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Thermal and optical properties of newly synthesized dicholesteryl esters with a phenylene oxide link in the normal and solidified cholesteric phases

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A series of liquid crystalline compounds with a central phenylene oxide group to which two cholesteryl groups are attached via two alkanoate spacers has been synthesized and investigated. All the compounds except the one with ethanoate spacers showed a cholesteric phase as a single mesophase. The phase transition temperatures, the corresponding enthalpy changes and the wavelengths of selective reflection associated with the cholesteric phases showed a strong odd–even effect as a function of the spacer length. By rapid cooling of the compounds from the cholesteric phase to 0°C, solid films maintaining a cholesteric molecular order were obtained. At room temperature, the solid film showed stable cholesteric colours controlled by changing the temperature at which the rapid cooling was begun. Heating the cholesteric solid film of the compound with hexanoate spacers gave two forms of crystals above 80°C, whose ratio changed depending on the colour of the starting solid films. This result suggests the existence of two conformational isomers in the liquid crystalline state. Since it is possible repeatedly to fix stable red, green and blue colours by thermal treatment of this compound, we may apply it to a rewritable full colour recording in the thermal mode.

1. Introduction

Some polymeric and non-polymeric liquid crystals with relatively high molecular masses form stable liquid crystalline glasses [1, 2]. This property of some liquid crystals has attracted attention since it can be applied to optical filters or rewritable optical recording, where optical anisotropy is utilized statically or changed dynamically, respectively [3, 4]. Irreversible fixing of the molecular ordering in a liquid crystalline manner has successfully been attained by polymerization of liquid crystalline monomers in the liquid crystalline state [5–8]. On the other hand, compounds for rewritable optical recording need to possess the property of stable and reversible fixing of the molecular ordering in the glassy state and high speed molecular realignment in the liquid crystalline state.

Due to the chiral structure of the molecule, the molecular alignment of the cholesteric phase shows a helical periodic structure. Due to this structural feature, light at the wavelength satisfying $\lambda = np$ (n and p stand for the mean refractive index of the liquid crystal and the helical pitch of the molecular order, respectively) in a wavelength range $\Delta\lambda = p\Delta n$ (Δn = anisotropy of the refractive index) is divided into right and left handed circularly polarized components. One component of light with the same rotation sense of the electric field vectors as the helical sense of the molecular ordering and light in other wavelength ranges is transmitted; the other component is reflected [9].

Some authors have already demonstrated that some dicholesteryl esters with a diyne group give a cholesteric phase that forms a cholesteric glass which is stable at room temperature, and that various colours are fixed, these being selected from almost the entire visible region by changing the temperature at which the cooling started [10–12]. Furthermore, the stability of the molecular order in the glassy state depends on the length and odd or even parity of the carbons in the alkylene chain connecting the diyne moiety and one of the cholesteryl groups [13].

Many other dimesogenic and trimesogenic cholesteric liquid crystals have been synthesized. For example,

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Barrell II *et al.* reported the synthesis and the phase transitions of dicholesteryl adipate, phthalate and sebacate [14]. Rault *et al.* [15] and Marcelis *et al.* [16] independently synthesized a series of dicholesteryl alkanedioates with the $(CH_2)_n$ ($n = 1$–8) chain and reported the effect of the carbon numbers in the alkylene chain on the phase transitions and the optical properties. Marcelis *et al.* further introduced a biphenyl group as the third mesogenic group to bis(dihydrocholesteryl) alkanedioates and reported the effect of the length of the alkylene chains on the phase transitions [17]. However, there have been only limited studies focusing on the relationship between the molecular structure and the stability of the cholesteric glassy state [18].

We now describe the synthesis, the phase transitions and the effect of the alkylene spacer length on the stability of the liquid crystalline glassy state of our newly synthesized dicholesteryl alkanedioates containing a phenylene oxide unit in the central part.

2. Experimental

2.1. *Measurements*

^{1}H NMR spectra were recorded with a Jeol GSX 270 NMR spectrometer. A Seiko Instrument DSC 120 system was used for the differential scanning calorimetry (DSC) measurements. Most of the measurements were carried out with a heating/cooling rate of 5°C min^{-1}. A Nikon polarizing microscope equipped with a Mettler FP82HT hot stage was used for visual observations. A Shimadzu UV-3100S and a Jeol spectrophotometer were used to obtain the UV-Vis spectra.

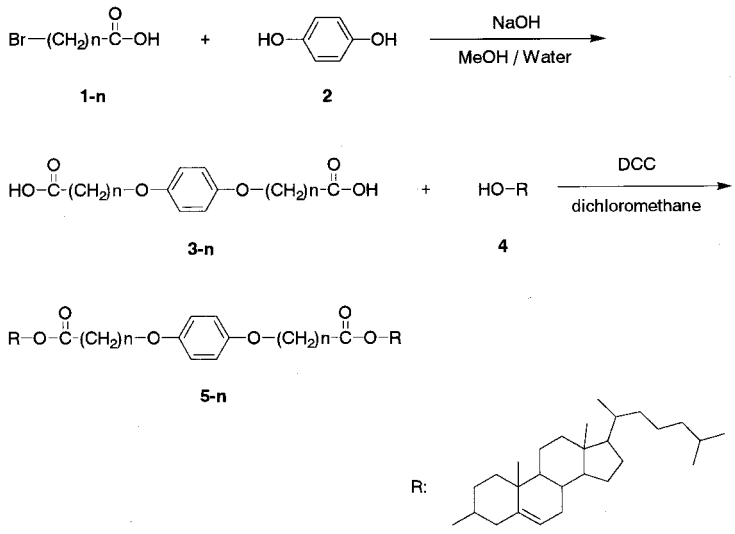
2.2. *Synthesis of dicholesteryl ester (route A)* [19]

As indicated in scheme 1, hydroquinone **2** (30 mmol) and NaOH (120 mmol) were dissolved in water (10 ml) and the solution was stirred for 2 h at 60°C. A solution of bromoalkanoic acid, **1-*n*** (60 mmol in 2.5 ml of water) was added dropwise over 1 h to the reaction mixture. The resulting precipitate was filtered off and dissolved in hot water. The mixture was acidified with dilute HCl, and the precipitate was filtered off and recrystallized from MeOH to give compounds **3-*n***. Yields were 13, 15, 23, 9 and 20% for compounds **3-1**, **3-5**, **3-7**, **3-10** and **3-11**, respectively. To a solution of cholesterol **4** (7 mmol) in 30 ml of dichloromethane was added a solution of the diacid **3-*n*** (3.5 mmol), dicyclohexylcarbodiimide (7 mmol) and 4-dimethylaminopyridine (7 mmol) in 15 ml of dichloromethane. The mixture was stirred at room temperature for 23 h. After removal of the precipitate by filtration, the solution was concentrated under vacuum. The crude product was purified by column chromatography (silica gel/dichloromethane) to obtain **5-*n*** as colourless solids. Yields were 24, 45, 41, 45 and 24% for compounds **5-1**, **5-5**, **5-7**, **5-10** and **5-11**, respectively.

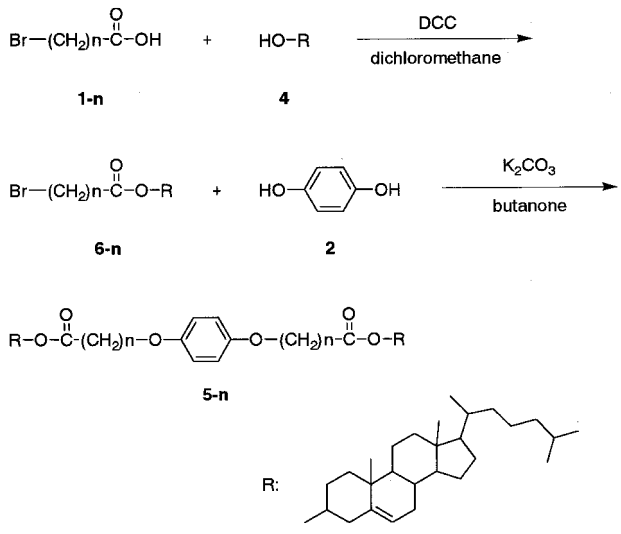
2.3. *Synthesis of dicholesteryl ester (route B)* [17]

To a solution of cholesterol **4** (70 mmol) in 280 ml of dichloromethane was added a solution of ω-bromoalkanoic acid **1-*n*** (70 mmol), dicyclohexylcarbodiimide (70 mmol) and 4-dimethylaminopyridine (7 mmol) in 120 ml of dichloromethane. The mixture was stirred at room temperature for 12 h. After removal of the precipitate by filtration, the solution was concentrated under vacuum. The crude product was then purified by column chromatography (silica gel/dichloromethane) to give colourless solids, **6-*n***. Yields were 57, 77, 55, 74, 70 and 87% for esters **6-4**, **6-5**, **6-6**, **6-7**, **6-8** and **6-9**, respectively.

A mixture of hydroquinone (1 mmol), the cholesteryl ester, **6-*n*** (2 mmol) and anhydrous potassium carbonate



Scheme 1.



Scheme 2.

(4 mmol) in 20 ml of butanone was heated at reflux for 16 h. After removal of the precipitate by filtration, the solution was concentrated under vacuum. The crude product was purified by column chromatography (silica gel/dichloromethane) to give colourless solids, **5-*n***. Yields were 30, 40, 45, 55, 67, 32 and 30% for diesters **5-3**, **5-4**, **5-5**, **5-6**, **5-7**, **5-8** and **5-9**, respectively.

5-1: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.65–1.99 (m, 82H), δ 2.32–2.35 (d, 4H), δ 4.53 (s, 4H, CH_2O), δ 4.72 (m, 2H, CHO), δ 5.37 (m, 2H, CH=), δ 6.83 (m, 4H, aromatic). Elemental analysis: calculated ($C_{64}H_{98}O_6$), C 79.78, H 10.25%; found, C 79.62, H 10.49%.

5-3: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.67–2.10 (m, 86H), δ 2.31 (d, 4H), δ 2.48 (t, 4H), δ 3.94 (t, 4H, CH_2O), δ 4.60 (m, 2H, CHO), δ 5.37 (m, 2H, CH=), δ 6.81 (m, 4H, aromatic). Elemental analysis: calculated ($C_{68}H_{106}O_6$), C 80.11, H 10.48%; found, C 80.03, H 10.73%.

5-4: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.68–2.03 (m, 90H), δ 2.29 (t, 8H), δ 3.89 (t, 4H, CH_2O), δ 4.59 (m, 2H, CHO), δ 5.37 (m, 2H, CH=), δ 6.82 (m, 4H, aromatic). Elemental analysis: calculated ($C_{70}H_{110}O_6$), C 80.25, H 10.58%; found, C 80.07, H 10.79%.

5-5: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.67–2.03 (m, 94H), δ 2.27 (q, 8H), δ 3.89 (t, 4H, CH_2O), δ 4.61 (m, 2H, CHO), δ 5.37 (m, 2H, CH=), δ 6.83 (m, 4H, aromatic). Elemental analysis: calculated ($C_{72}H_{114}O_6$), C 80.39, H 10.68%; found, C 80.20, H 10.79%.

5-6: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.67–2.03 (m, 98H), δ 2.28 (t, 8H), δ 3.89 (t, 4H, CH_2O), δ 4.59 (m, 2H, CHO), δ 5.36 (m, 2H, CH=), δ 6.80 (m, 4H, aromatic). Elemental analysis: calculated ($C_{74}H_{118}O_6$), C 80.53, H 10.78%; found, C 80.49, H 10.94%.

5-7: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.68–2.03 (m, 102H), δ 2.29 (q, 8H), δ 3.89 (t, 4H, CH_2O), δ 4.61 (m, 2H, CHO), δ 5.37 (m, 2H, CH=), δ 6.81 (m, 4H, aromatic). Elemental analysis: calculated ($C_{76}H_{122}O_6$), C 80.65, H 10.87%; found, C 80.57, H 11.09%.

5-8: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.68–2.05 (m, 110H), δ 2.29 (q, 8H), δ 3.89 (t, 4H, CH_2O), δ 4.61 (m, 2H, CHO), δ 5.37 (m, 2H, CH=), δ 6.81 (m, 4H, aromatic). Elemental analysis: calculated ($C_{78}H_{126}O_6$), C 80.77, H 10.95%; found, C 80.92, H 11.00%.

5-9: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.67–2.03 (m, 110H), δ 2.28 (q, 8H), δ 3.89 (t, 4H, CH_2O), δ 4.61 (m, 2H, CHO), δ 5.37 (m, 2H, CH=), δ 6.81 (m, 4H, aromatic). Elemental analysis: calculated ($C_{80}H_{130}O_6$), C 80.98, H 11.03%; found, C 80.88; H 11.17%.

5-10: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.67–2.03 (m, 114H), δ 2.27 (m, 8H), δ 3.89 (t, 4H, CH_2O), δ 4.61 (m, 2H, CHO), δ 5.37 (m, 2H, CH=), δ 6.83 (m, 4H, aromatic). Elemental analysis: calculated ($C_{82}H_{134}O_6$), C 81.00, H 11.11%; found, C 81.15, H 11.25%.

5-11: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.67–2.03 (m, 118H), δ 2.27 (q, 8H), δ 3.89 (t, 4H, CH_2O), δ 4.61 (m, 2H, CHO), δ 5.37 (m, 2H, CH=), δ 6.81 (m, 4H, aromatic). Elemental analysis: calculated ($C_{84}H_{138}O_6$), C 81.10, H 11.18%; found, C 81.13, H 11.45%.

2.4. *Preparation of liquid crystals in the glassy state*

A powdered sample (3 mg) sandwiched between two thin glass plates was placed on a hot stage and heated to the cholesteric temperature. While maintaining the sample at this temperature, the top glass plate was gently moved sideways to form a Grandjean texture. The sample was then dipped into ice-water to obtain a solid coloured film between the two glass plates.

3. Results and disscussion

3.1. *Synthesis*

Dicholesteryl esters **5-*n*** can be synthesized by either one of two routes, A or B, shown in schemes 1 and 2. For route A, dicarboxylic acid **3-*n*** was first obtained by the reaction of hydroquinone and a bromoalkanoic acid in methanol in the presence of sodium hydroxide. The diacid was then esterified with cholesterol using DCC as coupling reagent to afford compounds **5-*n***. In route B, an ω-bromoalkanoic acid was first esterified with cholesterol using DCC. Then the bromo ester obtained was reacted with hydroquinone in butanone in the presence of potassium carbonate. The yields for both steps in route A after purification were low, perhaps due to the low solubility of the dicarboxylic acids **3-*n*** in butanone, while route B provided higher yields.

3.2. *Phase transitions*

The phase transitions of the synthesized compounds were studied by differential scanning calorimetry and polarizing optical microscopy (POM)—see table 1.

Table 1. Phase transition temperatures (°C) of the **5-*n*** compounds upon cooling and heating measured by DSC. The corresponding enthalpy changes (mJ mol^{-1}) are in parentheses. Cr = crystal: N* = cholesteric: I = isotropic.

Compound	Cr → N* or I	N* → I	I → N* or Cr	N* → Cr
5-1	185 (35.0)	—	156 (−28.1)	—
5-3	139 (16.3)	179 (3.3)	178 (−2.6)	115 (−13.4)
5-4	130 (24.9)	145 (0.3)	139 (−3.2)	108 (−34.7)
5-5	145 (23.1)	180 (3.2)	180 (−4.5)	121 (−21.3)
5-6	133 (31.4)	148 (0.4)	147 (−1.0)	112 (−26.6)
5-7	128 (19.2)	161 (3.8)	159 (−4.4)	109 (−17.0)
5-8	113 (36.7)	131 (1.6)	131 (−1.9)	95 (−25.5)
5-9	107 (27.3)	142 (3.4)	138 (−3.9)	91 (−21.4)
5-10	110 (29.2)	122 (0.2)	123 (−1.9)	91 (−31.2)
5-11	105 (11.2)	134 (3.0)	133 (−3.0)	93 (−22.3)

Compound **5-1** showed just one endotherm upon heating and no liquid crystalline phase. The compounds other than **5-1** showed a mesophase that was verified as cholesteric by POM observations of the textures. These phases were enantiotropic, forming both upon heating and cooling. Figure 1 shows a typical DSC trace obtained for **5-5** during heating and cooling. Upon heating, endothermic peaks at which the compound changes from the crystalline to the cholesteric phase and from the cholesteric to the isotropic phase are observed at 145 and 180°C, respectively. Upon cooling, two exotherms are observed at 180 and 120°C. The large hysteresis for the transition between the cholesteric and crystalline phases can be explained by the relatively large molecular mass (1076) of **5-5** for a non-polymeric LC. By the introduction of a phenylene oxide group in place of the diyne group, the liquid crystalline property is changed from monotropic to enantiotropic [10, 13].

Figure 2 shows the relationship between the number of methylenes on one wing of the compounds and the phase transition temperature upon cooling. The odd–even effect is clearly seen for both phase transitions from the isotropic to the cholesteric and from the cholesteric to the crystalline state. The isotropization temperatures are higher and the liquid crystalline temperature regions are wider for the compounds with an odd number of carbons than for those with an even number of carbons in one of the alkylene chains. The enthalpy changes for the phase transitions also show the odd–even effect of the carbon number in a wing spacer. The compounds with odd parity show larger enthalpy changes for the I–N* transition than those with even parity, which means that the former compounds form a more stable cholesteric (N*) phase.

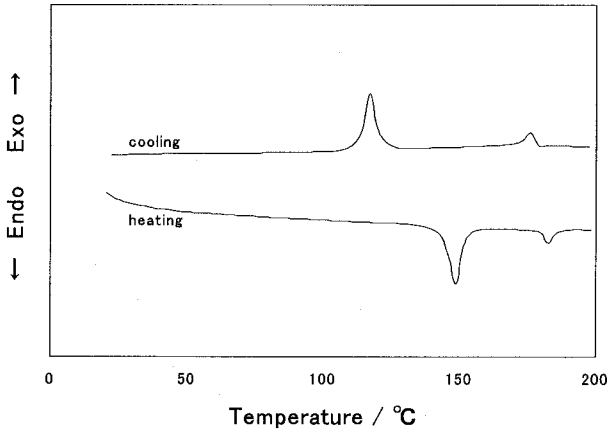


Figure 1. DSC thermogram of compound **5-5** upon second heating and second cooling.

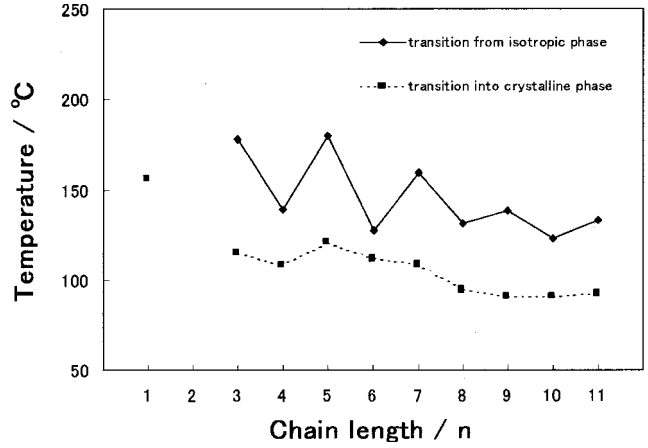


Figure 2. Phase transition temperatures of compounds **5-*n*** measured by DSC during cooling plotted versus the number of methylene units in one of the flexible wing linkages.

The odd–even effect in the physical properties of twin, triplet and other simpler mesogens is usually ascribed to a difference in the preferred conformation of the compounds in the mesophase and its effect on the ordering in the phase [17]. If the alkylene spacers are in the preferred all-*trans*-conformation, compounds with an odd number of carbons in the alkylene spacers have a more extended structure with the axes of all the cholesteryl and phenylene oxide groups parallel, while those with even numbers of carbons in the spacers have

a Z-shaped conformation. The extended conformation induces a better packed molecular order with a larger intermolecular interaction in the liquid crystalline phase, and this is the origin of the more stable cholesteric phase. For the N*–Cr transition, the compounds with odd parity methylenes showed smaller enthalpy changes than those with even parity. This could be caused by the fact that, coming from the better packed N* phase into the crystalline phase of the compounds with odd number spacers, there is less change in order than for those with even number spacers. These arguments also apply in the heating processes from crystal to cholesteric phase.

3.3. *Cholesteric solid state*

The compounds **5-*n*** were solidified while maintaining the liquid crystalline molecular order by rapidly cooling the liquid crystalline phase (see the experimental section for details of the film preparation). The solid film obtained showed iridescent colours which depended on the temperature at which the rapid cooling was started. Figure 3 shows the reflection spectra of **5-5** in the solidified cholesteric film (A) and in the normal cholesteric phase (B), respectively. Solidification slightly broadens the spectrum, but the peak wavelength remains. Broadening may be due to the disturbance in the direction of the helical axis of the molecular order.

Figure 4 shows the transmission spectra of the solid films of **5-5** reflecting red, green and blue light. By changing the temperature at which the rapid cooling was started, any colour could be fixed in the solid film. The colour or helical molecular order in each of the solid films obtained with **5-*n*** ($n = 3$, 5, 8, 9, 10, 11) is stable at room temperature for at least 1 month. However, the colour of the film disappeared once the film was heated above 80°C and the compound acquired a white crystalline state. Further heating of the sample

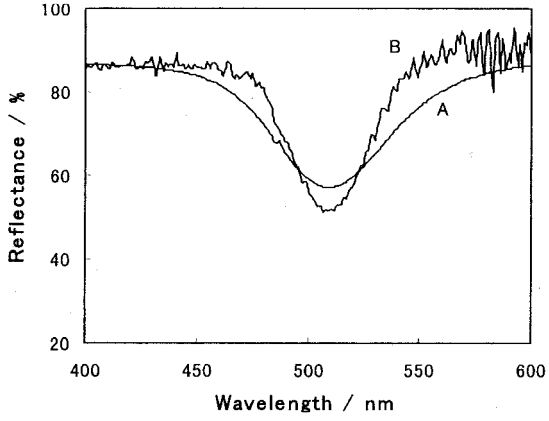


Figure 3. Comparison of reflection spectra of compound **5-5**. A: solid film obtained by rapid cooling from 150°C; B: liquid crystal in the cholesteric phase at 150°C.

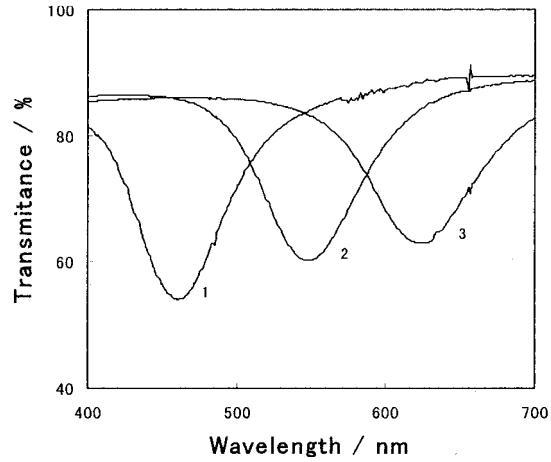


Figure 4. Transmission spectra of compound **5-5** sandwiched between glass plates in the coloured solid state, obtained by rapid cooling from different temperatures. 1: 180°C, 2: 140°C, 3: 126°C.

induced the phase transition from the crystalline to the normal cholesteric liquid crystalline state with colours that could be fixed again by cooling. Table 2 shows the transition temperatures for the compounds when passing from the cholesteric solid to the crystalline state on heating in a hot stage. The stabilities of the cholesteric solid states of the compounds **5-*n*** do not show an apparent odd–even effect in contrast to the dicholesteryl esters with a diyne group where an odd–even effect as a function of the carbons in the alkylene chains was observed [13], implying that those compounds which can have an extended conformation by assuming all-*trans*-alkylene chains have higher thermal stabilities in the cholesteric solid state. The phenylene oxide group in the compounds studied here may play an important role with regard to the intermolecular interactions stabilizing the cholesteric solid state and result in the odd–even effect being much smaller.

Table 2. Transition temperature for the compounds **5-*n*** from the cholesteric solid to the crystalline state as observed on heating in a hotstage.

Compound	Temperature/°C
5-1	—
5-3	68
5-4	—
5-5	80
5-6	—
5-7	67
5-8	78
5-9	83
5-10	80
5-11	82

Figure 5 shows the DSC thermograms obtained on heating the cholesteric solid samples of **5-5** obtained by rapid cooling from 175, 155 and 130°C. Two exothermic peaks are observed at 147 and 150°C, although a single exothermic peak at 145°C is observed for the freshly recrystallized compound. The ratio of the peak areas at 147 and 150°C is monotonously changed depending on the temperature at which the rapid cooling was started for the preparation of the solid film [13]. A similar phenomenon is observed for the dicholesteryl esters with a diyne unit. This may suggest the existence of two conformational isomers whose ratio is changed depending on the temperature in the normal cholesteric phase. The molecular conformation may be fixed upon rapid cooling and remain unchanged through to crystallization in the cholesteric solid state. This assumption will be further investigated in future work. In the DSC thermograms there are no apparent exothermic peaks around 80°C, the crystallization temperature on heating from the cholesteric solid state. Only a low and very broad increase in the baseline is seen. This is probably because the crystalline and cholesteric solid states are not energetically very different.

Figure 6 shows the relationship between the temperature at which the rapid cooling started and the wavelength of the peak in the transmission band. The reflection band appeared in the visible region for the compounds with an odd number of carbons in each alkylene chain, while it occurred in the ultraviolet region for compounds **5-8** and **5-10**. It was difficult to obtain cholesteric solid films for compounds **5-4** and **5-6** due to their rapid crystallization rate. Compounds **5-4** and **5-6** showed a reflection band around 300 nm that shifted towards longer wavelengths by decreasing the temperature in the normal cholesteric phase. Among the compounds with an odd number of carbons in each alkylene chain, the position of the reflection band, which significantly depends on the temperature, is shifted towards a longer wavelength as the length of the alkylene chain is shortened. On the contrary, the compounds with an odd number of carbons in each alkylene chain do not show a clear relationship between the position of the reflection band (which is not sensitive to temperature) and the length of the alkylene chain. This behaviour is similar to that reported by Marcelis *et al.* for triplet liquid crystals with a central biphenyl group to which two dihydrocholesteryl groups are attached via two flexible alkanoate spacers [17].

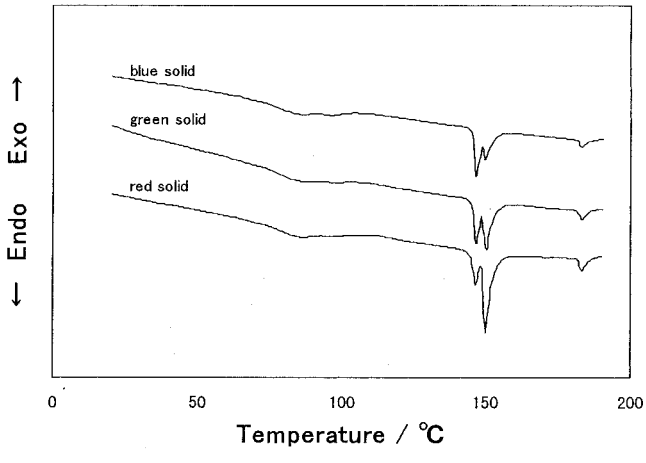


Figure 5. DSC thermograms of compound **5-5** on heating from the blue, green and red cholesteric solid states.

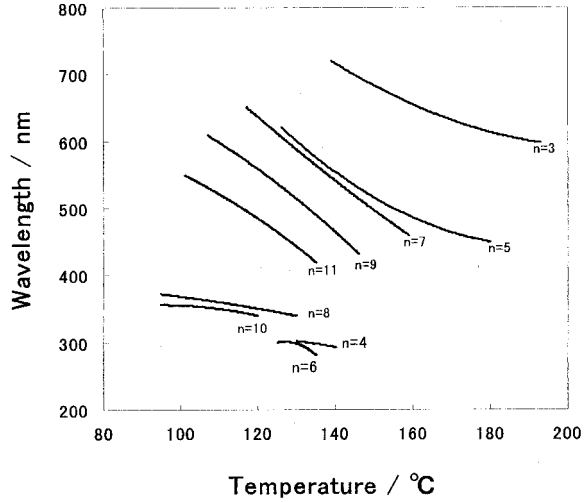


Figure 6. Relationship between the temperature at which rapid cooling was started and the wavelength of the peak in the transmission band for the solid cholesteric films.

4. Conclusions

The present study on dicholesteryl esters with a central phenylene oxide group has shown that there is a strong odd–even effect of the carbon number in the alkylene spacers on the temperatures and entropies of the phase transition and on the selective reflection wavelength. This effect is explained by proposing well- and badly-packed molecular order in the cholesteric phases due to the extended and Z-shaped molecular conformations of the compounds with an odd and even number of carbons in the spacers, respectively. The stability of the cholesteric solid does not show an apparent odd–even effect for the length of the spacers, suggesting the possibility of an important role of the phenylene oxide group with regard to the intermolecular interactions that stabilize the cholesteric solid state.

References

[1] For polymeric cholesterics: (*a*) FINKELMANN, H., KOLDEHOFF, J., and RINGSDORF, H., 1978, *Angew. Chem. int. Ed. Engl.*, **17,** 935; (*b*) TSENG, S.-L., LAIVINS, G. V.,

and GRAY, D. G., 1982, *Macromolecules*, **15,** 1262; (*c*) WATANABE, J., NAGASE, T., ITOH, H., ISHI, T., and SATOH, T., 1988, *Mol. Cryst. liq. Cryst.*, **164,** 135.

[2] For non-polymeric cholesterics: (*a*) TSUJI, K., SORAI, M., and SEKI, S., 1971, *Bull. chem. Soc. Jpn.*, **44,** 1452; (*b*) CHEN, S. H., SHI, H., MASTARANGLO, J. C., and OU, J. J., 1996, *Prog. polym. Sci.*, **21,** 1211; (*c*) KIHARA, H., KATO, T., and URYU, T., 1998, *Liq. Cryst.*, **24,** 413; (*d*) OSTUNI, E., and WEISS, R. G., 1999, *Liq. Cryst.*, **26,** 541; (*e*) KREUZER, F.-H., HÄBERLE, N., LEIGEBER, H., MAURER, R., STOHRER, J., and WEIS, J., 1997, *Organosilicon Chemistry III*, edited by N. Auner and J. Weis (Weinheim: Wiley-VCH), pp. 566–586; (*f*) PETRI, A., BRÄUCHLE, C., LEIGEBER, H., MILLER, A., WEITZEL, H.-P., and KREUZER, F.-H., 1993, *Liq. Cryst.*, **15,** 113; (*g*) CHEN, S. H., SHI, H., CONGER, B. M., MASTARANGELO, J. C., and TSUTSUI, T., 1996, *Adv. Mater.*, **8,** 12; (*h*) KASIS, D., CHEN, P. H. M., MASTARANGELO, J. C., CHEN, S. H., and BLANTON, T. N., 1999, *Chem. Mater.*, **11,** 1590; (*i*) FAN, F. Y., MASTARANGELO, J. C., KATSIS, D., CHEN, S. H., and BLANTON, T. N., 2000, *Liq. Cryst.*, **27,** 1239.

[3] WEDLER, W., DEMUS, D., ZASCHKE, H., MOHR, K., SCHÄFER, W., and WEISSFLOG, W., 1991, *J. mater. Chem.*, **1,** 347.

[4] PALFFY-MUHORAY, P., 1998, *Nature*, **391,** 745.

[5] TSUTSUI, T., and TANAKA, T., 1980, *Polymer*, **21,** 1351.

[6] SHANNON, P. J., 1984, *Macromolecules*, **17,** 1873.

[7] BROER, D. J., LUB, J., and MOL, G. N., 1995, *Nature*, **378,** 467.

[8] MÜLLER, M., ZENTEL, R., and KELLER, H., 1997, *Adv. Mater.*, **9,** 159.

[9] DE VRIES, H., 1951, *Acta. Cryst.*, **4,** 219.

[10] TAMAOKI, N., PARFENOV, A. V., MASAKI, A., and MATSUDA, H., 1997, *Adv. Mater.*, **9,** 1102.

[11] KRUK, G., TAMAOKI, N., MATSUDA, H., and KIDA, Y., 1999, *Liq. Cryst.*, **26,** 1687.

[12] TAMAOKI, N., MORIYAMA, M., and MATSUDA, H., 2000, *Angew. Chem. Int. Ed.*, **39,** 509.

[13] TAMAOKI, N., KRUK, G., and MATSUDA, H., 1999, *J. mater. Chem.*, **9,** 2381.

[14] BARRALL II, E. M., and JOHNSON, J. F., 1969, *Mol. Cryst. liq. Cryst.*, **8,** 27.

[15] RAULT, J., LIÈBERT, L., and STRZELECKI, L., 1975, *Bull. Soc. Chim. Fr.*, 1175.

[16] MARCELIS, A. T. M., KOUDIJS, A., and SUDHÖLTER, E. J. R., 1996, *J. mater. Chem.*, **6,** 1469.

[17] MARCELIS, A. T. M., KOUDIJS, A., and SUDHÖLTER, E. J. R., 1995, *Liq. Cryst.*, **18,** 851.

[18] MARCELIS, A. T. M., KOUDIJS, A., and SUDHÖLTER, E. J. R., 1996, *Thin solid Films*, **284-285,** 308.

[19] POKROVSKII, L. I., and FROLOV, S. S., 1961, *J. appl. Chem. USSR.*, **34,** 2024.