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Three Dimensionally Ordered Polymer Networks with a Helicoidal Structure

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ABSTRACT: It is demonstrated that densely cross-linked polymer networks with a helicoidal order in the nematogenic bridging units can be created by photoinitiated polymerization of liquid-crystalline diacrylates containing a chiral dopant. The natural pitch of the monomeric mixture is controlled by the dopant concentration, while the total rotation angle of the molecular helix and thus the actual pitch of the material between two unidirectionally rubbed substrates are supplementarily adjusted by the angle between the director at both interfaces and by the film thickness. During polymerization of a monomeric film the rotation angle remains constant, while the pitch may decrease due to polymerization shrinkage.

I. Introduction

It is common knowledge from low molar mass liquid crystals (LC) that the presence of a chiral center in the molecular structure yields a cholesteric phase, in which the molecules are arranged in a helicoidal structure along an axis perpendicular to their longitudinal axis. Chirality may also be induced by the addition of small amounts of chiral material to a nematic LC.¹⁻⁴ This phenomenon is widely applied in LCD devices, where the total twist angle of the LC molecules is determined by the combination of the concentration of the chiral dopant and by the rubbing direction of and the distance between the coated substrates.¹ Based on the same concept, cholesteric LC side-chain polymers have been made by linking a chiral substituent to the polymer backbone.⁵⁻⁷ In addition, linear cholesteric polymers have been synthesized either thermally^{8,9} or photochemically¹⁰ by bulk polymerization of cholesteryl acrylates.

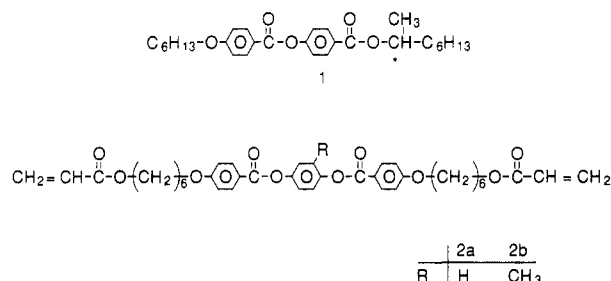
On the other hand, it is known that photoinitiated bulk polymerization of a liquid-crystalline acrylate monomer in its macroscopically oriented state leads to a highly ordered LC side-chain polymer film.^{11,12} When the same method is used to polymerize diacrylates in their mesophase, one obtains oriented polymer networks, which maintain their ordering up to high temperatures.^{13,14}

It is the aim of this work to polymerize LC diacrylates in the cholesteric phase in order to demonstrate the possibility of creating a densely cross-linked polymer network with a helicoidal superstructure of the rodlike units between the acrylate main chains. The intention is that through the use of LC diacrylates the type of ordering achieved in the monomeric phase at a given temperature is frozen-in during polymerization, enabling an exact control of the molecular arrangement. In that case loss of ordering or changes in the helicoidal structure during temperature cycling are blocked by the presence of chemical cross-links.

II. Experimental Section

The influence of the left-handed chiral material L-4-[[4-(hexyloxy)benzoyl]oxy]benzoic acid 2-octyl ester (1; S811, Merck) on the ordering of the mesogenic diacrylates **2a** and **2b** synthesized as described in refs 13 and 14 is studied. The chemical structures of these materials are given in Chart I. The diacrylates are stabilized by 100 ppm hydroquinone monomethyl ether. The photopolymerization, performed with a UV short-arc mercury lamp with a power output of 0.8 W/cm² (Ultracure 100, EFOS Inc.) illuminating the samples for 3 min, is activated by the presence of 1 wt % of 2,2-dimethoxy-2-phenylacetophen-

Chart I



none in the mixtures. The procedures for making the eutectic blend consisting of 20 wt % **2a** and 80 wt % **2b**, hereafter referred to as **3**, and for measuring the transition temperatures by differential scanning calorimetry are also given in ref 14. The natural pitch, p_0 , of the helicoidal structure is measured with the Cano wedge method.^{1,15,16} Its value is calculated from the distance between the Grandjean-Cano disclinations, which reflect a discontinuous step of π radians in the rotation angle of the LC material inserted between a uniaxially rubbed flat and plano-convex substrate coated with ZLI 2650 (Merck) polyimide. In order to make twisted polymer films with a variable twist angle, cells are constructed consisting of two glass substrates each provided with a uniaxially rubbed polyimide layer and assembled at a known angle between the rubbing directions. The cell spacing is controlled to 6 μm by the incorporation of chopped glass fibers and interferometrically measured with an accuracy of 0.2 μm . Thermal expansion is measured with a Perkin-Elmer TMA-7.

III. Chiral Properties of Monomers

In order to study the chiral properties of the monomer **2a** and the eutectic blend **3**, various amounts of the chiral dopant **1** are added. Since both the monomer and the blend are crystalline at room temperature (RT), their properties are determined at elevated temperatures, being 120 °C for monomer **2a** and 100 °C for blend **3**. The relationship of these temperatures with the melting and clearing point of the materials can be deduced from Table I. This table also demonstrates the influence of the chiral dopant on the transition temperatures. For the highest concentration studied, the melting temperature hardly changes, while the clearing temperature decreases by 11 °C for **2a** and by 6 °C for **3**. In the case of **2a**, the monotropic transition from nematic to smectic is lowered by 12 °C.

The chiral properties of these mixtures are characterized by the pitch of the resulting helicoidal structure, defined as the distance of a 2π screw rotation of the molecular packing and measured by the Cano wedge

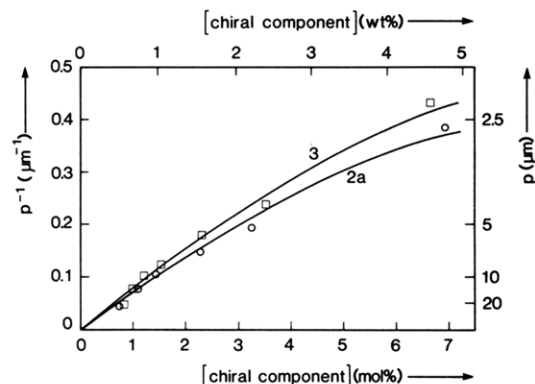


Figure 1. Natural pitch, p_0 , of the helicoidal structure in monomers 2a and 3 versus the concentration of chiral dopant 1.

Table I
Transition Temperatures ($^{\circ}\text{C}$) of the Studied Compounds and the Influence of the Chiral Dopant 1^a

compd	Cr \rightarrow S	S \rightarrow N	N \rightarrow I
1	48		
2a	108	(86)	155
2b	86		116
3	80		120
2a + 6.96 mol % 1	106	(74)	144
3 + 6.67 mol % 1	81		114

^a The values in parentheses indicate monotropic transitions.

Table II
Temperature (T) Dependence of the Natural Pitch (p_0) of 3 Provided with 6.67 mol % of Dopant 1

T , $^{\circ}\text{C}$	p_0 , μm	T , $^{\circ}\text{C}$	p_0 , μm
113	2.35	60	2.17
100	2.31	40	2.16
80	2.27		

method.^{1,15,16} Figure 1 illustrates at low concentrations a nearly linear dependence of the reciprocal pitch on the concentration of the chiral component, which is in agreement with observations on conventional LCs.¹⁶⁻¹⁸ There is some influence of the type of diacrylate on the pitch-concentration dependence. In view of the approved influence of LC hosts for a wide range of materials,¹⁸ the measured difference between the two acrylate systems is only marginal.

As shown in Table II, the pitch decreases only slightly with decreasing temperature in the range relevant for polymerization. In fact, the measured change in pitch over this temperature range nearly falls within the experimental inaccuracy. On the other hand, the pitch differences we measured fit very well into the broad class of various temperature behaviors for the pitch of low molar mass twisted LC materials.^{19,20}

IV. Chiral Properties of Polymers

By UV irradiating the twisted monomer in the wedge cell the helicoidal ordering of the photo-cross-linked polymer is investigated. The continued existence of a twisted structure in the resulting polymeric network is clearly illustrated by the photographed Grandjean texture shown in Figure 2. Measurements of the distance of the disclination lines toward the center of the wedge cell revealed no change during polymerization, which, of course, implies that the total rotation angle remains constant. For a constant angle of rotation the change in pitch is directly correlated to the change in film thickness, analogous to stretching or compressing a coiled spring.

In our experiment, however, no change in pitch occurred since lateral polymerization shrinkage is prohibited by

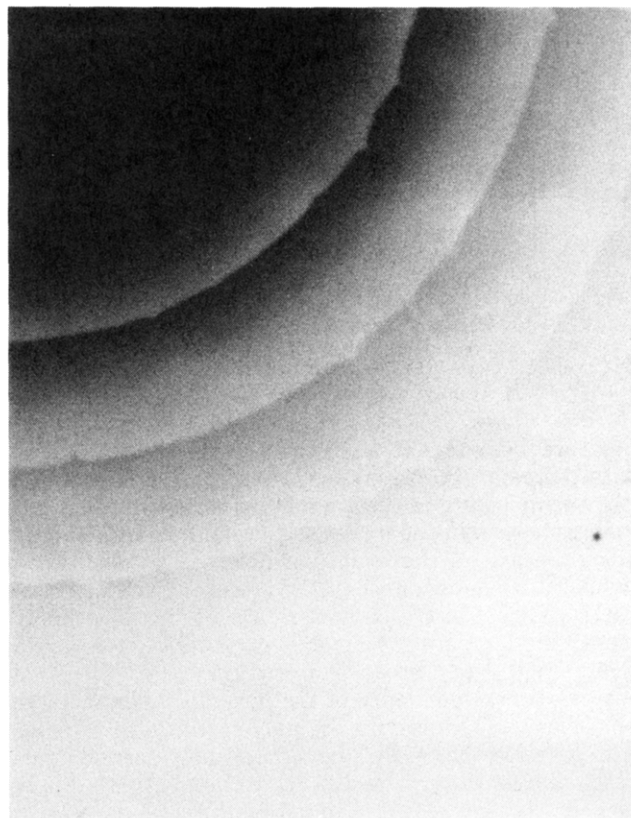


Figure 2. Segment of the circular Grandjean-Cano disclination lines observed through a polarizing microscope between crossed polarizers. The actual color shifts from dark blue in the center to pale blue at the edge.

the configuration of the measuring cell, for which the boundary surfaces are fixed by the glass to glass contact at the center. Here, the material is restricted to shrink in the plane of the substrates resulting in some radial cracks at the periphery of the film, but, in general, the existence of polymerization shrinkage reduces the film thickness and as such the pitch. The amount of shrinkage for the LC monomers is determined by interferometrically measuring the spacing between two free-moving glass substrates before and after UV irradiation. For both a twisted ($p_0 = 5.2 \mu\text{m}$) and a nontwisted sample of monomer 2a the film thickness decreases with $(10 \pm 1)\%$ during photopolymerization at a temperature of 120°C . So, within the experimental accuracy no effect of the presence of a twist on the polymerization shrinkage is found. The value of 10% lateral displacement corresponds to the estimated volume shrinkage of the monomers at this temperature. The phenomenon that volume shrinkage rather than linear shrinkage should be incorporated is explained by the small spacing relative to the surface dimensions and by the fact that gelation of the reacting monomer, prohibiting radial flow, occurs already in an early stage of the polymerization. Because of the difference in thermal expansion between the solid and the liquid state, the amount of lateral reaction shrinkage reduces to about 8% for a polymerization temperature of 100°C . These results determine the change in pitch during polymerization of twisted monomeric films.

Heating a free-standing polymeric film from RT to 250°C also did not change the total angle of rotation in the chiral order. In accordance with our expectations, a change in rotation is hindered by the highly cross-linked network connecting all the rodlike moieties. Again, the fact that the total rotation angle remains constant with temperature does not necessarily mean that the pitch is tem-

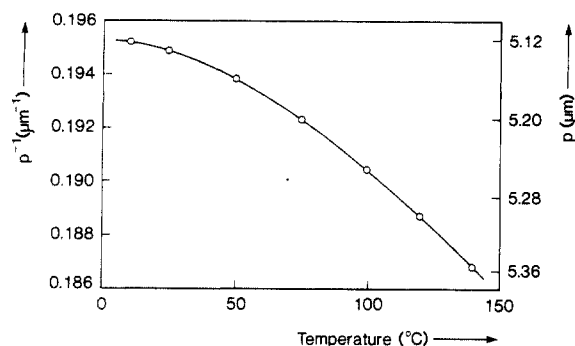


Figure 3. Temperature dependence of the pitch p of poly(2a) + 2.23 mol % 1, polymerized at 120 °C.

perature independent, since the film thickness may vary with temperature. Therefore, the variation of the pitch with temperature is determined by measuring the thermal expansion in the direction perpendicular to the foil along the axis of the molecular helix. This results in a temperature dependence of the pitch as given in Figure 3. In contrast to the cholesteric linear side-chain polymers,⁵ the temperature dependence of the pitch is relatively small over a broad temperature range. The small temperature dependence of the pitch in the monomeric phase is even reduced during polymerization.

In practice, the twisted monomer is polymerized at elevated temperatures near 100 °C, while the twisted polymer film is used at RT. Therefore, the total decrease in pitch is a combined effect of the polymerization and thermal shrinkage. As a result one has to take into account a reduction in pitch of about 13% for a sample polymerized at 120 °C and of about 10% for a sample polymerized at 100 °C.

V. Optical Properties of Twisted Films

Films were prepared using the cell technology described above. The total twist angle of the monomeric mesogens is defined by the angle between the bounding monomeric molecules at the bottom and top substrate, aligned along the rubbing direction. Cells were filled with various mixtures of the UV-polymerizable monomers and the cholesteric material. The concentration of the latter is dictated by the desired total twisting angle, ϕ_T , of the cell and its thickness, d . Due to the anchoring forces at the interfaces, some deviation of the ideal dopant concentration is acceptable since it only leads to dilation or contraction of the natural pitch, which do not affect ϕ_T . The birefringence, Δn , of the polymeric films, defined as the difference between the extraordinary and ordinary refractive index of the homogeneously oriented film, can be regulated by the UV-polymerization temperature.¹⁴ Thus, foils of twisted polymer are produced with controllable rotation angle, thickness, and birefringence.

The optical properties of these polymer films are evaluated by measuring the transmission as a function of the wavelength (λ) by means of a UV-vis spectrophotometer using polarized light. The shape of the resulting spectra is compared to the calculated one predicted by the Gooch-Tarry theory,²¹ which states that the transmission of a nontilted, uniformly twisted LC sample between parallel or crossed polarizers is a damped sinusoidal function of the total twist angle and of the quantity $d\Delta n/\lambda$. An example of such a calculated Gooch-Tarry curve is shown in Figure 4 for both a 180° and a 240° twisted film between crossed polarizers with the first polarizer parallel with or at 30° to the front director, respectively. The measured UV-vis spectra of our twisted polymer films

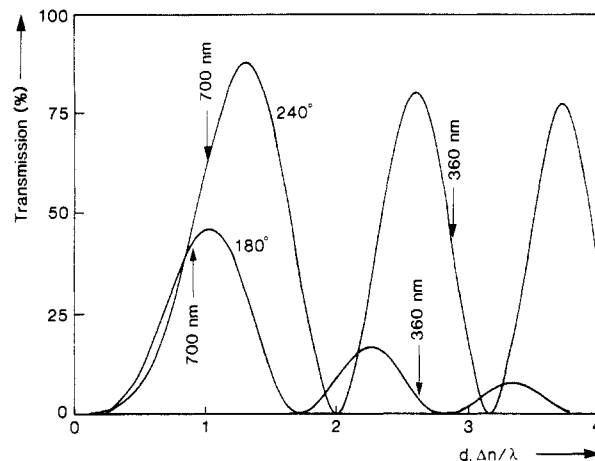


Figure 4. Transmission as a function of $d\Delta n/\lambda$, calculated by the Gooch-Tarry theory,²¹ for 180° and 240° twisted LC samples.

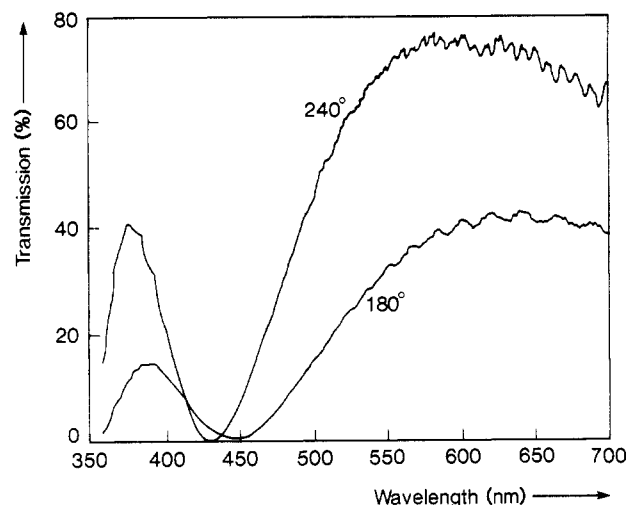


Figure 5. Transmission curve between crossed polarizers of poly(3) with twist angles of 180° and 240°, respectively. More specific data are given in Table III.

Table III
Data on the Polymer Films Poly(3), Used for Studying the Optical Behavior^a

ϕ_T , deg	[1], mol %	T_P , °C	Δn	d , μm
180	1.01	113	0.107	5.9
240	1.50	60	0.130	5.5

^a ϕ_T gives the total twist angle, [1] the concentration of the chiral dopant, T_P the polymerization temperature, and d the film thickness. The birefringence Δn is determined at a wavelength of 589 nm.

should correspond to subsections of this figure, the boundaries of which depend on the particular $d\Delta n$ value. This correspondence is checked experimentally by using polymer films, the parameters of which are summarized in Table III. The arrows in Figure 4 confine the subsections corresponding to the wavelength range of the actual measured spectra given in Figure 5.

It is clear that the shape of the curves as well as the height of the maxima confirm that the 180° and 240° rotation is indeed obtained in the twisted polymeric films. Moreover, from the position of the minima and maxima in Figure 4, the corresponding λ in Figure 5, and the separately measured film thickness, d , the birefringence of the films can be calculated as a function of wavelength. Figure 6 shows the results of such a calculation and compares them with the dispersion of Δn as measured on

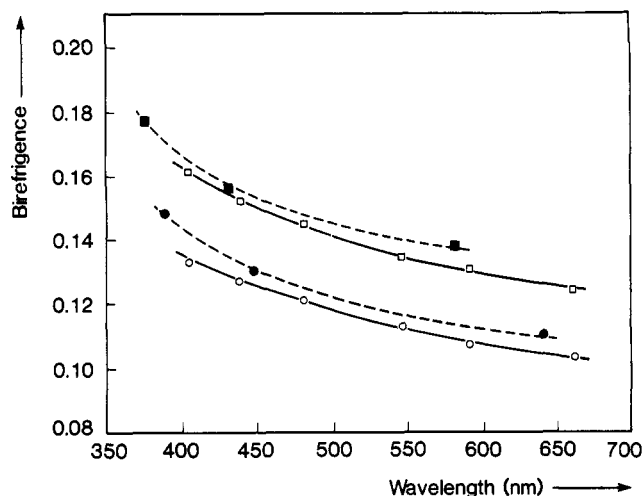


Figure 6. Dispersion of the birefringence of poly(3) polymerized at 60 °C (□, ■) and 113 °C (○, ●), respectively. The solid lines connect data measured with a polarizing microscope equipped with a tilting compensator; the dashed lines connect data calculated from Figures 4 and 5 using the Gooch-Tarry theory.

the corresponding homogeneously oriented samples ($\phi_T = 0$) with a tilting compensator mounted in a polarizing microscope. The Δn data obtained with both methods are quite well in agreement among themselves. The small discrepancy between the dashed and the solid line falls within the expected inaccuracy of the thickness measurement. The relatively sharp increase of Δn at shorter wavelengths is thought to be due to the anomalous dispersion close to the absorption band of the polymer at 265 nm.

VI. Conclusions

Analogous to the situation in conventional nonpolymerizable nematic LC mixtures, the addition of a chiral component induces a molecular helix in a direction perpendicular to the long axis of LC diacrylate molecules. Photoinitiated free-radical chain polymerization of these monomers leads to densely cross-linked polymer networks with a twisted superstructure.

The natural pitch of the monomer is determined by the concentration of chiral dopant and shows a small temperature dependence. During polymerization of a monomer film the molecular twist is frozen-in, while the pitch changes with a factor equal to the volume shrinkage. Heat-

ing of the polymeric network does not affect the molecular ordering. The change in pitch is now determined by the thermal expansion of the polymer film.

The optical properties of these twisted polymer films are characterized by a number of parameters: the birefringence, which is adjusted by the polymerization temperature, the total angle of rotation, which is controlled by the concentration of the dopant and the angle between the rubbing directions on the top and bottom substrate, and the thickness of the film. The transmissive behavior between crossed polarizers agrees well, at least qualitatively, with the Gooch-Tarry theory predicting the optical behavior of twisted nematic LC samples.

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