is an LCP product with exceptional mechanical and physical properties [16].



MRI-COMPATIBLE CATHETERS AND LCP MONOFILAMENT

Zeus' LCP monofilament is high grade advanced polymer fiber that presents many preferable and

advantageous traits for use in catheter construction for medical applications. In recent years, elimination of metals in catheter construction has become a point of emphasis to enable catheterization during magnetic resonance imaging (MRI) medical procedures [23, 24]; these procedures generally preclude the use of metal components. As the norm, catheters are constructed over a mandrel in four layers: a thin-walled chemically etched liner (usually PTFE), braiding reinforcement, jacketing material (such as Pebax® or nylon), all of which are covered by a layer of heat shrink (such as Zeus FluoroPEELZ™) (**Fig. 16**). The heat shrink is applied to reflow the underlying jacketing into the braid and bond the jacket to the etched PTFE. This bonding secures the jacketing, braiding, and PTFE liner to complete the construction, and the heat shrink is then removed. Historically, catheter braiding reinforcement has been made of metal such as stainless steel wire because of its strength. The finished catheter should possess significant strength and rigidity for pushability yet be sufficiently flexible to navigate the human vasculature. Catheterization procedures requiring soft tissue detailed structural visualization using these devices, however, use x-ray and thus expose patients and clinicians to ionizing radiation. To address this concern, Zeus LCP monofilament fiber is being used as catheter reinforcement braiding in lieu of stainless steel or other metal braiding. The LCP braiding provides significant structural stiffness while allowing the catheter to retain other preferable flexibility traits. Utilizing the non-metal LCP reinforcement means that soft tissue visualization procedures performed in conjunction with catheterization can be done using non-radiological MRI.



As a replacement for common metal braiding such as stainless steel wire to achieve MRI compatibility, Zeus LCP monofilament fiber was evaluated for a number of relevant characteristics. As described previously, the unique self-aligning nature of the LCP molecules during extrusion produces an inherent fortifying of fiber tensile strength. To assess this feature, LCP monofilament was compared to similar size Type 304V stainless steel (SS) wire, a wire type commonly used in catheter construction. Wire used as catheter braiding is chosen in varying degrees of hardness depending on the application of the particular catheter. For the comparisons described here, spring tempered, annealed, and 1/4 hard SS wire of round and rectangle profiles were used.

Tensile strength was initially measured for a 0.003" strand of round monofilament LCP fiber and 0.003" round SS annealed wire. The Zeus LCP fiber exhibited slightly superior tensile strength of 1.2 GPa compared to 1.0 GPa for the 0.003" round SS annealed wire (**Table 1**). A 0.003" \times 0.001" rectangle profile 1/4 hard SS wire was also measured and showed a tensile strength of 1.0 GPa. For further comparison, tensile strength of 0.003" round spring

tempered and 0.001" \times 0.003" rectangle spring tempered SS wires was measured. Spring tempering is performed to produce a wire with high spring-like stiffness to resist bends and kinks. As expected, the tensile strength of the spring tempered SS wires was higher than the LCP and annealed SS wires. The spring tempered round SS wire tensile strength was 2.3 GPa while the tensile strength of the 0.001" \times 0.003" rectangle spring tempered SS wire measured at 2.1 GPa. Although the spring tempered SS wire exhibited greater tensile strength for the round and rectangle profiles compared to the LCP, annealed, and 1/4 hard SS wires, spring tempered wire is not always preferable for catheter braiding because this wire possesses very high stiffness and rigidity; these traits can limit the catheter's ability to follow small radius bends that are frequently encountered in human vasculature. On the other hand, the non-metal LCP braiding inherently possesses significant flex capability because of its non-rigid nature. Indeed, tensile testing showed that the LCP is capable of providing substantial strength and support as catheter braiding equivalent to comparable sized annealed SS wire braiding.

		Zeus LCP Fiber	SS wire (spring tempered)	SS wire (annealed)	SS wire (spring tempered)	SS wire (1/4 hard)
Fiber Profile / Shape		Round	Round	Round	Rectangle	Rectangle
Size (diameter)	inches	0.003	0.003	0.003	0.001 × 0.003	0.001 × 0.003
	mm	0.0762	0.0762	0.0762	0.0254 × 0.0762	0.0254 × 0.0762
Average Tensile Strength	ksi	174.0	333.6	145.0	304.6	145.0
	GPa	1.2	2.3	1.0	2.1	1.0
Average Elongation at Break (%)		1.7	1.7	31.1	3.1	1.7
Average Tensile Modulus	ksi	10,877.8	29,399.1	19,507.6	27,470.1	21,886.2
	GPa	75.0	202.7	134.5	189.4	150.9

Table 1: Properties comparison of catheter braiding materials: Zeus LCP monofilament fiber and 304V stainless steel wire. Averages were calculated from five replicate trials. Tensile strength was measured according to ASTM D2256 guidelines. ksi = 1000 × psi; GPa = 10⁹ × pascal; mm = millimeter.

Another essential characteristic for catheters is torsional response, or torquability. This quality refers to the catheter's ability to transmit twisting or torsional force (torque) applied at the proximal end by the user to the distal end of the catheter. Torquability is vital to allow operators to navigate body spaces during catheterization procedures to reach the target site. Considering the manner in which reinforcement braiding may affect the catheter's torquability, braiding material elongation was measured for the LCP and the annealed, spring tempered, and 1/4 hard SS wires described above.

Measuring elongation at breakage, the 0.003" strand of round monofilament LCP fiber elongation was 1.7 %. This result was comparable to the 1.7 % elongation observed for the spring tempered 0.003" round wire and for the 1/4 hard 0.001" × 0.003" rectangle profile wires. Elongation at break for the annealed 0.001" × 0.003" rectangle wire was 3.1 %. The elongation of the 0.003" annealed SS round wire was substantially higher than the other SS wires and the LCP at 31.1 %. Note that the LCP fiber exhibited comparable elongation to the spring tempered (hardest) round SS wire at 1.7 %. Together, these data show that the LCP fiber is at least as resistant to stretching as SS wire for

catheter braiding. This stretch resistance of the LCP is even more pronounced when the LCP is compared to annealed SS round wire (1.7 % and 31.1 %, respectively). For catheter braiding, this low elongation (and high tensile modulus) implies efficient torsional response of the catheter – highly desirable when executing difficult catheterization procedures.

Following tensile strength and elongation measurements, tensile modulus was determined for the LCP fiber and for the SS wire for further comparison. Tensile modulus provides a gauge or means to assess the overall stiffness of a material and its resistance to deformation. Stiff material has a high tensile modulus, and a flexible material has a low tensile modulus. Stiff catheter braiding is desirable to provide the necessary pushability of the device but can be limiting to the catheterization procedure if overly stiff. The tensile modulus determined for the 0.003" LCP fiber was 75.0 GPa. Tensile modulus for the SS wire varied according to wire profile but increased with increasing hardness of the material. For the 0.003" annealed (softest) round SS wire, the tensile modulus was 134.5 GPa; for the 1/4 hard 0.001" × 0.003" rectangle SS wire, the modulus was 150.9 GPa; for the

0.001" × 0.003" rectangle spring tempered SS wire, 189.4 GPa; and for the 0.003" spring tempered round SS wire, 202.7 GPa. The highest tensile modulus observed for the spring tempered (hardest) round SS wire was expected. However, noteworthy still is the substantial tensile modulus of the LCP fiber at 75.0 GPa. This result suggests that the LCP has the required stiffness necessary for catheter shaft support as braiding while retaining some flexibility allowing catheter manipulation. Additionally, the degree of stiffness implied by the tensile modulus of the LCP would also have a beneficial effect upon the catheter's torquability.

While LCP monofilament fiber is intended as a replacement for metal componentry in catheters, other non-metal materials have been used in this application with varying degrees of success due to their mechanical and electrical properties. These materials include polyesters and other aramid polymers such as polyether ether ketone (PEEK) for braiding and guidewires [25-27]; and nylon [28], Kevlar® [29, 30], polyethylene terephthalate (PET), and blends of PET for braiding [31]. Relating these materials to the LCP monofilament, it is quickly apparent that the LCP monofilament fiber possesses superior tensile strength to all of these materials with the exception of Kevlar® (Table 2). For the PET, PEEK, and Nylon 6, the

LCP monofilament exhibits two orders of magnitude reater tensile strength and is equivalent on this level to the Kevlar®. The Kevlar® material, however, owes its higher strength to the fact that it is a multifilament. Secondly, the LCP fiber has greatly reduced elongation properties compared to PET, PEEK, and Nylon 6. Only the multifilament Kevlar® approaches the LCP monofilament for minimal elongation at 3.6 % compared to 1.7 % for the LCP fiber. Regarding the overall stiffness of these materials, an essential quality for catheter components, the LCP fiber shows greater than ten-fold higher tensile modulus than PEEK, PET, and Nylon 6 at 75.0 GPa compared to 2.9 GPa, 3.4-4.2 GPa, and 1.7-2.28 GPa for PET, PEEK, and Nylon 6, respectively. The LCP monofilament also exhibits slightly greater tensile modulus than the 70.5 GPa for the Kevlar®. For of the materials described here, which are already being used for catheter componentry, the LCP monofilament fiber possesses better mechanical properties in nearly every category. These qualities of the LCP – exceptional stiffness, strength, minimal elongation, and non-metallic – make it a preferred material for catheter construction to produce a rigid device but without sacrificing necessary flexibility.

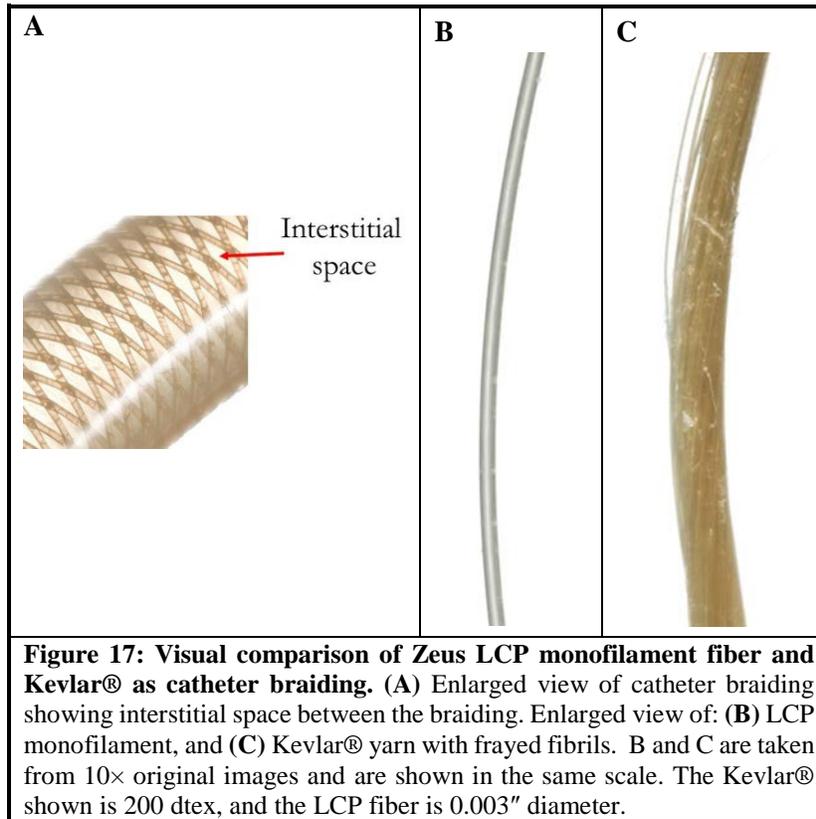
		Zeus LCP Fiber	PET	PEEK	Nylon 6	Kevlar® 29
Average Tensile Strength	ksi	174.0	4.9	7.98 – 13.9	6.3 – 9.2	424
	MPa	1200	33.9	55.0 – 95.5	45.0 – 67.7	2900
Average Elongation at Break (%)		1.7	84.3	19.3 – 35.0	76.3	3.6
Average Tensile Modulus	ksi	10,877.8	424.0	499 – 612	245.0 – 331.0	10.2
	GPa	75.0	2.9	3.4 – 4.2	1.7 – 2.28	70.5
Shrinkage (%)		<0.01	0.5 – 1.1	1.2	1.4	<0.1

Table 2: Properties comparison of LCP monofilament and several non-metal materials commonly used in catheter construction. Polymer data is from: <http://www.matweb.com/>. PET, PEEK, and Nylon 6 data were for unreinforced material. Range values are due to the range of grades tested. PET, PEEK, and Nylon 6 shrinkages were linearly measured at temperatures not exceeding 302 °F; LCP fiber shrinkage was linearly measured at 390 °F (199 °C) and at 482 °F (250 °C). Kevlar® 29 fiber was 1500 denier / 1000 filaments / dtex 1670; data was taken from Du PONT [32]. ksi = 1000 × psi; MPa = 10⁶ × pascal; GPa = 10⁹ × pascal; mm = millimeter.

In addition to the properties measured above, another essential property of these materials, shrinkage, was assessed. Under usual circumstances, catheter shrinkage is of minor consequence. However, with repeated uses from autoclaving, irradiation, or other sterilization procedures, shrinkage nevertheless does occur [33]. This hallmark is affected by the catheter material as well as the braiding used as structural reinforcement. For the LCP monofilament, shrinkage was measured at temperatures well above what would be required for autoclaving. The LCP monofilament fiber displayed < 0.01 % shrinkage at 390 °F (199 °C) and at 482 °F (250 °C) after 10 minutes exposure at these temperatures (**Table 2**). The Kevlar® multifilament and PET exhibited the next best minimal shrinkage at < 0.1 % and 0.5-1.1 %, respectively, both at temperatures below 350 °F (177 °C). Even though these shrinkage values were from temperatures lower than those at which the LCP shrinkage was measured, they were at least one order of magnitude higher than the shrinkage of the LCP monofilament fiber. Shrinkage of the PEEK and Nylon 6, also measured at temperatures below 350 °F (177 °C), were two orders of magnitude higher than the LCP monofilament fiber shrinkage. These comparisons show that the LCP monofilament is a superior alternative to either of the non-metal material options described above for catheter reinforcement where shrinkage may be a concern such as from sterilization procedures.

Another aspect regarding catheter rigidity and stiffness affecting its performance concerns its construction. The manner of catheter construction directly impacts its

pushability, torquability, and usable flexibility towards guiding the catheter to the target site. In this context is the nature of the braiding used for the catheter reinforcement. While Kevlar®, a multifilament yarn, displays several competitive traits with respect to the LCP monofilament, it is prone to fraying (**Fig. 17C**). As part of the final catheter construction, a layer of heat shrink is applied over the jacketing which covers the braiding (**Fig. 16A**). This heat shrink is applied not only to secure the underlying components together but also to reflow the jacketing material to create a bond to the etched PTFE liner underneath the braiding. Bonding to the underlying PTFE is accomplished by the penetration of the jacket in its reflow state through the interstitial space – the space between the individual braided strands – of the braiding weave (**Fig. 17A**). Although the braiding pitch can be varied, the characteristic fraying associated with Kevlar® functions as a partial occlusion preventing a more complete penetration of the melted jacket to the underlying etched PTFE catheter layer. The LCP monofilament fiber is much less prone to fraying during the braiding process with proper selection of fiber guides such as eyelets and pulleys. This minimized fraying of the LCP fiber thus provides more efficient jacket penetration during reflow and allows a more complete bond to the underlying PTFE liner. The increased bonding through the LCP braiding means that a catheter constructed with LCP fiber is more apt to possess the desired torquability characteristics and rigidity preferred by clinicians as an MRI-compatible option.



For manufacturers, LCP presents many desired traits regarding manufacturability and braiding. Like Kevlar®, many common multifilament yarns and other single fibers can exhibit fraying from tiny fibrils that branch off from the primary fiber. This fraying can manifest itself in “bird nesting” during the manufacturing process resulting in production stoppages. LCP monofilament, however, is much less prone to fraying due to its liquid crystalline and monofilament nature and thus does not exhibit “bird nesting.” As a consequence, LCP monofilament is easily integrated into industry-standard braiding machines such as those made by Steeger USA LLC and requires little or no process changes. Additionally, with respect to stainless steel braiding, braid termination of the LCP is much easier because the LCP braiding does not unravel at the cut ends as stainless steel. LCP fiber braid termination can simply

be secured via glue such as cyanoacrylate. The LCP monofilament fiber can be wound on Steeger and Wardwell bobbins as well as DIN 160 spools. For braiding manufacturers, LCP monofilament thus represents an attractive and smooth-transitioning production option.

With the favorable outlook regarding LCP monofilament and MRI-compatible catheters, manufacturers and clinicians have taken a renewed interest. As a result, LCP monofilament and LCP-constructed catheters have been evaluated by several manufacturers, medical supply companies, and investigative medical personnel. For manufacturability, companies have reported that only minor modifications were necessary to braid LCP monofilament [34]. These manufacturers likewise stated that LCP does not experience the fraying and “bird nesting” commonly

associated with other fibers and yarns. From a medical perspective, clinicians have reported that LCP performs well providing the unique combination of stiffness and flexibility necessary for MRI deflectable catheter procedures [34]. LCP monofilament consequently provides an easily manufacturable braiding for catheters to allow radiation-free detailed soft tissue visualization procedures via MRI.

SUMMARY AND CONCLUSION

Liquid crystals represent a distinct state of matter between an amorphous liquid and a fully crystalline solid. The self-aligning nature of the liquid crystal mesogen molecules produces a variety of crystal types each with their specific behavior. Additionally, the arrangement of the crystals within the mesophase – nematic, smectic, or other crystal types – adds to the myriad of liquid crystal systems and functionalities. These functionalities can be affected by either heat for thermotropic liquid crystals or solvents for lyotropic liquid crystals, while certain liquid crystals can be affected by both means. This ability to affect the creation or dissolution of the liquid crystal provides a method to study as well as manipulate them for beneficial purposes.

With the realization that liquid crystal mesogen molecules possess certain common features – non-symmetrical, (usually) an aromatic ring, a hydrophobic region, and a hydrophilic region – attention was directed to molecules which have these features. This finding led to a proliferation of molecules described with a liquid crystal phase which had not previously been identified as such. Logically following these discoveries, molecules began to be synthesized for the specific purpose of producing a liquid crystal. These new molecules also brought about the understanding that they could be synthesized to produce mesophases with specific properties.

In light of the unique properties posed by liquid crystals, interest arose in creating more complex molecules which could be of benefit due to their liquid crystal nature. Citing their specific mesogen features, polymers of liquid crystals were produced which also exhibited distinct properties apart from ordinary or simple polymers. As polymers, these molecules exhibit a variety of arrangements and connectivities that distinguish their behavior. As an LCP, these polymers are best described as a sub-category of thermoplastics. Their characteristic two

melting points present a processing window suitable for manufacture. While initially difficult to produce, additives can be introduced to increase manufacturing ease and impart or tailor other properties for specific uses.

The LCP monofilament fiber produced by Zeus Industrial Products, Inc., represents a new offering as an LCP product. Made from *p*-HBA and HNA, Zeus' proprietary processing has overcome a typically difficult-to-process material to produce a monofilament fiber with exceptional mechanical properties. The rod-like mesogens of this LCP form a nematic crystal in their mesophase which self-align and longitudinally orient themselves in the direction of extrusion. Furthermore, the polymeric chains of this LCP possess high chain continuity and crystallinity while in its mesophase. This result is a fiber with remarkable strength and stiffness.

This LCP monofilament fiber addresses an urgent need in the medical field: to produce a catheter that is fully compatible with MRI. As braiding reinforcement for these catheters, the Zeus LCP monofilament fiber outcompetes common polyester, nylon, or other polymer materials in terms of strength, tensile modulus (stiffness), elongation, and shrinkage by at least an order of magnitude. In the case of Kevlar®, which is a multifilament, the LCP monofilament is at least comparable regarding mechanical properties. However, the LCP separates itself from Kevlar® with its increase in bondability of the reflowed Pebax® or nylon jacket covering during the heat shrink application step of catheter construction. As a monofilament, the LCP is much less prone to fraying and allows superior penetration of the jacketing to the underlying PTFE. As a replacement for stainless steel wire braiding, the LCP also exhibits favorable characteristics: It retains a degree of flexibility as necessary for a deflectable catheter but also provides the substantial strength required for stiffness, torquability, and pushability. With respect to stainless steel, the LCP monofilament behaves as an amalgam between annealed (soft) stainless steel and spring tempered (hard) stainless steel yet is not metallic.

Catheters constructed with the Zeus LCP monofilament have received highly positive reviews from manufacturers and medical professionals. Manufacturers report that the Zeus LCP fiber is easily integrated into existing braiding machines. They have commented positively regarding the lack of fraying and “bird nesting” that is commonly associated with other fibers or multifilament yarns that

may be used in catheter construction. Availability on Steeger and Wardwell bobbins and on DIN 160 spools is also a highly desired trait of the LCP fiber. Finally, clinicians report that catheters braided with Zeus' LCP monofilament fiber exhibit the exceptional torquability and stiffness they require, thus this non-metallic fiber is well-suited for a deflectable MRI-compatible catheter.

ABOUT THE AUTHOR



Dr. Kevin J. Bigham is the Technical Writer for Zeus. Kevin earned his undergraduate degrees in Chemistry and Biochemistry from the College of Charleston before going on to graduate training at the Medical University of South Carolina. There, he earned his PhD with concentrations in Biomedical and Pharmaceutical Sciences. Dr. Bigham brings his broad experience and scientific knowledge spanning the manufacturing sector to biomedical research to produce varied content for the company's technical and lay audiences.

ABOUT ZEUS

Zeus is the world's leader in polymer extrusion technologies. For over 50 years, Zeus has been serving the medical, aerospace, energy exploration, automotive, and fiber optics industries. Headquartered in Orangeburg, South Carolina, Zeus employs approximately 1,250 people worldwide and operates multiple facilities in North America and internationally. You can find us at www.zeusinc.com.

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