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PHOTO-CONTROLLED DIFFUSION IN REACTING LIQUID CRYSTALS: A NEW TOOL FOR THE CREATION OF COMPLEX MOLECULAR ARCHITECTURES

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Abstract: Diffusion enforced photo-assembling during polymerization of a chiral-nematic monomer blend yields a cholesteric network in which the helical pitch gradually changes over the cross-section of the film. The polarization selective reflection band of cholesterics can be made much wider than those of single pitch materials and may expand over the whole visible wavelength. The paper discusses the photo-controlled diffusion process in thin films, the important process parameters and some of the properties of the molecular architectures obtained.

INTRODUCTION

A convenient technique to produce polymer films with control over the molecular order is photopolymerization of liquid-crystalline (LC) monomers (Refs.1,2,3,4). Preferably, they form crosslinked networks maintaining their molecular order up to high temperatures. The various LC phases of the reactive mesogens provide different molecular organisations, all being accessible for fixing by polymerization (Refs.5,6,7). Already three decades ago it was suggested to crosslink reactive LCs in the mesophase (Refs.8,9). Thermally initiated polymerization of LC diacrylates yielded polymer networks with a stable birefringent texture (Refs.10,11,12,13). However, the temperature of curing often conflicted with the temperature of the mesophase. Therefore photo-initiation is preferred instead. The monomers are processed without premature polymerization and the desired molecular order is subsequently fixed by exiting a dissolved photoinitiator. The first reports on LC photopolymerization were on mono-acrylates forming linear side-chain LCPs (Refs.14,15,16,17,18), however often the initial LC order was not maintained because of phase transitions upon polymerization and/or cooling to ambient temperature. For that reason photopolymerization of polyfunctional LCs became important. For instance, photo-induced chain-crosslinking of monolithically ordered nematic diacrylates resulted in stable polymer networks with preservation of texture and order

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(Refs.1,2,3). Photo-cationic crosslinking of LC diepoxides (Refs.19,20) and divinylethers (Refs.21,22,23) led to similar results. The optical properties of aligned LC networks are similar to those of low-molar-mass LCs. They are transparent, exhibit a high birefringence (Ref.3) and selective reflection in the case of cholesteric order (Ref.7). A number of their optical applications have been published (Refs.24,25,26). The mechanical properties are, apart from their anisotropy, of the same order as those of isotropic networks, i.e. stable materials but not that extreme values as found for the modulus and strength of main chain LCPs (Ref.27).

A new tool for creating more complex molecular architectures than realised by LC order alone is photo-induced diffusion simultaneously to the polymerization (Ref.28). The use of photo-initiation enables spatial modulation of polymerization. In the plane of the film the light intensity can be locally controlled by using photomasks (Refs.28,29) or holography (Ref.30). Differences in light intensity create composition gradients in blends of reactive mesogens. The composition gradient induces diffusion and therewith local changes in properties such as refractive index, birefringence, reflection wavelength or switching ability.

Also into the third dimension, i.e. perpendicular to the plane of the films, monomer diffusion during polymerization can create interesting molecular structures. Thereto light is modulated by small amounts of absorbers with a high extinction in the UV region of the photoinitiator (Ref.31). The intensity gradient causes monomer to diffuse over the film thickness and alters the properties in that direction. This new process will be discussed in this paper. It will be applied to a cholesteric film enforcing the cholesteric pitch to vary over the cross-section of the film. Optical films are thus created which reflect circularly polarized light over a broad spectral bandwidth.

DIFFUSION-ENFORCED PHOTO-ASSEMBLING

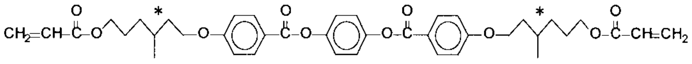
Mechanism

The aim is to demonstrate that it is possible to introduce a variation in the properties over the cross-section of a film of an LC network by using photo-induced diffusion. As an example the pitch of the helix of a cholesteric network will be varied continuously over the thickness such that the band width of cholesteric reflection will be broadened from the single pitch value of around 40 nm to one which expands over for instance the whole visible spectrum, i.e. 400 nm. The driving force for diffusion is a UV-intensity gradient over the film thickness in combination with a difference in reactivity between a helix-winding chiral monomer and a helix-unwinding nematic monomer. The UV-intensity gradient can be established by a small amount of dye which absorbs in the same region as the photoinitiator, i.e. around 340 nm but transmits light in the visible part of the spectrum avoiding coloration. A reactivity difference is obtained by selecting a chiral diacrylate and a nematic monoacrylate. The number of active sites per molecule determines the capture probability and thus the reactivity of the individual monomer molecules. This means that upon polymerization of a blend of these molecules, the chiral monomers are depleted (= converted into polymer) faster than the nematic ones.

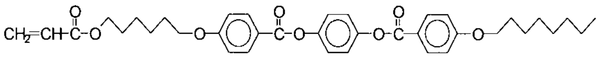
Upon UV irradiation in the presence of a dye the reaction is much faster at the side of the film nearest to the lamp. Due to the difference in reactivity the chiral diacrylate especially depletes here faster than the monoacrylate. This depletion introduces a concentration gradient causing diffusion. The top of the film is thus enriched by the pitch-tightening chiral material whereas the bottom will be enriched by the helix unwinding nematic mono-acrylate. When the polymerization progresses, ultimately all monomeric molecules become bonded to the network and the gradient remains fixed.

Monomer formulation

UV irradiation of the chiral LC diacrylate **1** in the presence of 1 wt-% photoinitiator **3** produces a cholesteric network with a helical pitch of 180 nm (Ref.7). The reflection wavelength of this material is too small for practical applications (282 nm) but can be shifted to the visible region by blending with a nematic, e.g. monoacrylate **2**. The latter has a wide nematic temperature range which, when added to **1**, broadens the processing temperature window.



Chiral LC diacrylate **1**: Cr 70 Ch 92 I



Nematic monoacrylate **2**: Cr 100 N 175 I

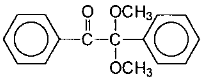
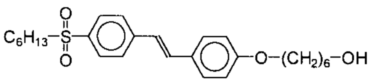


Photo-initiator **3**

(Irgacure 651 / Ciba-Geigy)



Dye **4** (Ref.32)

Table I. Absorbance maximum λ_{max} and extinction coefficients ε at λ_{max}, 350 nm and 365 nm, respectively.

Compound	λ_{max} (nm)	ε_{max} ($l.mol^{-1}.cm^{-1}$)	ε_{350} ($l.mol^{-1}.cm^{-1}$)	ε_{365} ($l.mol^{-1}.cm^{-1}$)
3	345	236	206	134
4	334	31524	24864	8170

When mixtures of **1** and **2** are applied at buffed substrates, planarly aligned, clear cholesteric films are formed. At appropriate mixing ratios they reflect circularly polarized light in the visible region. The influence of the initial composition on the cholesteric pitch and the reflection band is shown in Fig. 1. For this study it proved to be convenient to select a monomer blend reflecting around the center of the visible spectrum (e.g. **1**/**2** ≈ 60/40). In the presence of 1 wt-% **3** this blend photopolymerizes rapidly to a stable cholesteric network. The position of the band shifts somewhat, but not more than 10%, towards lower wavelengths due to polymerization shrinkage (Refs.5,7), but the bandwidth remains the same. Without pitch-gradient the formed cholesteric network has a narrow reflection band as illustrated in Fig. 2.

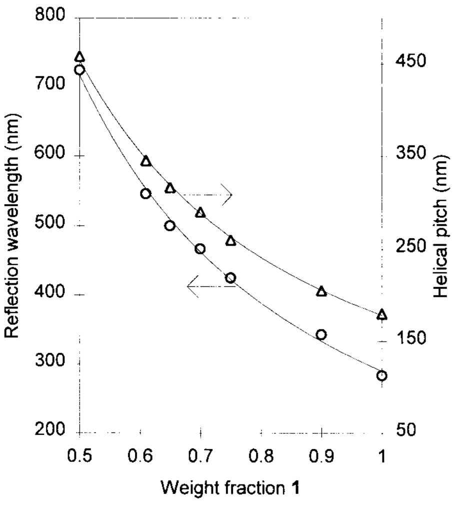


Figure 1 Reflection wavelength of the cholesteric network as a function of amount of chiral monomer.

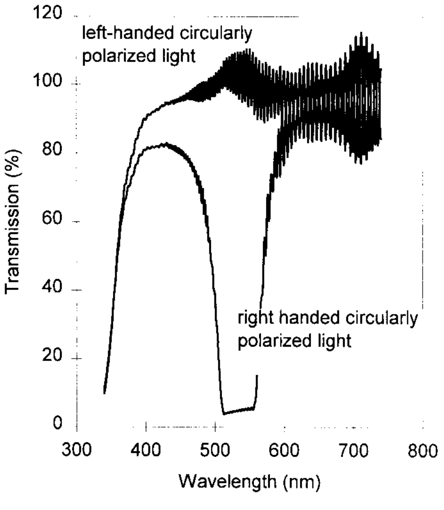


Figure 2 Example of a reflection band of cholesteric network containing 62 % **1**.

Formation of the helix gradient during polymerization

In order to create a gradient in UV intensity dye **4** is added to the monomer blend. Table I compares the optical properties of the photoinitiator and the added dye. The absorption maxima are chosen to be close to each other, however the extinction of the dye is much larger. This leads to a sharp drop in light intensity at the wavelengths of interest, i.e. 350 or 365 nm. Fig. 3 illustrates how the UV intensity decreases when light of these wavelengths penetrates into a 20 μm thick cholesteric film with 1 wt-% photoinitiator **3** at two different dye concentrations. Without dye the decrease of the intensity I in relation to the incident intensity I_o is small and solely due to absorption by the photoinitiator. When the dye is added the intensity rapidly drops off with the distance z from the film surface nearest to the lamp.

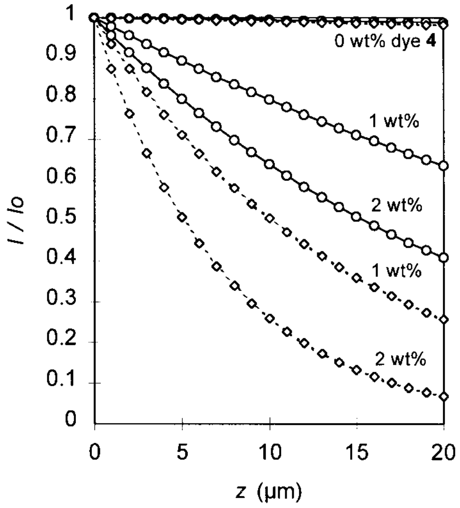


Figure 3 Relative light intensity I/I_o as a function of distance z from the surface calculated for 350 (◊) and 365 nm (o), respectively

Table II Maximum polymerization rate averaged over total film thickness as function of dye concentration.

Dye **4** (wt-%)	$\bar{R}_p$ (% C=C /s)
0	21.7
1	7.8
2	4.7
4	3.0

(Polymerization conditions: [**1**]/[**2**]= 60/40; 1wt-% **3**; I_o = 7 mW/cm2 at 365 nm).

When the polymerization is proceeded in the presence of the dye, the overall polymerization rate decreases exponentially. This is illustrated by Table II which shows the polymerization rates as measured by photo-DSC. These measurements represent the rates averaged over the total sample thickness. The local polymerization rate R_p scales with the local intensity I according to $R_p \propto I^a$ with a being between 0.5 and 1 depending on the termination mechanism of the chain-addition reaction. Combining the data from Fig. 3 and Table II it can be estimated that $\log R_p$ scales with $-z^a$ with a close to 0.5. Of course this is only valid in a relatively early stage of the reaction. At higher conversions the kinetics become more and more dominated by monomer mobility due to viscosity effects and partial linkage of the bi-functional monomers to the network and the rate differences over the thickness are expected to level off.

Before polymerization the composition is uniform and the sample shows a narrow reflection band. However as soon as the polymerization is initiated in the presence of the dye, the local polymerization rate differences cause the most reactive component, i.e. monomer **1**, to be depleted faster at small z. Therefore these areas are enriched by the chiral monomer and the helical pitch tends to tighten. Consequently, the areas at large z become enriched with nematic **2** and the pitch become larger. As a result, one observes broadening of the reflection band during polymerization more or less symmetrically around the position of the initial band. Therefore reflective polymer films may be formed with very large band widths as illustrated in Fig.4. Already with 1 wt-% dye the bandwidth can be increased from 42 to 381 nm. This implies that for this specific sample the cholesteric pitch increases from 0.27 at the top to 0.46 μm at the bottom of the film.

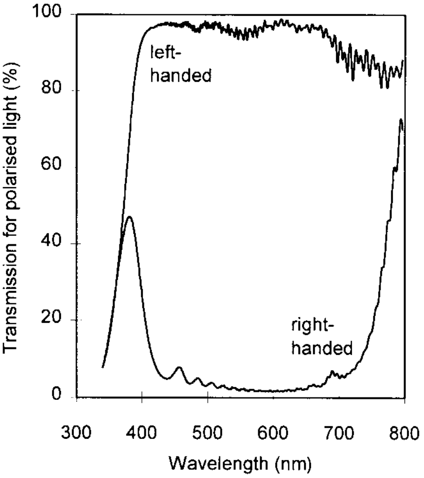


Figure 4 Broad-band polarized reflection at a 15 μm cholesteric film polymerised in the presence of 1 wt-% dye **4**

As the intensity gradient is the driving force for monomer diffusion, the bandwidth increases at increasing dye concentration. This is illustrated in Fig.5 for two intensities of 365nm UV generated by a Philips PL10 fluorescent lamp. It also shows that, as the formation of a gradient is diffusion driven, the polymerization and the diffusion rate should be very well balanced to get optimum effects. At high UV intensity the integral polymerization proceeds fast and diffusion hardly gets any chance to occur. Consequently, the reflection band remains narrow. At low UV intensity the effect becomes much more pronounced and bandwidths of 400nm or more are established already at small dye concentrations. When 350 nm fluorescent light (Philips TL08) is used, the intensity drop over the thickness is more pronounced (Fig. 3) which means that broader bands are formed at relatively high UV intensities (Fig. 5).

Taking the transition temperatures and the thermal stability of the monomer mixtures into account, the polymerization temperature can be varied to some extent. In general the polymerization rate increases with temperature at low temperatures (< 70 °C) because of viscosity effects and decreases at high temperatures (> 120 °C) for thermodynamic reasons (Ref.3). When polymerised in a region where R_p is relatively temperature independent the band width increases with polymerization temperature because of an increasing diffusion rate of the monomers. This is shown in Table III. Also the band position changes somewhat with polymerization temperature which is related to the temperature dependence of the monomeric reflection band (Ref.7). After polymerization the position of the reflection is stable and changes only minor with temperature, correlated to the thermal volume expansion (Ref.5).

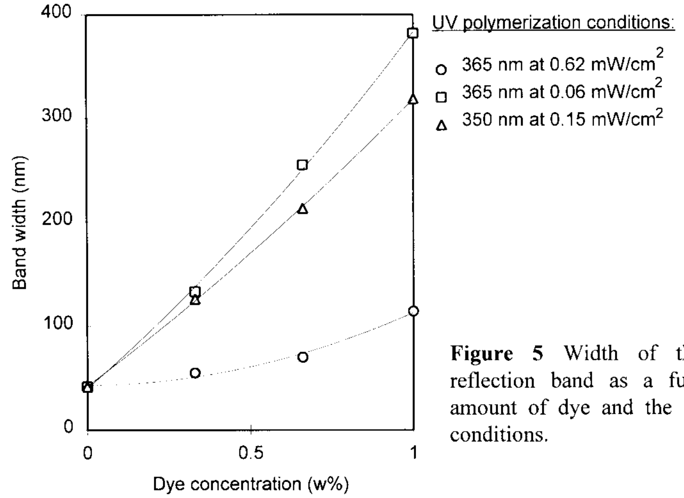


Figure 5 Width of the cholesteric reflection band as a function of the amount of dye and the polymerization conditions.

Table III Band position and width as a function of polymerization temperature (**1**/**2**=60/40; 1 wt-% dye; I_0= 0.06 mW/cm² at 365 nm).

Polymerization temperature (°C)	Center of the reflection band (nm)	Band width (nm)
80	569	346
90	584	359
100	596	381

Properties of helix-gradient cholesteric networks

The pitch-gradient cholesteric networks expanding their reflection band evenly over the total visible spectrum are clear, colourless and have a metallic appearance. They transmit only 2% right-handed circularly polarized light. Left-handed circularly polarized light is fully transmitted. The films are well suited as reflective polarizers. The bandwidth is variable and the band position can be located in the range from ultraviolet to the infrared by changing composition and polymerization conditions. The reflective polarizer is selective for circularly polarized light which, if desired, can be converted into linearly polarized light by adhering a quarter-wave retardation foil. This is used in prototype LCDs enabling the generation of polarized light with efficiencies much higher than 50% which is the physical limit for the current dichroic polarizers (Ref.33).

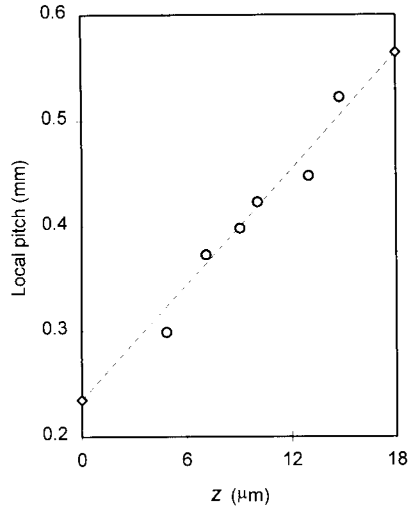


Figure 6 Local pitch measured by SEM (o) and calculated from reflection spectra (◊).

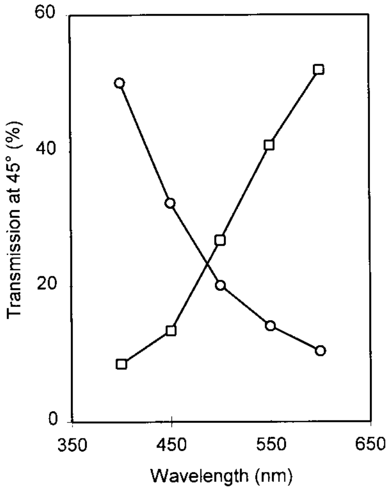


Figure 7 Transmission of circularly polarized light at oblique angle of 45° with positive (□) and a negative (o)pitch gradient, resp.

Scanning electron microscopy pictures (Ref.31) showed that the pitch increases over the thickness with the smallest pitch nearest to the position of the UV source at polymerization. As one example, for an 18 µm film (**1**/**2**=65/35) the reflection band ranged from λ_1=374 to λ_2=880 nm. From these values the smallest pitch p_1 can be calculated to be $p_1=\lambda_1/n_o$= 0.24 µm and the largest pitch $p_2=\lambda_2/n_e$= 0.56 µm. These data are plotted in Fig.6

together with the local pitch data measured at the SEM-pictures of a cross-section of the film. It shows that the pitch changes more or less linearly with the distance z.

Another indication of a linear pitch gradient can be found when measuring the transmission for right-handed circularly light under an oblique angle. Fig. 7 shows that the transmission becomes higher when light is reflected deeper into the film. This can be explained by depolarisation of light by the angle-induced birefringence of the cholesteric film. The further the light must travel through the birefringent medium the more depolarised it becomes. The reflection of the elliptical polarized light is less and the transmission increases. Accounting for the dispersion of the refractive indices, the data points in Fig. 7 are modelled to be correlated with an almost linear pitch gradient.

CONCLUSIONS

By photo-assembling of reactive liquid crystals, using simultaneous diffusion and polymerization, interesting new polymeric molecular architectures can be built which vary their properties over the thickness of the film. As an example it is demonstrated that a cholesteric network can be formed in which the pitch of the molecular helix changes gradually in z-direction. Films of these networks exhibit a broad band polarization-selective reflection which can be applied to make reflective polarizing filters.

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