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Synthesis and photopolymerization of cholesteric liquid crystalline diacrylates

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The synthesis of chiral liquid crystalline diacrylates is described. By mixing one of them with non-chiral liquid crystalline diacrylates, cholesteric phases are obtained of which the wavelength of reflection can be chosen by the composition of the mixture. After isothermal photopolymerization of the mixture a crosslinked network is obtained with thermally stable properties.

1. Introduction

In previous publications we demonstrated the formation of uniaxially oriented polymeric networks by isothermal photopolymerization in the nematic state of aligned liquid crystalline diacrylates [1–3], diepoxides [4, 5] and divinyl ethers [6]. These networks show interesting anisotropic thermal and mechanical properties, such as a lower thermal expansion coefficient and a higher modulus in the direction of molecular orientation than in the lateral directions [7, 8]. Their anisotropic optical properties are mainly manifested by an almost temperature-independent birefringence Δn (for example, Δn changes only about 3 per cent between 50° and 200°C) [1], which is very useful for optical applications.

By adding small amounts of a chiral dopant before polymerization of the nematic diacrylates, networks with a helicoidal structure can be obtained [9]. A typical network obtained by adding 2 per cent of a chiral dopant has a pitch p of about 5 μm. The pitch increases by about 2 per cent when the sample is heated from 20°C to 100°C, as a result of the thermal expansion of the polymer. By increasing the amount of chiral dopant, p will decrease and ultimately will have a value equal to the wavelength of visible light. Such cholesteric materials reflect light of which the wavelength at maximum reflection for perpendicular incident light (λ_m) is given by

$$\lambda_m = p\sqrt{(n_e^2 + n_o^2)/2} \qquad (1)$$

and the bandwidth of the reflected band ($\Delta\lambda$) is given by:

$$\Delta\lambda = p(n_e - n_o), \qquad (2)$$

where n_e and n_o are the effective extraordinary and ordinary refractive indices of a uniaxially oriented nematic film, respectively [10].

The reflected light is circularly polarized, the polarization direction being the same as that of the helix of the cholesteric material. Light with the other polarization direction is transmitted. Clearly these properties make the material also very useful for optical applications.

Materials with a higher content of chiral dope, the so-called cholesteric anisotropic gels and plasticized networks, have been described before [11–13]. In the case of the anisotropic gels, which contain a small amount of reactive diacrylates, electrically induced colour changes and scattering can be induced [11]. In the case of the plasticized networks, which contain a larger amount of reactive diacrylate, optical recording by locally removing chiral molecules has been demonstrated [13]. The use of such a system in the production of cholesteric networks with thermal stability has also been demonstrated.

Cholesteric side chain polymers show thermally stable optical properties below the glass transition [14–16]. These materials can be stabilized more by crosslinking [17].

In this paper we will describe a crosslinked cholesteric network with thermally stable optical properties starting from chiral nematic diacrylates. In the case that the materials have a sufficiently small p, the wavelength of reflection can be chosen by the ratio of a blend of nematic and chiral nematic molecules and the temperature before polymerization. Corresponding to the nematic diacrylates, the structure can then be frozen in by isothermal photopolymerization. Nematic diacrylate **1 a** (see scheme 1) can be used to form the above-mentioned uniaxially oriented polymeric networks. It has a relatively broad thermotropic nematic phase of about 40°C [1]. Chiral centres have to be introduced in this compound, to induce the cholesteric phase. This can be done in the hexamethylene spacers between the mesogenic group and the

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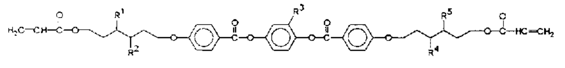
Scheme 1. Structures of the diacrylates mentioned in the text.



	R^1	R^2	R^3	R^4	R^5
1 a	H	H	H	H	H
1 b	H	H	CH_3	H	H
1 c	CH_3	H	H	H	H
1 d	H	CH_3	H	H	H
1 e	CH_3	H	H	H	CH_3
1 f	H	CH_3	H	CH_3	H

acrylate groups of **1 a**. In this way molecules **1 c** and **1 d** each containing one chiral centre, and molecules **1 e** and **1 f**, each containing two chiral centres per molecule, were designed. The synthesis of the nematic diacrylates **1 a** and **1 b** has been described in previous publications [1, 2]. The hexamethylene spacer was derived from 6-chlorohexanol. This means that in the chiral molecules in scheme 1, the spacer has to be derived from 3-methyl-6-chlorohexanol or 4-methyl-6-chlorohexanol. This paper describes the synthesis of these intermediates and the liquid crystals formed from them. The properties of the liquid crystals and their polymeric networks will also be discussed.

2. Experimental

2.1. *Synthesis*

All solvents were obtained from Merck. All other chemicals were obtained from Janssen Chimica except (*S*)-(−)citronellol which was obtained from Merck.

The syntheses of 4-(6-acryloyloxyhexyloxy)benzoic acid, 1,4-di-(4-(6-acryloyloxyhexyloxy)benzoyloxy)benzene **1 a** and 1,4-di-(4-(6-acryloyloxyhexyloxy)benzoyloxy)-2-methylbenzene **1 b** are described elsewhere [1, 2]. All diacrylates were more than 96 per cent pure according to HPLC. All products exhibit ^{1}H NMR spectra (300 MHz) that are in accordance with their structures.

2.1.1. (*S*)-*citronellyl chloride* **3**

A mixture of 64 g of (*S*)-(−)-citronellol **2**, 130 g of triphenylphosphine and 200 ml of carbon tetrachloride was heated under reflux for 16 h. After cooling, 400 ml of pentane were added and the precipitated phosphorus compounds were filtered off. After distillation, 51·2 g of the product (72 per cent) were obtained as a clear liquid (b.p. = 95–96°C, $p = 15$ mbar).

2.1.2. (*S*)-*4-Methyl-6-chlorohexanol* **4**

A solution of 50 g of (*S*)-citronellyl chloride **3** in 250 ml of methanol was ozonized at − 15°C. After termination of the ozonolysis, 9·5 g of sodium borohydride was added in portions to the vigorously stirred solution at such a rate that the temperature did not exceed 0°C. After addition of the sodium borohydride, the solution was stirred for another 2 h at room temperature and was then added to a mixture of 200 g of ice, 200 ml of water and 27 ml of sulphuric acid. The crude product which separates, was extracted into 250 ml of chloroform. The chloroform layer was shaken with 200 ml of a 10 per cent aqueous sodium bicarbonate solution, dried over magnesium sulphate and evaporated. After distillation, 30·2 g of the product (70 per cent) were obtained as a clear liquid (b.p. = 90–92°C, $p = 4$ mbar).

2.1.3. (*S*)-*Citronellyl acetate* **5**

Over a period of 30 min 22 ml of acetyl chloride were added to a solution of 43 g of (*S*-(−)-citronellol **2** and 45 ml of triethylamine in 150 ml of diethyl ether, precooled to 0°C. After stirring for another 30 min at room temperature, the mixture was filtered and the diethyl ether evaporated. After distillation of the residue 49·1 g of product (89 per cent) were obtained as a clear liquid (b.p. = 114°C, $p = 14$ mbar).

2.1.4. (*S*)-*6-Hydroxy-3-methylhexyl acetate* **6**

This product was obtained in 77 per cent yield from (*S*)-citronellyl acetate **5** in a similar way to that described for (*S*)-4-methyl-6-chlorohexanol **4**. It was not purified but used immediately in the next step.

2.1.5. (*S*)-*6-Chloro-3-methylhexyl acetate* **7**

32 g of crude (*S*)-6-hydroxy-3-methylhexyl acetate **6** were added to 41 ml of thionyl chloride over a period of 45 min. After boiling for 2 h, the excess of thionyl chloride was evaporated using a rotary evaporator. After distillation, 22·5 g of the product (62 per cent) were obtained as a clear liquid (b.p. = 124–127°C).

2.1.6. (*S*)-*4-(6-Hydroxy-3-methylhexyloxy)benzoic acid* **8–1**

6 g of sodium methoxide were added to a stirred solution of 20 g of ethyl 4-hydroxybenzoate in 100 ml of butan-2-one. After a clear solution had been obtained, 15 g of (*S*)-4-methyl-6-chlorohexanol **4** were added and the solution was boiled for 18 h. After evaporation of the butan-2-one, 100 ml of diethyl ether and 100 ml of water were added. After separation, the ether layer was shaken twice with 50 ml of a 10 per cent aqueous sodium hydroxide solution. After evaporation of the ether, the crude ester was mixed with a solution of 10 g of potassium hydroxide in 80 ml of water. The mixture was boiled for 2 h, cooled to room temperature, filtered an washed twice with 50 ml of ether. 30 g of ice were added to the aqueous layer. This layer was acidified with a 6 N hydrochloric acid solution, with vigorous stirring. The crude product

obtained after filtration was washed twice with 100 ml of water and dried at 75°C *in vacuo*. 22 g of the product (87 per cent) were obtained as a white powder.

2.1.7. *(S)-4-(6-Hydroxy-4-methylhexyloxy) benzoic acid* **8–2**

This product was obtained in 79 per cent yield from (*S*)-6-chloro-3-methylhexyl acetate **7** in a similar way to that described for (*S*)-4-(6-hydroxy-3-methylhexyloxy)benzoic acid **8–1**.

2.1.8. *(S)-4-(6-Acryloyloxy-3-methylhexyloxy)benzoic acid* **9–1**

Over a period of 30 min, 8·5 ml of acryloyl chloride were added to a stirred mixture of 22 g of (*S*)-4-(6-hydroxy-3-methylhexyloxy)benzoic acid **8–1**, 13 ml of *N,N*-dimethylaniline, 0·2 g of 2,6-di-*t*-butyl-4-methylphenol and 200 ml of 1,4-dioxan heated to 50°C. After stirring for 2 h at this temperature a homogeneous solution was obtained, which was added over a 30 min period to a vigorously stirred mixture of 0·5 l of water, 100 g of ice and 3 ml of concentrated hydrochloric acid. The precipitated crude product was washed for 30 min with 250 ml of water, and dried at 60°C *in vacuo* 24·5 g of the product (94 per cent) were obtained as a white powder.

2.1.9. *(S)-4-(6-Acryloyloxy-4-methylhexyloxy)benzoic acid* **9–2**

The product was obtained in 88 per cent yield from (*S*)-4-(6-hydroxy-4-methylhexyloxy)benzoic acid **8–2**. in a similar way to that described for (*S*)-4-(6-acryloyloxy-3-methylhexyloxy)benzoic acid **9–1**.

2.1.10. *(S)-(−)-1,4-di-(4-(6-Acryloyloxy-3-methylhexyloxy)benzoyloxy)benzene* **1f**

Over a period of 20 min, 8 ml of thionyl chloride were added to a mixture of 24·5 g of (*S*)-4-(6-acryloyloxy-3-methylhexyloxy)benzoic acid **9–1**, 0·5 ml of *N,N*-dimethylformamide, 0·1 g of 2,6-di-*t*-butyl-4-methylphenol and 15 ml of CH_2Cl_2, through which a stream of dry nitrogen was bubbled. After the addition of the thionyl chloride, the mixture became clear. After stirring overnight, the dichloromethane and thionyl chloride were evaporated, first at 40°C, then at room temperature in a high vacuum. The crude acid chloride was dissolved together with 17 ml of triethylamine in 130 ml of dichloromethane. After cooling the solution in an ice bath, 4·15 grams of hydroquinone were added in portions, at such a rate that the reaction temperature did not exceed 20°C. After stirring for 3 days at room temperature, a mixture of 40 g of ice, 40 ml of water and 3 ml of concentrated hydrochloric acid solution was added. After separation, the organic layer was washed with 80 ml of a concentrated sodium chloride solution. The organic layer was then eluted through magnesium sulphate (column diameter 35 mm, column height 20 mm) and over silica (same dimensions). A colourless solution was obtained which was evaporated at 30°C to yield the crude product as a white solid, 19 g (74 per cent) after crystallization from 150 ml of ethyl acetate at 0°C. HPLC showed that the product had a purity of 96 per cent.

2.1.11. *(S)-(−)-1,4-di-(4-(6-Acryloyloxy-4-methylhexyloxy)benzoyloxy)benzene* **1e**

This product was obtained in 66 per cent yield from (*S*)-4-(6-acryloyloxy-4-methylhexyloxy)benzoic acid **9–2** in a similar way to that described of (*S*)-(−)-1,4-di-(4-(6-acryloyloxy-3-methylhexyloxy)benzoyloxy)benzene **1f**.

2.1.12. *4-(Tetrahydropyran-2-yloxy)phenol* **10**

Over a period of 30 min, 90 ml of dihydropyran were added to a mixture of 110 g of hydroquinone, 8·5 g of toluene-4-sulphonic acid and 1 l of diethyl ether, with stirring. After stirring for another 2 h, the solution was filtered and nitrogen was bubbled through. The solution was shaken twice and nitrogen-purged solutions of 22·5 g of sodium hydroxide in 300 ml of water. The combined aqueous solutions were washed with 250 ml of diethyl ether and then cooled to 0°C with ice. 5 g of sodium bicarbonate were added and the vigorously stirred solution was slowly acidified with 64 ml of acetic acid. The precipitated crude product was washed twice with 300 ml of water and dried over silica *in vacuo*. The yield was 78 g (40 per cent).

2.1.13. *4-(4-(6-Acryloyloxyhexyloxy)benzoyloxy)phenol* **12**

A solution of 117 g of 4-(6-acryloyloxyhexyloxy)benzoic acid, 78 g of 4-(tetrahydropyran-2-yloxy)phenol **10**, 4·9 g of 4-dimethylaminopyridine and 0·3 g of 2,6-di-*t*-butyl-4-methylphenol in 600 ml of dichloromethane was cooled in an ice bath. 91 g of *N,N′*-dicyclohexylcarbodiimide were added. After stirring for 30 min, the ice bath was removed and stirring was continued for 16 h. After filtration, the dichloromethane was evaporated and the residual oil, which crystallized slowly, was recrystallized from 1200 ml of ethanol. Compound **11**, obtained in this way, was mixed with 750 ml of ethanol and 18 g a pyridinium toluene-4-sulphonate (0·072 mol). After the mixture had been stirred for 4 h at 60°C, a clear solution was obtained, which was poured into a vigorously stirred mixture of 750 g of ice and 1·5 l of water. The precipitated product was washed for 30 min with 1 l of water and then dried over silica *in vacuo*. The yield was 138·2 g (90 per cent) of a white powder.

2.1.14. *4-(4-(6-Acryloyloxyhexyloxy)benzoyloxy)-(4-(6-acryloyloxy-3-methylhexyloxy)benzoyloxy)benzene* **1 d**

This compound was obtained in 70 per cent yield after crystallization from 2-propanol in a similar way to that described for (*S*)-(−)-1,4-di-(4-(6-acryloyloxy-3-methylhexyloxy)benzoyloxy)benzene **1 f**. Equimolar amounts of 4-(4-(6-acryloyloxyhexyloxy)benzoyloxy)-phenol **12** and (*S*)-4-(6-acryloyloxy-3-methylhexyloxy)benzoic acid **9–1** were used.

2.1.15. *4-(4-(6-Acryloyloxyhexyloxy)benzoyloxy)-(4-(6-acryloyloxy-4-methylhexyloxy)benzoyloxy)benzene* **1 c**

This compound was obtained in 68 per cent yield after crystallization from 2-propanol using the method described for (*S*)-(−)-1,4-di-(4-(6-acryloyloxy-3-methylhexyloxy)benzoyloxy) benzene **1 f**. Equimolar amounts of 4-(4-(6-acryloyloxyhexyloxy)benzoyloxy)phenol **12** and (*S*)-4-(6-acryloyloxy-4-methylhexyloxy)benzoic acid **9–2** were used.

2.2. *Physical measurement*

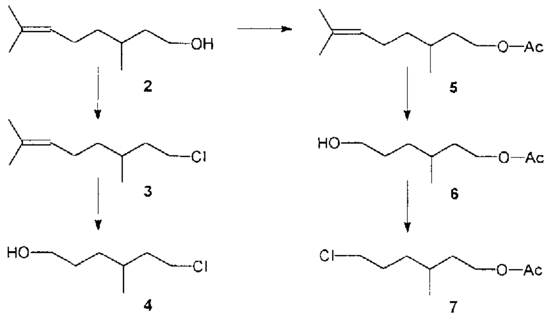
The diacrylates were stabilized by 200 ppm of 4-methoxyphenol and were made accessible for photopolymerization by the addition of 1 wt. % of Irgacure 651 (CIBA Geigy, Basel, Switzerland). Samples exhibiting the Grandjean texture were prepared by melting the monomers or their mixtures between polyimide-coated and rubbed glass substrates spacered at $6\,\mu m$. The photopolymerization was initiated by irradiation for 5 min using a fluorescent lamp (Philips, PL 10) with an intensity of 0·62 $\mathrm{mW\,cm^{-2}}$, measured at 365 nm, 20 cm away from the source.

A single-beam UV–VIS spectrometer (Unicam PU8755) was used in the optical characterization of the samples. A depolarizer, a polarization filter, a quarter-wave plate, a thermostatted sample holder with sample and a depolarizer were placed in the optical path in that order. Spectra were recorded between 360 and 860 nm, the active range of the polarizers. The sense of polarization was determined from the rotation direction of the polarizer relative to the optical axis of the quarter-wave plate required in the order to obtain maximum reflection.

3. Results and discussion

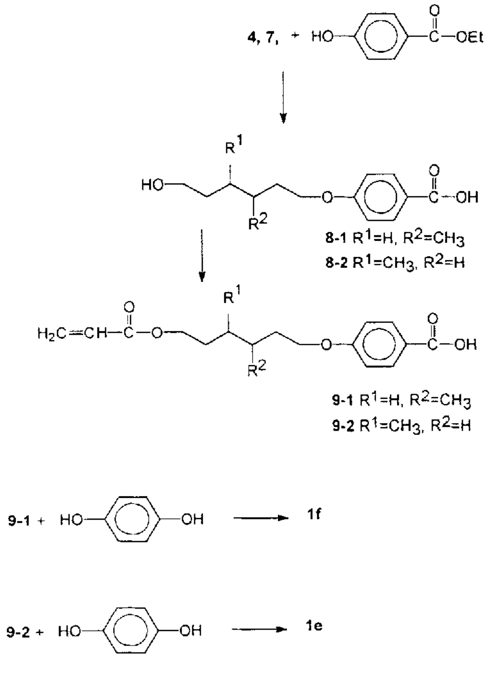
3.1. *Synthesis*

The synthesis of 4-methyl-6-chlorohexanol **4**, which forms the spacer in molecules **1 d** and **1 f**, is outlined in scheme 2. To obtain the chiral nematic phase, the enantiomeric excess necessary was introduced by using the commercially available (*S*)-(−)-citronellol **2**. To avoid isomerization of the double bond, citronellyl chloride **3** was formed under neutral conditions by using triphenylphosphine-carbon tetrachloride as the chlorinating agent. After ozonolysis of the double bond and reduction with sodium borohydride, **4** was obtained. 3-Methyl-6-chlorohexanol which was used to form the spacer in molecules. **1 c** and **1 e**, was obtained as its acetate **7**. The hydrolysis of the acetate was carried out in a later stage of the synthesis. Citronellyl acetate **5** was formed from **2** with the aid of acetyl chloride and triethylamine. It was converted into alcohol **6** similar to the conversion of **3** into **4**. **7** was formed from **6** through reaction with thionyl chloride.

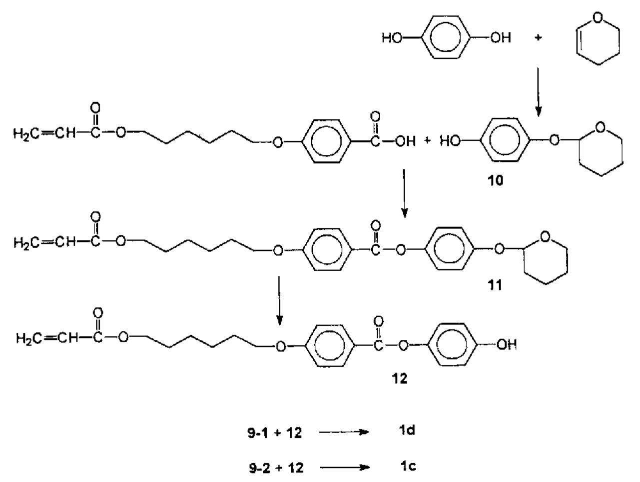


Scheme 2. Formation of (*S*)-4-methyl-6-chlorohexanol **4** and (*S*)-6-chloro-3-methylhexyl acetate **7** from (*S*)-citronellol **2**.

The chlorides **4** and **7** were used to form the corresponding intermediate acids **8–1** and **8–2**, respectively, by reaction with ethyl 4-hydroxybenzoate, followed by hydrolysis of the ester (see scheme 3). The acetate group originally present in chloride **7** was cleaved in this



Scheme 3. Formation of the symmetric diacrylates **1 e** and **1 f**.



Scheme 4. Formation of the asymmetric diacrylates **1 c** and **1d**.

reaction. Scheme 3 also shows the formation of the acrylate-containing acids **9–1** and **9–2** from **8–1** and **8–2**, respectively, by reaction with acryloyl chloride and dimethylaniline. After formation of the acid chlorides from **9–1** and **9–2**, diacrylates **1 e** and **1 f** were made respectively by reaction with hydroquinone.

The synthesis of the two diacrylates **1 c** and **1 d** containing one chiral centre per molecule is outlined in scheme 4. Hydroquinone with one hydroxyl group protected as a tetrahydropyranyl ether **10** was esterified with 4-(6-acryloyloxyhexyloxy)benzoic acid to form intermediate **11**. This was deprotected to form the phenol **12**. After esterification of **12** with the chiral acids **9–1** and **9–2**, diacrylates **1 d** and **1 c**, respectively, were formed.

3.2. *Properties*

The transition temperatures of the diacrylates are given in the table. The values of the melting point (T_M) and the clearing point (T_C) were determined from second heating DSC curves. Orthoscopic measurements revealed that all chiral diacrylates were in the cholesteric phase, having the characteristic Grandjean texture. In the case of chiral diacrylate **1 d**, DSC revealed a transition at T_T in the supercooled state. The higher-order phase was not analysed further, but is thought to be a chiral smectic phase denoted as S_X^*. A nematic isomer of **1 d** prepared from a racemic mixture of citronellol **3** showed the same transitions as **1 d**. Below T_T the focal conical texture of a smectic C phase was observed. The same phase was observed below the transition point of the non-chiral diacrylate **1 a** [1]. Therefore it is possible that the chiral diacrylate **1 d** forms a chiral smectic C phase (S_C^*) below the transition at T_T.

Transition temperatures for diacrylates **1 a**–**1 f**. T_M, melting point; T_C cleaning point; T_T N or N*–smectic transition temperature (see text).

Compound	T_M/°C	T_T/°C	T_C/°C
1 a	108	87	155
1 b	86		116
1 c	90		132
1 d	66	63	125
1 e	53		88
1 f	69		97

Upon melting of diacrylate **1 d**, a red colour appeared. Spectroscopic measurements revealed that the compound reflects right-handed circularly polarized light with $\lambda_m = 620$ nm at 110°C. No colour formation was observed upon melting of diacrylate **1 c**. This compound also reflects right-handed circularly polarized light, but at a longer wavelength ($\lambda_m = 862$ nm at 120°C). Due to the position of the chiral centre in **1 c**, which is one methylene group further away from the mesogenic centre than in **1 d**, the observation that the reflection wavelength, and thus the pitch in **1 c**, was larger than that of **1 d** is in agreement with similar effects described in the literature [18]. With both compounds **1 c** and **1 d**, reflection wavelength decreases with increasing temperature. This is a common effect observed with cholesteric molecules [18]. Because of the relatively high λ_m, these materials are not suitable for mixing with nematic diacrylates to obtain visible light reflection.

Similar non-sterol cholesteric compounds with the same absolute configuration, but with the distance between the chiral centre and the aromatic core differing by one atom, have oppositely twisted helices, according to rules proposed in the literature [19]. Since both diacrylates **1 c** and **1 d** were derived from *S*-citronellol and the chemistry applied (see scheme 2) had no effect on the absolute configuration, the absolute configuration of both diacrylates is also *S*. As seen in scheme 1, the chiral centre of **1 c** is one methylene group further away from the aromatic core than that of **1 d**. This means that this rule does not hold for these diacrylates.

Diacrylates **1 e** and **1 f** exhibit much smaller pitches. They only reflect visible light when mixed with other compounds, such as one of the nematic diacrylates **1 a** or **1 b**. Due to a big difference between the temperature ranges of the mesophases for **1 a** and **1 e** or **1 f**, such mixtures suffer from phase separation by crystallization of **1 a**. To obtain a broad mesophase, a eutectic mixture of **1 a** and **1 b** can be used. The mixture containing 20 per cent of **1 a** and 80 per cent of **1 b** has a much broader, stable mesophase than pure **1 b** [2]. Figure 1 shows the reflection wavelength at 85°C as a function of composition of **1 f** in the eutectic mixture. In this figure, the same data are plotted as the reciprocal wavelength ($1/\lambda_m$); the result is a straight line. This allows extrapolation to 100 per cent of **1 f**, which leads to a λ_m of about 290 nm for the pure

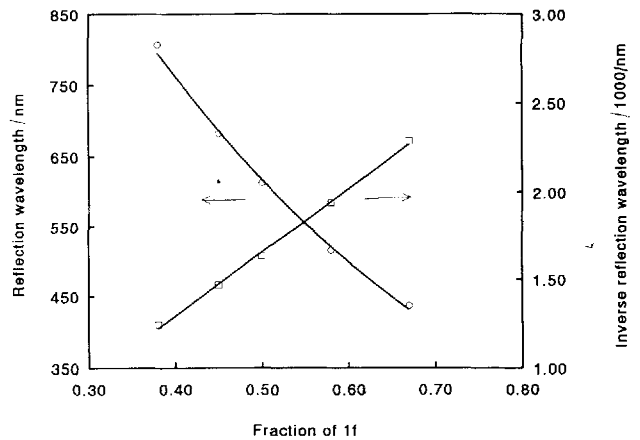


Figure 1. Reflection wavelength (○) and reciprocal reflection wavelength (□) at 85°C as a function of the amount of **1 f** in the eutectic mixture formed from **1 a** and **1 b**.

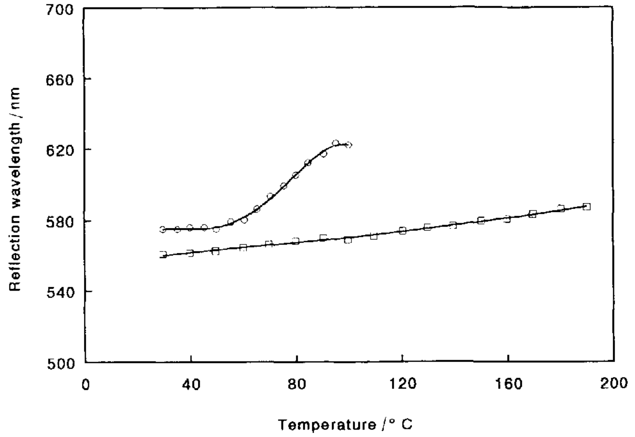


Figure 2. Dependence of the reflection wavelength on the temperature of a 1 : 1 blend of **1 f** and the eutectic mixture formed from **1 a** and **1 b** before polymerization (○) and after polymerization at 85°C (□).

compound, a value which falls outside the measuring range of our optical set-up. In the same temperature range, blends of **1 e** and the eutectic mixture yield a λ_m of about 350 nm. These diacrylate mixtures reflect right-handed circularly polarized light, as do the pure diacrylates **1 c** and **1 d**. Because **1 f** has a shorter pitch than **1 e** and is more readily obtainable through synthesis, the properties of this compound were investigated further.

In figure 2 the dependence of the reflection wavelength on temperature of a 1 : 1 blend of **1 f** and the aforementioned eutectic mixture is shown. This figure shows that above 50°C, the reflection wavelength of a 1 : 1 mixture of **1 f** and the eutectic mixture increases with increasing temperature. This is contrary to the effect of temperature on the reflection wavelength of **1 d**. A tentative explanation for this difference is as follows: the helix formation

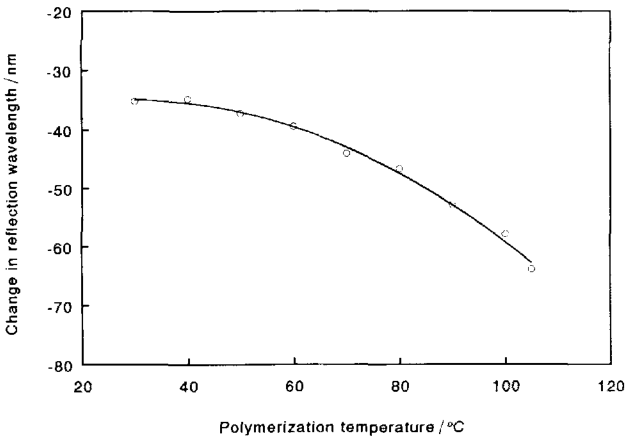


Figure 3. Difference in reflection wavelength between the monomer mixture at the polymerization temperature and the polymer at 20°C as a function of the polymerization temperature of a 1 : 1 blend of **1 f** and the eutectic mixture formed from **1 a** and **1 b**.

is determined by a balance between mesogenic interactions tending to give unwound (unidirectional) properties and twist-forming interactions due to packing caused by the chiral groups. In the case of **1 d**, the mesogenic interaction leading to higher order at lower temperature, especially near the cholesteric–smectic transition [18], may prevail over the twisted packing caused by the *single* chiral group. This might be also the case with the mixtures containing **1 f** at temperatures below 30°C, but this could not be measured due to crystallization of the samples. Between 50° and the clearing temperature, the twisted packing caused by the *two* chiral groups in **1 f** may prevail over the mesogenic interaction, which means that on lowering the temperature, the twisted packing results in a smaller pitch. Of course the role of **1 a** and **1 b** in the mixture should also be evaluated before a final explanation of these effects can be given.

Because these diacrylates were designed to make polymeric networks and because the optical properties of these networks are easier to determine, most of the measurements have been performed on the polymers.

3.3. *Polymerization*

After isothermal photopolymerization of a 1 : 1 mixture of **1 f** and the eutectic mixture, a decrease in the reflection wavelength is observed at all polymerization temperatures, as shown in figure 3. During polymerization the density increases which results in a higher average refractive index. This should lead to an increase in the reflection wavelength. The contrary was observed, which means that the pitch decreased considerably, probably due to polymerization shrinkage or to a better ordering of the molecules during polymerization or, to a small extent, due

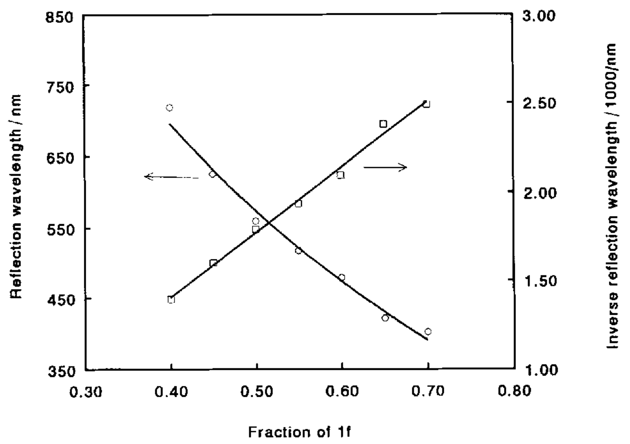


Figure 4. Reflection wavelength at 20°C (○) and reciprocal reflection wavelength (□) of polymers formed at 85°C as a function of the amount of **1 f** in the eutectic mixture formed from **1 a** and **1 b**.

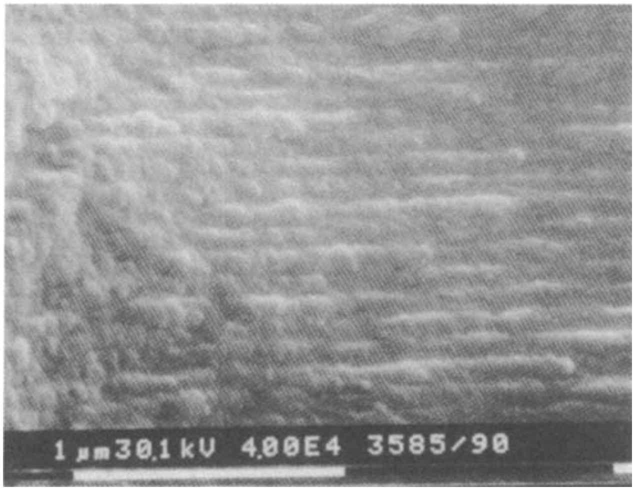


Figure 5. SEM photograph of a polymer formed from pure **1 f** polymerized at 85°C.

to shrinkage of the polymer when cooled to 20°C, the temperature at which these polymers were investigated. Figure 2 shows the last mentioned effect as the dependence of the reflection wavelength on the temperature after polymerization of the 1 : 1 mixture. A small temperature effect is observed on the refection wavelength (0·1 nm °C^{-1}). Due to the thermal expansion of the polymer, the pitch will increase with increasing temperature while the refractive index will decrease. These two effects more or less compensate one another and result in the observed low temperature effect.

Figure 4 shows the reflection wavelength at 20°C of polymers formed at 85°C as a function of the amount of **1 f** in the eutectic mixture. A comparison of this figure with figure 1 shows that all compositions of **1 f** in the eutectic mixture give a decrease in the reflection wavelength during polymerization. In figure 4 the data are also plotted as the reciprocal wavelength, which results in a straight line. Extrapolation yields a reflection wavelength of 280 nm for the pure compound after polymerization, a value which falls outside the measuring range of our optical set-up. In order to check this value, SEM pictures were taken of the cross-section of the polymer film of pure **1 f** obtained after fracture in liquid nitrogen. Figure 5 shows the result. Bands are visible because of differences in texture between the fracture surfaces parallel and perpendicular to the mean molecular axes. From this picture a pitch of 180 nm can be deduced for the molecular helix. The polymer has an average refractive index $(n_e^* + n_o^*)/2$ of 1·59. With the aid of relation 1 a reflection wavelength of 282 nm can be calculated, which confirms the validity of the extrapolation from the optical data.

Figure 5 also shows the substantial homogeneity of the cholesteric bands observed over the whole fractured cross-section. This homogeneity explains the high degree of transparency of the polymer films obtained with a low defect concentration and high contrast (1 : 20) in the separation of right- and left-handed circularly polarized light, which ultimately makes them suitable for the production of optical components in polarization and colour optics.

4. Conclusions

Nematic diacrylates **1 a** can be made cholesteric by introducing methyl groups at the 3- or 4-position in the hexylene spacer between the mesogenic group and the acrylate group. Only in the case of introduction of a methyl group into both spacers are molecules with a small pitch obtained. Mixtures of these molecules with nematic diacrylates show reflection bands in the visible region. The position of the band can easily be controlled through either the temperature of the monomer mixture or by the composition of the monomer mixture. After isothermal photopolymerization, a material is obtained whose reflection wavelength is almost temperature independent, which makes such materials suitable for application in passive optical components such as reflectors, circular polarizers and notch filters.

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