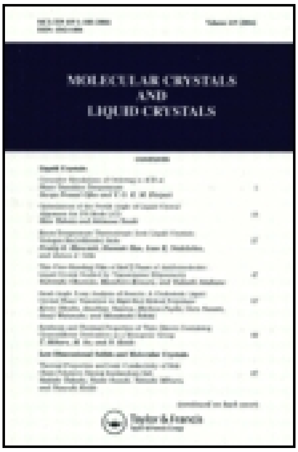

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The Use of Cholesterically-Ordered Polymer Networks in Practical Applications

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The Use of Cholesterically-Ordered Polymer Networks in Practical Applications

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Cholesteric polymer films produced by the photo-initiated polymerization of liquid-crystalline diacrylates containing a small amount of chiral dopant are demonstrated to be applicable as foils to compensate for the wavelength dependence of the transmission of supertwisted nematic liquid-crystal displays and to possess the appropriate thermal behaviour for use as a coating or encapsulation material for low-stress packaging of electronic devices.

Keywords: cholesterically-ordered network, cholesteric liquid crystals

1. INTRODUCTION

Recently, we have demonstrated that UV-photo-initiated polymerization of liquid-crystalline (LC) diacrylates yields highly-ordered densely-crosslinked polymer networks.[1–3] Subsequently, the possibility of adding a small amount of chiral material to the monomeric LC diacrylate to induce a helicoidal order in the polymeric network was described.[4] The main advantages of materials obtained via this process versus thermally or photo-chemically synthesized main-chain or side-chain cholesteric polymers is the control on the molecular arrangement by freezing-in the type of ordering in each of the monomeric phases and the temperature independence of the helicoidal structure.

This new kind of cholesteric polymer network is applicable in a large number of optical devices. In general, it may replace the low-molar-mass cholesteric LC materials in products where the temperature dependence and the electric or magnetic switching behaviour are not essential for operation. Because of their temperature independence, the cholesteric polymer networks are excellent candidates for use in passive optical components such as reflective colour filters, notch filters and devices for polarization rotation.

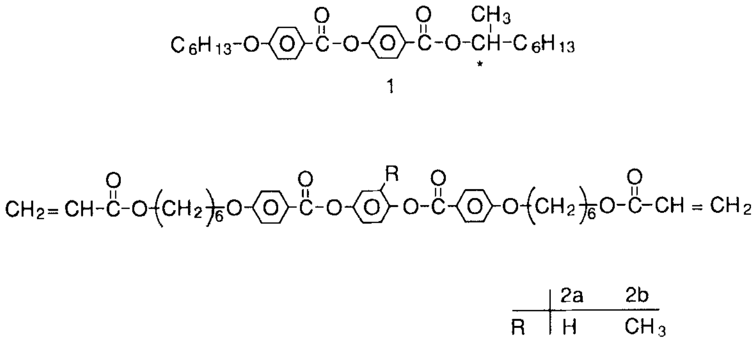
Analogous to the LC monomeric-polymeric gel systems, as studied in Reference 5, cholesteric networks containing unbound LC molecules can be produced by adding, apart from the chiral material, various amounts of non-reactive LC material to the monomeric diacrylate, which is subsequently UV-polymerized. This technique causes the cholesteric polymer network to become partly temperature dependent in a controllable way and switchable by an external electric or magnetic field by its interaction with the unbound molecules. Consequently, these systems can be used as scattering displays,[6,7] in thermometrical applications such as digital thermometers of different kinds and in thermographical analyses used as a diagnostic tool in medicine and manufacturing testing.

This paper concentrates on only two of the applications of the cholesteric polymer network described above. The first device demonstrates that the optical properties of such a cholesteric polymer film are effective in compensating for the wavelength dependence of the transmission of supertwisted nematic (STN) displays. In the second example we show that the specific thermal expansion behaviour of these materials meets the requirements for low-stress packaging of electronic components.

2. EXPERIMENTAL

The chemical structures of the materials used are shown in Scheme 1. For most of our purposes a left-handed ordering is induced in the eutectic blend **3** of the mesogenic diacrylates **2a** and **2b** (synthesized at Philips Research Labs)[1] by adding various amounts of the chiral material **1** (S811, Merck). In general, these monomeric mixtures also contain 100 ppm hydroquinone monomethyl ether as stabilizer and 1 wt% of 2,2-dimethoxy 2-phenylacetophenone as photoinitiator.

Cells consisting of two glass substrates, each coated at the inner side with the ZLI 2650 (Merck) polyimide, and rubbed with a velvet tissue in one direction, are filled with the monomeric LC material. The LC molecules near the bottom and top substrate are then oriented along these rubbing directions. By varying the angle between these directions, the total rotation angle of the mean molecular axis of the cholesteric phase can be altered. The thickness of the cell is controlled by introducing chopped glass fibres with a known diameter between the glass plates. Subsequently, the monomeric films are polymerized by a 3 min illumination of a UV short-arc mercury lamp with a power output of 0.8 W/cm^2. The temperature during UV-polymerization is controlled by a Mettler FP82 hot stage. The resulting



Scheme 1

solid polymer film can be removed from the glass substrates so that measurements can be performed on free standing films.

The transmission as a function of wavelength is recorded with a UV-VIS spectrophotometer (Philips PU 8740) equipped with a set of sheet polarizers, a depolarizer behind the lamp and one in front of the detector. The refractive indices are determined at a wavelength of 589 nm with an Abbe refractometer. The optical retardation, given by the film thickness times the birefringence, is measured for non-twisted films by means of a rotatory compensator in a polarizing microscope. Interference filters are provided in order to determine the dispersion of the retardation. Measurement of the pitch, being the distance of a rotation of the director over 2π radians, by means of the Cano-wedge method has been described earlier.[4,8] The thermal expansion behaviour is measured on samples with a thickness of about 60 μm using a Perkin Elmer TMA-7 apparatus.

3. COMPENSATION FOILS FOR STN DISPLAYS

The wavelength dependence of the transmission of STN displays,[9] in which the director of the planarly oriented LC molecules rotates from bottom to top substrate over an angle in the range from 180 to 270°, has been a problem for many years. It is known nowadays that this wavelength dependence can be compensated by constructing a double-cell configuration,[10] consisting of two identical cells with opposite twist directions positioned on top of each other such that the directors at either side of the intermediate substrate are mutually perpendicular. When no electric field is applied to the cells, this configuration appears perfectly black between a set of crossed polarizers. The system becomes bright on application of an external voltage to one of the cells. Its transmission results from the remaining birefringence of the non-addressed cell, the optical retardation of which has to be optimized in order to reduce the wavelength dependence and to appear as uncoloured white.

Since one of the two cells in the double-cell configuration does not need to be switched by an external electric field, it can be replaced by a solid polymer film, yielding a lower weight display. Uniaxially oriented polymer films, however, compensate the optical retardation of the STN display only in a limited wavelength range.[11,12] Compensation over a wider wavelength range is realized by introducing an optimized combination of two polymer films[13] or by approximating the second cell by a uniformly twisted stack of uniaxial foils.[14]

The wavelength dependence of the transmission of a STN display is completely neutralized when using a cholesteric polymer film, if this cholesteric film can be made identical to the STN cell, except with an opposite twist. We will demonstrate that our cholesteric polymer networks fulfil this condition.

3.1 Twist Angle

A first requirement of the compensation film is that its twisting direction and total twist angle ϕ_T are accurately adjustable. In the monomeric state ϕ_T is determined by the angle between the rubbing direction on the substrates of the cell, by the distance between the substrates and by the natural pitch *p* of the cholesteric phase. As illustrated in Table I, *p* is controlled by varying the amount of chiral dopant added to the monomeric LC diacrylate,[4] while the chemical structure of the chiral dopant unambiguously determines the twisting direction. It is important to note that the values of *p*, as given in Table I, are determined at 100°C, because the LC diacrylate used is only mesogenic at elevated temperatures.[1–4] The change of the natural pitch in the mesogenic temperature range of **3** with 4.63 wt% **1** is illustrated in Figure 1. It shows that *p* decreases with decreasing temperatures, a tendency which has also been observed for other low-molar-mass LC materials.

The total twist angle, adjusted for the cholesteric monomer by the parameters mentioned above, becomes fixed during UV-polymerization. The fact that ϕ_T does not change at all is demonstrated by the comparison of Figure 2a and b, showing a segment of the Cano-Grandjean disclination lines before and just after polymerization at 100°C, respectively. Figure 2c, taken at a temperature of 260°C, shows that ϕ_T of the polymer film remains constant at high temperatures.

However, this does not mean that the pitch of the cholesteric polymer also remains constant upon polymerization and as a function of temperature. Due to polymerization shrinkage[4] *p* decreases during polymerization by about 10% as can be deduced from the arrow in Figure 1 for blend **3** polymerized at 100°C. The marginal change of *p* with temperature, which is related to the thermal expansion in the direction perpendicular to the film, is also included in Figure 1 for this polymerized cholesteric network.

3.2 Optical Retardation

Crucial for the compensation of the wavelength dependence of the transmission of STN displays is the adjustment of the optical retardation of the foil to that of the display. In the monomeric state the optical retardation $d\Delta n$ is controlled by the thickness *d* of the monomeric film, determined by the use of glass fibres between the substrates, and by the birefringence Δn, which varies with temperature as illustrated in Figure 3a for blend **3**.

TABLE I

Natural pitch *p* of the cholesteric monomer consisting of various amounts of chiral dopant **1** into the diacrylate blend **3**, measured at 100°C

[**1**](*wt*%)	*p*(μm)
0.50	27.0
0.68	13.8
0.81	10.2
1.02	8.2
1.54	5.4
2.28	4.4
4.63	2.3

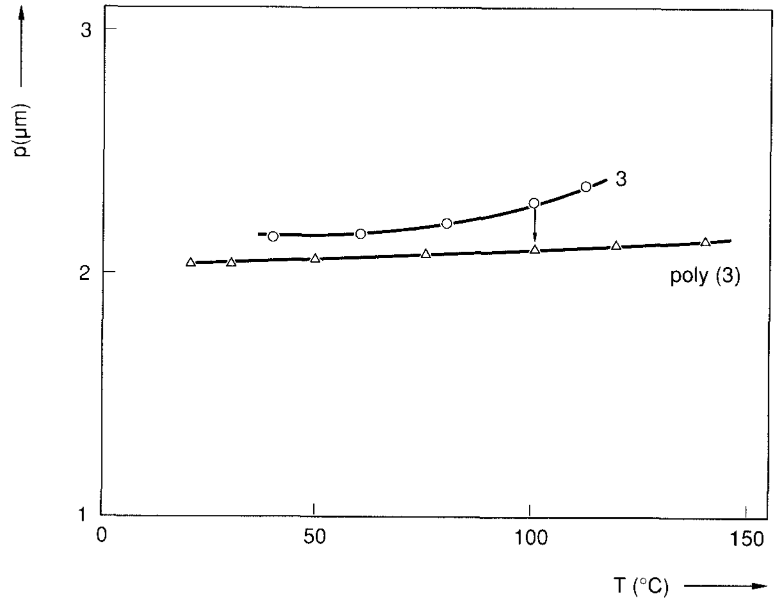


FIGURE 1 Change of the natural pitch p of blend **3** with 4.63 wt% **1** as a function of temperature in the monomeric (○) and polymeric (Δ) phase. The arrow indicates the change in p during polymerization at 100°C.

The resulting $d\Delta n$ value slightly changes during polymerization. The decrease in thickness is caused by the polymerization shrinkage in the direction perpendicular to the foil, which amounts to about 10% in the case of a film between substrates. The birefringence of a polymer film of blend **3** measured at the polymerization temperature, T_p, is presented in Figure 3b and shows a decreasing tendency with increased T_p. The change in birefringence $\delta(\Delta n)$, deduced from Figures 3a and b as the Δn after minus before polymerization, i.e. $\delta(\Delta n) = \Delta n_{after} - \Delta n_{before}$, depends on the type of LC material and on the polymerization temperature, as given in Figure 3c. For low values of T_p or high initial order the birefringence decreases slightly during polymerization, while for high values of T_p or a low initial order the opposite behaviour occurs.[2]

Finally, the cholesteric polymer network will be used as a compensation foil at room temperature (RT). Consequently, one has to take into account an additional change of the optical retardation of the polymer film over the temperature interval from polymerization to RT. It turns out that this change is negligible since the decrease in thickness due to thermal shrinkage compensates for the increase in birefringence due to an increased molecular density. From all this information it becomes possible to calculate the desired $d\Delta n$ value of the monomeric state corresponding to the $d\Delta n$ value required for the cholesteric compensation foil.

3.3 Optical Properties

The optical behaviour of a twisted birefringent medium between a set of polarizers has been described by the Gooch-and-Tarry (GT) theory,[15] yielding, for a given

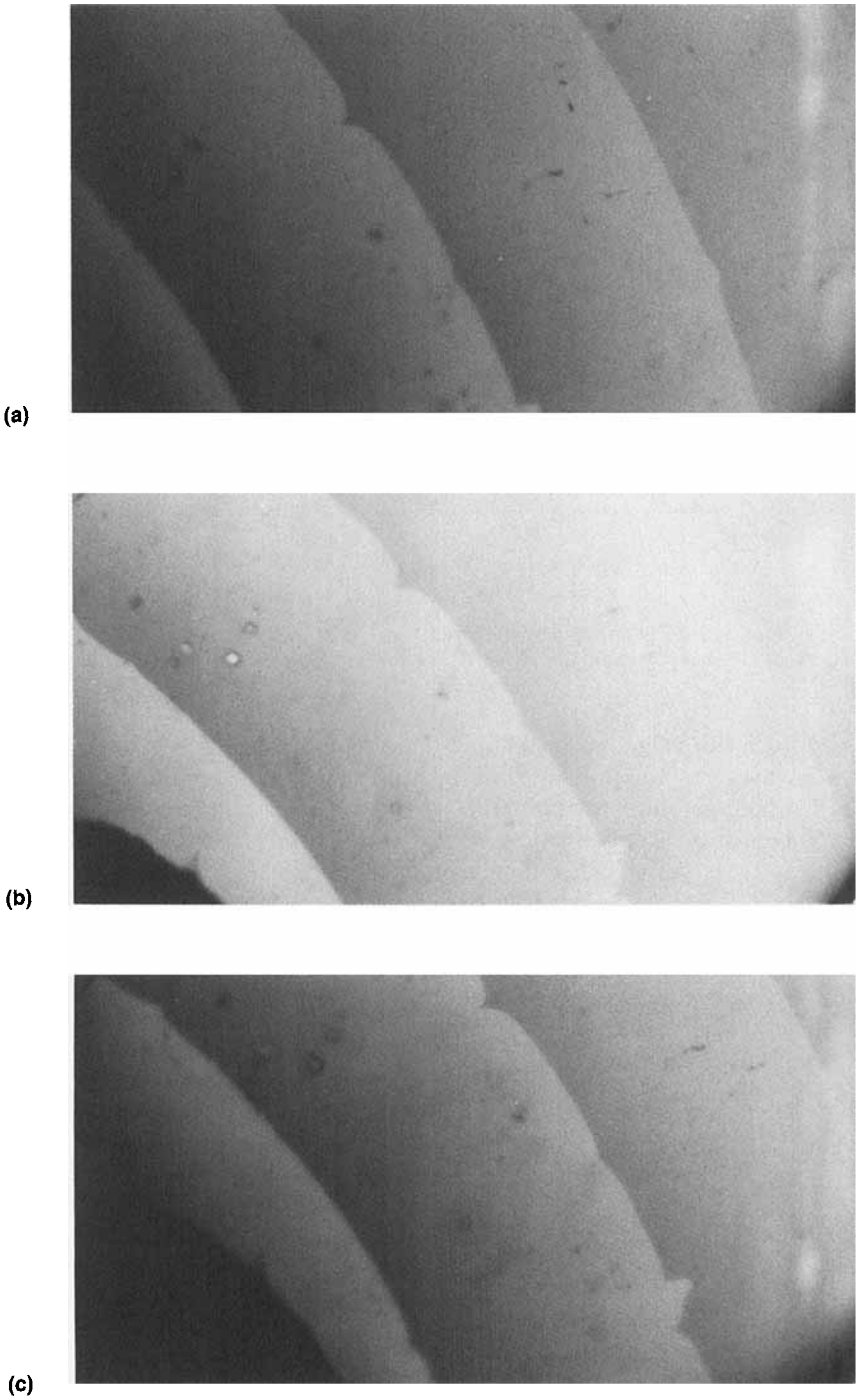


FIGURE 2 Photographs of the Cano-Grandjean disclination lines observed between a flat and a plano-convex rubbed substrate of **2a** in the monomeric state at 100°C (a), in the polymeric state at RT (b) and in the polymeric state at 260°C (c).

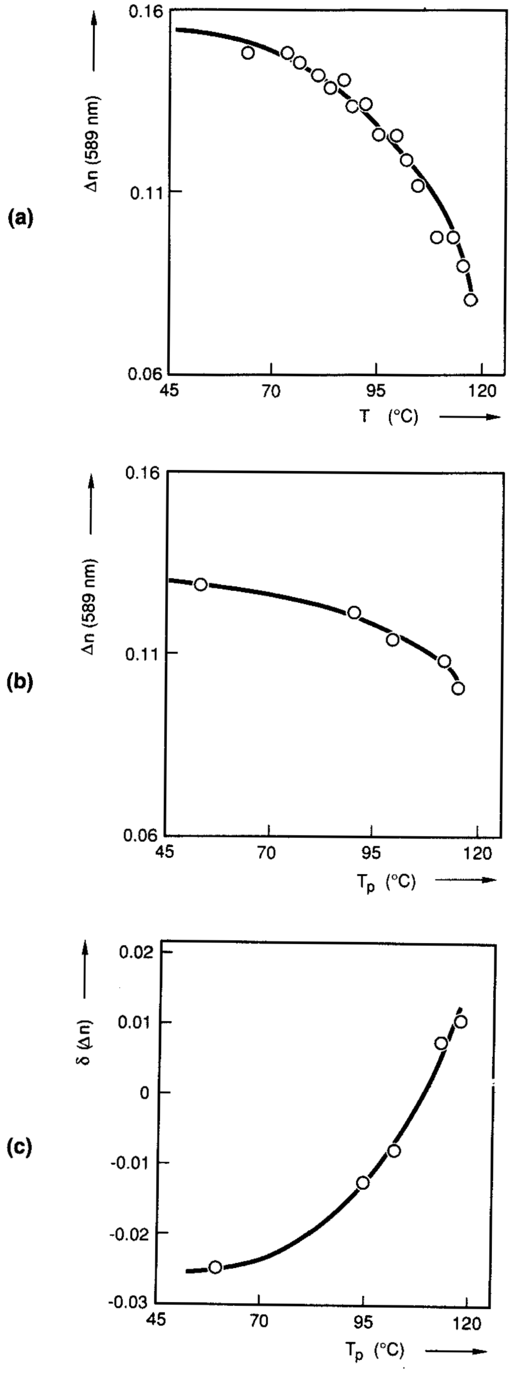


FIGURE 3 Birefringence Δn of blend **3** as a function of temperature in the monomeric phase (a), in the polymeric phase at the polymerization temperature indicated (b) and the change in birefringence $\delta(\Delta n)$, defined as Δn after minus before polymerization, i.e. $\delta(\Delta n) = \Delta n_{after} - \Delta n_{before}$, as a function of the polymerization temperature (c).

twist angle, an expression of the transmission as a function of $d\Delta n/\lambda$, in which λ is the wavelength. For a 240° twisted medium between a set of crossed polarizers with the front polarizer at 30° to the director at the front substrate, the resulting curve is shown by the solid line in Figure 4. The bullets in this figure represent the transmission measured at different wavelengths of a 240° twisted polymer film, made from blend **3** with 1.0 wt% **1** in a cell with a gap of 5.5 μm and polymerized at 60°C. The wavelengths are converted into a $d\Delta n/\lambda$ value by determining the retardation of the polymer foil, taking into account its dispersion. Apart from some deviation in the intensity, there is good agreement in the shape of both curves. This demonstrates that the optical properties of this twisted polymer foil correspond to the expected behaviour for a 240° STN LC cell.

The fact that these cholesteric polymer networks can be used as compensation foils for STN displays is further proven in Figure 5, which shows the on-state and off-state transmission of a right-handed 180° STN display provided with the corresponding left-handed 180° twisted polymer film. In the bright state the transmission is solely due to the optical retardation of the polymer foil which is 0.73 μm at 420 nm, and thus is not optimized to colourlessness in this case. In the dark state the transmission is nearly wavelength independent and has only an averaged value of 1%, which is comparable to the off-state transmission of an optimized double-cell STN display.[10]

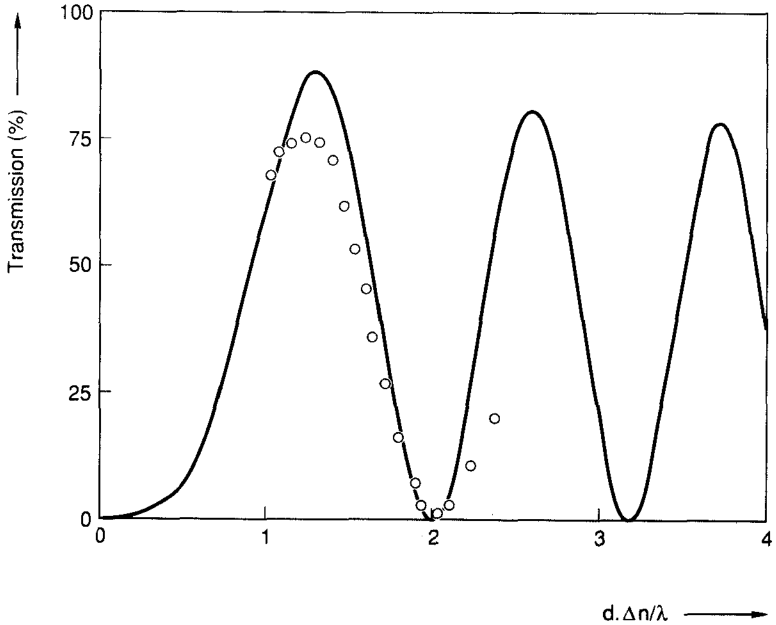


FIGURE 4 Transmission as a function of $d\Delta n/\lambda$ for a 240° twisted medium between crossed polarizers with the front polarizer at 30° to the front director as calculated according to the GT theory (solid line) and as measured at a poly(**3**) film (bullets).

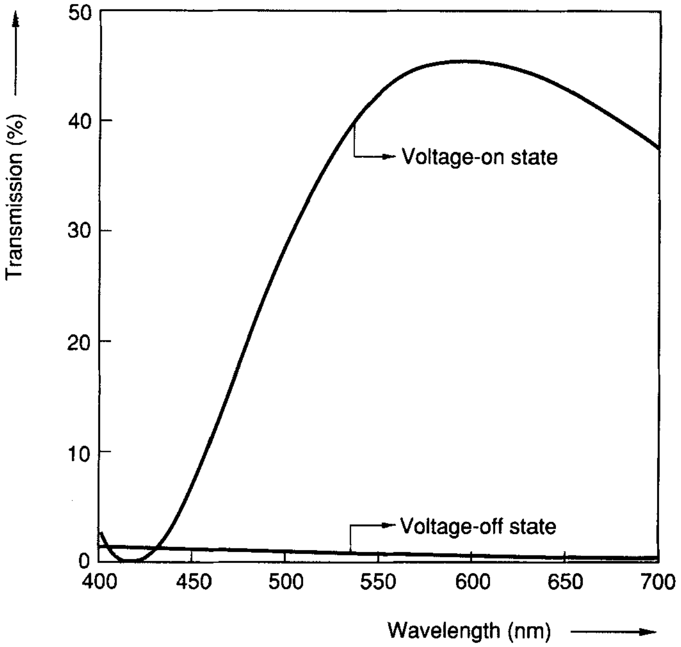


FIGURE 5 On-state and off-state transmission as a function of wavelength for a right-handed 180° STN LCD provided with a corresponding left-handed 180° twisted poly(**3**) film.

4. LOW-STRESS PACKAGING

It is well-known that the linear thermal expansion coefficient of polymers with a uniaxial ordering of the macromolecules is greatly reduced, so that along this direction a low expansion or even a thermal contraction may be observed.[16] However, for a number of applications a low thermal expansion in only one direction is insufficient. For example, in the case of coating or encapsulation of electronic devices a reduction of the thermal expansion in the two dimensions of the plane of the substrate is required in order to limit thermal stresses. This condition is fulfilled by using a helicoidally ordered polymeric network instead of a uniaxially ordered one.[16] The low thermal expansion or even contraction in the plane of the film at high temperatures is then accomplished by the loss of the high uniaxial ordering averaged over all the directions perpendicular to the normal of the foil. The linear thermal expansion measured in the three main directions of a rectangular sample of poly(**2a**) are compared in Figures 6 and 7 for the uniaxially and helicoidally ordered film, respectively. The y-axis is defined perpendicular to the film for both samples, while the x- and z-direction lie in the plane of the film. For the uniaxially oriented sample the z-axis is related to the orientation direction. It shows that the polymeric network uniaxially oriented along z exhibits at higher temperatures a thermal contraction only in this direction, whereas the helicoidally ordered polymeric network yields a small contraction in the two dimensions of the film, x and z, and a large expansion in the direction perpendicular to the film y.

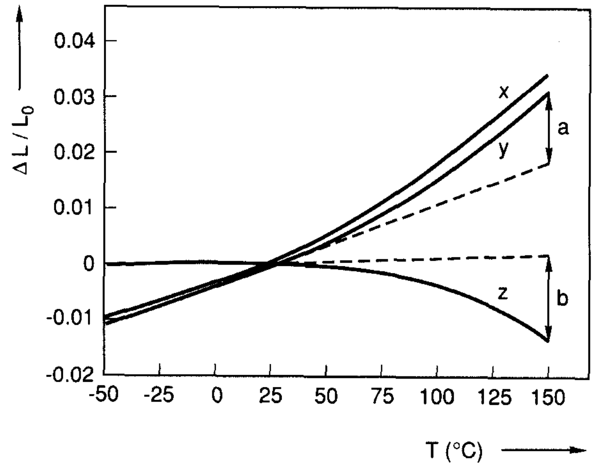


FIGURE 6 Change of length relative to the length at RT of uniaxially ordered poly(**2a**) as a function of temperature in the x, y and z direction (solid lines). The dotted lines represent the estimated contribution of the volume expansion. a = $(\Delta L/L_0)_y$ at 150°C = 0.012, b = $(\Delta L/L_0)_z$ at 150°C = -0.016.

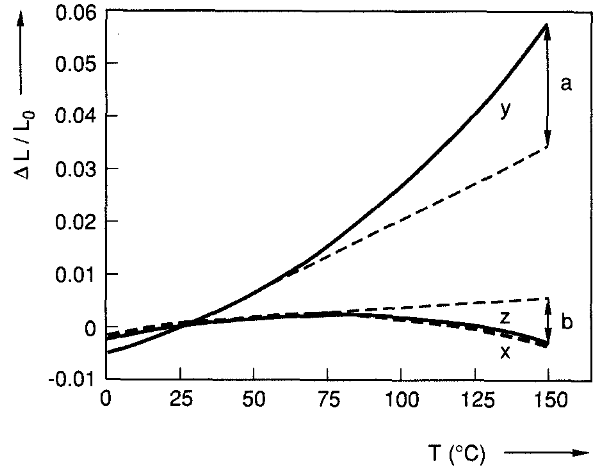


FIGURE 7 Change of length relative to the length at RT of helicoidally ordered poly(**2a**) + 2.2 wt% of **1** as a function of temperature in the x, y and z direction (solid lines). The dotted lines represent the estimated contribution of the volume expansion. a = $(\Delta L/L_0)_y$ at 150°C = 0.020, b = $(\Delta L/L_0)_z$ at 150°C = -0.007.

In this comparison it is rather surprising that the expansion along x and z for the cholesteric polymer network differs from the averaged expansion along x and z in the uniaxial polymer network. Moreover, one would expect that the linear expansion in the y-direction is equal for both the uniaxially and the helicoidally ordered polymeric films. Figures 6 and 7, however, clearly illustrate that the larger expansion in the y-direction for the cholesteric film compensates for the overestimated expansion in x and z, such that the volume expansion as calculated from the linear behaviour in the three dimensions, is equal for both samples. This observation means that the difference in the linear thermal properties of both kinds of polymer networks should be related to a different behaviour of their order parameter as a function of temperature. We will illustrate this on the base of a model, first mentioned in Reference 16.

According to this model, we can correlate the relative change in length $\Delta L/L_0$ in the orientation direction to a change δ in the order parameter by the relation

$$-\Delta L/L_0 = 1 - \left[\frac{2\delta}{2\langle P_2\rangle + 1} + 1\right]^{1/2} \tag{1}$$

in which the value of δ is determined from the change in birefringence over the same temperature range, assuming that Δn is proportional to the order parameter. For the uniaxially oriented polymer the relative change in length along z upon heating from RT to 150°C as due to a relative change in order parameter is resumed in Table II.[16] Assuming for a moment the absence of volume expansion the linear thermal behaviour along x and y, i.e. in the directions perpendicular to the orientation, is given by the expression

$$\left(\frac{\Delta L}{L_0}\right)_x = \left(\frac{\Delta L}{L_0}\right)_y = \sqrt{\frac{1}{\left(\frac{\Delta L}{L_0}\right)_z + 1}} - 1 \tag{2}$$

which for a small change in the relative length $(\Delta L/L_0)_z << 1$, is approximated by

$$\left(\frac{\Delta L}{L_0}\right)_x = \left(\frac{\Delta L}{L_0}\right)_y = -\frac{1}{2}\left(\frac{\Delta L}{L_0}\right)_z. \tag{3}$$

In Table II the thermal expansion in the three directions as estimated using these relations is compared to the experimental values, which are determined under the rough assumption that the contribution of volume expansion in that direction is a linear function, given by the expansion behaviour below the glass transition temperature T_g, where the change in order parameter is negligible. The contribution

TABLE II

The ratio of the order parameters (S_0 represents the order parameter at RT, while S_T gives the order parameter at 150°C) and the relative change in length ($\Delta L/L_0$) in three dimensions for a uniaxially and a helicoidally oriented polymer film upon heating from RT to 150°C

	S_T/S_0	calculated $\Delta L/L_0$			measured $\Delta L/L_0$		
		y	x	z	y	x	z
uniaxial	0.95	0.008	0.008	-0.015	0.012	0.012	-0.016
twisted	0.92	0.011	-0.006	-0.006	0.020	-0.007	-0.007

of volume expansion estimated in this way is indicated by a dotted line in Figures 6 and 7.

A similar analysis can be performed for the cholesteric polymer film if the birefringence as a function of temperature is known. Since it is impossible to determine the optical retardation of a twisted birefringent medium with a rotatory compensator, one is left with the measurement of the refractive indices in order to determine the birefringence. In Figure 8 the effective ordinary (n_o^*) and extraordinary (n_e^*) refractive index of the cholesteric film are given as a function of temperature. These data enable the calculation of the uniaxial refractive indices (n_o and n_e) by the relations[17]

$$n_o = n_e^* \tag{4}$$

$$n_e = \sqrt{2n_o^{*2} - n_e^{*2}} \tag{5}$$

Using expression (1) one finds then for the assumed uniaxial orientation a relative contraction of -0.022 along this direction. According to the approximations mentioned above and the resulting expression (3), this leads to a relative expansion of 0.011 in the y direction perpendicular to the film. The relative change in length along x and z in the plane of the film will be the average of the relative contraction along the orientation direction and the relative expansion in the direction perpendicular to it. In practice, this results in the expression

$$\left(\frac{\Delta L}{L_0}\right)_x = \left(\frac{\Delta L}{L_0}\right)_z = \frac{1}{2}\left\{\left(\frac{\Delta L}{L_0}\right)_{u.o.} - \frac{1}{2}\left(\frac{\Delta L}{L_0}\right)_{u.o.}\right\} = \frac{1}{4}\left(\frac{\Delta L}{L_0}\right)_{u.o.} \tag{6}$$

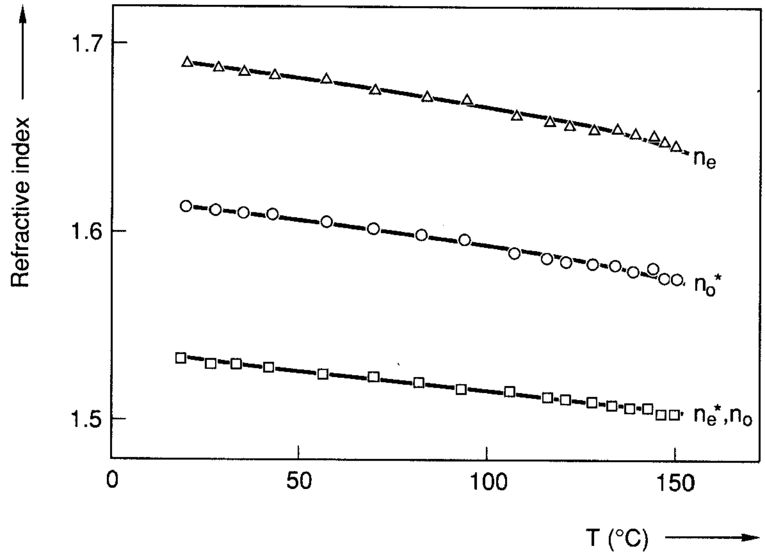


FIGURE 8 Temperature dependence of the extraordinary n_e^* and ordinary n_o^* refractive indices of cholesteric poly(**2a**) with 7 wt% **1** as measured at a wavelength of 589 nm and of n_e and n_o as derived according to equations (4) and (5).

in which $(\Delta L/L_0)_{u.o.}$ is the relative change in length for the assumed uniaxial orientation, in this case equal to -0.022. This yields a value for $(\Delta L/L_0)_x$ or $(\Delta L/L_0)_z$ of -0.006. These estimated data, together with the corresponding experimental values, are also included in Table II. The difference between theory and experiment in the case of the expansion along y for both the uniaxial and twisted films can probably be explained by the inaccuracy introduced by approximating the volume expansion in this direction by the extrapolated expansion behaviour below T_g. For strongly expanding films the linear approximation is too rough and should be replaced by a curved relation, taking into account a higher volume expansion above T_g. In the two in-plane directions there is good agreement between the calculated and measured thermal shrinkage.

5. CONCLUSIONS

We have demonstrated the possibility of creating densely-crosslinked cholesteric polymer networks by a process of UV-polymerization of LC diacrylates containing an amount of chiral dopant. Two of a number of potential applications of this process have been discussed.

Because of the control over its thickness by the use of chopped glass fibres, over its birefringence by the polymerization temperature, and over its total angle of rotation by the amount and kind of chiral dopant and by the rubbing direction at both substrates, such a cholesteric polymer film is an excellent candidate for the compensation of the wavelength dependence of the transmission of STN LCDs. It has the advantage of enabling a light-weight product with a performance equal to that of a double-cell configuration. The temperature dependence of the transmission of the display may be induced in the intrinsically temperature independent cholesteric polymer film by using a chiral LC monomeric-polymeric gel system, as described in Reference 5, instead of a pure LC diacrylate.

The peculiar behaviour of the thermal expansion in two directions parallel to the substrate opens the opportunity to use these cholesteric films in the coating or encapsulation of electronic devices. Because of the helicoidal conformation in the molecular packing, they fulfil the requirement of a nearly zero expansion or contraction within the plane of the film upon heating to high temperatures.

Acknowledgments

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