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Liquid Crystal Polymer Optics

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SUMMARY: In this paper we give a concise overview of various optical applications of Liquid Crystalline side-chain polymers. The possibility to tune the LC structure and phase-diagrams, as well as the availability of methods to create specific structures in the director field, allows materials to be developed for data-storage media and as optical compensation films for LC display applications.

Introduction

The molecular structure of side-chain LCP's can be tailored to achieve controlled production of multidomain, homeotropic, uniform planar and (S)TN film morphologies. Such films are useful for various optical applications such as analogue and digital storage and for the production of compensation films for liquid crystal displays.

The reason that side-chain LCP's are used for electrical and optical applications is due to their ease of processing. Assuming that structure-property relations are known the molecular architecture can be tuned to achieve the processing that leads to the desired properties. In obtaining insight into the structure-property relations use can be made of existing polymer expertise e.g. for making aramid fibers (Twaron®, Kevlar®) that are processed from liquid crystalline solution, and for coatings where use can be made of existing expertise in relation to film formation and adhesion. The activities in this field of optical applications originated from the accidental discovery of liquid crystallinity in an NLO side-chain polymer that was developed for Electro-Optical switching using the Pockels effect. Further investigation of this polymer resulted in the development of LCP based analog and digital storage media. Subsequently the "optical films" project started in 1993 which has led to the Twistar™ production plant coming on-line in 1999.

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Side-Chain Liquid Crystal Polymers

A schematic structure of a side chain LCP is shown in fig. 1, where the mesogenic groups are attached via a spacer to a polymer backbone, the headgroups of the pendent mesogens can be chosen so as to influence the occurring phase diagrams, e.g. by inclusion of dipoles (CN or NO_2) or alkoxy-tails of varying length.

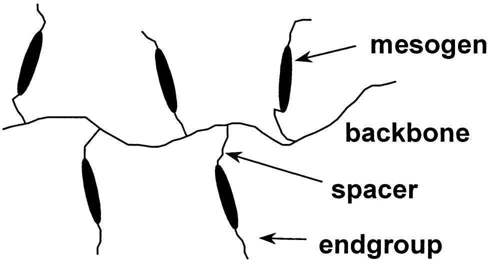

Fig. 1: Schematic structure of a side chain liquid crystal polymer.

The tuning of the physical properties of side-chain LCP's is achieved by systematic modification of the polymer structure. The backbone flexibility – and specific interactions of the mesogens – influences the glass-transition temperature. The structure of the mesogens, spacers and endgroups determines the types of LC phases that occur. The mesogenic groups to a large extent determine the birefringence and dichroism via the collective orientational order occurring in the various LC phases.

Structure property relations. The initially used NLO side-chain LCP was based on hydroxynitrostilbene mesogens attached to a polyester backbone, see fig.2.

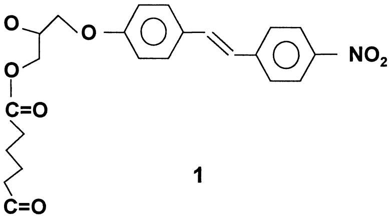

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Fig 2. NLO side-chain LCP, **1** with hydroxynitrostilbene mesogens attached to an aliphatic polyester backbone.

This material has a phase diagram G_N 45 N 85 I and was successfully used for the first-generation data-storage films using multiple scattering of light. In addition due to the dichroism of the side group also polarization dependent absorption could be demonstrated in this material. However, due to cis-trans isomerization the properties of this type of polymer were found to be unstable and alternatives materials were designed. One of these is the group of side-chain polyethers with alkoxyphenylbenzoate mesogens (fig.3).

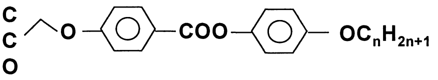

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Fig. 3: Side-chain polyether **2** with alkoxyphenylbenzoate mesogens.

It was found that the n = 1 and 4 homologues of **2** only have a nematic phase while the longer alkoxy tails lead to S_A and S_C phases. By systematically varying the composition of random copolymers more complicated phase diagrams (fig.4) can be obtained with reentrant N and S_A phases. Note the rather low glass transition temperatures of about 25 °C due to the high flexibility of the polyether backbone.

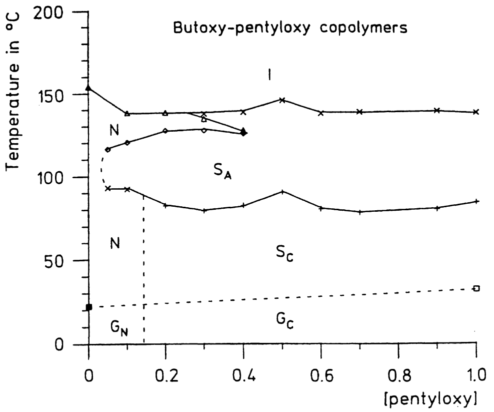

Fig. 4: Phase diagram for butoxy/pentoxy random copolymers of **2** (ref.1).

The figure shows that certain compositions of such copolymers can give rise to complicated phase sequences with re-entrant Nematic or Smectic-A phases, respectively for 90/10 butoxy/pentoxy and 70/30 butoxy/pentoxy ratios.

The examples discussed above demonstrate that a precise tailoring of polymer structure to the required properties for application and processing can be achieved, where side-chain LCP's allow independent variation of T_g, T_c and the phase diagram. The optical properties that can be modified are the birefringence, dichroism, absorption and the optical dispersion. In particular this allows the polymer properties to be matched to the optical characteristics of an active LCD cell.

Applications

Analogue data storage. Analogue data storage films can be produced with these materials. This storage method was developed in a Brite-Euram subsidized collaboration between Akzo, GEC, Laserscan and the universities of Hull and Leeds. The storage principle results from the phenomenon that birefringence causes a multidomain nematic texture to have an opaque appearance due to multiple scattering of the incident light[2)]. When a region in the sample is briefly heated into the isotropic phase (e.g. by using an IR laser) it becomes optically transparent and if the cooling rate is high enough the isotropic texture can be "frozen in" below the Tg of the polymer (fig.5).

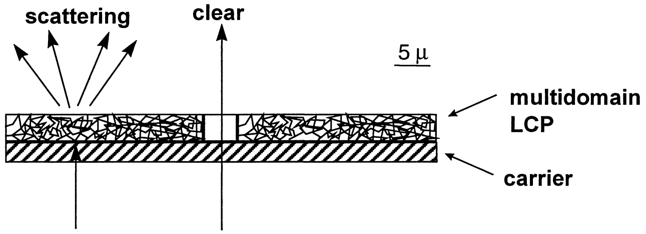

Fig. 5: Schematic structure of an analogue data storage film with an opaque multidomain nematic texture and transparent laser-written isotropic features.

This storage principle requires a minimum layer thickness of about 5-10 µm to achieve sufficient scattering contrast$^{2)}$ and therefore, due to the required focal-depth for laser writing, the optical resolution is limited to about 5 µm. This sort of optical resolution limits the application of multiple scattering films to analogue data storage of text and images, e.g. as a laser writable microfiche or for "smart labels".

Digital data storage. For digital media a resolution of about 0.5 µm is required, which can be achieved using homeotropic alignment of dichroic mesogens (fig.6). In this case the contrast between unwritten homeotropically aligned and written isotropic regions of the sample occurs by the change in absorption due to the dichroism of the mesogens or of solute dichroic dye molecules.

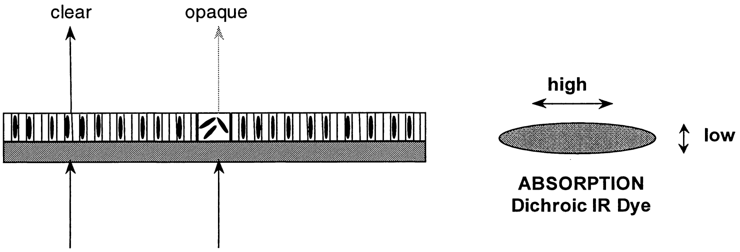

Fig. 6: Schematic structure of an digital data storage film with homeotropic alignment of the mesogens.

Here the contrast is determined by the degree of alignment of the solute IR-dye, as induced by the orientational order of the LC matrix, and depending on the dye concentration the films thickness can be less than 1 µm. Therefore the focal depth of the writing laser beam can be much smaller than in the case of scattering media and the resolution requirements for digital media can be met.

Compatibility with existing compact disk standards requires a certain contrast between written and unwritten regions of the sample and this imposes constraints on the orientational order of the dichroic dye. The measure for this is the "dichroic ratio" R which is the ratio of the optical densities for parallel and perpendicular polarised light (as measured with respect to the director in an uniform planar aligned sample), and this can be expressed in terms of the effective $<P_2>$ order parameter of the IR absorbing solute dye or mesogen:

$$R = \frac{OD_{//}}{OD_{\perp}} = \frac{2 < P_2 > +1}{1 - < P_2 >} \quad (\text{and conversely} < P_2 > = \frac{R-1}{2+R})$$

In the case of CD application the dichroic ratio has to be above 8.7 and therefore this requires high $<P_2>$ values of at least 0.72. Although achieving this was found to be technically possible it was discovered that there are easier methods, not using LCP's, to make recordable digital storage media – so that this particular application of side-chain LCP's was not investigated further.

Twistar - Optical retardation layers. Another example of an optical application of SCLCP's is their use for the manufacture of compensation films for STN liquid crystal displays. The principle is schematically shown in figure 7.

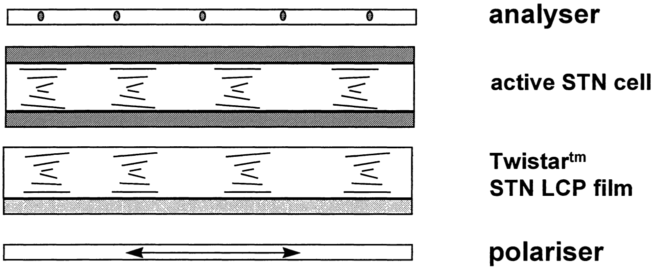

Fig. 7: Schematic structure of a liquid crystal display active cell combined with a Twistar SCLCP optical retardation layer that has a mirror image structure.

In the double cell shown in fig. 7 the optical characteristics of the active cell are to a large extent compensated by the inverse optical characteristics of the mirror image compensation layer. Such compensation can be achieved by using an additional STN cell complete with glass supporting substrates, and this gives rise to the so-called D-STN configuration. However, as the compensating element does not have to be switched it is found to be more convenient to use stretched birefringent polycarbonate films instead, this gives the F-STN type display. In our work we have developed a side-chain LCP based compensation element, optically similar to the D-STN configuration but with the advantages of a film compensated display, viz. reduced price & weight, and enhanced mechanical stability.

By tuning the layer thickness, the birefringence, the twist, and the optical dispersion of the compensation layer to that of the active cell it is possible to compensate for the wavelength dependent transmission and twisting power of the active cell. In addition the clearing temperature of the SCLCP in the compensation layer can be tuned to be the same as of the active cell so that a temperature independent compensation is achieved[3)], see fig.8. Clearly this is not possible using the more conventional stretched polycarbonate films, in the F-STN geometry, as the birefringence of such materials does not show the required temperature dependence.

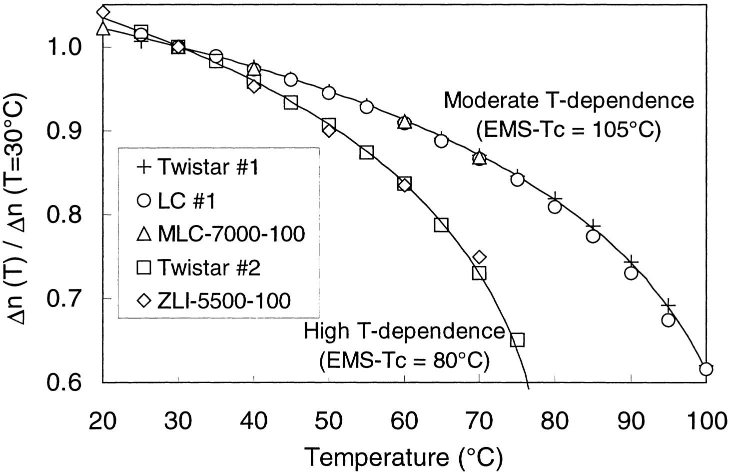

Fig.8: Temperature dependent birefringence of some side-chain LCP's compared to that of commercially available low molar mass liquid crystal blends, designed for use in the active LCD cell.

To illustrate the effect of temperature compensation on the optical performance, fig. 9 shows the difference in contrast between a display containing a T-matched and a non-T-matched STN compensating element[4)]. While it is possible to achieve full compensation at ambient temperatures, the non-T-matched display shows considerable degradation of the contrast at elevated temperatures compared to a display containing a Twistar™ T-matched compensator[4].

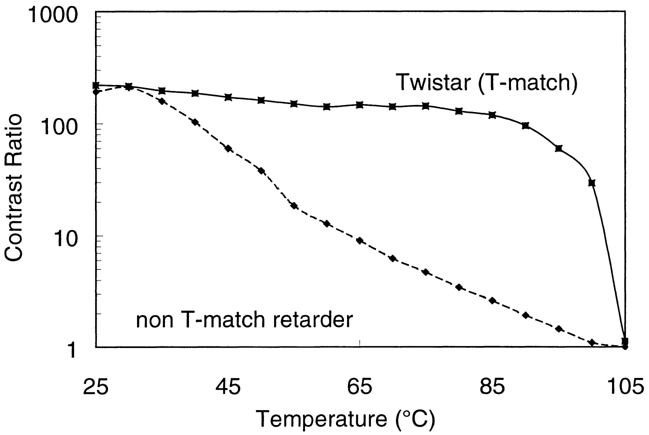

Fig.9: Contast versus temperature for a T-matched and non-T-matched STN display.

Discotwistar - the next generation. To further improve the performance of optical retardation films use can be made of negative birefringent materials containing discotic mesogenic groups. An example of such a group is schematically shown in figure 10, some additional information on this type of material can be found in[5].

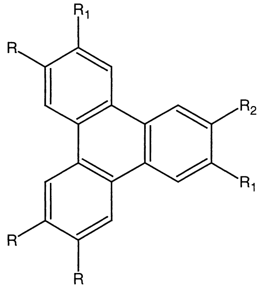

Fig. 10: Triphenylene discotic core group **3**, where R, R_1 and R_2 represent various tails containing additional phenyl rings and (meth)acrylate functionality's or chiral centres.

These materials can be processed to form partially crosslinked layers with a (S)TN texture, see fig.11 for a schematic structure. Due to the negative birefringence of the discotic nematic films it is possible to compensate the birefringence of the active mirror image (S)TN cell for all viewing angles so that the entire assembly is dark in the "off" state. This is due to the fact that a negative birefringent material has the opposite symmetry with regard to the indicatrix compared to positive birefringent calamitic LC materials, i.e. for discotic nematics the ordinary indices of refraction (the two components ⊥ to **n**) are larger than the extraordinary index (// to **n**). This property should lead to an improvement of the optical contrast compared to standard Twistar™ compensated displays where full compensation of the optical properties of the active cell only occurs for normally incident light.

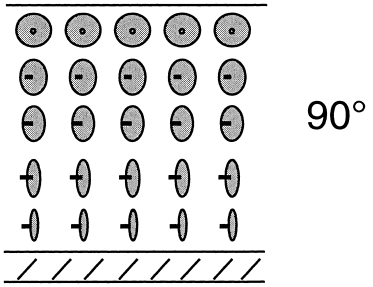

Fig.11: Schematic structure of a discotic nematic TN layer.

The particular challenge in making twisted negative birefringent elements is to design a robust processing method to obtain the required (S)TN configuration with discotic nematic materials. The current state affairs is that it was found to be possible to make a twisted negative birefringent film of **3** with a twist of 100°, a birefringence of -0.12 and a retardation of 500-600 nm, see fig. 12.

Fig.12. Negative birefringent sample with a twist of 100°, a birefringence of -0.12 and a retardation of 500-600 nm.

Conclusions

A variety of applications of side-chain LC polymers and discotic networks has been identified where use is made of the flexibility of the molecular design to tune the polymer materials to a specific processing method and required performance in a device. This allows the optics of liquid crystal polymers to be used to design new products or to improve on existing ones.

Acknowledgement

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