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SYNTHESIS AND OPTICAL CHARACTERIZATION OF CHOLESTERIC POLYMER NETWORKS

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Abstract The synthesis of some novel chiral liquid crystalline diacrylates and triacrylates is described. Photopolymerization of mixtures with nematic di- and triacrylates leads to polymer networks in which the helical structure of the cholesteric mesophase is frozen in. The reflection wavelength of the cholesteric phase is controlled by the composition of the mixtures and was determined by UV-VIS spectroscopy. The angular dependence of the reflection wavelength of the polymer networks and the corresponding colorimetric coordinates were evaluated.

INTRODUCTION

Among the different types of liquid cyrstalline (LC) mesophases the cholesteric phase plays an important role because of their ability to selectively reflect circular polarized light[1]. If the reflection wavelength is in the visible range of the spectrum, the mesophase appears coloured. The wavelength of the maximum reflection (λ_R) is related to the pitch p of the cholesteric helix by

$$\lambda_R = \bar{n}\, p \qquad (1)$$

where $\bar{n}$ is the average refractive index of the cholesteric phase.

The appearence of cholesteric phases is not limited to chiral mesogenes. Cholesteric phases can also be induced by adding chiral dopants to a nematic phase[2]. In this case the pitch of the helix p is inversely proportional to the concentration of the chiral dopant x_{ch}. β is called the helical twisting power (HTP).

$$\frac{1}{p} = \beta\, x_{ch} \tag{2}$$

For many electro - optical applications it is necessary to stabilize the cholesteric mesophase by dispersing low molecular weight liquid crystals in a polymer matrix[3] or by covalent fixation of the mesogenes in side chain LC-polymers[4,5]. Low molecular weight LCs can be dispersed in a polymer matrix to obtain polymer - dispersed liquid crystals (PDLC) which possess higher stability against shock and other types of cell deformation. Such systems are nowadays used in reflective colour displays[6]. Variations of the PDLCs are anisotropic gels where a small amount of a mesogenic monomer is dissolved in a nematic or cholesteric LC and crosslinked by photopolymerization. This kind of LCs can be used for optical storage[7] or electro-optical device applications[8].

In densely crosslinked cholesteric polymer networks obtained by photopolymerization of cholesteric diacrylate mixtures, the cholesteric structure is permanently frozen-in[14]. These networks exhibit no temperature dependence of the reflection wavelength. They can be used for decorative purposes and in passive optical components like reflection colour filters.

In this paper we describe the synthesis of densely crosslinked polymer networks from mixtures of nematic and cholesteric di- and triacrylates. We investigated the dependence of the reflection wavelength from the content of the chiral dopant. Furthermore the angular dependence of the reflection wavelength and the colorimetric coordinates have been determined.

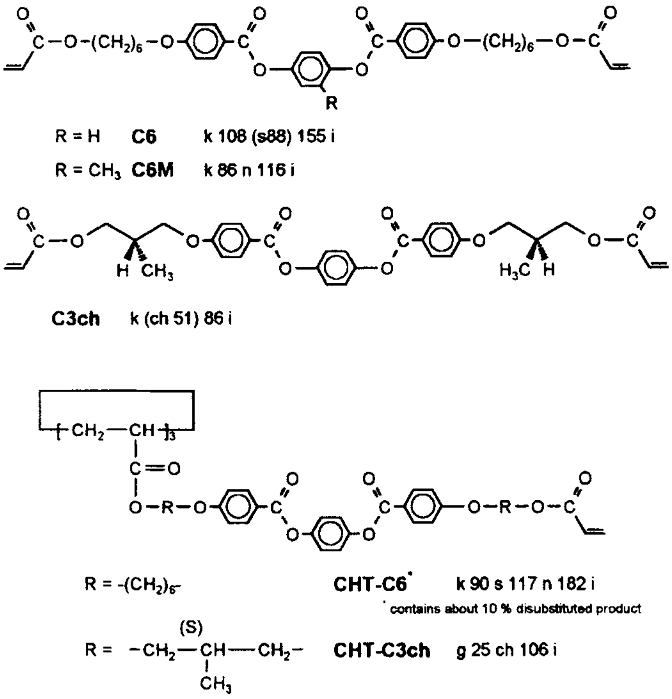
EXPERIMENTAL

The chemical structures of all monomers used throughout this study are shown in scheme 1. Cholesteric networks were prepared by adding 2 wt% of 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651, Ciba Geigy) as photoinitiator and 0.5 wt% sulfur as stabilizer to a mixture of the corresponding di- and triacrylates. After a uniform Grandjean texture is obtained by shearing the mixtures between two glass slides, the photopolymerization was initiated with a 150 W Xe arc lamp. A precision hot stage (Gestigkeit PZ 28-2) was used to insure polymerization at a well defined temperature. UV-VIS absorption spectra were taken with a Hitachi U-3000 UV-VIS spectrometer. For reflection measurements an Instruments Systems Optische Meßtechnik Spectro 320 UV-VIS spectrometer equipped with a goniometer was used. A Perkin Elmer DSC 7 was used to determine the phase transition temperatures of the monomers.

RESULTS AND DISCUSSION

Synthesis of the monomers

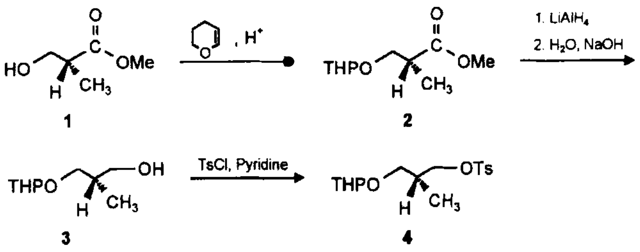
The chemical structures of the LC diacrylates and triacrylates used in this study are shown in scheme 1. The synthesis of the nematic diacrylates **C6** and **C6M** has already been described[9,10]. The synthesis of the chiral tosylate **4** which is used for the chiral C3-spacer in the diacrylate **C3ch** and triacrylate **CHT-C3ch** is outlined in scheme 2. The synthetic pathway ensures the retention of the configuration without appreciable reduction of the optical purity of the starting material. According to the known synthesis of a chiral C2-spacer starting from ethyl lactate[11], we first protected the hydroxyl group by adding dihydro-2H-pyran to **1** under acid catalysis. After reduction of the ester group and tosylation of the resulting alcohol **3** the chiral tosylate **4** is obtained. It is used to form the corresponding acid **6** by reaction with ethyl 4-hydroxybenzoate, followed by hydrolysis of the ester and cleavage of the hydroxyl protecting group (scheme 3).



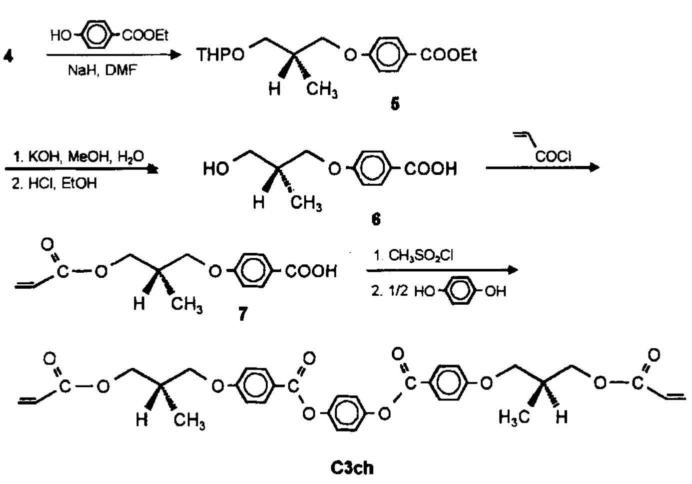
SCHEME 1 Chemical structures and phase transition temperatures of the LC di- and triacrylates

After formation of the acrylate - containing acid 7 by reaction with acryloyl chloride, the chiral diacrylate mesogene **C3ch** is formed by esterification of 7 with hydroquinone.

Scheme 4 shows the synthesis of the nematic and chiral triacrylates based on cyclohexane tricarboxylic acid. Hydroquinone with one hydroxyl group protected as tetrahydropyranyl ether is esterified with the acrylate containing acids **7a** and **7b**. Cleavage of the hydroxyl protecting group yields the phenoles **10a** and **10b**, which are esterified with the THP - protected acids **9a** and **9b**. After deprotection of the hydroxyl groups **11a** and **11b** are obtained. Reaction of **11a** and **11b** with an isomeric mixture of 1,3,5 - cyclohexane tricarboxyloyl chloride yields the desired triacrylates **CHT-C6** and **CHT-C3ch**, respectively.



SCHEME 2 Synthesis of the chiral C3-spacer

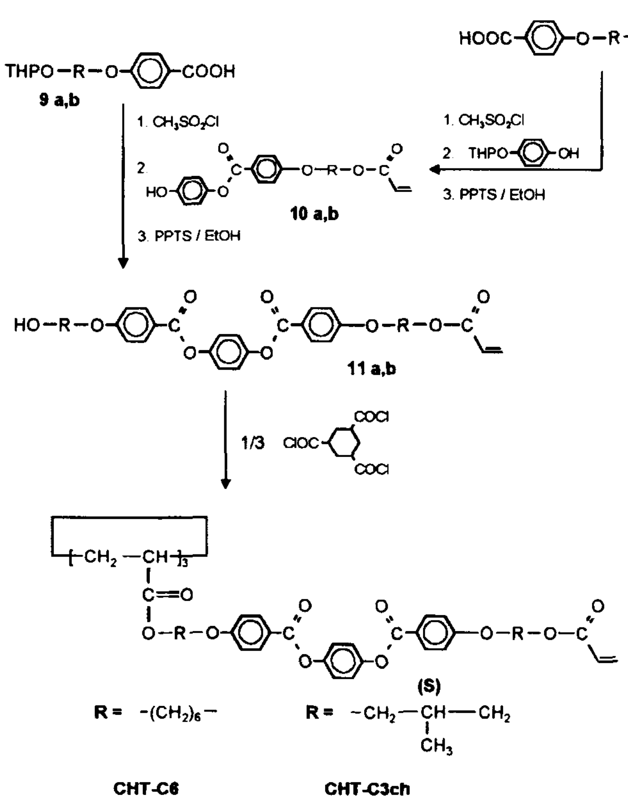


SCHEME 3 Formation of the chiral triacrylate **C3ch**

Cholesteric polymer networks

For the investigation of the wavelength dependence from the content of the chiral dopant x_{ch}, mixtures of nematic and chiral acrylates were made. These mixtures were placed between two glass slides. After heating to the isotropic state, the mixtures were cooled to the polymerization temperature by placing the sample on a precision hot stage. The polymerization of the mixture was initiated by UV irradiation. By this procedure, densely crosslinked networks with a helical structure are obtained.

In table 1 the composition of the networks and the polymerization conditions are summerized.



SCHEME 4 Syntheses of the nematic and chiral triacrylates **CHT-C6** and **CHT-C3ch**

Figure 1 shows the reflection wavelength λ_R and the inverse reflection wavelength λ_R^{-1} at room temperature as a function of the **CHT-C3ch** concentration in **NW III** The reflection wavelength λ_R decreases with increasing content of the chiral triacrylate **CHT-C3ch** as theoretically predicted by eq. 2.

The inverse reflection wavelength λ_R^{-1} shows a linear dependence for small amounts of **CHT-C3ch** up to $x_{ch} \approx 0.4$. At higher contents of the chiral triacrylate the slope of the curve increases which is in contrast to polymer networks with cholesteryl acrylates and diacrylates where the slope decreases[12].

TABLE 1 Compositions and polymerization conditions of the networks **NW I - NW III**[a)]

Network	Nematic monomer	Chiral monomer	Polymerization temperature (°C)
NW I	**C6**	**C3ch**	115
NW II	**C6M**	**C3ch**	80
NW III	**CHT-C6**	**CHT-C3ch**	115

[a)] Irradiation time: 5 min

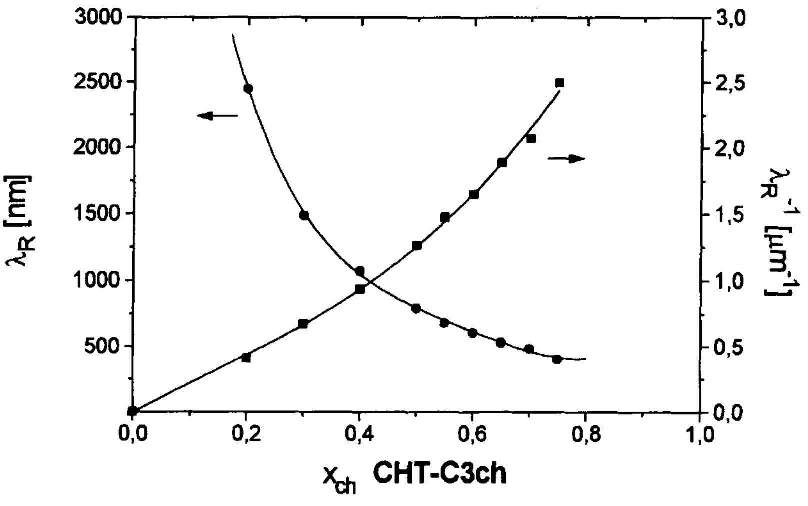


FIGURE 1 Reflection wavelength λ_R and inverse reflection wavelength λ_R^{-1} as function of x_{ch} **CHT-C3ch** in **NW III**

Another point of investigation was the angular dependence of the reflection wavelength of our cholesteric polymer networks. For this purpose we recorded UV-VIS reflection spectra. In figure 2 the arrangement of sample, light source and detector is shown.

Figure 3 shows the dependence of the maximum of reflection from the viewing angle β in **NW III** with different amounts of **CHT-C3ch**. The spectra in figure 3 (b) were recorded with fixed angle of illumination (α = - 60°), whereas the curves in figure 3 (a) are valid for a moved light source and moved detector 15° of gloss (- α = β + 15°).

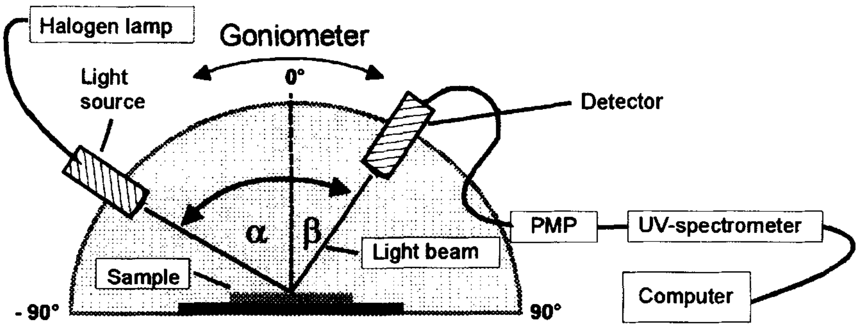


FIGURE 2 Determination of the reflection wavelength.

Note the definition of the illumination angle α and the observation angle β: α counts counterclockwise and β clockwise!

For the wavelength dependence of the maximum reflection λ_R equation (3), which corresponds to Bragg's law applies (γ is the angle between helix axis and incidence)

$$\lambda_R(\gamma) = \bar{n}\, p \cos\gamma \qquad (3)$$

In reality not all helix axes are oriented perfectly perpendicular to the surface but exhibit an orientation distribution. If we consider an air - LC boundary, cholesteric reflection is obtained for α ≠ β, too. The dependence of λ_R from α and β, the angles of incidence and observation, is then given by (4)[1,13]:

$$\lambda_R(\alpha,\beta) = \bar{n}\, p \cos\left\{\frac{1}{2}\left[\arcsin\left(\frac{\sin\alpha}{\bar{n}}\right) + \arcsin\left(\frac{\sin\beta}{\bar{n}}\right)\right]\right\} \tag{4}$$

Figure 3 (a) shows that the variation of λ_R with changing viewing angle becomes smaller if we go from red to green and finally to blue cholesteric networks. This is also the case for a fixed illumination source (ref. figure 3 b).

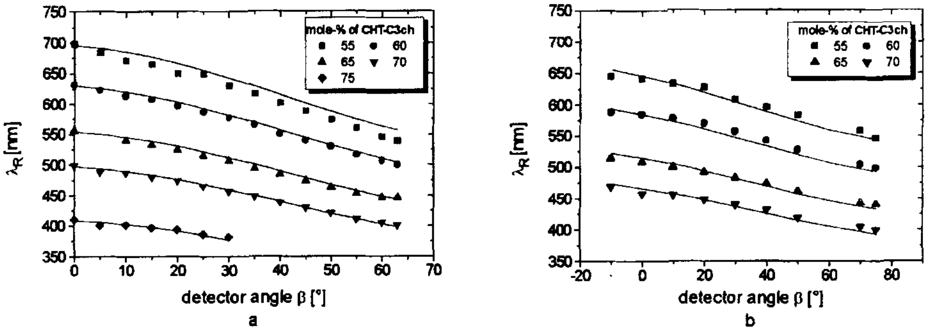


FIGURE 3 Reflection wavelengths of **NW III** with various amounts of **CHT - C3ch**

(a) Angle of illumination (α) and observation (β) are 15° of gloss

(b) Variation of λ_R with the observation angle (β) of observation for a fixed angle of illumination

Comparing the two cases of moved and fixed illumination for the same network composition, one observes that the starting wavelength is always smaller in the second case.

In both cases the experimental values fit well with the calculated lines using equation (4), assuming a refractive index $\bar{n}$ of 1.55. So the cholesteric polymer networks show the same behavior as low molar mass cholesterics with respect to the angular dependence of the reflection wavelength[1]. This is a prove that the optical properties of the cholesteric monomer mixtures are not destroyed during photopolymerization of the di- and triacrylates. The optical properties of the monomer LCs are fully transfered to the highly crosslinked polymer networks.

Integration of the reflection spectra from 380 to 780 nm delivers the colour coordinates x,y of the samples according to DIN 5033 (CIE 1931). Figure 4 shows the change of the colour coordinates of three different cholesteric networks **NW III** for the case of moving light source and moving detector.

As the spectral bandwidths of the samples are quite narrow (typically ≈ 50 nm) the chromaticity loci are close to those of monochromatic light. Only for large angles the colour moves in the direction of the light source E.

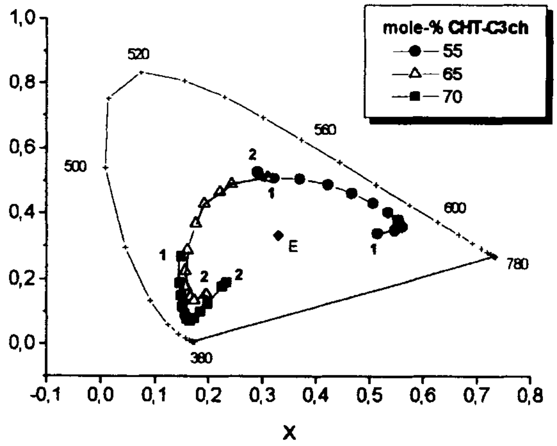


FIGURE 4 Colour coordinates according to DIN 5033 (CIE 1931) for three **NW III** (moved light source and moved detector 15° of gloss ref. figure 3a). 1 indicates the starting point of the detector at 0°, 2 the end point.

This effect can be explained qualitatively: with increasing illumination angle the specular reflection at the air - LC boundary increases and so the amount of light which is reflected by the cholesteric decreases. So the portion of white light added to the reflection colour of the cholesteric increases leading to a desaturation of the colour and to coordinates closer to the white light source E.

CONCLUSIONS

The mesogenic diacrylate **CHT-C3ch** with two chiral spacers exhibits a monotropic cholesteric phase. It can be used as dopant for the nematic diacrylates **C6** and **C6M** to induce an enantiotropic cholesteric phase over a wide monomer composition. Further stabilization of the cholesteric phase of the pure chiral monomer is achieved by attaching three mesogenes to a cyclohexane tricarboxylic acid core (**CHT-C3ch**).

Mixtures of the novel chiral di- and triacrylates with nematic di- and triacrylates show reflection in the visible region. The colour can be varied over the whole visible range by changing the monomer composition.

Photopolymerization of the mixtures leads to cholesteric polymer networks with the same optical properties as the corresponding low molar mass cholesterics. In these networks the cholesteric phase is permanently frozen - in. Such materials can be used as passive optical components such as reflection colour filters or for decorative purposes.

Acknowledgement

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