ADVANCED
MATERIALS

Liquid Crystals—State of the Art

By Heino Finkelmann*

A century ago, in 1888, the liquid crystalline state of matter was discovered. One might suppose from this that liquid crystals have begun to grow old. Actually the reverse holds: liquid crystals have increased our possibilities for producing advanced materials par excellence. The realization of super-molecular organization in the liquid crystalline state offers additional dimensions for tuning the physical properties of organic or organometallic materials including macromolecular systems. Therefore the molecular design of liquid crystals to create materials with exceptional properties is a challenging task for chemists in cooperation with physicists, materials scientists and engineers.

What are the main aspects of liquid crystalline materials currently under investigation? Although the different basic molecular geometries and constitutions causing the formation of the liquid crystalline state are known, so far only systems built up by rigid rod-like molecules have proven to be suitable for new applications. This holds for low molar mass as well as for polymeric liquid crystals.

Low molar mass liquid crystals in the nematic phase, in which the rigid rod-like molecules are ordered with respect to their long molecular axis, have been intensively studied both experimentally and theoretically during the last few decades. This was mainly due to their potential applications in optoelectronics, especially for low energy consuming displays: by applying an electric field the preferred orientation of the molecules can be altered (due to the liquid state), which causes a change in the (anisotropic) optical properties. Although this process had already been developed early in the seventies, remarkable progress in the layout of the display cell and in thin film transistor (TFT) technology calls for new designs of liquid crystals. Their chemical constitution has to be optimized with respect to the anisotropic phase properties such as viscosity, dielectric and elastic constants. Several new classes of nematics have been designed, which give a increased output in display technology: super-twisted-nematic (STN) displays are available having high resolution (e.g. for computers) and TFT displays give excellent picture quality for pocket color TV sets or for projection of TV pictures.

Liquid crystals research currently focuses not only on nematics but also on the ferroelectric chiral smectic phases, especially the chiral smectic-C phase. In this phase the rod-like molecules also have long range positional order within layers, with the long molecular axis tilted relative to the layer normal. These ferroelectric liquid crystals allow the production of very fast switching displays, which compete with TFT displays for TV screens. Only a few years ago little was known about these smectics, especially with regard to the relationship between the chemical constitution of the molecules and the temperature regime of the smectic-C phase. Since then intensive research by chemists and physicists has allowed the systematic synthesis and blending of smectics, which can serve technological demands, especially of the optoelectronics industry.

Polymeric liquid crystals have attracted much attention during the last few years. The combination of polymer-specific properties with the anisotropic physical properties of the liquid crystalline state offers wide-ranging possibilities for the design of new materials. Two different types of polymers—both based on rigid rod-like monomer units, yet completely different in application—have been examined: the "LC-main-chain polymers", where the rod like monomer units are within the polymer backbone, and the "LC-side-chain polymers", where the rod like moieties are attached as side groups to the backbone.

Contents

---

[*] Prof. Dr. H. Finkelmann
Institut für Makromoleculare Chemie der Universität
Stefan-Meier-Strasse 31, D-7800 Freiburg (FRG)

LC-main-chain polymers exhibit an orientational long range order of the polymer main chains in the nematic state. A shear gradient—e.g. during a spinning process—causes a macroscopic alignment of the preferred orientation of the macromolecules. Fibers can be easily obtained, where the polymer main chains are highly ordered in the direction of the fiber axis. This yields outstanding mechanical properties. Due to the orientation of flow the (anisotropic) viscosity was also observed to be lower than the viscosity of amorphous melts, which makes the processing of these materials easier. Furthermore, injection molded samples have very small thermal expansion coefficients in the solid (partially crystalline) state and, as a result, can be used as construction elements, since they hardly change their dimensions with temperature.

For LC-side-chain polymers the most remarkable property is the vitrification process of the liquid crystalline polymer melt. Liquid crystalline polymers—smectic or nematic—do not change their structure when frozen in the glassy state and consequently become *anisotropic glasses*. This means that the liquid crystalline polymer melt can be macroscopically or locally aligned by external electric or magnetic fields and vitrified to the ordered, anisotropic glass, giving solid materials with anisotropic physical properties. The vitrification of ordered ferroelectric chiral smectic-C polymers, for example, might give a completely new class of materials. Furthermore their non-centrosymmetric phase structure makes them suitable for applications in nonlinear optics. Research in this field is, however, still in its infancy.

The enormous potential of LC-side-chain polymers, especially for optical applications, is demonstrated by an example recently developed in our laboratory. The chemical crosslinking of the linear LC-side-chain polymers yields liquid crystalline elastomers ("rubbers"). Mechanical deformation of these elastomers by stretching or compressing causes a macroscopic orientation of the liquid crystalline molecules similar to the electric field orientation of low molar mass liquid crystals. Elastomer films can be prepared, whose macroscopic optical properties are similar to the optical properties of an anisotropic single crystal having the same dimensions. There is, however, an additional feature to these elastomers: a local deformation of the macroscopically aligned film causes a local change of the optical properties. This is schematically shown in Figure 1. If the plane surface of the film is brought into contact with a "stamp", which has a defined pattern of micron dimensions, the pattern deforms the elastomer surface and consequently the local direction of the optical axis. This can be directly observed in a polarizing microscope with crossed polarizers as shown in Figure 2. It is obvious that this offers a relatively simple technique for producing elements for the integrated optics. Light conducting pathways can be mechanically pressed into the liquid crystalline elastomer film (similar to the production of a record) and durably stored in the glassy state.

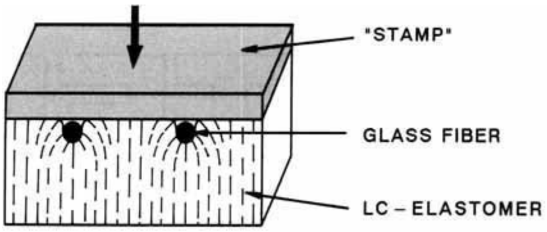

Fig. 1. Schematic drawing of the local deformation of the optical axis of an LC-elastomer by a "stamp" for application as planar light conductor for integrated optics. In this example a smooth stamp presses a glass fiber (10 μm diameter) into the elastomer surface. The arrow indicates the viewing direction parallel to the optical axis (of the undisturbed elastomer) as shown in Figure 2.

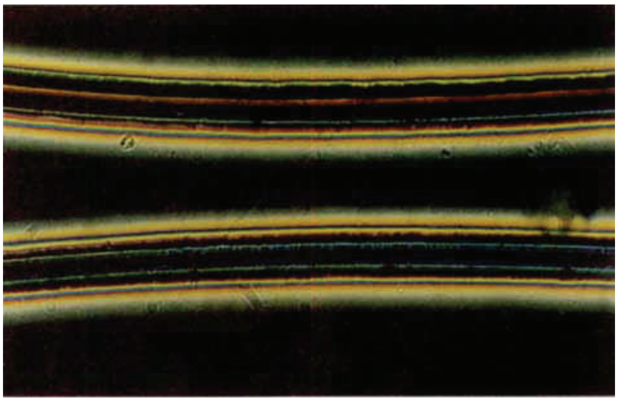

Fig. 2. Polarizing photomicrograph (crossed polarizers) of a locally deformed LC-elastomer. The local change of the birefringence is indicated by the interference pattern. The black area denotes regions where the optical axis of the elastomer is parallel to the viewing direction.

Although the liquid crystalline state of matter was discovered one hundred years ago, it was for many decades regarded only as a laboratory curiosity. The developments in the last twenty years impressively demonstrate the outstanding potential of liquid crystals as technologically relevant advanced materials.

Prof. Dr. Heino Finkelmann is Professor of Polymer Chemistry at the University of Freiburg, FRG. Born in 1945 in Gronau/Alfeld, he first became an engineer. Starting in 1969, he then studied chemistry at the Technical University of Berlin (Diplom in 1972) and at the University of Paderborn, where he earned his PhD under the supervision of H. Stegemeyer. He spent three postdoctoral years with H. Ringsdorf at the University of Mainz, and moved to the Technical University of Clausthal in 1978. Immediately after the Habilitation in 1984 in Clausthal he was offered his current position. He has been awarded the Carl-Duisberg-Gedächtnispreis of the Gesellschaft Deutscher Chemiker and the "Dozentenstipendium" of the Fonds der Chemischen Industrie. Professor Finkelmann is a member of the Scientific Committee of the 12th International Liquid Crystals Conference to be held in Freiburg from 15–19 August 1988.