Liquid crystal polymers under fire

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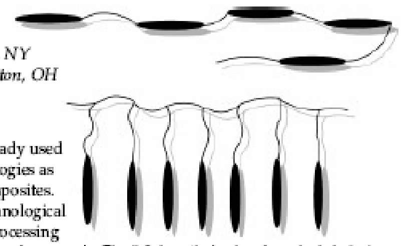


(Fig. 1) Schematic drawing of a main chain (top) and side-group LC polymer.

There are many types of molecules which show an intermediate (or meso-) phase before they crystallize on cooling. The molecules in these *mesophases* behave like liquids and flow, but also exhibit the anisotropic properties of crystals such as birefringence and the molecular order that can scatter X-rays. Such low molecular weight compounds can form anisotropic molecules and have been known for more than 100 years as liquid crystals (LC).

From the beginning, LC material research has been a fantastic adventure for scientists and not without reason. F. Reinitzer described [1] his new compounds when observed under a microscope as living materials and there are indeed several important biological systems based on liquid crystalline order. Since that time many thousands of mesogens have been synthesized thanks to the boundless imagination of chemists. From 1965 onwards, the invention of effective electro-optical displays based on LC's has increased research significantly in new directions.

Low molar mass liquid crystals have become everyday items and there are now attempts to exploit LC polymers because of their advantages in displays, optical devices and other applications (e.g. the solidification and vitrification properties allows drawing these materials into complex shapes with inherent anisotropy). There are many different ways of attaching the mesogenic groups to a polymer backbone. Figure 1 shows a schematic of the two standard LC polymers. These polymers can form films, make high modulus fibers and produce coatings with special features for different requirements. They are already used in such widely different technologies as displays and high modulus composites.

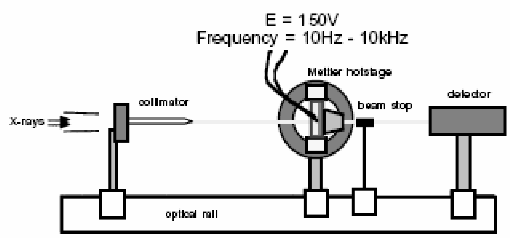
Despite the considerable technological progress in the synthesis and processing of polymers, there is little known about the basic principles of anisotropic molecules which possess certain mesophases, that is, occupy different arrangements in the LC state. Part of this lack of understanding is due to the many ways in which LC polymers can be constructed and the effect this structure has on LC behavior. In particular this is reflected in the absence of solid state structure analysis of side-group polymers whereas many structures of crystalline main chain polymers were solved.

For structural applications of LC side-group polymers, attention has been paid almost exclusively to their mechanical properties. In this case, the question of the basic relationship between molecular and macroscopic behavior is of secondary importance. However, to obtain more knowledge about the processing of such materials for new developments in holography, electro-optical devices [2] or light induced data storage, the entire structure must be very well understood [3,4]. To understand LC behavior, the molecular structure and organization of each molecular component of the polymer chain is important [5,6].

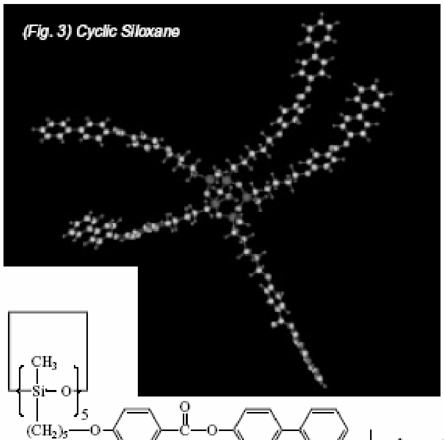
There are also advantages to having materials with properties between the low molar mass liquid crystals and LC polymers for adjusting such behavior as relaxation times on switching in external fields. For this reason oligomeric liquid crystals and compounds based on cyclic backbones with low molecular weights are being designed which exhibit an advantageous combination of glass forming and low melt viscosity properties. These oligomers (in ferroelectric form) are able to switch as fast as low molecular weight compounds and still exhibit the behavior of polymers [7]. To date it is not possible to predict *a priori* the kind or number of LC phases from a given architecture even with all the data available. This skill would be a strong advantage to our program for the synthesis of new LC polymers and oligomers. It would enable the tailoring of new materials with special properties for a variety of uses.

With the use of fast, real-time observations like those made possible by synchrotron sources, a new window is opening not only on the time scale of measurement but also on a new understanding of the nature of LC polymers. One of the dreams of a polymer crystallographer, to follow static and dynamic behavior and to observe those results simultaneously, can now be realized. We can now directly monitor the response of a polymer LC under applied external electric fields, for example. Within a few days, data is available which might usually take months or years to be collected. It is thus our primary aim with the CHESS work to gain more insight into the dynamics and structure-property relationships of LC compounds.

We had several days of beamtime available last fall. Like all CHESS runs, there were some unexpected developments while debugging our equipment. For example, with the modifications to A1, the new hutch size required changes to our usual procedures and experimental setup. Our prized Huber vanished and with the help of the excellent CHESS staff we pieced together what we needed and could study our materials with the device shown in Fig. 2.



(Fig. 2) Experimental setup for the electric field alignment, heating, and x-ray data collection on LC polymers.



(Fig. 3) Cyclic Siloxane

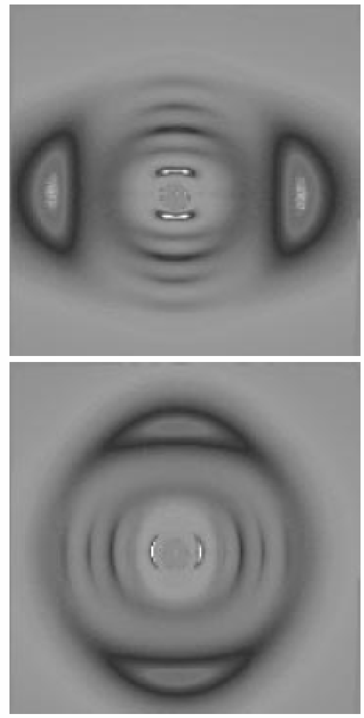
There is much data available on the switching behavior of LC materials in E-fields by polarizing optical microscopy (POM) which has been extensively used. With this method the molecular structure is not probed but only the macro structure of the investigated system i.e. birefringence before and after switching. With our experimental setup it is now possible to look at the microstructure of the system where we can directly follow the motion of molecules on switching.

The Mettler hotstage is used both for heating samples and for mounting electrodes. With this arrangement it was possible to investigate the polymers in the different LC phases. Furthermore, frequency and voltage were simultaneously applied to study the alignment of liquid crystal materials. The electrodes are separated by a 120 - 150 micron thick Kapton™ film. With an AC-field of about 1V/micron, low molecular weight compounds, oligomers and polymers could be oriented easily.

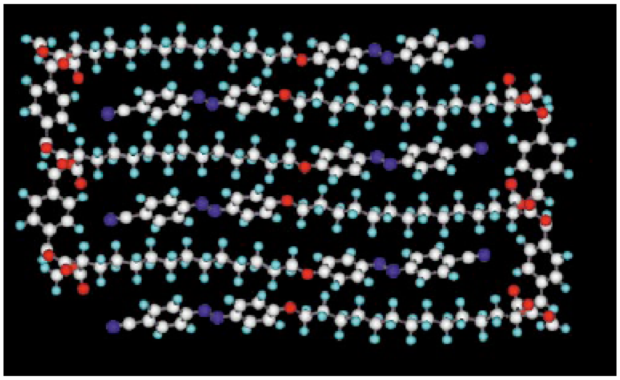
The samples were loaded into the 150 micron gap between electrodes where the polymer was held by capillary forces. From a previous CHESS run it was known that low molecular weight compounds and oligomers such as cyclosiloxanes (Fig. 3) with a molar mass not higher than 3000 g/mol were suitable for aligning in the applied E-field of 1V/micron [8]. For one of these cyclic siloxanes we again found switching on changing the frequency of the applied field, but we were all awake even at 2 A.M. when on cooling the sample changed orientation by 90° without changing frequency (Fig. 4). With a phase transition from nematic to smectic C, the side-groups changed their direction from a homeotropic to planar orientation. This process is reversible, and only observable using real-time diffraction techniques. Aside from changing our fundamental understanding of liquid crystals, this observation could in the future affect display and certain memory technologies.

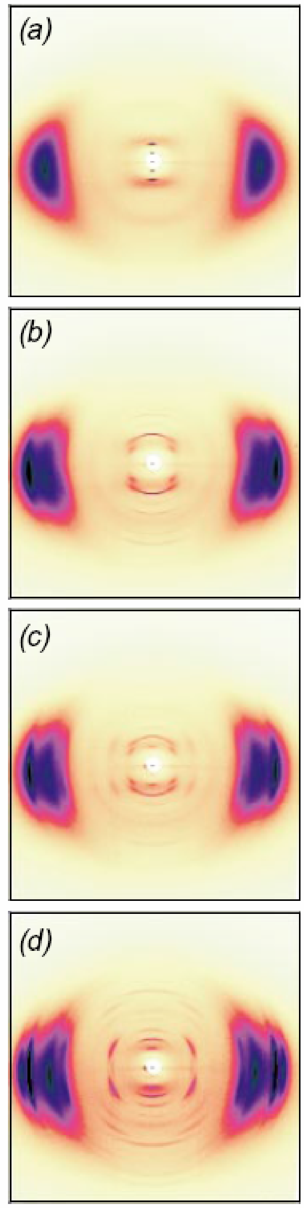
Based on our experience, it was doubtful whether linear polymers with polar end groups attached to the side-groups would show similar results. Figure 5 shows the structure of the poly(malonate) investigated. Nevertheless, the surprising response of the cyclosiloxane and the strong dipoles built into the poly(malonate) prompted us to again examine the effect of electric field on the LC polymer.

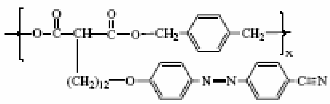
The X-ray patterns of the poly(malonate) clearly demonstrate that it is possible to align the mesogens in the mesophase and even retain the orientation in the crystalline phase (Fig. 6). Furthermore, there is an unusual behavior of the meridional layer reflections (vertical di-



(Fig 4) X-ray patterns of aligned cyclosiloxane in the nematic phase (top) and in the smectic C phase (bottom) upon cooling (applied E-field is vertical).







(Fig. 5, above) Possible molecular organization of a side-group poly(malonate). (Electric field is horizontal)

rection) when the polymer crystallizes. While the small angle smectic layer spots (6a) disappear, diffuse layer line reflections grow parallel to the meridian. When crystallization is complete (6d) the small angle smectic layer reflections again occur. This must be the result of a dramatic symmetry change on crystallization which confounds the common picture of crystallization from a LC to a solid phase. The conventional view of the direct buildup of a third dimension of order is not possible with these results. Without CHESS we were only able to see patterns 6a and d but not the intermediate images which suggested a simple phase change.

To be able to use a synchrotron source like CHESS has opened a new door to getting a better insight on the behavior and driving forces behind LC materials. Not only are the basic principles better understood with this approach, but there are also new phenomena which make these materials attractive for special devices (see flip in orientation on cooling Fig. 4). We have observed new dynamic behavior in LC materials and been able to probe them in ways never before considered. The advantage of being able to prepare new materials and analyze their behavior in remarkable detail using CHESS is a great privilege. With the new data from our last run, we are reassessing our basic strategies for LC design and expect that our next generation of materials will be even more exciting.

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