Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Cholesteric Networks Containing Free Molecules

R. A. M. Hikmet [a] & B. H. Zwerver [a]
[a] Philips Research Laboratories, P. O. Box 80.000, 5600JA, Eindhoven, The Netherlands

Version of record first published: 04 Oct 2006.

To cite this article: R. A. M. Hikmet & B. H. Zwerver (1991): Cholesteric Networks Containing Free Molecules, Molecular Crystals and Liquid Crystals, 200:1, 197-204

To link to this article: http://dx.doi.org/10.1080/00268949108044241

Mol. Cryst. Liq. Cryst., 1991, Vol. 200, pp. 197–204
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Cholesteric Networks Containing Free Molecules

R. A. M. HIKMET and B. H. ZWERVER

Philips Research Laboratories, P.O. Box 80.000, 5600JA Eindhoven, The Netherlands

(Received September 26, 1990; in final form December 28, 1990)

Two-component liquid crystalline (LC) mixtures containing LC diacrylates and chiral molecules with no reactive groups were made. Upon photopolymerisation of the mixtures, cholesteric networks containing up to 28% w/w chiral molecules which were not chemically attached to the networks were created. Temperature dependence of the optical properties of the polymerised systems was found to be determined to a large extent by the network molecules which also dominated the behaviour of the chiral molecules which were not chemically attached to the network. The cholesteric networks were stable and even when heated up to elevated temperatures, they preserved their helicoidal structure.

Keywords: cholesteric, networks, photopolymerisation, chiral diacrylate

INTRODUCTION

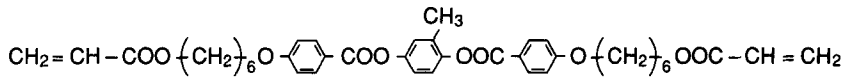
Recently the use of low molar mass liquid crystalline (LC) diacrylates in the production of anisotropic gels and plasticised networks was demonstrated.[1] These systems were produced by *in-situ* photopolymerisation of a LC mixture containing LC diacrylates[2,3] and LC molecules without reactive groups. In this way anisotropic networks containing molecules which are not chemically attached to the network were made. Orientation of the molecules could be obtained by a surface treatment, in electric and magnetic fields.[4] The systems obtained in this way possessed anisotropic electrical[5] and optical properties.[1] This new kind of material can have a wide range of applications, including optical components, and a new display principle is possible based on their anisotropic electrical and optical properties.[5]

The properties of cholesteric LC polymers[6,7] and polymeric networks with a helicoidal structure[8] have already been described. Here the production and the optical properties of a cholesteric system composed of a network and a large number of free molecules are described. Furthermore, the influence of the presence of the anisotropic network on the behaviour of the isotropic chiral molecules will be discussed.

EXPERIMENTAL

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

C6M



CB15

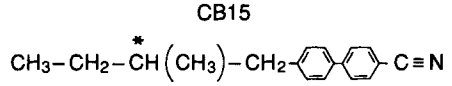


FIGURE 1 Molecular structure of the monomers.

diacrylate C6M has been described before 2. CB15 was purchased from Merck. The monomers were provided with a 2% w/w photoinitiator α,α-dimethoxydeoxybenzoin (Irgacure 651 Ciba Geigy). Photopolymerisation of the mixtures was initiated using a high pressure Hg lamp (intensity 10 $mWcm^{-2}$ at 366 nm). Optical measurements were carried out using a polarizing microscope. Sample temperatures were regulated using a Mettler FP5 hot stage. An Abbé refractometer which could be heated up to 140°C was used for the refractive index measurements. UV-VIS spectrometry was carried out using a Philips PU 8740 UV-VIS spectrometer. Planar-oriented cholesteric samples were obtained in glass cells provided with uniaxially rubbed polyimide layers on their inner surfaces and spaced with 7 μm fibres.

RESULTS AND DISCUSSION

Monomeric Mixtures

Cholesteric-isotropic transition temperatures T_c for the mixtures of C6M and CB15 are shown in Figure 2. This behaviour is typical of mixtures of two nematics,[9] showing that T_c decreases with increasing concentration of CB15, which shows a monotropic cholesteric phase.

In Figure 3, refractive indices for the mixture containing 28% w/w CB15 are shown as a function of temperature. Cholesteric ordinary ($n_{c,o}$) and extraordinary ($n_{c,e}$) refractive indices of the material were measured using the refractometer. These indices are related[6] to the refractive indices (n_o, n_e) of a uniaxially oriented nematic phase as

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

$$n_e = [2n_{c,o}^2 - n_o^2]^{1/2} \tag{2}$$

In Figure 3, it can be seen that for a given material, n_o remains almost unchanged as a function of temperature, while n_e decreases rapidly with increasing temperature, as also commonly observed for LC systems.[9] Refractive indices also depend on the composition of the mixtures and increase with increasing CB15 content of

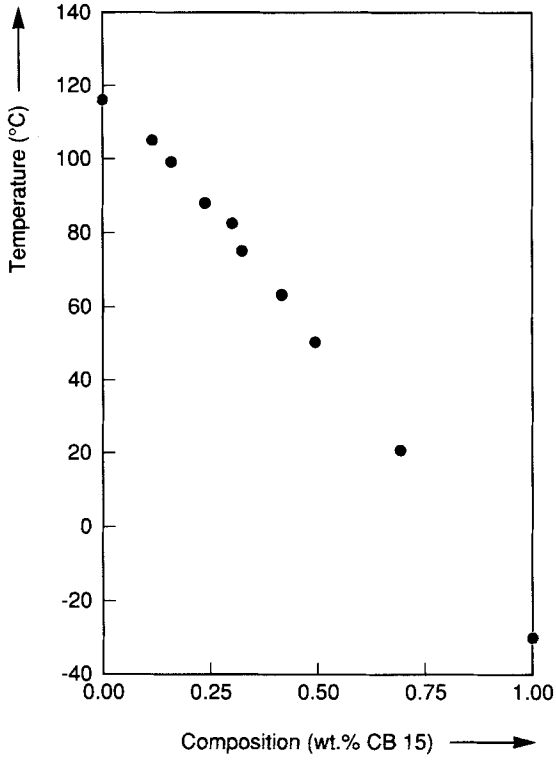


FIGURE 2 Phase diagram of C6M and CB15.

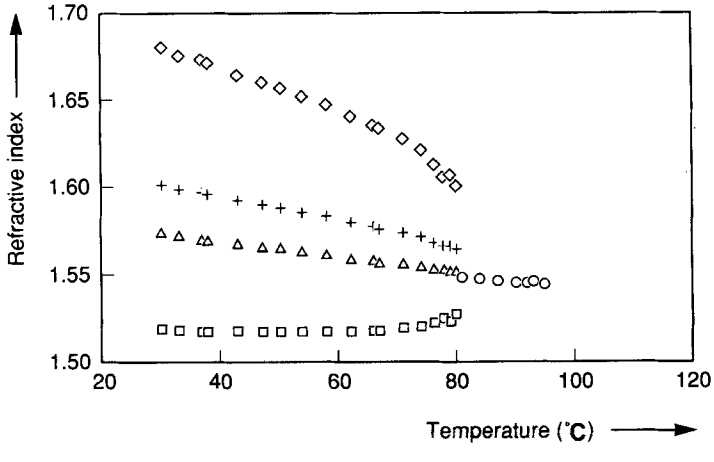


FIGURE 3 Refractive indices of the mixture containing 28% w/w CB15. □ = n_o, ◇ = n_e, + = $n_{c,o}$, △ = $\bar{n}$, ○ = n_{iso}.

the system at a given reduced temperature. The order parameter S for the mixtures was estimated from the refractive indices using[10] the equation below:

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

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the molecular polarizabilities in the direction parallel and perpendicular to the optical axis 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 was estimated from Haller plots,[11] which predict a linear relationship between $S(\alpha_{\parallel} - \alpha_{\perp})/\bar{\alpha}$ and $(1 - T/T_c)$. These values were then used to plot Figure 4, in which the order parameter for 28% w/w CB15 mixture is plotted as a function of the reduced temperature. This is also a typical behaviour observed for LC molecules where the order parameter decreases with increasing temperature before discontinuously becoming zero at the T_c.

Cholesteric phases have the property of selectively reflecting circularly polarized light. The wavelength of maximum reflection (λ_m) is related to the pitch by

$$\lambda_m = pn_{c,o} \tag{4}$$

The effect of the temperature and CB15 concentration on λ_m is shown in Figure 5. It can be seen that λ_m is highly dependent on the temperature and the chiral CB15 content of the system. Therefore, by adjusting these parameters any desired value for λ_m can be obtained.

Polymerised Mixtures

Cholesteric networks containing free molecules were formed by photopolymerisation of the mixtures. As CB15 molecules are quite stable to UV radiation, no

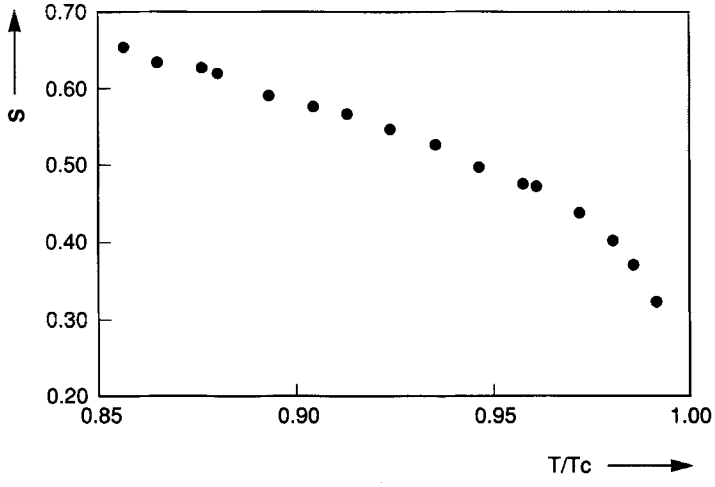


FIGURE 4 Order parameter as a function of reduced temperature for the mixture containing 28% w/w CB15.

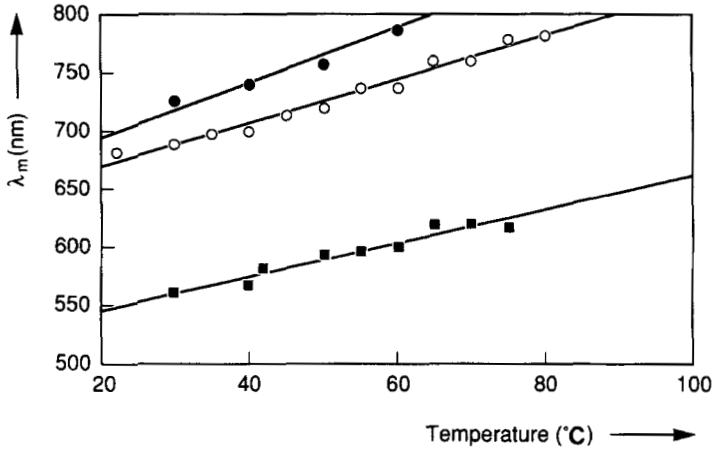


FIGURE 5 Wavelength of maximum reflection at normal incidence as a function of temperature for mixtures containing various amounts of CB15. ● = 20 w/w, ○ = 23% w/w, ■ = 28% w/w.

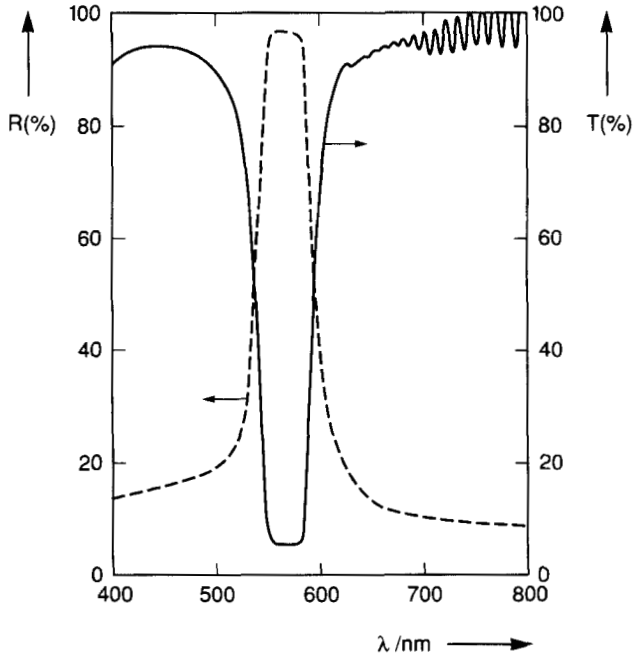


FIGURE 6 Reflectance and transmittance measured as a function of wavelength for a sample containing 28% w/w CB15 polymerized at 30°C.

degradation or chemical bonding of these molecules to the network formed by C6M was observed. Further details regarding the polymerisation of diacrylates in the presence of molecules without reactive groups can be found in Reference (1). In Figure 6, reflectance and transmittance spectra measured at room temperature using right-circular polarized light are shown for a mixture containing 28% w/w

CB15, which was polymerised at 30°C. The right-handed polarized light is totally reflected, whereas the left-handed polarized light is transmitted. The position of λ_m for polymerised samples in cells showed only a little temperature dependence as opposed to the behaviour observed for unpolymerised samples. The effect of polymerisation temperature is shown in Figure 7, where the refractive indices are plotted as a function of temperature for the mixture containing 28% w/w CB15, which was polymerised at various temperatures. In this figure it can clearly be seen that for a given sample, both n_e and n_o decrease with increasing temperature. When the refractive indices of the samples polymerised at various temperatures are compared at a given temperature, it is seen that n_e decreases, whereas n_o increases with increasing polymerisation temperature. When the birefringence $(n_e - n_o)$ of the layers in the cholesteric structure is compared at the temperature of polymerisation before and after polymerisation, at all temperatures, the birefringence decreases upon polymerisation. These effects are related to changes in the density and the order parameter. In order to estimate the order parameter of the polymerised samples, their refractive indices were used in Equation 1, together with the polarizability term obtained for the unpolymerized sample. This method gives a good estimation for the average order within the system as shown for a uniaxially system.[1] In Figure 8, the order parameter is plotted as a function of temperature for the sample polymerised at various temperatures. Here it can be seen that the order parameter of the polymerised samples is influenced to a much lesser extent by temperature and decreases slightly with increasing temperature. The order parameters of the polymerised samples also depend to a large extent on the polymerisation temperature and decrease with increasing polymerisation temperature. When the order parameters of the samples are compared, before and after polymerisation, at the temperature of polymerisation, it can be seen that in all cases, upon polymerisation, the order parameter shows a small decrease. The fact that

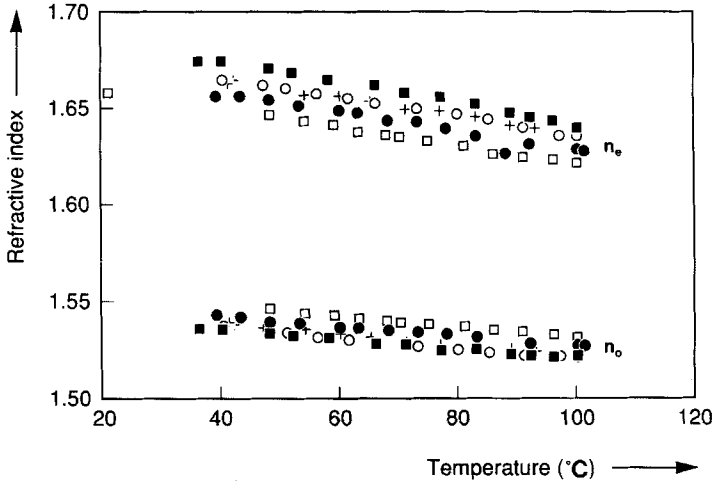


FIGURE 7 Refractive indices of the mixture containing 28% w/w CB15 after polymerisation at various temperatures. ■ = 30°C, ○ = 40°C, + = 50°C, ● = 60°C, □ = 70°C.

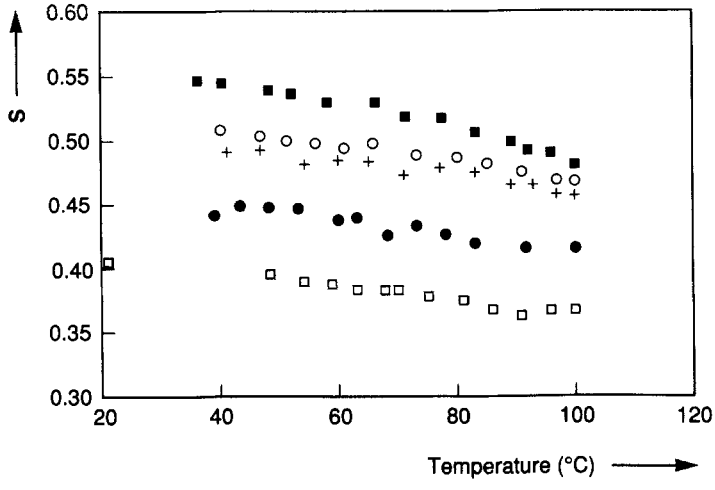


FIGURE 8 Order parameter as a function of temperature for the mixture containing 28% w/w CB15 after polymerisation at various temperatures. ■ = 30°C, ○ = 40°C, + = 50°C, ● = 60°C, □ = 70°C.

TABLE I

Optical properties of the mixture containing 28% w/w CB15 before and after polymerisation.

T °C	p(mon) nm	p(pol) nm	λ_m(pol) nm	$\Delta\lambda$(pol) nm
30	349	337	543	63
40	357	343	551	60
50	374	362	583	58
60	380	372	598	56
70	394	378	606	48

28% w/w of the molecules within the system contain no reactive groups indicates that these molecules to a large extent remain oriented within the cholesteric network. Indeed, infrared measurements[1] on the uniaxially oriented samples showed that the LC molecules without reactive groups remain highly oriented at temperatures far above their T_c.

Furthermore, we have estimated the pitch using Equation 4. In Table I, the pitch is plotted as a function of temperature for unpolymerised samples and for polymerised samples. The temperatures in this table also correspond to the polymerisation temperatures. Here it can be seen that there is a small change in the pitch which is in the order of 3%. This value is of the same order as the polymerisation shrinkage obtained for oriented networks in the direction perpendicular to the molecular orientation.[11] The bandwidth $\Delta\lambda$ of the reflected light was also estimated. Table I shows that with increasing polymerisation temperature, this also decreases, complying well with the equation[9] below

$$\Delta\lambda = p(n_e - n_o) \tag{5}$$

Following polymerisation, when samples were cooled down to room temperature,

$\Delta\lambda$ remained almost unchanged. In this way, therefore, it is possible to control the λ_m and $\Delta\lambda$ by adjusting the dopant concentration and the temperature of polymerisation, making it possible to manufacture optical components with the desired properties.

CONCLUSIONS

It has been shown that cholesteric networks containing chiral molecules which are not chemically attached to the network can be made. As all the compositions of the system did not cause an appreciable light scattering, they looked very clear. In the systems, the behaviour of the chiral molecules was found to be dominated by the network. The chiral molecules remain oriented in the cholesteric network upon polymerisation at temperatures above the T_c of the chiral molecules. Upon polymerisation, the birefringence of the cholesteric layers and the pitch decreased slightly. Optical properties of the cholesteric systems such as $\Delta\lambda$ and λ_m, became permanently fixed upon polymerisation and showed only a slight temperature dependence. In this way it is therefore possible to make optical components by choosing a cholesteric system and fixing its optical properties permanently.

References

1. R. A. M. Hikmet, accepted for publication in *Liquid Crystals.*
2. D. J. Broer, J. Boven, G. N. Mol and G. Challa, *Makromol. Chem.*, **190**, 2255 (1989).
3. D. J. Broer, R. A. M. Hikmet and G. Challa, *Makromol. Chem.*, **190**, 3201 (1989).
4. E. B. Priestly, P. J. Wojtowicz and P. Sheng, *"Introduction to Liquid Crystals"*, (Pendulum Press, London), Chap 12, 1974.
5. R. A. M. Hikmet, *J. Appl. Phys.*, **68**, 4406 (1990).
6. H. Finkelmann and G. Rehage, *Makromol. Chem., Rapid Commun.*, **1**, 31 (1980).
7. H. Finkelmann, H. Benthack and G. Rehage, *J. Chim. Phys.*, **80**, 16 (1983).
8. D. J. Broer and I. Heynderickx, *Macromolecules*, **23**, 1021 (1990).
9. H. Kelker and R. Hatz, *"Handbook of Liquid Crystals"* (Verlag Chemie, Weinheim), 1980.
10. I. Haller, H. A. Huggins, H. R. Lilienthal and T. R. McGurie, *J. Phys. Chem.*, **22**, 950 (1973).
11. R. A. M. Hikmet, B. H. Zwerver and D. J. Broer, accepted for publication in *Polymer.*