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Phase Transition of Cholesteryl Fluoroalkanoates

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Phase transitions were studied by differential scanning calorimetry and polarized microscopy for various cholesteryl fluoroalkanoates; cholesteryl ω-monohydrofluoroalkanoates (CHFA) [$C_{27}H_{45}OCO(CF_2)_nCF_2H$, $n = 1, 3, 5$ and 7] and cholesteryl perfluoroalkanoates (CPFA) [$C_{27}H_{45}OCO(CF_2)_mCF_3$, $m = 1$ and 6]. There were observed one mesophase in $n = 7$ of CHFA and two mesophases in $m = 6$ of CPFA monotropically on cooling, but no mesophase in the other samples. The crystal structures were also determined for a homologous series of CHFA. The crystal form was monoclinic in all samples except of CHFA of $n = 3$, but the lattice constant exhibited a complicated change with increasing length of the ester, n.

INTRODUCTION

In the preceding paper[1] on mesomorphism of cholesteryl halopropionates, we reported that the mesomorphism is governed with the halogen atom substituted in the propionate groups, especially the position of substituent; cholesteryl β-monohalopropionates showed a liquid crystal phase, but the α-monohalopropionates do not. Furthermore, it is of interest that cholesteryl 2,2,3,3-tetrafluoropropionate exhibited no mesophase, because Murza *et al.*[2] observed a monotropic mesophase on cooling in the homologous series of cholesteryl perfluoroalkanoates (CPFA) [$C_{27}H_{45}OOC(CF_2)_mCF_3$, $m = 1$–6], whereas Barrall *et al.*[3] found no mesophase in cholesteryl perfluorobutylate ($m = 2$).

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The purpose of this work is to prepare various cholesteryl fluoroalkanoates and to clarify their mesomorphisms. The cholesteryl derivatives used here are cholesteryl ω-monohydrofluoroalkanoate (CHFA) [$C_{27}H_{45}OOC(CF_2)_nCF_2H$, $n = 1$–7] and CPFA ($m = 1$ and 6).

EXPERIMENTAL

CHFA of $n = 1$ was prepared by a dehydration reaction from cholesterol and 2,2,3,3-tetrafluoropropionic acid in benzene in the same procedure described previously.[1] The other CHFA's ($n = 3, 5, 7$) and CPFA of $m = 6$ were synthesized by a dehydrogenchloride reaction from cholesterol and the corresponding fluoroalkanoyl chloride in chloroform with *N*, *N*-dimethylaniline. The crude samples were purified by several recrystallizations from chloroform–acetone (1 : 3) solution. CPFA of $m = 1$ was synthesized by a dehydration reaction from cholesterol and perfluoropropionic acid in benzene. The crude sample was purified by recrystallizing several times alternately from ligroin and chloroform–acetone (1 : 3) solution.

All samples were identified to be the objectives from IR, NMR and F-NMR for the perfluoroalkanoates, and elementary analysis, and judged to be thoroughly pure by a thin layer chromatograph, DSC, IR, NMR and the elementary analysis. The results of elementary analyses in CHFA and CPFA are as follows: In CHFA, $n = 1$; 9.28%H, 70.11%C (calc. 9.01%H, 70.01%C), $n = 3$; 7.83%H, 62.45%C (calc. 7.54%H, 62.52%C), $n = 5$; 6.68%H, 56.96%C (calc. 6.49%H, 57.14%C), $n = 7$; 5.62%H, 52.79%C (calc. 5.69%H, 53.07%C), and in CPFA, $m = 1$; 8.69%H, 67.63%C (calc. 8.52%H, 67.64%C), $m = 6$; 5.85%H, 53.54%C (calc. 5.79%H, 53.71%C). The single crystals for X-ray studies were grown by a very slow evaporation method from acetone solution.

Phase transitions were measured by a differential scanning calorimeter (Perkin Elmer, DSC IB) calibrated with gallium and indium, and by a polarized light microscope with a hot stage. DSC measurements were carried out at a heating/cooling rate of 10 °C/min in a wide temperature range from −70 °C over the melting point, T_m, as follows; after the crystals was first cooled, the first heating process was run up to the melting point and the other thermal processes were successively done. The crystal structure was determined from X-ray diffraction photographs taken by Weissenberg camera and precession camera with Ni filtered CuKα radiation at 25 °C.

RESULTS AND DISCUSSION

Phase transition parameters obtained are listed in Table I, and DSC charts of several samples are shown in Figure 1. In CHFA, no liquid crystal state is observed for $n = 1$, 3 and 5 on either heating and cooling, and one liquid crystal state is seen only on cooling for $n = 7$. In $n = 3$ and 7, an exothermic peak is observed just below T_m on the more than 2nd heating processes (see DSC curves and c2 in Figure 1). These might be explained by a recrystallization phenomenon just below T_m.[4,5] Since the exothermic peak was not observed on the first heating process from the crystals, the crystals frozen from the melt may be unstable and may produce some recrystallization near the melting point. The $n = 5$ sample shows apparently one crystal transition appearing near −18 °C on the first heating and −52 °C on the first cooling. However, the crystal transition was not distinctly observed on the more than 2nd heating processes in the present DSC work. This means that the crystals frozen from the melt show no distinct crystal transition on the DSC charts, perhaps because of the unstable crystal state.

In phase transitions of CPFA, there are some discrepancies between the present results and the other past reports. In $m = 1$ sample, although Murza *et al.*[2] observed a mesophase between 76 and 79 °C on cooling monotropically, no liquid crystal phase is observed in this work. In cholesteryl perfluorobutylate ($m = 2$), Barrall *et al.*[3] observed no liquid crystal state, but Murza *et al.*[2] found a liquid crystal state at the temperature range of 63 and 66 °C on cooling. These discrepancies may be caused by the impurity of samples, since phase transition is known generally to be very sensitive to the purity of sample.[6,7] Barrall *et al.* describes in their paper that the absence of liquid crystal state in perfluorobutylate ($m = 2$) does not originate in the impurity of their sample. Actually, the interpretation that some impurity prefer to induce a mesophase on cooling seems to be rather reasonable.[7] Cholesteryl perfluorooctanoate ($m = 6$) shows two liquid crystal phases monotropically on cooling, whereas Murza *et al.* observed one mesophase between 86 and 93 °C on cooling. Previously we indicated that the halogen atom substituted at α-position of cholesteryl alkanoate losses the endowments forming liquid crystal state of cholesteryl halopropionate, because of the increase of molecular breadth by the α-halogen atom. The appearances of mesophase in $m = 6$ of CPFA and $n = 7$ of CHFA mean that the contribution of fluoroalkanoate group to the length of molecule prevails over the steric effect of the α-halogen atom.

TABLE I

Phase transition parameters of cholesteryl fluoroalkanoates

Sample		T_t °C	T_m °C	ΔS_t J · K^{-1} · mol^{-1}	ΔS_m J · K^{-1} · mol^{-1}		$T_{I\text{-}L}$ °C	$T_{L\text{-}L}$ °C	T_f °C	T_t °C	$\Delta S_{I\text{-}L}$ J · K^{-1} · mol^{-1}	$\Delta S_{L\text{-}L}$ J · K^{-1} · mol^{-1}	ΔS_f J · K^{-1} · mol^{-1}	ΔS_t J · K^{-1} · mol^{-1}	Ref.
CHFA															
$n = 1$	1h		150		70	1c			132				−64		
	2h		146		61	2c			132				−63		
	3h		146		61	3c			132				−61		
$n = 3$	1h		110		77	1c			82				−46		
	2h	70	108	−17	78	2c			82				−48		
	3h	66	108	−17	70	3c			81				−49		
$n = 5$	1h	−18	100	25	79	1c			77	−53			−58	−5.5	
	2h		100		70	2c			78	−52			−61	−4.0	
	3h		100		74	3c			76	−54			−60	−5.6	
$n = 7$	1h		118		88	1c	88		83		−4.7		−68		
	2h	96	117	−11	98	2c	88		83		−5.6		−61		
	3h	94	117	−9.3	93	3c	88		83		−3.8		−59		
CPFA															
$m = 1$	1h		152		76	1c			138				−56		
	2h		150		67	2c			138				−54		
	3h		149		62	3c			139				−53		
			101				79		76						Murza *et al.*[2]
$m = 2$	1h		114.7		67.9	1c			100.3				−67.2		Barrall *et al.*[3]
	2h		114.2		68.6	2c			100.1				−67.2		
	1h		108			1c	66		63						Murza *et al.*[2]
$m = 6$	1h		106		83	1c	100	85	65		−9.6	−6.3	−52		
	2h	103	105	9.6	77	2c	100	85	65		−7.9	−5.5	−52		
	3h	103	105	10	69	3c	100	85	64		−9.6	−4.6	−49		
			104				93		86						Murza *et al.*[2]

T_t and ΔS_t: transition temperature and the entropy change, T_m and ΔS_m: melting point and the entropy change, $T_{I\text{-}L}$ and $\Delta S_{I\text{-}L}$: isotropic-liquid crystal phase transition and the entropy change, $T_{L\text{-}L}$ and $\Delta S_{L\text{-}L}$: liquid crystal-liquid crystal phase transition temperature and the entropy change, T_f and ΔS_f: freezing point and the entropy change, 1h, 2h and 3h: 1st, 2nd, and 3rd heating process, 1c, 2c and 3c: 1st, 2nd and 3rd cooling process.

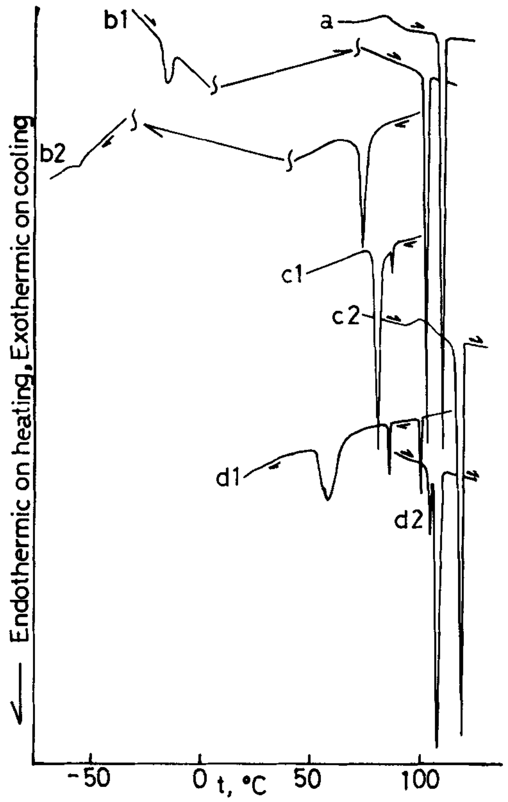

FIGURE 1 DSC curves of several samples. a: the 2nd heating process for $n = 3$ of CHFA, b1 and b2: the 1st heating and the 1st cooling processes for $n = 5$ of CHFA, respectively, c1 and c2: the 1st cooling and the 2nd heating processes for $n = 7$ of CHFA, respectively, d1 and d2: the 1st cooling and the 2nd heating processes for $m = 6$ of CPFA, respectively.

Plots of the melting point, T_m, and the entropy change, ΔS_m, versus n in CHFA are shown in Figure 2. The value of T_m descends with increasing n, but elevates at $n = 7$. This may be connected with the molecular packing in the crystals. Table II lists the crystal data of CHFA crystals. The lattice dimensions show much difference between samples. Crystal structures in a homologous series of cholesteryl alkanoate are known to change by chain length of the alkanoate group.[5,8] Particularly it is noted that the structure is a monolayer arrangement in the shorter chains than the octanoate and a bilayer arrangement in the longer chains. Furthermore, the appearance of smectic phase in the higher chains than the octanoate has been connected with the bilayer arrangement in the crystals. In the case of

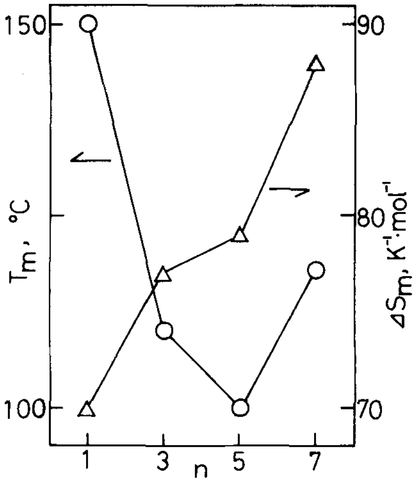

FIGURE 2 Plots of melting point, T_m, and the entropy change, ΔS_m, versus n in CHFA.

CHFA, the chain length of the ester appears to affect the crystal structure complicatedly. The crystals of $n = 1$ and 5 resemble each other in the lattice constants and in the existence of crystal transition. In $n = 5$, one crystal transition is observed as described already, and in $n = 1$, the existence of the two crystal transitions at −94 and −130 °C has been found from our X-ray and dielectric studies.[9,10] On the other hand, no crystal transition has been observed in $n = 3$ and 7. The values of c in the lattice constants of $n = 3$ and 7 are roughly four times and twice of those of $n = 1/5$, respectively. While, the values of a, b and β in $n = 3$ and 7 resemble each other, although the crystal system was attributed to be orthorhombic in $n = 3$ and monoclinic in $n = 7$. The single crystal grown from acetone solution has a long and slender shape like a sword in all samples, and the longest line of the

TABLE II

Crystal data (25°C) and melting point, T_m, of CHFA

		Lattice constant					
n	T_m °C	a A	b A	c A	β degree	System	Space group
1	150	12.5	9.33	13.3	106.6	monoclinic	$P2_1$ or $P2_1/m$
3	110	6.21	11.2	46.6	90.0	orthorhombic	$P2_12_12$
5	101	12.6	9.39	15.0	91.3	monoclinic	$P2_1$ or $P2_1/m$
7	118	6.37	11.1	27.7	91.0	monoclinic	$P2_1$ or $P2_1/m$

edges corresponds with the *b* axis in $n = 1$ and 5, and with the *a* axis in $n = 3$ and 7, respectively. Thus, the crystal structure of CHFA might be roughly classified by two groups, $n = 1$ and 5, and $n = 3$ and 7. Consequently, the relation between the crystal structure of CHFA and the chain length of the ester can not be understood straightforwardly as that in cholesteryl alkanoate. More detailed structural work is in progress.

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