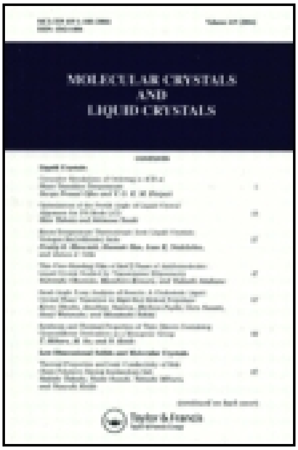

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Synthesis and Thermal. Properties of Cholesteryl 4-n-Alkoxy-3-methoxybenzoates

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Synthesis and Thermal Properties of Cholesteryl 4-*n*-Alkoxy-3-methoxybenzoates

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A homologous series of new liquid crystalline compounds, cholesteryl 4-*n*-alkoxy-3-methoxybenzoate were synthesized from vanillin and their mesomorphic properties were studied by differential scanning calorimetry, polarizing microscopy and x-ray diffractometry. Each of the homologues from cholesteryl 3,4-dimethoxybenzoate ($n = 1$) to cholesteryl 4-*n*-hexyloxy-3-methoxybenzoate ($n = 6$) showed a cholesteric-nematic phase (N_{Ch}). The other higher homologues (from $n = 7$ to $n = 18$) indicated smectic A (S_A) and N_{Ch} phases. The temperature region of smectic phases increased with the increase of the chain length of the *n*-alkoxyl group. Transition temperatures in each of the homologues were lower than those in a corresponding non-3-methoxy substituted benzoate ester, due to the destabilizing effect of the lateral methoxyl group. The effect was more significant on the homologues having a shorter *n*-alkoxyl chain. It was also found that these esters formed a glassy state by quenching from mesophases and/or the isotropic liquid phase. The change of the glass transition temperature on each homologue (from $n = 1$ to $n = 6$) suggested the effect of the chain length of the *n*-alkoxyl group on the formation of the glassy state.

Keywords: liquid crystals, thermal properties, differential scanning calorimetry, cholesteric phase, smectic A phase, glassy state

INTRODUCTION

In one of our studies intended to obtain new functional monomers and polymers using chemicals obtained from plant materials,[1,2,3] we have been paying attention to the synthesis of liquid crystalline compounds, especially from degradation products of lignin.[4] Although, lignin as well as cellulose, is one of the two major components of the plant, the liquid crystalline compounds, whose structural units are related to lignin, have scarcely been reported. The basic structural units of lignin are the 4-hydroxyphenyl, 3-methoxy-4-hydroxyphenyl (guaiacyl) and 3,5-dimethoxy-4-hydroxyphenyl (syringyl) groups. It is known that 4-hydroxybenzaldehyde, vanillin and syringaldehyde are obtained as degradation products of lignin. The synthesis of liquid crystals using the above compounds is useful for the effective utilization of lignin.

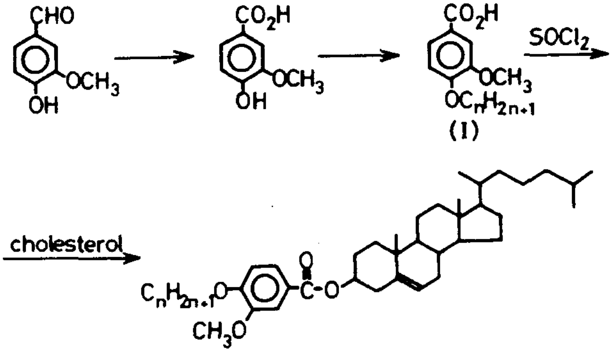
A homologous series of 4-*n*-alkoxybenzoic acids, derived from 4-hydroxybenzaldehyde, are well known as thermotropic liquid crystalline compounds and their physical properties have been studied by many researchers.[5,6,7] We synthesized a homologous series of 4-*n*-alkoxybenzoic acid derivatives from vanillin and syringaldehyde.[8] However, the liquid crystalline properties were not observed for these compounds.[8] It is supposed that the large methoxyl group attached to the aromatic ring prevents the formation of the molecular stacking which leads to the stable mesophase. In order to reduce the effect of the methoxyl group, the acids were converted to the ester carboxylic acids by reaction with 4-hydroxybenzoic acid. The ester carboxylic acid derived from vanillin, 4-(4′-*n*-alkoxy-3′-methoxybenzoyl)-oxybenzoic acids, were found to exhibit liquid crystalline properties. By means of polarizing microscopy, either the nematic or smectic phases were observed, depending on the chain length of *n*-alkoxyl group.[4]

In this report, we describe the synthesis and thermal properties of a homologous series of cholesteryl esters of 4-*n*-alkoxy-3-methoxybenzoic acids, which were prepared from vanillin. Since Reinitzer[9] first discovered that cholesteryl benzoate showed liquid crystalline properties, various kinds of aromatic cholesteryl esters have been synthesized.[10] However, it is still worthwhile to investigate those cholesteryl esters having a chemical structure related to lignin. This is because one might expect a marked change of the transition temperature owing to the large methoxyl group attached to the aromatic ring. In this paper, the thermal behaviour of each homologue cholesteryl 4-*n*-alkoxy-3-methoxy benzoate was investigated in detail by differential scanning calorimetry. Polarizing microscopy and X-ray diffractometry were also used for the investigation.

EXPERIMENTAL

Sample preparation

A homologous series of cholesteryl 4-*n*-alkoxy-3-methoxybenzoates were synthesized according to the synthetic route shown in Scheme 1.



Cholesteryl 4-n-Alkoxy-3-methoxybenzoate
(II)

Scheme 1 Synthesis of cholesteryl 4-*n*-alkoxy-3-methoxybenzoate.

4-*n*-Alkoxy-3-methoxybenzoic acids(I) were prepared by the alkylation[11] of vanillic acid, which is the oxidation product of vanillin. The following procedure for the preparation of 4-*n*-octyloxy-3-methoxybenzoic acid examplifies the method used.

4-Hydroxy-3-methoxybenzoic acid (vanillic acid) (3.36g, 0.02mol) was dissolved in ethanol (80ml). To this, a solution of potassium hydroxide (2.24g, 0.04mol) in water (10ml) was added by stirring. The resulting mixture was refluxed. Then, *n*-octyl bromide (4.13g, 0.0214mol) was added dropwise. After the addition was completed, the mixture was further refluxed for 23 hrs. An additional amount of potassium hydroxide (0.25g) in water (2.5ml) was added and the mixture was heated under reflux for a further 2 hrs. Then, the mixture was cooled and poured into the cold 3N hydrochloric acid (ca. 500ml) while stirring. The precipitated product (white solid) was filtered and washed with water several times. Recrystallization of the crude product from methanol gave pure 4-*n*-octyloxy-3-methoxybenzoic acid as white crystalline needles. The yield was 3.64g (65%).

Cholesteryl 4-*n*-alkoxy-3-methoxybenzoate (II) was prepared by the same esterification method as that for the 4-(4′-alkoxy-3′-methoxybenzoyl)-oxybenzoic acids.[4] The acids (I) were converted to the corresponding acid chlorides with thionyl chloride. The reaction of acid chlorides with cholesterol gave the esters (II). The following example is representative.

The mixture of 4-*n*-octyloxy-3-methoxybenzoic acid (0.523g, 1.87mmol) and thionyl chloride (2ml) was heated under reflux for ca. 3 hrs while stirring. The excess of thionyl chloride was then removed by distillation. The residual acid chloride was diluted with dry pyridine (5ml). The resulting solution was added slowly to a solution of cholesterol (0.796g, 2.06mmol) in dry pyridine (5ml) at 0°C by stirring. The reaction mixture was stirred overnight at room temperature. Then the mixture was poured into cold 3N hydrochloric acid (200ml). The product was extracted with ether. The ether extract was washed with water several times and dried over anhydrous sodium sulfate. The ether was evaporated under reduced pressure and the residue was dissolved in a minimum amount of *n*-hexane. This was chromatographed on a column of silica gel, eluting with *n*-hexane/ether (98:2, v:v). The ester thus obtained was recrystallized several times from hexane. The yield was 0.449g (60%).

For example, the analytical data for cholesteryl 4-*n*-octyloxy-3-methoxybenzoate obtained by IR and ^{1}H NMR spectroscopy are as follows.

IR (KBr) ν_{max} 1710(ester C═O), 1270(C—O)cm^{-1}; ^{1}H NMR (CD$_3$Cl) δ 0.70(s, 3H, —CH$_3$), 0.87(d, J5.4Hz, 6H, —(CH$_3$)$_2$), 0.93(d, J5.4Hz, 3H, —CH$_3$), 1.08(s, 3H, —CH$_3$), 1.14 – 2.67(m, 40H, —CH$_2$— and —$\underset{|}{\mathrm{C}}$H—), 3.91(s, 3h, —OCH$_3$), 4.06(t, J6.6Hz, 2H, —OCH$_2$—), 4.78(m, 1H, —O$\underset{|}{\mathrm{C}}$H—), 5.42(m, 1H, —CH = $\underset{|}{\mathrm{C}}$—), 6.85(d, J8.2Hz, 1H, Ar), 7.52(d, J1.9Hz, 1H, Ar), 7.65(dd, J1.9 and 8.2Hz, 1H, Ar)ppm.

The purity of the product was checked by thin-layer chromatography and elementary analysis. Anal. Calcd for $C_{43}H_{68}O_4$ (cholesteryl 4-*n*-octyloxy-3-methoxybenzoate): C, 79.58; H, 10.56. Found: C, 79.98; H, 10.24

Differential scanning calorimetry

Thermal analysis was carried out using a differential scanning calorimeter (DSC), Perkin-Elmer Model II, equipped with a low temperature cell. The sample weight was about 4mg. Temperature was varied from 240 to 430K. The transition temperatures measured with DSC were calibrated using a melting temperature (429.8K) of indium metal as the standard. The scanning rate was 10K/min.

Polarizing microscopy

Microscopic observation was made using a polarizing microscope, Leitz model Orthoplan-Pol, equipped with a rotating stage. Each specimen was heated on a heating block mounted on the rotating stage. A colour plate (450 μm) was used as a test plate to determine interference colours. The temperature of the heating block was controlled using a thermo-regulator, Shimaden Model DSM-0210P, the accuracy of which was within ±0.1K.

X-ray diffractometry

X-ray diffractometry was carried out using a Rigaku Denki Co. x-ray diffractometer Geigerflex 2028. X-ray diffraction patterns were recorded with a scintillation counter using CuKα radiation operated at 35 KV and 20 mA.

RESULTS AND DISCUSSION

The yields of the esters based on 4-*n*-alkoxy-3-methoxybenzoic acids are shown in Table I. Because of the formation of by-products, the yields were moderate (mainly 50–60%). Through observation by x-ray diffractometry and polarizing microscopy, the cholesteryl esters grown in solution were found to be crystals.

Figure 1 shows DSC curves of cholesteryl 4-*n*-propoxy-3-methoxybenzoate over a temperature range of 240K to 465K. As the temperature increased, the DSC curve of the sample recrystallized from the *n*-hexane solution exhibited two endothermic transitions (Run 1). A rather large peak can been seen at about 415K and a small peak at 453K. In the cooling curve (Run 2) two exothermic peaks can be seen at 452 and 367K. Re-heating (Run 3) gave the same pattern of DSC curve as that of Run 1.

When the sample recrystallized from the hexane solution was heated under a polarizing microscope, the crystal melted at around 415K. At a temperature from 415K to 450K, a fan-shape texture was observed. By a comparison of obtained micrographs with those previously reported,[12] the mesophase represented by the above texture was attributed to the cholesteric-nematic (N_{Ch}) phase. Therefore, the

TABLE I

The yields of synthesized choleteryl esters

Cholesteryl ester	Carbon number	Alkoxyl group	Yield (%)
II	1	CH_3O—	58
	2	C_2H_5O—	63
	3	n—C_3H_7O—	64
	4	n—C_4H_9O—	61
	5	n—$C_5H_{11}O$—	65
	6	n—$C_6H_{13}O$—	59
	7	n—$C_7H_{15}O$—	61
	8	n—$C_8H_{17}O$—	60
	9	n—$C_9H_{19}O$—	65
	10	n—$C_{10}H_{21}O$—	58
	11	n—$C_{11}H_{23}O$—	70
	12	n—$C_{12}H_{25}O$—	55
	13	n—$C_{13}H_{27}O$—	59
	14	n—$C_{14}H_{29}O$—	60
	15	n—$C_{15}H_{31}O$—	55
	16	n—$C_{16}H_{33}O$—	61
	17	n—$C_{17}H_{35}O$—	58
	18	n—$C_{18}H_{37}O$—	57

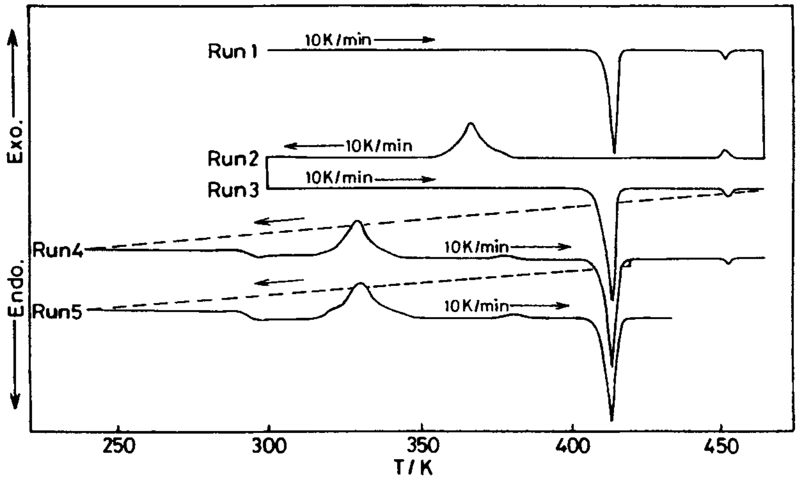


FIGURE 1 DSC curves of cholesteryl 4-*n*-propoxy-3-methoxybenzoate.

main peak in Runs 1 and 2 is attributed to the crystal-N_{Ch} phase transition. The small peak at 453K represents the N_{Ch}-isotropic liquid phase transition. Run 4 shows the heating curve of the sample, which was quenched from the isotropic liquid state to 240K. At 290K, an endothermic jump in the curve was observed. Two exothermic peaks appeared at 330K and 378K before the endothermic crystal-N_{Ch} phase transition peak at 414K.

Usually, the formation of the glassy state is achieved by the rapid cooling of the sample from the liquid state.[13] Therefore, the anomaly at 290K seems to be caused by a glass transition. It is known that an enthalpy relaxation can be observed among glassy samples.[14] The relaxation takes place when the glassy sample is annealed at a temperature below the glass transition temperatures or slowly cooled from the liquid state. In order to confirm the glass transition clearly, the quenched sample was annealed at a temperature below the inflection point (285K for 25min).

Figure 2 shows the heating curve of the quenched and the annealed samples over a temperature range from 280 to 310K. In the annealed sample, a small endotherm, as well as the endothermic jump, was newly observed (Run 6). This endotherm suggests that an enthalpy relaxation took place during the annealing. Consequently it is considered that, with cholesteryl esters, the liquid crystalline state is transformed to the glassy state on cooling. This consideration is also supported by the fact that the temperature of the inflection point increased with the increase of the heating rate. Thus, the DSC pattern of Run 4 of Figure 1 indicates that the sample form the glassy state

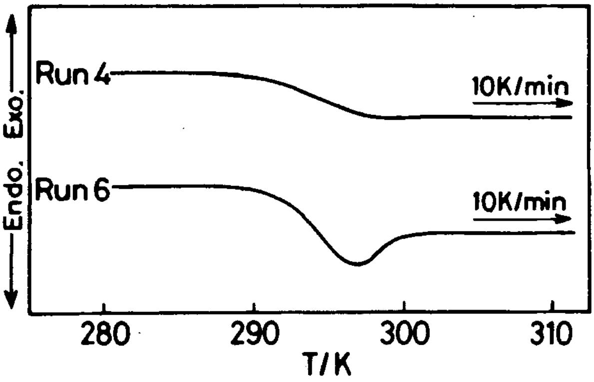


FIGURE 2 DSC curves of cholesteryl 4-*n*-propoxy-3-methoxybenzoate at around glass transition temperature.

by quenching. The X-ray diffraction of the quenched sample showed the typical halo pattern. This phenomenon also indicated the formation of the glassy state. The glassy state of the liquid crystal was first found among cholesteryl hydrogen phthalate (CHP),[14] and after that, found for nematic[15] and smectic liquid crystals.[16] The above fact suggests that the samples synthesized in this experiment can be classified as glassy liquid crystals. Run 5 in Figure 1 shows the heating curve of the sample which was cooled rapidly to 240K from the cholesteric phase (420K). In this case, also, an endothermic jump was observed at around 290K. This suggests that this sample easily forms the glassy state, whether it is in the isotropic or liquid crystalline state before quenching. A similar situation was found in certain other homologues.

Figure 3 shows the DSC curve of cholesteryl 4-*n*-decyloxy-3-methoxybenzoate over a temperature range from 240K to 440K. On heating, the curve of a solution-grown sample (Run 1) showed three endothermic transitions. The pattern of the curve suggests the existence of two kinds of mesophases. In order to identify the kind of mesophase, microscopic observation was carried out. Over a temperature region from 380K to 400K, a number of small, clear fan-shapes were observed, surrounded by homeotropic areas which appeared as a dark background. By a comparison of obtained micrographs with those previously reported, it was found that the texture was the same as that of the smectic A phase in cholesteryl myristate.[17]

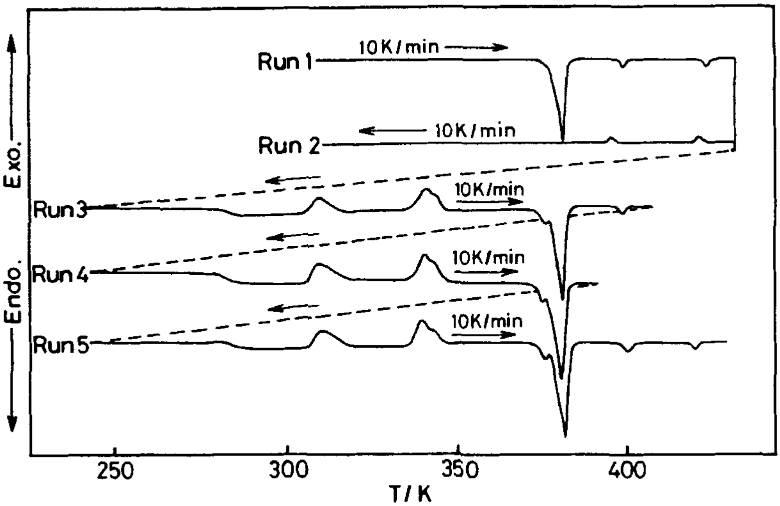


FIGURE 3 DSC curves of cholesteryl 4-*n*-decyloxy-3-methoxybenzoate.

Then, these small fan-shapes turned suddenly into large fan-shapes at 400K, and the background area vanished and merged into the fan-texture, which was at the same phase as already described in the former section. These observations suggest that the largest endothermic peak at 380K can be attributed to the crystal-smectic A (S_A) phase transition, while the other relatively small peaks at 400K and 424K can be attributed to S_A-N_{Ch} and N_{Ch}-isotropic liquid phase transitions, respectively. On cooling (Run 2), two small exothermic transitions, corresponding to two small endotherms on heating, were observed at 422K and 396K. However, no other thermal anomaly was observed above 300K. On microscopic analysis, it was supposed that, on cooling, the liquid crystalline state was super-cooled and was finally transformed into a glassy state without crystallization. Run 3 in Figure 3 is the heating DSC curve of the sample which was cooled rapidly from the isotropic liquid to 240K. At 279K, a glass transition was observed as in the case of the *n*-propoxy homologue, and two exothermic peaks appeared at 310K and 340K. By means of microscopy, the quenched sample was seen to be dark under a crossed polarizer at a temperature below 310K, and a crystalline texture gradually appeared at 310K. On this account, the exothermic peak is attributed to cold-crystallization. The exothermic peak at 340K is supposed to be pre-melt crystallization, although no significant change was observed under microscopy. Runs 4 and 5 in Figure 3 are the heating curves of samples which cooled rapidly to 240K from the N_{Ch} and S_A phases, respectively. The patterns of both curves are similar to that of Run 3. An endothermic jump at around 280K was observed in both cases.

Figure 4 shows the stacked DSC heating curves of the solution-grown samples of the cholesteryl esters. Figure 5 also shows the stacked cooling curves of the samples cooled from the isotropic liquid state. Each of the homologues from cholesteryl 3,4-dimethoxybenzoate ($n = 1$) to cholesteryl 4-*n*-hexyloxy-3-methoxybenzoate ($n = 6$) displays a N_{Ch} phase as mentioned previously in the case of the ester ($n = 3$), while the homologues-(from $n = 7$ to $n = 15$) show S_A and N_{Ch} mesophases.

The transition temperatures of samples quenched from the isotropic liquid state are listed in Table II. The glass transition, cold-crystallization and pre-melt crystallization temperatures were observed.

The plot of transition temperatures of the samples quenched from the isotropic liquid state versus the number of carbon atoms in the *n*-alkoxyl group is shown in Figure 6. The transition temperatures of the crystalline-N_{Ch} and the crystalline-S_A transitions decreased as the

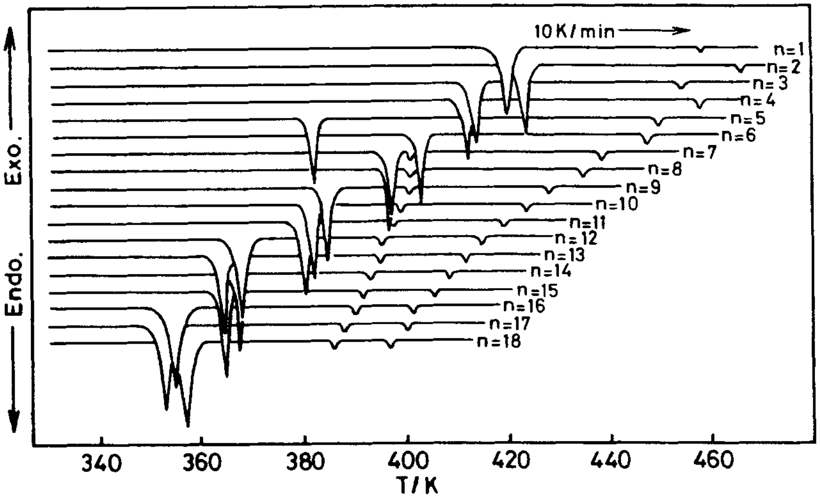


FIGURE 4 Stacked DSC heating curves of solution-grown samples.

chain length increased, although they did not give a smooth curve as did other transition temperatures. The transition temperatures of the S_A-N_{Ch} transition were almost the same for the first three homologues ($n=7$, 8, 9); they then decreased gradually. The smectic range increased with the increasing length of the alkoxyl chain. An odd-even effect of the N_{Ch}-isotropic transition temperatures was clearly ob-

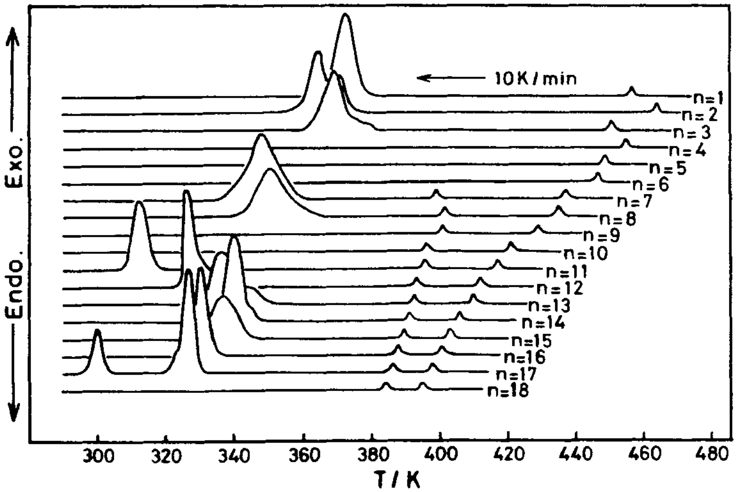


FIGURE 5 Stacked DSC cooling curves of samples from the isotropic liquid state.

TABLE II

Transition temperatures of samples quenched from the isotropic liquid state

Carbon number	Alkoxyl group	Tg	Transition Temperature (K)			
			T_{CC}	$T_{C\text{-}N_{Ch}}(S_A)$	T_{S_A}-N_{Ch}	$T_{N_{Ch}}$-I
1	CH_3O—	306	332	420.5	—	459
2	C_2H_5O—	299.5	327	423.5	—	467
3	n—C_3H_7O—	290.5	330.5	414	—	453.5
4	n—C_4H_9O—	288	336.5	409	—	455.5
5	n—$C_5H_{11}O$—	284.5	338.5	397	—	450.5
6	n—$C_6H_{13}O$—	280.5	335	399	—	447.5
7	n—$C_7H_{15}O$—	280	325.5	396.5	401	438.5
8	n—$C_8H_{17}O$—	279.5	324.5	395.5	401	434.5
9	n—$C_9H_{19}O$—	280.5	327	383.5	400.5	428.5
10	n—$C_{10}H_{21}O$—	279.5	311	380.5	398.5	424.5
11	n—$C_{11}H_{23}O$—	281	298	379.5	398.5	420
12	n—$C_{12}H_{25}O$—	—	—	360.5	397	416
13	n—$C_{13}H_{27}O$—	—	—	366.5	395.5	413
14	n—$C_{14}H_{29}O$—	—	—	368	394	409
15	n—$C_{15}H_{31}O$—	—	—	364.5	392	406
16	n—$C_{16}H_{33}O$—	—	—	356.5	390.5	403
17	n—$C_{17}H_{35}O$—	—	—	356.5	389	400.5
18	n—$C_{18}H_{37}O$—	278.5	315 326.5	358.5	386.5	397.5

*Tg: Glass Transition Temperature

T_{CC}: Cold Crystalization Temperature

$T_{C\text{-}N_{Ch}(S_A)}$: Transition Temperature from Crystal to Cholesteric-nematic (Smectic A) Phase

$T_{S_A\text{-}N_{Ch}}$: Transition Temperature from Smectic A to Cholesteric-nematic Phase

$T_{N_{Ch}\text{-}I}$: Transition Temperature from Cholesteric-nematic Phase to Isotropic Liquid

served for the homologues with short alkoxyl chains, and thereafter the temperature decreased smoothly as the chain length increased. Such odd-even alternation for the N_{Ch}-isotropic transition was also found in homologous series of other cholesterol derivatives.[18]

Dave *et al.* synthesized a homologous series of cholesteryl *p*-n-alkoxybenzoate and studied its mesomorphic properties.[19] In the series, the first six members show only the cholesteric phase and the higher members from cholesteryl *p*-n-heptyloxybenzoate exhibit the smectic and cholesteric-nematic mesophases. The smectic mesophase region increases with the increase of the alkoxyl chain length. These results are almost the same as ours except for the transition temperatures. Each of the homologous series of cholesteryl 4-*n*-alkoxy-3-methoxybenzoate has lower transition temperatures than those of the

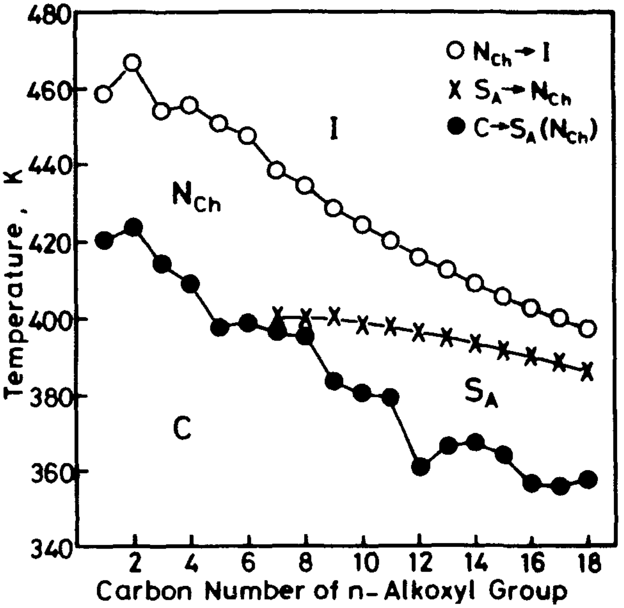


FIGURE 6 Relationships between transition temperatures and carbon number of *n*-alkoxyl chain of samples quenched from the isotropic liquid state. C: Crystalline phase, N_{Ch}: Cholesteric-nematic phase, S_A: Smectic A phase, I: Isotropic liquid.

corresponding non-3-methoxy substituted benzoate ester. This phenomenon is attributed to the effect of the lateral substituent of the aromatic ring of mesogenic compounds which has been studied systematically in certain types of compounds.[20] The lateral substituents usually have two opposing effects on the thermal stability of the mesophase. One is the stabilizing effect by increasing the molecular polarizability. The other is the destabilizing effect by increasing the breadth of the molecule. The second of these effects normally predominates.[20] In the case of the methoxyl group, although there are few examples, it can be expected that the group decreases the thermal stability significantly because of its relatively large size compared with other substituents, i.e., the halogen, methyl, nitro groups, etc. Actually we found that 3-methoxy derivatives of 4-*n*-alkoxybenzoic acid showed no liquid crystalline properties[8] although 3-fuluoro derivatives did.[21] For cholesteryl derivatives, the effect of the lateral substituents was also studied by Dave *et al.*[22] They synthesized different cholesteryl benzoate derivatives having substituents in ortho-, metha-, and para-positions of the phenyl ring and investigated their mesomorphic properties. As a result, it was found that the substitution in the ortho- and the metha-positions in cholesteryl benzoates reduced the thermal stability of the compounds. Therefore our results agree well with those of Dave *et al.*

By comparing the transition temperatures of cholesteryl 4-*n*-alkoxy-3-methoxybenzoates with those of the analogues non-3-methoxy substituted ones, it was found that the decrease of the N_{Ch}-isotropic transition temperature by the introduction of the methoxyl group on the 3-position of the phenyl ring became smaller with the increase of the chain length of the *n*-alkoxyl group($n=1$, 82.5K; $n=7$, 56.5K; $n=16$, 50K). The effect of the lateral methoxyl group was more significant on the esters having a shorter *n*-alkoxyl chain. However, the existence of the 3-methoxyl group did not change the kinds of mesophase. In both series of the compounds, the first six members showed only one mesophase (N_{Ch}) and the others showed S and N_{Ch} phases.

As listed in Table II, in each of the homologues except for esters from $n=12$ to $n=17$, the glass transition was observed. The glass transition temperature gradually decreased from cholesteryl 3,4-dimethoxybenzoate ($n=1$) to cholesteryl 4-*n*-hexyloxy-3-methoxybenzoate ($n=6$) with the increase of the carbon number of the *n*-alkoxyl group. However, it was almost constant for the esters having carbon numbers above 6. No effect of the chain length of *n*-alkoxyl group on the glass transition temperature was observed. As previously mentioned, the esters ($n>6$) showed two kinds of mesophase, S_A and N_{Ch} phases. However, the others showed only one N_{Ch} phase. Therefore, the effect of the chain length on the glass transition temperature was found only when the ester had the N_{Ch} phase. This indicated that the kind of mesophase affected the formation of glassy state of the ester.

From the above results, it is concluded that the homologous series of cholesteryl 4-*n*-alkoxy-3-methoxybenzoates, which were newly synthesized in this study, showed liquid crystalline properties. Temperatures of the first-order phase transitions were decreased by the methoxyl group introduced into the aromatic ring and also by the length of the paraffinic chain. At the same time, it was found that the ester formed the glassy state by quenching from mesophases and/or the isotropic liquid phase. By contrast to the melting and/or liquid crystal transitions, the temperature of glass transition was constant, when the ester showed the smectic phase, suggesting the effect of the kind of mesophases on the formation of liquid crystal glass.

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