

Optical storage effect due to photopolymerization of mesogenic twin molecules

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The photopolymerization of diacrylate mixtures containing a nematic twin compound and a chiral dopant leads to perfectly stable, highly crosslinked cholesteric networks. The Bragg reflection spectra of the respective monomer and polymer mixtures were measured and the influences of the chemical structure, the temperature and the concentration of chiral dopant on the reflection wavelength was studied. Subsequent UV exposures of different parts of the sample at different temperatures are suitable to generate colored patterns. Deposition of several cholesteric films with different Bragg wavelengths results in additive color mixing. © 2000 American Institute of Physics. [S0021-8979(00)06605-6]

I. INTRODUCTION

The discovery of liquid crystals by Reinitzer^{1,2} was probably due to an interesting color effect which attracted his attention. Today, we know that this color effect is based on Bragg reflection which occurs due to the helical structure of the director field in cholesteric and blue phases.^{3,4} If the pitch p of the helix is of the order of a few hundred nm, the Bragg wavelength

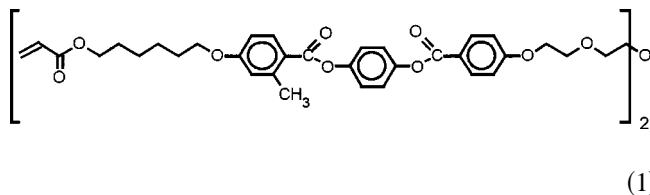
$$\lambda = 2nd \cos \theta \quad (1)$$

is in the visible range. The distance d in Eq. (1) is the spatial periodicity of the structure ($d=p/2$ for the cholesteric phase), the quantity n is an average refractive index, and θ is the direction of light propagation with respect to the pitch axis. Since Reinitzer's observation, the selective reflection and the associated phenomenon of very high optical activity were the subject of many fundamental studies and the basis for many practical uses of cholesteric liquid crystals. The applications include the optical detection of temperature,^{5,6} infrared holography,⁷ electrooptic displays,⁸ laser-written images,⁹ high density optical storage due to wavelength multiplexing,¹⁰ pigments for car paintings,¹¹ and organic polarizers.¹² Some of these possible applications have motivated the search for suitable cholesteric oligomers and polymers. One major group of extensively studied compounds are side chain oligomers with a siloxane backbone where transitions can be thermally induced and frozen in a glass-like state.^{13,14} An approach to obtain thermally very stable cholesteric layers is the *in situ* photopolymerization of multifunctional monomers which leads to the formation of highly crosslinked networks.¹⁵⁻¹⁹ A hot topic in this area is the development of new materials which allow to control the

color of the cholesteric selective reflection either by adjusting the temperature^{20,21} or by illuminating samples which contain a light-sensitive chiral dopant.²²⁻²⁷ Two of us (K. K. and P. S.) have recently described the synthesis and mesogenic properties of functionalized mesogenic dimers,²⁸ which are suitable for photopolymerization. One of the practical problems of crosslinkable mesogenic monomers is their crystallization at room temperature which destroys the alignment of the liquid crystal. Our new compounds show the advantage of forming a liquid crystalline glass state. The glass transition temperatures are rather low so that fixation of the liquid crystalline state can be easily achieved by photopolymerization at room temperature. In the present article, we describe optical studies of cholesteric mixtures containing these compounds and their respective polymer networks.

II. EXPERIMENT

The materials investigated are induced cholesteric mixtures, each consisting of a nematic host and a chiral dopant. The molecules of the nematic and the chiral component contain acrylate units which can react in a free radical mechanism to give a crosslinked polymer network. The two nematic compounds used in this study show the following structures and transition temperatures.

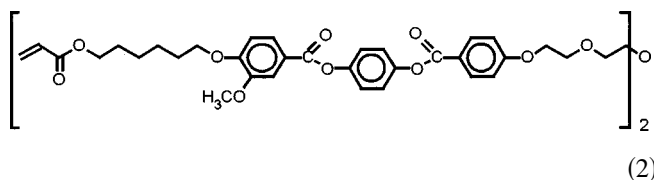


Phase transition temperatures (second heating):
 $g-17^\circ\text{C}$ $N137^\circ\text{C}$ I

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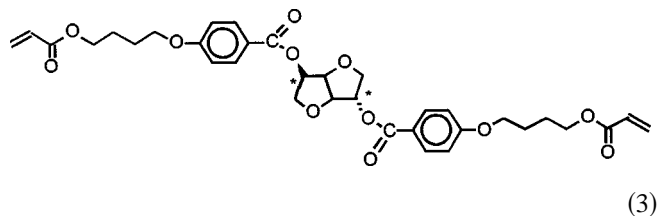
TABLE I. Bragg wavelengths of the investigated samples (M: monomer mixture; P: polymer; R, G, B: red, green, and blue, respectively; T_i : clearing temperature; T_{poly} : temperature of the photopolymerization).

Sample	Nematic component	Chiral component	Clearing point (T_i)/ polymerization temperature (T_{poly})	Photoinitiator	λ_{max} (293 K) (nm)
MR1	90 mol % (1)	10 mol % (3)	$T_i=115^\circ\text{C}$	No	648
MG1	88 mol % (1)	12 mol % (3)	$T_i=119^\circ\text{C}$	No	574
MB1	86 mol % (1)	14 mol % (3)	$T_i=123^\circ\text{C}$	No	482
PR1	90 mol % (1)	10 mol % (3)	$T_{\text{poly}}=30^\circ\text{C}$	Yes	694
PG1	88 mol % (1)	12 mol % (3)	$T_{\text{poly}}=30^\circ\text{C}$	Yes	604
PB1	86 mol % (1)	14 mol % (3)	$T_{\text{poly}}=30^\circ\text{C}$	Yes	498
MR2	87 mol % (2)	13 mol % (3)	$T_i=94^\circ\text{C}$	No	636
MG2	83.5 mol % (2)	16.5 mol % (3)	$T_i=90^\circ\text{C}$	No	494
MB2	82 mol % (2)	18 mol % (3)	$T_i=86^\circ\text{C}$	No	456
PR ₂ ₃₀ ^{°C}	87 mol % (2)	13 mol % (3)	$T_{\text{poly}}=30^\circ\text{C}$	Yes	654
PG ₂ ₃₀ ^{°C}	83.5 mol % (2)	16.5 mol % (3)	$T_{\text{poly}}=30^\circ\text{C}$	Yes	492
PB ₂ ₃₀ ^{°C}	82 mol % (2)	18 mol % (3)	$T_{\text{poly}}=30^\circ\text{C}$	Yes	460
PR ₂ ₇₀ ^{°C}	87 mol % (2)	13 mol % (3)	$T_{\text{poly}}=70^\circ\text{C}$	Yes	610
PG ₂ ₇₀ ^{°C}	83.5 mol % (2)	16.5 mol % (3)	$T_{\text{poly}}=70^\circ\text{C}$	Yes	468
PB ₂ ₇₀ ^{°C}	82 mol % (2)	18 mol % (3)	$T_{\text{poly}}=70^\circ\text{C}$	Yes	432



Phase transition temperatures (second heating):
g-2 °C N 114 °C I

These twin monomers were synthesized with the aim to generate molecules, which show a nematic phase at room temperature. Due to the workup from solution, a melting point at (1) 54 °C or (2) 88 °C is detected during the first differential scanning calorimetry (DSC) heating run. Upon cooling, no recrystallization occurs and only T_g are observed. Details about the synthesis of these compounds are given elsewhere.²⁸ In contrast to liquid crystalline polymers, these reactive monomers have the advantage of a low viscosity which allows to achieve a uniform orientation, easily. In order to induce a cholesteric phase, we used the following crosslinkable chiral sorbitol derivative:²⁹



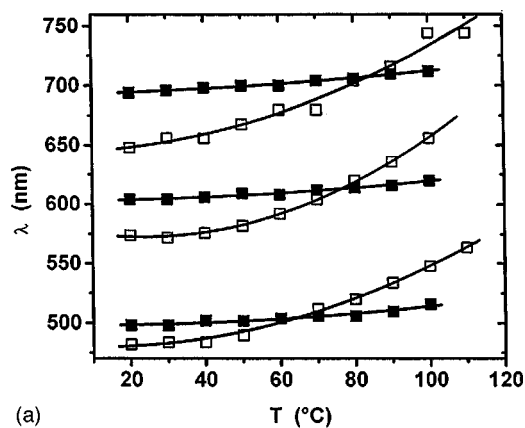
which induces a right-handed (clockwise) helical structure and is characterized by a very high helical twisting power. By varying its concentration between 10 and 20 mol %, the selective reflection can be adjusted within the entire visible range.

The optical properties of two-component mixtures of the chiral compound (3) in the nematic hosts (1) and (2) were investigated. Before polymerization, 0.9 wt % of a photoinitiator (Irgacure 651, Ciba Geigy) was added. The respective mixture was cast on a glass slide, heated to the isotropic state, and covered with a second glass slide. After cooling

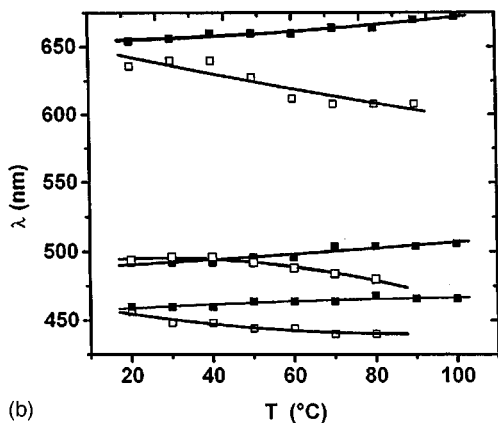
below the clearing point, a uniform Grandjean texture was achieved by shearing. The polymerization is initiated with a metal halogen UV lamp (UV type A). The distance between lamp and sample was about 40 cm, the intensity 10 mW/cm² in the range 320–400 nm. The reflection spectra of both the monomer mixtures and the polymer films were measured using a diode array spectrophotometer (Photo Research, model PR650). For reflectivity measurements, the spectra were divided by the lamp spectrum. Uncorrected spectra were used to calculate the chromaticity coordinates. In order to test the optical storage capability, we exposed only parts of the sample to the UV radiation using a mask.

III. RESULTS AND DISCUSSION

Monomer mixtures with red, green, and blue selective reflection were prepared (Table I). The Bragg wavelength of the monomer mixture can be adjusted by choosing an appropriate concentration of the chiral dopant (3). All the monomer mixtures show a distinct temperature dependence of the Bragg wavelength (Fig. 1). Surprisingly, the respective temperature coefficient is positive for mixtures of the compounds (1) and (3), but negative for mixtures of the compounds (2) and (3). A negative temperature coefficient of the cholesteric pitch is typical for systems which show a smectic phase at lower temperatures. Thus, we speculated that mixtures of the compound (2) are more likely to form smectic phases than the mixtures of compound (1). For all investigated mixtures, the photopolymerization leads to highly crosslinked polymer networks which are very stable and show a temperature independent selective reflection (Fig. 1). The wavelength of the selective reflection of the polymer depends on the temperature at which the sample was polymerized, e.g., the Bragg wavelength of the sample PR₂₇₀^{°C} which was photopolymerized at 70 °C is 44 nm smaller than the Bragg wavelength of the sample PR₂₃₀^{°C} which was obtained from the same monomer mixture (MR2) by polymerization at 30 °C (Table I).



(a)



(b)

FIG. 1. Temperature dependence of the Bragg wavelength. (a) Mixtures of the compounds (1) and (3). The curves with open squares show the temperature dependencies of the monomer mixtures MR1, MG1, and MB1 (Table I). The solid squares indicate the values for the respective polymer mixture PR1, PG1, and PB1. (b) Mixtures of the compounds (2) and (3). As in (a), the curves with open symbols show the temperatures dependencies of the monomer mixtures (MR2, MG2, MB2). Solid squares correspond to samples polymerized at 30 °C (PR_{230 °C}, PG_{230 °C}, PB_{230 °C}).

The spectral bandwidth of the reflection spectra and the maximum reflectivity depend mainly on the quality of the alignment and the sample thicknesses. Figure 2 shows the reflectivity of monomer and polymer mixtures for different

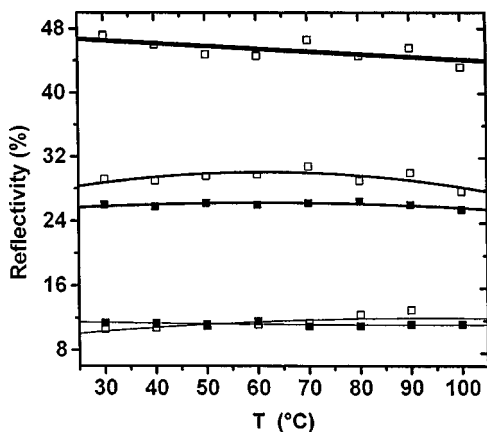


FIG. 2. Temperature dependence of the reflectivity of samples exhibiting the same composition, but different sample thickness. Thin line: sample without spacer (1–2 μm), medium: 6 μm spacer, thick line: 50 μm spacer. Lines with open squares correspond to the monomer mixture, solid squares correspond to the respective polymer.

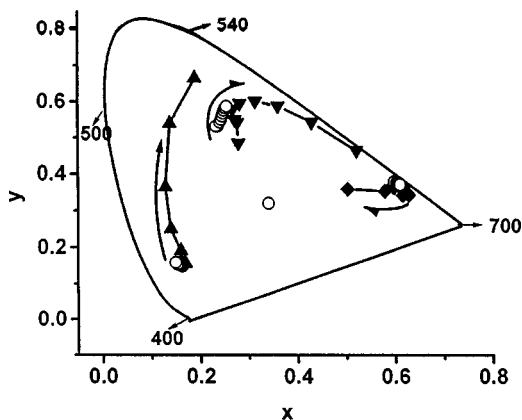


FIG. 3. Chromaticity coordinates of the reflectivity. (♦) Sample MR1 (Table I), (▼) MG1, (▲) MB1, (○) respective polymers (PR1, PG1, PB1).

samples thickness of mixtures with component (1). The reflected intensity at the Bragg wavelength was divided by the intensity of the incident linearly polarized light. We expect a maximum value of 50% for the reflectivity shown in Fig. 2, because only right circularly polarized light of the incident light is reflected by the cholesteric sample. Thin samples (1–2 μm) without spacer show a much smaller reflectivity, whereas the 50 μm sample is in the saturation range. For a sample without spacer and a sample with 12 μm nominal thickness, the reflectivity of the polymer (squares in Fig. 2) is the same as the reflectivity of the respective monomer mixture (curves with open squares). This behavior indicates that the uniform alignment of the pitch axis perpendicular to the substrates is maintained during the polymerization. The spectral bandwidth of the selective reflection was found to be between 50 and 70 nm. This is in good agreement with the expectation $\Delta\lambda/\lambda = \Delta n/n$ which is valid for large sample thickness.

In order to characterize the subjective color impression of the reflecting polymer films, we calculated the chromaticity coordinates corresponding to the reflection spectra (Fig. 3). It can be seen that the chromaticity coordinates are close to the coordinates of pure spectral colors. The three curves in Fig. 3 show the shift of the chromaticity coordinates due to the temperature dependence of the selective reflection. These curves demonstrate that a large variety of colors is accessible. Three polymer films obtained from the three monomer mixtures show only little variations of their chromaticity coordinate because of the temperature-independent wavelength of selective reflection (open circles).

The possibility of freezing the cholesteric structure in a permanent, rigid state due to the photopolymerization gives rise to interesting optical storage effects (Fig. 4). If only a part of the monomer sample is exposed to UV radiation, the unexposed part remains in the monomer state and can be polymerized under different conditions, e.g., at a different temperature. For the second exposure, one may choose a temperature below or above the clearing point (Fig. 4). In the first case, two regions with different wavelength of selective reflection occur. In the latter case, regions with and without selective reflection appear. Similar effects have been reported previously for cholesteric gels¹⁷ or polymerized lyo-

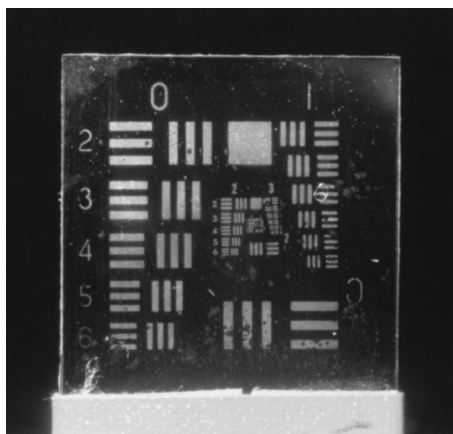


FIG. 4. Samples polymerized using chromium masks. Mixture containing 88 mol % of compound (1) and 12 mol % of compound (3). Polymerization temperatures are 20 and 130 °C.

tropic systems²⁰ or other systems based on cellulose derivatives.²¹ For our system, we tested the spatial resolution of the optical storage effect using a chromium mask which shows striped patterns with different spacings. A grating with a period of 30 μm was well resolved by the different regions occurring in our sample. This resolution could only

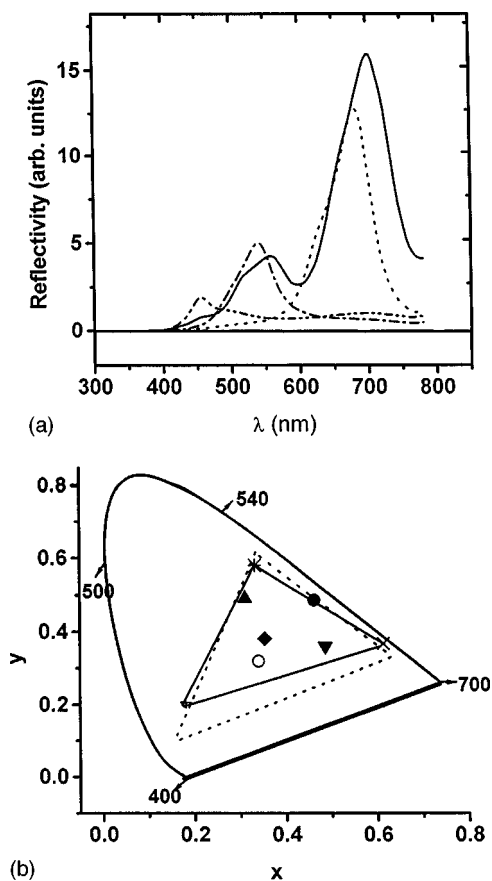


FIG. 5. (a) Reflectivity spectra of the separate polymer films (broken lines) and the stack of three films (solid line). (b) Chromaticity coordinates of the polymers made of compounds (1) and (3). (*) Separate films, (\diamond , \bullet , ∇ , \blacktriangle) stacks of two or more films. The triangle of solid lines indicate the range of colors accessible with our cholesteric films. The dashed triangle shows the range of a commercial television set for comparison.

be obtained in samples without photoinitiator, for which a longer exposure time >6 min was necessary. We suppose that even the low intensity of the scattered light in the shadow of the mask is sufficient to initiate the radical reaction in mixtures which contain the photoinitiator.

For a good spatial resolution, it is necessary to minimize the distance between the mask and the liquid crystal layer. Thus, eventually, we tried to polymerize thin cholesteric films with a free surface and adjusted the distance between the mask and the sample by glass spacers. In this case, we found that the polymerization can be initiated only if the sample is held in an argon atmosphere. Since O_2 captures radicals, it is essential for this radical polymerization reaction to exclude oxygen. Instead of using a mask, a holographic setup was successfully applied to generate gratings with a period of a few μm .

Since cholesteric films are transparent for the light which is not selectively reflected, it is possible to stack several films on top of each other, either in order to read the information from the films separately using a wavelength multiplexing scheme¹⁰ or in order to add the colors reflected from different films, thereby mixing colors. In order to test the latter possibility, we measured the reflectivity spectra and color coordinates of stacked films. The latter were obtained in the following way. A cholesteric sample between two orienting glass substrates was polymerized and one of the substrates was removed after polymerization. Subsequently, another monomer mixture was placed on the remaining substrate, partially coating the first polymer film, and covered with a new glass substrate. Then, the sample was exposed to UV radiation again. Examination of the films shows that the reflection spectrum of two stacked films is approximately the sum of the reflection spectra of the two separate films [Fig. 5(a)]. Consequently, additive color mixing of the light reflected from stacked cholesteric polymer films is possible. The chromaticity coordinate corresponding to the reflection spectrum of a stack of films is a linear combination of the chromaticity coordinates of the separate films [Fig. 5(b)]. Thus, three basic colors can be used in order to achieve any color within the triangle formed by their respective chromaticity coordinates. The range accessible by our cholesteric films is quite promising for achieving a large variety of colors.

IV. CONCLUSION

The presented results indicate that the chiral mixtures of mesogenic twin molecules with acrylate groups are suitable to get stable, highly crosslinked polymer films exhibiting the well-known selective reflection of circularly polarized light. To optimize the color effect, it is necessary to use a medium cell thickness $d \approx 10\text{--}20 \mu\text{m}$. In samples without photoinitiator, it is possible to generate fine patterns by using a mask and polymerizing different parts of the sample at different temperatures. The half width of the selective reflection bands shows that wavelength intervals of $\Delta\lambda = 50\text{--}70$ nm are reasonable for applications which require wavelength multi-

plexing. The chromaticity coordinates are promising for achieving a variety of reflection colors due to additive color mixing.

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