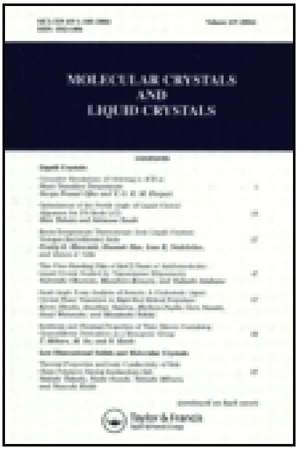


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Light Induced Colour Change of Cholesteric Copolymers**

Martin Brehmer [a] [b], Johan Lub [a] & Peter Van Dewitte [a]

[a] Philips Research Laboratories, Prof. Holstlaan 4, 5656, AA Eindhoven, The Netherlands

[b] University of Wuppertal, Dept. of Chemistry and Institute of Materials Science

Version of record first published: 04 Oct 2006

To cite this article: Martin Brehmer, Johan Lub & Peter Van Dewitte (1999): Light Induced Colour Change of Cholesteric Copolymers**, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 331:1, 333-340

To link to this article: http://dx.doi.org/10.1080/10587259908047531

Mol. Cryst. Liq. Cryst., 1999, Vol. 331, pp. 333-340
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Light Induced Colour Change of Cholesteric Copolymers**

MARTIN BREHMER*, JOHAN LUB and PETER VAN DEWITTE

Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven,
The Netherlands

We demonstrate an easy method for the colour patterning of cholesteric liquid crystalline copolymers based on photoisomerization of a chiral comonomer. The UV dose determines the reflection colour. If two chiral compounds with opposite twist sense are copolymerized, an inversion of helical twisting sense can be observed during photoisomerization.

Keywords: Cholesteric LC Polymers; Pitch Control; Photoisomerization

INTRODUCTION

Cholesteric Liquid Crystals draw attention because of their ability to reflect visible light. This effect is of interest for several applications. Amongst them are reflective polarizers, [1] reflective displays and smart reflectors.[2,3]

It would be interesting to have cholesteric samples that reflect different colours in different areas independently of the temperature. One approach to achieve this effect is to make use of the thermochromic effect of cholesteric liquid crystals. By crosslinking parts of the sample at different temperatures or by quenching locally heated samples to temperatures below the glass transition

---

* Present address: University of Wuppertal, Dept. of Chemistry and Institute of Materials Science.

temperature, different colours can be achieved and stabilized.[4-6] Disadvantages of these methods are the laborious process and the difficulty to produce detailed structures.

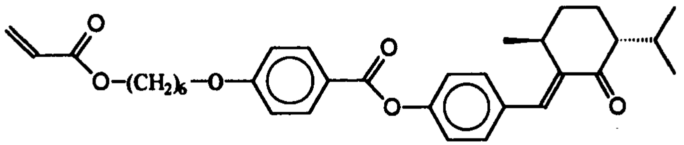
A promising method to obtain colour changes is to change the structure of the chiral dopant locally. Recently, the light induced racemisation of low molar mass binaphthyl compounds was used for colour structuring: In the enantiomeric pure state the binaphthyl compounds possess high twisting powers while the fully racemized compounds do not have any helical twisting power.[7]

An attractive alternative is to use the UV induced isomerization of double bonds. For most photoisomerizable chiral compounds the E and the Z isomers have different helical twisting powers. Recently an inversion of the handedness of a chiral nematic helix was reported.[8] Menthone derivatives give a large shift of the helical pitch upon E-Z isomerization.[9,10] Furthermore, their high twisting power is attractive.

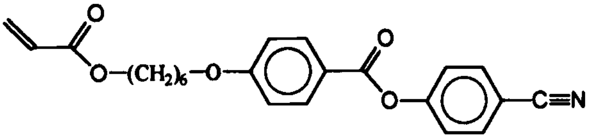
Our objective was to investigate the possibility to use co-polymers containing a menthone derivative I and solutions of those co-polymers in low molar mass LC-mixtures for locally changing the reflection colour. The achiral monomer II is known to give nematic homopolymers.[11] Furthermore, monomer I was copolymerized with chiral monomer III, which gives a helix of opposite handedness. With the resulting copolymers it should be possible to observe an inversion of the helix during irradiation.

RESULTS AND DISCUSSION

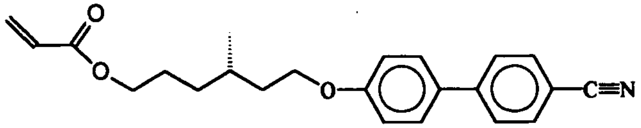
Polymers (IV-VII) with different amounts of menthone derivative I and the achiral monomer II were prepared by radical polymerisation (Table 1).[10] Polymers with an M_n of 6.000-7.000 g/mol were obtained. The glass



I



II



III

transition temperatures gradually rised with increasing contents of the menthone derivative from 20° to 40°. The clearing point of the polymers decreased with an increasing amount of the menthone derivative. This is due to the non mesogenic properties of the chiral unit. Polymers **VII** and **VIII** are isotropic out of the same reason.

The helical twisting power β_p (Table 1) of the polymers V-VII at room temperature is proportional to the amount of chiral monomer I. The value for a single chiral group β_m is determined by the induced pitch p and the weight fraction x of the chiral molecule via the equation $\beta = 1 / px$. In diluted solutions of the polymers in E7 there is no visible effect of the polymer structure on the HTP of the chiral unit. Irradiation at 365 nm leads to a conformational change from E to Z.[10,12] As is clear from Table 1, this is accompanied by a large decrease in the helical twisting power β.

TABLE 1 Properties of copolymers IV - VII

	x1)	phase transitions2)	$\beta_p/\mu m^{-1}$ 3) (polymer chain)	β_m/mm^{-1} 3) (chiral unit)	$\beta_i/\mu m^{-1}$ 3) (chiral unit irradiated4))
IV	0	g 23 N 113 I	-	-	-
V	0.15	g 18 N* 102 I	2.5	15.3	2.9
VI	0.33	g 18 N* 89 I	6.6	16.7	2.8
VII	0.50	g 35 I	10.5	18.1	2.4
VIII	1	g 40 I	14.9	14.9	1.4

1) molar ratio of menthone derivative, 2) determined by DSC, g = glassy state, N = nematic, N* = cholesteric, I = isotropic, 3) helical twisting power calculated from pitch measured in wedge cells (0.02-0.1 %wt polymer in E7), 4) irradiated at 365 nm (60 min.).

Due to the large twisting power of the menthone derivative I, copolymer V, containing only 15% of this derivative, reflects UV light. Upon irradiation with UV light (λ= 365 nm) at room temperature, the reflected colour of the sample changed very slowly. A complete reorientation from a blue to an infrared reflecting helix took 5 days. This slow effect can be explained by the high viscosity of the polymers at room temperature, which hinders a fast reorientation of the mesogens. When the sample was heated to 60°C, the colour changed within 15 minutes. The reflection colour of the sample was dependent on the dose of UV light and could be changed from ultraviolet to infrared. The shift of the reflection colour was followed with a UV-vis spectrometer (Fig. 1a). A decrease of transmission corresponds with the reflection of left handed circularly polarized light. The shift of the reflection wavelength with UV exposure is clearly visible. A gradual broadening of the reflection band with UV exposure can be observed. The samples became more light scattering at these exposure times. Both effects indicate a loss of orientation.

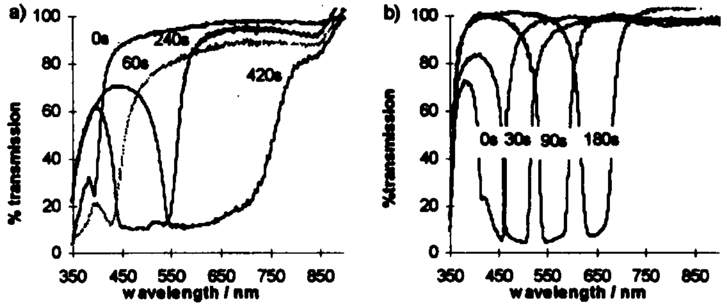


FIGURE 1a: Transmission spectra as a function of UV exposure time of samples prepared from polymer V. b: Transmission spectra as a function of UV exposure of samples prepared from a 50% (w/w) solution of polymer VI in E7.

The solution of copolymer VI in the nematic host E7 (50% w/w) showed a similar behaviour upon irradiation (Fig. 1b). The colours could be shifted over the whole visible spectrum. Due to the low viscosity of this mixture, the pitch changed instantaneously at room temperature. There was no visible change of orientation. The reflected colours remained iridescent. Examples of structured samples of the mixture copolymer VI / E7 can be seen in Fig. 2.

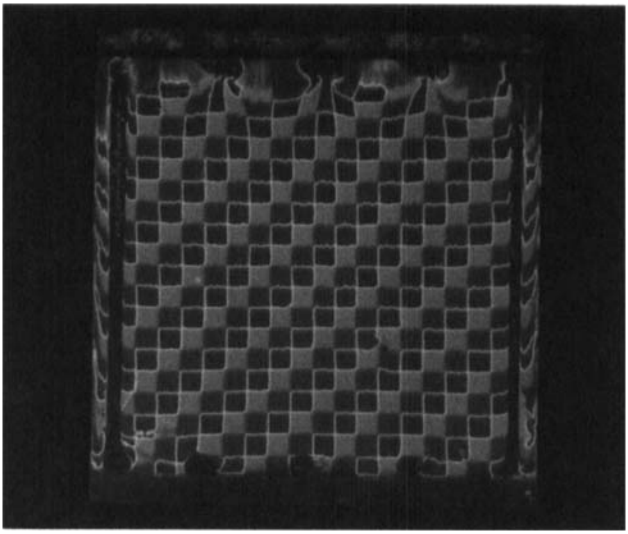


FIGURE 2: Photograph of a cell filled with mixture of polymer V and E7 (50%wt.) irradiated through a greyscale mask (size of the cell is 3 x 3 cm). (See Color Plate II at the back of this issue)

The pitch of the helix can be compensated or even reversed by a second compound with opposite twisting direction. For that purpose monomer **I** was copolymerized with compound **III** in different ratios. (Table2)

The homopolymer of **III** (**IX**) shows a 5 times smaller helical twisting power than homopolymer **VIII**. In Polymer **X** the pitch is partly compensated. It reflects blue light. The reflection is shifted into the UV region after irradiation. Polymer **XI** has a larger pitch.The reflection colour can now be shifted from red to blue.

TABLE 2

	x(I)	phasetransitions	β/mm^{-1} 3) (polymer chain)	β/mm^{-1} 3) (polymer chain irradiated4))
IX	0	g 12 N* 49 I	4.8	
X	0.07	g 20 N* 61 I	3.0	3.9
XI	0.13	g 22 N* 65 I	1.2	2.8
XII	0.22	g 24 N* 67 I	1.7	2.o

notes: see TABLE 1

Polymer XII with the highest content of menthenone derivative I showed a green reflecting cholesteric phase. The handedness is opposite to that of polymers IX-XI. After irradiation with UV light the colour vanished. Microscopic observation showed, that the material became nematic after 2 min. Further irradiation led to the appearence of a blue reflection. Before irradiation compound I determined the pitch, and after irradiation compound III. Thus we developed a process in which layers can be patterned with different colours and different twisting senses.

EXPERIMENTAL PART

Polymers IV - VII were synthesized according to ref. [10]. E7 was obtained from Merck (Poole, GB).Samples for irradiation experiments were sandwiched between two polyimide (AL1051, JSR, Japan) coated, antiparallel rubbed, glass plates. The HTP was determined using the Grandjean Cano method, by filling a 1% (wt) solution of the polymers into wedge shaped cells

(EHC, Japan (tanα=0.0083). The irradiation in the near UV region was done with a Philips SP 500 W Mercury Lamp with an intensity of 5.6 mWcm^{-2} at λ=365 nm..

ACKGNOWLEDGEMENT

Martin Brehmer wishes to thank the E.C. for granting a Marie Curie Fellowship.

References

[1] D. J. Broer, J. Lub, G. N. Mol, *Nature,* **1995**, *378*, 467–469.

[2] D.-K. Yang, J. L. West, L.-C. Chien, J. W. Doane, *J. Appl. Phys.*, **1994**, *76*, 1331.

[3] R. A. M. Hikmet, H. Kemperman, *Nature,* **1998**, *392*, 476.

[4] G. Maxein, H. Keller, B. M. Novak, R. Zentel, *Adv. Mater.* **1998**, *3*, 341.

[5] N. Tamaoki, A. Parfenov, A. Masaki, H. Matsuda *Adv. Mater.* **1997**, *9*, 1102.

[6] P. Palffy-Muhoray, *Nature* **1998**, *391*, 745.

[7] F. Vicentini, J. Cho, L.-C. Chien, *Liq. Cryst.* **1998**, *24*, 483.

[8] B. I. Feringa, N. P. M. Huck, A. M. Schoevars, *Adv. Mater.* **1996**, *8*, 68.

[9] S. N. Yarmolenko, L. A. Kutulya, V. V. Vashenko, L. V. Chepeleva, *Liq. Cryst.* **1994**, *16*, 877.

[10] P. v. d. Witte, J. Lub, J. C. Galan, *Liq. Cryst.* **1998**, *24*, 819.

[11] M. Portugall, H. Ringsdorf, R. Zentel, Makromol. Chem. **1982**, *183*.

[12] L. A. Kutulya, S. N. Yarmolenko, V. V. Vashchenko, L. V. Chepeleva, L. D. Patsenker, O. A. Ponomarev, *Russ. J. Phys. Chem. (eng. Trans.)*, **1995**, *69*, 80.