Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Phase Behavior of Novel Liquid-Crystalline Salts Containing a Cholesteryl Group

N. Kimura [a] , N. Takeshima [a] , Y. Nishio [a] & H. Suzuki [a]

[a] Department of BioEngineering, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata, 940-21, Japan

Version of record first published: 24 Sep 2006.

To cite this article: N. Kimura , N. Takeshima , Y. Nishio & H. Suzuki (1996): Phase Behavior of Novel Liquid-Crystalline Salts Containing a Cholesteryl Group, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 287:1, 35-45

To link to this article: http://dx.doi.org/10.1080/10587259608038741

Mol. Cryst. Liq. Cryst., 1996, Vol. 287, pp. 35–45
Reprints available directly from the publisher
Photocopying permitted by license only

Phase Behavior of Novel Liquid-Crystalline Salts Containing a Cholesteryl Group

N. KIMURA, N. TAKESHIMA, Y. NISHIO and H. SUZUKI

Department of BioEngineering, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-21, Japan

(Received September 25, 1995; in final form December 12, 1995)

The phase behavior of liquid-crystalline salts having a cholesteryl group was investigated by differential scanning calorimetry and polarized-light microscopy. Cholesteryl hydrogen succinate (CHS) and cholesteryl hydrogen phthalate (CHP) were used as a mesogenic core, and a series of normal aliphatic amines with $12 \sim 18$ carbons were used as a flexible tail. The salts were prepared as a stoichiometric 1:1 complex of a cholesterol derivative and an amine from mixed solutions in ethanol by solvent evaporation. CHS exhibited a monotropic cholesteric phase, while the salts of CHS with amines showed a mesophase in both cooling and heating cycles and it was frozen into a glassy state at temperatures below 0°C without changing the anisotropic organization. A similar state of glassy liquid crystal was noted for CHP *per se* and its salts with amines. The temperature range where a fluid liquid-crystalline phase appeared was mostly wider in the salt systems, when compared with the cases using the cholesterol derivatives alone. An odd-even oscillation phenomenon was perceived in the dependence of the mesophase-isotropic transition temperature and enthalpy of the salts on the carbon number of the amine component.

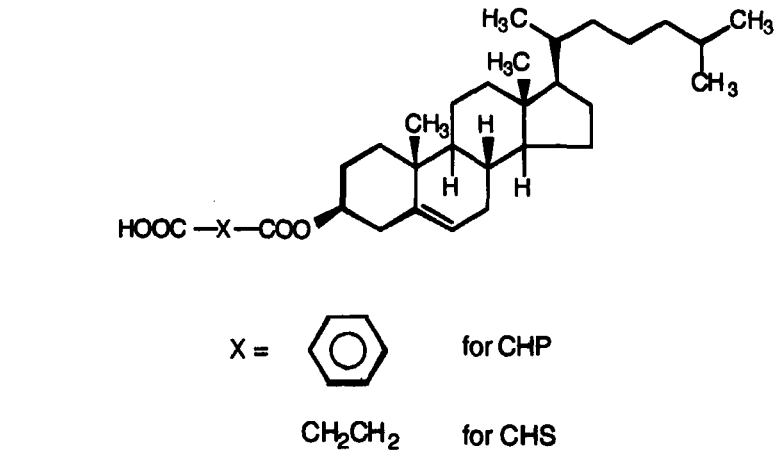
Keywords: Cholesterol derivative, aliphatic amine, complex salt, phase behavior, glassy liquid crystal.

1. INTRODUCTION

Recently, much attention has been focused on the liquid crystal formation via molecular assemblies among different chemical compounds. For instance, it has been reported that the electrostatic interaction between cationic and anionic molecules,[1,2] or the hydrogen bonding between proton donating and accepting molecules,[3,4] can stabilize mesophases. In these binary systems, the thermal properties such as phase-transition temperatures, and a temperature range of mesophase formation can be easily controlled by varying the species of constituent molecules, instead of complicated chemical reactions to design liquid-crystalline materials.

The present paper is concerned with the phase behavior of liquid-crystalline salts formed via ionic interaction between aliphatic amines and monocholesterylesters of dicarboxylic acids. Although aliphatic amines have often been utilized as flexible tails in several salt systems showing liquid crystallinity,[1,2] there has been no attempt to adopt them for the complexation with ionic steroids acting as a mesogenic core. In this work, we used cholesteryl hydrogen phthalate (CHP) and cholesteryl hydrogen succinate

(CHS) as cholesterol derivative samples, both having a functional carboxylic group at their terminal end, as formulated below:



In-particular, CHP is the first low-molecular-weight compound that was reported explicitly to form a stable "glassy liquid crystal"[5]; however, the complete scheme of phase transition does not still seem to be established. In this present study, first the thermal behavior of CHP is described in detail in comparison with that of CHS, and then our major insight is provided into the formation and stability of glassy mesophases in the salt systems of CHP and CHS with normal aliphatic amines having 12–18 carbons. The dependence of transition parameters (temperature and enthalpy) on the carbon number of the amines is discussed.

2. EXPERIMENTAL SECTION

2.1. Materials

CHP and CHS were purchased from Tokyo Kasei Kogyo Co. and purified by recrystallization from ethanol. It was ascertained that the recrystallized cholesterylesters gave almost the same data of melting as described in earlier literature.[6,7] Normal aliphatic amines, $C_nH_{2n+1}NH_2$ ($n = 12$ to 18, hereafter abbreviated as C_n-amine), were also purchased from Tokyo Kasei Kogyo Co. and employed without further purification.

2.2. Instrumentation

Differential scanning calorimetry (DSC) measurements were performed on a Seiko Instrument DSC 210 equipped with a SSC 5020 control system. Thermograms were measured at a heating and cooling rate of 20 °C min^{-1}. The temperature reading was calibrated with an indium standard.

Fourier transform infra-red (FT-IR) spectra were recorded on a Shimazu FT-IR 8100M combined with a diffuse reflectance instrument (DRS-8000).

Polarized optical microscopy was conducted with an Olympus BHS-751P microscope equipped with a Mettler FP82 hot-stage. Samples were usually sandwiched between a slide and cover glass.

2.3. Preparation of Salts of Cholesterol Derivatives with Amines

Each component was dissolved in ethanol at 1 wt% by stirring at room temperature (~ 25 °C), and two different solutions were then mixed to yield equimolar amounts of cholesterylester and amine. Cholesterylester/amine salts were obtained as a laminate product on a glass tray, each cast from the corresponding mixed solution by solvent evaporation at 25 °C.

3. RESULTS AND DISCUSSION

3.1. Phase Behavior of CHP

Selected DSC thermograms of CHP are compiled in Figure 1. On heating the sample (K_I) crystallized from ethanol solution, it melted solely into an isotropic liquid at 167 °C without giving any indication of mesophase formation. On cooling the CHP melt, however, an explicit transition of the isotropic phase (I) into a mesophase (M) took place at 87 °C. When the corresponding cooling process was monitored with a polarizing microscope, the development of a Grandjean plane texture was observed at ca. 90 °C, following transient appearance of a focal conic texture. Thus the CHP mesophase may be assigned as a cholesteric type. Upon continued cooling the mesomor-

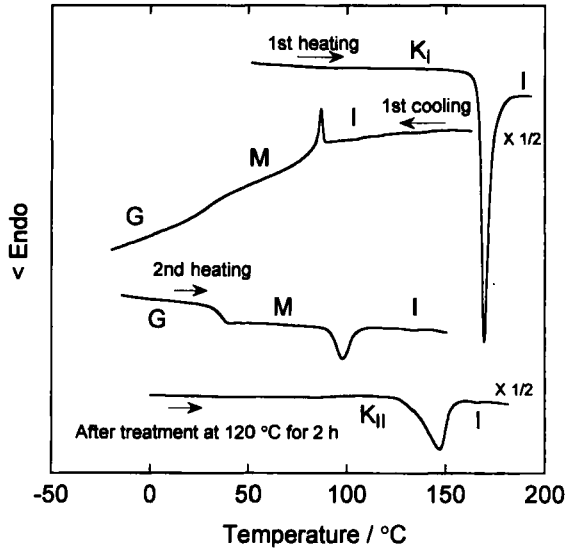
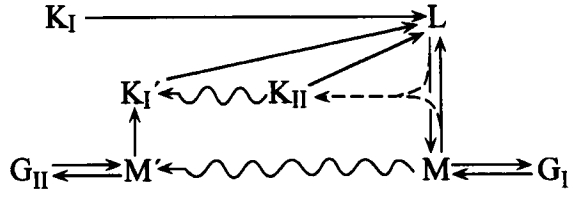


FIGURE 1 DSC thermograms of CHP. The heating and cooling rates are 20°C min^{-1}.

phic CHP, it was transformed into a glassy state (G_I) at ca. 30 °C without crystallizing nor losing its anisotropic texture, implying that a "glassy liquid crystal" was realized. In the second heating scan, the ordered glass changed into the cholesteric mesophase with fluidity at 31.6 °C and eventually into isotropic liquid at 91.4 °C. These temperatures are, respectively, taken as the glass transition temperature (T_g) and the mesophase-isotropic phase transition temperature (T_{MI}) of CHP. Additional cooling and heating cycles were sometimes carried out and the response of the DSC traces was essentially reproducible after the first heating scan. Accordingly, it can be said that CHP shows an "enantiotropic" behavior concerning the thermotropic mesophase formation, once the as-prepared crystal is melted. This behavior is diagrammed as "L⇌M⇌G_I" in Scheme 1. Formerly, Barrall II *et al.*[6] reported that CHP exhibited two liquid-crystalline states, a smectic phase as well as a cholesteric phase, in a cooling process from the isotropic melt, while Tsuji *et al.*[5] perceived the formation of only one liquid-crystalline phase for this compound. The latter result may be supported by the present investigation with high-sensitive calorimetry, combined with careful optical observations.

If CHP is subjected to some mechanical or annealing treatment via the mesophase state (M), different routes of phase transition become open, as is summarized in Scheme 1. Annealing CHP at 105–125 °C immediately after the mesophase-isotropic transition, a crystalline phase (K_{II}) was induced. The melting point of the organized crystal ranged usually from 135 to 145 °C (see example in Fig. 1). For many other compounds[8] capable of forming a glassy liquid crystal, the state being accomplished mostly by rapid quenching of a fluid mesophase, it is very familiar to observe a transformation of the mesophase into a crystal after the onset of the glass transition on heating. Contrary to those cases, the thermally-induced crystallization of CHP obeyed kinetics so slowly that an appreciable exothermic signal hardly emerged at any temperature lower or higher than the mesophase-isotropic transition temperature (~ 92 °C), in the present DSC measurements conducted at a rate of 20 °C min^{-1}.

In the case where the CHP mesophase (M) was sheared strongly at ca. 50–80 °C between glass plates and cooled quickly below room temperature, it was transformed into a glassy solid (G_{II}) with an oriented nematic-like structure. On continuously heating the oriented glass in a DSC scan, a clear crystallization exotherm was observed with the peak maximum at ~ 115 °C, after passing through a glass (G_{II})-mesophase (M') transition at ~ 30 °C. The crystal (K_I') thus generated, ultimately melted into an isotropic liquid at ca. 160 °C, this temperature being rather close to the melting point of the solution-grown CHP crystal (K_I). The crystalline allomorph K_I' was also obtain-



SCHEME 1 Phase transitions of CHP: ---→, annealing treatment; →, mechanical treatment; →, usual thermal treatment.

able through mechanical grinding of the crystal K_{II} induced by prolonged heat-treatment at 105–125 °C.

3.2. Phase Behavior of CHS

DSC thermograms and a scheme of phase transition of CHS are shown in Figure 2 and Scheme 2, respectively. This cholesterylester exhibited a typical "monotropic" liquid-crystalline behavior. The original sample melted at 173 °C into isotropic liquid. On cooling from the isotropic state, a mesophase appeared in quite a narrow temperature range of 155–146 °C, accompained by a Grandjean plane texture under a polarizing microscope. Further cooling resulted in complete crystallization from the mesophase; no glassy state was realized in contrast with CHP. Additional heating and cooling scans monitored substantially the same transition behavior as stated above.

3.3. Phase Behavior of Amines

All the aliphatic amines used in this study showed no liquid crystallinity, and only a crystal-isotropic liquid phase transition was possible in a temperature range of 30–55 °C (estimated on heating).

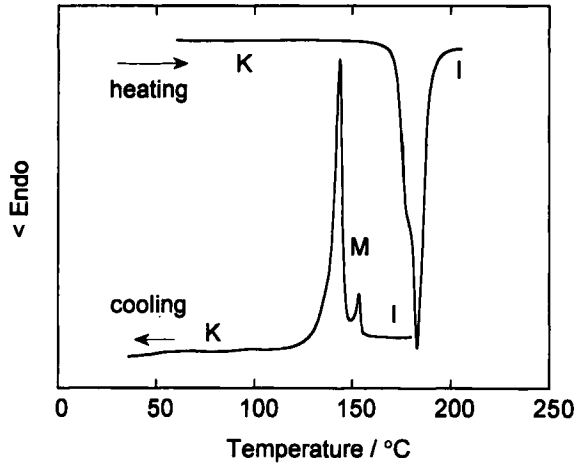
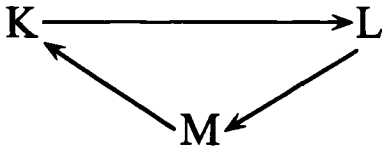


FIGURE 2 DSC thermograms of CHS obtained at a scaning rate of 20 °C min^{-1}.



SCHEME 2 Phase transitions of CHS.

3.4. Salt Formation and Phase Behavior of Amine/Cholesterylester Mixtures

In Figure 3, FT-IR spectra of an equimolar mixture of CHS and C_{18}-amine cast from ethanol solution are displayed in an enlarged scale for two specific frequency regions and compared with the corresponding data for the two constituent species. Complete formation of a salt in the mixture is evidenced by the disappearance of an N–H stretching band at 3333 cm^{-1} and a C=O stretching band at 1711 cm^{-1}, i.e., by the absence of isolated amine and acid carbonyl group. A similar spectral change was confirmed for other combinations of the cholesterylesters and aliphatic amines used in this study. The salt formation followed an exact stoichiometric relationship of 1:1 complexation between the two species; because one of the two specific IR signals mentioned above remained at a prolate fraction in the case where samples were prepared at non-equimolar mixing ratios. At elevated temperatures above 190 °C, however, all the salts prepared were liable to undergo chemical reactions such as dehydration between carboxyl groups and amide formation between a carboxyl and an amino group. Through FT-IR measurements for a few selected salts heat-treated at various temperatures for 10 min, it was ascertained that the salts of CHS with amines were chemically stable up to 160 °C while 140 °C was a critical temperature for the amine/CHP series. Thus the phase behavior of the two series of salts was examined, keeping the temperature below the critical values specified above.

Transition parameters evaluated for the C_n-amine/CHS and C_n-amine/CHP salt systems by DSC measurements are listed in Table 1, each almost reproducible data determined after the first heating. All the salts showed no transition signal originating from the constituent amine and cholesterylester themselves. Instead, a single glass transition and a mesophase (M)-isotropic (I) phase transition were clearly observed. A typical example of DSC thermograms is shown in Figure 4; the data were obtained

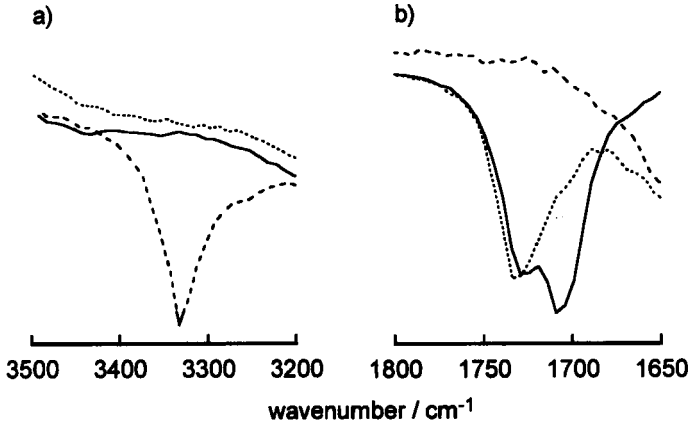


FIGURE 3 FT-IR spectra of CHS, C_{18}-amine, and a salt of C_{18}-amine/CHS, depicted in an enlarged scale for two frequency regions: a) N–H stretching region and b) C=O stretching region. —, CHS; – – –, C_{18}-amine, ..., C_{18}-amine/CHS.

TABLE I
Transition parameters for C_n-amine/Cholesterol derivative systems, determined by DSC measurements

n	T_g[a)]°C	T_{MI}[a)]°C	ΔH_{MI}[b)] kJ mol^{-1}
		CHS (cooling)	
–	–	155.2	2.3
		C_n-Amine/CHS (2nd heating)	
12	−3.9	97.6	2.7
13	4.7	96.2	4.6
14	1.0	109.3	5.2
15	−0.7	109.0	4.1
16	11.7	118.7	6.1
17	−4.7	98.8	4.8
18	3.7	121.2	7.0
		CHP (2nd heating)	
–	31.6	91.4	3.3
		C_n-Amine/CHP (2nd heating)	
12	17.7	79.5	3.7
13	27.3	78.0	3.8
14	25.0	87.1	8.2
15	23.6	90.3	7.0
16	24.0	95.3	10.4
17	12.7	88.6	6.8
18	19.1	89.0	9.9

[a] Estimated as the onset point of each transitional signal in DSC curves.
[b] Calculated per unit molar salt from the area of an endothermic peak.

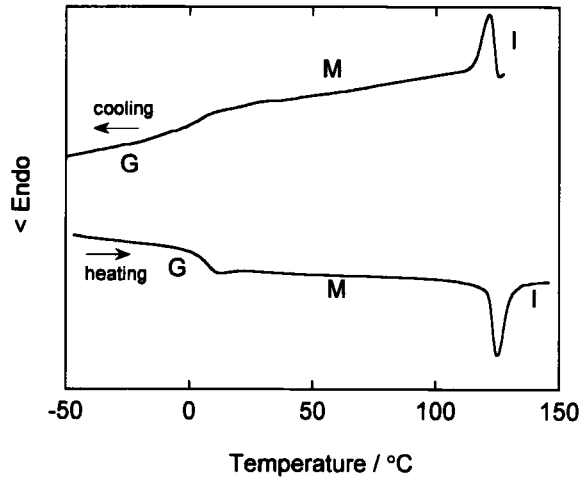


FIGURE 4 DSC thermograms of a C_{18}-amine/CHS salt sample, obtained after the first heating scan.

for a C_{18}-amine/CHS salt in the first cooling and subsequent heating scans. As is apparent here, the amine/CHS system exhibited a mesophase not only on cooling but also on heating, unlike the thermal behavior of CHS alone. Furthermore, the temperature range allowing for the relevant material to be in a liquid-crystalline state became

extraordinarily wide by the salt formation. Such stabilization of the cholesterol-based mesophase was not observed in a case where the amine component was replaced by a normal alcohol (e.g., stearylalcohol) as an aliphatic chain component instead of amines,[9] probably due to lack of an effective interaction of the hydroxyl group with a carboxyl group of the cholesterylester component.

Polarized microscope observations revealed that all the salts examined preferred a molecular arrangement to orient perpendicularly rather than parallel to the surface plane of a slide glass in the liquid-crystalline state. This may be ascribed to the homeotropic character of aliphatic amines serving as a long tail of the complex salts. On cooling to room temperature or lower temperatures, the salt samples solidified into a glassy state with the original liquid-crystalline order preserved therein. Thus, both C_n-amine/CHS and C_n-amine/CHP salts can become a "glassy liquid crystal", though the molecular alignment is different from the planar orientation distribution noted for unmixed CHP.

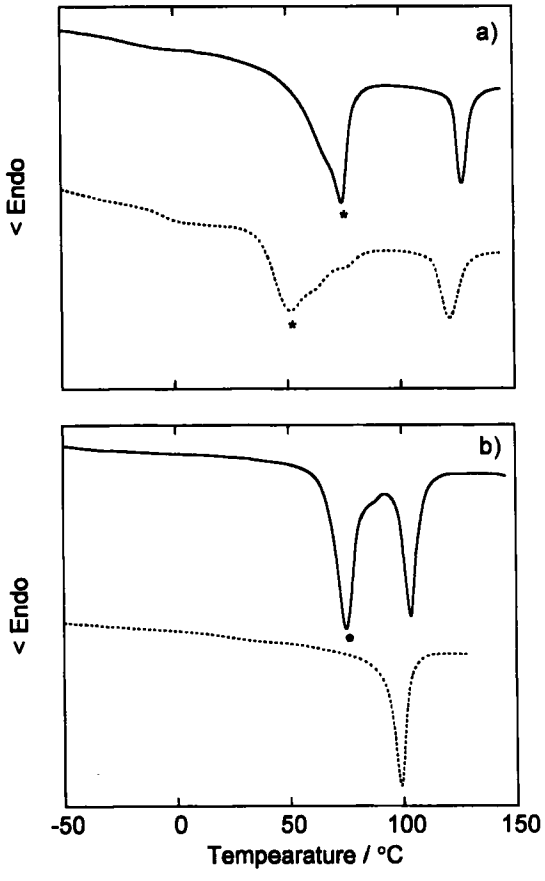


FIGURE 5 DSC thermograms obtained on heating as-cast salts and annealed ones of a) C_{18}-amine/CHS and b) C_{18}-amine/CHP: ——, as-cast samples; – – –, samples annealed for 7 days at 25°C (CHS salt) or at 50°C (CHP salt) after cooling from the isotropic liquid state above 120°C. Endothermic peaks marked by asterisks show a crystal-mesophase transition.

The crystallinity of amine/cholesterylester salts was admitted in some restricted samples: as-cast ones of both C_n-amine/CHS and C_n-amine/CHP series, and C_n-amine/CHS salts annealed at above T_g in the initially uniform, liquid-crystalline state. Figure 5 illustrates DSC thermograms of annealed salts of C_{18}-amine/CHS and C_{18}-amine/CHP in the first heating process, together with data for the corresponding as-cast samples. The annealing treatment was carried out by storing samples over a period of 7 days at 25 °C (for C_{18}-amine/CHS) or at 50 °C (for C_{18}-amine/CHP), each higher than the T_g of the respective salt by 20–30 °C, after cooling from the isotropic molten state above 120 °C. In the DSC data for the as-cast samples of both series, we can see two endothermic peaks. A larger peak located in a lower temperature side ($\sim$ 75 °C) is associated with a crystal-mesophase transition, and the other one refers to a mesophase-isotropic phase transition, both of which were identified by polarized optical microscopy. The crystal-mesophase transition signal appeared again in a DSC scan for annealed samples of C_{18}-amine/CHS, whereas never for annealed C_{18}-amine/CHP salts, as can be seen from the comparison of the two data denoted by broken-line curves in Figure 5. This result demonstrates a general trend that the supercooled mesomorphic state of the salts of CHP with amines was more stable than that of the amine/CHS series. Even in the latter series, however, the crystallization proceeded so slowly that it was hardly detectable in the continuous heating and cooling cycles, as already shown in Figure 4.

Figure 6 shows a construction of plots of the mesophase (M)-isotropic (I) transition parameters, T_{MI} and ΔH_{MI} listed in Table 1, as a function of the carbon number n of the amine component of complex salts. A striking effect of odd-even oscillation can be clearly seen in the ΔH_{MI} versus n plots for both C_n-amine/CHP and C_n-amine/CHS

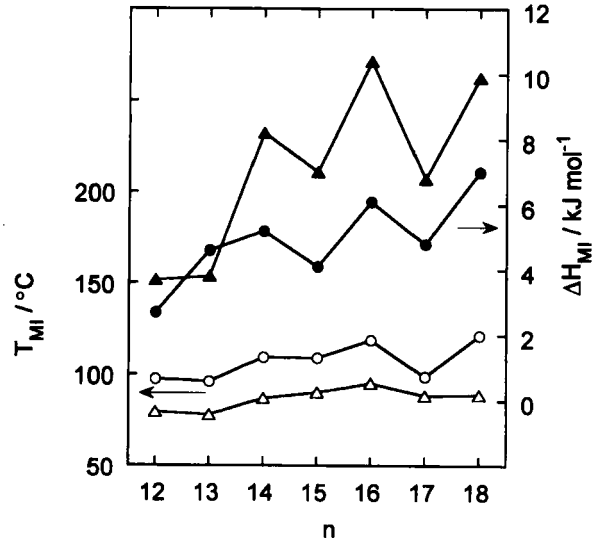


FIGURE 6 Variation of the M-I transition temperature T_{MI} and M-I transition enthalpy ΔH_{MI} as a function of the carbon number n of the aliphatic amine component. Open and filled symbols represent T_{MI} and ΔH_{MI}, respectively: ○ and ●, data for C_n-amine/CHS salts; Δ and ▲, data for C_n-amine/CHP salts.

series. The same effect holds for many liquid-crystalline molecules with a linear alkyl chain dangling at the end of a mesogenic group. Accordingly the above finding further supports the view that the normal aliphatic amines serve as tail rather than as solvent for the cholesterol derivatives CHP and CHS.

An odd-even effect is also perceived in the T_{MI} versus n plots; however, the dependence seems to follow a variation manner of rather subtle oscillation, especially for the C_n-amine/CHP series. A similar dependence was observed for the glass transition temperature (T_g) versus n plots.

Generally, liquid crystals of ionic salts prefer to assume a layered structure such as a smectic type of assembly,[10] due to micro-phase separation between ionic and non-ionic parts of the constituent molecules. For the salts studied in this paper, we have not undertaken an accurate identification of the type of the liquid crystal. For elucidation of the details of the liquid-crystalline structure, another measurement, e.g., X-ray diffraction analysis, will be required. Further investigations of the present systems and related ones are now in progress.

4. CONCLUSIONS

As a consequence of a precursory investigation, schemes of the phase transitions of cholesteryl hydrogen phthalate (CHP) and cholesteryl hydrogen succinate (CHS) were completed successfully. These cholesterylesters complexed normal aliphatic amines (C_n-amines; $n = 12$–18) stoichiometrically, through ionic interaction between carboxylic acid and amino groups. The resulting salts of C_n-amine/CHP and C_n-amine/CHS, each produced at an equimolar ratio, showed a mesophase over an extraordinarily wide temperature range in both heating and cooling processes. The liquid-crystalline characteristics of the complex salts made a striking contrast, especially to that of CHS alone exhibiting a monotropic transition behavior. It was reasonably assumed that the C_n-amine component serves as a flexible tail for the mesogenic steroid cores, also responsible for an observed tendency of homeotropic orientation in the mesomorphic ordered state of the salts. At room temperature or lower temperatures, all the salts examined were transformed into a glassy state with the liquid-crystalline organization preserved therein, as was also the case for CHP *per se*. The anisotropic glassy state was considerably stable, compared with those reported in the literature for many other liquid-crystalline molecules, as was supported by the absence of crystallization in a usual DSC heating scan. Values of the transition parameters, T_{MI}, T_g, and ΔH_{MI}, assessed for the two series of salts varied in an odd-even oscillation manner as a function of the carbon number of the C_n-amine component, particularly clearer in the transition enthalpy versus n plots.

References

1. V. Busico, P. Corradini, and M. Vacatello, *J. Phys. Chem.*, **86**, 1033 (1982); **87**, 1631 (1983).
2. Y. Matsunaga and K. Nishida, *Bull. Chem. Soc. Jpn.*, **61**, 3435 (1988); M. Ito, Y. Matsunaga, H. Matsuzaki, and S. Shimojima, *ibid.*, **62**, 3919 (1989); J. Kawamata, Y. Matsunaga and K. Ohtsu, *Mol. Cryst. Liq. Cryst.*, **257**, 27 (1994).

3. T. Kato, and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **111**, 8533 (1989); U. Kumar, T. Kato, and J. M. J. Fréchet, *ibid.*, **114**, 6630 (1992).
4. H. Kressse, I. Szulzewsky, S. Diele, and R. Paschke, *Mol. Cryst. Liq. Cryst.*, **238**, 13 (1994); H. Kresse, I. Szulzewsky, P. Mandt, and R. Frach, *ibid.*, **257**, 19 (1994).
5. K. Tsuji, M. Sorai and S. Seki, *Bull. Chem. Soc. Jpn.*, **44**, 1452 (1971).
6. E. M. Barrall II, J. S. Porter and J. F. Johnson, *Mol. Cryst. Liq. Cryst.*, **8**, 27 (1969).
7. T. Takahashi, T. Yamane and Y. Nishio, *Kobunshi Ronbunshu*, **41**, 159 (1984).
8. M. Sorai and S. Seki, *Mol. Cryst. Liq. Cryst.*, **23**, 299 (1973); N. Kirov, M. P. Fontanta and N. Affanassieva, *ibid.*, **89**, 193 (1982); S. Takenake and H. Yamasu, *J. Chem. Soc., Faraday. Trans.*, **90**(11), 1537 (1994); H. Shi and S. H. Chen, *Liq. Cryst.*, **18**, 733 (1995).
9. R. Yamazaki, N. Kimura, Y. Nishio and H. Suzuki, unpublished results.
10. S. Ujiie and K. Iimura, *Polym. J.*, **25**, 347 (1993).