

# MORPHOLOGICAL HIERARCHY IN LIQUID CRYSTALLINE POLYMERS

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### LIQUID CRYSTAL PHASE

Liquid crystalline phase has order intermediate to the complete disorder of liquids and long ranged three dimensional order of crystalline solids. Thus a liquid crystal can flow like a liquid but the molecules within the liquid are arranged and oriented in a crystal like way. Molecules which exhibit the liquid crystal behavior are known as *mesogens*. Mesogens are usually organic compounds with a highly anisotropic molecular shape or polymers composed of units having a high degree of rigidity in the backbone or in the side chains. The mesogens do not exist in the liquid crystalline phase all the time. Liquid crystals can be classified into either *thermotropic* or *lyotropic* liquid crystals. The thermotropic mesogens exhibit a phase change on the basis of the changes in temperature and the lyotropic mesogens do so due to changes in concentration.

The most common liquid crystal phases are the *nematic* phase and the *smectic* phase. In the nematic phase the molecules have no positional order but long range orientational order. Thus the molecules may flow like a liquid and be arranged randomly but still be pointing in the same direction. In the smectic phase along with the orientational order the mesogens are also grouped into layers and thus have long range positional order. In the smectic A phase, the molecules are perpendicular to the layer planes and in the smectic C phase the molecules have a slight tilt.<sup>1,2</sup>

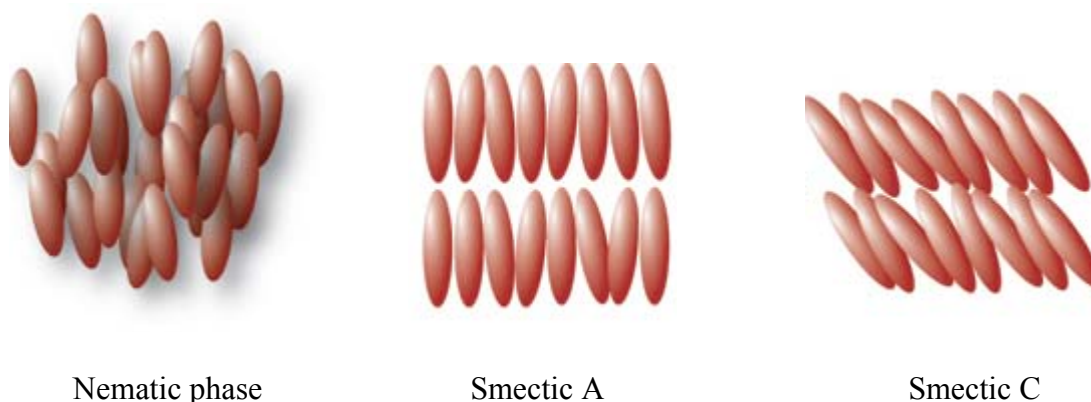


Fig 1: Three commonly observed types of liquid crystal phases<sup>1,2</sup>

Polymer liquid crystals are materials which combine the versatility of polymers with the liquid crystalline behavior. In order for the flexible polymers to show liquid crystalline behavior rigid rod like or disc like mesogens must be incorporated in the chain structure of the polymers. The placement of these mesogens gives rise to main chain or side chain polymer liquid crystals. Main chain PLCs are formed when the rigid mesogen is incorporated in the backbone of the polymer chain. Normally the mesogen consists of aromatic rings which impart the necessary stiffness through steric hindrance and resonance. Eg aromatic polyesters.

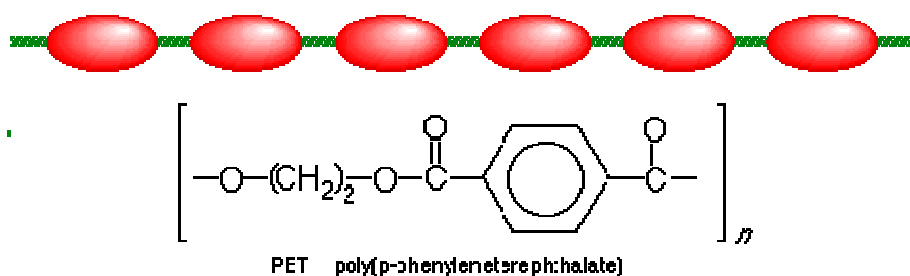


Fig 2 : Main chain LCP<sup>3</sup>

Side chain LCPs have the mesogen attached to the side of the main backbone chain through the spacer block. The mesogen again consists of aromatic rings joint together by some functional group and the spacer consists of a sequence of methylene groups. The mesogens are able to orient although the polymer main chain may be in the entangled form due to the presence of the spacer groups. The spacer group provides the flexibility or the mesogen to move.

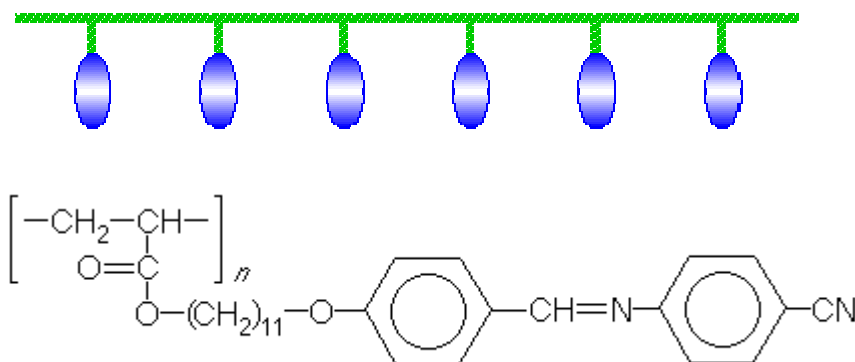


Fig 3: Side chain LCP<sup>3</sup>

## MORPHOLOGICAL HIERARCHY IN ORIENTED LCPs

The liquid crystalline polymers comprise a broad class of materials but can be classified into lyotropic aramids such as poly (p-phenylene terephthalamide) or PPTA (commercialized as Kevlar), ordered lyotropic aromatic heterocyclic polymers and the thermotropic aromatic polyesters.<sup>4</sup> All these LCPs possess high orientation and modulus. Microscopy studies of the highly oriented thermotropic polyesters and Kevlar revealed a distinct surface skin and a regular fibrillar internal structure. This meant that the structures had a high aspect ratio and were tape-like and uniaxially oriented.<sup>4</sup> These fibrillar structures were observed for fibers, films, ribbons and all other extruded thermotropic polyesters.



Fig 4: The fibrillar structure of a fractured Kevlar fiber<sup>4</sup>

The existence of structural hierarchy in Kevlar fibers was first put forth on the basis of electron microscopy and electron diffraction studies by Dobb.<sup>5</sup> Using selected area microscopy and dark field imaging techniques associated with it established that the supramolecular architecture of these fibers consisted of a system of sheets pleated regularly along its long axis and arranged radially.

Sawyer and Jaffe developed this hierarchical approach in terms of the observed fibrillar nature of Kevlar and thermotropic polyesters. Extensive microscopic analysis using polarized light microscopy (PLM), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) supplemented by electron diffraction studies allowed the delineation of different size scales of these fibers. The size scales of the fibers observed

were 5 microns in diameter (macro fibrils), 0.5 microns or 500 nm (fibrils) and 0.05 microns or 50 nm (micro fibrils). This matched the size scales observed for Kevlar too where the micro fibril was observed to be around 30-40 nm. This gave rise to a structural hierarchy in these fibers which can best be explained by figure 5.

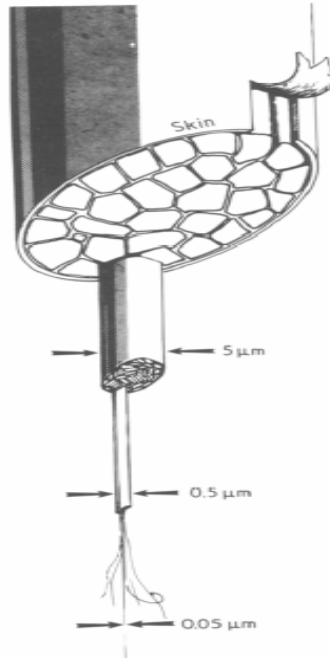


Fig 5: The proposed hierarchy in LCP fibers<sup>4</sup>

In case of molded parts and extrudates the same fibrillar hierarchy hold and is further complicated by the presence of a skin-core pattern with the skin oriented and the core less well oriented.

It was believed that the micro fibrils existed from before the use of sample preparation techniques. Also the size scale of the micro fibril agreed for the range of samples that were studied. On the other hand the morphology of the macro fibrils depended more on the process parameters and gradients like temperature and stress. Thus fibrils were fiber like in fiber samples, tape like in extrudates and sheet like in injection molded samples.<sup>4</sup>

Although this fibrillar hierarchical model was initially proposed only for the thermotropic polyesters it was soon extended for lyotropic polyesters like Kevlar, rigid rod like polymers and even to highly oriented extended chain structures such as polyethylene which were processed by conventional techniques.<sup>6</sup>

Later studies revealed that the micro fibrils existed within larger fibrillar units and not as separate entities. This confirmed that micro fibrils were not formed as a result of some deformation or sample preparation technique.<sup>6</sup> Also the micro fibrils were observed to be tape-like in both Vectran and Kevlar instead of a round fibrous shape with a width of around 10 nm and a thickness of about 3 nm.<sup>7</sup> This was confirmed by three dimensional imaging by a scanning tunneling microscopy study.<sup>7</sup>

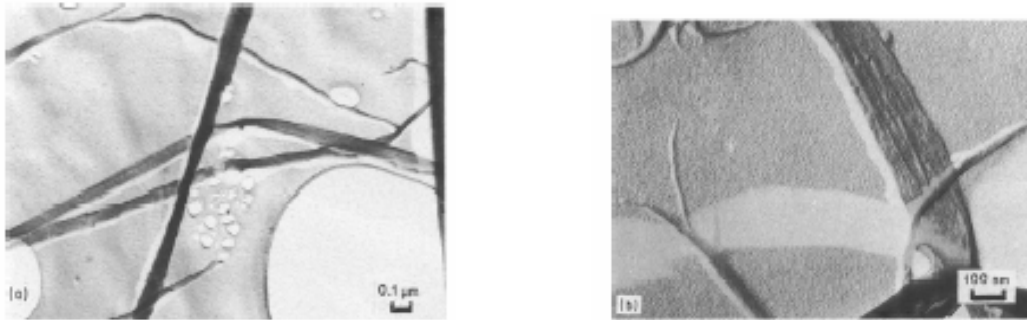


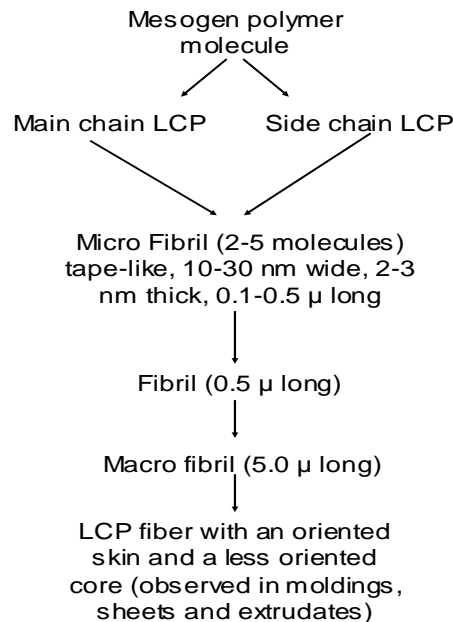
Fig 6: TEM images of (a) Vectran and (b) Kevlar showing the tape like nature of the microfibrils and illustrating the fact that they are present within larger fibrils<sup>7</sup>

Although on the higher size scale both the fibrils and the micro fibrils were oriented in the direction of the fiber axis, imaging revealed that the perfect orientation does not hold on the local level. The fibrils and the micro fibrils meander in and out of the longitudinal plane and show a worm like trajectory rather than a rigid rod like model which can be inferred from the tape like nature of the micro fibrils.<sup>7</sup> This behavior is similar to the worm like chain model for polymers which is an intermediate to the rigid rod like model and the completely random coil model used for polymer coils.

Comparison with the molecular indicated that the micro fibrils were 2-5 molecules long and were thus macromolecular. Previously micro fibrils were observed for natural minerals and were imaged by using the earliest TEM.<sup>8</sup> Later on they were developed for biological materials like cellulose<sup>9</sup> and conventional random coil polymers before the same concept was applied to the LCP behavior. In all cases the general shape of the molecular chain is very large compared to its width and thickness. This gave rise to the idea that the micro fibril was a replication of the molecular chain. This made the micro fibril the smallest structural unit associated with the mechanical properties and the

properties such as compressive strength, tensile strength and fracture are related to the shape and orientation of micro fibrils.

Thus it is possible to express the hierarchy in liquid crystal polymers in the form of the following flow chart.



Thus to summarize upto this point the report describes the hierarchy observed in the morphology of liquid crystal polymers. The current research focus is no longer solely directed towards the synthesis of new liquid crystal structures but is more towards understanding the structure property relationships shown by this class of materials. As an example of this the report will discuss certain interesting observations which relate the liquid crystalline morphology and its effects on spider silk.

## SPIDER SILK AND LIQUID CRYSTALLINE BEHAVIOR

Spider silk is known to be extraordinarily strong and has a tensile strength comparable to that of engineering steel. It has a breaking stress comparable to Kevlar but inspite of all this the relative density is 1.3 as compared to 7.8 for steel.<sup>11</sup> A spider uses this silk for a variety of applications which require a different set of properties. This is achieved by

subtle variations in the chemical composition of silk and parameters involved in the processing of the material in the fluid state.

The structure of spider silk shows components with a well ordered hierarchical morphology. Silk is a pure protein called as fibroin and a simplified version of the molecular structure is shown in fig. 7.

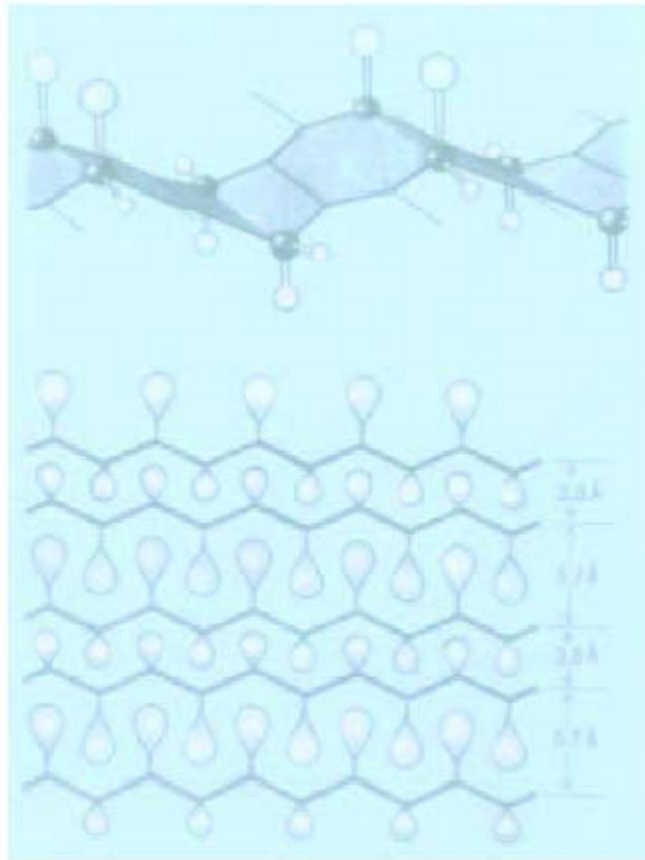


Fig 7: The  $\beta$  pleated sheet secondary structure of spider silk protein<sup>10</sup>

Crystalline blocks of  $\beta$ -sheet structure are a part of rubbery, disoriented matrix of random chain material.<sup>10</sup> In each of the pleats the polypeptide strands lie in an anti-parallel array and they are linked to each other by hydrogen bonding between the carbonyl group of one chain and the  $-NH$  group of its neighbor. In case of silk fibroins nearly half the amino acid residues are glycines, another third are alanines and the remainder is serines. In these fibroins there is an alternating pattern where every other amino acid is a glycine so that all the R-groups one side of the sheet are hydrogen atoms which gives it a mild hydrophilic character. Alanine makes up the remainder of the amino acids making the other side of the sheet rich in methyl groups and consequently more hydrophobic. These



sheets can thus stack together with an alternation in spacing which introduces a further complexity in the structure.

Thus it can be seen that spider silk structure shows morphology inherent to most protein structure. There is a primary structure comprising of amino acid chain backbones. The secondary interactions are in the form of the various hydrogen bonds and Van der Waal's interactions that occur between the carbonyl and the amide groups. Further complications arise in the form of hydrophobic and hydrophilic interactions that occur between the stacks of  $\beta$ -sheets giving rise to a tertiary structure.

There exists a liquid crystalline phase in this complex hierarchy of a biological structure which greatly alters the spinning parameters of the spider silk. However the unbranched polypeptide chain of silk does not have any rigid rod like molecules which can contribute towards liquid crystalline behavior. This can be explained on the basis of the silk spinning process. Initially the proteins are synthesized from individual ribosomes in a hydrated state. This is followed by the development of the crystalline domain in the downstream side of the gland which is dispersed in the fluid hydrated matrix. As this solution is concentrated the asymmetry leads to spontaneous alignment and the entire phase becomes liquid crystalline. This liquid crystalline material is then extruded through spinnerets and the material hardens.<sup>12</sup>

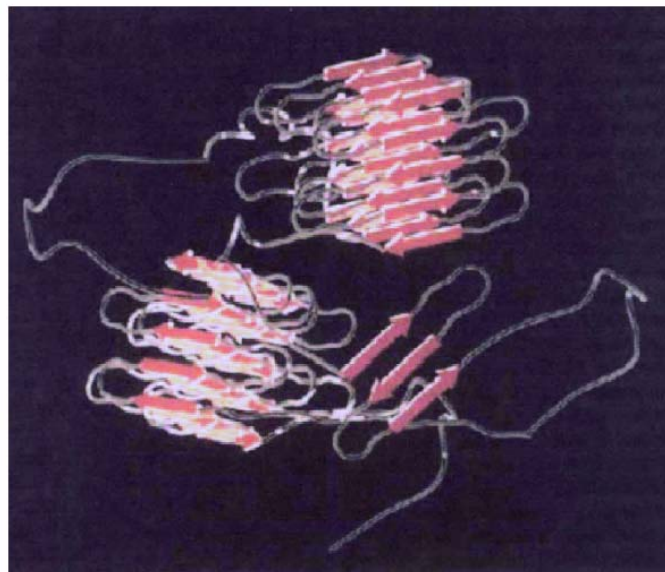


Fig 8: The morphology of silk structure with the crystalline beta sheet domains suspended in a rubbery, random matrix

This introduction of the liquid crystalline phase in the complex hierarchy of biological silk has a huge impact on the natural spinning process. The tendency to retain short range order in the LC phase helps the elimination of defects and allows the material to stay aligned after extrusion. The pressure required to spin the thread is reduced drastically because the LC phase is non-Newtonian in nature and the effective viscosity of the mesophase is very low. Thus an extremely strong silk fiber is spun by the spider in very moderate processing conditions which is in sharp contrast to the synthetic manufacture of Kevlar, Teflon or Rayon which require drastic processing conditions.<sup>10, 12</sup>

The existence of liquid crystal phase in the complex hierarchy of biological spider silk is a topic of intensive research. The motivation behind this is the possibility of spinning extremely strong fibers in relatively 'benign' or 'green' processing conditions.

## **CONCLUSIONS**

The report summarizes the morphological hierarchy exhibited by conventional liquid crystalline polymers such as Kevlar and Vectran. A model common to both thermotropic and lyotropic LCPs has been discussed. It depicts a fibrillar hierarchy in these moldings, extrudates and sheets of these materials. There is a distinct delineation of the fibers into micro fibrils, fibrils and macro fibrils and the size scales for each have been discussed. In addition to this the presence of a liquid crystalline phase as an additional part of the hierarchy of natural spider silk has been described. It is clear that the presence of this phase is responsible for the synthesis of high strength silk fibers in perfectly moderate processing environments.

## References:

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