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Liquid crystalline compounds having a tribranched structure: substituted malonic esters consisting of two Schiff's base units and a cholesteryloxyalkyl substituent

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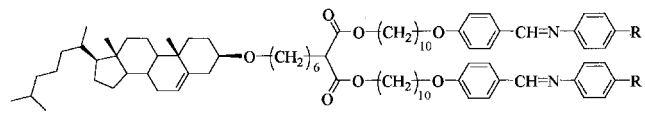
New tribranched thermotropic liquid crystal compounds were synthesized and their liquid crystalline properties studied by differential scanning calorimetry, X-ray diffraction and polarizing optical microscopy. The compounds are the bis-{10-[4-(4-alkylphenyliminomethynyl)-phenoxy]decyl} 2-[6-(cholesteryloxy)hexyl]malonates and the corresponding alkoxy derivatives. These compounds contain three mesogenic units, two identical Schiff's base type mesogens and one cholesteryl either moiety, interconnected in a tribranched structure via spacers. The cholesterly moiety is attached to the malonic acid core through an oxyhexamethylene spacer while the two Schiff's-base moieties are attached through oxydecamethylene spacers. The terminal alkyl group of the Schiff's base unit is either a butyl or decyl group, and the alkoxy terminal group is either a butoxy or decyloxy chain. All the compounds form only an enantiotropic smectic phase, most probably of the smectic C type. The larger spacings determined by small angle X-ray diffraction range from 3.3 to 4.1 nm, which are much shorter than the end-to-end distance (5.9–7.4 nm) of the molecules estimated using molecular models assuming an all *trans* extended conformation for all the alkyl spacers.

1. Introduction

Recently, the liquid crystalline (LC) properties of non-symmetric dimers have been reported by ourselves [1–8] and others [9–18]. These compounds consist of two different mesogenic units connected linearly through linking spacers such as polymethylene groups. The LC behaviour of this type of compound is rather intriguing because there is no simple relationship between the mesophases formed by the dimers and those formed independently by the constituent mesogens. In other words, the correlation between the structure of non-symmetric dimers and their LC behaviour is yet to be established. Moreover, some of the non-symmetric dimers reported by ourselves exhibit incommensurate phases and a series of very complicated, multiple phase transitions prior to isotropization [2–4, 6–8]. The LC properties of some hydrogen-bonded non-symmetric dimers have also been reported by ourselves [19].

In this article, we report the synthesis and LC properties of four tribranched compounds consisting of two identical Schiff's base mesogenic groups and a cholesterol moiety connected via a central malonic acid unit and polymethylene spacers: the bis-{10-[4-(4-alkyl or alkoxyphenyliminomethynyl)phenoxy]decyl} 2-[6-(cholesteryloxy)hexyl]malonates.



TM-C$_4$: $R = n$-C_4H_9
TM-C$_{10}$: $R = n$-$C_{10}H_{21}$
TM-OC$_4$: $R = O$-n-C_4H_9
TM-OC$_{10}$: $R = O$-n-$C_{10}H_{21}$

TM in the acronyms refers to tribranched malonate derivatives. The central branching point is located on the central methylene group of the malonic acid moiety. The LC properties and phase transitions of the compounds have been studied using differential scanning calorimetry (DSC), polarizing optical microscopy, and small angle and wide angle X-ray diffraction (SAXD and WAXD, respectively).

2. Experimental

2.1. *Characterization and instrumentation*

The IR and NMR spectra of intermediates and final products were recorded on a Bomem MB FTIR instrument and a Varian Gemini 300 spectrometer, respectively. Elemental analysis was performed using an

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Eager 200 elemental analyser. Thermal properties were examined by differential scanning calorimetry (Mettler DSC 821, heating rate 5°C min^{-1}) under a nitrogen atmosphere and also on a polarizing microscope (Olympus BH-2) equipped with a hot-stage (Mettler FP-82HT) controlled by a Mettler FP-90 controller. X-ray diffraction patterns of the mesophases were obtained using synchroton radiation (1.542 Å) at the Pohang Synchrotron Laboratory, Pohang, Korea.

2.2. *Synthesis*

The scheme summarizes the synthetic route to the title compounds; preparative details are given below.

2.2.1. *Di-[10-(4-formylphenoxy)decyl]malonate,* **2**

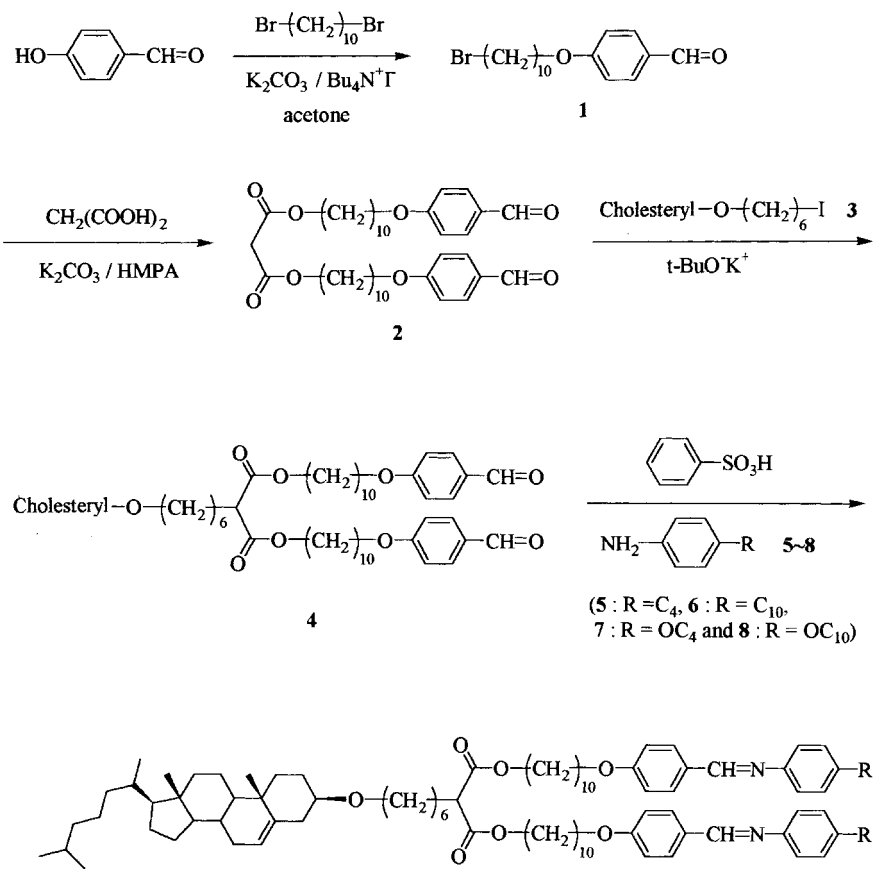
Malonic acid (1.30 g, 1.25×10^{-2} mol) and 4-(10-bromodecyloxy)benzaldehyde, **1** [20] (13.0 g, 3.81×10^{-2} mol) were dissolved in hexamethylphosphoric triamide (HMPA) (100 ml) containing K_2CO_3 (4.4 g) [21]. After stirring the mixture for 32 h at room temperature, it was poured into excess water, and the product extracted with diethyl ether. The solvent was removed under reduced pressure, and the crude product purified by chromatography on a silica gel column using a mixture of ethyl acetate and hexane (1:3 by volume) as eluent; yield 4.80 g (76.8%), m.p. 37°C. IR (KBr, cm^{-1}): 2932 and 2854 (aliphatic C–H stretch), 1749 (ester C=O stretch), 1691 (aldehyde C=O stretch), 1599 and 1510 (aromatic C=C stretch), 1259 and 1011 (C–O stretch). ^{1}H NMR ($CDCl_3$, δ ppm): 3.37 (s, 2H, $\underline{CH_2}$–(COO–)$_2$), 4.04 (t, 4H, Ar–O$\underline{CH_2}$–), 4.14 (t, 4H, COO$\underline{CH_2}$–), 6.97–7.84 (d, 8H, Ar), 9.88 (s, 1H, ArCHO). Elemental analysis: calc. for $C_{37}H_{52}O_8$ C 71.13, H 8.39; found C 71.18, H 8.53%.

2.2.2. *Cholesteryl-(6-iodohexyl) ether,* **3**

Compound **3** was prepared in two steps following the literature method [22]; thus cholesteryl-(6-*p*-tosyloxyhexyl) ether was first prepared and then reacted with sodium iodide to give **3**.

2.2.3. *Di-[10-(4-formylphenoxy)decyl] 2-[6-(cholesteryloxy)hexyl]malonate,* **4**

Compound **2** (4.40 g, 7.04×10^{-2} mol) was dissolved in dry tetrahydrofuran (150 ml), and dry tetrahydrofuran (7.7 ml) containing 1 mol % of potassium *t*-butoxide was added dropwise. A solution of **3** (4.20 g, 7.04×10^{-3} mol) dissolved in dry tetrahydrofuran (100 ml) was added over a period of 30 min to the reaction mixture. The mixture was heated at reflux overnight under a dry nitrogen



Scheme. Synthetic route to the tribranched LC compounds.

atmosphere. The solvent was removed by distillation under reduced pressure. The residue was mixed with distilled water (400 ml) and poured into excess 0.1M HCl. The product was isolated by extraction using diethyl ether. Removal of the diethyl ether by distillation gave the crude product which was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane (1:4 by volume) as eluent; yield 5.1 g (67%), m.p. 48°C. IR (KBr, cm^{-1}): 2933 and 2852 (aliphatic C−H stretch), 1740 (ester C=O stretch), 1691 (aldehyde C=O stretch), 1601 and 1512 (aromatic C=C stretch), 1265 and 1014 (C−O stretch). ^{1}H NMR ($CDCl_3$, δ ppm): 3.11 (m, 1H, −CH−O), 3.31 (t, 1H, −CH−$(COO-)_2$), 3.43 (t, 2H, cholesteryl−OCH_2), 4.03 (t, 4H, Ar−OCH_2−), 4.12 (t, 4H, COOCH_2−), 5.34 (m, 1H, H-6), 6.97–7.84 (m, 8H, Ar), 9.87 (s, 2H, ArCHO). Elemental analysis: calc. for $C_{70}H_{108}O_9$ C 76.88, H 9.95; found C 76.83, H 10.03%.

2.2.4. *Bis-{10-[4-(4-butylphenyliminomethyny l)-phenoxy]decyl} 2-[6-(cholesteryloxy)hexyl]-malonate,* ***TM-C^4***

Compound **4** (1.1 g, 1.01×10^{-2} mol) and 4-butylaniline 90.45 g, 3.02×10^{-3} mol) were dissolved in benzene (80 ml) containing benzene sulphonic acid (0.02 g). The mixture was heated at reflux for 24 h under a dry nitrogen atmosphere whilst the water formed was removed using a Dean–Stark trap [23]. The volume of the reaction mixture was reduced to about 20 ml by distillation of the benzene. The residue was poured into ethanol (150 ml) causing the product to precipitate. The crude product obtained by filtration was purified by recrystallization from acetone; yield 1.2 g (89%), m.p. 84°C. IR (KBr, cm^{-1}): 2932 and 2851 (aliphatic C−H stretch), 1732 (ester C=O stretch), 1610 and 1512 (aromatic C=C stretch and C=N stretch), 1257 and 1018 (C−O stretch). ^{1}H NMR ($CDCl_3$, δ ppm): 2.61 (t, 4H, Ar−CH_2−), 3.11 (m, 1H, −CH−O), 3.32 (t, 1H, −CH−$(COO-)_2$), 3.43 (t, 2H, cholesteryl−OCH_2), 4.00 (t, 4H, Ar−OCH_2−), 4.12 (t, 4H, COOCH_2−), 5.34 (m, 1H, H-6), 6.96–7.84 (m, 16H, Ar), 8.39 (s, 2H, −CH=N−). Elemental analysis: calc. for $C_{90}H_{134}N_2O_7$ C 79.72, H 9.96, N 2.07; found C 79.73, H 9.92, N 2.10%.

All the other **TM** compounds were prepared in exactly the same manner and therefore only their spectroscopic and elemental analysis data are given.

2.2.5. *Bis-{10-[4-(4-decylphenyliminomethyny l)-phenoxy]decyl} 2-[6-(cholesteryloxy)hexyl]-malonate,* ***TM-C^{10}***

Yield 93%, m.p. 83°C. IR (KBr, cm^{-1}): 2923 and 2851 (aliphatic C−H stretch), 1731 (ester C=O stretch), 1610 and 1512 (aromatic C=C stretch, and C=N stretch), 1257 and 1018 (C−O stretch). ^{1}H NMR ($CDCl_3$, δ ppm): 2.61 (t, 4H, Ar−CH_2−), 3.11 (m, 1H, −CH−O), 3.32 (t, 1H, −CH−$(COO-)_2$), 3.43 (t, 2H, cholesteryl−OCH_2), 4.00 (t, 4H, Ar−OCH_2−), 4.12 (t, 4H, COOCH_2−), 5.34 (m, 1H, H-6), 6.93–7.82 (m, 16H, Ar), 8.38 (s, 2H, −CH=N−). Elemental analysis: calc. for $C_{102}H_{158}N_2O_7$ C 80.37, H 10.45, N 1.84; found C 80.36, H 10.47, N 1.85%.

2.2.6. *Bis-{10-[4-(4-butoxyphenyliminomethyny l)-phenoxy]decyl} 2-[6-(cholesteryloxy)hexyl]-malonate,* ***TM-OC^4***

Yield 91%, m.p. 126°C. IR (KBr, cm^{-1}): 2936 and 2851 (aliphatic C−H stretch), 1732 (ester C=O stretch), 1609 and 1512 (aromatic C=C stretch, and C=N stretch), 1251 and 1020 (C−O stretch). ^{1}H NMR ($CDCl_3$, δ ppm): 2.60 (t, 4H, Ar−CH_2−), 3.11 (m, 1H, −CH−O), 3.32 (t, 1H, −CH−$(COO-)_2$), 3.43 (t, 2H, cholesteryl−OCH_2), 3.95–4.03 (m, 8H, Ar−OCH_2−), 4.12 (t, 4H, COOCH_2−), 5.34 (m, 1H, H-6), 6.89–7.82 (m, 16H, Ar), 8.39 (s, 2H, −CH=N−). Elemental analysis: calc. for $C_{90}H_{134}N_2O_9$ C 77.88, H 9.73, N 2.02; found C 77.84, H 9.78, N 2.09%.

2.2.7. *Bis-{10-[4-(4-decyloxyphenyliminomethyny l)-phenoxy]decyl} 2-[6-(cholesteryloxy)hexyl]-malonate,* ***TM-OC^{10}***

Yield 90% m.p. 110°C. IR (KBr, cm^{-1}): 2920 and 2850 (aliphatic C−H stretch), 1735 (ester C=O stretch), 1608 and 1512 (aromatic C=C stretch, and C=N stretch), 1253 and 1023 (C−O stretch). ^{1}H NMR ($CDCl_3$, δ ppm): 2.61 (t, 4H, Ar−CH_2−), 3.11 (m, 1H, −CH−O), 3.32 (t, 1H, −CH−$(COO-)_2$), 3.43 (t, 2H, cholesteryl−OCH_2), 3.94–4.02 (m, 8H, Ar−OCH_2−), 4.12 (t, 4H, COOCH_2−), 5.34 (m, 1H, H-6), 6.87–7.81 (m, 16H, Ar), 8.39 (s, 2H, −CH=N−). Elemental analysis: calc. for $C_{102}H_{158}N_2O_9$ C 78.72, H 10.23, N 1.80; found C 78.63, H 10.72, N 1.86%.

3. Results and discussion

3.1. *Synthesis*

The four **TM** compounds were prepared successfully via the multistep synthetic route shown in the scheme. The structures of all the intermediates and final compounds were confirmed by elemental analyses and IR and NMR spectroscopy. The only structural differences in the **TM** compounds are the lengths of the terminal chains and the absence or presence of the ether oxygen in the amine ring. A common feature is that they are all esters of a substituted malonic acid.

3.2. *Thermal transitions*

The DSC traces of **TM-C$_4$**, **TM-C$_{10}$**, **TM-OC$_4$** and **TM-OC$_{10}$** are shown in figure 1. All the traces show

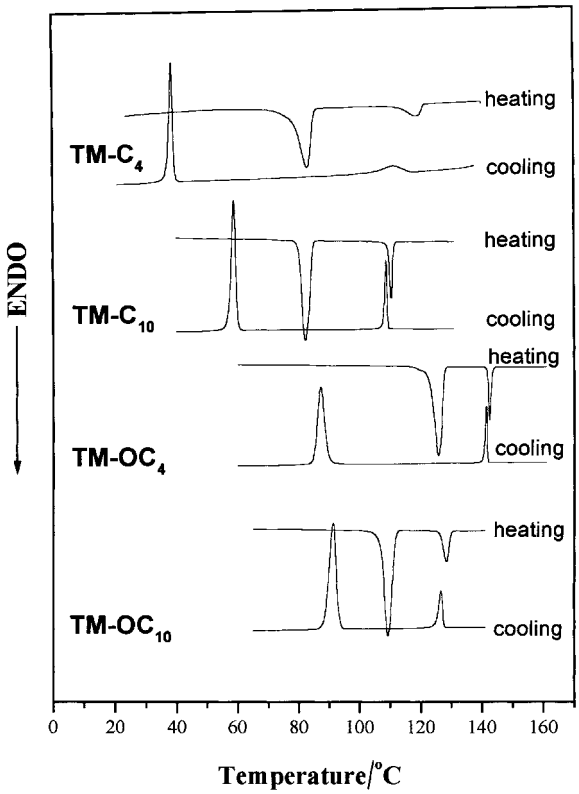
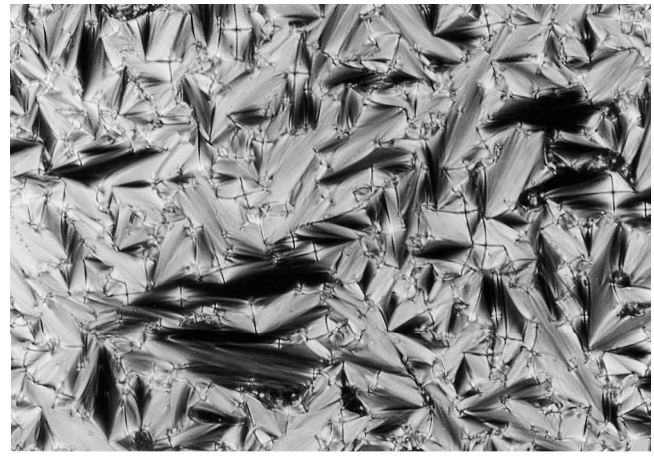
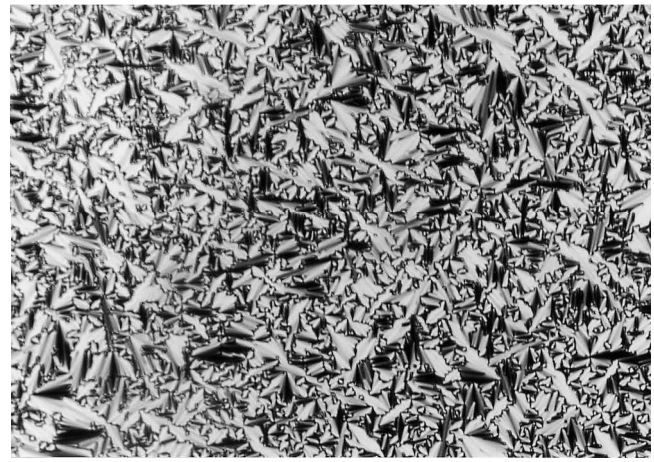


Figure 1. DSC traces of the tribranched **TM** compounds.



(a)



(b)

Figure 2. Optical photomicrographs of the fan textures exhibited by the mesophases of (*a*) **TM-C$_4$** (1st cooling, 80°C), (*b*) **TM-OC$_4$** (1st cooling, 120°C); magnification 200×.

two endothermic transitions on heating and two exothermic transitions on cooling. In other words, each contains two reversible transitions. The low temperature transition corresponds to melting and the higher temperature transition to isotropization. These assignments were confirmed by viewing the samples on a hot-stage attached to a polarizing microscope. As has always been observed for other compounds, crystallization from a LC melt exhibits a significant degree of supercooling. It is also noted that the isotropization endotherm of **TM-C$_4$** was broader than that of the other compounds.

The table summarizes the transition temperatures of the **TM** compounds and the associated thermodynamic data. The transition temperatures decrease on increasing the length of the terminal chains, and the reductions shown by the **TM-OC*n*** compounds are significantly larger than those shown by the **TM-C*n*** compounds. The T_m and T_i values of the **TM-OC*n*** compounds are significantly higher than those of the **TM-C*n*** compounds, indicating stronger intermolecular interactions for the former. Such a trend is very common in many other homologous series [24–28]. In addition, it is noted that

Table. Thermodynamic data for the phase transitions of the tribranched TM compounds heating and cooling rate 5°C min^{-1}; atmosphere N_2 flow rate 15 ml min^{-1}.

	T_m	T_i	ΔH_m		ΔH_i		ΔS_m	ΔS_i	$\Delta S_i/R$
Compound	°C	°C	J g^{-1}	kJ mol^{-1}	J g^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	J mol^{-1} K^{-1}	(mesogenic unit)
TM-C$_4$	84.2	118.6	48.8	66.2	7.7	10.4	185	26.7	1.77
TM-C$_{10}$	82.5	110.5	52.8	80.4	12.5	19.0	226	49.5	2.02
TM-OC$_4$	126.2	142.8	74.5	103.4	13.1	18.1	259	43.6	1.74
TM-OC$_{10}$	109.3	128.4	57.7	89.8	11.9	18.5	235	46.1	1.85

the mesophase temperature ranges of the **TM-C*n*** compounds are much wider than those of the **TM-OC*n*** compounds. The magnitude of the enthalpy (ΔH_i) and the entropy changes (ΔS_i) associated with isotropization range from about 15 to 24% of the corresponding values (ΔH_m and ΔS_m) for melting. These values are rather high when compared with monomeric and dimeric LC compounds [1, 5, 24, 27]. This suggests that the mesophases exhibited by the tribranched compounds may possess a higher degree of order than shown by monomeric and dimeric LC compounds. When the values are scaled by the number of the mesogenic units, i.e. $\Delta S_i/R/3$, they range from 1.7 to 2.0 (see the table). Similar observations have also been made for linear liquid crystal trimers and tetramers [29].

3.3. *Nature of the mesophases*

Figure 2 shows the optical textures of the mesophases exhibited by **TM-C$_4$** and **TM-OC$_4$**. Similar fan textures were observed for **TM-C$_{10}$** and **TM-OC$_{10}$** and appear to be characteristic of smectic phases. Figures 3 and 4 show X-ray diffraction patterns for each compound obtained in the solid, mesophase, and isotropic states. A close examination of the X-ray diffraction patterns of the LC phases reveals that the compounds form the same LC phase. All the patterns show a sharp peak in the small angle region and a very broad one in the wide angle region (*c.* $2\theta = 15$–$22°$; 5.9–4.4 Å), which suggests that they form a fluid smectic phase. In addition, a very small, and probably second order, diffraction peak is detected in all the diffraction patterns of the LC phases. The layer spacings estimated from the small angle peaks are 27.6, 28.1, 31.0 and 32.1 Å, respectively, for **TM-C$_4$**, **TM-C$_{10}$**, **TM-OC$_4$** and **TM-OC$_{10}$**. These values are significantly smaller than the end-to-end distance of the molecules estimated assuming anti-*trans* conformations for all the CH_2 groups in the skeleton, i.e. for **TM-C$_4$** 58.8 Å, **TM-C$_{10}$** 71.7 Å, **TM-OC$_4$** 60.8 Å, and **TM-OC$_{10}$** 73.6 Å; they are also less than the half skeletal lengths of 30.5, 37.8, 31.6, and 38.9 Å for **TM-C$_4$**, **TM-C$_{10}$**, **TM-OC$_4$** and **TM-OC$_{10}$** respectively. It is believed therefore, that these slightly bent compounds are tilted (*c.* 25–28°) in the smectic layer. It is suggested that the cholesterol branch is bent back so as to lie parallel with the other two arms containing the Schiff's-base mesogenic units [30]. In other words, the LC phases are of the smectic C type. As expected, the diffraction patterns of the isotropic phases exhibit only a very broad diffraction peak in the wide angle region. A weak diffraction peak at about $2\theta = 1.5°$ observed in the pattern for **TM-C$_{10}$** at 100°C appears to have arisen from incompletely melted crystals.

If this phase assignment is valid, one may imagine that the present compounds should form a chiral smectic C mesophase due to the presence of the cholesterol moiety linked to the middle methylene position of the central malonic acid structure. We could not however observe an electro-optic response from any of the compounds; they revealed no ferroelectric switching properties. Although we do not yet know exactly why these compounds are not electro-optically responsive, it can be surmised that the presence of the extremely large cholesterol moiety in the middle branch hampers the field-induced molecular

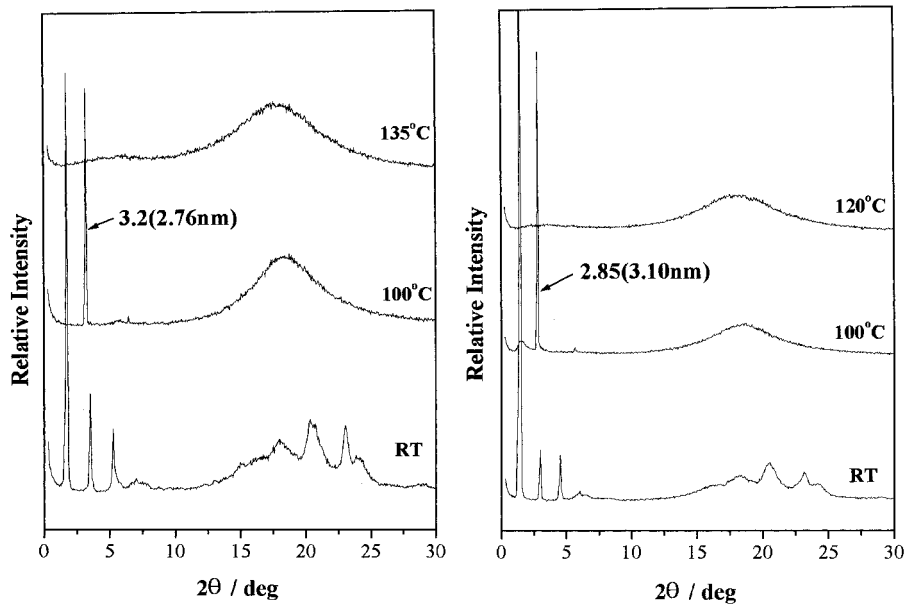


Figure 3. X-ray diffraction patterns of (*a*) **TM-C$_4$**, (*b*) **TM-C$_{10}$**.

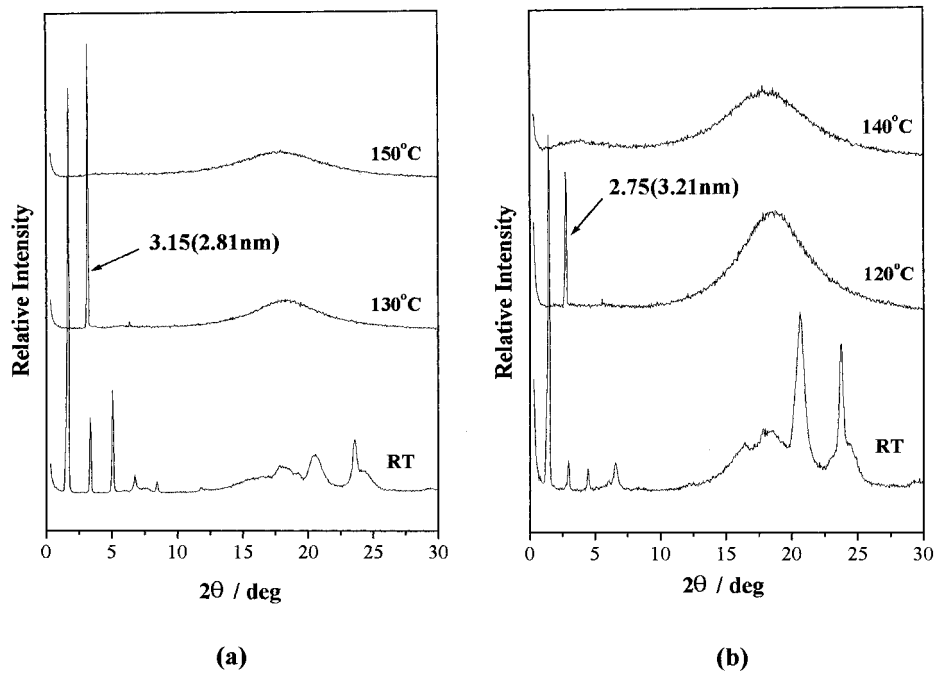


Figure 4. X-ray diffraction patterns of (*a*) **TM-OC$_4$**, (*b*) **TM-OC$_{10}$**.

reorientation. Moreover, even the initial molecular alignment for electro-optic measurements may not be easily achieved. Further investigation is necessary before a definitive answer to this question can be given.

4. Conclusion

A series of new tribranched compounds has been investigated in this study. These compounds are composed of two identical Schiff's-base type mesogens and a cholesterol moiety connected through polymethylene spacers emanating from a central malonic acid core. All the compounds studied in this work form only a fluid smectic phase, most probably of smectic C type. They did not however, exhibit ferroelectric switching, probably due to the presence of the bulky cholesterol branch which can interlock the molecules in the LC phase hindering molecular alignment and also molecular reorientation in the presence of the electric field.

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