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POLYMER NETWORKS CONTAINING CHOLESTERYL COMPOUNDS OF DIFFERENT FUNCTIONALITY

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ABSTRACT

The synthesis of densely crosslinked polymer networks with a helicoidal structure from various cholesteryl compounds is described. By mixing nematic diacrylates with cholesteryl compounds of different functionality, cholesteric phases are obtained. The reflection wavelength can be varied by the composition of the mixture. Isothermal photopolymerization leads to crosslinked networks with different fixation of the cholesteryl compounds to the network depending on their functionality. The influence of temperature and organic solvents on the reflection wavelength as well as the angular dependence of the reflection wavelength have been investigated.

INTRODUCTION

Among the liquid crystalline (LC) compounds used in optical applications, cholesteric materials play an important role because of their interesting optical properties such as the selective reflection of circularly polarized light [1]. The wavelength maximum of the reflected light (λ_m) for perpendicular incidence is given by:

$$\lambda_m = \bar{n}p \tag{1}$$

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

Cholesteric mesophases are usually induced by adding chiral molecules to nematic compounds. With increasing amount of the chiral dopant, the pitch of the cholesteric helix and therewith the reflection wavelength decreases. So the color can be varied by changing the amount of chiral dopant.

In recent years, cholesteric polymer networks have achieved increasing interest [2–6]. Such anisotropic films are made by adding chiral molecules to nematic diacrylates, resulting in a cholesteric monomer mixture which is subsequently photopolymerized in the ordered cholesteric mesophase. After polymerization, networks with a frozen-in helicoidal structure are obtained. Since the chiral dopants usually have no polymerizable groups, they are not covalently bound to the polymer network.

Low molar mass cholesterics show a strong temperature dependence of the reflection wavelength, which can be used to manufacture thermometers. In contrast to low molar mass compounds, cholesteric side-chain polymers exhibit only a weak temperature dependence of the reflection wavelength below their glass transition temperature. In densely crosslinked cholesteric polymer networks, the reflection wavelength and therewith the color of the films is temperature independent, what makes them excellent candidates for the use in passive optical components [3]. Cholesteric networks containing free chiral molecules have been tested in optical storage applications [5] and for electrically induced color changes [6].

In this paper we describe the synthesis of densely crosslinked cholesteric polymer networks with three different cholesteryl compounds. The networks were prepared by in-situ photopolymerization of a LC mixture containing a nematic diacrylate and cholesteryl compounds without and with one and two acrylate groups.

The cholesteric networks show reflection in the whole visible range. The dependence of the reflection wavelength on the amount of added cholesteryl compound as well as the temperature and angular dependence of the reflection wavelength are described.

EXPERIMENTAL

Synthesis

Ethyl 3,4-dihydroxybenzoate was purchased from ABCR; the other chemicals were from Fluka or Aldrich. Acryloyl chloride was distilled twice before use. Toluene was dried over potassium. All other chemicals were used without further purification.

The syntheses of 1,4-di-(4-(6-acryloyloxyhexyloxy)benzoyloxy)benzene **1a** and 1,4-di-(4-(6-acryloyloxyhexyloxy)benzoyloxy)-2-methylbenzene **1b** have been described elsewhere [7, 8].

Cholesteryl Acrylate **3**

According to the procedure described in [9], cholesteryl acrylate **3** is obtained only in low yield. Here we present an improved procedure for the preparation of **3**.

To a solution of 7.73 g cholesterol, 3.81 mL *N*,*N*-dimethylaniline and 40 mg of 2,6-di-*tert*-butyl-*p*-cresol (inhibitor) in 50 mL of dry toluene, and 2.44 mL of freshly distilled acryloyl chloride dissolved in 10 mL dry toluene were added dropwise at room temperature. After stirring for 1 hour, a white precipitate was formed.

The temperature was raised to 80°C and the mixture was stirred for another 17 hours. After removal of the solvent, the residue was dissolved in 100 mL $CHCl_3$. The organic phase was washed twice with 50 mL saturated sodium hydrogen carbonate solution and with 50 mL water. After removal of the solvent the residue was recrystallized from 150 mL ethanol to give colorless crystals (yield: 85%).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 2936, 2907, 2886, 2868, 2862, 2820, 1717 (C=O), 1639 (C=C), 1466, 1410, 1298, 1206, 984, 966, 804.

^1H NMR (DMSO) δ (ppm): 0.67 (s, 3H, Chol-H), 0.8–1.0 (m, 11 H, Chol-H), 1.2 (s, 3H, Chol-H), 1.5–2.1 (m, 24 H, Chol-H), 2.35 (m, 2H, Chol-H), 4.65 (m, 1H, Chol-H), 5.35 (m, 1H, Chol-H), 5.77 (dd, 1H, OCOCH=CH_2), 6.08 (dd, 1H, OCOCH=CH_2), 6.35 (dd, 1H, OCOCH=CH_2).

Ethyl 3,4-Di-[2-(tetrahydro-2-pyranyloxy)ethoxy]benzoate **7**

A mixture of 12.75 g ethyl 3,4-dihydroxybenzoate **5**, 24.8 g 1-chloro-2-(tetrahydro-2-pyranyloxy)ethane **6**, 38.7 g potassium carbonate, and 2.0 g potassium iodide in 250 mL cyclohexanone was refluxed with vigorous stirring for 5 hours. The solution was hot filtered and the solvent was removed under reduced pressure. The crude oil was used without further purification.

3,4-Di-(2-hydroxyethoxy)benzoic Acid **8**

The crude ester **7** was dissolved in 250 mL methanol and a solution of 15.71 g KOH in 30 mL water was added. Then the mixture was refluxed for 17 hours. After removing the methanol, the residue was dissolved in 200 mL of 0.5 N NaOH and washed three times with 80 mL diethylether. The water phase was acidified with concentrated HCl whereby a precipitate was formed. To remove the tetrahydropyranyl blocking group, the acidified mixture was refluxed for 1 hour. After removal of half of the water, **8** precipitated and was further purified by two recrystallizations from 100 mL water to give colorless crystals (yield: 70%).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3500–2500 (COOH), 3354 (OH), 3945, 2873, 1674 (C=O), 1598, 1589, 1517, 1442, 1309, 1278, 1232, 1141, 1085, 1043, 766.

^1H NMR (DMSO) δ (ppm): 3.7 (m, 4H, CH_2OH), 4.05 (m, 4H, ArOCH_2), 4.9 (s, 2H, OH), 7.05 (d, 1H, Ar—H), 7.5 (d, 1H, Ar—H), 7.55 (dd, 1H, Ar—H).

^{13}C NMR (DMSO) δ (ppm): 59.51, 59.58, 70.40, 70.60, 112.59, 114.29, 123.06, 123.48, 147.90, 152.55, 167.16.

3,4-Di-(2-acryloyloxyethoxy)benzoic Acid **9**

8.37 g of **8** were added to a solution of 9.33 g *N,N*-dimethylaniline in 120 mL 1,4-dioxane. At 60°C, 3.78 g acryloyl chloride were added slowly. After 2 hours of stirring, **9** was isolated by pouring the solution into 400 mL ice-water and recrystallization from 100 mL 2-butanol (colorless crystals, yield: 60%).

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3500–2500 (COOH), 2960, 2878, 1728 (C=O), 1676 (C=O), 1639 (C=C), 1588, 1526, 1443, 1415, 1302, 1278, 1232, 1196, 1143, 1055, 974, 952.

^1H NMR (DMSO) δ (ppm): 4.25 (m, 4H, ArOCH_2), 4.45 (m, 4H, CH_2-OCOCH=CH_2), 5.95 (2dd, 2H, OCOCH=CH_2), 6.15 (2dd, 2H, OCOCH=CH_2), 6.35 (2dd, 2H, OCOCH=CH_2), 7.1 (d, 1H, Ar—H), 7.5 (d, 1H, Ar—H), 7.58 (dd, 1H, Ar—H).

^{13}C NMR (DMSO) δ (ppm): 62.82, 63,05, 66.96, 67.36, 113.68, 115.74, 123.97, 124.19, 128.24, 131.96, 147.74, 152.36, 165.55, 167.08.

Cholesteryl 3,4-Di-(2-acryloyloxyethoxy)benzoate 4

2.66 g cholesterol were dissolved in 40 mL dry CH_2Cl_2 in an argon atmosphere. After adding 1.56 g dicyclohexylcarbodiimide at room temperature, the solution was refluxed for 17 hours. 2.41 g of **9** and 100 mg 4-dimethylamino pyridine were added, and refluxing was continued for an additional 4 hours. After filtration and removal of the solvent, the residue was dissolved in 150 mL CH_2Cl_2 and washed twice with 40 mL of 2 N HCl and twice with 40 mL saturated sodium hydrogen carbonate solution. After removal of the solvent, the residue was recrystallized from 80 mL 2-propanol to yield 2.34 g (47%) colorless crystals.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 2951, 2870, 2852, 1716 (C=O), 1637 (C=C), 1620, 1600, 1517, 1415, 1274, 1186, 1137, 878, 809.

^1H NMR (DMSO) δ (ppm): 0.68 (s, 3H, Chol-H), 0.8–2.1 (m, 38H, Chol-H), 2.45 (d, 2H, Chol-H), 4.26 (m, 4H, ArOCH_2), 4.5 (m, 4H, $CH_2OCOCH{=}CH_2$), 4.8 (m, 1H, Chol-H), 5.38 (m, 2H Chol-H), 5.85 (2dd 2H, $OCOCH{=}CH_2$), 6.12 (2dd, 2H, $OCOCH{=}CH_2$), 6.42 (2dd, 2H, $OCOCH{=}CH_2$), 6.9 (d, 1H, Ar-H), 7.6 (d, 1H, Ar-H), 7.66 (dd, 1H, Ar-H).

^{13}C NMR (DMSO) δ (ppm): 11.90, 18.78, 19.37, 21.15, 2.52, 22.73, 23.91, 24.33, 28.00, 28.20, 32.02, 35.80, 36.30, 36.76, 37.16, 38.35, 39,59, 39.90, 42.46, 50.27, 56.37, 56.65, 62.73, 62.97, 67.53, 68.05, 74.61, 114.17, 116.94, 122.71, 124.53, 124.80, 125.90, 128.17, 128.25, 130.96, 139.82, 148.47, 152.94, 165.37, 165.83.

Film Preparation and Measurements

LC mixtures were prepared by addition of 2 wt% 2,2-dimethyl-2-phenyl-acetophenone (Irgacure 651, CIBA Geigy) to the monomers and stabilized with 0.5 wt% sulfur. In order to thoroughly mix the compounds, the monomers, sulfur, and the photoinitiator were dissolved in methylene chloride. Then the solvent was evaporated. Samples exhibiting a Grandjean texture were prepared by melting these mixtures between two glass substrates and shearing uniaxially until a uniform orientation was obtained. Polymerization was performed under isothermal conditions using a precision hot stage (Gestigkeit PZ 28-2). The photopolymerization was initiated by irradiation for 5 minutes using a 150-W xenon high-pressure lamp (Osram XBO 150 W/s 4) with an intensity of 8 mW/cm^2.

For the detection of the reflection wavelength a Hitachi U-3000 spectrometer was used in the UV-VIS region. In the NIR region we used a Perkin-Elmer Lambda 9 UV-VIS-NIR spectrometer. The angular reflection measurements were made using an Instrument Systems Optische Messtechnik Spectro 320 UV-VIS spectrometer equipped with a goniometer.

Differental scanning calorimetry (DSC) was carried out using a Perkin-Elmer DSC-7. 1 wt% sulfur was added to the samples in order to prevent thermal polymerization.

To investigate in the influence of organic solvents on the reflection wavelength of the polymer films, they were treated with methylene chloride or toluene for 10 minutes. After drying the films in vacuum at 40°C, UV-VIS spectra were recorded.

RESULTS AND DISCUSSION

We have prepared three different LC networks from the nematic diacrylates **1a** and **1b** and cholesteryl butyrate **2**, cholesteryl acrylate **3** with one, and the novel cholesteryl compound **4** with two polymerizable acrylate groups. The properties of the different networks are described in the following sections.

Cholesteric Network Containing Cholesteryl Butyrate as Free Molecule

First, two cholesteric networks with free chiral molecules are described. Several examples for such networks from nematic diacrylates and nonpolymerizable chiral molecules have been published before [2, 3, 5].

The cholesteric networks were made by adding a chiral dopant to a nematic LC diacrylate and subsequent photopolymerization of the mixture in the oriented cholesteric phase. The networks are formed by the nematic diacrylate whereas the chiral dopant is incorporated as a free molecule as shown in Fig. 1.

In Scheme 1 the structures of the nematic diacrylates and chiral dopants are shown. A number of such polymer networks have already been described.

Broer [2] used a mixture of **1a** and the chiral dopant **S 811** or the eutectic blend of the nematic diacrylates **1a** and **1b** and **S 811** [3]. The amounts of the chiral

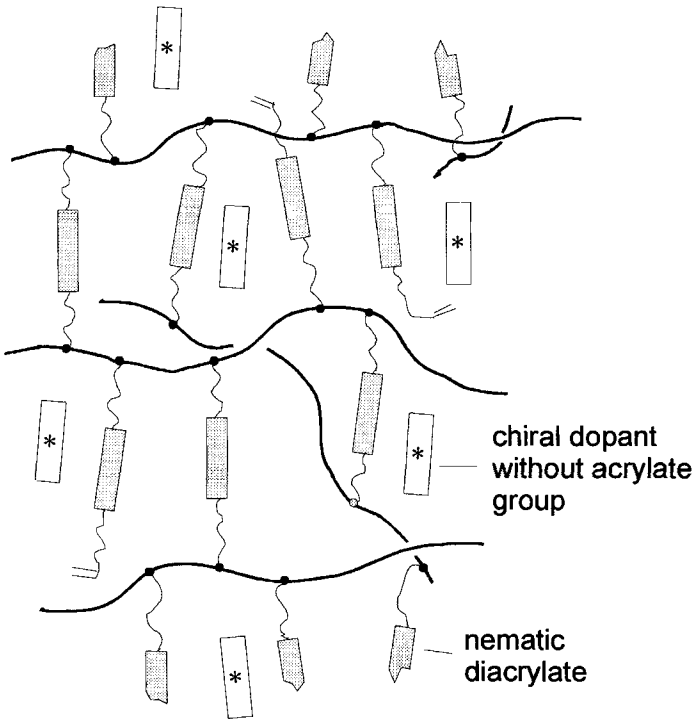
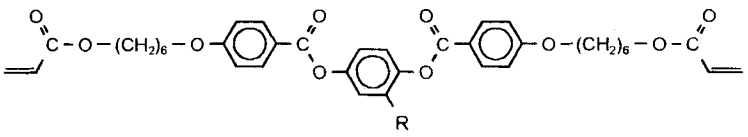


FIG. 1. Model of a cholesteric network from a nematic diacrylate and a nonpolymerizable chiral molecule.

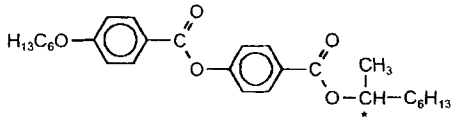
Nematic diacrylates:



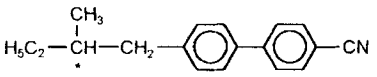
1a R = H
1b R = CH_3

	R	phase transitions [°C]
1a	H	k 108 (s 88) n 155 i
1b	CH_3	k 86 n 116 i

Chiral dopants:



S 811



CB15

SCHEME 1. Structures of the nematic diacrylates and chiral dopants mentioned in the text.

dopant were below 10 mol% in both cases. At such low concentrations the reflection wavelength of the cholesteric phase is in the IR region. It is not possible to obtain reflection in the visible region with that system since mixtures with more than 30 mol% of **S 811** exhibit no enantiotropic cholesteric phase.

Hikmet [4-6] synthesized cholesteric networks from the nematic diacrylate **1b** and the chiral dopant **CB15**. Mixtures containing 28 wt% **CB15** show visible reflection with a maximum at 560 nm and have a clearing temperature of 82°C. Increasing the amount of **CB15** leads to a further blue shift, but the clearing temperature decreases rapidly and is below room temperature at a **CB15** content above 70 wt%.

Our aim was to find monomer mixtures which can be polymerized at one single temperature over the whole concentration range and which lead to cholesteric polymer networks with a selective reflection in the visible.

To fulfill these demands, a chiral dopant must possess the following properties. It should be a mesogen itself to insure the existence of a cholesteric mesophase in mixtures with a nematic diacrylate even at high concentrations. If the helical twisting power (HTP) of the system is high enough, it is not a problem to get reflection in the whole visible range by variation of the amount of chiral compound.

Furthermore, the mesophase of the chiral molecule should be within or at least overlap with the mesophase of the nematic diacrylate. This allows for the polymerization of mixtures with varying monomer ratios at one temperature.

Cholesteryl butyrate **2**, whose structure is shown in Scheme 2, fulfills these requirements and was used in combination with the nematic diacrylate **1a** in our experiments.

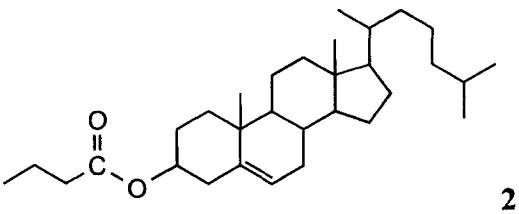
Polarizing microscopy of mixtures of **1a** and **2** showed that the whole visible range of cholesteric reflection is accessible between a content of 30 mol% (red) and 60 mol% (blue) of **2** and that all samples can be polymerized at a temperature of 115°C.

Up to a content of cholesteryl butyrate **2** of 30 mol% the polymerized films are transparent after cooling to room temperature. Using a polarizing microscope, a frozen-in Grandjean texture was observed.

With an increasing amount of **2**, the polymer films became more and more turbid. The reason is that recrystallization of the cholesteryl butyrate **2** separates it from the polymer network after polymerization. This process is reversible upon heating. The sample becomes transparent and selective reflection of the cholesteric phase is again observed. The melting and recrystallization of cholesteryl butyrate within the helicoidal network can be followed under a polarizing microscope.

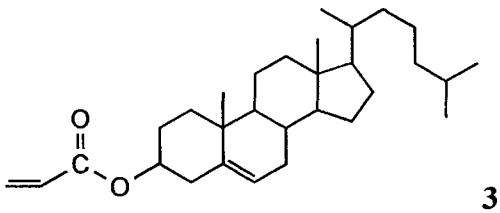
Recrystallization is one major disadvantage of networks containing free chiral molecules. Another disadvantage is that free chiral molecules can be removed from the network by evaporation or by solvents, resulting in a blue shift of the reflection wavelength, which is a major disadvantage for many applications.

Hikmet and Zwerver [5] explained this blue shift as due to a volume shrinkage of the polymer network after removal of free molecules carried out by heating the polymer film to 200°C for 15 minutes. This effect can be used for optical data storage by evaporation of volatile chiral molecules from a network with laser light [5].



2

k 102 ch 113 i [10]



3

k 121 ch 126 i [9]

SCHEME 2. Structure of cholestryl butyrate **2** and cholesteryl acrylate **3** and its phase transitions.

A change of the reflection wavelength is not desirable for cholesteric networks. As the networks are treated with solvents (for example, used as color pigments), free molecules will be washed out, resulting in a wavelength shift of the reflection.

We investigated this point by extracting the networks for 10 minutes in CH_2Cl_2. Prior to this procedure and after drying the polymer films, UV-VIS spectra of the films were recorded. The results are shown in Fig. 2 for a polymer network made from a mixture of 70% of nematic diacrylate **1a** and 30% of cholesteryl butyrate **2**. The reflection wavelength decreases from 720 nm (red) before treatment with CH_2Cl_2 to 565 nm (green) afterward. This effect can be explained as follows.

The swelling of the polymer networks in CH_2Cl_2 is accompanied by a dissolution of the incorporated cholesteryl butyrate. As a consequence of the resulting volume shrinkage, a blue shift is observed.

These two effects, turbidity of the polymer networks because of recrystallization and the change of the reflection wavelength after solvent treatment, make them unsuitable for application. So we synthesized networks where the chiral dopant has at least one polymerizable acrylate group and therefore became permanently fixed to the polymer backbone during polymerization.

Cholesteric Polymer Networks with Monofunctional Cholesteryl Derivatives

A model of a cholesteric polymer network made of a nematic diacrylate and a chiral monoacrylate is shown in Fig. 3. In order to attach the chiral molecule to the network, it must contain at least one acrylate group. We again used a cholesteryl derivative, cholesteryl acrylate **3**.

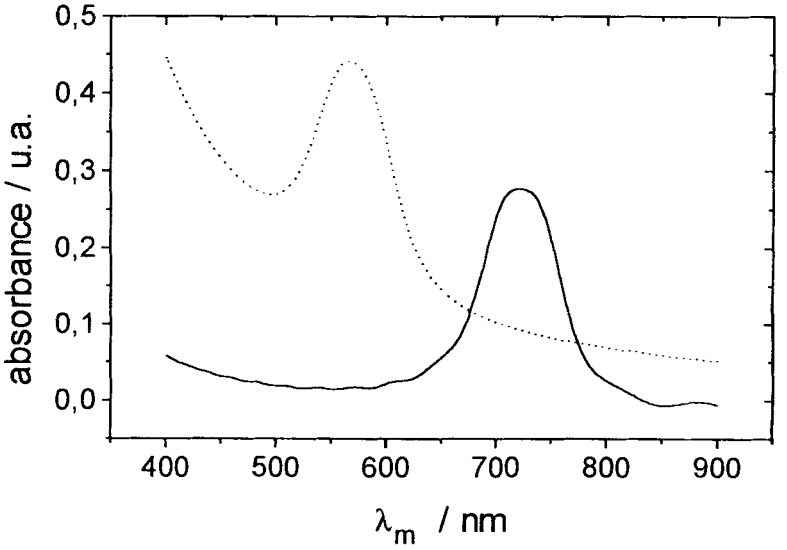


FIG. 2. Absorbance of a cholesteric network from 70 mol% of **1a** and 30 mol% of cholesteryl butyrate **2** before (——) and after (- - -) extraction with methylene chloride.

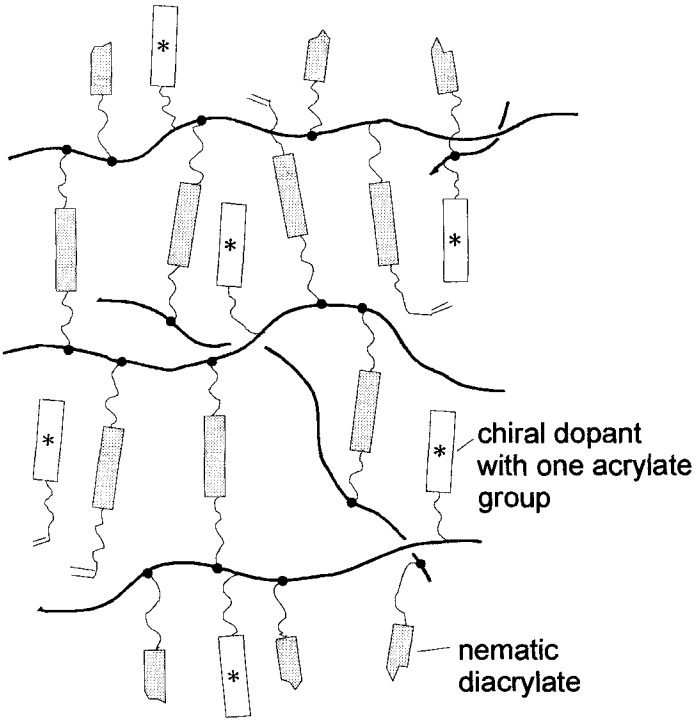


FIG. 3. Model of a cholesteric network from a nematic diacrylate and a chiral monoacrylate.

It has a cholesteric mesophase between 121 and 126°C [9], which is within the nematic phase of the diacrylate **1a**, and so a polymerization temperature of 115°C could be used for all monomer mixtures. We polymerized mixtures with a chiral dopant **3** content of from 10 to 70 mol%. In all cases transparent films were obtained after polymerization.

No clearing temperature is observed if these films are heated on the hot stage of a polarizing microscope. The networks are stable up to their thermal decomposition at about 250°C.

For application as color pigments it is advisable that the reflection color can be adjusted within the whole visible range by variation of the monomer mixtures. Figure 4 shows the reflection wavelength (λ_m) as a function of the amount of cholesteryl acrylate **3**. The inverse reflection wavelength ($1/\lambda_m$) is also included in this figure. It can be seen from Fig. 4 that the reflection wavelength of the cholesteric polymer films is inversely proportional to the amount of chiral additive **3**.

By varying the composition of the initial monomer mixture in the range between 30 and 70 mol% of **3**, the whole visible range is accessible. Because of the enhanced crosslink density in these networks, no transition to an isotropic state is observed.

The reflection color of the networks should not be affected by organic solvents. In contrast to the networks mentioned before, in which the chiral dopant is

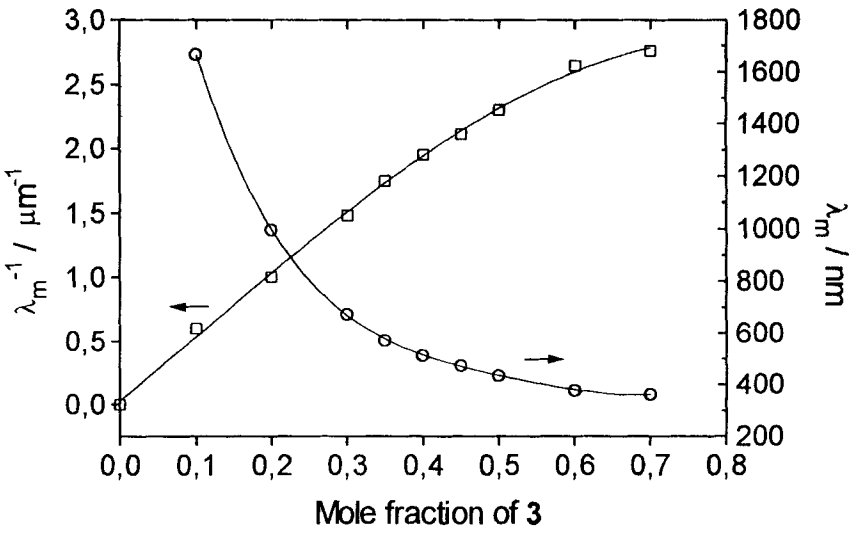


FIG. 4. Reflection wavelength (○) and inverse reflection wavelength (□) at room temperature as a function of the amount of **3** in networks with **1a**.

incorporated as a free molecule, it should be attached to the polymer network if cholesteryl acrylate is used. Therefore we expected no significant shift of the reflection wavelength after extracting the polymer films in organic solvents.

The reflection maxima of the networks before and after extraction in xylene are shown in Table 1.

Surprisingly, these networks also show a drastic change of the reflection wavelength. As in the networks with cholesteryl butyrate **2**, a shift to a shorter wavelength is observed. That means that soluble parts are still present, although the chiral dopant has a reactive acrylate group and should be attached to the network. But during polymerization the viscosity of the network increases rapidly and reaches infinity at the gel point. Consequently, not all acrylate groups are able to react. So unreacted monomer or short soluble polymer chains present are washed out during the solvent treatment. The resulting shrinkage of the network leads to a decrease of the reflection wavelength.

TABLE 1. Maximum Reflection of Cholesteric Polymer Networks with Different Monomer Ratios of **1a** and **3** Before and After Treatment with Xylene [14]

mol% 3,	λ_m (before)	λ_m (after)	$\Delta\lambda_m$
35	622	530	92
40	545	449	96
50	447	362	85

Polymer Networks Containing a Cholesteryl Derivative with Two Polymerizable Groups

In the cholesteric networks described before, the network density decreases with an increasing amount of the chiral dopant cholesteryl acrylate **3** because it has only one polymerizable acrylate group and does not participate in the crosslinking reaction. This leads to an undesirable shift of the reflection wavelength when the polymer networks are treated with organic solvents.

Keeping this in mind, we synthesized polymer networks from monomer mixtures where both the nematic and chiral monomer had two reactive acrylate groups, so we were sure to obtain densely crosslinked polymer networks at any monomer ratio.

A model of such a polymer network is shown in Fig. 5. In contrast to the crosslinked polymers described before, this network should, because of the bifunctional monomers, contain no or only negligible amounts of molecules which are not covalently bound to the network and can be washed out. Furthermore, the crosslink density does not decrease with an increasing amount of the chiral dopant, and so the mechanical properties of the network do not become worse.

In 1995 Lub described a cholesteric polymer network using a chiral diacrylate with the chiral center located in the spacer [11]. We also presented such networks [12]. Recently we made cholesteric networks from nematic and chiral triacrylates where the chiral center is situated in the spacer, too [13].

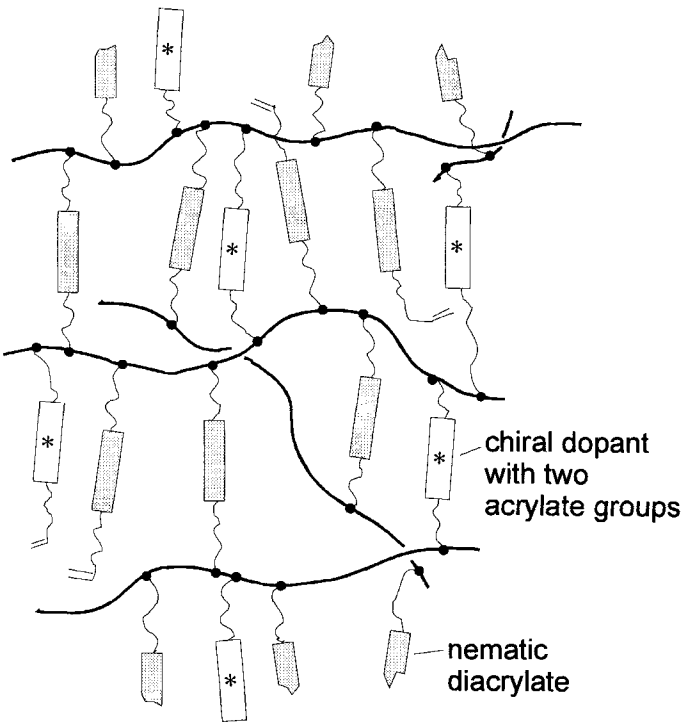


FIG. 5. Model of a cholesteric network from a nematic and a chiral diacrylate.

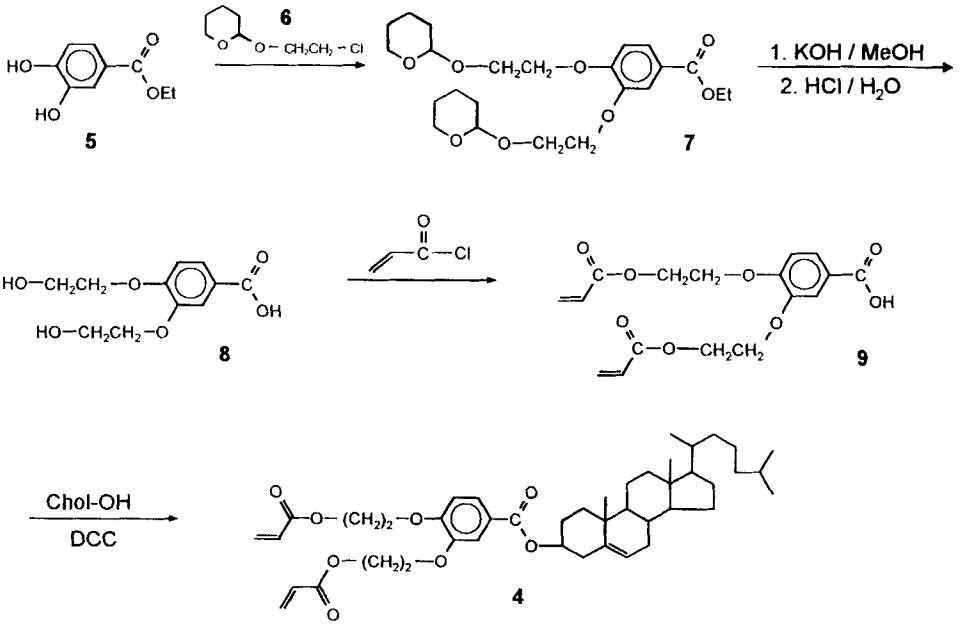
In this paper we used a novel cholesteryl diacrylate **4**. The synthesis of **4** is shown in Scheme 3.

The C2 spacers are introduced by etherification of the hydroxyl groups of **5** with tetrahydropyranyl-protected 2-chloroethanol **6**. Hydrolysis of the ethyl ester and cleavage of the tetrahydropyranyl blocking group leads to the dihydroxy acid **8**. This synthetic pathway was chosen because a direct introduction of the C2 spacer with 2-bromoethanol failed. In the next step the two hydroxy groups in **8** are esterified with acryloyl chloride to yield the diacrylate **9**. The final esterification with cholesterol using the DCC method gives the desired cholesteryl diacrylate **4**.

The diacrylate **4** exhibits a cholesteric mesophase between 73 to 99°C and was used in combination with the nematic diacrylate **1b** (k 86 n 116 i) because the mesophases of the two molecules overlap in a broad temperature range. To determine the polymerization temperature of this system, mixtures with 30, 50, and 70 mol% of **4** were made and the phase transitions were measured by DSC. The transition temperatures are summarized in Table 2. As a consequence of these measurements, we polymerized the mixtures at 80°C.

In Fig. 6 the reflection wavelength and the inverse reflection wavelength are plotted versus the mole ratio of compound **4**. The reflection wavelength decreases with an increasing amount of cholesteryl diacrylate **4**. The inverse reflection wavelength shows a linear dependence for small amounts of **4**. The curve saturates at higher contents. Compared to Fig. 4 the reflection wavelengths are shifted to longer wavelengths and the inverse reflection wavelengths are smaller.

As the HTP of cholesteryl acrylate **3** and cholesteryl diacrylate **4** are similar, two other factors can be responsible for this effect. First, the polymerization tem-



SCHEME 3. Synthesis of the cholesteryl derivative **4**.

TABLE 2. Phase Transition Temperatures of Different Monomer Mixtures of **1b** and **4**

1b, mol%	**4**, mol%	Phase transitions, °C
70	30	k 66 ch 98 i
50	50	k 60 ch 89 i
30	70	k 67 ch 84 i

perature for monomer mixtures containing **4** is lower, which leads to a red shift of the reflection. Second, nematic diacrylate **1b** has a lateral methyl side group in the core of the mesogenic unit. Therefore, the twisting power of the chiral dopant toward the nematic diacrylate is smaller compared to **1a**, again resulting in a red shift of the reflection.

Because both the nematic molecule and the chiral dopant possess two polymerizable groups, we expect no extractable material in the network. We proved this to be a fact by measuring the spectra before and after extracting the polymer films in xylene. For the polymer network containing 45 mol% of cholesteryl diacrylate **4**, the UV-VIS spectra are shown in Fig. 7. As can be seen, no shift of the reflection wavelength or broadening of the transmission band occurs. The crosslink density is high at any monomer ratio and no soluble fraction exists after polymerization.

For the use of the cholesteric polymers as decorative pigments, the angular dependence of the reflection wavelength plays an important role. If all helices are oriented perpendicular to the substrate surface, the angular dependence is given by Eq. (2) [14, 15]:

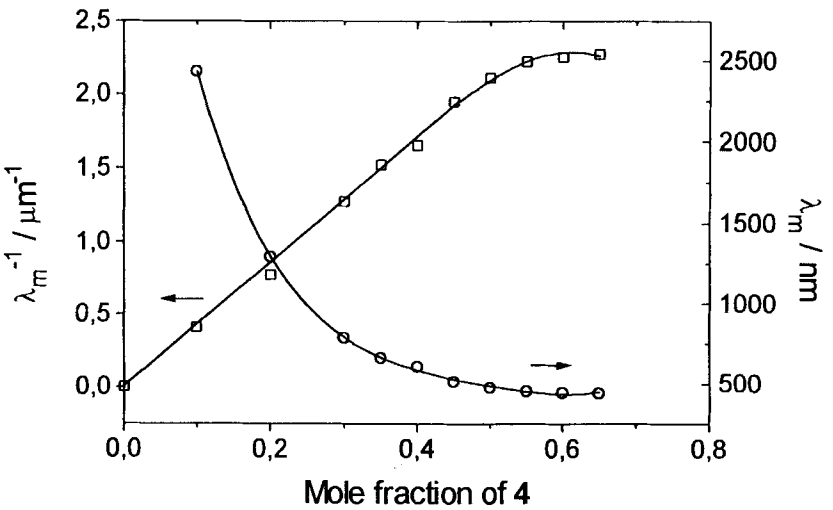


FIG. 6. Reflection wavelength (○) and inverse reflection wavelength (□) as a function of the amount of **4** in polymer networks with **1b** (at room temperature).

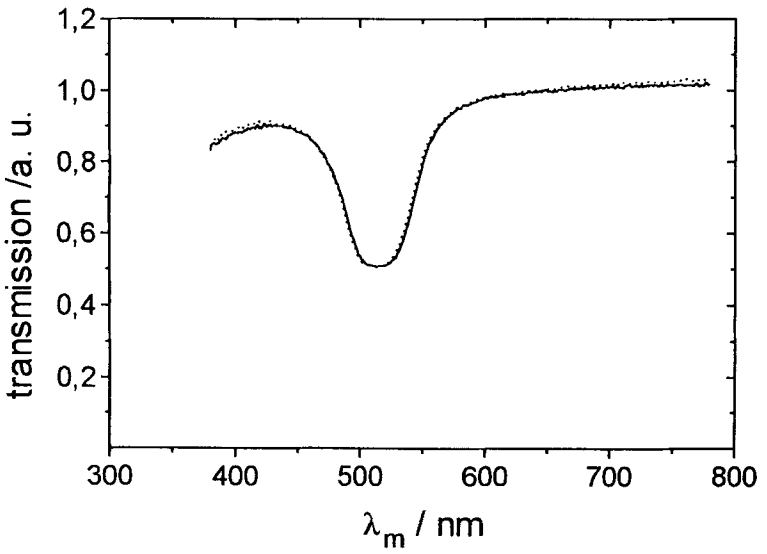


FIG. 7. Transmission spectra of a cholesteric network containing 45 mol% cholesteryl diacrylate **4** and 55 mol% **1b** before (——) and after (- - -) extraction in xylene.

$$\lambda_m = \bar{n}p \cos \gamma \tag{2}$$

where λ_m is the reflection wavelength, $\bar{n}$ is the average refractive index of the cholesteric phase, p is the pitch of the helix, and γ is the angle between the helix axis and the direction of observation.

In reality, not all helices are oriented ideally perpendicular to the surface, but are slightly tilted. The angular dependence is then described by Eq. (3) [1, 16]:

$$\lambda_m(\alpha,\beta) = \bar{n}p \cos\left\{\frac{1}{2}\left[\arcsin\left(\frac{\sin\alpha}{\bar{n}}\right) + \arcsin\left(\frac{\sin\beta}{\bar{n}}\right)\right]\right\} \tag{3}$$

where α is the angle of incidence, β is the viewing angle, p is the pitch of the cholesteric helix, and $\bar{n}$ is the average refractive index of the cholesteric phase.

We measured the angular dependence of the reflection wavelength of such densely crosslinked cholesteric polymer networks with different amounts of the cholesteryl diacrylate **4**. To exclude spectral reflectance, the samples were measured in an arrangement of light source and detector 15° of gloss (see Fig. 8).

The results of the measurements are shown in Fig. 9. In the polymer film containing 35 mol% of the cholesteryl derivative **4**, the reflection maximum changes from 691 mm at 0° detection angle to 549 nm at 60°, whereas at a 55 mol% content of **4** it only changes from 473 to 393 nm.

That means that the spectral change of the reflection wavelength with varying viewing angle decreases with decreasing pitch of the cholesteric helix. In the example shown, the shift is 142 nm in a polymer film containing 35 mol% of **4** and only 80 nm in the film with 55 mol% of **4**.

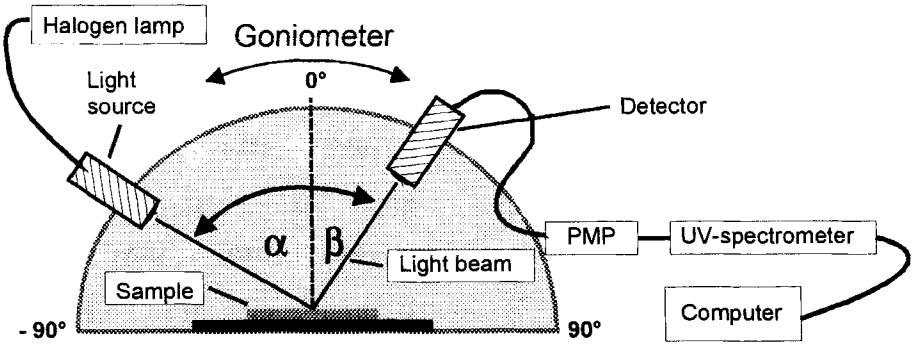


FIG. 8. Arrangement of sample, light source, and detector for reflection measurements.

The reflection maxima can be fitted with Eq. (3). As can be seen from Fig. 9, there is good agreement between the measured and the calculated values if we assume a $\bar{n}$ of 1.5, which is common for cholesteric phases of the type we used [1].

The good agreement shows that there is no difference in the optical properties of low molar mass cholesterics for which Eq. (3) has been deduced and cholesteric polymer networks. The helicoidal structure of the monomer mixture is not destroyed during rapid photopolymerization of the acrylate groups. It is frozen-in permanently in the polymer networks without loss of the optical properties.

In order to determine the temperature dependence of the reflection wavelength of the polymer networks, we recorded UV-VIS spectra for different temperatures from room temperature to 100°C. The result of this measurement is shown in Fig.

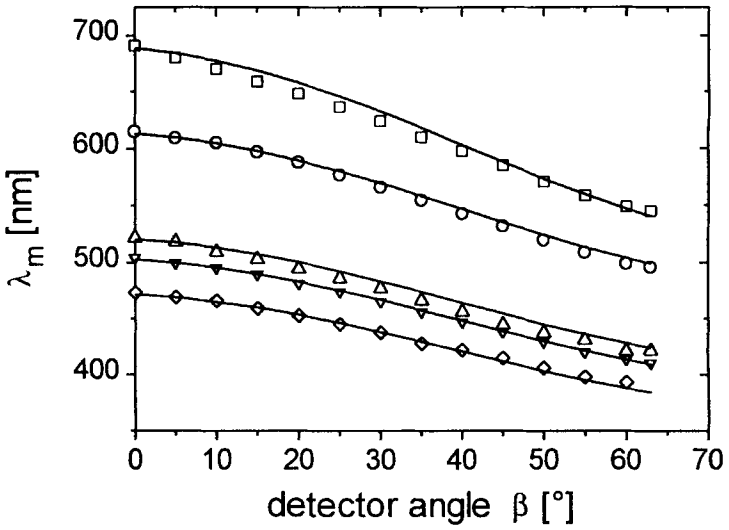


FIG. 9. Angular dependence of the reflection wavelength for polymer films with different amounts of **4** (mol%); (□) 35, (○) 40, (△) 45, (▽) 50, (◇) 55. Solid lines: Fit according to Eq. (3), $\bar{n} = 1.5$.

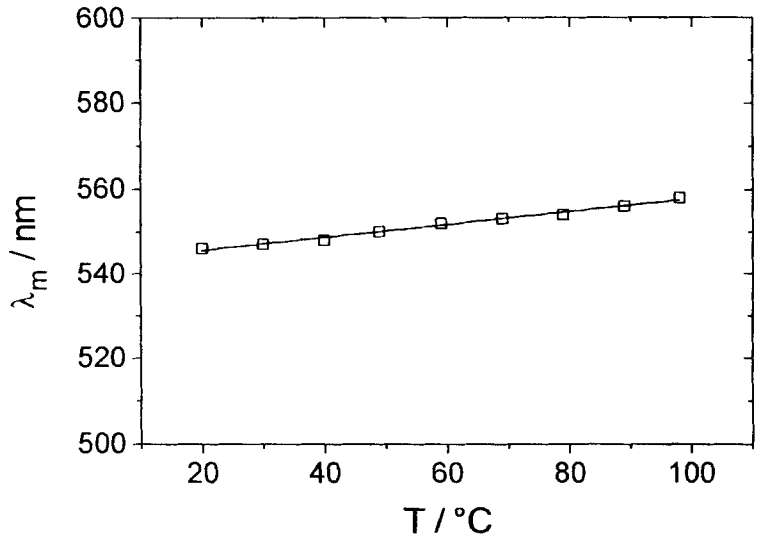


FIG. 10. Reflection wavelength λ_m as a function of the temperature T for a network consisting of 55 mol% **1b** and 45 mol% **4**.

10 for the network made from 55 mol% of **1b** and 45 mol% of **4**. In contrast to the behavior of the monomer mixture which exhibits a strong decrease of the reflection wavelength with increasing temperature, the reflection wavelength of the polymer film increases only slightly with temperature. As can be seen from Fig. 10, the dependence is linear and the wavelength changes from 546 nm at 20°C to 558 nm at 98°C, which means an increase of about only 2%.

Whereas in the monomer mixture the interaction between the nematic and chiral molecules leads to stronger twisting of the helix and therefore to a smaller pitch, this interaction is no longer possible in the crosslinked network. Only the thermal expansion of the film influences the pitch of the cholesteric helix and results in an increase of the reflection wavelength.

CONCLUSIONS

We have shown that at least difunctional monomers are necessary to obtain densely crosslinked cholesteric polymer networks. In such materials, all the molecules are part of the polymer network and no soluble fraction exists.

Networks from mixtures of the nematic diacrylate **1b** and the novel difunctional cholesteryl derivative **4** in different ratios show a reflection over the whole visible range. Mixtures of **1b** and **4** have been photopolymerized at a temperature of 80°C. The reflection wavelength of the films is not affected by solvent treatment or by heat.

The angular dependence of the reflection wavelength can be fitted by Eq. (3), which has been deduced for low molar mass materials. This shows that the optical properties of the cholesteric monomer mixture are not altered during polymerization. The helicoidal structure of the phase is permanently frozen-in.

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