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Electrooptical characterizations of polymer stabilized cholesteric liquid crystals

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Abstract

Several monomers were added to a cholesteric liquid crystal to obtain after irradiation a polymer stabilized cholesteric texture (PSCT). For that use, two monomers were synthesized. The influence of the nature of the monomer (nematic or cholesteric) and of its structure is investigated as well as parameters such as the UV irradiation. Some of the characteristics of the PSCT can be correlated to the interactions between the polymer network and the low molecular mass liquid crystal molecules. A broadening of the reflection band can also be obtained with such monomers and is also discussed with the aspect of the interactions polymer network/liquid crystal molecules. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Monomer; Polymer; Cholesteric liquid crystal

1. Introduction

Liquid crystal dispersions are being studied intensively because of their numerous applications (large area flat panel displays, privacy windows,…). In polymer-stabilized liquid crystals (PSLC) [1–3], a monomer is dissolved in a low-molar-mass liquid crystal, aligned in a suitable state and photopolymerized. The monomer is generally dispersed in small amounts (typically a few percent in weight) to create a polymer network through the sample. Polymer stabilized cholesteric formulations have a reflective state usually improved by a suitable orientation layer (rubbed polyimide layer), they become scattered when the voltage is increased and transparent when the liquid crystal molecules are homeotropic. If the voltage is suddenly cut off, the liquid crystal molecules return to their planar orientation; otherwise the scattering state is reached. Thanks to the polymer network, the scattering state is stable and there is no further relaxation towards the planar state [3]. Systems in which the monomer concentration is higher (up to at least 40%) can also be made [4].

Several kinds of monomers can be used. They can be either nematic or cholesteric, and have the main following functional groups: acrylates [5–7], epoxides [8] or ethers [9,10]. The functionality of the monomers proves to be important.

Our aim is to study several liquid crystal monomers to be used as a stabilizer of the liquid crystals textures. The influence on the electrooptical behavior of the monomer concentration and of its structure is investigated as well as parameters such as the intensity of irradiation.

Such monomers can also be used to induce a broadening of the reflection band. Polymer stabilized cholesteric texture (PSCT) materials reflecting a great part of the visible range could be used for instance as glazings that could allow obtaining energy gains. The broadening can be due to the existence of two populations of nematic molecules [11]. Some of them are linked to the polymer network and others no. They do not have the same pitch and the overlap of both corresponding reflection bands can lead to a broadening. Broer [12,13] and Hikmet [14,15] obtained broadband reflection by creating a pitch gradient across the sample. We proved the existence of such a mechanism based on the existence of a UV gradient through the sample and have studied the parameters of the broadening [16]. Experiments on the broadening of the reflection band are also carried out.

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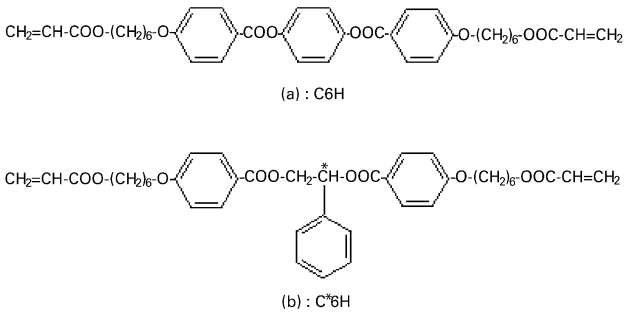


Fig. 1. Formulae of the synthesized monomers C6H (a) and C*6H (b).

2. Experiments and results

Our aim is to study several liquid crystal monomers as a stabilizer of the liquid crystals textures and to see if a modification of the structure of the monomer can lead to changes of the electrooptical behavior of the corresponding PSCT.

2.1. Experiments

2.1.1. Synthesis of the monomers

Two diacrylate monomers are synthesized, one is nematic and the other one is chiral. Their formulae are represented in Fig. 1. The nematic monomer called C6H (Fig. 1a) is synthesized according to the process given by Broer (see Fig. 2a) [17]. The chiral monomer called C*6H (Fig. 1b) is obtained by replacing the hydroquinone of the last step by the chiral *S*-styrene glycol (see Fig. 2b).

Another monomer called C6M is also tested: the only difference with the monomer C6H is the existence of a methyl group on the central phenyl group (Fig. 3).

2.1.2. Characterizations of the monomers

The synthesized compounds are analyzed after each step of the synthesis by infrared spectroscopy (IR) and gas chromatography (GC)/mass spectroscopy (MS) to check their purity and that the correct compounds are obtained.

The final compounds are also analyzed by IR. GC/MS

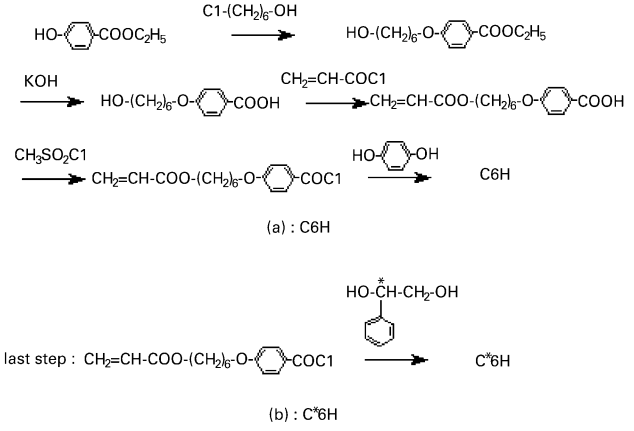


Fig. 2. Steps of the synthesis of the monomers C6H (a) and C*6H (b).

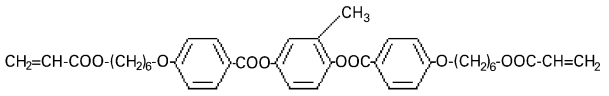


Fig. 3. Formula of the monomer C6M.

analysis are carried out but it proves impossible to vaporize the monomers due to their very high molecular weight. Concerning MS analysis (not coupled with GC) in electronic impact, the molecular peak is not registered but the combination of the other peaks allows to make sure that the appropriate compounds are synthesized. ^{1}H NMR (nuclear magnetic resonance) experiments on the two monomers are also carried out as well as differential scanning calorimetry (DSC) measurements.

^{1}H NMR spectra are registered on a spectrometer Bruker AMX 400 and the IR spectra on a spectrometer Nicolet 460 with a DTGS detector. DSC is carried out with a Perkin–Elmer DSC-2C (heating rate: 5 K min^{-1}) and the GPC/MS with a Hewlett-Packard 5890 series II/ MSD 5971A.

Table 1 gives the ^{1}H NMR, IR and DSC results for the synthesized products and has compared them with the

Table 1
IR-TF, ^{1}H NMR and DSC measurements of the monomers C6H and C*6H — comparison with the literature values

Monomer C6H

IR-TF 1% in KBr (cm^{-1}): 3434 (vw, OH); 3110, 3080, 3051 (vw, CH ar); 2944, 2933, 2914, 2867 (w, CH al), 1725 (s, C=O); 1634 (w, C=C al); 1605, 1512, 1502 (m, m, w, C=C ar); 1405 (w, CH_8=CH); 1311, 1207 (w, m, acrylate); 1298, 1256, 1168 (w, s, vs, C–O); 1077 (m); 1005 (m); 846 (w, 2H adj); 764 (w, CH_2CH_2; 691 (w); 650 (w)

IR-TF (literature values): 2940, 2860, 1720, 1636, 1600, 1510, 1500, 1425, 1410, 1300, 1255, 1200, 1170, 1080, 1000, 850, 840, 760, 650, 630

^{1}H NMR (400 MHz, $CDCl_3$): 8.13 (d, 9 Hz, 4H, ar); 7.24 (s, 4H, ar); 6.95 (d, 8.8 Hz, 4H, ar); 6.38 (dd, 17, 3, 1.5 Hz, 2H, vinyl); 6.11 (dd, 17.3, 10.5 Hz, 2H, vinyl); 5.81 (dd, 10.5, 1.5 Hz, 2H, vinyl); 4.17 (t, 6.7 Hz, 4H, $COOCH_2$); 4.04 (t, 6.6 Hz, 4H, $PhOCH_2$); 1.83 (q, 6.7 Hz, 4H, $COOCH_2CH_2$); 1.71 (q, 6.6 Hz, 4H, $PhOCH_2CH_2$); 1.4–1.57 (m, 8H, inner CH_2CH_2)

^{1}H NMR (literature values): 8.18 (d, 4H); 7.25 (s, 4H); 7 (d, 4H); 6.5–5.8 (m, 6H); 4.22 (t, 4H); 4.01 (t, 4H); 1.9–1.3 (m, 16H)

DSC (°C): T(solid/nematic) = 107, T(nematic/isotropic) = 145 (not very obvious)

DSC (literature values): T(solid/nematic) = 108, T(nematic/isotropic) = 155

*Monomer C*6H*

IR-TF 1% in KBr (cm^{-1}): 3497 (vw, OH); 3065, 3034 (vw, CH ar); 2943, 2864 (m, m, CH al); 1777 (w); 1721 (s, C=O); 1634 (w, C=C al); 1605, 1511, (s, s, C=C ar); 1409 (s, CH2=CH); 1311, 1198 (m, s, acrylate); 1298, 1255, 1168 (w, s, vs, C–O); 1102 (s); 986 (s); 848 (m, 2H adj); 811 (m); 769 (m, CH_2CH_2); 700 (m, 5H adj)

^{1}H NMR (400 MHz, $CDCl_3$): 8.01 (d, 8.8 Hz, 2H, ar); 7.98 (d, 8.8 Hz, 2H, ar); 7.44 (dd, 7, 1.7 Hz, 2H, ar); 7.37 (td, 7, 1.7 Hz, 3H, ar); 6.92 (d, 8.7 Hz, 2H, ar); 6.9 (d, 8.7 Hz, 2H, ar); 6.38 (dd, 17.3, 1.4 Hz, 2H, vinyl); 6.1 (dd, 17.3, 10.4 Hz, 2H, vinyl); 5.8 (dd, 10.4, 1.4 Hz, 2H, vinyl); 5.09 (dd, 5.3, 3.3 Hz, 1H, C*H); 4.5 (dd, 11.7, 3.3 Hz, 1H, C*H–CH_2); 4.39 (dd, 8.3, 11.7 Hz, 1H, C*H–CH_2); 4.16 (t, 6.6 Hz, 4H, $COOCH_2$); 3.95–4.05 (m, 4H, $arOCH_2$); 1.81 (q, 6.6 Hz, 4H, $COOCH_2CH_2$); 1.69 (q, 6.9 Hz, 4H, $arOCH_2CH_2$); 1.4–1.55 (m, 8H, inner $(CH_2)_2$)

DSC (°C): T(chiralnematic/isotropic) = 67°C, T polymerization = 175°C

Table 2
Optical rotation measurements for compound C*6H and its precursor

	Solvent	Cell	T (°C)	Concentration (mg ml^{-1})	α (589 nm)
S-styrene glycol	Cyclohexanone	1dm	25	9.8	47.3
C*6H	Cyclohexanone	1dm	25	5	− 2

literature [17]: the experimental values are in good agreement with the literature ones. We can therefore conclude that the correct compounds were synthesized with a good purity.

Table 2 sums up the results concerning the optical rotation measurements for chiral compound C*6H and its precursor.

2.1.3. Samples' preparation

The nematic liquid crystal used has a positive dielectric anisotropy. Table 3 sums up its main characteristics. A chiral dopant is added to the nematic to obtain cholesteric materials. Levogyre and dextrogyre dopants are used: they only differ by the sign of their specific rotation. The monomer is added to the liquid crystal with a small amount of photoinitiator (Irgacure 907: 2% weight of monomer). The three monomers (C6M, C6H and C*6H) are incorporated into the mixtures.

A polyimide layer is deposited on the ITO-coated substrates and is rubbed. The samples' thickness (8.5 μm) is controlled by the use of spacers in the active layer.

The cells are filled with the liquid crystal mixtures by capillary action and are then irradiated at 4.6, 0.6 or 0.06 mW cm^{-2}. The composition of the mixtures is x% nematic liquid crystal/(100 − x)% chiral dopants/y monomer.

2.1.4. Analysis of the samples

The electrooptical behavior of the samples is analyzed either directly by using a spectrophotometer UV–visible HP8453E, or by analyzing the reflected intensity with a microscope OLYMPUS BH-2 outfitted with a photomultiplicator HAMAMATSU H5702-50. A multimeter HP34401A converts the light intensity into a voltage.

In order to understand the electrooptical behavior of the samples, the interactions between the polymer network and the liquid crystal molecules are determined by estimating the contact angle of a liquid crystal drop on the corresponding polymer film.

2.2. Results

2.2.1. Electrooptical studies

To study the influence of the structure of the monomer on the voltage response of the PSCTs, several aspects of the electrooptical behavior of the samples are taken into account:

- the dependence of the threshold voltage with the monomer concentration is analyzed since the threshold voltage is directly linked to the network density [18];
- it is also important to study the influence of the UV intensity for the network morphology depends on the intensity of irradiation [19–20]. Moreover, modifications of the reflection band can happen after irradiation [11–16];
- the last point to be studied concerns the return of the liquid crystal molecules to the planar orientation after switching.

The results are first analyzed for each monomer tested, then compared and discussed in the following part.

2.2.1.1. Use of the monomer C6H. The threshold voltage depends strongly on the monomer concentration since increasing slightly the monomer concentration induces higher and higher threshold voltages (Fig. 4).

There is almost no influence of the UV intensity on the threshold voltage whatever the prepolymer concentration is as it is shown in Fig. 5 representing the electrooptical behavior of the sample with 10% C6H. A broadening of the reflection band takes place and decreases with the UV intensity (Figs. 6 and 7). Picture 1 represents the texture of the gel after the irradiation.

The return to the planar state after switching is damaged even for 1% of monomer as shown in Picture 2. Increasing the monomer concentration leads to an even worse behavior.

2.2.1.2. Use of the monomer C6M. The threshold voltage is very dependent on the monomer concentration even for very small concentrations (1%) as shown in Fig. 8.

Table 3
Properties of the nematic liquid crystal

	Melting point (°C)	Clearing point (°C)	Optical anisotropy		Dielectric anisotropy	
			n_0 (20°C)	Δn (20°C)	$\epsilon_{\parallel}$ (20°C)	$\Delta\epsilon$ (20°C)
Liquid crystal	< −20	96	1.52	0.219	16.1	11.8

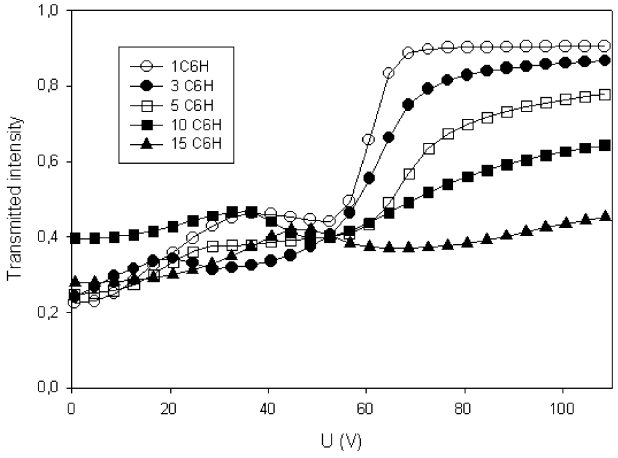


Fig. 4. Influence of the monomer C6H concentration on the threshold voltage (4.6 mW cm^{-2}).

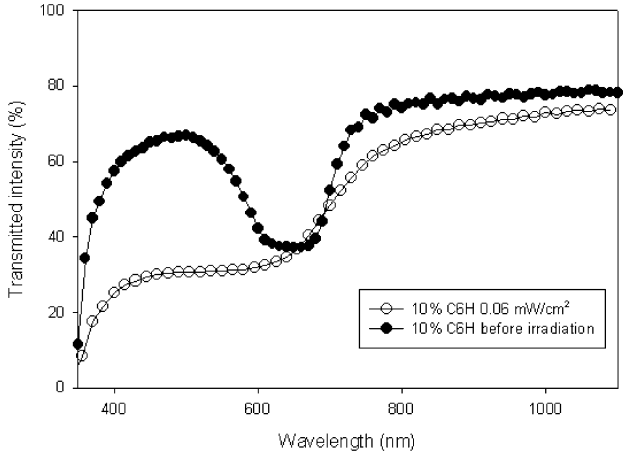


Fig. 6. Broadening of the reflection band (10% C6H) — 0.06 mW cm^{-2}.

Concerning the influence of the irradiation intensity, it proves that increasing the UV intensity leads to almost no change of the threshold voltage (Fig. 9) but a broadening of the reflection band happens after irradiation (Fig. 10). The broadening is all the more important as the UV intensity is low and that the monomer concentration is high (Fig. 11). An important point is that the reflected intensity is not the same according to the analyzed side of the sample (Fig. 10): the reflected wavelength is higher from the closer side to the UV source. Pictures 3 and 4 show that the reflected intensity is red from the closer side to the UV source (Picture 3) and green from the other side (Picture 4).

As for the return to the planar state after switching the sample to the homeotropic state, it is damaged whatever the monomer and the UV intensity are (Picture 5).

*2.2.1.3. Use of the monomer C*6H.* The first two monomers being nematic, the electrooptical behavior is the same whatever the sign of the specific rotation of the chiral dopant is. On the contrary, the monomer C*6H is chiral. Two cases are therefore distinguished because the pitch of the cholesteric helix is much more dependent on the monomer concentration if the specific rotations have opposite signs. A band broadening is therefore more likely to happen in that case [16].

The *first* set of experiments concerns the case of a monomer and of chiral dopants having specific rotations with the same sign.

In that case, there is almost no dependence of the threshold voltage with the monomer concentration even for the high concentrations (Fig. 12).

After irradiation, there is an important modification of the liquid crystal's pitch (Fig. 13). There is a shift of the pitch towards the higher wavelengths. Modifying the UV intensity slightly changes the location of the pitch but leads to no change of the threshold voltage (Fig. 14). A slight broadening happens and is all more important as the UV intensity is low and the monomer concentration high (Fig. 15). Picture 6 shows that the texture of the gel after irradiation is not homogeneous.

Concerning the return to the planar state when the voltage is cut off, it is good for the sample with 1% monomer as

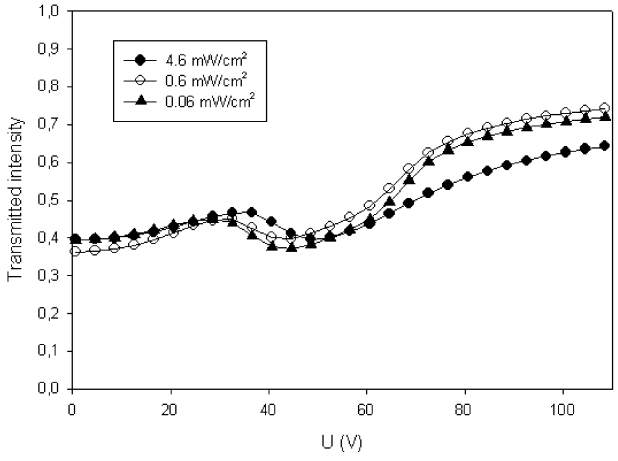


Fig. 5. Influence of the UV intensity on the electrooptical behavior (10% C6H).

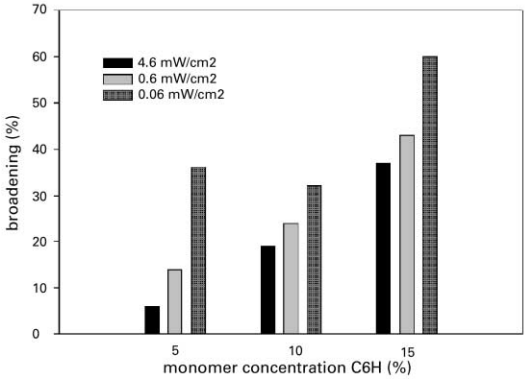
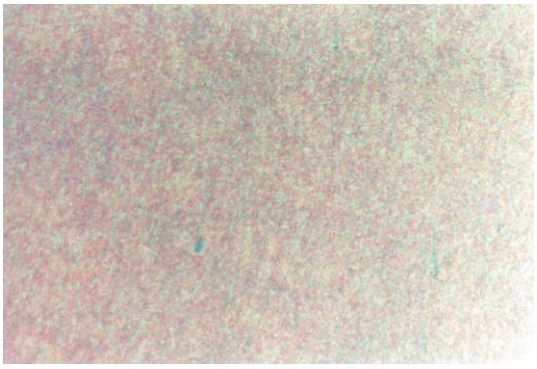
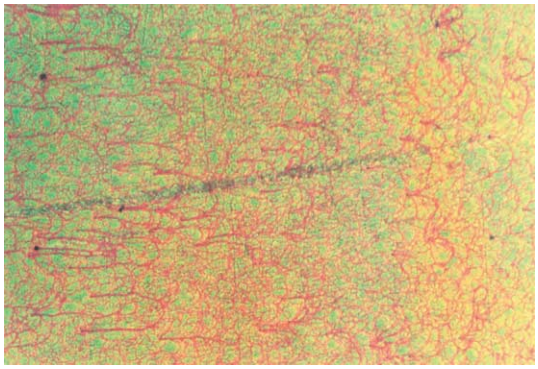


Fig. 7. Broadening of the reflection band with the monomer C6H concentration and the UV intensity.



Picture 1. Reflection view of a sample with a broadening 10 % C6H 0.06 mW cm^{-2}.



Picture 3. Reflection view of a sample with a broadening — 10% C6M — 0.06 mW cm^{-2} — UV side face.

shown in Picture 7. The other samples with higher concentrations are still reflective but remain slightly scattering when the voltage is cut off. Moreover, by enforcing a mechanical pressure to them, they recover their planar state with a little degradation of the return to the planar state (Picture 8).

The *second* set of experiments concerns the case of a monomer and of chiral dopants having specific rotations of opposite signs.

The threshold voltage of such samples is also absolutely independent on the monomer concentration (Fig. 16).

After irradiation, there is a shift of the reflection wavelength as it was observed in the first set of experiments but in that case towards the smaller wavelengths (Fig. 17). The threshold voltage is independent on the UV intensity as shown in Fig. 18. There is almost no broadening of the reflection band after irradiation and the textures of the gel looks like the ones observed in the first set of experiments but appear to be more homogeneous.

As for the return to the planar state after switching, it is exactly the same as the one observed in the first set of experiments.

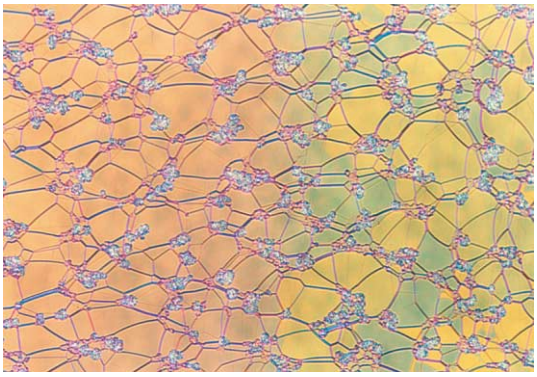
3. Qualitative study of the interactions between the liquid crystal molecules and the polymer network

To estimate the strength of the interactions between the polymer network and the low molecular mass liquid crystal molecules, the monomers C6H, C6M and C*6H (with a small amount of photoinitiator) are deposited in a thin layer on a glass lamella. They are covered by a plastic sheet and polymerized: the plastic sheet is used to avoid the inhibition of the polymerization by the oxygen. The plastic sheet is then removed and the spreading of a drop of the nematic low molecular mass liquid crystal is estimated.

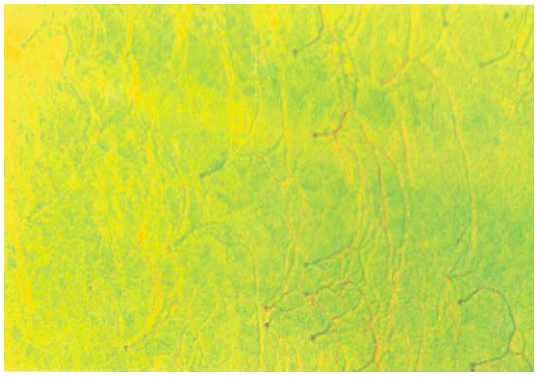
With the monomers C6H and C6M, there is a total spreading of the drop on the film suggesting very strong interactions between the polymer film and the liquid crystal molecules. On the contrary, the spreading is much less important with the monomer C*6H (contact angle 20°) showing that the interactions with the polymer film are probably lower.

4. Discussion

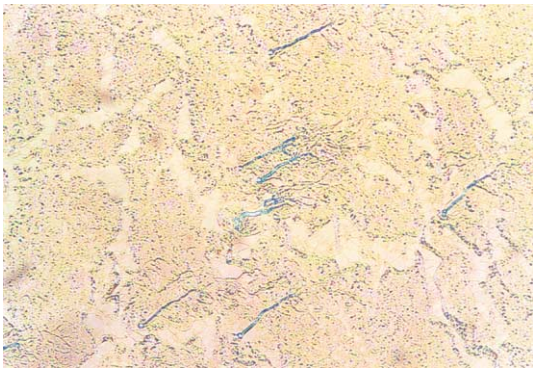
The most important result from the above experiments is that a very slight modification of the structure of the monomer can lead to differences of the electro-optical behavior of the samples. The interactions between the polymer network and the liquid crystal molecules are considered to explain the electro-optical behavior especially the dependence of



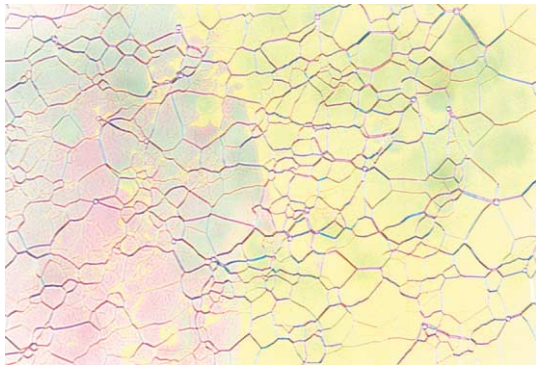
Picture 2. Reflection view of a sample with 1% C6H (4.6 mW cm^{-2}) — return after switching.



Picture 4. Reflection view of a sample with a broadening — 10% C6M — 0.06 mW cm^{-2} — opposite side (same sample as Picture 3).



Picture 5. Reflection view of a sample with 1% C6M — 4.6 mW cm^{-2} — return after switching.



Picture 7. Reflection view of a sample with 1% C*6H (4.6 mW cm^{-2}) — return after switching.

the threshold voltage with the monomer concentration and the quality of the return to the planar state after switching. The broadening of the reflection band is also discussed.

4.1. Electrooptical behavior — interactions between the polymer network and the liquid crystal molecules

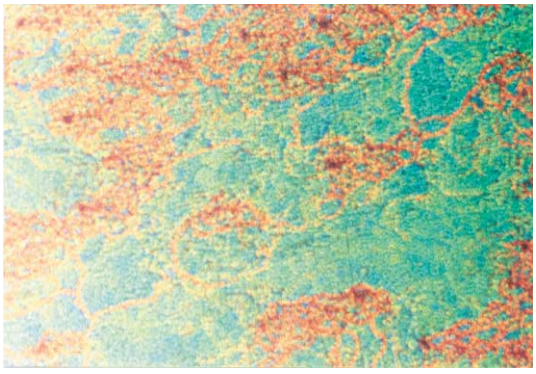
With the monomers C6H and C6M, there is a spreading of the drop of the liquid crystal on the polymer film: it suggests that the interactions between the polymer network and the liquid crystal molecules are very strong. It could therefore explain why there is an important dependence of the threshold voltage with the monomer concentration for both of them (Figs. 4 and 8).

Concerning the monomer C*6H, we have seen that the threshold voltage does not depend on the monomer concentration (Figs. 12 and 16): it suggests that the interactions between the liquid crystal molecules and the polymer network are weak. The spreading of a drop of nematic liquid crystal is rather important (contact angle 20°) but is much lower than the one obtained with the monomers C6H and C6M. In these conditions, the fact that the interactions between the polymer network and the liquid crystal molecules are lower could explain why there is no dependence of the threshold voltage with the monomer concentration.

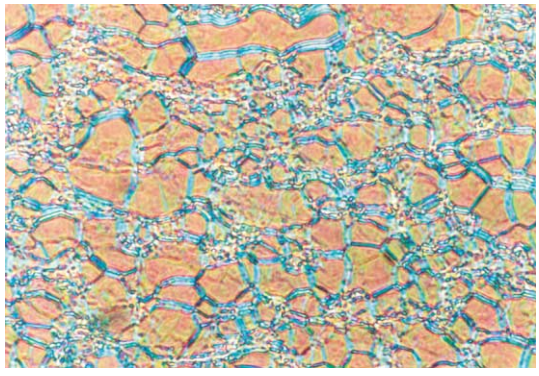
The fact that the interactions between the nematic molecules and the network formed with the monomer C6H seem to be stronger than with the monomer C*6H can be correlated to the structure of the molecules. The lateral presence of phenyl groups in the network formed with the monomer C*6H could lead to a decrease of the interactions with the liquid crystal molecules. Concerning the presence of a methyl group on the central phenyl group, it does not seem to modify these interactions.

The return to the planar state after switching is damaged even for 1% monomer with the monomers C6H (Picture 2) and C6M (Picture 5). The interactions of the liquid crystal molecules with the polymer network are very strong and could therefore lead to a degradation of the polymer network.

On the contrary, the return is not disturbed for 1% monomer C*6H (Picture 7) but for higher concentrations, the sample is reflective but also scattering. By enforcing a mechanical pressure to the sample, the molecules recover partially their planar orientation showing that the interactions of the molecules with the network are not strong enough to lead to a return to a planar state. The interactions being lower, the polymer network is less damaged with an applied voltage (Picture 8).



Picture 6. Reflection view of a sample 10% C*6H — 4.6 mW cm^{-2}.



Picture 8. Reflection view of a sample with 3% C*6H (4.6 mW cm^{-2}) — return after switching.

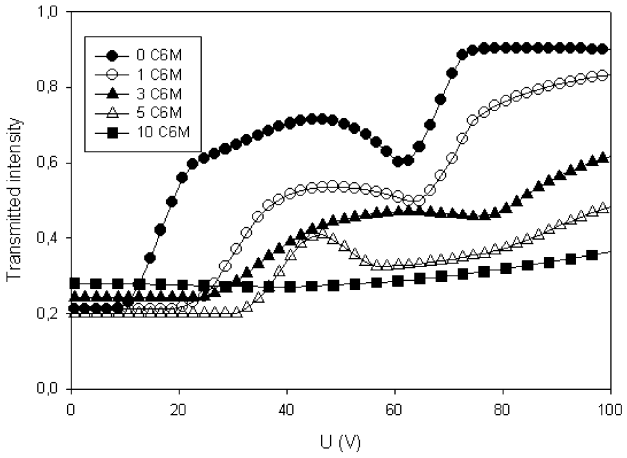


Fig. 8. Influence of the monomer C6M concentration on the threshold voltage (4.6 mW cm^{-2}).

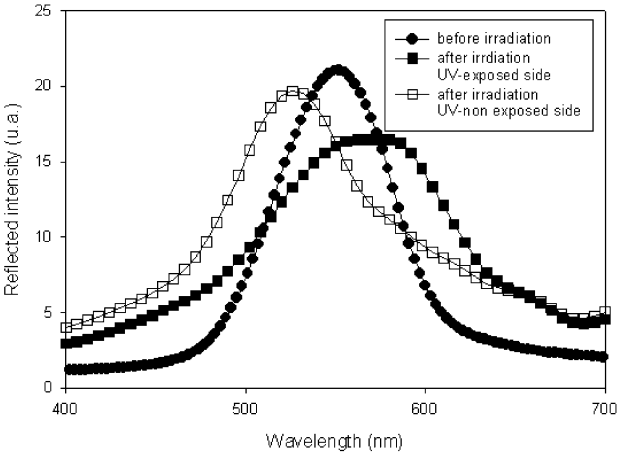


Fig. 10. Broadening of the reflection band (10% C6M — 0.06 mW cm^{-2}).

4.2. Broadening of the reflection band

To have a broadband film, it is necessary to create a pitch gradient across the sample [16]. The mechanism of broadening that we have put forward is the following one. Using a small UV intensity leads to the creation of a UV gradient across the sample. The monomer is therefore preferentially consumed near the closer strip to the UV source: it leads to a diffusion gradient of the monomer from the remotest areas towards the closest areas relatively to the position of the UV source. In the areas close to the UV source, there is an enrichment in monomer whereas in the remoter areas, there is an impoverishment. In the areas close to the source, the polymerization consumes the monomer but due to the strong interactions between the liquid crystal molecules and the network, the pitch is blocked. Due to the gradient diffusion, some monomer diffuses again towards these areas leading to a modification of the pitch but again the monomer is consumed and the pitch blocked. An inhomogeneous polymer network is therefore created through the sample leading to the existence of a pitch gradient. A broadening around the initial reflection band therefore happens. According to such a mechanism, we can expect that mixtures with a strong dependence of the reflection wavelength with the monomer concentration will induce higher broadenings.

Figs. 19–21 show the dependence of the wavelength of the selective reflection of mixtures with the monomer concentration before irradiation.

First case. Use of a nematic or of a chiral monomer with chiral dopants with specific rotation of same sign.

The dependence of the reflection wavelength with the monomer concentration is rather low in the three cases of the experiments (Figs. 19–21 — black curve, respectively, for the monomers C6H, C6M and for the monomer C*6H). The chiral monomer behaves as a chiral dopant: the pitch therefore decreases with the monomer concentration. The monomers C6H and C6M being nematic, the pitch of the mixture increases with the monomer concentration.

According to the above mechanism to explain the formation of a pitch gradient, the higher the monomer

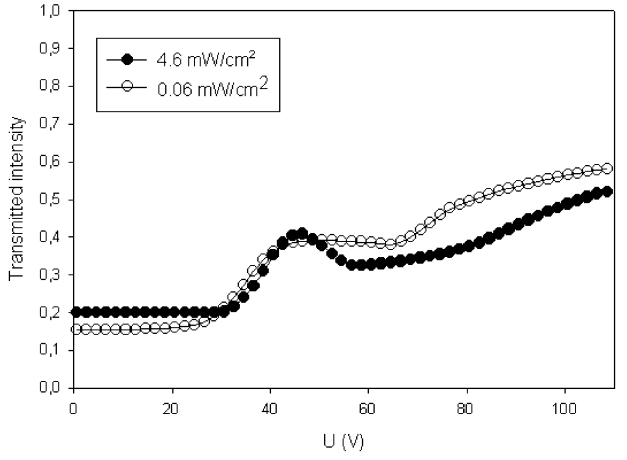


Fig. 9. Influence of the UV intensity on the electrooptical behavior (5% C6M).

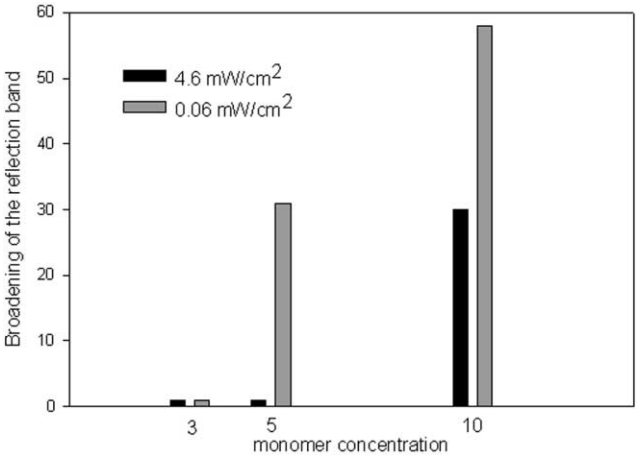


Fig. 11. Broadening of the reflection band with the monomer C6H concentration and the UV intensity.

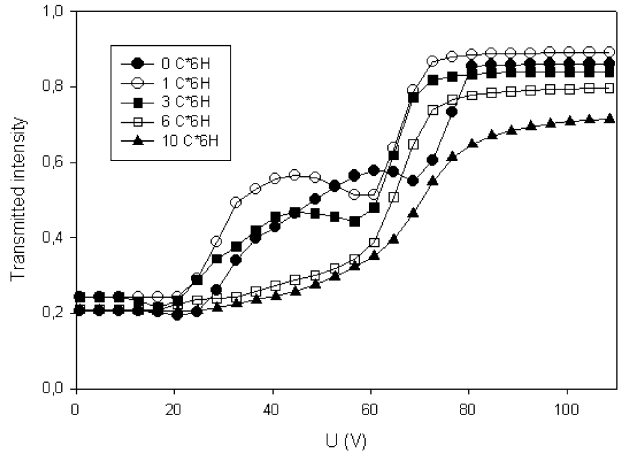


Fig. 12. Influence of the monomer C*6H concentration on the threshold voltage (4.6 mW cm^{-2}).

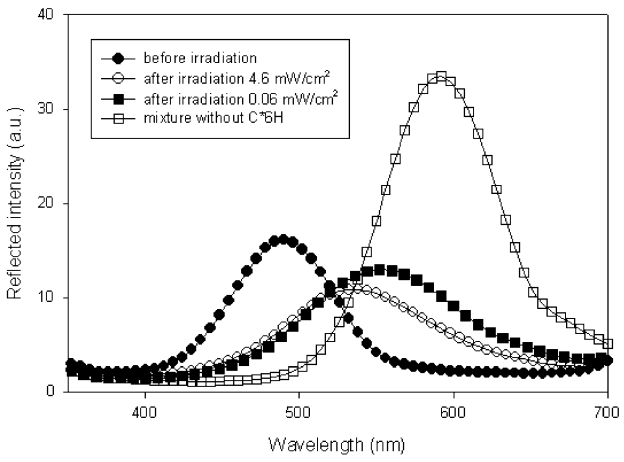


Fig. 13. Shift of the reflection band after irradiation (10% C*6H).

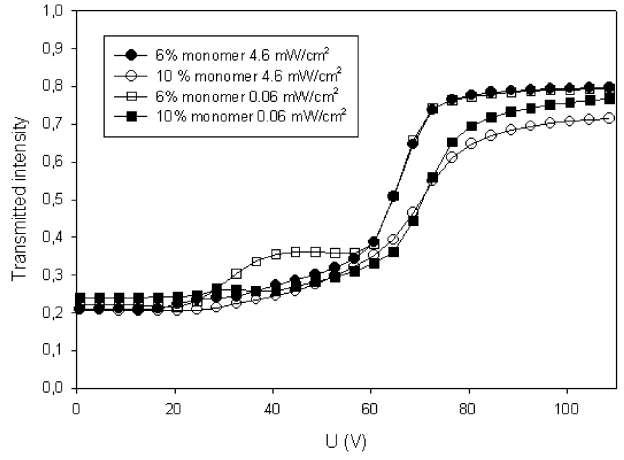


Fig. 14. Influence of the UV intensity on the electrooptical behavior (6 and 10% C*6H).

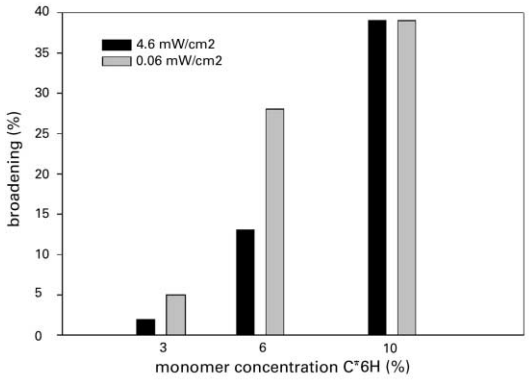


Fig. 15. Broadening of the reflection band with the monomer C*6H concentration and the UV intensity.

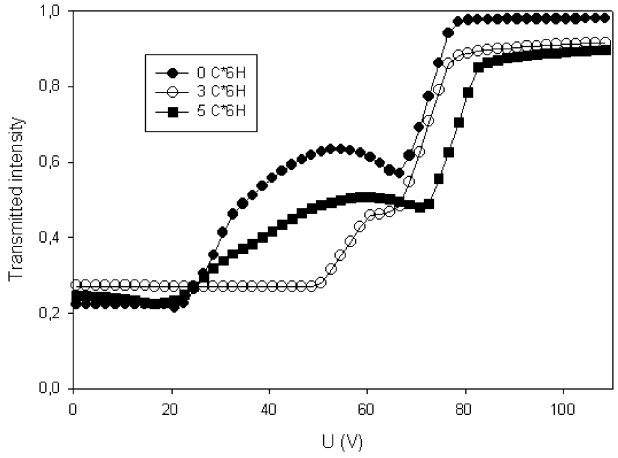


Fig. 16. Influence of the monomer C*6H concentration on the threshold voltage (4.6 mW cm^{-2}).

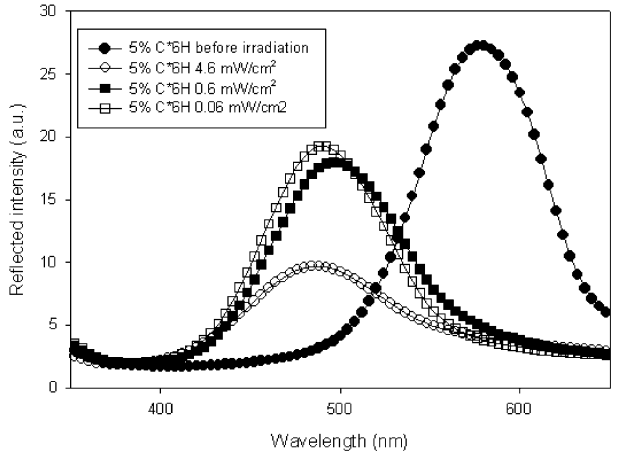


Fig. 17. Shift of the reflection band after irradiation (5% C * 6H).

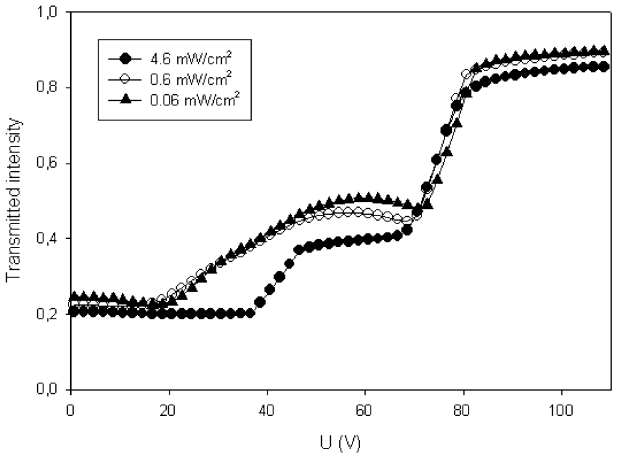


Fig. 18. Influence of the UV intensity on the electrooptical behavior (5% C * 6H).

concentration is, the lower the UV intensity is and the more broadened the reflection band is (Figs. 7, 11 and 15). Indeed, such conditions leads to the creation of a higher monomer consumption gradient and therefore to a higher diffusion gradient.

We have to notice that the texture of the gels after irradiation is different in the three cases studied:

- For the monomer C6M, it was shown that the reflected intensity from both sides of the samples is not the same (Fig. 10, Pictures 3 and 4): the reflected wavelength is higher for the closest side of the UV source. It is relevant with the above mechanism for the broadening of the reflection band: there is a diffusion of the nematic monomer towards the closest side of the UV source which leads to a higher pitch in these areas.
- For the monomer C6H, the broadening is more important on the left side of the peak before irradiation for a concentration of 10% (Fig. 6) and is symmetric in the same conditions for 15% monomer. There is no obvious visual difference between the two sides of the samples (Picture 1).

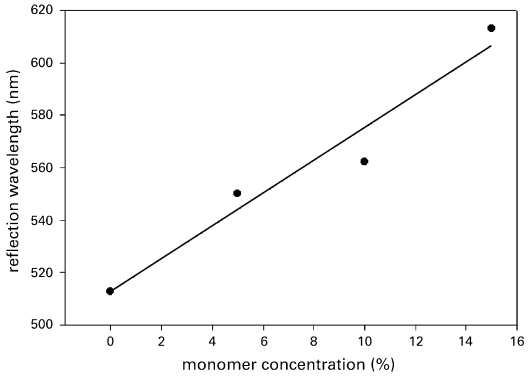


Fig. 19. Reflection wavelength vs. monomer C6H concentration.

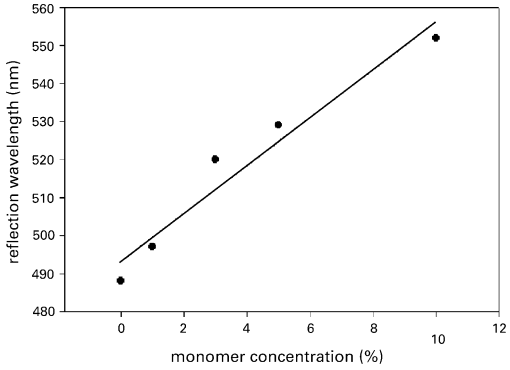


Fig. 20. Reflection wavelength vs. monomer C6M concentration.

- Concerning the monomer C*6H, after irradiation, there is a shift of the peak towards the higher wavelengths that is to say towards the peak corresponding to the mixture without monomer (Fig. 13): it suggests that the interactions between the polymer network and the liquid crystal molecules are weak. The texture is not homogeneous (Picture 6) and confirms that conclusion. Around the oily-streaks (where the polymer grows preferentially), there are red areas; that color corresponds to the reflection wavelength of the liquid crystal mixture without monomer. It suggests that the interactions between the network and the liquid crystal molecules are not strong enough to block the pitch. The rather weak broadening that happens seems to be due to the existence of two populations of liquid crystal molecules with different pitches, ones are close to the polymer network and others farther. The fact that the threshold voltage does not depend on the monomer concentration (Fig. 12) seems to confirm that the interactions network-liquid crystal molecules are rather weak.

The mechanism of the broadening above mentioned does not therefore seem to apply to all cases.

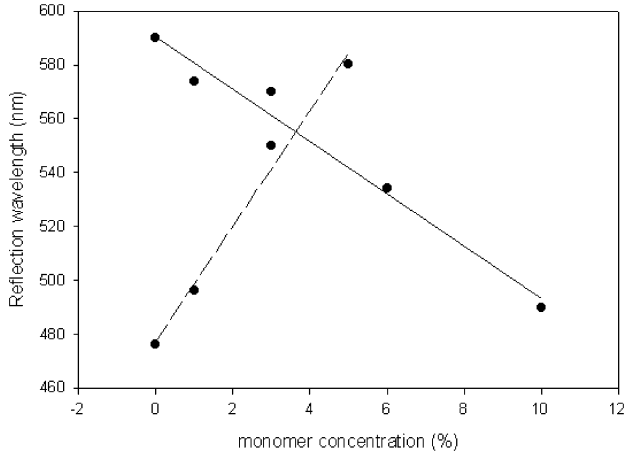


Fig. 21. Reflection wavelength vs. monomer C*6H concentration (solid curve: first experiments; dash curve: second experiments).

Nevertheless, we have to underline that the broadening is not very important probably because the dependence of the reflection wavelength with the monomer concentration is not very important.

Second case. Use of a chiral (C*6H) monomer and chiral dopants with a specific rotation of opposite sign.

In that case, the dependence of the reflection wavelength with the monomer concentration before irradiation is much more important (Fig. 21 — dash curve).

Almost no broadening happens: after irradiation, there is a shift of the pitch towards the smaller wavelengths that is to say towards the peak corresponding to the mixture without monomer (Fig. 17). These observations are relevant with the previous ones (no dependence at all of the threshold voltage with the monomer concentration — Fig. 16). We can suppose that the interactions between the polymer network and the liquid crystal molecules are not strong enough to block the pitch and to consequently lead to a significant pitch gradient according to the mechanism already mentioned.

The broadening of the reflection band was more important with the dopants having a specific rotation with the same sign as the monomer (Fig. 15) which can be attributed to the existence of a less homogeneous texture of the gel (Picture 6).

We can therefore conclude that there are two conditions to obtain an important broadening of the reflection band: an important dependence of the reflection wavelength with the monomer concentration and rather strong interactions between the polymer network and the liquid crystal molecules in order to block the pitch.

5. Conclusions

Parameters such as the interactions between the polymer network and the liquid crystal molecules appear to have a big influence on the electrooptical behavior, i.e. the dependence of the threshold voltage with the monomer concentration and the quality of the return of the liquid crystal molecules to the planar state after switching. A slight modification of the structure of the monomer leads to important changes of the electrooptical behavior of the samples. The monomers have therefore to be carefully designed.

A broadening of the reflection band can be obtained but again the structure of the monomer is important. A chiral monomer is more suitable to obtain a broadening of the reflection band because it allows having an important dependence of the pitch of the liquid crystal with the monomer concentration. But it appears that there is another condition to obtain a broadening: the interactions between the polymer network and the liquid crystal molecules have to be strong enough to block the pitch in order to create a pitch gradient. The monomer's structure is therefore important.

Acknowledgements

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References

[1] Doane JW, Yang DK, Yaniv Z. Japan Display '92, 1992. p. 73.
[2] Yang DK, Doane JW. SID' 92 DIG?, 1992. p. 759.
[3] Yang DK, Chien LC, Doane JW. Conference Record of International Display Research Conference, SID, 1991. p. 49.
[4] Hikmet RAM, Poels HLP. Liq Cryst 2000;27(1):17.
[5] Broer DJ, Gossink RG, Hikmet RAM. Makromol Chem 1990; 183:45.
[6] Broer DJ, Mol GN, Challa G. Makromol Chem 1991;192:59.
[7] Lub J, Broer DJ, Hikmet RAM, Nireop KGJ. Liq Cryst 1995;18(2):319.
[8] Broer DJ, Lub J, Mol GN. Macromolecules 1993;26:1244.
[9] Hikmet RAM, Lub J, Higgins JA. Polymer 1993;34(8):1736.
[10] Andersson H, Gedde UW, Hult A. Mol Cryst Liq Cryst 1994;243:313.
[11] Leroux N, Fritz WJ, Doane JW, Chien LC. Mol Cryst Liq Cryst 1995;261:465.
[12] Broer DJ, Mol GN, Van Haaren JAMM, Lub J. Adv Mater 1999;11(7):573.
[13] Broer DJ, Lub J, Van Nostrum CF, Wienk MM. Recent Res Dev Polym Sci 1998;2:313.
[14] Hikmet RAM, Kemperman H. Nature 1998;392:476.
[15] Hikmet RAM, Kemperman H. Liq Cryst 1999;26(11):1645.
[16] Guillard H, Sixou P. Liq Cryst 2001;28(6):933.
[17] Broer DJ, Boven J, Mol GN. Makromol Chem 1989;190:2255.
[18] Hikmet RAM, Poels HLP. Liq Cryst 2000;27(1):17.
[19] Rajaram CV, Hudson SD, Chien LC. Chem Mater 1995;7:2300.
[20] Dierking I, Kosbar LL, Lowe AC, Held GA. Liq Cryst 1998;24(3):397.