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J. Lub [a] , A. Omenat [b] , A. Ruiz-melo [b] & M. C. Artal [b]

[a] Philips Research Laboratories, Prof. Holstlaan 4, 5656, AA Eindhoven, The Netherlands

[b] Dpto. Química Orgánica-Quimica Fisica, Instituto de Ciencia de Materiales de Aragön. Universidad de Zaragoza, 50009, Zaragoza, Spain

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Synthesis and Photopolymerization of Cholesteric Liquid Crystalline Vinyl Ethers

J. LUB*, A. OMENAT†, A. RUIZ-MELO† and M. C. ARTAL†

Philips Research Laboratories, Prof. Holstlaan 4,
5656 AA Eindhoven, The Netherlands

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The synthesis of three cholesteric divinyl ethers is described. One of them is suitable for forming polymeric networks by isothermal cationic photopolymerization. Such networks exhibit temperature-stable reflection bands. By mixing with nematic divinyl ethers before polymerization, the reflection wavelength of such networks can be chosen by the relative amount of both types of divinyl ethers.

Keywords: Cholesteric liquid crystals; vinylethers; photopolymerization

1. INTRODUCTION

In a previous publication we demonstrated the formation of cholesteric networks by isothermal photopolymerization of mixtures of chiral nematic and nematic diacrylates [1]. Cholesteric materials reflect light whose wavelength at maximum reflection for perpendicular incident light (λ_m) is given by:

$$\lambda_m = \mathbf{p}\sqrt{(\mathbf{n}_e^2 + \mathbf{n}_o^2)/2}.$$

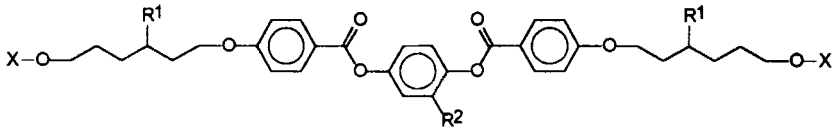
where p is the pitch of the helicoidal structure of the cholesteric material, and n_e and n_o are the effective extraordinary and ordinary refractive indices,

* To whom correspondense should be sent.
† Present address: Dpto. Química Orgánica-Química Física. Instituto de Ciencia de Materiales de Aragón. Universidad de Zaragoza. 50009 Zaragoza, Spain.

respectively, of a uniaxially oriented nematic film [2]. The reflected light is circularly polarised, the polarisation direction being the same as that of the helix of the cholesteric material. Light with the other polarisation direction is transmitted. The reflection wavelength of the cholesteric network can be chosen by the composition of the diacrylate mixture before polymerisation. This was done by using a cholesteric component with a very short molecular pitch such as **3a** (see Tab. I), which resulted in a virtual reflection in the UV region, which could not be measured due to the absorption of the aromatic rings.

Larger reflection wavelengths could be chosen, increasing the pitch by adding nonchiral nematic material. Also the structure of the cholesteric liquid crystal strongly determines the pitch. Isomers of **3a** with the chiral centre one carbon atom further away from the mesogenic group [1] or on the carbon atom closest to the mesogenic group [3] led to material with larger pitches. It is also possible to choose the reflection wavelength by changing the temperature. After isothermal photopolymerization, a material is obtained whose reflection wavelength is almost temperature-independent.

TABLE I Phase transitions of divinyl ethers **2a, b** and **4a, b** and their analogues diacrylates **1a, b** and **3a, b**. (C = crystalline, N = nematic, Ch = cholesteric and I = isotropic)



	R^1	R^2	X	phase transitions (°C)
1a	H	H	CH_2=CHCO	C - 115- N - 155 - I
2a	H	H	CH_2=CH	C - 117- N - 185 - I
1b	H	CH_3	CH_2=CHCO	C - 86 - N - 116 - I
2b	H	CH_3	CH_2=CH	C - 87 - N - 148 - I
3a	CH_3	H	CH_2=CHCO	C - 69 - CH - 97 - I
4a	CH_3	H	CH_2=CH	C - 103 - CH - 116 - I
3b	CH_3	CH_3	CH_2=CHCO	C - 45 - CH - 54 - I
4b	CH_3	CH_3	CH_2=CH	C - 55 - CH - 91 - I

This makes such materials suitable for applications in passive optical components such as reflectors, circular polarizers and notch filters [1,4]. The bandwidth $\Delta\lambda$ of the reflection band is given by [2]:

$$\Delta\lambda = \mathbf{p}(\mathbf{n}_e - \mathbf{n}_o)$$

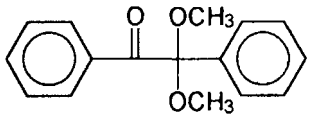
It is possible to make this bandwidth broader by using special photopolymerization techniques resulting in films with a pitch gradient [4,5]:

$$\Delta\lambda = \mathbf{p}_1\mathbf{n}_e - \mathbf{p}_2\mathbf{n}_o,$$

where $\mathbf{p}_1$ and $\mathbf{p}_2$ are the largest and the smallest pitch, respectively.

The use of liquid crystalline divinyl ethers may have some advantages over diacrylates. Table I shows the phase transitions of nematic vinyl ethers **2a** and **2b**. They exhibit melting points similar to the corresponding diacrylates **1a** and **1b**, respectively, but the clearing points are 30°C higher [6]. This means that vinyl ethers can be applied over a much broader temperature range than acrylates. It is also possible that structures containing acrylate groups which are monotropic, become enantiotropic if they contain vinyl ether groups. For cholesterics this implies that with a much broader temperature range, tuning of the reflection wavelength by varying the temperature can be done over a broader wavelength range. Mesogenic groups which are not applicable with acrylates can be used with vinyl ethers; for example, making low temperature polymerizable liquid crystals possible.

Photopolymerization of liquid crystalline divinyl ethers is performed with a cationic initiator system containing Irgacure 651 **5** and iodonium salt **6**



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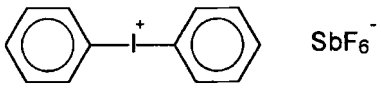


6

[6]. **5** is added due to the fact that it absorbs in the near UV region while cationic initiator **6** only in the far UV. The exact mechanism of this cationic initiator system is not completely clear [7]. A disadvantage of the system is its temperature instability. Above 100°C thermal decomposition leads to thermal polymerisation during alignment of the molecules, resulting in optically imperfect films [6].

The aim of this article is to describe the synthesis and properties of cholesteric divinyl ethers, and their photopolymerization products. Analogues to the most successfully studied chiral liquid crystalline diacrylate **3a**, we have started our research with the corresponding three-ring divinyl ether. As a result of the predicted extension of the liquid crystalline temperature range, we may achieve more freedom in the molecular design. This encourages us to study apart from the three-ring mesogens also two-ring mesogens for the same application.

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 Tagasako Int. Co. (Japan).

The syntheses of 2-methyl-1,4-phenylene bis(4-(6-vinyloxyhexyloxy)benzoate) **2b** [6] and (S)-4-methyl-6-chlorohexanol **7** out of (S)-citronellol [1] are described elsewhere. The synthetic routes to compounds **4a** and **4b** are shown in scheme 1. The synthetic route to compound **10** is shown in scheme 2. All divinyl ethers were more than 96% pure according to HPLC. ^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ with TMS as internal standard using a Bruker DPX 300 spectrometer. All intermediate products exhibit ^{1}H-NMR spectra (300MHz) that are in accordance with their structures.

2.1.1. (S)-6-chloro-4-methyl-hexylvinyl ether 8

A mixture of 57.6 g of (S)-6-chloro-4-methyl-1-hexanol **7**, 215 ml of ethyl vinyl ether and 2.15 g of mercuric acetate was stirred at 37°C under a nitrogen atmosphere overnight. 2 g of potassium carbonate was added and the reaction mixture was stirred at room temperature for 30 min. After filtration over celite, the solution was evaporated at reduced pressure. After purification by column chromatography using silica and methylene chloride as the eluent, and distillation under reduced pressure (b.p. = 100°C, 16 mm Hg), 41 g of the product (61%) was obtained as a colourless liquid.

2.1.2. (S)-4-(3-methyl-6-vinyloxyhexyloxy)benzoic acid 9

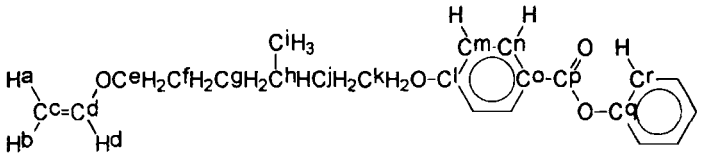
A mixture of 43 g of ethyl 4-hydroxybenzoate, 14 g of sodium methoxide and 250 ml of butanone was stirred until a clear solution was

obtained. To this solution 41 g of (S)-6-chloro-4-methyl-hexyl vinyl ether **8** and 7.5 g of sodium iodide were added. The reaction mixture was refluxed under a nitrogen atmosphere for 24 h. The crude intermediate ester obtained after filtration and evaporation was mixed with 250 ml of ether and 200 ml of water. The ethereal layer was extracted with a 10% aqueous solution of sodium hydroxide, dried over magnesium sulphate and evaporated. The white solid obtained was mixed with a solution of 16.6 g of potassium hydroxide in 180 ml of water and 45 ml of ethanol. The reaction mixture was refluxed for 2 h, cooled down to room temperature and acidified by careful addition of 5% hydrochloric acid, until the mixture was slightly acidic; the product precipitated as a white solid. It was washed with water and pentane. After drying under vacuum over silica, 51 g of the product (88%) was obtained as a white powder.

2.1.3. (S, S)-1,4-phenylene bis(4-(3-methyl-6-vinyloxyhexyloxy) benzoate) 4a

5.6 g of (S)-4 (3-methyl-6-vinyloxyhexyloxy)benzoic acid **9**, 1.1 g of hydroquinone and 400 mg of 4-*N*, *N*-dimethylaminopyridine were dissolved in 60 ml of methylene chloride. The mixture was cooled in an ice bath and 4.12 g of dicyclohexylcarbodiimide was added. The reaction mixture was stirred under nitrogen overnight and filtered through a pad of silica. After evaporation, and recrystallization from ethanol, 3.8 g of the product (60%) was obtained as white needles.

^{1}H-NMR: 8.14 (*d*, 4H, J = 8.6, H^n), 7.26 (*s*, 4H, H^r), 6.97 (*d*, 4H, J = 8.6, H^m), 6.45 (*dd*, 2H, $J_1 = 15$, $J_2 = 7.1$, H^d), 4.18 (*dd*, 2H, $J_1 = 15$, $J_2 = 2.3$, H^a), 4.10 + 4.12(*m*, 4H, H^k), 3.95 (*dd*, 2H, $J_1 = 7.1$, $J_2 = 2.3$, H^b), 3.7 (*t*, 4H, J = 7.0, H^e), 1.95–1.25 (*m*, 14H, $H^j + H^h + H^g + H^f$), 1.0 (*d*, 6H, J = 7.0, H^i)

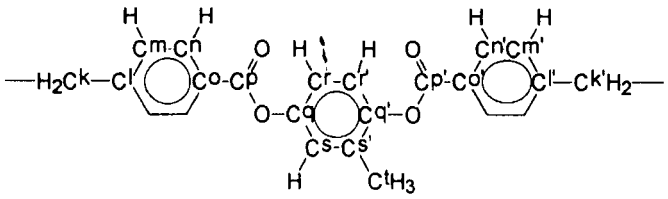


^{13}C-NMR: 164.8 (C^p), 163.5 (C^l), 151.9 (C^d), 148.4 (C^q), 132.3 (C^n), 122.6 (C^r), 121.5 (C^o), 114.3 (C^m), 86.3 (C^c), 68.2 (C^e), 66.4 (C^k), 35.9 (C^j), 33.2 (C^g), 29.6 (C^h), 26.5 (C^f), 19.5 (C^i).

2.1.4. (S, S)-2-methyl-1,4-phenylene bis(4-(3-methyl-6-vinyloxyhexyloxy) benzoate) 4b

This compound was prepared as described for **4a**, replacing hydroquinone by 1.24 g of methylhydroquinone. It was obtained in 49% yield as a white powder. The NMR data which are different from those of **4a** are given below:

^{1}H-NMR: 8.16 (*d*, 2H, J = 8.6, H$^{n'}$), 8.14 (*d*, 2H, J = 8.6, H^{n}), 7.17 (*d*, 1H, J = 8.5, H$^{r'}$), 7.13 (*d*, 1H, J = 2.5, H^{s}), 7.08 (*dd*, 1H, J_1 = 8.5, J_2 = 2.5, H^{r}), 6.99 (*d*, 2H, J = 8.6, H$^{m'}$), 6.96 (*d*, 2H, J = 8.6, H^{m}), 4.15–4.08 (*m*, 4H, H^{k} + H$^{k'}$), 2.24, (*s*, 3H, H^{t}).



^{13}C-NMR: 164.9 (C^{p}), 164.5 (C$^{p'}$), 163.5 (C^{l} and C$^{l'}$), 148.4 (C^{q}), 147.1 (C$^{q'}$), 132.3 (C^{n} and C$^{n'}$), 131.8 (C^{s}), 124.1 (C$^{s'}$), 122.9 (C$^{r'}$), 121.4 and 121.6 (C^{o} and C$^{o'}$), 120.0 (C^{r}), 114.3 (C^{m} and C$^{m'}$), 68.5 (C^{k} and C$^{k'}$), 16.4 (C^{t}).

2.1.5. (S)-4-(6-hydroxy-3-methylhexyloxy)phenol 11

To a refluxing mixture of 8.9 g of (S)-6-chloro-4-methyl-1-hexanol **7**, 11 g of hydroquinone, 3 g of sodium iodide and 50 ml of ethanol was added, dropwise, 10 ml of an aqueous 20% sodium hydroxide solution. After 6 hours the mixture was cooled down and evaporated. To the crude reaction mixture was added 160 ml of an aqueous 5% sodium hydroxide solution and 100 ml of ether. After separation, the aqueous layer was acidified with 2.5 N hydrochloric acid. The product was extracted with dichloromethane. The dichloromethane layer was extracted twice with water, dried over magnesium sulphate and evaporated. 6.3 g of the product was obtained as a light yellow oil (56%).

2.1.6. (S)-4-(6-vinyloxy-3-methylhexyloxy)phenol 12

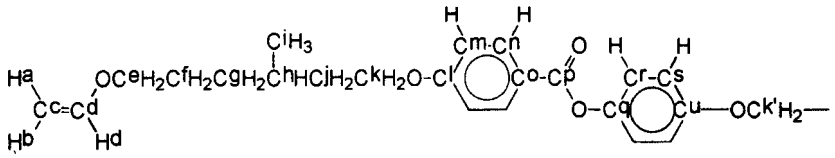
A mixture of 6.3 g of (S)-4-(6-hydroxy-3-methylhexyloxy)phenol **11**, 15 ml of ethyl vinyl ether and 0.14 g of mercuric acetate was stirred at 37°C under nitrogen overnight. The mixture was cooled down to room temperature,

filtered through a pad of silicagel and evaporated. The product was purified by column chromatography using silicagel and methylene chloride as eluent. 2.4 g of the product (56%) was obtained as a clear oil.

2.1.7. (S, S)-4-(6-vinyloxy-3-methylhexyloxy)phenyl)-4-(6-vinyloxy-3-methylhexyloxy)benzoate 10

2.7 g of (S)-4-(3-methyl-6-vinyloxyhexyloxy)benzoic acid **9**, 2.4 g of (S)-4-(6-vinyloxy-3-methylhexyloxy)phenol **12** and 200 mg of 4-*N*,*N*-dimethylaminopyridine were dissolved in 40 ml of methylene chloride. The mixture was cooled in an ice bath and 2.0 g of dicyclohexylcarbodiimide was added. The reaction mixture was stirred under a nitrogen atmosphere overnight and filtered through a pad of silica. The solvent was evaporated and the product purified by column chromatography (silica and methylene chloride as eluent). 3.2 g of the product (65%) was obtained as a white solid after stirring with cold ethanol.

^{1}H-NMR: 8.12 (*d*, 2H, J = 8.6, H^n), 7.10 (*d*, 2H, J = 8.6, H^m), 6.98 (*d*, 2H, J = 8.6, H^r), 6.9 (*d*, 2H, J = 8.6, H^s), 6.45 (*dd*, 2H, J_1 = 15.0, J_2 = 7.1, H^d), 4.18 (*dd*, 2H, J_1 = 15.0, J_2 = 2.3, H^a), 4.12 (*m*, 2H, H^k), 4.05 (*m*, 2H, $H^{k'}$), 4.00 (*dd*, 2H, J_1 = 7.1, J_2 = 2.3, H^b), 3.67 (*t*, 4H, J = 7.0, H^e), 1.95–1.25 (*m*, 14H, $H^j + H^h + H^g + H^f$), 0.99 (*d*, 6H, J = 7.0, H^i).



^{13}C-NMR: 165.2 (C^p), 163.3 (C^l), 156.7 (C^u), 151.9 (C^d), 144.4 (C^q), 132.2 (C^n), 122.4 (C^r), 121.8 (C^o), 115.0 (C^s), 114.2 (C^m), 86.3 (C^c), 68.3 (C^e), 66.5 (C^k), 66.4 ($C^{k'}$), 36.1 (C^j), 33.2 (C^g), 29.6 (C^h), 26.5 (C^f), 19.5 (C^i).

2.2. Physical Measurements

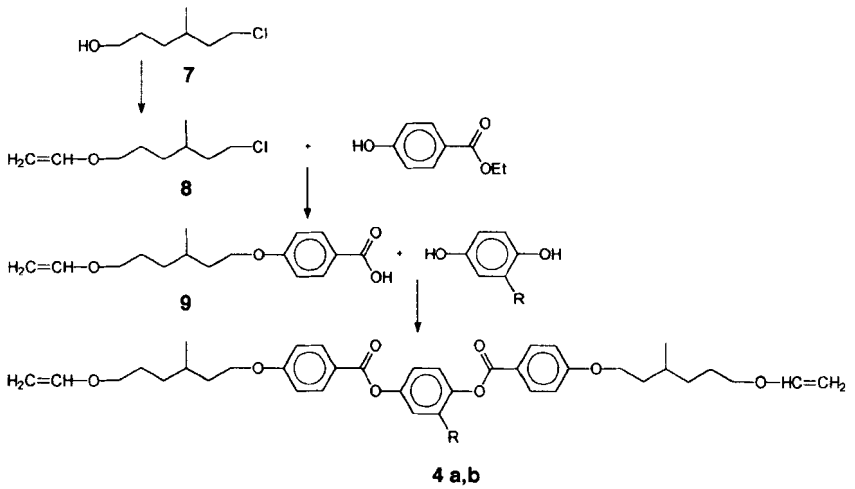
Samples exhibiting the Grandjean texture were prepared by melting the monomers or their mixtures between polyimide-coated and rubbed glass substrates spacered at 6 μm. The photopolymerization was initiated by 5 minutes irradiation using a fluorescent lamp (Philips, PL10) with an intensity of 0.62 $mW \cdot cm^{-2}$, measured at 365 nm, 20 cm away from the source.

A single-beam UV-VIS spectrometer (Unicam PU8755) was used in the optical characterisation of the samples. A depolarizer, a polarisation filter, a quarter-wave plate, a thermostatted sample holder with sample and a depolarizer are 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 polarisation was determined by the direction of rotation between polarizer and the optical axis of the quarter-wave plate in order to obtain maximum reflection.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Properties of 4a and 4b

The synthesis of **4a** which is the divinyl ether analogue of diacrylate **3a** is outlined in scheme 1. The starting product: (S)-4-methyl-6-chlorohexanol **7**



SCHEME 1 Synthesis of cholesteric divinyl ethers **4a** ($R = H$) and **4b** ($R = CH_3$).

was obtained starting from (S)-citronellol as described in a previous publication [1]. The reaction steps are the same as those for the synthesis of **2b** where 6-chlorohexanol and methylhydroquinone were used instead of **7** and hydroquinone, respectively [6].

The liquid crystalline properties of **4a** are shown in Table I. Contrary to the non-chiral divinyl ethers **2a** and **2b** its melting point is considerably higher than that of its acrylate analogue **3a**. The isotropic transition is

indeed higher than that of **3a**. The high melting point of **4a** makes the compound not very suitable for photopolymerization due to the thermal instability of the initiator system described above. In order to obtain a compound with a lower melting point, suitable to be photopolymerized, **4b** was prepared, replacing hydroquinone by methylhydroquinone. Table I shows that this compound has a much broader cholesteric phase than its acrylate analogue **3b**. In fact its thermotropic phase is broader and observed at lower temperatures than that of acrylate **3a**. This shows clearly the attractiveness of the vinyl ethers over acrylates.

In order to measure the pitch of **4b** it was mixed with nematic divinyl ether **2b** and the reflection wavelengths were measured as transmission losses as described for **3a** [1]. Figure 1 shows the reflection wavelength (λ_{max}; the centre of the reflection band) as a function of the reduced temperature (T_r) for mixtures. The reduced temperature being defined as:

$$T_r = (T + 273)/(T_{CH\text{-}I} + 273),$$

where $T_{CH\text{-}I}$ is the clearing point of the mixture. The positive temperature effect on the reflection wavelength and thus on the pitch of the mixtures is believed to be due to a stronger twist-forming interaction of the chiral groups than the unidirectional unwinding action of the mesogenic groups

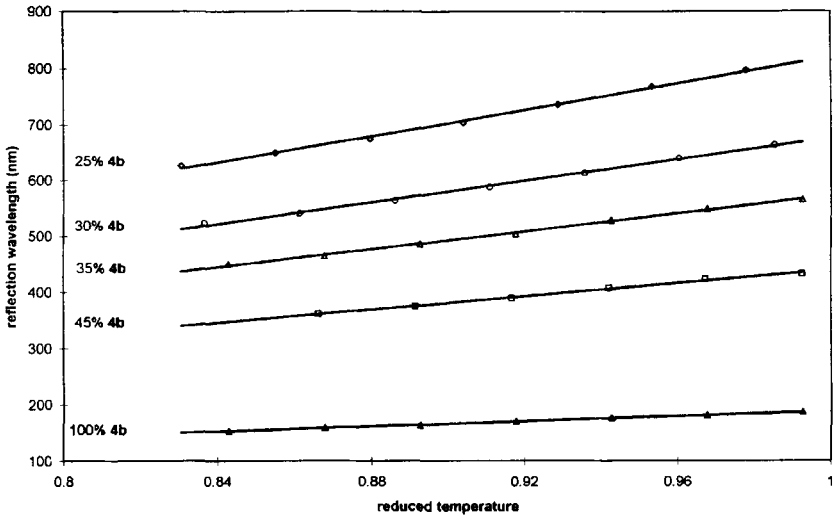


FIGURE 1 λ_{max} measured as a function of reduced temperature for mixtures of **2b** and **4b** with weight percentages of **4b** as indicated. The values for 100% of **4b** were obtained by extrapolation.

[1]. This indicates the absence of a smectic transition in these mixtures near the temperature range of the measurements [3]. Extrapolating the data of Figure 1 for various reduced temperatures to pure **4b**, the reflection wavelength λ^{100} for pure **4b** can be determined assuming:

$$\lambda^{100} = 100 * \lambda_{max}/\mathbf{c}$$

where **c** is the weight percentage of **4b**. At $\mathbf{T}_r = 0.9$, $\lambda^{100} = 170$ nm. Using an average refractive index for these type of materials of 1.55 [6], the pitch can be calculated to be 110 nm. In the same way a pitch of 180 nm for diacrylate **3b** was obtained using mixtures with **1b** [8]. Both materials were made from the same batch of citronellol and therefore had the same enantiomeric excess, thus the difference finds its origin in the difference of polymerizable groups. Both **3b** and **4b** reflect right-handed circularly polarised light.

3.2. Photopolymerization of a Mixture of 2b and 4b

In order to study the effect of photopolymerization on the reflective properties of a mixture of **2b** and **4b** (70/30 w/w), these monomers were mixed with 1% of each of the abovementioned initiator components and photopolymerized at different temperatures. With the aid of photo-DSC, conversions of more than 85% could be calculated from the measured reaction enthalpy [9], indicating the formation of highly crosslinked networks [6]. Figure 2 shows the effect of photopolymerization on the temperature stability of the reflection wavelength. The monomer mixture exhibits a positive temperature effect of 1.60 nm/°C. After polymerisation this value had diminished till 0.13 nm/°C. Furthermore, the monomer mixture had an isotropic transition at 130°C above which the reflection of light ceased. The properties of the polymer are much more stable. Even after heating to 220°C there was no change in the reflective properties of the materials. Figure 2 also shows that upon polymerisation the reflection wavelength decreases. This effect is greater at higher temperatures. Due to polymerisation shrinkage the density, and thus the refractive index, will increase. This should lead to a longer reflection wavelength. On the other hand, polymerization shrinkage will lead to a shorter pitch. This last effect is probably dominant. Similar effects were observed with acrylates [1].

3.3. Synthesis and Properties of 10

In order to find out whether it is possible to make divinyl ethers with lower melting points than **4b**, one of the rings of the mesogenic group of the

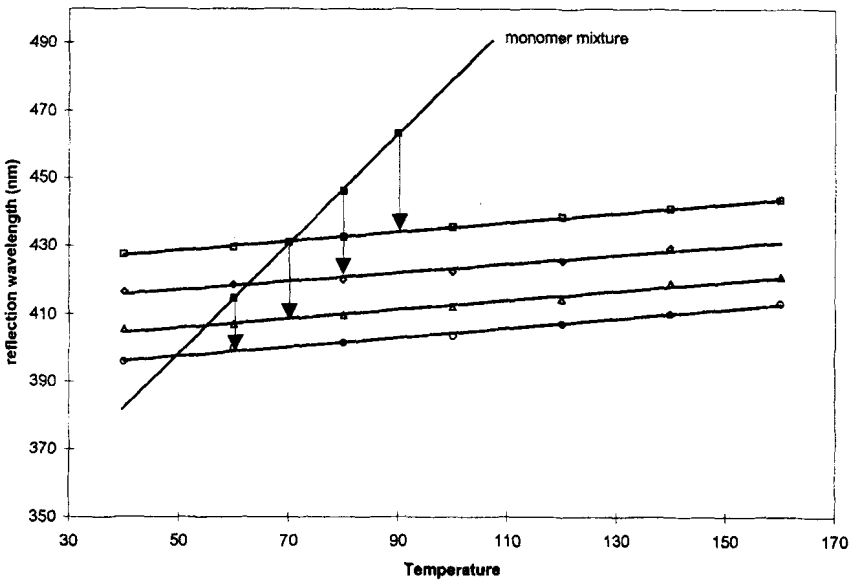
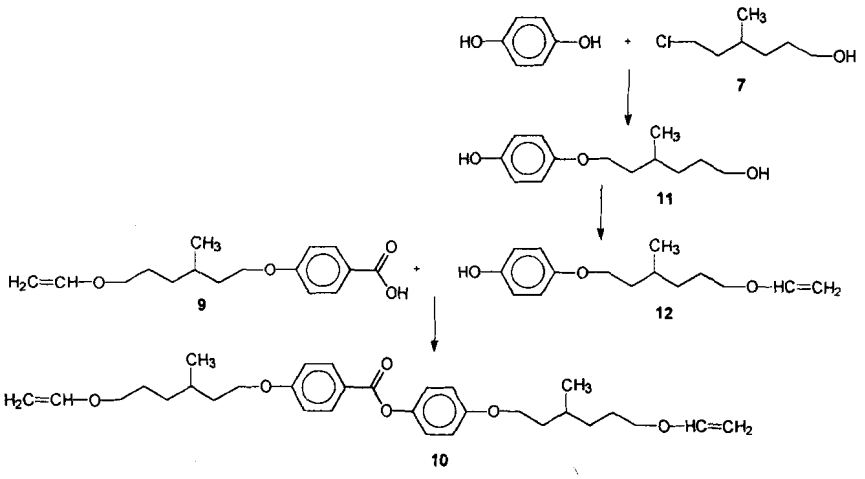


FIGURE 2 Reflection wavelength as a function of temperature of a monomer mixture of **4b** and **2b** containing 30% of **4b** and after polymerisation of this mixture at temperatures indicated by the arrows.

molecules of Table I was left out. The synthesis of this molecule **10** is outlined in scheme 2.



SCHEME 2 Synthesis of cholesteric divinyl ether **10**.

In order to make phenolic vinyl ether **12**, the starting product was again **7**, which produced phenolic alcohol **11** upon etherification with hydroquinone. Introduction of the vinyl ether group was done in the same way as the formation of **8** out of **7**, namely transetherification with ethyl vinyl ether catalysed by mercuric acetate [6]. In this reaction the phenolic hydroxyl function turned out to be unreactive. The final product **10** was obtained by esterification of **12** with acid **9** using dicyclohexylcarbodiimide catalysed by dimethylaminopyridine. **10** showed the following transitions: Cr-I: 58°C and CH-I: 10°C. Thus this compound is monotropic and has a higher melting point than **4b**.

In order to determine the pitch of this compound it was mixed with nematic divinyl ether **2b** and the reflection wavelengths were measured as described above. The results of these measurements are shown in Figure 3. Probably due to the latent smectic character of **10** (e.g. the pitch unwinding character of the Smectic-A phase), the positive temperature effect on the reflection wavelength decreases at lower temperatures [3]. In the same way as described for **4b**, the reflection wavelength for pure **10** was obtained by extrapolation and is shown also in Figure 3. At $\mathbf{T}_r = 0.9$ it has a value of

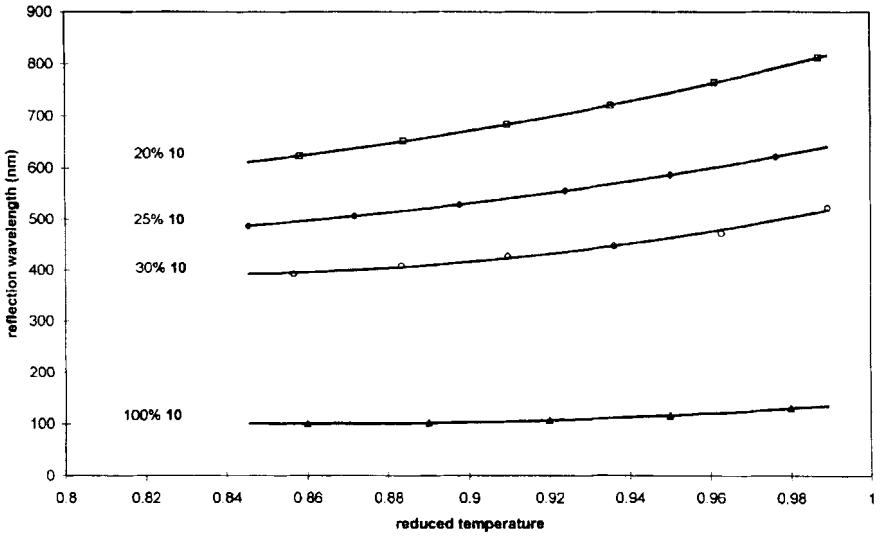


FIGURE 3 λ_{max} measured as a function of reduced temperature for mixtures of **2b** and **10** with weight precentages of **10** as indicated. The values for 100% of **10** were obtained by extrapolation.

110 nm which is shorter than the value obtained for **4b** (170 nm). Compared to compound **4b** this compound does not exhibit better properties: its synthesis is more laborious, its melting point is as high and the isotropic transition is observed at much lower temperatures.

CONCLUSIONS

Of the three newly described cholesteric divinyl ethers **4a**, **4b** and **10**, **4b** has the best properties for use in making polymeric cholesteric films. Its melting point is much lower than that of **4a** and low enough to make alignment possible in the presence of cationic photoinitiators without suffering unwanted thermal polymerisation prior to complete alignment. Compared to **10**, it is easier to synthesise and has a much broader liquid crystalline phase. Polymer networks made out of mixtures of **4b** and nematic divinyl ether **2b** by isothermal cationic photopolymerization exhibit nearly temperature-independent reflection wavelengths. This polymeric material therefore has comparable properties to that made from cholesteric diacrylate mixtures, but the monomers can be processed at more favourable temperatures.

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