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Cholesteric polymeric networks with steroids as chiral components

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Induced cholesteric polymeric networks with steroids as chiral components were prepared with the aim of finding steroid esters which show distinctly higher helical twisting power (HTP) than cholesteryl 3,4-di-(2-acryloyloxyethoxy)benzoate. Isothermal photopolymerization led to crosslinked networks. The HTPs of the networks were determined by measuring the reflection wavelengths and their dependence on the molar fraction of the chiral compound. The relationship between the HTP of the cholesteric polymeric networks and the molecular structure of the chiral steroid ester is discussed. A high HTP can be attributed to the definite alignment imposed by the large substituents on the long axis of the steroid nucleus.

1. Introduction

More than 200 000 natural and synthetic steroids are known. Physiologically important steroid hormones such as androgens, estrogens, gestagens and corticosteroids belong to this class of substance. In 1888 Reinitzer found that cholesteryl benzoate had a 'double melting point' [1]. Closer investigation of the melting behaviour of this compound led to the discovery of the cholesteric mesophase and marked the inception of liquid crystal science [2]. Since then, many steroidal compounds have been shown to exhibit liquid crystal behaviour. Their chirality and today's easy accessibility from plant sources make them very interesting candidates for applications in modern technology. A recent application of liquid crystalline steroids is in cholesteric colour-flop pigments for the automobile industry [3]. For this purpose the cholesteric mesophase is fixed in a polymer network by photopolymerization.

A cholesteric mesophase is usually induced from a nematic phase by addition of a chiral dopant [4]. The orientation of a cholesteric phase can be frozen in a liquid crystalline network by photopolymerization [5–8]. In this process liquid crystalline monomers with two polymerizable groups, e.g. acrylate groups, are polymerized in their oriented mesophase by UV irradiation in the presence of photoinitiators. The characteristic feature of a cholesteric mesophase is the helical ordering of the molecules, and due to its helical structure the cholesteric phase shows a selective reflection of light.

This effect is fundamental for the unique optical properties of cholesteric liquid crystals. By irradiation of a cholesteric mesophase with white light, certain wavelengths are reflected dependent on the the pitch p of the helix and the viewing angle [9]. In induced cholesteric phases the reflection wavelength can be easily controlled by the amount of the chiral dopant. The more chiral dopant the mixture contains, the shorter is the reflection wavelength (blue shift). Liquid crystal pigments are used in effect-lacquers [10]. They show bright colours and an intensive colour-flop effect due to the angular dependence of the reflection wavelength [11]. At increasing angles of observation, a blue shift of the reflection wavelength is observed.

The advantage of the use of steroid esters for induced cholesteric phases lies in their high tendency to form cholesteric mesophases which possess a sufficiently high helical twisting power (HTP) to cover the whole visible reflection range. We were interested in the search for steroid esters which show a distinctly higher HTP than cholesteryl 3,4-di-(2-acryloyloxyethoxy)benzoate (**15**); see the table. In this way it is possible to induce a suitable cholesteric phase from a nematic phase with a smaller amount of the chiral compound, and in this way,

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Table 1. Glass transition temperatures, melting points, specific rotations and helical twisting powers of the chiral compounds **1**–**15**.

Compound	T_g/°C[a]	T_m/°C[b]	$[\alpha]_D^{22}$/°[c]	HTP/μm^{-1}[d]
1	16		+ 30	− 6.6
2	15		+ 71	− 7.3
3	5		+ 22	− 10.1
4	2		− 7	− 10.5
5	17	120[e]	+ 47	− 11.0
6	− 16		+ 16	− 11.0
7	− 5	55[e]	+ 28	− 12.2
8	10	[f]	+ 32	− 12.4
9	− 17		− 14	+ 12.8
10	− 7		− 12	− 13.9
11	− 17		+ 16	− 14.5
12	2		+ 134	− 19.9
13		55[e]	+ 18	− 24.4
14	− 1		− 34	− 26.0
15		[g]	− 5	6.1

[a] T_g: glass transition temperature, DSC measurement, 10 K min^{-1}.
[b] T_m: melting point, DSC measurement, 10 K min^{-1}.
[c] $[\alpha]_D^{22}$: specific rotation determined using a $CHCl_3$ solution at 1.0 g/100 ml.
[d] HTP: helical twisting power determined by optical spectroscopy on cholesteric networks prepared from the chiral compounds **1**–**15** and the nematic bisacrylate **16** (for explanations see text).
[e] Recrystallization occurred in the next DSC run at 75°C (**5**), 35°C (**7**) and 34°C (**13**).
[f] DSC run, first cooling: **8**, I 49°C Ch 43°C Cr.
[g] Cr 73°C Ch 99°C I.

problems of mixing a nematic liquid crystal and the chiral dopant are reduced. The relationship between the HTP of the cholesteric polymer networks and the molecular structure of the steroid esters will be discussed.

2. Results and discussion

The chiral steroid esters **1**–**14** were synthesized for the first time; see figure 1. The compounds **1**–**5**, **7**, **8** and **10** were obtained by esterification of the corresponding steroid with 3,4-di-(2-acryloyloxyethoxy)benzoic acid in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC). The reaction of the steroids with 3,4-di-(2-acryloyloxyethoxy)-phenylpropionyl chloride, 4-(6-acryloyloxyhexoxy)phenylpropionyl chloride, 3,4-di-(2-acryloyloxyethoxy)benzoyl chloride and 4-(6-acryloyloxyhexoxy)benzoyl chloride yielded **6** (R_3), **9**, **13** (R_4) **12** (R_1) and **11**, **14** (R_2). As can be seen in the table, the compounds **1**–**12** and **14** possess a glass transition (T_g) in the range − 17°C to + 17°C. The pregnenolone ester **8** in the first DSC cooling run shows a cholesteric phase between 49°C and 43°C.

The chiral compounds **1**–**14** were added to give a concentration of 2–55 mol % in the nematic monomer **16** (see figure 2) whose synthesis was described before [5]. The mixture was applied together with 2 wt % of 2,2-dimethoxy-2-phenylacetophenone as photoinitiator, to a glass slide, heated to form the cholesteric mesophase and oriented by shearing between two glass slides. Photopolymerization was carried out for 4 min with UV light at a reduced temperature $T^* = 0.95$. The phase transitions of the unpolymerized mixtures of **16** with the chiral compounds **1**–**14** were obtained by polarizing optical microscopy.

The optical properties of the photopolymerized cholesteric networks were investigated. The reflection wavelengths in the UV-Vis/NIR region were measured as a function of the molar fraction of the chiral compound and in this way the HTP of the cholesteric helix could be obtained. The strength of the chiral induction in an induced cholesteric polymer network is defined as follows:

$$HTP = \bar{n}(d\lambda_m^{-1}/dx)_{T^*}$$

where $\bar{n}$ = mean refractive index of the cholesteric network, λ_m = maximum of the reflection wavelength, x = molar fraction of the chiral compound and T^* = reduced temperature ($T^* = T/T_c$, T = measured temperature, T_c = clearing temperature) [12]. The HTP values for all the cholesteric networks are given in the table. Figure 3 shows the maximum of the reflection wavelength as a function of the molar fraction of the (20*R*)-pregn-5-ene-3β,20-diol ester **14**.

3-Hydroxyestra-1,3,5(10)-triene ester **7** showed a higher HTP than the more polar estradiol ester **1** and estrone ester **2**. Therefore polar interactions between the chiral dopants **1**, **2**, and **7** and the nematic compound **16** have no influence on the HTP. This could be confirmed by the androstenolone ester **3** and 3β-hydroxypregn-5-ene ester **4**. The more polar 17-keto function of **3** did not result in a higher HTP in comparison with **4**. The double bond in position 5 of **3** has a small influence on the HTP compared with 3β-hydroxyandrost-5α-an-17-one ester **5**. The aromaticity of the steroidal A ring of **2** results in a smaller HTP in comparison with **3**. The esterification of pregnenolone with 3,4-di-(acryloyloxyethoxy)benzoic acid in **8** and 3,4-di-(acryloyloxyethoxy)-phenylpropionic acid in **6** has only a small influence on the HTP. The two additional carbon atoms of the substituent R_4, 4-(6-acryloyloxyhexoxy)phenylpropionyl, in the (20*R*)-pregn-5-ene-3β,20-diol ester **9** cause a dramatic decrease of the HTP compared with the moiety R_2, 4-(6-acryloyloxyhexoxy)benzoyl, in **14** and a change of the screw sense. The presence of the carbon atoms 20 and 21 in **14** leads almost to a doubling of the HTP in comparison with the androst-5-ene-3β,17β-diol ester **11**. The steroid compounds esterified with 3,4-di-(acryloyloxyethoxy)benzoic acid **1**–**5**, **7**, **8** and **10** show a higher

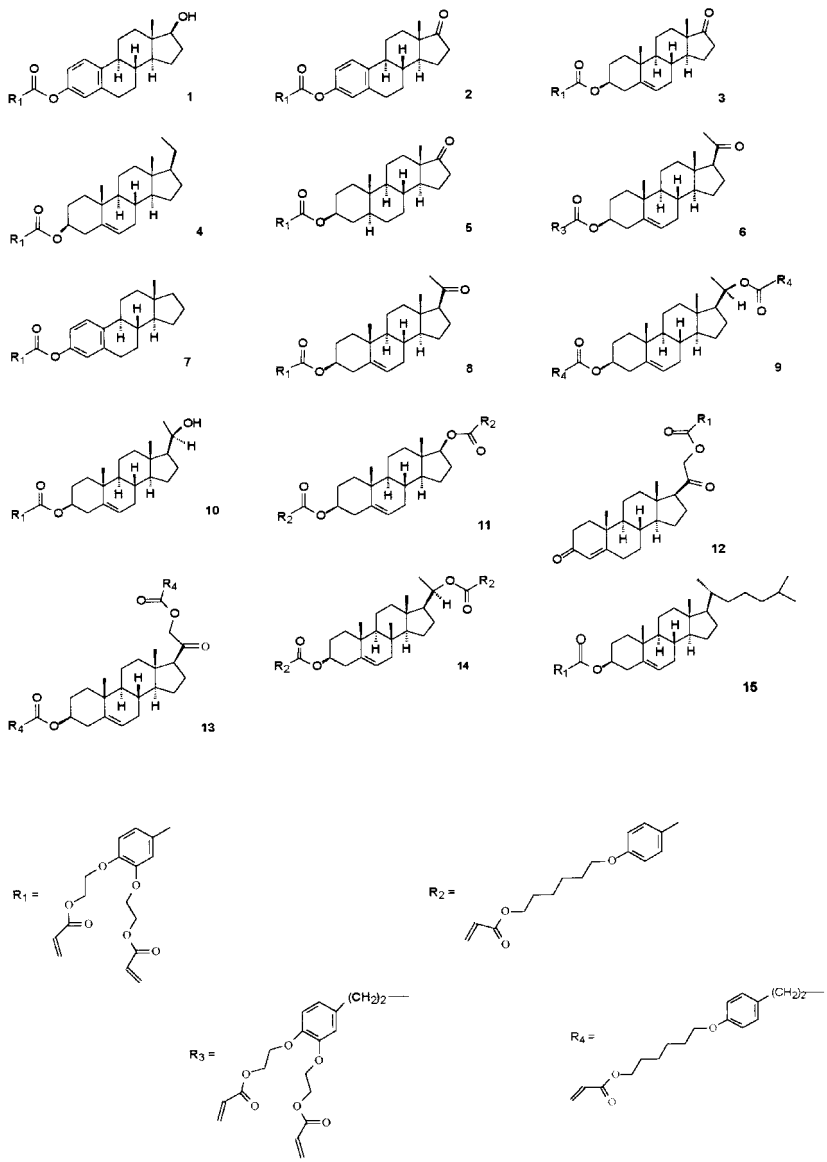
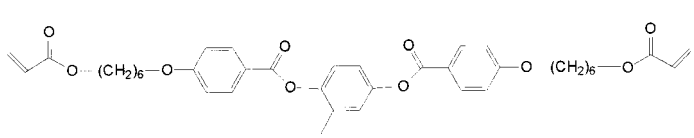


Figure 1. Chemical structures of the new chiral steroid esters **1**–**14** and **15**.

HTP in the induced cholesteric polymer networks with the nematic monomer **16** than cholesteryl 3,4-di-(2-acryloyloxyethoxy)benzoate (**15**) (HTP = 6.1 μm^{-1}) [13]. The six additional carbon atoms 22–27 of the cholesterol side chain of **15** cause a decrease of the HTP compared with **4**. The diester **14** possesses a 4.3 times higher HTP than cholesteryl 3,4-di-(2-acryloyloxye thoxy)-benzoate (**15**). Therefore we have been able to synthesize steroid esters with a distinctly higher HTP in comparison with the cholesteryl ester **15**.

It is known that the guest in a nematic solvent prefers an orientation with its long axis parallel to the nematic director [14]. Substituents increasing the molecular dimensions of the steroid nucleus in the direction of the



16

Cr 78°C N 118°C I

Figure 2. The nematic bisacrylate monomer **16**.

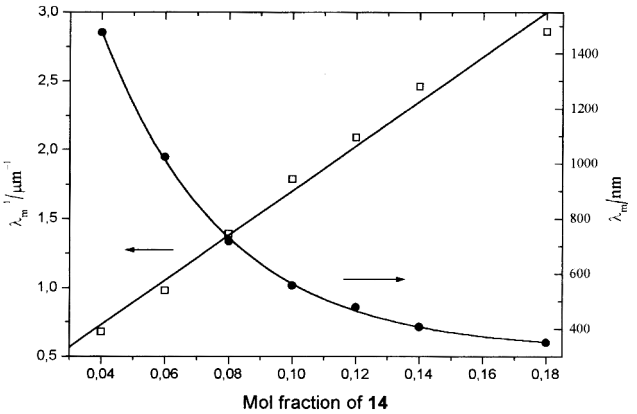


Figure 3. Reflection wavelength λ_m and inverse reflection wavelength λ_m^{-1} as a function of the molar fraction of dopant **14** in a polymeric network consisting of the nematic diacrylate **16** and **14**.

long axis (C-3 → C-16) should favour orientations of the steroidal dopant along the nematic director. Therefore the intermolecular chirality transfer [15] should be more effective with dopants which possess large substituents in the direction of long axis of the steroid molecule. The high HTP values of **13** and **14** can be attributed to the definite alignment imposed by the large substituents in the 3- and 21-positions of the steroid nucleus. The higher flexibility of the side chains of **9** due to the two additional carbon atoms of the substituent R_4 compared with **14** results in a decrease of the HTP. An optimal intermolecular chirality transfer from **9** to the nematic molecule **16** is prevented due to the formation of conformers of **9** in which the side chains are not situated in the direction of the long axis of the steroid.

3. Experimental

Estradiol, estrone, androstenolone and pregnenolone were purchased from Fluka Chemie AG (Buchs, Switzerland), 11-desoxycorticosterone and pregnenolon-21-yl acetate from Sigma Chemie GmbH (Taufkirchen, Germany) and 3β-hydroxyandrost-5α-an-17-one from Aldrich Chemie GmbH (Taufkirchen, Germany).

The compounds **1**–**5**, **7**, **8** and **10** were synthesized by esterification of the steroid alcohols with 3,4-di-(2-acryloyloxyethoxy)benzoic acid in the presence of DCC. The steroid alcohol (0.15 mol), the acid (0.15 mol), a catalytic amount of 4-*N*,*N*-dimethylaminopyridine (DMAP) and 2,6-di-(*tert*-butyl)-*p*-cresol as polymerization inhibitor were dissolved under an argon atmosphere in dry methylene chloride. The mixture was cooled to 0°C and dry DCC (0.15 mol) was added. The reaction was followed by thin layer chromatography on silica gel sheets 60 F_{254} (Merck). When the reaction was finished, the mixture was filtered and the filtrate washed several times with aqueous $KHCO_3$ and aqueous NaCl, dried over Na_2SO_4 and concentrated to dryness to obtain the crude product which was then purified by flash chromatography on silica gel. The yields were 50–60%.

The reaction of the corresponding steroid alcohol with 3,4-di-(2-acryloyloxyethoxy)phenylpropionyl chloride (0.15 mol), 4-(6-acryloyloxyhexoxy)phenylpropionyl chloride (0.30 mol), 3,4-di-(2-acryloyloxyethoxy)benzoyl chloride (0.15 mol) and 4-(6-acryloyloxyhexoxy)benzoyl chloride (0.30 mol) gave **6** (R_3), **9**, **13** (R_4) **12** (R_1) and **11**, **14** (R_2). The acid chloride (0.15 or 0.30 mol) was slowly added at room temperature to a solution of steroid alcohol (0.1 mol), pyridine (1 mol), a catalytic amount of DMAP and 2,6-di-(*tert*-butyl)-*p*-cresol as polymerization inhibitor in dry methylene chloride. The mixture was heated under reflux for 5 h. The work-up was the same as that described above and the yields were 50–60%. The products were characterized by one- and two-dimensional NMR experiments.

Pregnenolone and estrone reacted with tosylhydrazone to give the hydrazones which were then reduced with catecholborane to 3β-hydroxypregn-5-ene and 3-hydroxyestra-1,3,5(10)-triene [16–18]. The two steroids were used for the synthesis of 3β-hydroxypregn-5-ene ester **4** and 3-hydroxyestra-1,3,5(10)-triene ester **7**. Pregnenolon-21-yl acetate was hydrolyzed to 21-hydroxypregnenolone which was transformed into **13**. The reduction of pregnenolone with $NaBH_4$ [19] yielded (20*R*)-pregn-5-ene-3β,20-diol which was esterified to give **9**, **10** and **14**.

The transition temperatures were determined on a Nikon Diaphot 300 polarizing microscope equipped with a Mettler FP 80 hot stage. The cholesteric phase was identified by its characteristic texture. The DSC curves were measured using a Perkin Elmer DSC 7. The heating rate for all measurements was 10 K min^{-1}.

To obtain the HTP values, thin film polymer samples were prepared from the nematic compound **16** and different amounts of chiral dopant, giving a series of mixtures with 5 and 10 mol% concentration steps, except for the mixtures **13** and **14** where we used concentration steps of 2 mol%. The monomer mixtures and 2 wt% 2,2-dimethoxy-2-phenylacetophenone as photoinitiator were heated to the LC phase. After uniaxial orientation between two glass slides, photopolymerization in the cholesteric phase was carried out at a reduced temperature of $T_{red} = 0.95$ by UV irradiation for 4 min using a 150 W xenon high pressure lamp (Osram XBO 150 W/s 4) with an intensity of 8 mW cm^{-2}. The HTP was determined by UV-Vis/NIR reflection spectroscopy. For the detection of the reflection wavelengths, a Hitachi U-3000 spectrometer was used in the UV-Vis region. A Perkin Elmer Lambda 19 UV-Vis/NIR spectrometer was used in the NIR region. The angular reflection measurements were made by an Instrument Systems Optische Messtechnik Spectro UV-Vis spectrometer

equipped with a goniometer. The screw sense of the cholesteric helix was obtained by means of a right and a left handed circular polarizer as shown in [20].

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References

[1] Reinitzer, F., 1888, *Monatsh. Chem.*, **9,** 421.
[2] Lehmann, O., 1889, *Z. Phys. Chem.*, **4,** 462.
[3] Häbele, M., Haas, W., and Kreuzer, F.-H., 1991, EP 466 183.
[4] Goosens, W. J. A., 1971, *Mol. Cryst. liq. Cryst.*, **12,** 237.
[5] Broer, D. J., Hikmet, R. A. M., and Challa, G., 1989, *Makromol. Chem.*, **190,** 3201.
[6] Broer, D. J., Boven, J., Mol, G. N., and Challa, G., 1989, *Makromol. Chem.*, **190,** 2255.
[7] Broer, D. J., Mol, G. N., and Challa, G., 1991, *Makromol. Chem.*, **192,** 59.
[8] Broer, D. J., and Heynderickx, I., 1990, *Macromolecules*, **23,** 2474.
[9] Solladie, G., and Zimmermann, R. G., 1984, *Angew. Chem.*, **96,** 335.
[10] Bunning, T. J., and Kreuzer, F.-H., 1995, *Trends polym. Sci.*, **3,** 318.
[11] Eberle, H.-J., Miller, A., and Kreuzer, F.-H., 1989, *Liq. Cryst.*, **5,** 907.
[12] Finkelmann, H., and Rehage, G., 1980, *Makromol. Chem. rapid Commun.*, **1,** 733.
[13] Stohr, A., and Strohriegl, P., 1997, *J. macromol. Sci. pure appl. Chem.*, **A34,** 1125.
[14] Sackmann, E., Krebs, P., Rega, H. V., Voss, J., and Moehwald, H., 1973, *Mol. Cryst. liq. Cryst.*, **24,** 283.
[15] Kuball, H.-G., Müller, T., Brüning, H., and Schönhofer, A., 1995, *Mol. Cryst. liq. Cryst.*, **261,** 205.
[16] Hutchins, R. O., Milewski, C. A., and Maryanoff, B. E., 1973, *J. Am. chem. Soc.*, **95,** 3662.
[17] Kabalka, G. W., and Baker Jr., J. D., 1975, *J. org. Chem.*, **40,** 1834.
[18] Kabalka, G. W., and Chandler, J. H., 1979, *Synth. Commun.*, **9,** 275.
[19] Kumar, V., Amann, A., Ourisson, G., and Luu, B., 1987, *Synth. Commun.*, **17,** 1279.
[20] Stegemeyer, H., 2000, *Nachr. Chem.*, **48,** 1052.