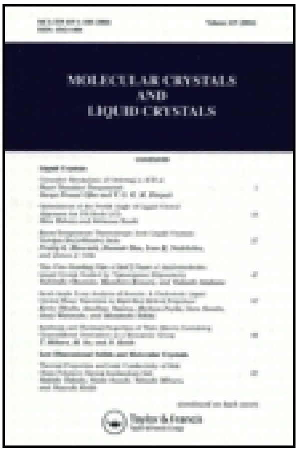

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CREATION OF SUPRAMOLECULAR THIN FILM ARCHITECTURES WITH LIQUID-CRYSTALLINE NETWORKS

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Abstract In-situ photopolymerization of liquid-crystalline networks offers the opportunity to fix the molecular organisation of any LC phase in a thin plastic film. In addition to that, one has access to a number of additional techniques to affect the molecular organisation during or after the polymerization process which makes it possible to create odd molecular architectures in a controlled way. A number of these techniques are discussed in this paper.

INTRODUCTION

The anisotropy of their optical properties form the basis of many applications of liquid crystals (LCs) in optical devices. Besides the active optical switching ability of low molar mass LCs in light valve applications, the frozen-in molecular textures of polymeric LCs are highly useful for the generation of passive optical functions.[1] Well-known examples are retardation foils, polarizing beam splitters or bi-focal lenses by nematic polymers, dichroic mirrors by cholesterics and half-lambda plates or STN compensation foils by twisted nematics. The control over the molecular structure in thin films inspires daily to the invention of new optical devices, which can be either cheaper than their inorganic-based (e.g. quartz) predecessors, or which can also be completely new only to be made by the access to the molecular organization in LC materials.

A process which enables a very secure control over the ordering of the molecules within one single layer is in-situ photopolymerization of liquid-crystalline monomers[2]. With an appropriate choice of reactive liquid crystals and by the use of the existing alignment techniques one can form thin films consisting of stable polymeric networks, in which the original LC monomeric units are very well ordered in mono-domains, i.e. over long distances with a low defect concentration. Besides 'simple' freezing-in of different types of LC phases one has with this process access to the formation of completely new molecular structures hardly to made by any other process. It is the aim of this paper to show some of the tools which we have worked out to adjust the molecular architecture to our imagination and to inspire to the discovery of completely new optical devices to be realized by these structures.

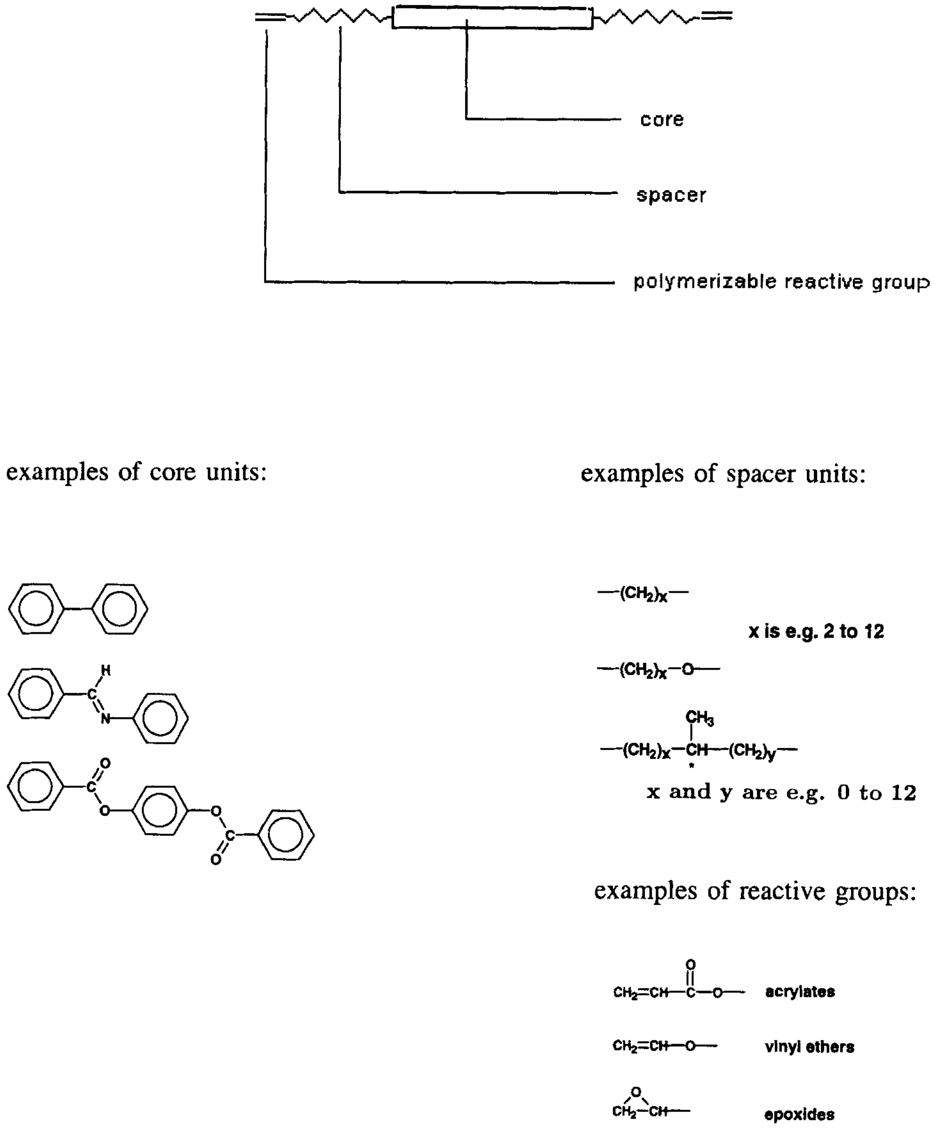

Figure 1 Some examples of the basic moieties of reactive liquid crystals

FORMATION OF ORIENTED LIQUID-CRYSTALLINE NETWORKS

The process of in-situ photopolymerization of LC monomers has been reviewed previously[3] and needs here only a short introduction. Basically one starts with liquid-crystalline molecules containing one, but preferably two polymerizable end-groups. Some elemental structures are shown in Figure 1. These monomers can be aligned and brought into a monolithic oriented structure just as ordinary liquid crystals by means of treated substrate surfaces and/or external fields. In this oriented state the monomer is irradiated with UV light, which excites a dissolved photoinitiator generating the reactive particles (either free radicals or cations depending on the reactive groups selected), which initiate the polymerization reaction. The polymerization reaction itself is, at least in the nematic, cholesteric or the most common smectic phases, not much affected by the molecular ordering and the polymerization proceeds fast and to a high conversion. During polymerization the molecular organization is maintained such that the ultimate polymeric texture corresponds with the one of the initial monomer.

Although in the nematic state of LC diacrylate monomers the mean molecular distance between the monomeric units decreases during polymerization the order parameter is not subjected to large changes. In fact at a relatively low degree of order of the monomers close to the isotropic transition, e.g. $<P_2>$ is smaller than 0.6, the order parameter tends to increase during polymerization whereas at higher initial order the order parameter remains the same or even might decrease somewhat due to steric hindrance of the polymer chains formed. This means that although the isotropic transition temperature of the LC networks, if any, is shifted to temperatures far above the limits of degradation, the order parameters of the nematic networks are between 0.6 and 0.8. The birefringence Δn of most of the materials studied sofar lies in between 0.1 and 0.2. A commercialized application based on this Δn is a polarizing beam splitter consisting of two glass prisms adhered together with a monolithic film of a nematic network.[4]

Besides the formation of nematic networks also cholesteric[5], smectic[2], ferroelectric[6] and blue phases[7] have been photopolymerized and their applications have been studied. An interesting extension of the possibilities of the LC networks is the addition of non-reactive low molar mass LCs to the reactive system.[8] The so-formed LC gels are of great interest because, unlike the fully crosslinked LC networks, they still can be switched by means of an external field. Another feature is that the photopolymerization process is ultimately suited for mould replication. This technique enables the formation of special surface reliefs in the oriented thin films.

MOLECULAR ARCHITECTURES BY COMBINING ORIENTATION TECHNIQUES

The LC monomers can be monolithically aligned by the orientation techniques currently used for LCs, such as by a polymer coated and subsequently rubbed substrate, by a surfactant treated substrate or by an electrical field or a magnetic field. In general the application of these techniques yields uniaxially aligned polymer structures of which the polar angle of director with the plane of the film can be chosen freely. This on itself is already of interest as in most other techniques to make oriented films the director is set by a machining direction like the flow in an extrusion process. However, even more interesting molecular architectures can be formed when different of the above mentioned alignment techniques are combined. The molecular textures which are then formed are quite normal for those who are working with LC materials but are unique for plastic films. This is especially the case when they can be made in a controlled way.

In a first simple example use can be made of two polyimide coated substrates of which the rubbing directions are mutually different.[9] When the LC monomer is brought between these substrates the director of LC orientation at the boundaries is determined by the rubbed polyimide and the director gradually changes from one to the other, just as is known for e.g. normal TN cells. But now the orientation can be fixed by photocrosslinking. When necessary chiral dopants can be used to guide the LC monomers in the twisting direction to prevent domain formation. Actually, by this method every rotation angle can be fixed and this technique is ultimately useful for the manufacturing of halfwave plates and STN compensation foils.[10]

Exploring the techniques worked out for LC display applications further, interesting architectures can also be formed using alignment by rubbed polyimide coatings on structured electrodes. As in the displays the director can be modulated in the plane of the film of nematic LC monomer and also this molecular organization can be frozen-in.

More bizarre architectures have been formed on melting the LC monomer between a rubbed substrate at one side and a surfactant treated substrate at the other.[7] This yields polymer films in which the molecules tumble over 90° in the plane of the cross-section of the film. Tumbling over 180° can even be obtained if the LC monomer is molten between two rubbed substrates and placed in a perpendicular external field, e.g. a magnetic field. Depending on the film thickness, the field strength and the elastic constants the director changes from planar to perpendicular and to planar again. Of course, also the reverse architecture can be made by using surfactant treated substrates in a parallel magnetic field. An example is demonstrated in Figure 2 which shows the transmission spectra between polarizers (Gooch and Tarry curves) of a 6.7 μm thick film of poly(C6M) (methyl substituted 1,4-phenylene bis{4-(6-(acryloyloxy)hexyloxy) benzoate, Philips[11]) aligned at the interfaces with rubbed polyimide and in the centre by a 1.5 Tesla magnetic field. At the both edges the director tumbles from planar to homeotropic over a thickness of approximately 1.2 μm which provides the typical transmission curves. Transmission depends the effective optical retardation and on the mutual polarizer directions in relation to the edge directors. It is of course especially the typical viewing angle dependence which adds the birefringence of the homeotropically aligned part to the effective optical retardation which is interest for this type of films.

MOLECULAR ARCHITECTURES BY A LITHOGRAPHIC APPROACH

Because use is made of a photo-crosslinking reaction the polymerization can be carried out locally by modulation of the light intensity in the plane or over the cross-section. This can be performed by using masks[2,12] or by interference (holography) techniques[13]. Chess board type of structures can be made by local irradiation of a uniaxially aligned LC monomer and a subsequent re-orientation of the unexposed area, e.g. by rotation of the direction of the external field, and a flush post-exposure of the total area to polymerize also the remaining monomers.

Interesting structures can be formed if the molecular ordering in the unexposed areas is altered by a change of the temperature. In this way for instance anisotropic islands can be formed in an isotropic sea. Especially when cholesteric LC monomeric mixtures are used with a steep temperature dependence of the pitch of the molecular helix, the pitch can be locally altered and coloured patterns can be formed highly useful for patterned reflective colour filters. It has been demonstrated that reflection of the whole visible wavelength range can be established in one single film where the transition from one wavelength of reflection to another may proceed within one micron.

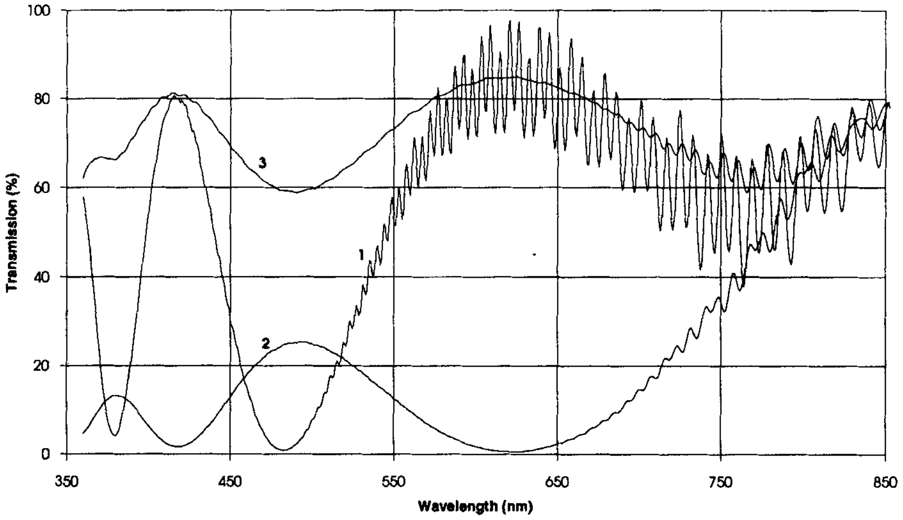

Figure 2 Transmission between two polars of poly(C6M) with a director tumbled over 180°. (1) between crossed polars with rubbing direction at 45°, (2) between crossed polars with the rubbing directions parallel to first polar, and (3) between parallel polars and parallel rubbing directions.

MOLECULAR ARCHITECTURES BY DIFFUSION

Diffusion during polymerization

When a lithographic approach is chosen to structurize the LC networks, an interesting addition is found in using diffusion processes during polymerization. For instance in the case of two monomers with a different reactivity, which can also be a LC diacrylate and a non-reactive liquid crystal, the high-reactive monomer tends to diffuse to the illuminated areas, whereas the low-reactive monomer diffuses to the dark parts as the polymerization proceeds. This causes controlled fluctuations in the concentration of the two (the low and the high reactive) components in the plane of the film. When monomers with different properties, e.g. refractive indices, transition temperatures, sign of the dielectric constant, etc., are selected, a film is formed in which the properties are thereby modulated in the plane of the film.

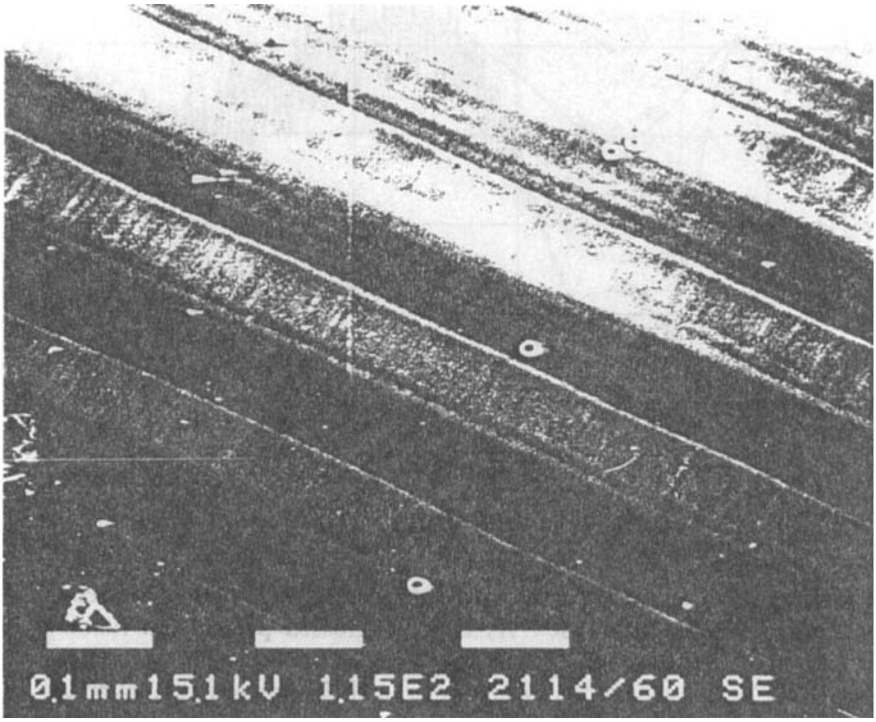

Figure 3 SEM photograph of the surface reliefs in an LC network obtained after the process of diffusion during and extraction after polymerization

In an example the low-reactive monomer is a non-reactive LC (K15, Merck Ltd, UK) which is 1:1 blended with C6M and UV irradiated (Philips PL10 at 15 cm) through a line mask for 10 minutes after which the mask was removed and a flush exposure was given to the total sample. By this process a film is formed containing lines which are alternatingly rich and poor with K15 as this materials diffuses during polymerization to the non-illuminated areas. After polymerization the K15 can be removed almost completely from the film by extraction with a suitable solvent, e.g. ethanol. In that case local shrinkage occurs predominantly at the K15 rich area which yields the special surface reliefs in the oriented LC networks shown in Figure 3.

Covering these surfaces with other, non-diffusing monomers (LC or isotropic) which can be photopolymerized gives special 3D architectures which can, for instance, be used as anisotropic gratings. Of course if the diffusing monomers have properties (refractive indices, clearing temperature) which are sufficiently different from each other, the extraction process can be avoided and the grating can be produced in one step in one single film being very attractive for the production of optical components.

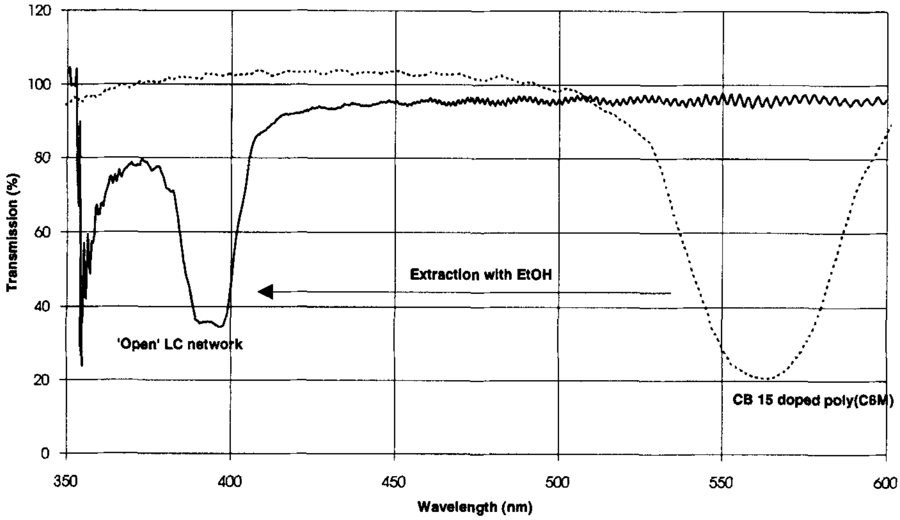

Figure 4 Shift in cholesteric reflection wavelength during creation of an 'open' network by extraction of the mobile component in the CB15 doped C6M network.

Diffusion after polymerization

Another technique to control the molecular architecture is to use diffusion after the polymerization of the LC network has taken place. In general the LC networks have a high crosslink density which means that diffusion processes will be slow and the amount of diffusible material low. In order to make the LC network more accessible for diffusion it should first be 'opened'. Thereto the LC network can preferably be formed in the presence of non-reactive LCs which can be removed later by evaporation[14] or solvent extraction as described above. The thus produced 'open LC network' can be easily refilled by diffusion of other molecules of a size not much larger than the original removed molecule into the network again. An example of this technique is the formation of a cholesteric network from a nematic LC diacrylate and a chiral non-reactive LC. The pitch, and thus the angle of reflection of such a film can be adjusted by the ratio between the two components. This is for instance illustrated in Figure 4 which shows the reflection wavelength of polymerized nematic diacrylate C6M (methyl substituted 1,4-phenylene bis{4-(6-(acryloyloxy)hexyloxy) benzoate, Philips[11]) modified with the chiral non-reactive LC CB15 (Merck Ltd). After polymerization the blend has a reflection wavelength of 565 nm.. When the chiral component is removed from the polymer by extraction in ethanol at room temperature the pitch becomes smaller which can be concluded from the blue shift of the wavelength of reflection to 395 nm. On itself this is already a remarkable event as the chirality seems to increase when the chiral component is removed. It however can be understood quite easily when one realizes that the directors at the boundaries are fixed whereas the film thickness decreases due to

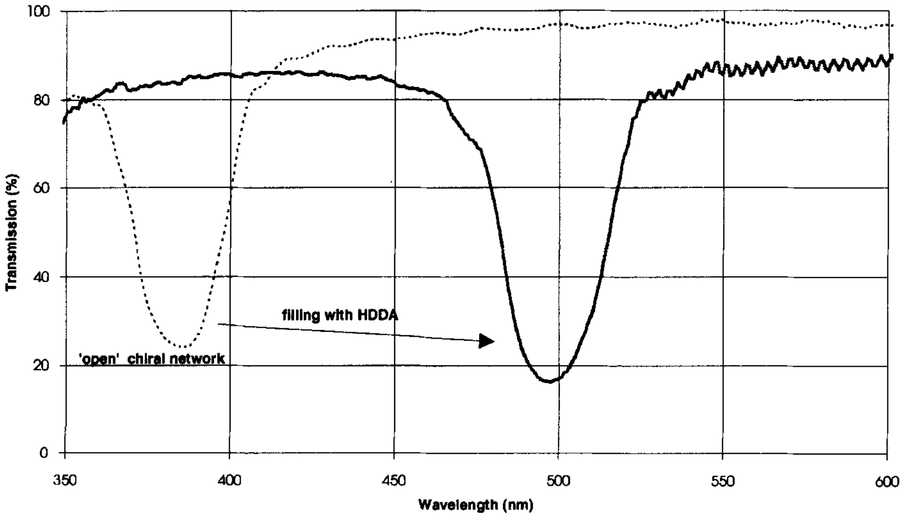

Figure 5 Shift of the cholesteric reflection wavelength by diffusion of HDDA into the 'open' LC network

shrinkage. Due to the extraction process this network has an open structure which can now be refilled by another monomer which is not necessarily chiral or even liquid crystalline as is demonstrated in Figure 5. Here hexanediol diacrylate (HDDA) is used to take open sites which the moved CB15 have left. This causes re-swelling of the film, again with fixed boundary conditions, and therefore an expansion of the molecular helix. The attractiveness of using a photo-reactive monomer as diffusing material is that at the end of the process the new situation can be fixed again by a UV irradiation. With HDDA the wavelength of reflection does not obtain the original value from before the extraction/diffusion processes, partly because the HDDA does not fit in all open sites, partly because the average refractive indices somewhat lowered and partly because during the polymerization of HDDA some polymerization shrinkage occurred..

The re-filling of the 'open' LC network occurs in most cases with a concrete swelling front which means that during the diffusion process there exist two helices with a different pitch on top of each other. As we preferably swell with a photopolymerizable monomer besides the end-situation also any intermediate situation can be fixed at any time by a simple UV exposure yielding odd architectures in which within one layer one chiral helix with its specific pitch is built on top of another helix with a different pitch.

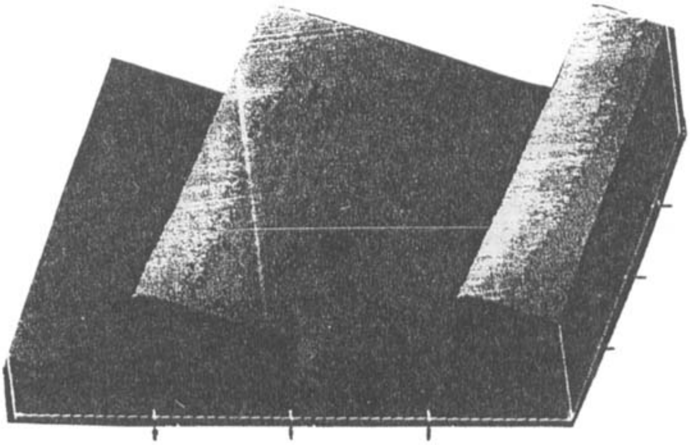

Figure 6 STM of a LC network replica of a saw-tooth shaped mould. The marks at the bottom axis indicate a distance of 2 μm.

MOLECULAR ARCHITECTURES BY REPLICATION

A current process to make films with special surface reliefs is photoreplication.[15,16] Conventional photo-curable monomers are squeezed between a mould and a substrate and subsequently photopolymerized. After removal of the mould the surface of the photosetting resin is a negative image of the mould surface. By this process sub-micron surface structures can be made. It has been demonstrated that the same process can be used to modify the surface of films of aligned LC networks by pressing LC monomers to a mould which is provided with a rubbed polyimide layer. Figure 6 shows a STM of a replica in poly(C6M) of a saw-tooth shaped mould. The director is in this case along the step lines. The picture indeed demonstrates that high resolution surface reliefs can be produced in this way, enabling to make fresnel-type of designs of otherwise more voluminous components as large area polarizing-beam-splitting wedges. Of course, again more complicate structures can be made if the surface replicated layers are stacked with new anisotropic or isotropic top layers giving the tools for the production of very complicated 3-D architectures.

CONCLUSION

Various techniques have been presented to control the molecular architecture in three dimensions in transparent films of monolithically oriented liquid-crystalline networks. These methods can be used as a stand-alone tool to adjust the molecular orientation for producing optical components. But even more complicated molecular structures can be build if these techniques are combined with each other.

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