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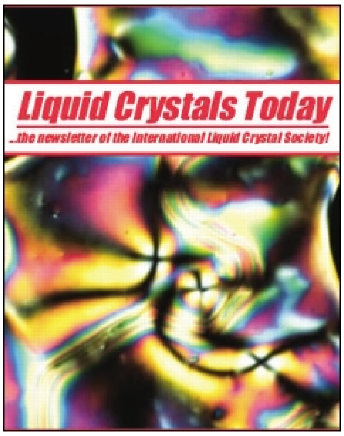

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Applications of Liquid Crystal Polymers: *Part 1: Fibre Spinning*

S. J. Picken[a]
[a] Physical Chemistry Department, Akzo Nobel Central Research, Arnhem, The Netherlands

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Applications of Liquid Crystal Polymers:

Part 1: *FIBRE SPINNING*

**S.J. Picken, Akzo Nobel Central Research, Physical Chemistry Department RGP,
P.O. Box 9600, 6800 SB Arnhem, The Netherlands**

Two categories of liquid crystal polymers (LCPs) should be distinguished. On the one hand we have side-chain LCPs, where the mesogenic groups are attached to a polymer backbone, and on the other hand we have main-chain LCPs where the polymer chain itself contains the mesogenic groups. In the latter case we may either have a continuous semiflexible polymer chain or an alternating sequence of rigid aromatic mesogens and flexible aliphatic spacers. In Fig. 1 the various types of polymer liquid crystal are shown with some possible chemical structures.

As regards applications of LCPs, the present situation is that continuous main-chain LCPs are being used for high-strength high-modulus fibre spinning and for high-precision injection moulding, and that side-chain LCPs show considerable potential for optical applications. With side-chain LCPs it is possible to make optical films with a well defined birefringence, twist, tilt, and optical dispersion, that can be used as passive components in liquid crystal displays for improvement of the viewing angle and the contrast. Also, there are developments to use uniformly oriented LCP layers in digital storage media, such as compact disks (audio and CDR) and optical video tape. Finally, there may be use for chiral LCPs to construct loss-free polarizing light sources and colour filters. From the above it will be clear that LCPs are interesting not only from a scientific point of view. Here we will not discuss the financial side further and will focus more on the scientific and technological aspects. This first part will deal with fibre spinning and in a following contribution some applications of side-chain LCPs will be presented.

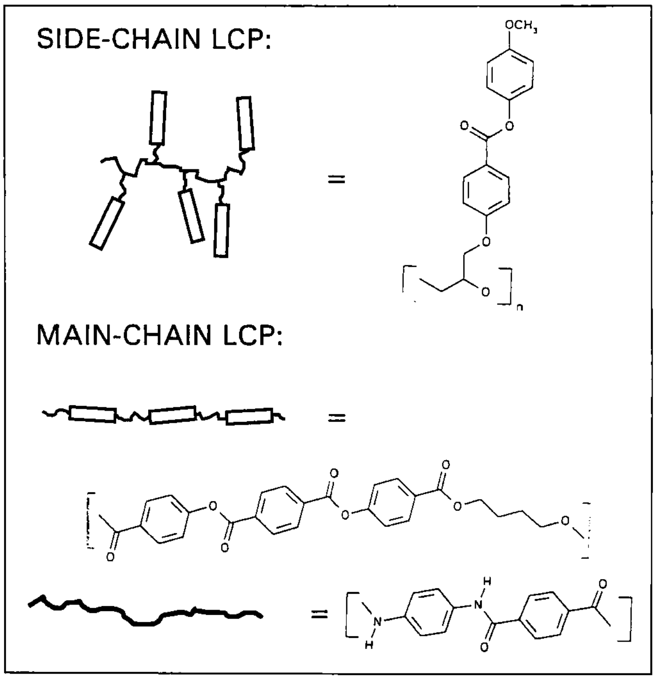

Figure 1. Side-chain and main-chain liquid crystal polymers: *(top)* methoxybenzoate-ester substituted side chain polyether, *(middle)* alternating rigid – flexible main chain polyester, *(bottom)* semiflexible aramid PPTA poly(phenylene-terephthal-amide).

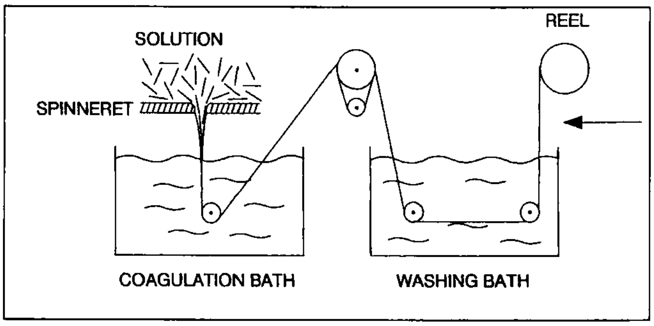

Figure 2. Dry-jet air-gap spinning process used for aramid fibre spinning

Main-chain LCPs for fibre-spinning

In 1958, in the same edition of the *Discussions of the Faraday Society* as the historic paper by Sir Charles Frank on the elasticity of nematic liquid crystals, Conmar Robinson [1] described the occurrence of liquid crystallinity in a solution of PBLG or poly(L-benzyl-glutamate). In the following years this led to the development of PBLG fibre-spinning at Courtaulds. About 10 years later other possibilities for fibre spinning using LCPs were discovered at DuPont and Akzo based on sulphuric acid solutions of PPTA, poly(*p*-phenylene-therephthal-amide), see Fig.1, and similar aromatic poly-amides (aramids). Unlike the PBLG spinning process which never developed to a commercial stage, aramid fibre spinning is of great importance and has led to a.o. Kevlar® and Twaron® fibres. The current yearly production of aramid fibres is about 30 000 tonnes. The applications of these high-strength high-modulus fibres are in composites, e.g. tyres, brake-linings, hoses, conveyer belts, concrete reinforcement, bridge construction, storage tanks, bullet proof vests, helmets; and for heat-resistant non-flammable textiles, e.g. flame-resistant clothing, upholstery for aerospace and public transport. In addition there are small scale applications in sport goods, such as skis, gloves, tennis racquets and the like.

Compared to traditional wet-spun fibres, e.g. the viscose solution-based Rayon fibres, that are spun from an isotropic polymer solution, aramid fibres distinguish themselves by the extremely high degree of molecular orientation that is present. This is due to the liquid crystallinity of the polymer solution used during the spinning process. The nematic solutions are spun in a dry-jet air-gap spinning process, see Fig. 2. In the air-gap the solution is subjected to an elongational flow that causes alignment of the director.

To obtain a high degree of molecular orientation along the fibre axis there are two requirements. Firstly, it is necessary that the molecular orientation with respect to the local director is very high in these solutions, and secondly it is necessary that during the elongation, or draw-down, process the director can be fully aligned. That this is indeed possible may be concluded from the fact that in the fibre that is formed during the aramid spinning process the order parameter S (or $<P_2>$) is about 0.95. This should be compared to the normal values for the order parameter in nematic liquid crystals which usually are in the range of 0.4–0.7. It will be clear that it is necessary to investigate in detail that such a high degree of orientation can be obtained during the aramid fibre spinning process. It should be noted that this high orientation is not specific to aramid polymer solutions but will generally occur in main-chain polymer liquid crystals, both in nematic polymer solutions and melts.

Orientational order in aramid solutions

As mentioned above the orientational order in aramid solutions may be extremely high [2], reaching values up to 0.95. The main reason for this is the rigidity of the continuous semi-flexible polymer chains which is much higher than that of mesogenic groups traditionally found in low-molecular weight nematics. To be more precise the length to width aspect ratio, in e.g. cyanobiphenyls, is about 3 whereas in aramid polymers this aspect ratio is more in the region of 60. For this reason and due to the high melting point of the pure polymer, which is above the degradation temperature of approximately 700°C, liquid crystallinity is only observed in solution. The solvent of choice for the aramid spinning process is concentrated sulphuric acid, where a nematic phase is found for polymer concentrations between about 8–20%, depending on temperature. Although this solvent may appear somewhat unpleasant at first, it should be realized that compared to many solvents used for polymers, sulphuric acid has the advantage that it is not volatile and is not toxic as such, although highly corrosive. In addition sulphuric acid has been handled on an industrial scale with little difficulty since the 17th century.

Examining the nematic aramid solutions in sulphuric acid it is found that the clearing temperature depends strongly on the polymer concentration, increasing by about 20°C for each per cent increase in concentration, see Fig. 3. From this result it can be extrapolated that for 20% polymer concentration the clearing temperature of the nematic solution is about 240°C, so that the nematic range in this case is from 50°C, the melting point of the crystal–solvate phase, to 240°C at the clearing point. Considering this wide range of the nematic phase it is easy to understand why the molecular orientation reaches the high value of $<P_2> = 0.95$. Interestingly such wide nematic ranges are not uncommon for polymer liquid crystals, both for main-chain as well as side-chain liquid crystal polymers. In Fig. 4 a texture of an aramid solution is shown using polarization microscopy. In this rather well aligned sample some disclination loops can be observed. Usually the textures of aramid solutions are less well developed and a rather featureless 'multidomain' texture is observed.

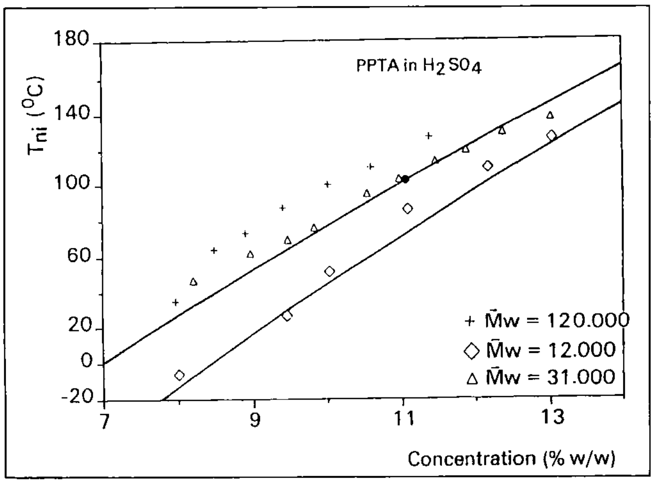

Figure 3. Dependence of the clearing temperature on polymer concentration, the drawn curves are from a simple mean field model described in [3].

Alignment of the director in an elongation flow field

Apart from the local high orientation of the molecules with respect to the director it is also necessary to fully align the director field during the spinning process. Although the details of flow of polymer liquid crystals are not yet fully understood it is nevertheless possible to describe the orientation process during shear flow by relatively simple means. The central observation required to do this is the fact that the director itself is a macroscopic property of the liquid crystal phase, i.e. it is hardly influenced by thermal motions. From this it may be expected that during deformation of the polymer nematic in a flow field the director orientation follows the overall deformation in an affine fashion. In such an affine deformation the assumption is that the local deformation of the sample is identical to the macroscopically applied strain. The result of this somewhat simplified picture is that the director field may be considered to be a highly deformable structure in the fluid that follows the external deformation with little or no resistance. Using this approach it is relatively simple to calculate what the effect of the applied elongational flow during the spinning process will be [2,3]. In Fig. 5 this affine

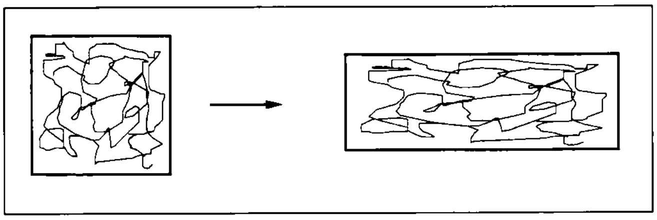

Figure 5. Affine elongational deformation process. The wiggly lines are an artists impression of an infinitely deformable director field.

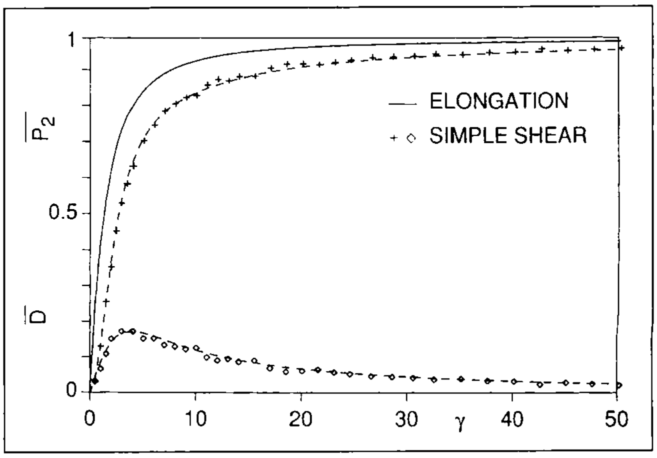

Figure 6. Director alignment order parameter $\bar{P}_2$ as a function of elongational strain L/L_0 λ = (= 1 + γ).

deformation process is shown graphically. In Fig. 6 the resulting degree of director orientation is shown in terms of the director order parameter $\overline{P_2}$ as a function of the elongation where $L/L_0 = \lambda = 1 + \gamma$. From experiments it is observed that for a draw ratio of 1 (no elongation) the director is already aligned by the flow through the spinneret. This pre-orientation, with $\overline{P_2} = 0.85$, may be imagined to be equivalent applying a virtual elongation λ of about 8. During the normal spinning process a further elongation of about 6 – 8 is applied in the air-gap so that an overall λ of approximately 50 is used. In this case the director alignment due to affine deformation is essentially complete with an expected $\overline{P_2}$ value of 0.993, see Fig. 6. For this reason in normal aramid spinning it is sufficient only to consider the molecular order parameter and to assume complete director alignment. If one applies a low draw-ratio then of course the director alignment does have to be taken into account.

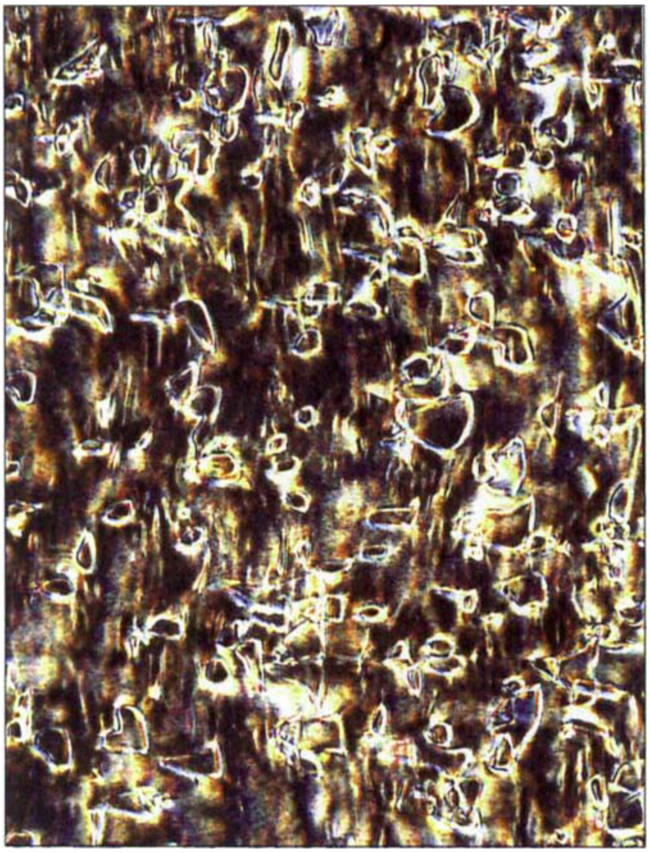

Figure 4. Polarization microscope texture of an aramid solution occurring after cessation of shear flow in the horizontal direction and subsequent annealing. The light lines are the (integer strength) disclination loops. The periodic colours are from the so-called band texture.

Mechanical properties and molecular orientation in the fibre

In the aramid spinning process the highly oriented nematic solution is coagulated in the water bath. It is found that the alignment that is present in the nematic phase is frozen in during the coagulation process and that the resulting order parameter of the aramid chains with respect to the fibre axis is about 0.95. The value of the order parameter in the solution can be modified either by changing the polymer concentration or by changing the temperature. The relevant temperature in this case is found to be the temperature of the water in the coagulation bath.

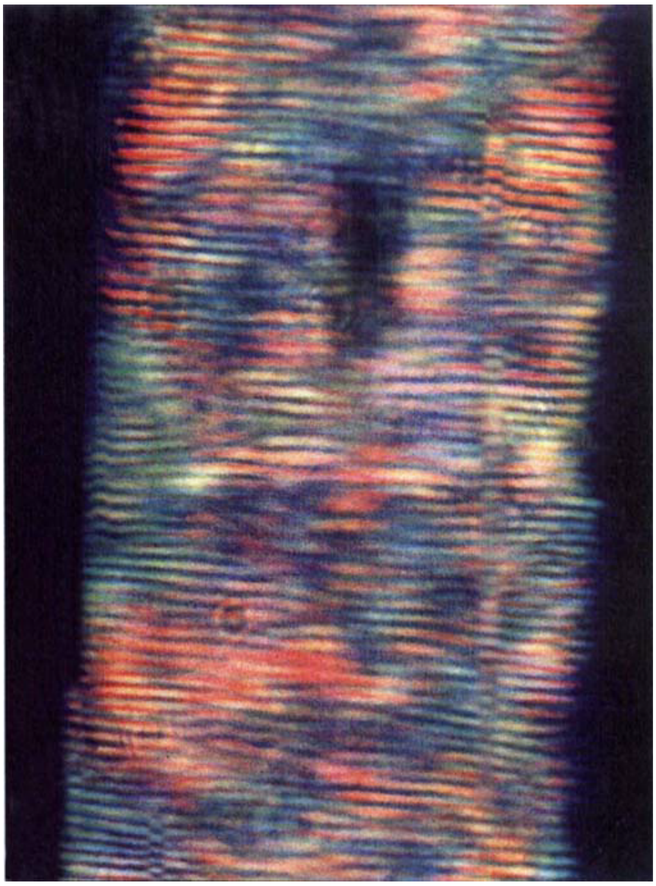

Figure 7. Polarization microscope image of a single aramid filament, diameter 12 μm, the fine periodic texture (period about 0.5 μm) is the pleated sheet structure, which results from small variations of the director alignment.

Due to the high degree of molecular alignment the mechanical properties of the polymer are highly anisotropic where the Young's modulus along the axis is about 100 GPa and the lateral modulus is about 1.8 GPa. The modulus along the fibre direction is to a good approximation given by [4]:

$$\frac{1}{E} = \frac{1}{e_c} + \frac{\overline{< \sin^2(\Theta) >}}{2g} = \frac{1}{e_c} + \frac{1 - \overline{< P_2 >}}{3g}$$

where e_c is the chain modulus of approximately 240 GPa and g is the shear modulus of about 2 GPa. Here the overall orientational order $\overline{<P_2>}$ is a product of the local molecular order with respect to the director and the director order parameter: $\overline{P_2}\,<P_2>$. From this equation it will be clear that extremely high orientational order is required before this has an appreciable effect on the modulus.

To conclude this somewhat concise introduction to fibre-spinning Fig. 7 shows the structure of an aramid filament. The longitudinal periodicity that occurs in such filaments is due to a variation of the optical axis (or director). The exact cause for this phenomenon is unknown but is thought to be due to the coagulation process.

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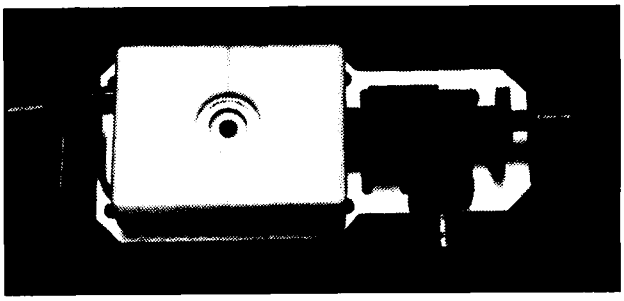

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