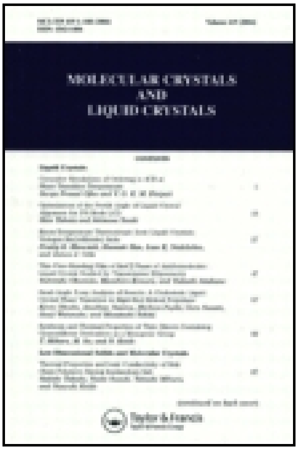

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Polymer Network Cholesteric Liquid Crystal Operating in the Near Infrared

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Polymer Network Cholesteric Liquid Crystal Operating in the Near Infrared

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A Polymer Stabilized Cholesteric Texture (PSCT) material operating in the near infrared can be used to modulate the infrared spectrum. We emphasize on the electrooptical behavior of such materials and especially on the study of parameters such as the prepolymer concentration or the UV intensity on the quality of the response. The influence of these parameters is discussed. The amplitude of the modulation with the liquid crystal pitch and the thickness of the active layer is also investigated. An important modulation is obtained in the range investigated (up to 3 microns).

Keywords: PSCT; cholesteric; infrared; prepolymer; modulation

INTRODUCTION

A material allowing to have a modulation of the near Infrared spectrum can be used for applications such as light shutters, infrared valves, night vision goggles or visible-to-infrared image converters. Several kinds of materials can be suitable for such applications.

Pure Nematic liquid crystals can be used to modulate the Infrared radiation [1,2]: these devices utilize homogeneous alignment of the nematic liquid crystal in Twisted Nematic (TN) systems [3]. Such materials use relatively thick liquid crystal layers, which greatly lengthens the response time. Moreover, they require polarizers which leads to a reduction in transmission. Ferroelectric liquid crystals allow to have a better contrast and short response times [4].

A modulation of the near infrared spectrum can also be obtained by using Polymer Dispersed Liquid Crystals in which the nematic liquid crystal is dispersed in droplets in a polymer matrix . Aspects such as the sample's thickness and the size of the liquid crystal droplets are essential for the modulation [5-8].

It is also possible to use systems with a cholesteric liquid crystal and only a few percent of polymer to create a polymeric network through the sample. Such displays have a Polymer Stabilized Cholesteric texture (PSCT) [9-11]. Polymer stabilized liquid crystals with a pitch in the near infrared spectrum have been studied [12]. Such systems offer several possibilities for the modulation of the IR radiation since three states are available: reflective in the infrared without voltage, scattering and transparent (homeotropic orientation of the liquid crystals molecules) with an applied voltage.

Our aim is to answer some of the questions concerning PSCTs in the near infrared spectrum such as :

- the possible choice of the selective reflection wavelength and of the broadness of the associated band
- the range of suitable pitches by taking into account the absorption of the substrate
- the modulation of the transmitted intensity with an applied voltage with the liquid crystal's pitch and the influence of parameters such as the liquid crystal's thickness and its pitch
- the prepolymer quantity that can be dissolved in the liquid crystal to keep a good electrooptical response
- the evolution of the threshold voltage with parameters like the UV intensity or the pitch

RESULTS AND DISCUSSION

Natural Broadness Of The Reflection Band

Cholesteric liquid crystals have the property of reflecting a part of the incident radiations thanks to their helical structure. The reflected wavelength is proportional to the pitch of the cholesteric liquid crystal.

The pitch of the cholesteric screw of the liquid crystal depends on the composition of the mixture: a cholesteric liquid crystal is obtained by adding chiral compounds to a nematic liquid crystal. The higher the concentration of the chiral compounds is, the smaller the reflection wavelength is.

The width of the reflection band depends on several parameters :

$\lambda = n_{par} * \text{pitch} = 0.25\,(n_e^2 + n_o^2)^{1/2} * \text{pitch}$; λ : 'average' wavelength

Δn : birefringence

$\Delta n = n_e - n_o$; n_e : liquid crystal extraordinary index

n_o : liquid crystal ordinary index

$\Delta\lambda = (\Delta n / n_{par}) * \lambda$; $\Delta\lambda$: reflection band width

In the infrared spectrum, the width of the reflection band is therefore proportional to the reflection wavelength. Indeed, it has been shown that the birefringence remains approximately constant in the IR region except for the resonance effects in the vicinity of molecular vibrational bands [1, 3]. Consequently, for the same liquid crystal and the same chiral dopants, the higher the pitch of the cholesteric liquid crystal is, the broader the reflection band is.

For the experiments, we have taken a nematic liquid crystal, we have added chiral compounds and 3% of a prepolymer (to create a polymeric network through the sample to stabilize the textures). We have changed the concentration of the chiral compounds to modify the wavelength of the reflection band. The width of the reflection band for each sample was measured. The results are summarized in the table 1 :

Reflexion in the	Mean reflexion wavelength λ (nm)	Reflexion band width $\Delta\lambda$ (nm)
Red	630	90
IR	950	130
	1550 (1.55 μm)	230
	1725 (1.725 μm)	240
	2065 (2.065 μm)	300
	3200 (3.2 μm)	450

TABLE 1 variation of the reflection band width with the wavelength

We can notice that there is a very good correlation between the experimental and the theoritical values of the bandwidth obtained for a nematic liquid crystal with a birefringence of 0.21. (figure 1) : the experiment values are slightly higher.

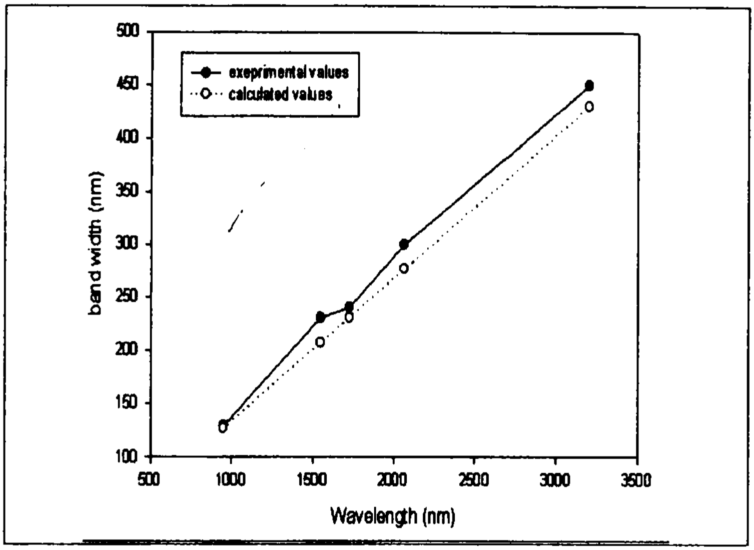


FIGURE 1 modulation of the reflection band width with the wavelength

It is therefore possible to modify the location of the reflection band and in the same time its bandwidth.

<u>Modulation Of The Initial Reflected Intensity : Relation Reflected Intensity Without Voltage – Pitch – Sample's Thickness:</u>

The percentage of reflected intensity can also be chosen. Indeed, the maximum reflected intensity that can be obtained is 50% since, due to the polarisation of light, only half of the initial radiations is reflected. The amount of reflected intensity depends on the number of pitches. For the same liquid crystal, we've changed the sample's thickness and measured the transmitted intensity to see the evolution of the band with the number of pitches of the cholesteric liquid crystal (figures 2a to d and table 2).

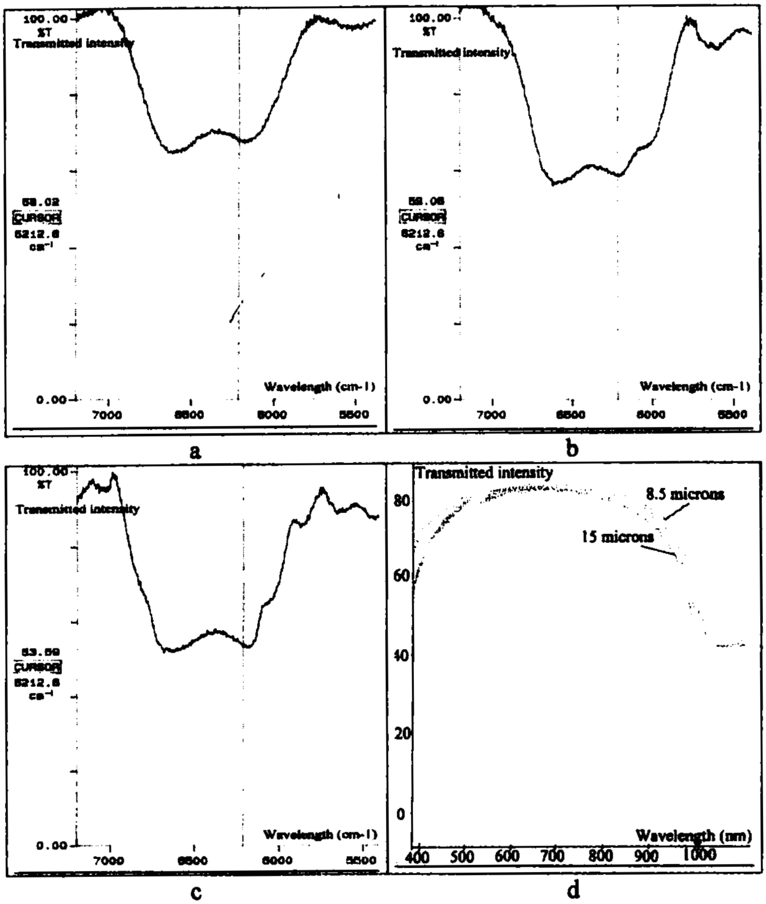


FIGURE 2 reflection band in various cases (a) : mean reflection wavelength 1.56μm – thickness 3.2 microns, (b) : mean reflection wavelength 1.56μm – thickness 8.5 microns, (c) : mean reflection wavelength 1.56μm – thickness 15 microns, (d) : mean reflection wavelength 1.05μm – thickness 8.5 and 15 microns

Due to the fact that the sample's thickness is not completely uniform on the whole sample, it is not possible to give the exact number of pitches :

Liquid crystal pitch (mean reflection wavelength)	Mean Sample's thickness	Number of pitch	% of transmitted intensity
1 μ (1.56 μm)	3.5	3-4	32
	8.5	8-9	41
	15	about 15	47
0.7 μ (1.05 μm)	8.5	about 12	48
	15	about 20	48

TABLE 2 modulation of the transmitted intensity with the number of pitch

According to the values obtained for the sample with a pitch of 0.7 μm, it appears that the maximum of reflected intensity is obtained for a number of pitch of at least 12. Concerning the other liquid crystal, this observation is relevant since a maximum reflected intensity is obtained for a number of pitch of about 15. For a number of pitch of about 8-9, the maximum is not reached. We can therefore conclude that the maximum reflected intensity is obtained for a number of pitch of about 10.

It is therefore possible to modulate the reflected intensity solely by changing the sample's thickness.

Absorption Of The Radiations By The Substrate

A major problem about the modulation of the infrared radiations concerns the substrate's absorption. The absorption by the substrate of the Infrared spectrum (to about 10 μm) was studied. ITO-coated glass substrates are not suitable because glass is not transparent and ITO is absorptive due to the free-carrier absorption which is proportionnal to λ^2 [1]. IR transmissive windows such as ZnSe [1], KRS-5 [1], CaF_2 [3], ZnS Claertran [3], NaCl [6] can be used. Concerning the conductive layers, Pt [6] or In_2O_3 [1] are suitable. Ge antireflective coatings allows to increase the transmission [5].

Experiments were carried out on ITO-coated glass substrates for our goal was first to check that PSCT materials can be suitable for a modulation of the infrared spectrum and first to study the influence of some parameters on the electrooptical behavior of the samples.

ITO-coated plastic substrates (PET or PC) can't be used for the same reason. The transmission of plastic substrates was investigated :

some proved to be suitable and others no such as cellulose or polycarbonate. A conductive layer that can be easily deposited was succesfully tested to replace the ITO conductive layer.

Experiments with substrates less absorbing in the Infrared will be discussed in another paper.

To conclude that part, we can say that it is therefore possible to choose the location of the reflection band in the infrared spectrum and also to modify the reflected intensity. We now have to study the modulation in the infrared spectrum with an applied voltage and the influence of parameters such as the pitch of the cholesteric liquid crystal or the sample's thickness.

Electrooptical Behaviour Of The Samples

Voltage behaviour – general considerations

Three possible states are available for Infrared cholesteric liquid crystals :

- a reflective state in the near infrared spectrum without voltage
- a scattering state when the voltage is applied
- a transparent state for higher voltages.

When the liquid crystal molecules are in the third state (homeotropic orientation), a return towards the planar or the scattering state can be obtained depending on the way the voltage is cut off. Schematically, if the voltage is cut off very quickly, the planar reflective state is reached but if it is cut more slowly, the final state is the scattering one.

The voltage behavior of a sample is illustrated on the figure 3.

Without voltage (figure 3a), the sample is reflective with a reflection band between 1.44 µm and 1.67 µm (band width : 230 nm). The transparency of the sample without voltage is very good.

When the voltage is increased, there is first a decrease of the reflection band (figures 3b and c) and the sample becomes scattering (figure 3c). The diffusion of the sample increases with the applied voltage (figure 3d) till the liquid crystals molecules are homeotropic (figure 3e): the sample is transparent and its transparency of the sample is very good (100% transmission).

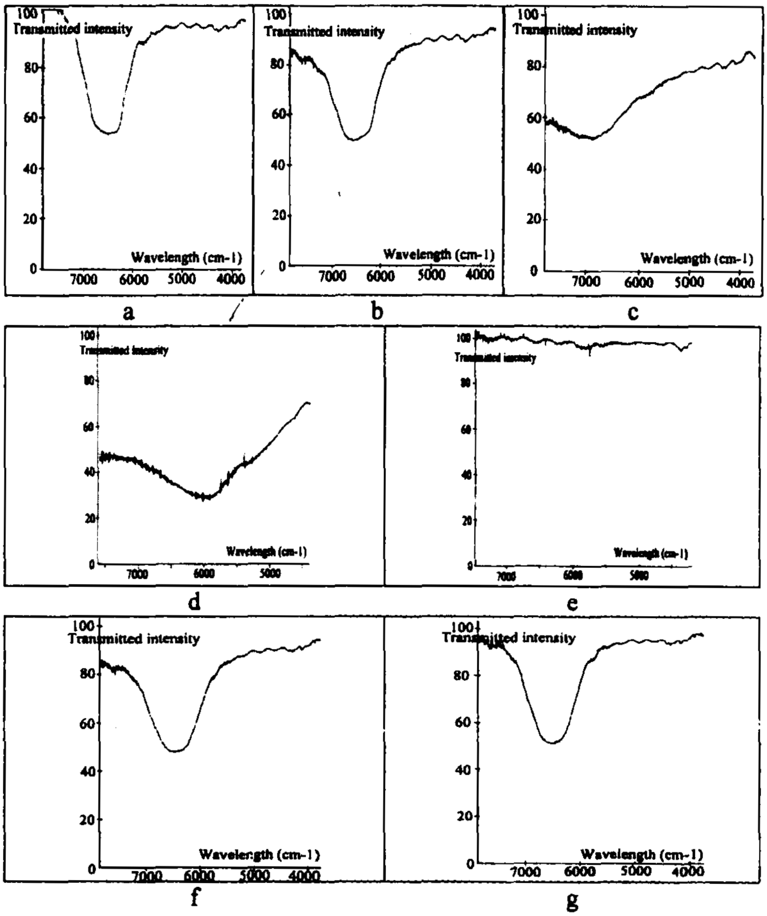


FIGURE 3 voltage behavior– Infrared sample – band width 230 nm [1.44μm – 1.67μm] – evolution of the transmitted intensity versus wavelength with the applied voltage
(a) 0V, (b) 6V, (c) 7.3V, (d) 25.2, (e) : 30V, (f) cut-off voltage – return to the planar state after 30 seconds, (g) cut-off voltage, return to the planar state after 5 minutes

When the voltage is cut off, the return to the reflective state happens very quickly due to a very fast coalescence of the planar domains. After thirty seconds (figure 3f), the transparency is more than 90% of the initial one; after 5 minutes, the sample has almost recovered its initial transparency (figure 3g).

It is therefore possible to have a modulation of the transmitted intensity with an applied voltage.

Modulation of the transmitted intensity with an applied voltage – influence of the pitch

Samples with different pitches were elaborated and the transmitted intensity investigated with an applied voltage. The voltage behaviour is the same as the one described above. The spectra corresponding to the highest modulation are shown on the figures 4 to 6 for respectively the samples with a mean reflection wavelength at 1.05 μm (4a and b), 2.2 μm (5a and b) and 3.5 μm (6a and b).

In all the cases, an important modulation of the intensity is obtained but some conclusions can be drawn : increasing the liquid crystal's pitch leads to a decrease of the modulation and to less steady states (particularly for the sample with the highest pitch).

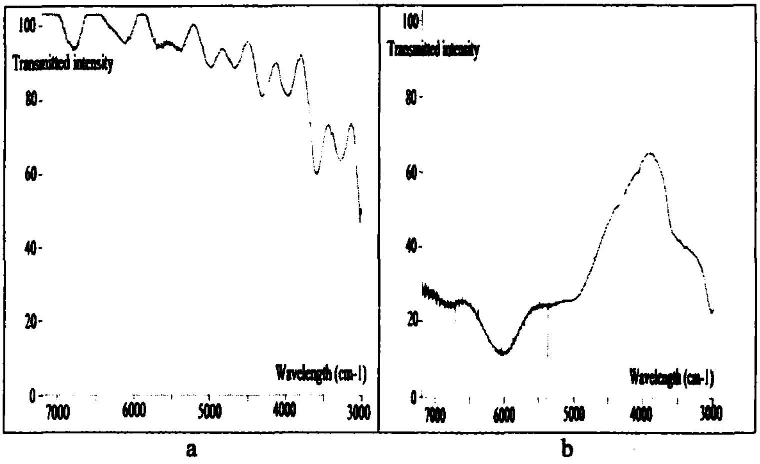
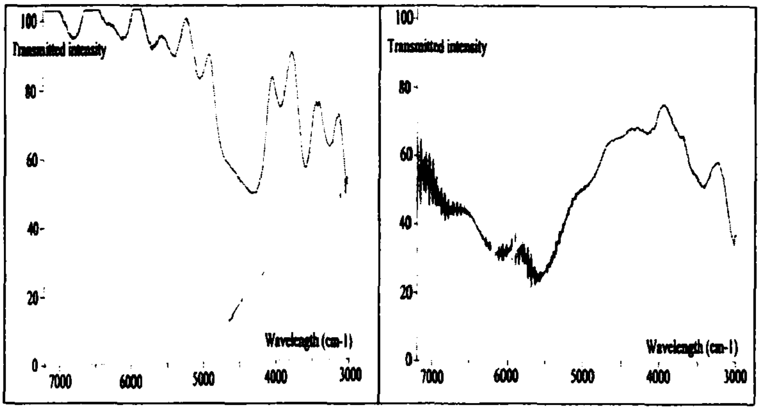
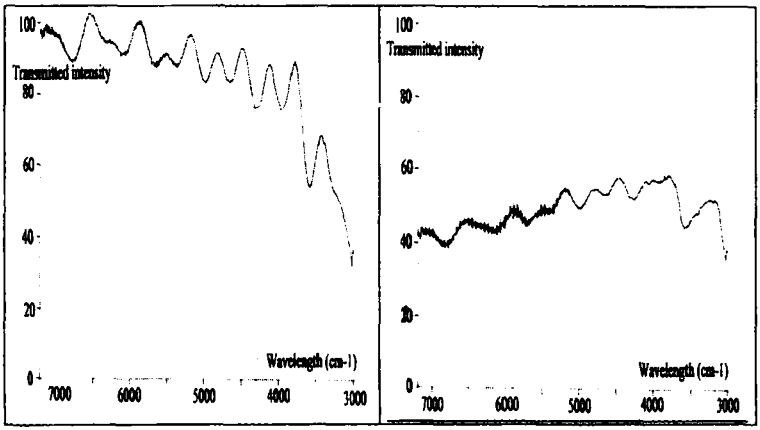


FIGURE 4 mean reflection wavelength 1.05μm (950 cm^{-1}) - 8.5μm
(a) transmitted intensity without voltage, (b) transmitted intensity with an applied voltage



a b

FIGURE 5 mean reflection wavelength 2.2μm (4550 cm^{-1})-8.5μm
(a) transmitted intensity without voltage, (b) transmitted intensity with an applied voltage



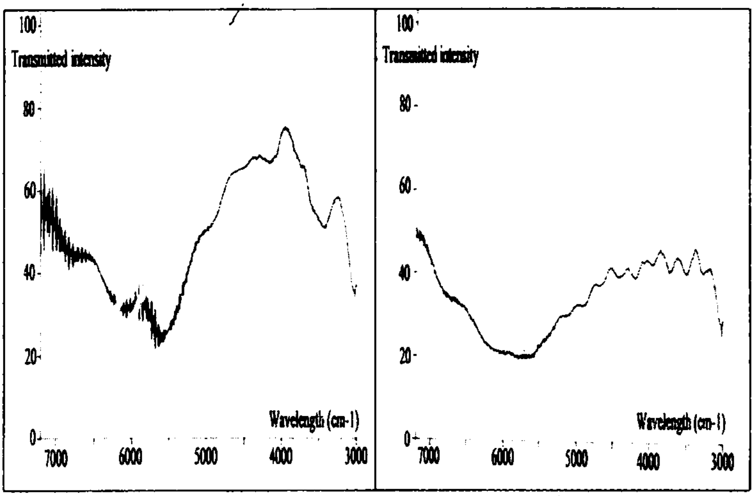
a b

FIGURE 6 mean reflection wavelength 3.5μm (2860cm^{-1})-8.5μm
(a) transmitted intensity without voltage, (b) transmitted intensity with an applied voltage

Modulation of the transmitted intensity with an applied voltage – influence of the sample's thickness

The influence of the sample's thickness on the modulation of the transmitted intensity was also investigated. The voltage behavior of a sample with a mean reflection wavelength at 2.2 μm was studied for sample's thicknesses of 8.5 (figure 7a) and 15 μm (figure 7b).

A more important modulation is obtained for the thicker sample, especially for the range corresponding to the highest wavelengths.



a b

FIGURE 7 mean reflection wavelength 2.2μm
(a) transmitted intensity with an apllied voltage 8.5 microns, (b) transmitted intensity with an applied voltage 15 microns

Threshold voltages – influence of the pitch and of the UV intensity

As it will be discussed in the part dedicated to the liquid crystal behavior when the voltage is cut off, the highest concentration of prepolymer than can be used is 3%. The influence of higher concentrations was therefore not investigated here.

The results are summarized in the table 3 (sample's thickness 15 microns).

Reflexion wavelentgh (μm)	0.06 mW/cm^2 2% prepolymer Us(V)	0.6 mW/cm^2 2% prepolymer Us(V)	0.6 mW/cm^2 3% prepolymer Us(V)
1.6	39	42	43
2	30	30	28
4	21	21	22

TABLE 3 threshold voltages

The threshold voltages are estimated by measuring the transmitted intensity versus the voltage at 545 nm.

Increasing the pitch leads to a decrease of the threshold voltages as it can be explained by considering the relation :

$E_c = \pi^2 (d / P_0) (K_{22} / \varepsilon_0 \Delta\varepsilon)$ with Ec threshold voltage, K_{22} twist elastic constant, ε_0 permittivity of the free space, $\Delta\varepsilon$ dielectric anisotropy of the cholesteric liquid crystal mixture, P_0 pitch of the liquid crystal and d sample's thickness.

There is no obvious influence of the UV intensity and of the prepolymer concentration on the threshold voltage.

Return to a planar orientation after switching the samples

All the results are summarized in the table 4 which gives the quality of the return to the planar state when the voltage is cut off :

Wavelength (μm)	0.06 mW/cm^2 2% prepolymer	0.06 mW/cm^2 3% prepolymer	0.6 mW/cm^2 2% prepolymer
1.6	bad	bad	good
2	bad	bad	good
3.2	bad	bad	good

Wavelength (μm)	0.6 mW/cm^2 3% prepolymer	4.6 mW/cm^2 2% prepolymer	4.6 mW/cm^2 3% prepolymer
1.6	bad	good	good
2	bad	good	bad
3.2	bad	/	/

TABLE 4...quality of the return to the planar orientation when the voltage is cut-off

The return to the planar orientation when the voltage is cut off can be damaged as it is shown on the pictures 1 (planar orientation) and 2 (locally disturbed orientation).

- *Influence of the pitch of the liquid crystal*

There is only one case where the pitch has an obvious influence on the quality of the sample (3% prepolymer – 4.6 mW/cm^2) : a good return is only obtained for the sample with smaller pitch. Increasing the pitch can therefore lead to a worse orientation of the liquid crystal molecules when the voltage is cut off. Nevertheless, it is not a factor as important as the UV intensity and the prepolymer concentration.

- *Influence of the UV intensity*

Decreasing the UV intensity induces an important degradation of the orientation of the liquid crystal molecules. For a very low intensity (0.06 mW/cm^2), a good return is never obtained whatever the pitch and the prepolymer concentration are. At 0.6 mW/cm^2, the return doesn't depend on the pitch but on the prepolymer concentration. At 4.6 mW/cm^2, the return depends on the prepolymer concentration but also on the pitch.

- *Influence of the prepolymer concentration*

In all the cases, better results are obtained for a prepolymer concentration of 2%. For the strongest irradiation, 3% prepolymer are suitable but not for all the other irradiations.

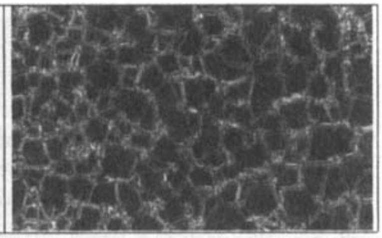
Relation between the polymer network morphology, the quality of the return to the planar state and the above parameters (prepolymer concentration, UV intensity and pitch of the cholesteric screw) : observations and discussion

- *Observations :*

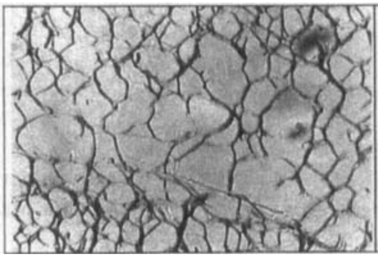
The picture 3 shows the texture of the sample (mean reflection wavelength 3.2 µm, 0.06mW/cm^2) at 35V. The liquid crystal molecules are homeotropic but the sample is weakly scattering. That scattering is due to the polymeric network : it forms thick strands. If the voltage is increased the strands are moving. When the voltage is cut off, there is a partial return in the larger voids between the polymer strands (the picture 4 represents the same area as picture 3 immediately after cutting off the voltage). The return to the planar orientation is disturbed close to the polymer network.

The light scattering in the homeotropic state is due to the formation of a network with thick strands.

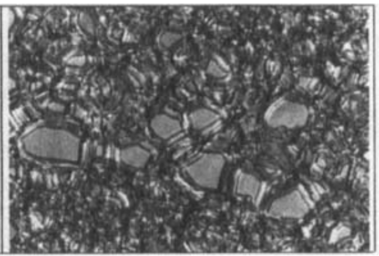
PICTURE 1 transmission view after switching of a sample with 2% prepolymer, mean wavelength 2 μm, UV irradiation 4.6 mW/cm^2



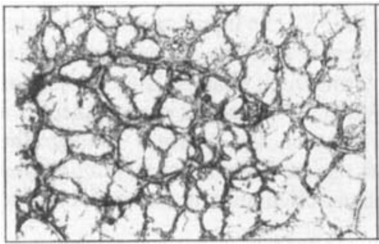
PICTURE 2 transmission view after switching of a sample with 3% prepolymer, mean wavelength 2 μm, UV irradiation 4.6 mW/cm^2



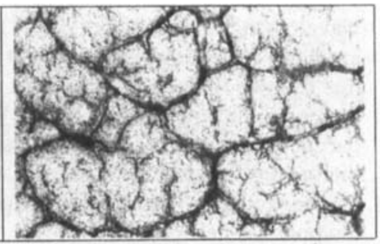
PICTURE 3 transmission view of a sample in the homeotropic state with 2% prepolymer, mean wavelength 3.2 μm, intensity of irradiation, 0.06 mW/cm^2



PICTURE 4 transmission view of the sample of picture 3 when the voltage is cut off



PICTURE 5 polymer network (3%), UV irradiation 4.6 mW/cm^2



PICTURE 6 polymer network (3%), UV irradiation 0.06 mW/cm^2

See Color Plate XXVI at the back of this issue.

The bad reorientation of the liquid crystal molecules when the voltage is cut off is linked to a worse reorientation close to the polymer network.

To sum up, we can say that :

Increasing UV intensity	Leads to a(n)	Improvement of the return
Increasing prepolymer concentration		Degradation of the return
Increasing the pitch		Slight degradation of the return

- Discussion : influence of the parameters

The morphology of the polymer network was investigated for the three intensities of irradiation. After polymerisation, the cells are put in a container with acetone. The solvent slowly replaces the liquid crystal and after a few hours it has completely replaced it. The acetone is therefore evaporated and the two strips carefully split. Such an extraction can lead to modifications of the polymer network [13]. Therefore several sets of experiments are necessary to make conclusions.

Concerning the modifications of the polymer network by the extraction procedure, it is observed that the higher the UV intensity is and the less damaged the polymer network is. It suggests that the polymer network obtained for very small intensities is more fragile.

Pictures 5 and 6 shows the morphology obtained for 0.06 mW/cm^2 (picture 5) and 4.6 mW/cm^2 (picture 6). For the highest intensity, the polymer network covers the whole surface with a relatively thick layer and has a few outgrowths. For the lowest intensity, the surface is also covered but the polymer layer seems much thinner, the outgrowths are more numerous, are larger and have a bigger size.

The same experiment was made with another prepolymer for the same concentration concentration and the same intensities. The conclusions remain the same : the polymer network morphology depends on the UV intensity. For a high UV intensity, the polymer network covers the surface, is very thin because there are a lot of nucleation spots and has less outgrowths. Decreasing the UV intensity leads to a network with less nucleation spots (the polymer network covers less the surface), the outgrowths are therefore higher, thicker and more numerous.

Such observations are relevant with the above observations concerning the damaging of the polymer network during the liquid crystal extraction : for high intensities, the network covers the surface and has only a few small outgrowths, it is therefore strongly linked to the surface and will be less damaged.

The quality of the return of the liquid crystal molecules to a planar orientation can also be explained by considering the same previous remarks.

Concerning the prepolymer concentration, for the same UV intensity, increasing the concentration leads to a network with higher outgrowths and also denser. Consequently, it is not surprising that a degradation of the electrooptical behavior is observed in all the cases.

CONCLUSIONS

A modulation of the infrared spectrum can be obtained with devices using cholesteric liquid crystals.

The electrooptical behavior of such materials was investigated relatively to several aspects :

- without voltage, it is possible to choose the location of the reflection band, its band width and the associated reflected intensity
- with an applied voltage, a modulation of the transmitted intensity is obtained. Parameters such as the liquid crystal's pitch and the sample's thickness were studied: a relatively small pitch and a thick liquid crystal layer are more suitable to lead to a significant modulation
- an optimization of the parameters (prepolymer concentration, UV intensity, liquid crystal's pitch) to have a good electrooptical response was carried out : low prepolymer concentrations and relatively high UV intensity allows to obtain the best behavior

Materials using IR liquid crystals are interesting because of properties such as low theshold voltages, good transparency. It has been shown that an important modulation of the transmitted intensity that can be obtained in the IR radiations range investigated (form 1.3 micron up to 3 microns).

The modulation of the transmitted intensity for higher wavelengths has now to be studied.

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