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Cholesteric gels formed by LC molecules and their use in optical storage

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Two-component liquid crystalline (LC) mixtures containing LC diacrylates and chiral molecules with no reactive groups were made. Upon photopolymerization of the mixtures cholestric networks containing LC molecules which were not chemically attached to the networks were created. By heating, molecules which were not chemically attached to the network could be removed leaving behind a three dimensional network with a helical structure containing no chiral molecules and changed optical properties. The changes in the optical properties of the system could also be induced locally using a laser beam, demonstrating the possibility of using the method for optical storage.

1. Introduction

The use of side chain type LC polymers for optical storage has been suggested in numerous reports [1–8]. Many of these reports deal with changing the orientation of the molecules in the nematic and smectic states [1–4, 8] in order to produce a contrast, whereas others [5–7] deal with cholesteric systems. In the case of nematics and smectics, the contrast is created by producing light scattering centres on a transparent background or vice versa by local heating using a laser. In the case of erasable systems combined use was made of a laser and an electric field. In the case of cholesteric media, the property of selective reflection of a band of circularly polarized light by these systems was made. In [5, 6], the contrast is produced by changing the orientation of the cholesteric pitch and, as a result, changing the position of the reflected light. Prins *et al.* [7] described a cholesteric system in which the helical structure could be locally destroyed by a photochemical reaction initiated by a laser.

Here we describe a cholesteric gel [9, 10] and changes induced in its optical properties following the removal of free molecules. These networks containing free molecules (gels) [11–13] were produced by *in-situ* photopolymerization of an LC mixture containing an LC diacrylate [14, 15] and LC molecules without reactive groups. In this way the orientation of the molecules could be obtained by a surface treatment and permanently fixed by cross-linking. Here the properties of cholesteric gels before and after the removal of the free molecules is described and their use in optical recording is suggested.

2. Experimental

The structures of the LC diacrylate (C6M) and the chiral molecule containing no reactive groups (CB15) used in this study are shown in figure 1. The diacrylate C6M

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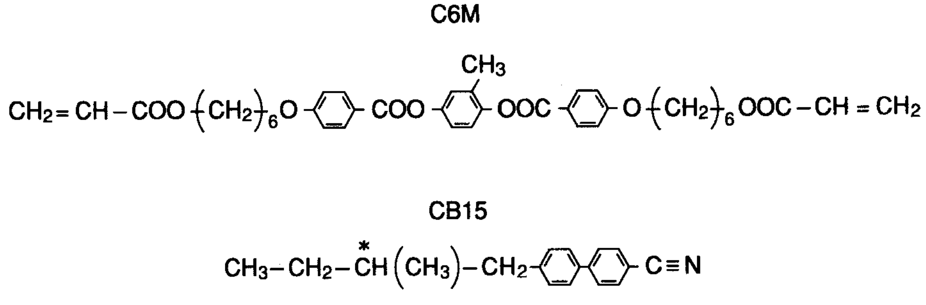

Figure 1. Molecular structure of the monomers.

was synthesized at Philips Research Laboratories and the details of the synthesis can be found in [14]. CB15 is a commercial product purchased from Merck Ltd, England. The monomers were treated with a 2 per cent w/w photoinitiator α, α-dimethoxy-deoxybenzoin (Irgacure 651 Ciba Geigy). Optical measurements were carried out using a polarizing microscope. Sample temperatures were regulated using a Mettler FP 5 hot stage. An Abbé refractometer which could be heated up to 140°C was used for the refractive index measurements. UV-VIS spectrometery was carried out using a Philips PU8740 UV-VIS spectrometer. Planar oriented cholesteric samples were obtained in glass cells which were provided with uniaxially rubbed polyimide layers on their inner surfaces and spaced with 7 μm fibres.

3. Results and discussion

3.1. *Polymerization of the mixtures*

In the present study, we used a mixture containing 28 per cent w/w CB15 molecules. The monomeric mixture was placed in a 7 μm cell. The photopolymerization of the mixture was initiated using a UV lamp. In this way a network with a helical structure containing free molecules (cholesteric gel) was formed. Details of the polymerization of diacrylates in the presence of molecules without reactive groups and the properties of the monomeric mixtures can be found in [9]. In figure 2, the wavelength of maximum reflection (λ_{max}) measured as a function of temperature for the monomeric mixture before and after polymerization at 60°C is shown. It can be seen that as opposed to the behaviour of the monomeric mixture which has a clearing temperature (T_c) of 83°C, the gel shows a reflection band even when it is heated well above the T_c of the monomeric mixture. It can also be seen that the λ_{max} for the monomeric mixture is very temperature sensitive, whereas for the polymerized sample (the gel), λ_{max} remains almost unchanged as a function of temperature. As also shown before [9, 10], here again the results indicate that upon polymerization the helical structure induced by the chiral dopant in the monomeric state became frozen-in by the creation of the three dimensional network with a helical structure. Consequently the behaviour of the polymerized system (the gel) becomes to a large extent determined by this temperature stable network.

In order to investigate the degree of order within the cholesteric gels, the refractive indices were measured using the Abbé refractometer. The measured cholesteric ordinary ($n_{c,o}$) and extraordinary ($n_{c,e}$) indices were used to calculate the ordinary n_o and extraordinary n_e refractive indices of the uniaxially oriented cholesteric layers as

$$n_o = n_{c,e} \tag{1}$$

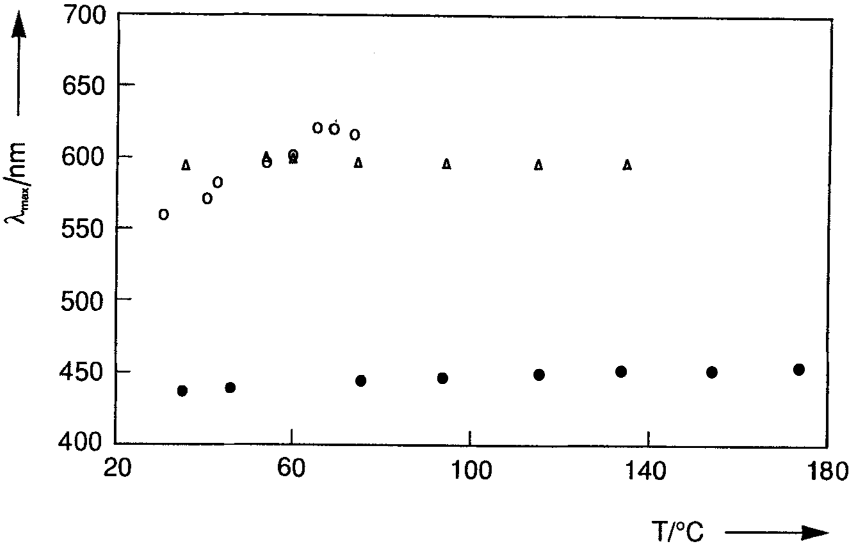

Figure 2. The wavelength of maximum reflection as a function temperature measured for a system containing 28 per cent w/w CB15. ○, before, △, after polymerization at 60°C and ●, after the removal of CB15 at 200°C from the gel.

and

$$n_e = (2n^2_{c,o} - n^2_{c,e})^{1/2} \qquad (2)$$

In figure 3 refractive indices as a function of temperature are shown for the gels polymerized at various temperatures. The order parameter S for the polymerised

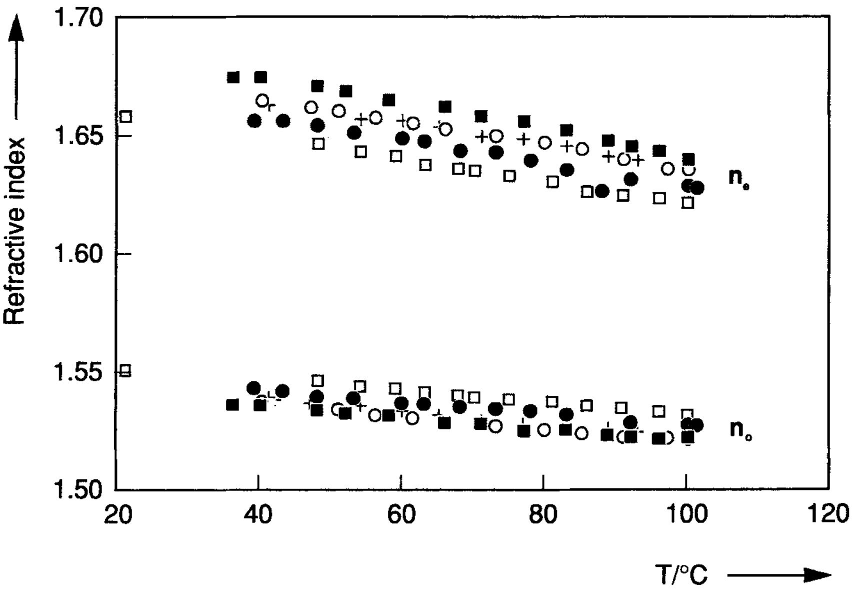

Figure 3. Refractive indices of the mixture containing 28 per cent w/w CB15 after polymerization at various temperatures. ■, 30°C; ○, 40°C; +, 50°C; ●, 60°C; □, 70°C.

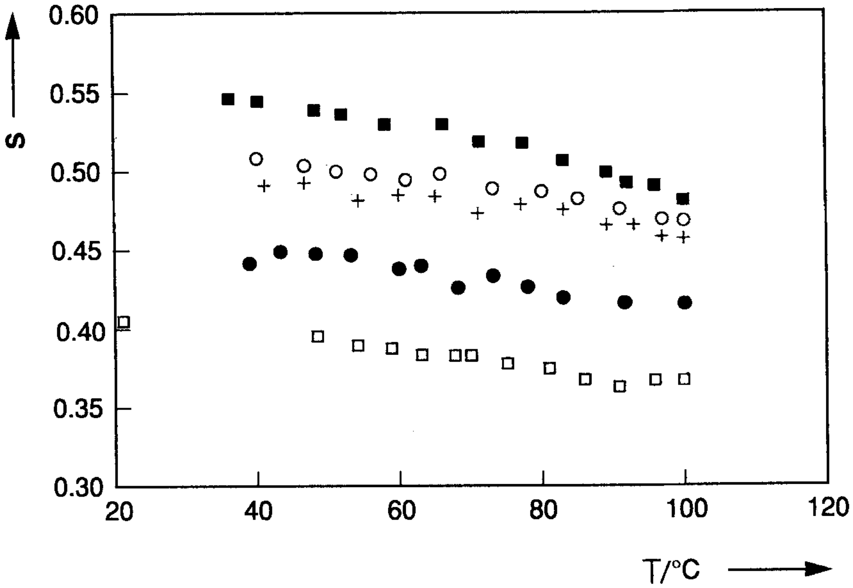

Figure 4. Order parameter as a function of temperature for the mixture containing 28 per cent w/w CB15 after polymerization at various temperatures. ■, 30°C; ○, 40°C; +, 50°C; ●, 60°C; □, 70°C.

samples was estimated from the refractive indices using the equation [16]

$$S = \left\{ \frac{\bar{\alpha}}{\alpha_{\parallel} - \alpha_{\perp}} \right\} \frac{n_e^2 - n_0^2}{\bar{n}^2 - 1}, \tag{3}$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the molecular polarizabilities in the directions parallel and perpendicular to the optical axies of the molecules respectively, and $\bar{\alpha}$ is the mean polarizability. The mean refractive index $\bar{n}$, is given by $\sqrt{[(2n_o^2 + n_e^2)/3]}$.

The polarizability term estimated for the monomeric mixture (1·84) was used in the calculations. This method gives a good estimation of the average order parameter within the system [15]. In figure 4 the order parameter is plotted as a function of temperature for samples polymerized at various tempertures. Here it can be seen that at a given temperature, the samples polymerized at higher temperatures have lower order parameters than samples polymerized at lower temperatures. However, the order parameters of the cholesteric gels decrease only slightly with increasing temperature, as opposed to the monomeric mixture which becomes isotropic at 83°C, showing the dominance of the network over the behaviour of the gels.

3.2. *Removal of CB15 out of the gels*

The cells containing the gels were opened leaving a gel layer adhering to one of the glass surfaces. When the gel layers, containing free molecules were heated up to high temperatures (200°C for 15 min), it was found that the reflected colour from the layers also changed irreversibly. Based on the disappearance of the IR band (2230 cm^{-1}) corresponding to the C≡N vibration band of the CB15 molecules and the weight loss corresponding to the initial weight fraction of CB15 used, it was concluded that the irreversible change upon heating was the result of the removal of the CB15 molecules. This point will become clearer later in the text. In figure 5, examples of the

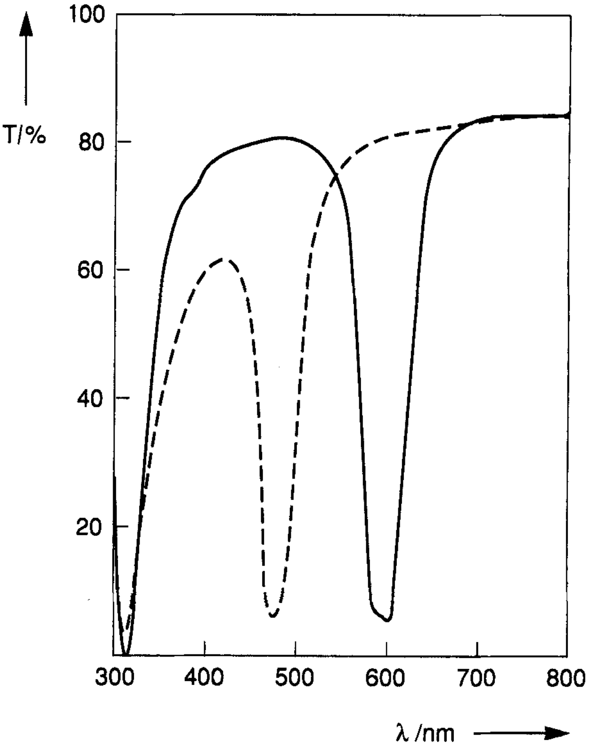

Figure 5. Transmittance measured as a function of wavelength for a sample containing 28 per cent w/w CB15 polymerized at 60°C before (——) and after (----) evaporation of CB15 molecules.

transmission spectra, obtained using right-handed circularly polrized light, are shown for the sample polymerized at 60°C before and after the removal of the CB15 molecules. The wavelength of maximum reflection λ_{max} is given by [17]

$$\lambda_{max} = pn_{c,o}, \tag{4}$$

where p is the cholesteric pitch. In figure 5 it is clear that upon the removal of CB15, λ_{max} decreases by 120 nm. In the table, the change in the λ_{max} and the cholesteric pitch, calculated using in equation (4) the refractive index values from figures 3 and 6, before and after the removal of CB15 molecules are given for a sample polymerized at various temperatures. It can be seen that upon the removal of the CB15 molecules, the cholesteric pitch decreases by about 30 per cent which also approximately corresponds to the initial volume fraction of CB15 molecules. The thicknesses of the gels were also measured, before and after the removal of the CB15, using mechanical means and the results conform well with the optical data (see the table) showing that the shrinkage is uniaxial in the direction of the film thickness, which also defines the direction of the cholesteric pitch. In the monomeric state it is well-known that the magnitude of the pitch is determined by the concentration of chiral dopant. The fact that in the present case the removal of the chiral component did not cause the destruction of the helical structure indicates that the helical network obtained during the polymerization of the monomeric mixture determines the behaviour of the gel before, as well as after the removal of the chiral dopant. This is further supported by the results in figure 2, where λ_{max} for the monomeric mixture before and after

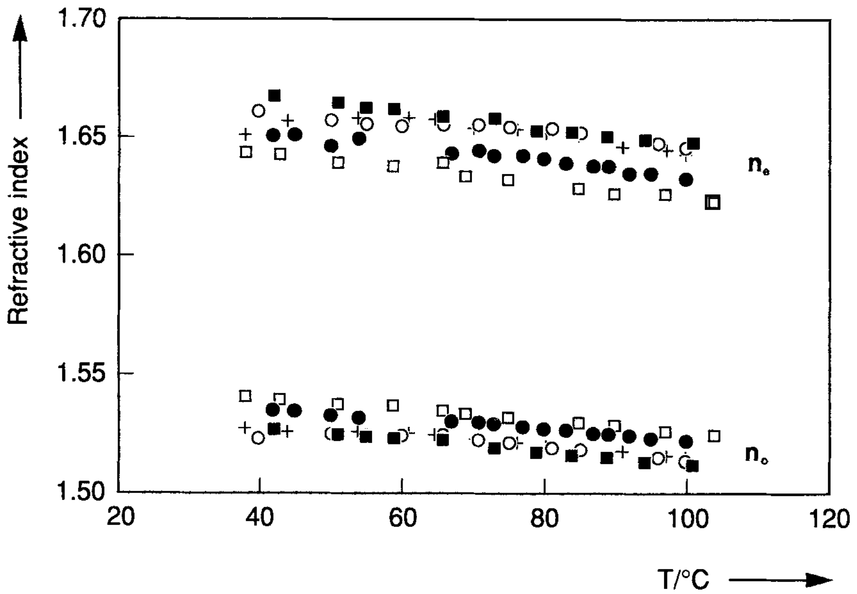

Figure 6. Refractive indices of the mixture containing 28 per cent w/w CB15 which were polymerized at various temperatures and after the CB15 molecules were evaporated at 200°C. ■, 30°C; ○ 40°C; +, 50°C; ●, 60°C; □, 70°C.

polymerization and after the removal of CB15 are plotted as a function of temperature. It can be seen that, while for the monomeric mixture λ_{max} shows a strong temperature dependence, for the gel and the network which remained after the removal of the CB15 molecules, the influence of temperature on λ_{max} is much smaller. Furthermore, the fact that the shrinkage was uniaxial in the direction of the helix and that the helical structure remained preserved upon the removal of the CB15 indicate that, as proposed before [10, 18], an alternating layered structure, consisting of CB15 and network molecules, exists within the gels. Upon the removal of the CB15 layers, the pitch decreases giving rise to a uniaxial shrinkage.

In order to estimate the order within the remaining network after the removal of the CB15 molecules, refractive indices of these networks were measured. In figure 6 refractive indices are shown as a function of temperature for the networks which were obtained by polymerization of the monomeric mixture at various temperatures followed by the removal of CB15 at 200°C. When figure 3 and 6 are compared, it can be seen that in all cases, at a given temperature n_o decreases, which n_e remains almost unchanged upon the removal of CB15 molecules. This indicates that the degree of

Optical properties of the mixture containing 28 per cent w/w CB15, which was polymerized at various temperatures before and after the evaporation of CB15 molecules. Properties after evaporation are indicated with *.

T/°C	λ_{max}/nm	λ^*_{max}/nm	p/nm	p^*/nm
30	543	380	337	236
40	551	422	343	263
50	583	433	362	269
60	598	449	372	281
70	606	462	378	288

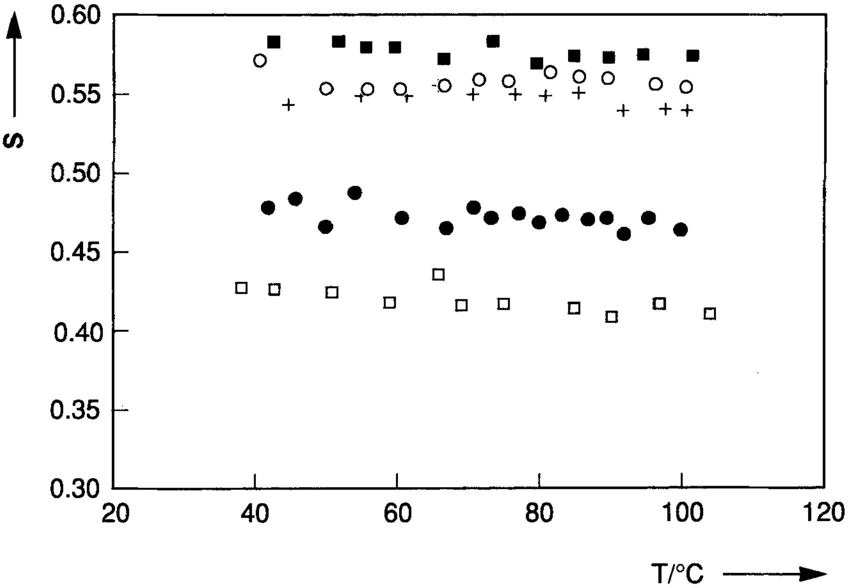

Figure 7. Order parameter as a function of temperature for the mixture containing 28 per cent w/w CB15 which were polymerized at various temperatures and after the CB15 molecules were evaporated at 200°C; ■, 30°C; ○, 40°C; +, 50°C; ●, 60°C; □, 70°C.

order within the system changes upon the removal. In order to estimate the degree of order within the systems following the removal of CB15 molecules, we used the values for the refractive indices in equation (2) together with the value of 1·92 [15] for the polarizability term obtained for the monomeric C6M. The results are shown in figure 7. When the values for the order parameter in this figure are compared with those in figure 4, it can be seen that upon the removal of the CB15 molecules at a given temperature, the mean order parameter increases. This can be due to either an increased order of the network molecules upon the removal of CB15 molecules or the possibility that the order parameter of the CB15 molecules is lower than that of the network molecules. The latter possibility is more likely since earlier publications [9–11] report that at temperatures above the isotropic transition temperature of a pure material, molecules which are not chemically attached to a network have a mean order parameter lower than that of the network.

Other optical properties of such a helical network containing no chiral component were also investigated and compared with the properties of the gels before the removal of CB15. In figure 8 the optical rotary power of the sample polymerized at 60°C, before and after the removal of CB15 molecules, is plotted as a function of wavelength. Here it can be seen that the dispersion curve moves to lower wavelengths upon the removal, while the shapes of the curves remain very similar. The angular dependence of $\lambda_{\max}$ for the sample polymerized at 60°C before and after the removal of CB15 is shown in figure 9. The angular dependence of the maximum reflection is given by [17]

$$\lambda_{\max} = \lambda_{m,o} \cos(\sin^{-1}(\sin\theta/n_{c,o})), \qquad (5)$$

where θ is the angle of incidence and $\lambda_{m,o}$ is the maximum reflection at $\theta = 0$. In figure 9 the solid lines represent the calculated values according to equation (5). The good

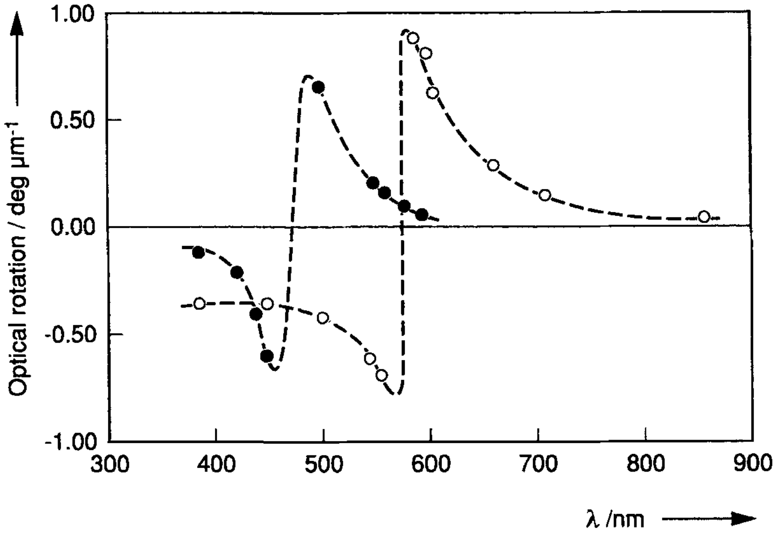

Figure 8. Optical rotation as a function of wavelength for a sample containing 28 per cent w/w CB15 polymerized at 60°C before (○) and after (●) evaporation of CB15 molecules.

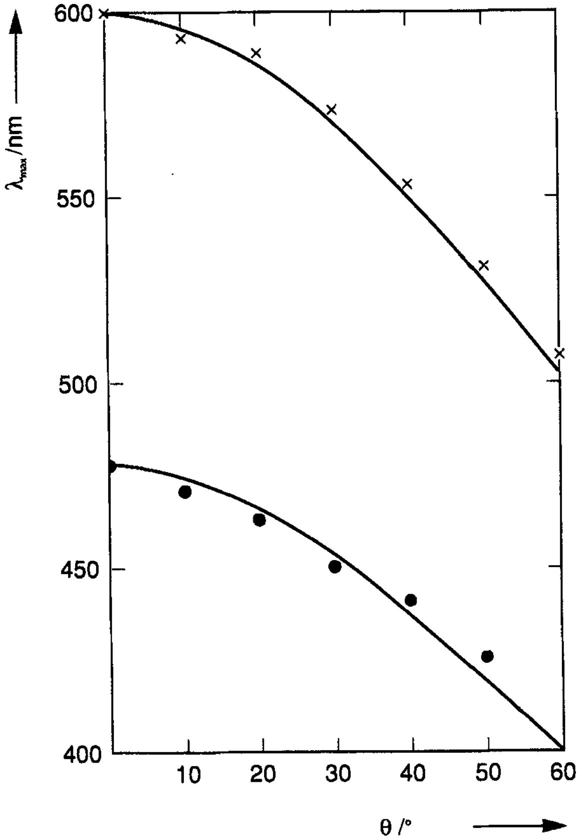

Figure 9. Angular dependence of λ_{maz} for a sample containing 28 per cent w/w CB15 polymerized at 60°C before (×) and after (●) evaporation of CB15 molecules.

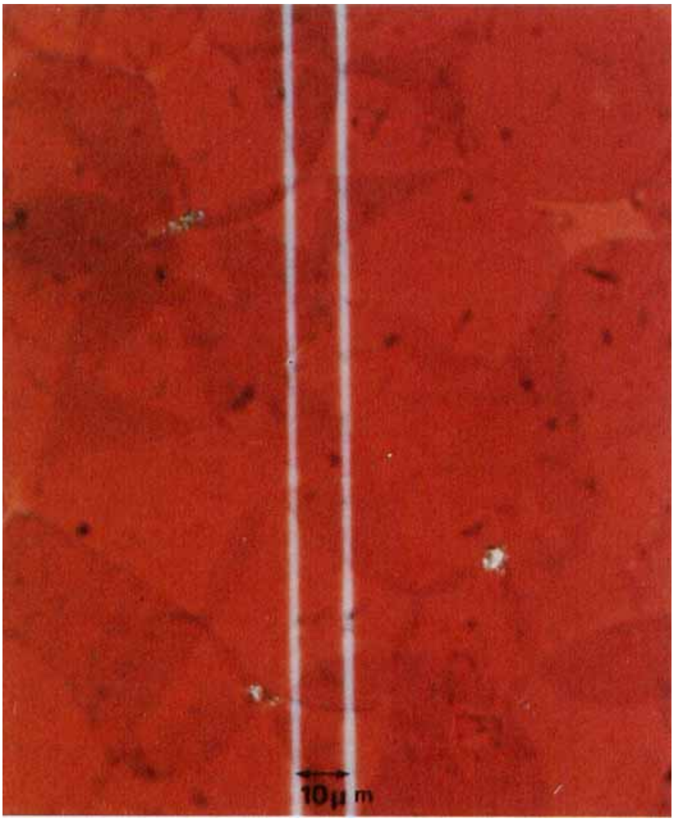

Figure 10. Optical micrograph of a cholesteric film with lines recorded by a laser beam.

agreement between the calculated values for the sample before and after the removal is quite apparent.

Here is is clear that these networks containing no chiral molecules, obtained by the removal of CB15 from the gels, showed good optical quality and behaved just like conventional cholesterics. This result, together with the fact that the films showed uniaxial shrinkage in the direction of the pitch, supports the theory [10, 18] that in these anisotropic gel systems there is a segregation on the microscopic scale whereby a sandwich structure consisting of planes containing cross-linked network and CB15 molecules exists. Upon the removal of the CB15 molecules, layers containing these molecules disappear giving rise to a decrease in the pitch, while preserving the quality of the remaining films and their cholesteric-like optical properties.

Having shown that the optical properties of the cholesteric gels could be changed by the removal of the CB15 molecules, we tried to write into such a cholesteric film by bringing about a local removal. For this purpose, a Nd : YAG/dye laser was used and the recording was made by moving the cholesteric film on an X–Y stage under the focused laser beam, $\lambda = 300$ nm. In figure 10 two lines 2 µm thick and 10 µm apart recorded using the laser beam are shown. The photograph was obtained between crossed polarizers and shows that recording on a micron scale on such films is possible. It is hoped that a method based on this principle can be used in optical recording, where digital information can be recorded by locally removing molecules which are not chemically bonded to the network.

4. Conclusions

Here it was shown that cholesteric networks containing chiral molecules which are not chemically attached to the network can be made. When these systems were heated to elevated temperatures, the molecules which were not chemically attached to the network molecules came out, leaving behind a three dimensional network containing no chiral molecules and so changing the optical properties of the system. It was found that the removal of the molecules resulted in a large decrease in the cholesteric pitch, whereas the change in the refractive indices of the system was much smaller. The networks obtained after the removal of the CB15 molecules showed good optical quality and behaved like conventional cholesterics. These observations provide an additional support to the theory [10, 18] that in anisotropic gels and plasticized networks, the molecules are confined between layers (or long channels) formed by the network molecules. The optical properties of the films could also be changed locally, making the materials suitable for recording purposes.

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