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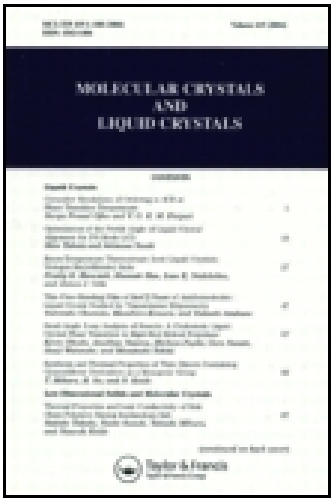

Molecular Crystals and Liquid Crystals

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Photo-Isomerizable Derivatives of Phenylethanediol and Cinnamic Acid: Useful Compounds for Single-Layer R, G, and B Cholesteric Color Filters

J. Lub [a], M. P. Ezquerro [a] & B. Malo [a]

[a] Philips Research Laboratories, Eindhoven, the Netherlands

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Photo-Isomerizable Derivatives of Phenylethanediol and Cinnamic Acid: Useful Compounds for Single-Layer R, G, and B Cholesteric Color Filters

J. Lub
M. P. Ezquerro
B. Malo
Philips Research Laboratories, Eindhoven, the Netherlands

This article describes the synthesis of derivatives of (R)-phenylethanediol and cinnamic acid. These molecules are photo-isomerizable and contain two acrylate groups that can form densely cross-linked cholesteric polymer films. The Z-isomers formed by irradiation of the E-isomeric cinnamic acid derivatives exhibit a much lower helical twisting power than that of the E-isomers. In this way, the reflection wavelength of cholesteric layers made with these molecules can be increased by irradiation. After polymerization, the cholesteric films are thermally stable and hence these molecules are suitable for use in cholesteric color filters that find application in liquid-crystalline displays.

Keywords: cholesteric liquid crystals; color filters; photo isomerisation; photo polymerisation

1. INTRODUCTION

Considerable attention has been given to cholesteric liquid-crystalline materials because of their ability to reflect circularly polarized light [1]. The development of photo-isomerisable chiral molecules in particular is of interest [2]. Such materials find application in the production of cholesteric color filters for use in liquid-crystalline displays because of the color change induced by ultraviolet (UV) light. Cholesteric films made with menthone derivative **1** (Fig. 1), for instance, change the color by means of E-Z photo-isomerization. The reflection wavelength

Address correspondence to J. Lub, Philips Research Laboratory, Prof. Holstlaan 4, 5656 AA Eindhoven, the Netherlands. E-mail: johan.lub@philips.com

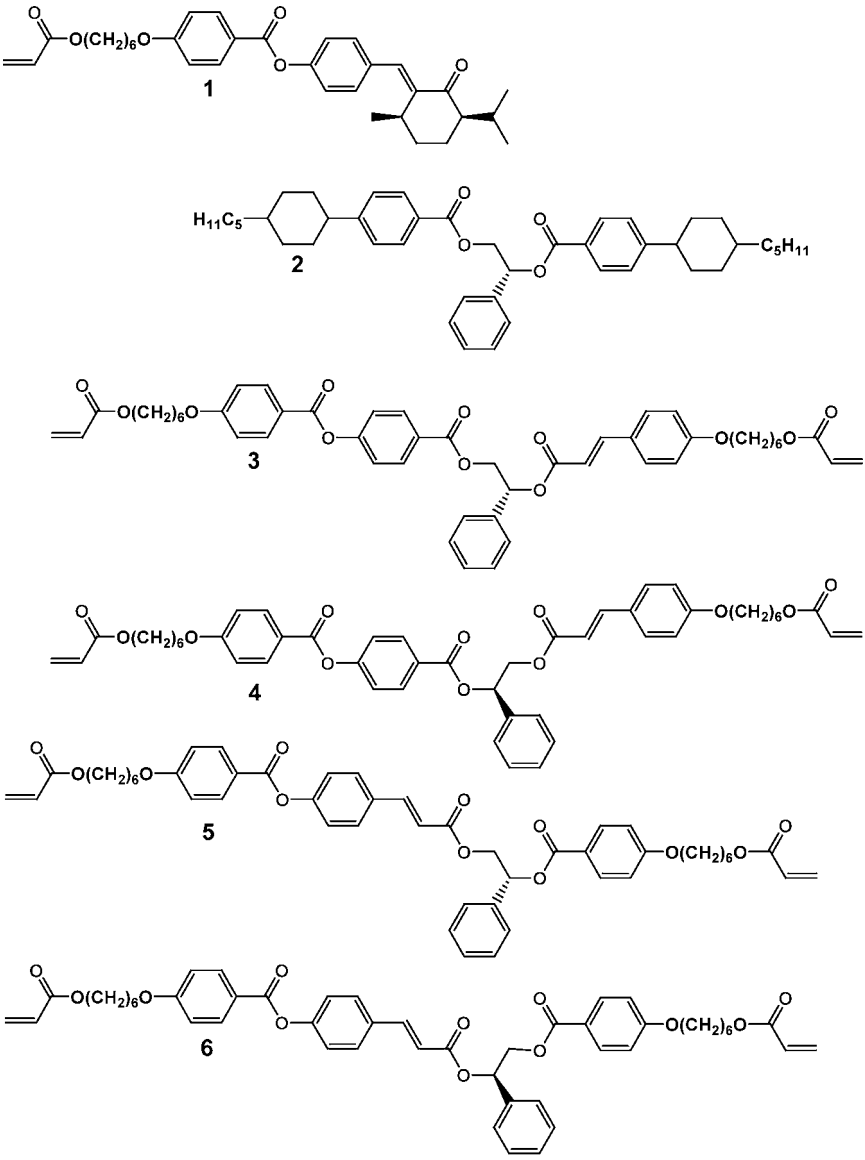

FIGURE 1 Structures of the chiral compounds.

(λ) of a cholesteric layer made from a mixture of **1** and nematic molecules is, therefore, defined by [3]

$$\lambda = n \times p = n(HTP_{E^\times} x_E + HTP_{z^\times} x_z)^{-1}, \quad (1)$$

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where n is the mean refractive index of the cholesteric mixture; p is the pitch of the helix of the cholesteric structure; x_E is the weight fraction of **1** (the E-isomer) present in the cholesteric mixture; x_Z is the weight fraction of photo-isomerized material (Z-isomer, obtained through photo-isomerization of **1**); HTP_E is the so-called helical twisting power, which is a property of **1**, that is, the reciprocal of the pitch of the helix for $x_E = 1$; and HTP_Z is the helical twisting power of the Z-isomer of **1**. The change in conformation upon E-Z photo-isomerization of **1** causes the reflection wavelength to increase, because the HTP_E of this compound is approximately $19\,\mu m^{-1}$, whereas HTP_Z is approximately $3\,\mu m^{-1}$ [4].

Thermal and UV stable films are required to produce cholesteric color filters. Therefore, compound **1** was added to a mixture of nematic di-acrylates and a photo-initiator [5,6]. When a substrate provided with a rubbed alignment layer is coated with the mixture, a blue reflecting film is formed. The photo-isomerization reaction was effected in a single UV irradiation step with the aid of a grayscale mask, with patterned areas having 100%, 0%, and intermediate transmission, leading to the red, blue, and green pixels, respectively [5,7]. The colors can be optimized through use of the correct irradiation dose for the green and red pixels. Subsequent photo-polymerization of the film containing the pixelated reflection colors leads to the formation of a stable cross-linked material. The process conditions were chosen to prevent the two photochemical processes (i.e., isomerization and polymerization from interfering with each other [5]. Photopolymerization will not start if air is present because of the inhibitive effect of oxygen on the acrylate polymerization reaction. The combination of this effect and the relatively low UV intensity needed for isomerization results in ready formation of the colors in air without any noticeable polymerization. The photopolymerization reaction was effected in an inert atmosphere (nitrogen or argon), in which it proceeded at a much higher rate than the isomerization process. This led to rapid fixation of the patterned cholesteric structure with no changes in its optical properties. The cross-linking resulted in a material that is stable under UV light and at elevated temperatures. These cholesteric color filters reflect colors of high color purity and appear to be interesting materials for new generations of liquid-crystalline displays (LCDs) [8,9].

However, the manufacture of LCDs imposes even more severe demands on the stability of the cholesteric color filter, as it involves high-temperature treatments (typically 200°C), such as Indium Tin Oxide (ITO) deposition directly onto the color filter, followed by the application and baking of a polyimide film on top of the ITO. During

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these processes, degradation of the filters was observed. This degradation is partly attributable to the thermal instability of the menthone-derived chiral moiety in **1** and partly attributable to the fact that this chiral compound is a mono-acrylate and hence leads to the formation of polymer networks with relatively low cross-link density upon photopolymerization [10,11]. In previous publications, we reported several alternative structures for compound **1**, in which the menthone moiety was replaced by various derivatives of cyclohexanone [12–14]. This previous research led to a better understanding of the structure–property relationship of these chiral materials, but most of them are either difficult to synthesize or exhibit *HTP* values that are too low for them to be used in color-filter manufacturing. We therefore searched for other molecules that are more stable. In addition, we anticipated that it would be advantageous to functionalize these new compounds with two acrylate groups rather than one. The increase in cross-link density would improve the thermal stability of cholesteric color filters.

Di-esters of phenylethanediol such as **2** are compounds with *HTP* values of up to 40 μm^{-1} [15]. Compounds containing two polymerizable groups with these structures were applied in cholesteric mixtures that formed polymeric networks reflecting visible light after photopolymerization [16,17]. Di-acrylates derived from isosorbide as chiral moiety and cinnamic acid as isomerizable moiety have been prepared and shown to be suitable for use in cholesteric color-filter manufacturing [11,18]. Thus, the cinnamic moiety is a useful isomerizable group.

To study the suitability of structures derived from phenylethanediol and cinnamic acid for use in cholesteric color filters, we decided to synthesize and investigate the properties of compounds **3, 4, 5**, and **6** (Fig. 1). These compounds are all structural isomers of each other. By comparing the properties of these compounds, the effect of the positions of both the phenyl group and the isomerizable cinnamate group in the molecule on the helical twisting power and on the photo-induced change in the helical twisting power can be studied.

Chiral compounds derived from menthone, such as **1**, or from isosorbide, described earlier for use in cholesteric color filters, form left-handed and right-handed helices, respectively [4,11]. It is very difficult to obtain cholesteric layers with an inverse helix because the mirror enantiomers of the chiral starting compounds, menthone and isosorbide, either cannot be obtained or are very difficult to prepare. For complex optical stacks, having freedom of choice in terms of the handedness of the helix may be advantageous [19]. Both enantiomers of the compounds described here are easily accessible because the materials originate from the readily available (R) and (S) mandelic acid. Thus, cholesteric layers with right-or left-handed helix layers

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can be made with equal ease using these types of compounds. Molecules **3, 4, 5**, and **6** are suitable for replacing the menthone-derived compound **1** in cholesteric mixtures. Some properties of cholesteric films made with these new di-acrylates are presented.

2. EXPERIMENTAL

2.1. Materials and Methods

Literature procedures were used to obtain 4-(6-acryloyloxy-hexyloxy)-benzoic acid (**7a**) [20], 4-(6-acryloyloxyhexyloxy)cinnamic acid (**7b**) [21], 4-(4-(6-acryloyloxyhexyloxy)benzoyloxy)benzoic acid, (**10a**) [11,18], and (R)-2-phenyl-2-(tetrahydro-pyran-2-yloxy)-ethanol (**14**) [22].

RM82 {(4-(6-acryloyloxyhexyloxy)benzoyloxy)-2-methylphenyl 4-(6-acryloyloxyhexyloxy)benzoate} and RM257 {(4-(3-acryloyloxypropyloxy) benzoyloxy)-2-methylphenyl 4-(3-acryloyloxypropyloxy)benzoate} were obtained from Merck. Darocur®. 4265 photo-initiator was obtained from Ciba Specialty Chemicals. All the other chemicals were obtained from Aldrich.

Absorption UV spectra were recorded in an acetonitrile solution using a Unicam UV2-100 spectrometer. The transmission spectra of the cholesteric films were recorded using a Perkin-Elmer spectrometer equipped with a combination of a linear polarizer and an achromatic $\lambda/4$ film.

NMR spectra were recorded with a Bruker DPX300 spectrometer in a deuterated dichloromethane or deuterated chloroform solution. The ^{1}H and ^{13}C NMR data were fully consistent with the required structures and confirmed the purity of all the final products. The spectra were interpreted with the aid of 2D $^{13}C-^{1}H$ correlation spectra. The isomerization measurements were done in dichloromethane. Irradiation of the NMR tubes was performed with a PL10 light source (Philips, $\lambda_{max} = 365\,nm$) or a TL08 light source (Philips, broadband, $\lambda = 350\,nm$).

FTIR spectra were recorded in a chloroform solution with an ATI Mattson Genesis II spectrometer. Compounds **3**, **4, 5**, and **6** showed similar spectra with the following peaks (in cm^{-1}): 2939 (CH_2), 1732 (C=O, benzoate, cinnamate, and acrylate), 1637 (C=C), 1605 and 1511 (aromatic rings), 1408 (CH_2-acrylate), 1250 (O-aromatic ring), and 984 ($CH{=}CH_2$).

Matrix Assisted Laser Desorption Ionisation Time of Flight (MALDI-TOF) mass spectra were recorded on a Voyager-De Pro machine using α-cyano-4-hydroxycinnamic acid as the matrix. Calculated for $C_{49}H_{52}O_{12}$ (compounds **3**, **4, 5**, and **6**) 832.35; found 832.32 ± 0.03.

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2.2. Synthesis

2.2.1. Synthesis of Ethoxymethyl 4-hydroxycinnamate (8b)

Chloromethyl ethyl ether (6.3 ml, 100 mmol) in 40 ml of dichloromethane was added dropwise to a solution of 16 g (100 mmol) of 4-hydroxycinnamic acid and 14 ml (100 mmol) of triethylamine in 80 ml of dichloromethane. The mixture was stirred overnight at room temperature. The mixture was extracted subsequently with 60 ml of water, with 60 ml of a 2.4 M HCl solution and with 60 ml of a saturated solution of sodium bicarbonate. After drying over magnesium sulphate, the solvent was evaporated, and 18.7 g of clear oil (84%), that slowly crystallized, were obtained.

2.2.2. Synthesis of 4-(4-(6-Acryloyloxyhexyloxy)benzoyloxy)-cinnamic Acid 10b

N,N-Dicyclohexyl carbodiimide (15.7 g, 75 mmol) was added to a mixture of 18.7 g (75 mmol) of ethoxymethyl 4-hydroxycinnamate (**8b**), 22.2 g (75 mmol) of 4-(6-acryloyloxy-hexyloxy)-benzoic acid (**7a**), 0.93 g (7.6 mmol) of 4-N,N-dimethylaminopyridine, and 200 ml of dichloromethane cooled in an ice-water bath. After removing the ice-water bath, the mixture was stirred at room temperature overnight. The mixture was filtered through a thin layer of silica and evaporated. The intermediate ethoxymethyl 4-(4-(6-acryloyloxyhexyloxy)benzoyloxy)cinnamate (**9b**) obtained after crystallization from ethanol was dissolved in 60 ml of hot ethanol together with 0.75 g (3 mmol) of pyridinium 4-toluenesulfonate. After stirring for 13 h at 60°C, 12.7 g of a white solid (40%) crystallized upon cooling to room temperature.

2.2.3. Synthesis of (R)-2-Hydroxy-2-phenylethyl 4-(4-(6-Acryloyloxyhexyloxybenzoyloxy)benzoate (12a)

N,N′-Dicyclohexyl carbodiimide (2.1 g, 10 mmol) was added to a mixture of 2.2 g (10 mmol) of (R)-2-phenyl-2-(tetrahydro-pyran-2-yloxy)-ethanol (**14**), 4.1 g (10 mmol) of 4-(4-(6-acryloyloxyhexyloxy) benzoyloxy)benzoic acid (**10a**), 0.12 g (1.0 mmol) of 4-N,N-dimethylaminopyridine, and 50 ml of dichloromethane stirred in an ice-water bath. After 2.5 h the ice bath was removed, and the mixture was stirred at room temperature for 24 h. The reaction mixture was filtered over a thin silica layer and evaporated. The crude intermediate (R)-2-(tetrahydropyran-2-yloxy)-2-phenylethyl 4-(4-(6-acryloyloxyhexyloxybenzoyloxy)benzoate (**11a**) obtained as an oil was dissolved in 35 ml of ethanol. Then 0.25 g (1.0 mmol) of pyridinium 4-toluensulfonate was added, and the mixture was heated at 60°C for 15 h. A white solid (3.2 g, 60%) precipitated upon cooling to 5°C.

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2.2.4. Synthesis of (R)-2-Hydroxy-2-phenylethyl 4-(4-(6-Acryloyloxyhexyloxybenzoyloxy)cinnamate (12b)

This product was obtained as a solid with 55% yield, in the same manner as described for (R)-2-hydroxy-2-phenylethyl 4-(4-(6-acryloyloxyhexyloxybenzoyloxy)benzoate (**12a**) starting from 4-(4-(6-acryloyloxyhexyloxy)benzoyloxy)cinnamic acid (**10b**) instead of 4-(4-(6-acryloyloxyhexyloxy)benzoyloxy)benzoic acid (**10a**).

2.2.5. Synthesis of (R)-2-Hydroxy-2-phenylethyl 4-(6-Acryloyloxyhexyloxy)benzoate (16a)

N,N′-Dicyclohexyl carbodiimide (4.1 g, 20 mmol) was added to a mixture of 4.4 g (20 mmol) of (R)-2-phenyl-2-(tetrahydro-pyran-2-yloxy)-ethanol (**14**), 5.8 g (20 mmol) of 4-(6-acryloyloxyhexyloxy)benzoic acid (**7a**), 0.24 g (2.0 mmol) of 4-N,N-dimethylaminopyridine, and 80 ml of dichloromethane stirred in an ice-water bath. After 2.5 h, the ice bath was removed, and the mixture was stirred at room temperature for 24 h. The reaction mixture was filtered over a thin silica layer and evaporated. The crude intermediate (R)-2-(tetrahydropyran-2-yloxy)-2-phenylethyl 4-(6-acryloyloxyhexyloxy)benzoate (**15a**) obtained as an oil was dissolved in 50 ml of ethanol. Then 1.0 g (4.1 mmol) of pyridinium 4-toluensulfonate was added, and the mixture was heated at 60°C for 15 h. After evaporation of the ethanol, the mixture was purified by column chromatography (silica/dichloromethane–ethyl acetate = 94:6). The product (4.2 g, 51%) was obtained as an oil.

2.2.6. Synthesis of (R)-2-Hydroxy-2-phenylethyl 4-(6-Acryloyloxyhexyloxy)cinnamate (16b)

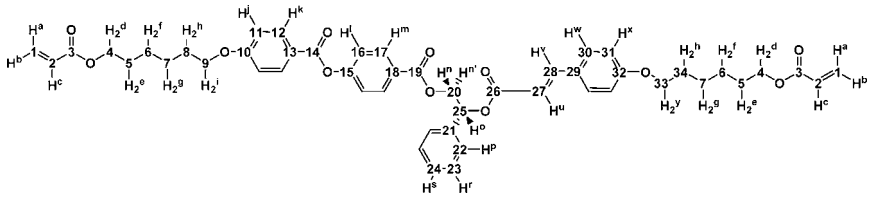
This product was obtained as a solid with 30% yield, in the same manner as described for (R)-2-hydroxy-2-phenylethyl 4-(4-(6-acryloyloxyhexyloxybenzoyloxy)benzoate (**12a**) starting from 4-(6-acryloyloxyhexyloxy)cinnamic acid (**7b**) instead of 4-(4-(6-acryloyloxyhexyloxy) benzoyloxy) benzoic acid (**10a**).

2.2.7. Synthesis of 2-(4-(6-Acryloyloxyhexyloxy) cinnamoyloxy)-2-(R)-phenylethyl 4-(4-(6-Acryloyloxyhexyloxy)benzoyloxy)benzoate (3)

N,N′-Dicyclohexyl carbodiimide (1.2 g, 6 mmol) was added to a mixture of 3.2 g (6 mmol) of (R)-2-hydroxy-2-phenylethyl 4-(4-(6-acryloyloxyhexyloxybenzoyloxy)benzoate (**12a**), 1.9 g (6 mmol) of 4-(6-acryloyloxyhexyloxy)cinnamic acid (**7b**), 0.07 g (0.6 mmol) of 4-N,N-dimethylaminopyridine, and 40 ml of dichloromethane stirred in an ice-water bath. After 2.5 h, the ice bath was removed, and the mixture was stirred at room temperature for 24 h. The reaction

mixture was filtered over a thin silica layer and evaporated. The product (4.0 g, 80%) was obtained after crystallization from ethanol.

^{1}H NMR (δ in ppm, relative to TMS, J in Hz): 8.13 (d, 2H, $J = 9.0$, H^k), 8.08 (d, 2H, $J = 9.0$, H^m), 7.69 (d, 1H, $J = 16.2$, H^v), 7.48 (d, 2H, $J = 7.2$, H^p), 7.47 (d, 2H, $J = 8.7$, H^w), 7.40 (m, 3H, H^r+H^s), 7.27 (d, 2H, $J = 9.0$, H^l), 6.97 (d, 2H, $J = 9.0$, H^j), 6.88 (d, 2H, $J = 8.7$, H^x), 6.42 (dd, 2H, $J_1 = 17.3$, $J_2 = 1.5$, H^a), 6.39 (d, 1H, $J = 16.2$, H^u), 6.32 (dd, 1H, $J_1 = 7.5$, $J_2 = 4.5$, H^o), 6.13 (dd, 2H, $J_1 = 17.3$, H^c), 5.82 (dd, 2H, $J_1 = 10.5$, $J_2 = 1.5$, H^b), 4.67 (dd, 1H, $J_1 = 7.5$, $J_2 = 12.1$, H^n), 4.61 (dd, 1H, $J_1 = 4.5$, $J_2 = 12.1$, $H^{n'}$), 4.18 (t, 4H, $J = 6.4$, H^d), 4.05 (t, 2H, $J = 6.4$, H^i), 3.98 (t, 2H, $J = 6.4$, H^y), 1.82 (q, 4H, $J = 6.4$, H^h), 1.72 (q, 4H, $J = 6.4$, H^e), 1.49 (m, 8H, H^f + H^g).



^{13}C NMR (δ in ppm, relative to TMS): 166.7 ($C^3 + C^{26}$), 165.9 (C^{19}), 164.7 (C^{14}), 164.1 (C^{10}), 161.5 (C^{32}), 155.4 (C^{15}), 145.8 (C^{28}), 137.2 (C^{21}), 132.8 (C^{12}), 131.7 (C^{17}), 131.0 (C^1), 130.3 (C^{30}), 129.1 (C^{23}), 129.0 ($C^2 + C^{24}$), 127.6 (C^{18}), 127.2 (C^{29}), 127.1 (C^{22}), 122.3 (C^{16}), 121.5 (C^{13}), 115.2 (C^{27}), 114.8 ($C^{11} + C^{31}$), 73.5 (C^{25}), 68.5 (C^9), 68.3 (C^{33}), 67.2 (C^{20}), 64.9 (C^4), 29.4 ($C^8 + C^{34}$), 28.9 (C^5), 26.1 ($C^6 + C^7$).

2.2.8. Synthesis of 2-(4-(6-Acryloyloxyhexyloxy)cinnamoyloxy)-1-(R)-phenylethyl 4-(4-(6-Acryloyloxyhexyloxy)benzoyloxy) benzoate (4)

This compound was obtained as a solid with 65% yield, in the same manner as described for 2-(4-(6-acryloyloxyhexyloxy)cinnamoyloxy)-2-(R)-phenylethyl 4-(4-(6-acryloyloxyhexyloxy)benzoyloxy)benzoate (**3**) starting from 4-(4-(6-acryloyloxyhexyloxy)benzoyloxy)benzoic acid (**10a**) and (R)-2-hydroxy-2-phenylethyl 4-(6-acryloyloxyhexyloxy)cinnamate (**16b**).

^{1}H NMR (δ in ppm, relative to TMS, J in Hz): 8.19 (d, 2H, $J = 9.0$, H^k), 8.13 (d, 2H, $J = 9.0$, H^m), 7.63 (d, 1H, $J = 16.2$, H^v), 7.50 (d, 2H, $J = 7.2$, H^p), 7.44 (d, 2H, $J = 8.7$, H^w), 7.40 (m, 3H, $H^r + H^s$), 7.30 (d, 2H, $J = 9.0$, H^l), 6.97 (d, 2H, $J = 9.0$, H^j), 6.87 (d, 2H, $J = 8.7$, H^x), 6.42 (dd, 2H, $J_1 = 17.3$, $J_2 = 1.5$, H^a), 6.33 (dd, 1H, $J_1 = 8.3$, $J_2 = 3.8$, H^n), 6.28 (d, 1H, $J = 16.2$, H^u), 6.13 (dd, 2H, $J_1 = 17.3$, H^c), 5.82 (dd, 2H, $J_1 = 10.5$, $J_2 = 1.5$, H^b), 4.64 (dd, 1H, $J_1 = 8.3$, $J_2 = 11.8$, H^o), 4.55 (dd, 1H, $J_1 = 3.8$, $J_2 = 11.8$, H^o), 4.18 (t, 4H,

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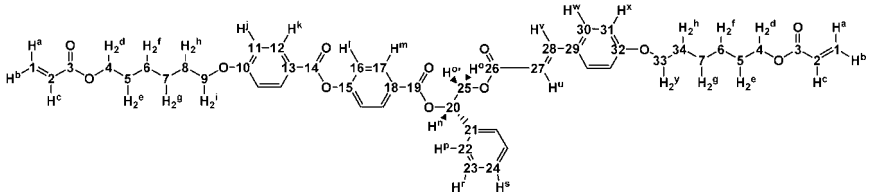
$J = 6.4$, H^d), 4.05 (t, 2H, $J = 6.4$, H^i), 3.98 (t, 2H, $J = 6.4$, H^y), 1.82 (q, 4H, $J = 6.4$, H^h), 1.72 (q, 4H, $J = 6.4$, H^e), 1.49 (m, 8H, $H^f + H^g$).

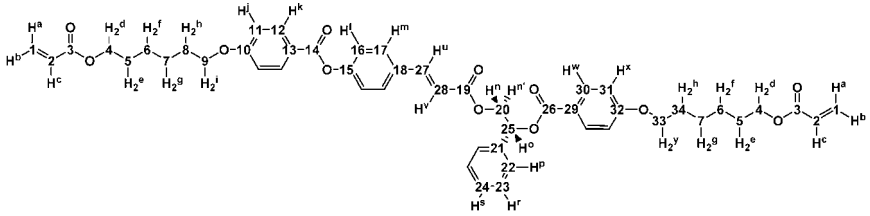


^{13}C NMR (δ in ppm, relative to TMS): 167.3 (C^{26}), 166.7 (C^3), 165.4 (C^{19}), 164.7 (C^{14}), 164.1 (C^{10}), 161.4 (C^{32}), 155.4 (C^{15}), 145.7 (C^{28}), 137.8 (C^{21}), 132.8 (C^{12}), 131.8 (C^{17}), 131.0 (C^1), 130.3 (C^{30}), 129.1 ($C^{23} + C^{24}$), 129.0 (C^2), 127.8 (C^{18}), 127.2 (C^{29}), 127.1 (C^{22}), 122.3 (C^{16}), 121.5 (C^{13}), 115.2 (C^{27}), 114.8 ($C^{11} + C^{31}$), 74.7 (C^{25}), 68.5 (C^9), 68.3 (C^{33}), 66.4 (C^{20}), 64.9 (C^4), 29.4 ($C^8 + C^{34}$), 28.9 (C^5), 26.1 ($C^6 + C^7$).

2.2.9. Synthesis of 2-(4-(6-Acryloyloxyhexyloxy)benzoyloxy)-2-(R)-phenylethyl 4-(4-(6-Acryloyloxyhexyloxy)benzoyloxy)-cinnamate (5)

This compound was obtained as a solid with 40% yield in the same manner as described for 2-(4-(6-acryloyloxyhexyloxy)cinnamoyloxy)-2-(R)-phenylethyl 4-(4-(6-acryloyloxyhexyloxy)benzoyloxy)benzoate (**3**) starting from 4-(6-acryloyloxyhexyloxy)benzoic acid (**7a**) and (R)-2-hydroxy-2-phenylethyl 4-(4-(6-acryloyloxyhexyloxybenzoyloxy)cinnamate (**12b**).

^1H NMR (δ in ppm, relative to TMS, J in Hz): 8.14 (d, 2H, $J = 9.0$, H^k), 8.05 (d, 2H, $J = 8.7$, H^w), 7.67 (d, 1H, $J = 16.2$, H^v), 7.54 (d, 2H, $J = 9.0$, H^m), 7.47 (d, 2H, $J = 7.2$, H^p), 7.40 (m, 3H, $H^r + H^s$), 7.22 (d, 2H, $J = 9.0$, H^l), 6.97 (d, 2H, $J = 9.0$, H^j), 6.91 (d, 2H, $J = 8.7$, H^x), 6.42 (dd, 2H, $J_1 = 17.3$, $J_2 = 1.5$, H^a), 6.40 (d, 1H, $J = 16.2$, H^u), 6.31 (dd, 1H, $J_1 = 8.3$, $J_2 = 3.8$, H^o), 6.13 (dd, 2H, $J_1 = 17.3$, $J_2 = 10.5$, H^c), 5.82 (dd, 2H, $J_1 = 10.5$, $J_2 = 1.5$, H^b), 4.64 (dd, 1H, $J_1 = 8.3$, $J_2 = 12.1$, H^n), 4.53 (dd, 1H, $J_1 = 3.8$, $J_2 = 12.1$, $H^{n'}$), 4.18 (t, 4H, $J = 6.4$, H^d), 4.05 (t, 2H, $J = 6.4$, H^i), 4.01 (t, 2H, $J = 6.4$, H^y), 1.82 (q, 4H, $J = 6.4$, H^h), 1.72 (q, 4H, $J = 6.4$, H^e), 1.49 (m, 8H, $H^f + H^g$).



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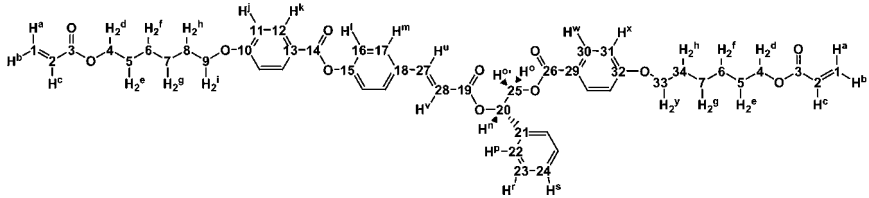
^{13}C NMR (δ in ppm, relative to TMS): 166.9 (C^{26}), 166.7 (C^{3}), 165.8 (C^{19}), 165.0 (C^{14}), 164.0 (C^{10}), 163.5 (C^{32}), 153.1 (C^{15}), 144.8 (C^{28}), 137.3 (C^{21}), 132.8 (C^{12}), 132.2 (C^{17}), 132.1 (C^{18}), 131.0 (C^{1}), 129.7 (C^{30}), 129.1 (C^{23}), 129.0 ($C^{2} + C^{24}$), 127.1 (C^{22}), 122.8 (C^{16}), 122.5 (C^{29}), 121.6 (C^{13}), 117.9 (C^{27}), 114.7 (C^{11}), 114.6 (C^{31}), 74.1 (C^{25}), 68.5 (C^{9}), 68.4 (C^{33}), 66.7 (C^{20}), 64.9 (C^{4}), 29.4 ($C^{8} + C^{34}$), 28.9 (C^{5}), 26.1 ($C^{6} + C^{7}$).

2.2.10. Synthesis of 2-(4-(6-Acryloyloxyhexyloxy)benzoyloxy)-1-(R)-phenylethyl 4-(4-(6-Acryloyloxyhexyloxy)benzoyloxy)-cinnamate (6)

This compound was obtained as a solid with 70% yield in the same manner as described for 2-(4-(6-acryloyloxyhexyloxy)cinnamoyloxy)-2-(R)-phenylethyl 4-(4-(6-acryloyloxyhexyloxy)benzoyloxy)benzoate (**3**) starting from 4-(4-(6-acryloyloxyhexyloxy)benzoyloxy)cinnamic acid (**10b**) and (R)-2-hydroxy-2-phenylethyl 4-(6-acryloyloxyhexyloxy)-benzoate (**16a**).

^{1}H NMR (δ in ppm, relative to TMS, J in Hz): 8.14 (d, 2H, $J = 9.0$, H^{k}), 7.96 (d, 2H, $J = 8.7$, H^{w}), 7.73 (d, 1H, $J = 16.2$, H^{v}), 7.58 (d, 2H, $J = 9.0$, H^{m}), 7.49 (d, 2H, $J = 7.2$, H^{p}), 7.40 (m, 3H, $H^{r} + H^{s}$), 7.24 (d, 2H, $J = 9.0$, H^{l}), 6.97 (d, 2H, $J = 9.0$, H^{j}), 6.88 (d, 2H, $J = 8.7$, H^{x}), 6.42 (dd, 2H, $J_1 = 17.3$, $J_2 = 1.5$, H^{a}), 6.50 (d, 1H, $J = 16.2$, H^{u}), 6.33 (dd, 1H, $J_1 = 7.4$, $J_2 = 4.5$, H^{n}), 6.13 (dd, 2H, $J_1 = 17.3$, $J_2 = 10.5$, H^{c}), 5.82 (dd, 2H, $J_1 = 10.5$, $J_2 = 1.5$, H^{b}), 4.64 (dd, 1H, $J_1 = 7.4$, $J_2 = 12.1$, H^{o}), 4.58 (dd, 1H, $J_1 = 4.4$, $J_2 = 12.1$, $H^{o\prime}$), 4.18 (t, 4H, $J = 6.4$, H^{d}), 4.05 (t, 2H, $J = 6.4$, H^{i}), 4.00 (t, 2H, $J = 6.4$, H^{y}), 1.82 (q, 4H, $J = 6.4$, H^{h}), 1.72 (q, 4H, $J = 6.4$, H^{e}), 1.49 (m, 8H, $H^{f} + H^{g}$).



^{13}C NMR (δ in ppm, relative to TMS): 166.7 (C^{3}), 166.4 (C^{26}), 166.3 (C^{19}), 165.0 (C^{14}), 164.0 (C^{10}), 163.5 (C^{32}), 153.1 (C^{15}), 144.9 (C^{28}), 137.1 (C^{21}), 132.8 (C^{12}), 132.2 (C^{18}), 132.1 (C^{17}), 131.0 (C^{1}), 129.7 (C^{30}), 129.1 (C^{23}), 129.0 ($C^{2} + C^{24}$), 127.2 (C^{22}), 122.8 (C^{16}), 122.3 (C^{29}), 121.6 (C^{13}), 118.2 (C^{27}), 114.7 (C^{11}), 114.6 (C^{31}), 74.1 (C^{20}), 68.5 (C^{9}), 68.4 (C^{33}), 66.7 (C^{25}), 64.9 (C^{4}), 29.4 ($C^{8} + C^{34}$), 28.9 (C^{5}), 26.1 ($C^{6} + C^{7}$).

2.3. Cholesteric Film Formation

Cholesteric layers with a thickness of about 3.5 μm were made by spin-coating at 800 rpm a solution containing 43% (w/w) solid material in

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xylene onto a glass plate coated with a rubbed alignment layer. The alignment layer induces a planar orientation of the liquid-crystalline molecules. The solid material consisted of 16–20 wt% of one of the chiral compounds **3, 4, 5**, or **6**, 1% of Darocur® 4265 and 79–83% of a 1:4 mixture of RM82 and RM 257.

The color change in the films before polymerization was effected in air by UV irradiation. A Philips HPA 400 S lamp that emits a broad spectrum in the near UV region was used. After irradiation and heating at 70°C for 1 min the film was polymerized in a nitrogen atmosphere using the same lamp. The polymerization process was completed by heating for 90 min at 150°C in a nitrogen atmosphere.

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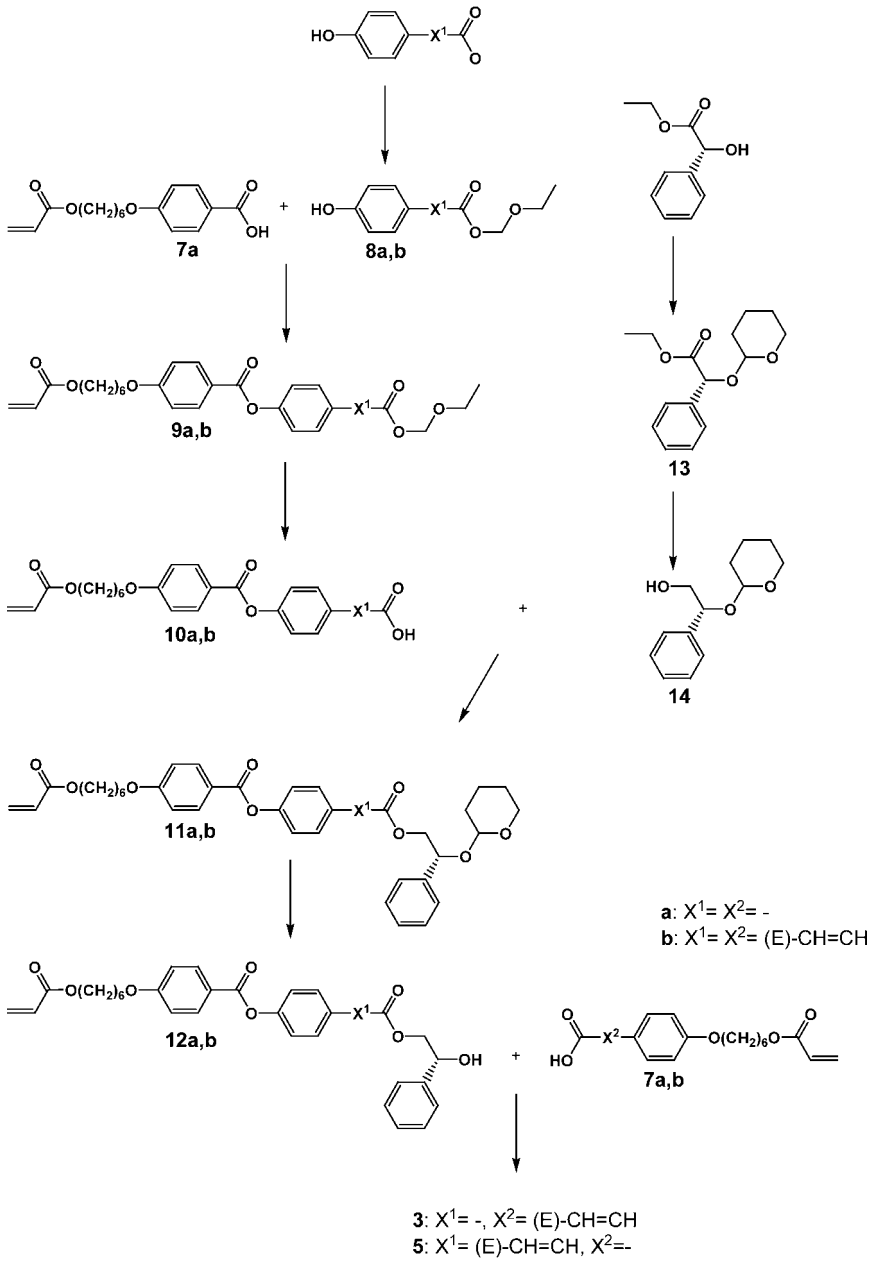
3. RESULTS AND DISCUSSION

3.1. Synthesis of 3, 4, 5, and 6

To obtain the final products, the two different hydroxyl groups of (R)-phenylethanediol had to be esterified selectively with two different acids. For this purpose, THP-protected derivative **14** was used. This compound was made starting from ethyl (R)-mandelate via intermediate **13** (see Scheme 1) using a known procedure [22]. By subsequent esterification with acid **10a** or acid **10b** followed by deprotection of **11a** or **11b** and then esterification with **7b** or **7a**, products **3** or **5** were prepared, respectively. Acids **10a** and **10b** were prepared starting from 4-hydroxybenzoic acid and 4-hydroxycinnamic acid, respectively. These acids were protected as ethoxymethyl esters **8a** and **8b** before esterification with the acrylate-containing acid **7a**. Deprotection of **9a** and **9b** was performed under very mild acidic conditions. Product **4** (see Scheme 2) was made in the same manner as **3**, but the esterification sequence was reversed. In the same way, **6** was made with the same acids used for the preparation of **5**.

3.2. Properties and Photochemistry of 3, 4, 5, and 6

All four new compounds are crystalline powders that form isotropic phases upon melting. Comparison of both types of isomers reveals that **3** and **5** have higher melting points than **4** and **6**, respectively (see Table 1). The central phenyl group in the moiety derived from phenylethanediol in compounds **3** and **5** is connected to the group derived from **10a** and **10b**, respectively, by an even number of atoms. In the case of the other two compounds, this connection is made by an odd number of atoms. This odd–even effect probably explains these differences in melting points.



SCHEME 1 Synthesis of compounds **3** and **5**.

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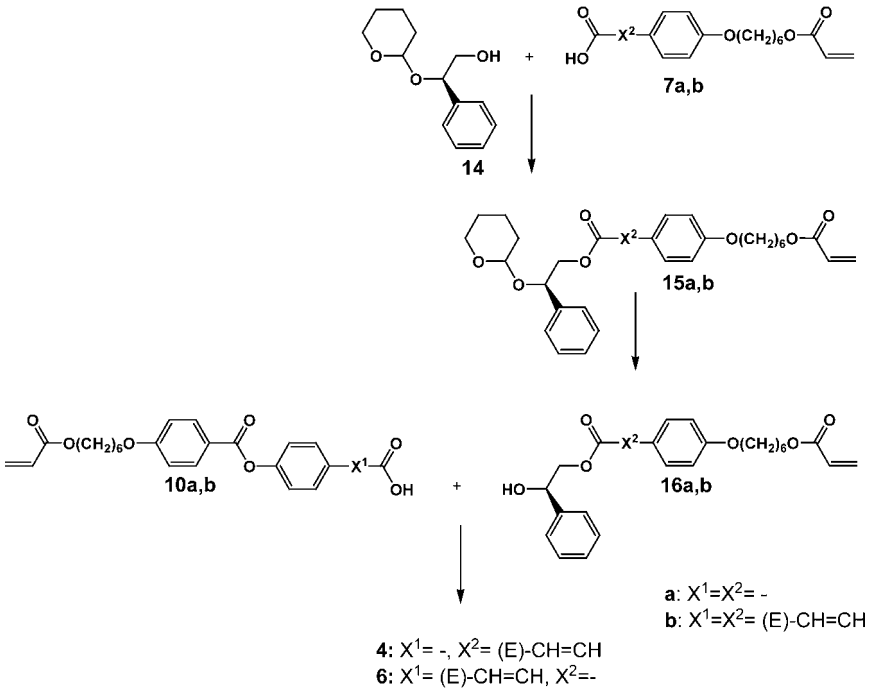

SCHEME 2 Synthesis of compounds **4** and **6**.

To study the photo-isomerization of these compounds, solutions in deuterated dichloromethane were irradiated and analyzed by ^{1}HNMR spectroscopy. The E-Z isomerization was followed as a function of irradiation time. The conversion was determined by integration of the new signals originating from the Z-isomer. In the case of **3** and

TABLE 1 Physical Properties of Menthone Derivative **1** and (R)-Phenylethanediol Derivatives **3**, **4**, **5**, and **6** and Conversion to the Z-Isomers after Irradiation, Measured by ^{1}H-NMR Spectroscopy

Compound	Mp (°C)	*HTP* (μm^{-1}) (after polymerization)	Conversion (%) measured from NMR spectra
1	76	−20	97
3	81	−19	30
4	53	−25	30
5	97	−18	38
6	80	−21	38

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5, a shift of about 0.4 ppm of the olefinic protons (H^u, see Experimental) was used. In the case of **4** and **6**, the shift of the signals of the olefinic protons of the Z-isomers were obscured by the signals of the acrylic group. In this case, the shift of one of the protons in the aromatic ring of the cinnamate moiety (0.1 ppm for H^x and 0.15 ppm for H^l, respectively) was used. Irradiating with a PL-10 lamp that emits light around 365 nm resulted in a 12% conversion of compounds **3** and **4** and no conversion of compounds **5** and **6**.

Figure 2 shows the UV spectra of **3** and **5** in acetonitrile solution. These spectra are identical to those of **4** and **6**, respectively. This shows that the position of the phenyl group in the moiety derived from phenylethanediol does not have an effect on the UV spectra of these compounds, but the position of the cinnamate moiety does. The extinction around 365 nm, especially of compounds **5** and **6**, is very low, **which might explain the low** conversion or even the lack of conversion of the photo-isomerization reaction. Comparison of the UV spectrum of **5** with that of **3** reveals a blue shift. The band at approximately 311 nm in Fig. 2 can be assigned to the cinnamate moiety of compound **3**. This band has shifted to about 276 nm in the case of compound **5**. This shift can be explained by the fact that the electron-donating alkoxy group, substituted in the para position of the cinnamate group

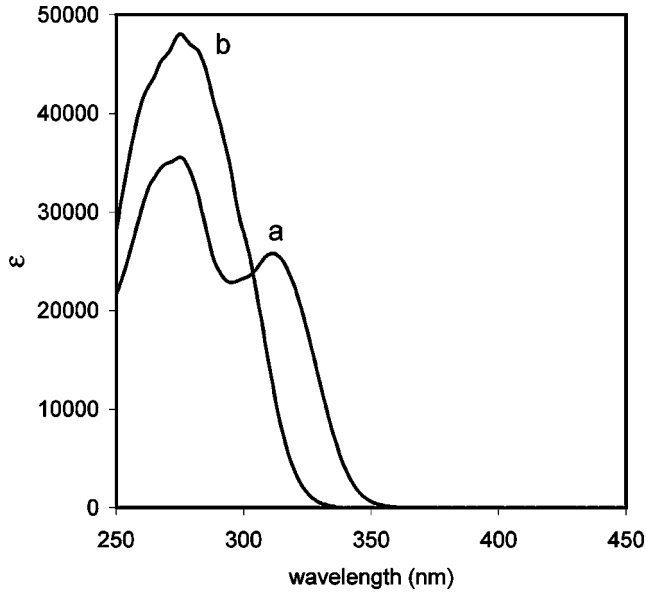

FIGURE 2 Absorption UV spectra of a solution of **3** (a) and **5** (b) in acetonitrile.

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of compound **3**, is replaced by a less electron-donating arylcarbonyloxy group in compound **5**. These spectral differences explain why **5** and **6** convert less than **3** and **4** upon irradiation with a PL-10 lamp.

The use of a TL-08 lamp emitting broadband around 350 nm, resulted in a much higher conversion in all cases because the emitted light coincides better with the absorption bands. The conversions for the four compounds are shown in Table 1. Compounds **3** and **4** show a conversion of 30% when they reach a photostationary state. The difference–UV spectra for several irradiation times between the irradiated and nonirradiated compound **3** are shown in Fig. 3. Similar spectra were obtained with compound **4**. Thus, the position of the phenyl group in the moiety derived from phenylethanediol did not observably affect the UV spectra and the photochemistry. Moreover, the isosbestic point at 269 nm indicates a clean isomerization process without side reactions, even after prolonged irradiation. The NMR spectra also indicate a clean isomerization reaction, because the NMR spectra did not change after forming the photostationary state.

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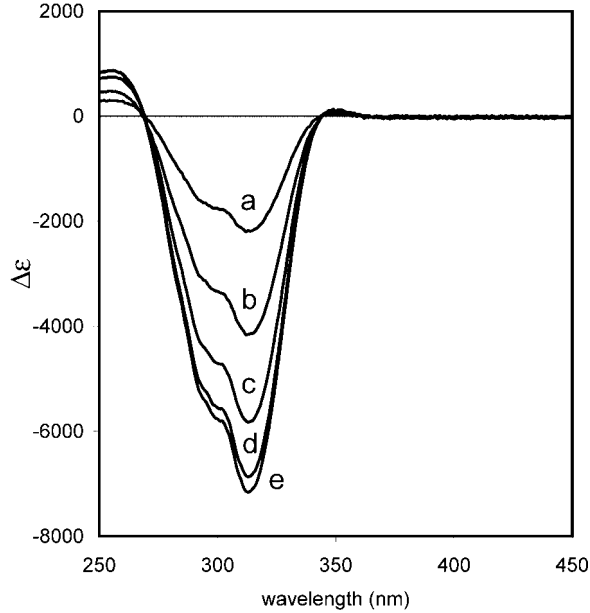

FIGURE 3 Absorption UV difference spectra of a solution of **3** in acetonitrile after irradiation for 1 min (a), 2 min (b), 4 min (c), 8 min (d), and 256 min (e) with a Tl-08 lamp.

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Table 1 demonstrates that compounds **5** and **6** show a 38% conversion of the photo-isomerization reaction when they reach a photostationary state. Contrary to compounds **3** and **4**, significant yellowing of the NMR solution occurred after prolonged irradiation, suggesting the occurrence of side reactions. However, the NMR spectra showed only minor changes upon prolonged irradiation. The difference–UV spectra for several irradiation times between the irradiated and non-irradiated compound **5** are shown in Fig. 4. These spectra clearly show a deviation from the isosbestic point (inset, Fig. 4) and an increase in the absorption above 350 nm upon prolonged irradiation. Similar results were obtained with compound **6**. Thus another photochemical process is operative, resulting in yellowing of the material. It is possible that the benzoyloxycinnamate group in compounds **5** and **6** is more susceptible to a photo-Fries rearrangement [23] than the benzoyloxybenzoate group in compounds **3** and **4**. This may explain the absence of by-products in the case of **3** and **4**. Concerning application in cholesteric color filters, these side reactions will not cause problems because they were only observed long after the formation of the photostationary state.

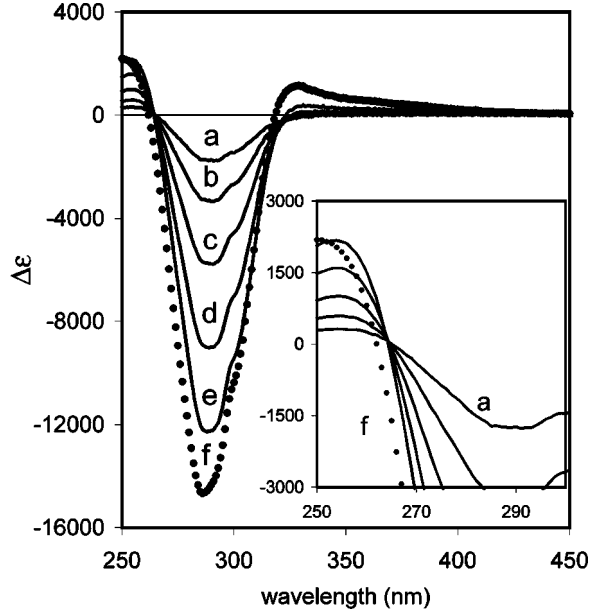

FIGURE 4 Absorption UV difference spectra of a solution of **5** in acetonitrile after irradiation for 2 min (a), 4 min (b), 8 min (c), 16 min (d), 32 min (e), and 256 min (f) with a Tl-08 lamp.

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3.3. Helical Twisting Power and Irradiated Cholesteric Layers

To determine the helical twisting power of the four compounds in cholesteric polymeric films, films consisting of mixtures of one of these compounds with nematic di-acrylates were copolymerized. For this purpose, cholesteric layers were made by spincoating a mixture of one of the chiral compounds with the nematic di-acrylates RM82 and RM257 and the photo-initiator in xylene on a rubbed polyimide layer. The advantage of using these nematic di-acrylates is that they do not crystallize rapidly, which makes it possible to handle the liquid film at room temperature (i.e., in the supercooled state). After heating at 70°C for about 1 min, good alignment was obtained and photopolymerization was performed at room temperature under nitrogen, followed by thermal polymerization at 150°C. From the transmission spectra, such as the one shown in Fig. 5 obtained with compound **5**, the reflection wavelength was determined as the center of the reflection band. The helical twisting power was then calculated according to Eq. (1), using a mean refractive index of about 1.6 of these materials after polymerization [24]. The *HTP* values are presented in Table 1

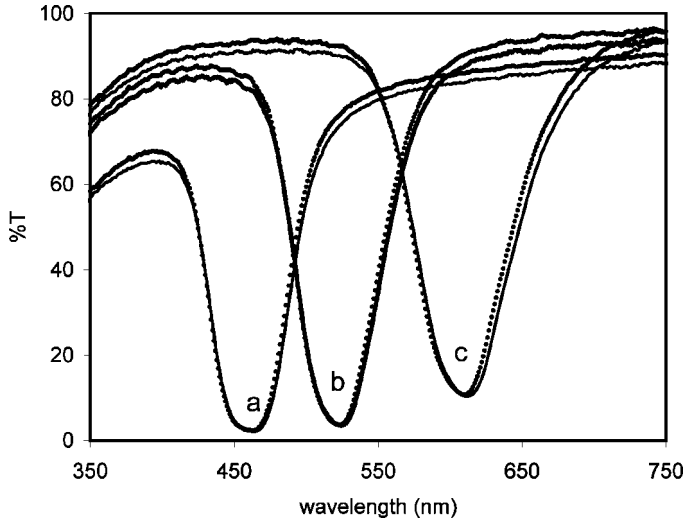

FIGURE 5 Transmission spectra of a 3.5-μm-thick cholesteric polymeric film consisting of a copolymer of RM82, RM257, and 19% of isomerizable compound **5**, without irradiation before polymerization (a), irradiation before polymerization (b), and (c) with irradiation times increasing in the order b < c. The dotted lines are the spectra of the same polymeric films, obtained after heating at 200°C for 6 h in a nitrogen atmosphere.

and were found to be around that of the menthone compound **1**, thus sufficient to generate a small pitch to obtain blue reflecting layers. The differences in *HTP* values between the four compounds are reversed in order of the melting points. This may point to some relationship with the odd–even effect referred to previously. However, it is still difficult to understand what molecular interactions determine the helical pitch, and because the differences are not very big, no real structure–property relationship can be deduced from these observations.

To generate the green and red colors, irradiation was performed in air on the wet blue monomer film before polymerization. Then the 70°C step was performed, followed by photopolymerization and the thermal (post-)polymerization step at 150°C, as described for the blue reflecting film. In all cases, the increase in pitch upon irradiation was big enough to have the colors disappear into the infrared region. This means that the conversion of 30% and 38% shown in Table 1 for compounds **3** or **4** and **5** or **6**, respectively, is sufficient for a pitch change of at least 50%. However, care should be taken when comparing the NMR experiments in dichloromethane with the experiment with the films. The different environments (i.e., dichloromethane solution versus wet film) and experimental conditions may influence the isomerization reaction. Future experiments where the properties of the Z-isomers are determined or where the irradiated films are analyzed before polymerization may give a better insight into the relationship between the conversion of the isomerization reaction and the helical pitch change. The most important conclusion from these experiments, however, is that all four compounds have *HTP* values that are high enough and have changes in the *HTP* values upon irradiation that are sufficient for the manufacturing of cholesteric colour filters.

Figure 5 (normal lines) shows the transmission spectra of cholesteric polymeric films made with **5**. The same spectra were obtained using one of the other three chiral compounds. The green and red colors were obtained by optimizing different irradiation times for these colors. In all cases, the reflected light was left-handed circularly polarized, which is in accordance with the observation of the left-handed helix in cholesteric mixtures with model compound **2** that was also derived from R-phenylethanediol [15].

The same polymer films were analyzed by spectroscopy after heating them at 200°C for 6 h. The spectra after this thermal treatment are also presented in Fig. 5 (dotted lines). Comparison of the spectra before and after the treatment reveals that no significant change in reflection wavelength or reflection intensity can be observed, thus these polymeric films are thermally very stable. Similar cholesteric films made with the menthone-derived compound **1** show blue shifts

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of up to 10 nm and a decrease in reflection intensity when thermally treated [10,18]. Thus, the films made with the new phenylethanediol-derived compounds exhibit a higher thermal stability, which is important when these films are processed further in the manufacturing of reflective LCDs [10].

Although the mechanism responsible for the thermal degradation of the films made with menthone derivative **1** has not yet been elucidated, the improved thermal stability of the films prepared from **3**, **4**, **5**, and **6** can be attributed to the higher cross-link density of the polymerized film, the greater stability of the chemical structure of the newly synthesized molecules, or a combination of both effects. To distinguish between these two effects, mono-acrylates derived from R-phenylethanediol and mono-acrylates with a structure similar to the di-acrylates RM82 and RM257 could be prepared and used. Mono-acrylates with structures similar to **3**, **4**, **5**, and **6** could be prepared fairly easily using non-acrylate-containing acids instead of the acids **7a**, **7b**, **10a**, and **10b** in Schemes 1 and 2. Future research will deal with these types of materials.

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4. CONCLUSIONS

Chiral isomerisable di-acrylates derived from (R)-phenylethanediol and cinnamic acid were prepared. The helical twisting power of these compounds blended with nematic di-acrylates is sufficiently high to form cholesteric films that reflect in the blue part of the visible spectrum. Upon irradiation of the E-isomeric cinnamic derivatives, the Z-isomer is formed. Because the *HTP* of these isomers is lower than that of the E-isomers, the color of the films changes. In this way, color patterning to form color filters can be carried out. The colored films can be handled at room temperature. After photopolymerization, thermally very stable films are obtained that will not lose their optical properties upon high-temperature processing during later steps in LCD manufacturing. A combination of the higher cross-link density of the polymerized film and the greater stability of the chemical structure probably account for the improved stability of the cholesteric films made with these new compounds compared with those made before with mono-acrylates derived from menthone. These compounds are very suitable for cholesteric color filter manufacture.

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