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The Synthesis of a Cholesteric Diacrylate using Enzymatic Resolution

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Chiral nematic or cholesteric diacrylates are used to form cholesteric networks. In order to be able to investigate the effect of the position of the chiral center in the spacer of these molecules on the molecular pitch, we synthesized a chiral liquid crystalline diacrylate whose chiral center was close to the mesogenic group. To obtain high enantiomeric excess, we applied an enzymatic resolution on one of the intermediates. The diacrylate showed a larger cholesteric pitch and a smaller cholesteric temperature range than other related compounds in which the chiral center of the same structure is positioned further away from the mesogenic group.

INTRODUCTION

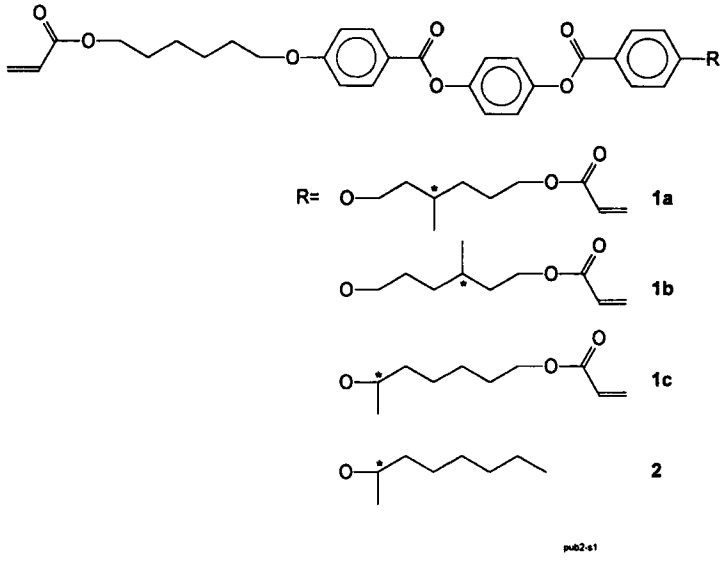
In a previous publication we demonstrated the formation of cholesteric networks by isothermal photopolymerization of mixtures of chiral nematic and nematic diacrylates[1]. Cholesteric materials reflect light whose wavelength at maximum reflection for perpendicular incident light (λ_m) is given by:

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

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, respectively, of a uniaxially oriented nematic film[2]. 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. The reflection wavelength of the cholesteric network can be chosen by the composition of the diacrylate mixture before polymerization. This was done by using a cholesteric component with a very short molecular pitch, which resulted in a virtual reflection in the UV region, which couldn't be measured due to the absorption of the aromatic rings. Larger reflection wavelengths could be chosen, increasing the pitch by adding non-chiral nematic matereial. After isothermal photopolymerization, a material is

obtained whose reflection wavelength is almost temperature independent. This makes such materials for applications in passive optical components such as reflectors, circular polarizers and notch filters[1,3].

In the same publication the synthesis and properties of diacrylates **1a** and **1b** (see Scheme 1and Tab. I) were described. These diacrylates contain a chiral center in only one of the spacer units between the mesogenic group and the acrylate groups. The reflection wavelength of these compounds is rather long. They are not suitable for preparing materials which can reflect light at any wavelength in the visible region. Compounds **1a** and **1b** are of interest because the effect of the position of the chiral center on the molecular pitch can be measured directly by spectroscopic measurements without having to make extrapolations from mixtures or by taking SEM pictures of polymerized samples. Table I shows that compound **1a** exhibits a shorter molecular pitch than compound **1b**. This is due to the fact that in **1b** the methyl group in the chiral center is one carbon atom further away than in **1a**. This



SCHEME 1 Structures of the four liquid crystalline diacrylates mentioned in the text.

TABLE I

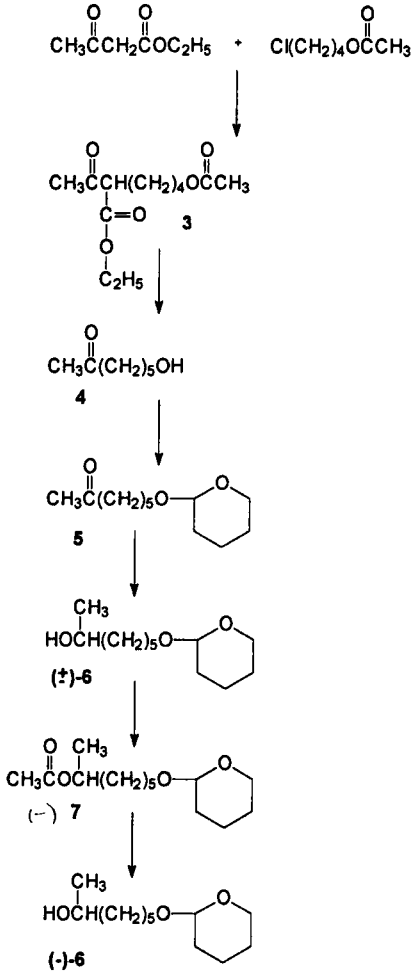
Physical properties of the diacrylates **1a-1c** and **2**. a: Conditions: $C = 10$g/100ml of chloroform. b: The following monotropic transition was found: $S_x - 63 - CH$

	phase transitions (°C)	λ_m (nm)/T (°C)	pol. direction of reflection	$[\alpha]_D^{25}$ [a]
1a	Cr-66-CH-125-I[b]	620/110	right-handed	−3.0°
1b	Cr-90-CH-132-I	860/120	right-handed	−4.3°
1c	Cr-80-CH- 83-I	820/ 70	right-handed	+2.5°
2	Cr-76-CH-102-I	890/ 90	right-handed	+2.6°

effect of the position of the chiral center on the molecular pitch is commonly observed with cholesteric molecules[4].

In order to investigate whether it is possible to synthesize isomers of **1a** and **1b**, which may result in a shorter pitch, we decided to prepare compound **1c** (see Scheme 1). In this compound the methyl group in the chiral center is two carbon atoms nearer to the mesogenic group than in **1a**.

The chiral spacers of **1a** and **1b** are derived from the commercially available S-citronellol. For the systems of **1c** an intermediate like **(-)−6** (see Scheme 2) is needed. We were unable to find a commercial source with a high enantiomeric excess to form this intermediate. Secondary alcohols with high enantiomeric excesses can be prepared via resolution of the racemic mixture using enzymes which preferen-



SCHEME 2 Synthesis and resolution of 7-(tetrahydropyran-2-yloxy)-2-heptanol **(-)-6.**

tially acetylate one of the enantiomers[5]. For our purpose we aimed to synthesize secondary alcohol (±)−**6**, we separate both enantiomers and use one of them to prepare **1c**. For reasons of comparison also chiral monoacrylate **2** using the commercially available R-2-octanol as a starting product is synthesized.

EXPERIMENTAL

All solvents were obtained from Merck. Porcine Pancreas Lipase was obtained from SIGMA (No L-3126). All other chemicals were obtained from Janssen Chimica. The following chemicals were prepared according to literature procedures: 4-hydroxyphenyl 4-(6-acryloyloxyhexyloxy) benzoate **8**[1] and 4-(tetrahydropyran-2-yloxy) benzoic acid **9**[6].

^{1}H and ^{13}C-NMR spectra were measured on a Bruker DPX 300 spectrometer, in $CDCL_3$ with TMS as internal standard. Chemical shifts are given in ppm, coupling constants J in Hz. The intermediate products exhibited ^{1}H-NMR spectra that are in accordance with their structures. chiral GC was performed at 160 °C, On a Chrompack WCOT Fused silica 50 m × 0.25 mm column coated with CP-Cyclodex B 236 M. Phase transitions were measured on a Perkin Elmer DSC-7 apparatus. A Reichert microscope provided with a Mettler FP52 hostage was used for texture measurements. The optical rotation with a AA-5 polarimeter of Optical Activity Ltd.

A single-beam UV-VIS spectrometer (Unicam PU8755) was used for the optical characterization of the samples. A depolarizer, a polarization filter, a quarter-wave plate, a thermostatted sample holder with a sample and a depolarizer were placed in the optical path in that order. Spectra were recorded between 360 and 900 nm. The sense of polarization was determined by the rotation direction between the polarizer and the optical axis of the quarter-wave plate in order to obtain maximum reflection. 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.

Synthesis of 7-Hydroxyheptanon-2 4

A mixture of 180 g of the sodium salt of ethyl acetoacetate (85% pure), 30 g of sodium iodide, 159 g of 4-chlorobutyl acetate and 500 ml of 2-butanone was refluxed for 24 hours. After evaporation of the 2-butanone, the crude diester **3** was obtained. 300 g of sodium carbonate and 1.5 l of water were added. After refluxing for 24 hours, the mixture was extracted three times with 200 ml of diethyl ether. The combined ether layers were dried over magnesium sulphate, evaporated and fractionated. 59 g of **4** (56%) were obtained as a clear oil, $bp = 92$°C at 1.0 mbar.

Synthesis of 7-(Tetrahydropyran-2-yloxy)heptanon-2 5

A mixture of 59 g of **4,** 63 ml of dihydropyran, 5 g of pyridinium 4-toluenesulphonate and 150 ml of dichloromethane was stirred at room temperature for 24 hours.

After two extractions with 100 ml of a 5% aqueous sodium bicarbonate solution and drying over magnesium sulphate, the solution was eluted over a short silica column and evaporated. 91 g of **5** (94%) was obtained as a light yellow oil, which was used in the next step without further purification.

Synthesis of Racemic 7-(Tetrahydropyran-2-yloxy)-2-heptanol (±)-6

To a solution of 91 g of **5** in 400 ml of ethanol, cooled in an ice bath was added 4.4 g of sodium borohydride in portions, at such a rate that the temperature didn't exceed 15 °C. After stirring for another two hours at room temperature, 25 ml of acetone was added to decompose the excess of sodium borohydride. After addition of 200 ml of a 10% sodium hydroxide solution, 500 ml of the water/ethanol mixture was evaporated. To the remaining slurry were added 200 ml of diethyl ether and 200 ml of water. After separation, the aqueous layer was extracted with 200 ml of diethyl ether.

The combined ether layers were extracted with 100 ml of a saturated sodium chloride solution, dried over magnesium sulphate and evaporated. 67 g of (±)-**6** (78%) was obtained as a clear oil after fractionation ($bp = 101-104$ °C at 0.3 mbar).

Resolution of 7-(Tetrahydropyran-2-yloxy)-2-heptanol (±)-6

A mixture of 21.6 g of racemic (±)-**6**, 10 g of Porcine Pancreas Lipase, 37 ml of vinylacetate, and 250 ml of benzene was stirred for 3 days at room temperature. After filtration over celite and evaporation, the acetate **7** was obtained after elution over aluminium oxide with hexane/dichloromethane 3:1. Chiral GC analysis showed that **7** had an enantiomeric excess of 98%. To obtain (-)-**6**, a mixture of **7**, 1.5 g of sodium hydroxide and 25 ml of methanol was refluxed for one hour. After evaporation , 60 ml of water and 75 ml of diethyl ether were added. After separation, the ether layer was extracted with 40 ml of a saturated sodium chloride solution, dried over magnesium sulphate and evaporated. 5.1 g of pure (-)-**6** (24% overall yield) was obtained after purification through distillation in a Kügelrohr apparatus. $[\alpha]_D^{25} = -4.74°$ ($C = 10$ gml^{-1}, in chloroform).

Synthesis of 4-(4-hydroxybenzoyloxy) phenyl 4-(6-acryloyloxyhexyloxy)benzoate 12

To a mixture of 7.7 g of 4-hydroxyphenyl 4-(6-acryloyloxyhexyloxy) benzoate **8**, 4.4 g of 4-(tetrahydropyran-2-yloxy) benzoic acid **9**, 0.25 g of 4-N,N- dimethylamino pyridine and 60 ml of dichloromethane, cooled in an ice bath, was added 4.5 g of dicyclohexylcarbodiimide. After stirring for 24 hours at room temperature, the mixture was filtered and evaporated. The pure intermediate **10**, obtained after crystallization from 2-propanol, was mixed with 100 ml of ethanol and 0.5 g of pyridinium -4-toluene sulphonate. The mixture was heated at 60 °C for 4 hours, upon which a clear solution was obtained. This hot solution was dropeed in a mixture of 100 g of ice and 300 ml of water. The precipitate was collected and washed with 100 ml of water. After drying, 8 g of **11** (80%) was obtained as a white powder.

Synthesis of 4-(4-(7-9tetrahydrapyran-2-yloxy)heptyl-2-oxy)benzoyloxy) phenyl 4-(6-acryloyloxyhexyloxy)benzoate 12.

To a mixture of 7.2 g of **11**, 3 g of **(-)-6**, 5.3 g of triphenylphosphine and 80 ml of dichloromethane, cooled in an ice bath, was added dropwise 3.2 ml of diethyl azodicarboxylate in 10 ml of dichloromethane. After stirring for 24 hours at room temperature, the dichloromethane was evaporated and the remaining solid was washed twice with 70 ml of ethanol. 8.5 g of **12** (87%) was obtained as white needles after crystallization from ethanol.

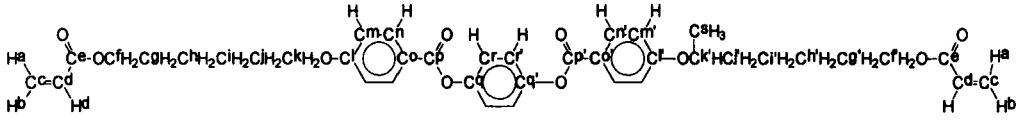
Synthesis of 4-(4-(7-hydroxyheptyl-2-oxy)benzoyloxy)phenyl 4-(6-acryloxyhexyloxy)benzoate 13

6.7 g of **13** (90%) was obtained after deprotection of **12** in the same way as described for the formation of **11** from **10.**

Synthesis of 4-(4-(7-acryloyloxy-2-yloxy)heptyle-2-oxy)benzoyloxy) phenyl 4-(6-acryloyloxyhexyloxy) benzoate 1c

To a mixture of 6.7 g of **13**, 1.7 ml of triethylamine and 35 ml of dichloromethane cooled to 0 °C, was added at once 1.0 ml of acryloyl chloride. After stirring overnight at room temperature a mixture of 25ml of water and 2 ml of concentrated hydrochloric acid was added. After separation, the organic layer was washed with 20 ml of a concentrated sodium chloride solution, dried over magnesium sulphate and eluted over a short silica column. 4.9 g of product **1c** (67%) was obtained as a white powder after crystallization from 2-propanol. Calculated for $C_{39}H_{44}O_{10}$: C, 69.6; H, 6.6; O, 23.8. Found: C, 69.5; H, 6.6; O, 24.1.

^{1}H-NMR: 8.14 (d, 2H, J = 8.6, $H^{n'}$), 8.13 (d, 2H, J = 8.6, H^{n}), 7.25 (s, 4H, H^{r} and $H^{r'}$), 6.97 (d, 2H, J = 8.6, $H^{m'}$), 6.95 (d, 2H, J = 8.6, H^{m}), 6.40 (dd, 2H, J_1 = 17.3, J_2 = 1.7, H^{a}), 6.13 (dd, 2H, J_1 = 17.3, J_2 = 10.2, H^{d}), 5.82 (dd, 2H, J_1 = 10.2, $J_2$41.7, H^{b}), 4.49 (m, 1H, H^{k}), 4.18 (t, 2H, J = 6.6, H^{f}), 4.16 (t, 2H, J = 6.6, H^{f}), 4.05 (t, 2H, J = 6.6, H^{k}), 1.9-1.4 (m, 16H, H^{g}, H^{h}, H^{i}, H^{j}, $H^{g'}$, $H^{h'}$, and $H^{j'}$), 1.35 (d, 3H, J = 7.0, H^{s}).



^{13}C-NMR: 166.3 (C^{e}), 164.8 (C^{p} + $C^{p'}$), 163.5 (C^{i}), 162.8($C^{i'}$) 148.4 (C^{q} + $C^{q'}$), 132.3 (C^{n} + $C^{n'}$), 130.5 (C^{c}), 128.6 (C^{d}), 122.6 (C^{r} + $C^{r'}$), 121.5 (C^{c}), 121.3 ($C^{o'}$), 115.2 ($C^{m'}$), 114.3 (C^{m}), 74.0 ($C^{k'}$), 68.1 (C^{k}), 64.5 (C^{f} + $C^{f'}$), 36.2 ($C^{j'}$), 29.0 (C^{j}), 28.6 (C^{g} + $C^{g'}$), 25.9, 25.7 (C^{h}, $C^{h'}$, and C^{i}), 25.1 ($C^{i'}$), 19.6 (C^{s}).

Synthesis of 4-(4-(octyl-2-oxy) benzoyloxy)phenyl 4-(6-acryloyloxyhexyloxy) benzoate 2

This compound was prepared in the same way as **12**, only **(-)-6** was replaced by

R-2-octanol. It was obtained as a white powder after crystallization from a mixture of ethanol and toluene (9:1). Calculated for $C_{37}H_{44}O_8$: C, 72.1; H, 7.2; O, 20.8. Found: C, 72.2; H, 7.2; O, 20.8.

NMR-data: the same numbering has been used as for compound **1c**. The methyl group which replaces the acryloyloxy group is numbered "t". Only the differences due to this replacement are indicated.

^{1}H-NMR: 1.9-1.3 (m, 18H, H^f, H^g, H^h, H^i, H^j, $H^{g'}$, $H^{h'}$, $H^{i'}$, and $H^{j'}$), 0.88 (t, 3H', J = 5.5, H').

^{13}C-NMR: 74.2 ($C^{k'}$), 36.3 ($C^{j'}$), 31.8 ($C^{g'}$), 29.2 ($C^{h'}$), 25.4 ($C^{i'}$), 22.6 ($C^{f'}$), 19.6 (C^t), 14.1 (C^s).

RESULTS AND DISCUSSION

The synthesis of alcohol (±)-**6** is outlined in scheme 2. Diester **3** was obtained by alkylation of ethyl acetoacetate with 4-chlorobutyl acetate. After saponfication and decarboxylation, hydroxyketone **4** was obtained, after which the hydroxy group was protected as tetrahydropyranyl (THP) ether **5**. After reduction, the racemic mixture of secondary alcohol (±)-**6** was obtained. With the aid of Porcine Pancreas Lipase in benzene, one of the enantiomers was acetylated with vinyl acetate to form **7**. After this acetate had been separated from the non-reacted alcohols by column chromatography, its enantiomeric excess was found to be more than 98% with chiral GC. Enantiomerically pure (-)-**6** was obtained after saponification of **7**. Although the exact configuration of (-)-**6** was not confirmed, it probably has the R configuration. Alcohols similar to (±)-**6** are acetylated by Porcine Pancreas Lipase to form the R enantiomers of the acetates[5]. Furthermore, the enantiomerically pure (-)-**6** exhibited a levorotary rotation in the polarimeter, which was also observed for R-2-octanol, the starting product to prepare acrylate **2**.

The total synthesis of **1c** is outlined in scheme 3. The mesogenic group containing the non-chiral spacer provided with the acrylate group **11** was prepared using intermediates **8** and **9**, which have already been described in previous publications[1,6]. The THP-protected intermediate **10** was formed from **7** and **8** with the aid of dicyclohexylcarbodiimide. This is an esterification procedure which is compatible with the THP group. To obtain **11**, the THP group was removed with the aid of pyridinium 4-toluenesulphonate in ethanol. The ester bonds in the mesogenic group and the acrylate group are stable under these deprotection conditions. If a stronger acid had been used for the deprotection, these ester bonds would also have been attacked. In order to avoid the risk of racemization, the coupling of **11** and (-)-**6** was performed with triphenylphosphine and diethyl azodicarboxylate. This procedure is known to proceed with full inversion of configuration[7,8]. The protected alcohol **12** thus obtained was deprotected to form **13** in the same way as the deprotection of **10** to form **11**. After reaction of **13** with acryloyl chloride, diacrylate **1c** was obtained. If we assume that **7** to has the R-configuration (see the above discussion), **1c** will have the S-configuration.

The synthesis of **2** was performed in the same way as the formation of **12** from **11** and (-)-**6**; replacing (-)-**6** by R-2-octanol. As pointed out before, this reaction pro-

ceeds with inversion of configuration. For that reason compound **2** exhibits the S-configuration.

Some physical properties of the new products **1c** and **2** and the known products **1a** and **1b** are shown in Table I. The polarization direction of the reflected light of **1c** and **2** is the same. Both compounds also exhibit the same rotation direction in the polarimeter. Because **2** has the S-configuration and, in view of what has been discussed in the previous section and the data from Table I, it is very well probable that **1c** also exhibits the S-configuration. Comparison of the properties of **1c** with those of **1a** reveals that the movement of the methyl group from the 3 position of the hexamethylene spacer in **1a** to the 1 position in **1c** makes the liquid crystalline properties poorer, only an enantiotropic cholesteric phase in a range of 3 °C is observed in the case of **1c** compared to 59 °C in the case of **1a**. The replacement of the terminal methyl group of **2** by an acrylate group in **1c** also has a strong effect on the temperature range of the cholesteric phase. The clearing point decreases 20 °C. This effect is frequently observed in comparison of similar liquid crystals with and without acrylate groups.

The reflection wavelength measured 10 °C below the clearing point of **2** is longer than that of **1c**. The origin of this effect is not known. Figure 1 shows the effect of temperature on the reflection wavelength of **1c**. To enable comparison with the data of **1a**, the reduced temperature (T_R) defined as:

$$T_R = (T + 273)/(T_{CH-1} + 273),$$

has been used, instead of the absolute temperature (in °C).

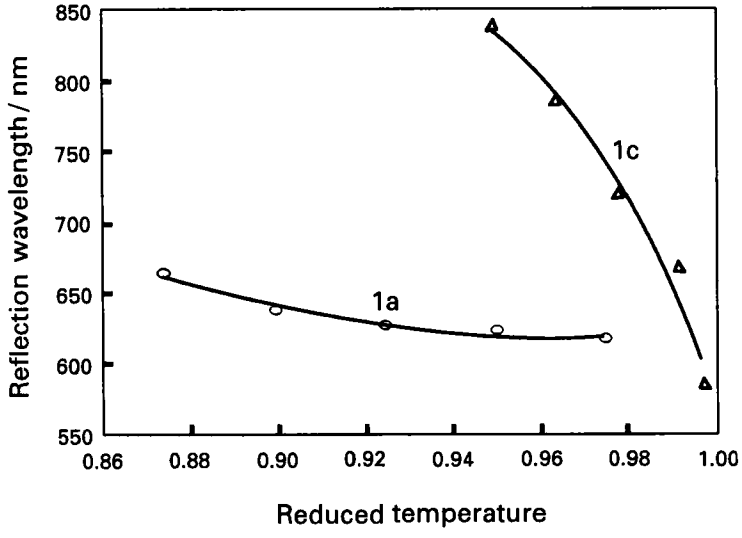
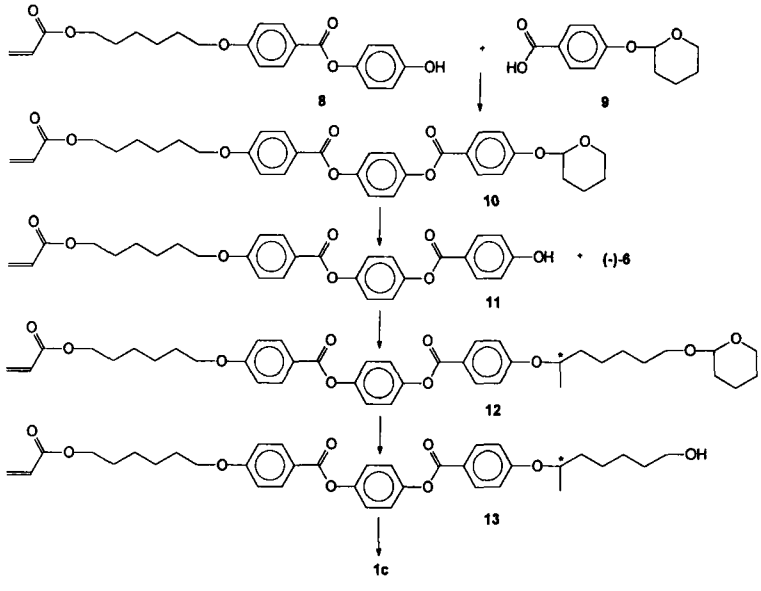


FIGURE 1 Dependence of the reflection wavelength on temperature for 4-(4-(6-acryloyloxy-3-methyl-hexyloxy) benzoyloxy) phenyl 1-(4-(6-acryloyloxyhexyloxy) benzoate **1a** (o) and 4-(4-(7-acryloyloxy-2-yloxy) heptyl-2-oxy) benzoyloxy)phenyl 4-(6-acryloyloxyhexyloxy) benzoate **1c** (Δ).

T_{CH-I} is the clearing point in °C. A strong negative temperature effect on the reflection waelength is observed. A similar curve is obtained for compound **2**. The temperature dependence of the reflection wavelength of **1a** is shown in the same figure. The pitch of cholesteric liquid crystals usually increases considerably with decreasing temperature near a cholesteric to smectic transition[4]. In the case of **1a** such a transition is found at $T_R = 0.84$. In the case of **1c** such a transition was not observed before crystallization at $T_R = 0.89$. A monotropic transition below this temperature which cannot be observed due to crystallization, is probably responsible for this strong temperature effect. Comparison of both curves reveals that the reflection wavelength and hence the pitch of **1c** is larger than that of **1a**. Thus, the decrease in the pitch caused by bringing the methyl group closer to the mesogenic group, as observed from compound **1b** to **1a**, does not continue when the methyl group is placed nearer to the mesogenic group. A similar effect was observed when two cholesteric liquid crystals from cyanobiphenyl where compared[9]. It would be interesting to prepare the isomer of **1a-1c** with the methyl group at position 2 of the hexamethylene spacer. In that case a shorter pitch than that of **1a** might be obtained, and a broader LC phase than that of **1c**. It is possible that the replacement of the oxygen atom between the spacer and the mesogenic group in **1c** by a methylene group may result in a decrease in the pitch. Such an effect has also been observed for a series of cholesteric liquid crystals derived from cyanobiphenyl[9].

If the non-chiral spacer of **1a** is replaced by a second chiral spacer, a cholesteric diacrylate is obtained with a short pitch. This replacement lead to a considerable decrease in the temperature range of the LC phase[1]. In the case of **1c**, this replace-



SCHEME 3 Synthesis of 4-4-(7-acryloyloxy-2-yloxy)heptyl-2-oxy)benzoyloxy) phenyl 4-(6-acryloyloxy-hexyloxy) benzoate **1c**.

ment would certainly lead to a compound with monotropic LC properties which is less suitable for applications. The fact that the pitch of **1c** is larger than that of **1a** also shows that no advantage can be gained from using cholesteric compounds derived from the 1-methylhexyl spacer over those derived from the 3-methylhexyl spacer, such as **1a**.

The methylheptyl group of compound **2** has been used to prepare ferroelectric liquid crystalline polymers[10,11]. The chemistry outlined in schemes 2 and 3may be useful for preparing chiral smectic monomers suitable for the formation of crosslinked polymers. Such polymers may exhibit a very stable spontaneous polarization and can be used as piezoelectric elements, as has been shown in previous publications[12,13]. Future work will focus on this type of monomers.

CONCLUSIONS

We have demonstrated the use of an enzymatic technique to prepare a precursor for a chiral spacer between the mesogenic groups and the acrylate group of a chiral liquid crystalline diacrylate. We also demonstrated that moving the methyl group in the chiral spacer from the third carbon atom relative to the mesogenic group of compound **1a**, to the first carbon atom in compound **1c** lead to a long pitch in the cholesteric phase, and to an enantiotropic phase over a much shorter temperature range.

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