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The smectogenity as a crucial factor of broadening of the selective light reflection peak in cholesteric photopolymerizable mixtures

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ABSTRACT

Cholesteric liquid crystals reflecting circularly polarised light are promising materials for creating flexible and compact polarisers. One of the issues of these systems is the narrow width of the photonic stop band. The range of selective light reflection can be increased by creating a gradient of the cholesteric pitch in the process of photopolymerisation of reactive cholesteric mixtures. The possibility of broadening the peak of selective light reflection during UV polymerisation of nematogenic diacrylate mixed with chiral monoacrylates was studied. The monoacrylates used had a different number of aromatic rings.

A broadening of the peak of selective light reflection was observed during the photopolymerisation of mixtures containing a chiral monomer with three benzene rings. While before irradiation the width of the selective reflection peak was about 100 nm, after irradiation it was broadened to about 300 nm. A mechanism is proposed for the formation of the helical pitch gradient in the cholesteric, in which the smectogenity of the system plays a crucial role. The obtained results open up new possibilities for creating flexible and thin circular polarisers operating in a wide spectral range.



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Introduction

Cholesteric liquid crystals are a helical supramolecular structure reflecting a circularly polarised light whose direction coincides with the direction of the twist of the helix [1-3].

One of the methods for producing cholesteric polymers is the copolymerisation of nematogenic and chiral monomers. Cholesteric polymers are promising materials for creating polarisers, light filters, and photo-tunable smart coatings. The advantages of these materials are flexibility and compactness. But the width of the range of selective light reflection $(\Delta \lambda)$ usually doesn't exceed tens of nanometres and is determined by the anisotropy of the refractive index (Δn) of the sample and the cholesteric chiral pitch (*P*) according to the following equation:

$$\Delta \lambda = \Delta n \times P \tag{1}$$

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Various methods have been developed for broadening the peak of selective light reflection to hundreds of nanometres in various spectral ranges [4–22]. For example, one approach is to create multilayer structures from several layers of cholesteric films, together covering a wide spectral range [4,23]. In this case, a combination of usually three of cholesteric liquid crystals with selective reflection in the blue, green, and red regions of the spectrum allows obtaining a sandwich structure with a total selective reflection of light up to 300–350 nm wide. Increasing of selective reflection bandwidth is also possible by obtaining the gradient of the helix pitch (ΔP); in this case only one cholesteric layer is used.

All these approaches are based on a direct relationship between the width of the peak of selective light reflection and the difference between the maximum (P_{max}) and minimum (P_{min}) pitch of the helix in the LC layer ($\Delta P = P_{max} - P_{min}$). For example, to form a different pitch of the helix *P*, stepwise polymerisation is carried out at different temperatures [10,14], or a temperature gradient is used in the polymerised layer [7]. In polymer-stabilised cholesteric LCs, switching to the broadband reflective state can be carried out under the influence of an electric field [11–13,24].

Another way to induce a partial untwists of the cholesteric helix and to achieve a local increase in chiral pitch P by the introduction of nanoparticles into the cholesteric mixture. These particles do not participate in the reaction but contribute to the uneven distribution of the chiral pitch during the polymerisation of the system due to deformation of the structure of the cholesteric helix [16,17]. The materials obtained in this way are promising for circular polarisers and filters operating in a wide spectral range [23].

Despite a large number of studies on this topic, obtaining cholesteric systems with a selective reflection peak of more than a hundred nm is still a non-trivial task, so the search for new approaches continues.

An effective method for broadening the peak of selective light reflection was proposed by Broer et al [18]. This approach is based on the different reactivity of mono- and diacrylates. The number of reactive double bonds per molecule (functionality) determines the probability of monomer capture by the growing polymer chain. As the authors suggest, during the polymerisation of a mixture, chiral bifunctional monomers turn into a polymer faster than nematic monofunctional ones. This leads to a decrease in the concentration of the chiral monomer in the upper part of the cholesteric layer and, as a result, diffusion of the unreacted chiral monomer into this region. An increase in the concentration of chiral diacrylate leads to a twist of the



Figure 1. (Colour Online) Illustration of the supramolecular cholesteric helix with constant pitch P_o and with a gradient of the pitch.

cholesteric helix. As a result, a gradient of the cholesteric helix pitch (Figure 1) is formed along the cross-section of the film, and the range of selective light reflection increases. This effect is enhanced with the introduction of a UV absorber, a substance partially absorbing light that initiates photopolymerisation.

A priori, it can be assumed that this approach should work for any cholesteric mixture with monomers of different functionality. Therefore, one of the objectives of this work was to verify the universality of the approach suggested by Broer et al. For this purpose, we obtained mixtures of nematogenic diacrylate and chiral monoacrylate of various structures (Figure 2).

Monomer **RM257** (Figure 2) was used as a nematogenic diacrylate, which has proven itself in a large number of publications devoted to polymerisable cholesteric systems. As chiral monoacrylates, we synthesised compounds **A6ZL-2** and **A6ZL-3** (the synthesis is described in Supporting information). The monoacrylates we used have a different number of benzene rings in the aromatic nucleus. A **Tinosorb S** UV absorber (see structure in Fig. S1) was introduced to create the gradient of UV light intensity across the polymerising layer.

The composition of the cholesteric mixtures (Table 1) was selected so that the peak of the selective reflection of light from the mixture was in the visible range. Photopolymerisation was initiated using **Irgacure 651** (Merck).

Thus, one of the objectives of this work is the study of the possibility of broadening the peak of selective light reflection in the case when the monoacrylate is used as the chiral monomer, and diacrylate - as the



Figure 2. (Colour Online) Nematogenic diacrylate **RM257** and chiral monoacrylate (n = 1 **A6ZL-2**; n = 2 **A6ZL-3**) (a); scheme of photopolymerisation of a mixture of monomers with the formation of a polymer network.

Table 1. Compositions, isotropization temperatures (T_{iso}), the position of the middle of the peak of selective reflection (λ_{max}), and the width of the peak ($\Delta\lambda$).

Nº	RM257	A6ZL-2	A6ZL-3	Tinosorb	lrgacure 651	Inh	T _{iso} , ⁰ C	$\lambda_{max\prime} \ nm$	Δλ, nm
1	69.7	25.0	-	3.2	1.2	0.9	63–65	492	88
2	62.1	-	33.0	2.9	1.1	0.9	98–100	569	133

nematogenic. We also aimed to check in such a way the universality of the approach developed by Broer et al. In addition, it is of interest to establish the influence of the structure of the chiral monomer, namely, the length of the aromatic fragment, on the width of the peak of selective light reflection after photopolymerisation of mixtures.

Experimental part

Materials

The chiral monoacrylates A6ZL-2 and A6ZL-3 were synthesised according to Scheme S1 in Supporting information. The nematogenic diacrylate 2-methyl-1,4-phenylenebis(4-(3- (acryloyloxy)propoxy)benzoate) (RM257, Merck), the UV polymerisation initiator Irgacure 651 (Merck), and the thermopolymerisation inhibitor Inh (Aldrich) (the structure of the initiator and inhibitor are shown in Fig. S1) were used without additional purification. A Tinosorb S UV absorber (BASF) was also introduced into the mixture to create a gradient of UV light intensity in the polymerising layer.

Samples preparation

Weighed portions of the starting materials were dissolved in $CHCl_3$ _ a good solvent for all components. Residual solvent was removed from the system by heating to 60°C in a muffle furnace, followed by drying in vacuum. For samples preparation glass substrates were coated with polyimide and rubbed in one direction using custom-made equipment. Glass cells were filled with a low molecular mass mixture using capillary forces. The gap thickness was fixed with spacers, glass balls with a diameter of d = 20 µm. Used cells are transparent for wavelengths above 300 nm. The polymerisation was initiated with UV light λ = 365 nm. Irradiation was carried out with a mercury lamp I = 1.0 mW/cm², t = 10 min, T = 60°C. Heating was performed to prevent the crystallisation of the individual components of the mixture.

Samples for X-ray and TEM studies were prepared by disassembling the cells after UV polymerisation, and the free-standing polymer films were used for further studies.

Photooptical investigations

Studies of the phase behaviour of low molecular weight mixtures were performed using a LOMO P-112 polarising microscope equipped with a Mettler TA-400 heating stage. A UV filter was used to prevent the photopolymerisation of the mixtures during the observations.

The spectra of selective reflection (transmission) of light of low molecular mass mixtures and polymer films were studied using a Unicam UV-500 UV-Vis spectrophotometer.

Structural investigations

The structure of the films was studied using transmission electron microscopy (TEM) and X-ray scattering.

The X-ray scattering experiments were carried out with a Xenox WAXS/SAXS System diffractometer equipped with a Genix3D radiation source (wavelength 1.54 Å, beam size $300 \times 300 \ \mu\text{m}^2$). Diffraction patterns were recorded using a two-dimensional Pilatus300k detector. The sample-to-detector distance was calibrated using several orders of the fundamental diffraction peak of silver behenate. The integration and processing of scattering curves was performed in the software package created by the authors in the Igor Pro software (Wavemetrics Ltd.) environment. The experiments were carried out in transmission geometry.

For studies using electron transmission microscopy (TEM), thinly cut sample films (80–100 nm) were prepared using a REICHERT-GUNG ultramicrotome with a DIATOME diamond knife and various cutting speeds (from 0.1 to 100 mm/s). For the structural study of samples in a plane orthogonal to the film surface, a series of successive sections (up to 50) in the transverse direction (at a speed of 2 mm/s) was carried out. The obtained sections were studied using a transmission electron microscope LEO 912 AB OMEGA (Karl Zeiss) with an accelerating voltage of 100 kV.

Results and discussion

Phase behaviour and optical properties of low molecular mass cholesteric mixtures

Polarisation optical microscopy was used for the primary identification of the mesophase (see Table 1). Both studied mixtures form a cholesteric mesophase showing a planar texture (Figure 3) with 'oily streaks' which is typical for cholesteric liquid crystal.



Figure 3. (Colour Online) Polarisation microscopy of mixture 2, room temperature, typical planar texture of a cholesteric liquid crystal.



Figure 4. (Colour Online) Transmittance spectra of low molecular mass cholesteric mixtures at 60°C.

The study of the spectral properties of low molecular mass mixtures shows the presence of characteristic peaks of selective light reflection with a maximum in the visible range (Figure 4). The maximum of the reflection peak for the first mixture was found at 492 nm and at 569 nm for the second.

Both mixtures can crystallise at room temperature over time; therefore, photopolymerisation was carried out at a temperature of 60°C.

Optical properties of cholesteric polymer networks

Let us consider the effect of UV irradiation and photopolymerisation on the optical properties of the studied systems. Figure 5 shows transmittance spectra of 20 μ m glass cells filled with mixture 1 and 2 before and after UV irradiation. As seen from these spectra, after photopolymerisation of mixture 2 based on the three-rings chiral monomer **A6ZL-3**, a significant broadening of the peak of selective light reflection was observed (Figure 5 (b), Table 2). In the same time, the broadening effect for mixture 1 was not detected (Figure 5(a)).

The structure of cholesteric polymer networks

Investigations of the influence of thickness of the samples on the optical properties of the final polymer films show no significant broadening of the selective reflection peak in cells of small cell thickness (5 μ m, Table 2). Irradiation with low-intensity light also did not cause changes in the optical characteristics of the films (Table 2).

Regarding the structural features of the obtained samples, let us compare XRD patterns of cholesteric films based on two mixtures presented on Figure 6.



Figure 5. (Colour Online) Transmittance spectra of cholesteric mixtures **1** (a) and **2** (b) before and after photopolymerisation (cell thickness d = 20 μ m, polymerisation conditions: I = 1.0 mW /cm², t = 10 min, λ = 365 nm).

Table 2. Optical characteristics of the cholesteric polymers based on mixture **1** and **2**; **d** is the thickness of the sample, **I** is the intensity of UV light, **t** is the irradiation time, λ_{max} is the position of the middle of the peak of selective reflection, $\Delta \lambda$ is the width of the peak at half maximum.

Mixture	d, µm	l, mW/cm ²	t, min	$\lambda_{max\prime}$ nm	Δλ, nm
1	20	1.0	10	481	86
2	20	1.0	10	554	278
	20	1.4	10	530	260
	5	1.8	10	504	112
	5	0.3	90	516	107

For a polymer film sample based on mixture 2, a clear ring-like reflex is observed in the small-angle region of the X-ray pattern (Figure 6(b)). This indicates the presence of smectic order elements. The corresponding interlayer spacing (33 Å) approximately equals the length of the side groups of the A6ZL-3 polymer (34–35 Å) and the nucleation of SmA₁* phase clusters is

observed. On the other hand, a polymer film based on chiral monomer A6ZL-2 does not show scattering at small angles (Figure 6(a)).

The data of transmission electron microscopy of a slice of polymer films based on mixture 2 reveal the formation of a chiral pitch gradient of the cholesteric liquid crystal helix in the layer (Figure 7). On irradiation side, the helix pitch is minimal and increases from the top to the bottom of the layer. The distance between the centres of the grey bands corresponds to half the step of the cholesteric helix. The causes of visibility of this periodicity on TEM images of slices of cholesteric polymer films are considered in the article [21]. For films based on mixture 1, a gradient was not detected.

Based on the obtained experimental data, we can assume the following mechanism for broadening the peak of selective light reflection during the photopolymerisation of cholesteric mixture 2. Under UV light



Figure 6. (Colour Online) X-ray diffraction patterns of cholesteric polymer films based on mixture 1 (a) and mixture 2 (b).



Figure 7. (*Colour Online*) The structure of the polymer film: a) a transmission electron microscope photo of the cross section of films based on chiral monoacrylate A6ZL-3; b) a schematic representation of the gradient of chiral pitch in the polymer film layer.

exposure due to the presence of a UV absorber Tinosorb, the UV light intensity is significantly higher in the upper layer of the cholesteric mixture and the polymerisation rate in this region is much higher. As previously shown [22], the process of photopolymerisation and crosslinking most often leads to slight shrinkage of the film and shift of the peak of selective reflection of light into the short-wavelength region and its fixation. In contrast, at the bottom part of the sample the polymerisation rate is lower and during the relatively slow formation of the polymer network, a helix is untwisting. This is due to the formation of SmA1 phase clusters in the resulting polymer (see Figure 6 (b)) and the increase of the twist elastic constant, which leads to the untwisting of the cholesteric helix. An additional factor enhancing the smectogenity of the mixture during photopolymerisation is the limitation of the translational mobility of the side groups during the formation of the polymer, which further enhances the tendency to the formation of layer-ordered elements.

Thus, after UV irradiation and photopolymerisation, a slight decrease in the helix pitch occurs in the top layer of the film, and a noticeable increase in the helix pitch in the bottom layer, which is in good agreement with spectral data (Figure 5(b)) and TEM results (Figure 7). An additional data confirming this mechanism is the absence of peak broadening for relatively thin layers of mixture 2 with a thickness of 5 μ m (Table 2). For mixture 1 based on a monomer with a short aromatic fragment, no smectic clusters were detected (Figure 6(a)), and, accordingly, peak broadening was not observed.

Thus, the key structural factor causing peak broadening is the appearance of smectic order clusters due to the presence of a long aromatic fragment in the chiral monomer. On the other hand, the absence of a broadening of the peak of selective light reflection for mixture 1 indicates that the approach proposed by Broer et al. [18] is not universal – the copolymerisation of nematogenic diacrylate and chiral monoacrylate does not always lead to a helix pitch gradient.

Conclusions

The effect of the structure of the chiral monomer and UV-initiated photopolymerisation of cholesteric mixtures of chiral monoacrylates and nematogenic diacrylate on the optical properties of the resulting polymer networks was studied. In particular, the effect of the length of the aromatic fragment of chiral monoacrylates on the width of the peak of selective light reflection has been established. A significant broadening of the peak of selective light reflection (about 300 nm) was found for mixtures containing chiral monoacrylate with three benzene rings in the aromatic fragment, while this effect was not observed for mixtures with a two-ring monomer. TEM data indicate that peak broadening is associated with the formation of a spiral pitch gradient along the film section.

Based on the results obtained, it was suggested that the smectogenic nature of the chiral monomer with three benzene rings in the aromatic core is a decisive factor in the formation of a broad peak of selective light reflection. This suggestion is supported by X-ray diffraction studies and TEM analysis. The resulting polymer films are promising materials for use as broadband circular polarisers (photonics and optoelectronics).

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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