LIQUID CRYSTAL POLYMERS AND ZEUS LCP MONOFILAMENT

Kevin J. Bigham, PhD

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INTRODUCTION

Most of us have heard the term *liquid crystal* (LC); we know it from liquid crystal displays of digital watches and clocks dating back to the 1970's. Since then, LCs have replaced almost all conventional displays for portable devices such as cell phones, personal computers, toys, and more recently for televisions. But have you ever heard of *liquid crystal polymers* (LCPs)? While these unusual molecules have been adapted to a variety of uses, they recently have garnered interest from a new sector: For nearly two decades, the medical industry has sought the development of catheters – typically constructed with metal componentry – which could be used for magnetic resonance imaging (MRI) medical procedures. MRI, however, generally precludes the use of metals. This article discusses LCPs and how we at ZEUS have exploited their unique character to produce an advanced monofilament fiber for the construction of a fully MRI-compatible catheter.

DISCOVERY

Despite their more recent commercialization, the discovery of liquid crystals can be traced back to the late 19th century to a pair of European scientists, Austrian Friedrich Reinitzer and German Otto Lehmann. First investigated by Reinitzer and corroborated by Lehmann a short time later, these scientists discovered that solid cholesteryl benzoate underwent multiple phase transitions as it was heated and cooled: As the solid was heated, it first became a hazy liquid; but with continued heating, the material became clear. The opposite effect was observed as the heated clear liquid was allowed to cool: first clear, then a hazy liquid, then a white solid. The troubling question for Reinitzer and Lehmann was the apparent two liquid states of the cholesteryl benzoate: hazy and clear. (Typically, solids melt at a very narrow melting point range of only a degree or two and phase or color transitions are immediate. Pure ice, for example, melts at exactly 32 °F). Reinitzer and Lehmann had in fact described two different melting points for the same material – a previously unknown phenomenon. When viewing the hazy liquid under a microscope, Lehmann described seeing crystallites – multiple small crystalline formations with irregular borders. When the hazy liquid was heated further and became clear, the crystallites disappeared. Lehmann realized that this first intermediate *fluid* seemed to be *crystalline* in nature which he suggested was new state of matter. He later termed his discovery a *liquid crystal*, and the observation of two melting points would become fundamental to its identification.

WHAT ARE LIQUID CRYSTALS?

What Reinitzer, Lehmann, and others had found was a new state of matter somewhere between a true solid and a liquid. This new in-between phase of matter thus became known as a *mesophase*, and the molecules within it were termed *mesogens*. These small to moderate size organic molecules arrange themselves in varying degrees of organization along an axis called the *director* (**Fig. 1**). The longer range order of the liquid crystal is typified by the director. However, not all of the mesogen molecules participate in this ordering giving the liquid crystal unique behavior as neither a solid nor liquid. Furthermore, researchers also realized that the mesogen positional orientation along the director was a fundamental element and resulted in different crystal formations.

In 1922, French mineralogist Georges Friedel proposed a classification system based upon mesogen alignment and accounting for the different behaviors of liquid crystal types. Friedel described several basic crystal forms which have since been expounded upon in great detail. Of particular interest here are *nematic* and *smectic* liquid crystal structures (**Fig. 2**). Nematic liquid crystal molecules maintain their directional orientation but do retain some freedom of movement within the liquid crystal. Smectic mesogens are arranged such that their principal axes are parallel with their centers of mass in one plane. Smectic liquid crystals show positional and directional order. The material properties of liquid crystals such as optical activity, magnetic, and electrical properties are affected by this orientation of molecules; this effect is called *anisotropy*. Conversely, for liquids or gases, which show complete disorientation or disorder of molecules in those states, they exhibit *isotropy* and their properties are isotropic (**Fig. 1**). Anisotropy is a second defining characteristic of liquid crystals.

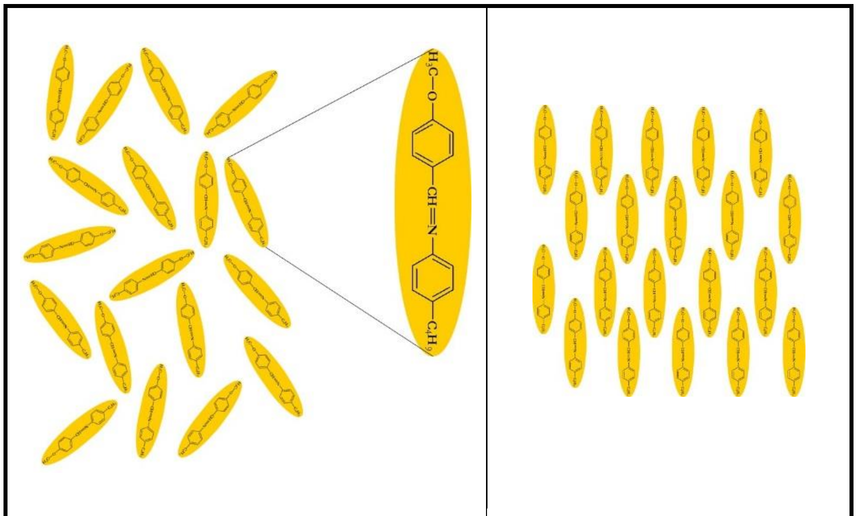

Figure 1: Diagram showing the arrangement of mesogen molecules along the director within a substance. **(A)** Liquid (isotropic) and **(B)** crystalline (solid, anisotropic) forms.

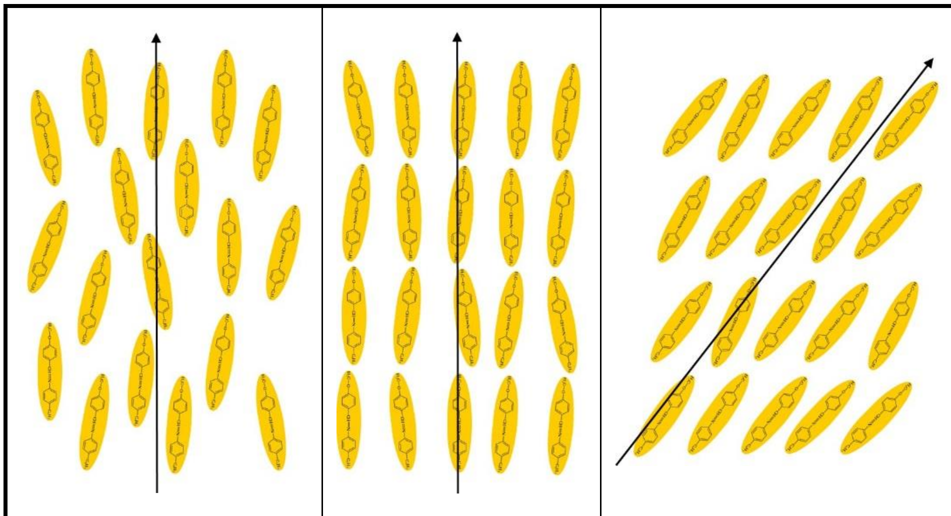

Figure 2: Diagram showing the arrangement of mesogen molecules within liquid crystal types. Liquid crystal forms exhibit directional alignment of their molecules and are anisotropic. **(A)** Nematic liquid crystal showing orientational order, **(B)** smectic A liquid crystal form, and **(C)** smectic C liquid crystal form. B and C possess orientational and positional order.

LIQUID CRYSTAL POLYMERS

With further study, investigators later realized that liquid crystals also formed from more complex polymeric molecules. As their name suggests, *liquid crystal polymers* (LCPs) are derived from liquid crystals to take advantage of their unique properties. These molecules consist of repeated monomer units but which are linked to form extended chain-like molecules. Most LCPs have a common fundamental structure consisting of three parts: a rigid mesogen core, a hydrophobic flexible linker on one end, and a hydrophilic moiety on the other end (**Fig. 3**). These chain structures aggregate and self-align to form LCPs just as single mesogen molecules do to form liquid crystals. However, the chain-like nature of LCPs dramatically affects enhanced intermolecular interactions resulting in profound effects upon LCP behavior unlike simple (non-polymeric) liquid crystals.

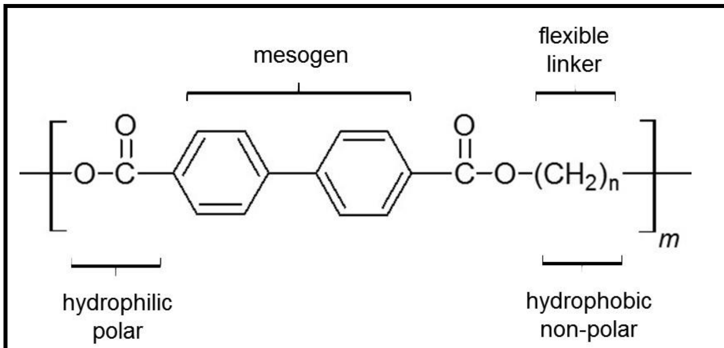

Figure 3: Representative example LCP monomer showing hydrophobic and hydrophilic regions, mesogen, and the flexible linker region.

LCPs AND THERMOPLASTICS

Of particular interest today are LCPs and their potential in thermoplastic applications. We are already familiar with many thermoplastics such as polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polytetrafluoroethylene (PTFE), polystyrene (PS), and Kevlar® (**Fig. 4**). These examples are all simple hydrocarbon chains, and with the exception of polystyrene, contain no ring components. Ring substituents are in fact another feature common to liquid crystal polymers, and polystyrene monomer is frequently incorporated into blends to produce LCPs. In their flow state during processing, LCPs distinguish themselves form typical thermoplastics because they retain significant crystallinity. This partial crystalline state of LCPs imparts many unique properties to these plastics such as exceptional strength, high temperature and chemical resistance, and toughness. Today you may find LCP plastics in a broad range of applications from aerospace parts, laser beam deflectors, to food containers.

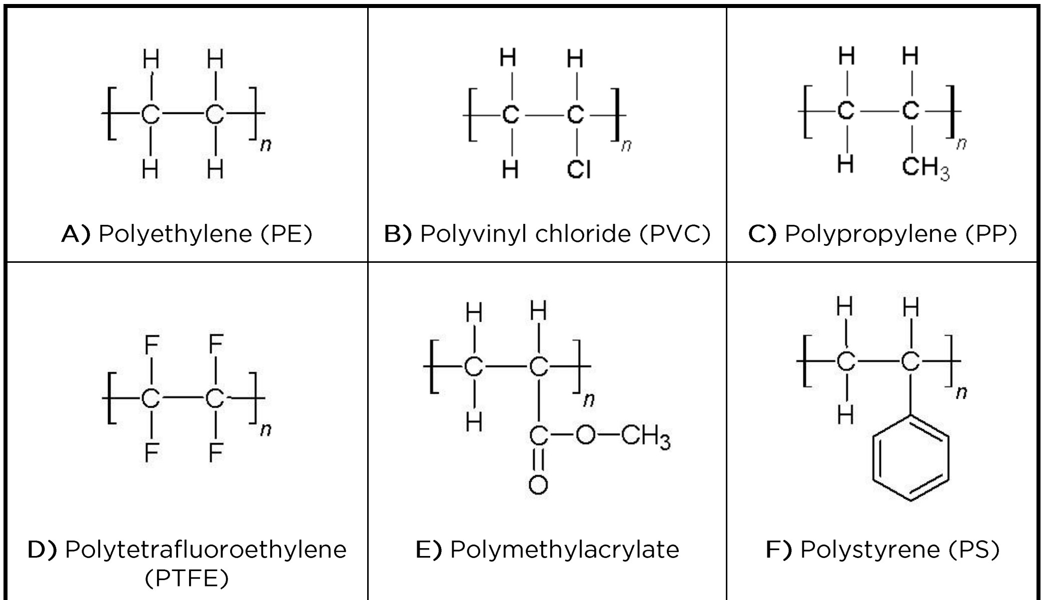

Figure 4: Representative thermoplastic polymer monomers. Of these, polystyrene is the most frequently incorporated into an LCP.

COMMERCIALIZATION

For manufacturability, most commercial LCPs incorporate *p*-hydroxybenzoic acid (*p*-HBA) as one of its monomers (**Fig. 5**). Processing typically involves various condensation methods and often incorporates other monomers such as bisphenol (BP), hydroquinone (HQ), 2,6-naphthalenedicarboxylic acid (NDA), terephthalic acid (TA), 6-hydroxy-2-naphthoic acid (HNA), isophthalic acid (IA), and others to facilitate synthesis (**Fig. 6**). Furthermore, the two melting points of liquid crystals – and of LCPs – provide a broader processing window for these unique polymer plastics. As examples, poly(4-hydroxybenzoic acid) is a high-melt polyester formed from the condensation of *p*-HBA monomers, and polybisphenol-A-teraphthatlate is produced from terephthalic acid (TA) and bisphenol A (BP) (**Fig. 5**). LCPs are in fact quite amenable to blend processing with polycarbonate, polyolefins, other polyester building blocks, and common fillers such as fiberglass and carbon . The ability to vary LCP composition not only expands their range of properties but also their potential applications.

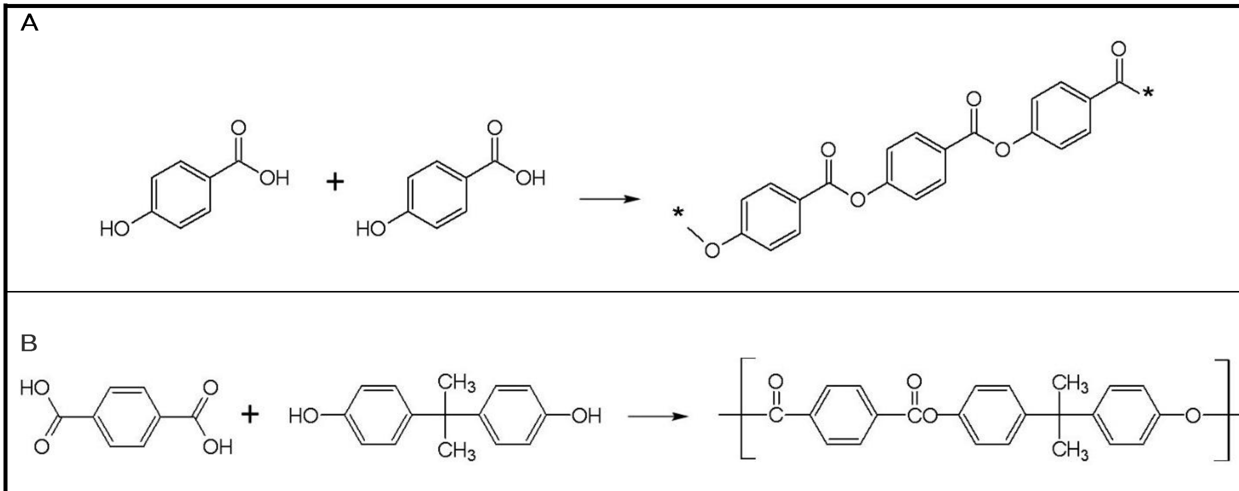

Figure 5: Example polyarylate polymer condensation reactions. **(A)** Polymerization of *p*-HBA monomers yield poly(*p*-hydroxybenzoic acid) polymer, and **(B)** Teraphthalic acid (TA) and bisphenol A monomers yield polybisphenol-A-teraphthatlate polymer (monomeric unit shown).

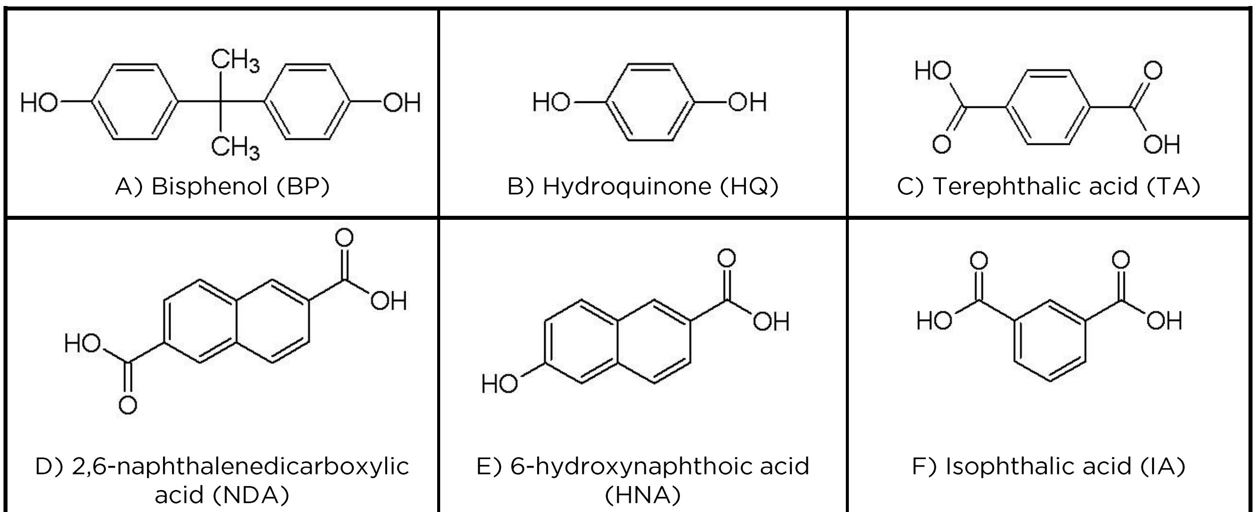

Figure 6: Common additives which can be combined with *p*-HBA for LCP syntheses and processing.

ZEUS LCP MONOFILAMENT

In view of the special material properties that are possible with LCPs, we at ZUES have developed an LCP polymer as an extruded monofilament fiber. While initially aimed towards medical applications, this product has potentially broad uses. ZEUS' LCP monofilament is produced from an exclusive method involving the condensation of *p*-HBA and HNA resulting in poly(4-hydroxybenzoic acid-*co*-6-hydroxy-2-naphthoic acid) (**Fig. 7**). This copolymer polyester is comprised of high-continuity chains and forms a random melt-processable (thermotropic) material. Structurally, this LCP fiber is composed of rod-like mesogens which form nematic liquid crystals. During extrusion, these self-aligning molecules become longitudinally arranged in the flow direction resulting in enhanced strengthening of the material (**Fig. 8**). The unique structural attributes and proprietary processing result in a LCP fiber with exceptional mechanical and physical properties.

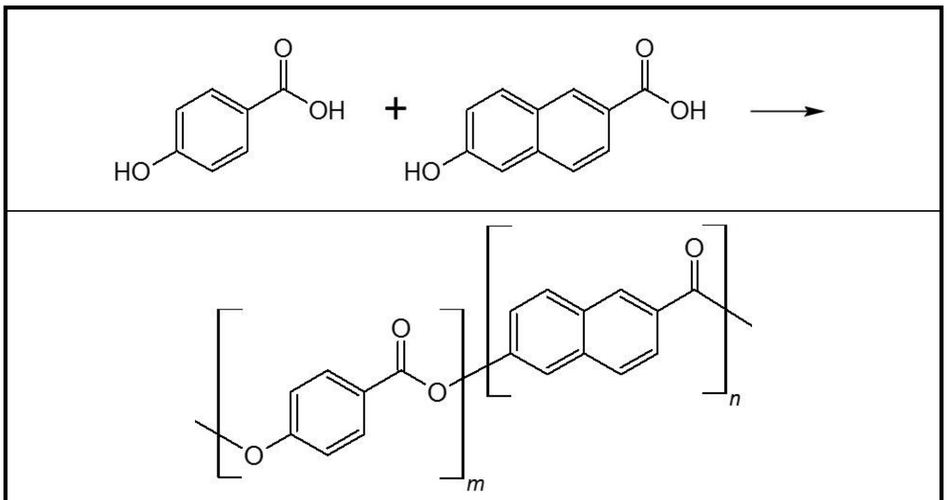

Figure 7: LCP condensation synthesis from *p*-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid.

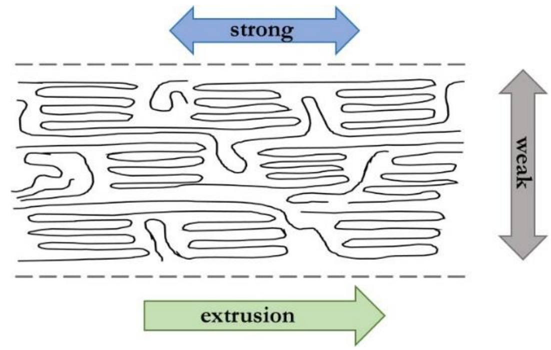

Figure 8: Representation of LCP alignment during extrusion and the effect on fiber strength. *Adapted from*: Holliday L: *The Stiffness of Polymers in Relation to Their Structure. In: Structure and Properties of Oriented Polymers*. Edited by Ward IM. Dordrecht: Springer Netherlands; 1975: 242-263).

MRI-COMPATIBLE CATHETERS AND LCP MONOFILAMENT

Since the development of magnetic resonance imaging (MRI) in the 1970's, there has been keen interest towards expanding its use in medical diagnostics. The most significant obstacle to this goal is that MRI generally precludes the use of metals in devices such as catheters which would be used under the MRI field. In such scenarios, the standard practice is to utilize x-ray for soft tissue visualization procedures requiring catherization because of the metal reinforcing braiding used in catheter construction. An obvious consequence of x-ray is that it exposes both patients and clinicians to ionizing radiation. What is needed instead are catheters which can be utilized under MRI to provide safer and higher quality visualization procedures.

To address the issue of MRI-compatibility and catheterization, a number of entities have sought to develop catheters with various non-metal braiding components. This effort has been ongoing for nearly twenty years and has produced only mixed results. In this context, ZEUS LCP monofilament fiber is being used as catheter reinforcement braiding in lieu of stainless steel or other metal and fiber braiding (**Fig. 9**). The goal of this LCP braiding is to provide the structural stiffness that clinicians require while allowing the catheter to retain preferrable traits such as flexibility for distal end deflectability. These catheters also must possess the strength and rigidity for pushability to navigate the human vasculture.

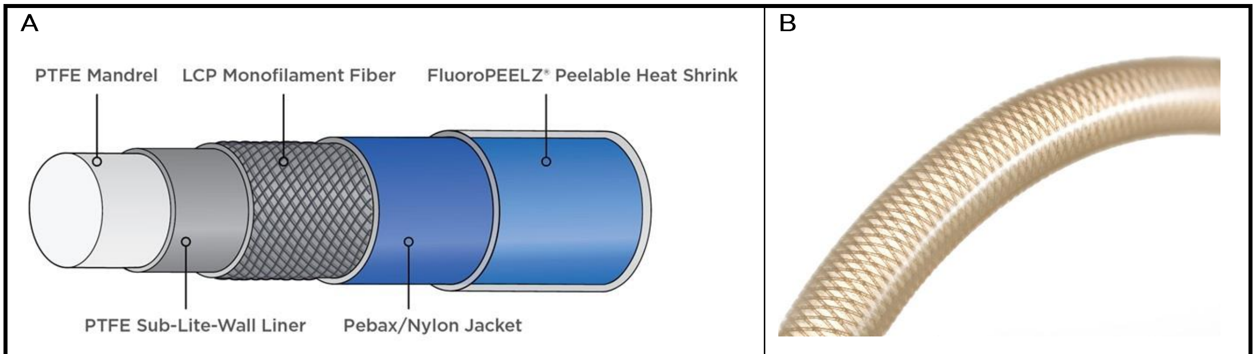

Figure 9: (A) Catheter constuction components showing how LCP monofilament catheter braiding is applied as structural reinforcement. **(B)** Enlargement of LCP monofilament fiber braiding after being applied to the catheter.

As a replacement for standard metal catheter braiding such as stainless steel wire, ZEUS LCP monofilament was compared to Type 304V stainless steel (SS) wire – a braiding wire type commonly used in catheter construction – for several relevant characteristics. Spring tempered, annealed, and 1/4 hard SS wire of round and rectangle profiles were used for these comparisons (**Table 1**). The LCP fiber exhibited superior tensile strength to both the annealed round and 1/4 hard rectangle SS wires and an elongation at break comparable to the SS round and 1/4 hard rectangle wires. The substantial tensile modulus of the LCP fiber of 75.0 GPa suggests that the LCP has the required stiffness necessary for catheter shaft support. These qualities translate into superior torsional and stiffness properties for the catheter while retaining a degree of flexibility for catheter manipulation – highly desirable traits for these devices.

		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	19507.6	27470.1	21886.2
	GPa	*75.0*	*202.7*	*134.5*	*189.4*	*150.9*

Table 1: Properties comparison of 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 = 10^9 × pascal; mm = millimeter.

To provide additional support and context for the use of this new material, the ZEUS LCP fiber was compared to several non-metal materials that have been used in catheter construction including polyether ether ketone (PEEK), nylon, Kevlar®, and polyethylene terephthalate. Of particular note is that PEEK, nylon, and PET are monofilaments while Kevlar® is a multifilament yarn. The ZEUS LCP monofilament outperformed all of the monofilament fibers with respect to tensile strength and modulus while exhibiting the least elongation at break and even showed superior tensile modulus to the Kevlar® multifilament (**Table 2**). The LCP also showed the least shrinkage among all of the fibers tested at temperatures up to 483 °F. Altogether, these comparisons show that the ZEUS LCP monofilament is a superior alternative to almost all other non-metal fibers recommended for catheter braiding.

		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
		1.2 GPa	*33.9 MPa*	*55.0 – 95.5 MPa*	*45.0 – 67.7 MPa*	*2.9 GPa*
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: Comparison of properties of the LCP monofilament fiber and several 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. ksi = 1000 × psi; MPa = 10^6 × pascal; GPa = 10^9 × pascal; mm = millimeter.

Another advantage that the LCP fiber has over other braiding material involves its manufacturability with respect to catheter construction. As a multifilament yarn, Kevlar® is prone to fraying, or "bird nesting," when used in braiding machines whereas the LCP monofilament shows almost no fraying. Secondly, the multifilament Kevlar® displays a degree of flattening when covered with heat shrink to reflow the catheter jacket material (such as Pebax or nylon) during the final stages of construction. This flattening or spreading out of the Kevlar® fibers partially occludes the interstitial space between the braiding and prevents thorough bonding of the jacket to the underlying liner (such as etched OD PTFE tubing) during reflow (**Fig. 10**). Insufficient bonding is a troublesome problem for catheter construction and can result in catheters with poor stiffness and torsional properties. As a monofilament, the LCP fiber allows superior penetration and bondability of the jacket to the liner during catheter construction and is sufficiently strong to provide the necessary torquability, stiffness, and deflectability that clinicians value most.

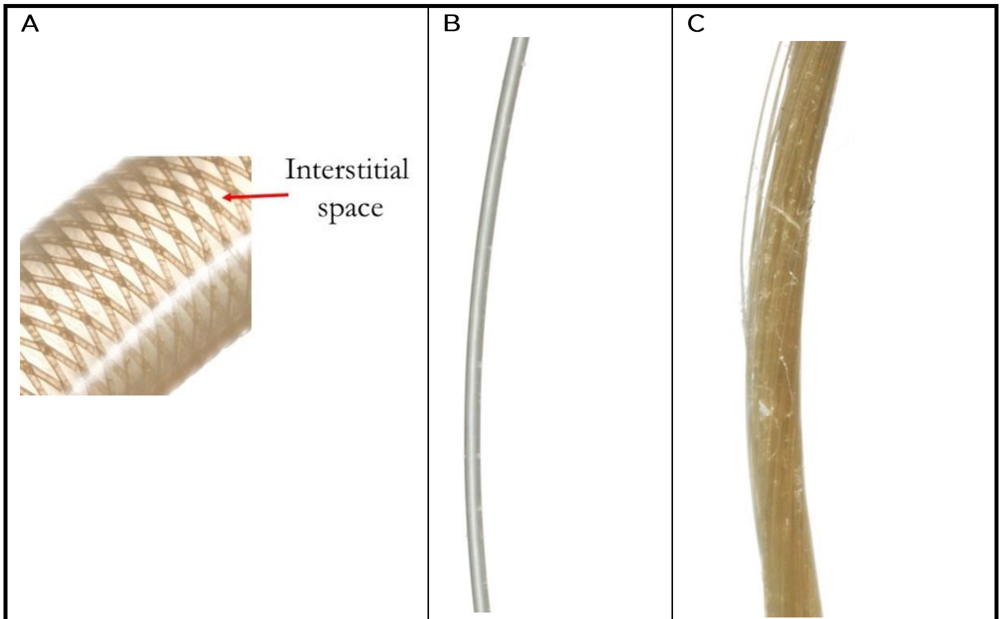

Figure 10: Comparison of Zeus LCP monofilament fiber and Kevlar® as catheter braiding. **(A)** Enlarged view of catheter braiding showing interstitial space between the braiding. Enlarged view of: **(B)** LCP monofilament, and **(C)** Kevlar® yarn with frayed fibrils. B and C are taken from 10× original images and are shown in the same scale. The Kevlar® shown is 200 dtex, and the LCP fiber is 0.003″ diameter.

SUMMARY

The LCP monofilament fiber produced by ZEUS represents a new offering as an LCP product and addresses an urgent need in the medical field: to produce a catheter that is fully compatible with MRI. The Zeus LCP fiber out competes common polyester, nylon, or other polymer products in terms of strength, tensile modulus (stiffness), elongation, and shrinkage by at least an order of magnitude. For the multifilament Kevlar®, the LCP monofilament is at least comparable regarding mechanical properties but separates itself from Kevlar® with its increased bondability of the reflowed jacket covering and liner during reflow. As a replacement for stainless steel for catheter braiding, the LCP also exhibits highly favorable characteristics: It retains a degree of flexibility necessary for a deflectable catheter but also provides substantial strength 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. Utilizing the non-metal LCP reinforcement means that soft tissue visualization procedures performed in conjunction with catheterization can be done using non-radiological MRI.

With this new opportunity, manufacturers and clinicians have taken a renewed interest in this significant step towards achieving a fully MRI-compatible catheter.

See the complete and fully referenced Technical Paper, "LCP Introduction to Liquid Crystal Polymers," here at our website.