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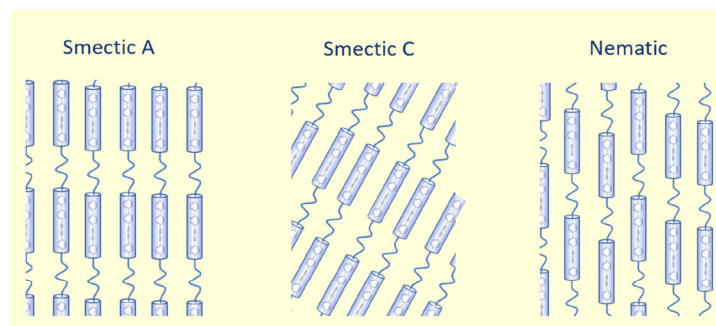
## LIQUID CRYSTAL POLYMERS (LCPs)

## PROPERTIES

Liquid crystalline polymers (LCPs) are a special type of thermoplastics that exhibit properties between highly ordered crystalline materials and amorphous disordered liquids over a well defined temperature range.

To date, thousands of LC polymers have been synthesized. However, only a small number have become commercially important LC materials. The three most common LCPs are semi-aromatic *copolyesters*, *copolyamides*, and *polyamides*. These polymers contain rigid rod-like or plate-like repeat units with a high length-to-width ratio, the so-called *mesogenic groups*, that are able to self-assemble into anisotropic liquid crystals (mesophases) upon cooling or action of an external field. Three very common LC mesophases are *nematic*, *smectic A* and *smectic C* (see below). Nematic mesophases show only unidimensional orientational order in the direction of the long (in rod-shaped) or disc-shaped molecular axes. This is typically the flow direction during processing of the LC resin. Smectic mesophases, on the other hand, show two-dimensional orientational order. These LC's have a lot in common with crystalline polymers. In crystalline polymers, molecules are arranged in layers (lamellae). The long axes of the (rod-like) molecules are either perpendicular (smectic A) or it is inclined at an angle (smectic C).

## EXAMPLES OF COMMON MESOPHASES



The most common LCPs are liquid crystalline polyesters which can be produced by polycondensation of an aromatic hydroxycarboxylic acid and an aromatic dicarboxylic acid with an aliphatic diol as a coreactant. The aromatic blocks form the liquid crystals in the copolymer while the aliphatic blocks act as flexible *spacers*. Several other flexible (hydrophobic) spacers such as aliphatic ethers and organosilicons can be part of the LCP. The spacers or flexible linkers impact the rigid mesogenic groups<sup>1</sup> to ease cooperative self-assembly. They also lower the melting point and increase the temperature range within which the liquid crystals are stable.

The properties of LCPs such as crystallinity, flexibility, and strength depend on the molecular weight distribution, average chain length and the type and length of the flexible linker or spacer. The properties can be further adjusted by copolymerization with other monomers and by addition of plasticizers and fillers and/or by blending with other polymers such as polycarbonates, polyolefins, and polyesters. The addition of plasticizers and fillers lowers cost, alters the performance and can facilitate processing. For example, addition of graphite improves resistance to chemicals whereas carbon fibers and glass fibers increase strength and rigidity; carbon black enhances electrical properties and electrostatic dissipation.

Many commercial self-reinforced LCPs can be processed using conventional injection molding and extrusion techniques. For fiber applications, LCPs are spun into fibers from lyotropic solutions or melts.<sup>2</sup> The extrusion of the liquid or LC polymers through spinnerets or small nozzles produces highly anisotropic plastic fibers that have very high tensile strength and elastic modulus.

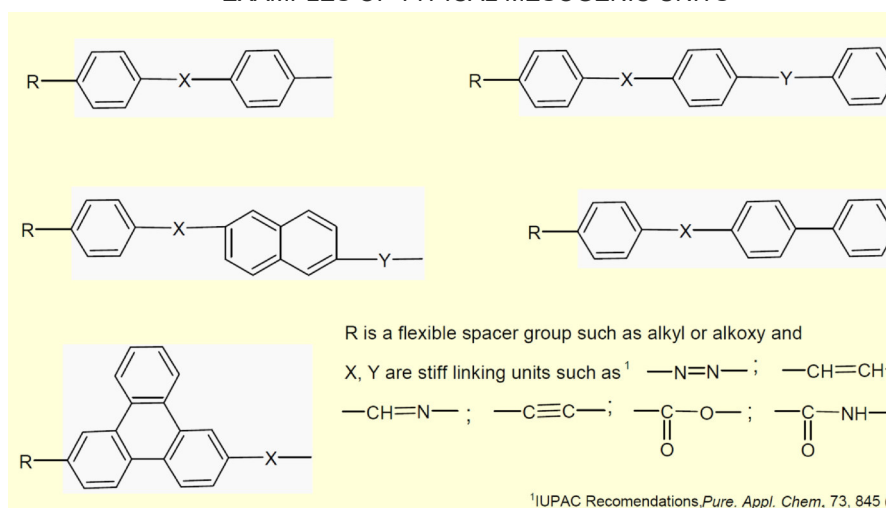
Modern plastics based on LC polymers are often referred to as superplastics because they possess much higher modulus (up to 60-70 GPa) and strength (up to 700 MPa) than conventional plastics. They also exhibit very low elongation at break (typically in the range of 1.5 - 2%), high stiffness and very low thermal expansion coefficients (CTE) with

noticeably lower than those of conventional non-liquid crystalline polymers and often comparable with the CTE of glasses.<sup>2</sup> For example, the tenacity of aromatic LC polyamide fibers is typically 2 to 3 times higher and the elongation is about 10 to 20 times higher than those of high-strength yarns based on aliphatic polyamides such as nylon 6. Aromatic polyamides have also a favorable strength-to-weight ratio due to their low density. For example, their specific strength is about 8 times higher than that of steel and comparable to those of carbon fibers and glass fibers.<sup>3</sup>

The enhanced mechanical properties of LCPs are the result of a more dense packing of the polymer chains in the liquid crystalline state due to the parallel alignment of the rigid mesogenic groups which is further enhanced by extrusion, spinning, etc. The highly ordered structure and the resulting low void density present in LCPs is also responsible for the much lower permeability and exceptionally good hydrolytic and chemical resistance including many (diluted) acids / alkaline solutions. A large number of common liquids and solvents.<sup>4</sup>

The anisotropic LC structure intermediate between the crystalline solid and disordered liquid state is unique to liquid crystalline polymers.<sup>5</sup> In the liquid crystalline state, the ordered grouping of the rigid segments is sufficient to impart some liquid-like behavior on the plastic, but the attractive forces between the aligned molecules are not strong enough to prevent movement of the rigid crystalline domains when exposed to external forces or fields. The high mobility of the crystals or for molecular rearrangement of the crystals and thus for manipulation of the anisotropic properties by mechanical means, heat, radiation, electromagnetic fields, and in some cases, even by the chemical environment. This behavior makes LCPs very desirable as functional materials for a broad spectrum of optic and optoelectronic applications.

#### EXAMPLES OF TYPICAL MESOGENIC UNITS



#### COMMERCIAL LIQUID CRYSTAL POLYMERS

The highest volume commercial LCPs are liquid crystalline polyesters. One of the cheapest is *self-reinforcing* polyester which can be produced by co-polycondensation of p-hydroxybenzoic acid and terephthalic acid and/or 4,4'-dihydroxydiphenyl with ethylene glycol as a coreactant. Important manufacturers of this type of LCP are Celanese and Solvay.

A common fully aromatic liquid crystalline polyester is based on copolyesters of p-hydroxybenzoic acid and 6,6'-naphthoic acid which is sold under several trade names. Two important manufacturers of polyester-based LCPs are Celanese and Kuraray which market these products under the trade names **Vectran™**, **Vectra®** and **Zenite LCP**. Various grades of these resins are available on the market including unreinforced, glass and carbon fiber reinforced, PPS (Vectra) as well as mineral, graphite and carbon black loaded. Many of these resins can be easily molded with processing techniques including injection molding, extrusion, co-extrusion and thermoforming.

An important LC polymer based on aromatic amide is poly(p-phenylene terephthalamide) also known as **Kevlar**. Other important manufacturers of aromatic polyamides are Honeywell (**Spectra®**), Teijin (**Twaron®**) and DuPont (**Kevlar®**). Commercially, these LC polymers are mainly sold in the form of fibers. The fibers are typically wet spun which is

extruding the dissolved resins through small orifices of spinnerets into an aqueous coagulation bath to extract them. The fibers are subsequently drawn at high temperature to increase their strength.

## APPLICATIONS

LC polymers are much more expensive than standard thermoplastics but have excellent mechanical and electrical properties and outstanding chemical resistance. They are used for very demanding applications in many industries. Examples include ultra-high-strength and lightweight fibers and cables, bulletproof vests, tennis strings, hockey sticks (carbon composite), snowboards, tire reinforcement, jet engine enclosures, brake and transmission friction parts, and gears.

LC polymers are also widely used as functional materials in all kinds of optical and optoelectronic devices because of their anisotropic material properties such as refractive index, birefringence, selective light reflection and transmission characteristics are tunable by temperature, mechanical stress, and electromagnetic radiation and fields. Important applications include temperature-sensing, data storage, display technology, telecommunication and numerous other optoelectronic products.

<sup>1</sup>Mesogens or mesogenic groups are the parts of the polymer that self-assemble and phase-segregate into a number of ordered domains. The rigid mesogens can be located in the main chain or in the side chains (branches) or they can be the polymer itself.

<sup>2</sup>V.P. Shibaev, A.Y. Bobrovsky, *Russ. Chem. Rev.*, 86 (11) 1024-1072 (2017)

<sup>3</sup>Kevlar® Aramid Fiber Technical Guide, H-77848 4/00

<sup>4</sup>The chemical resistance depends on the chemical structure and composition of the LCP as well as on the test condition such as temperature and time of exposure.

<sup>5</sup>The liquid-crystalline state is only retained within a certain temperature range. More specifically, the LC state exists only between the clearing temperature (or melting temperature, if a polymer is able to crystallize) and the isotropization temperature (T<sub>iso</sub>). Above T<sub>iso</sub> it loses its LC properties and behaves like an ordinary isotropic polymer melt whereas below its glass transition temperature (T<sub>g</sub>) the polymer behaves like a (semi-)crystalline solid but with anisotropic properties because the anisotropic structure is fully preserved below the T<sub>g</sub>.