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Phase Transition in a Homologous Series of Cholesteryl α,α,ω-Trihydrofluoroalkylcarbonate (CTHFAC)

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Phase transitions in a homologous series of cholesteryl α,α,ω-trihydrofluoroalkylcarbonates [$C_{27}H_{45}OC(O)OCH_2(CF_2)_pCF_2H$, p= 1,3,5,7] (CTHFAC) were studied by differential scanning calorimetry, polarizing microscopy and dielectric method. The p=5 and 7 compounds showed one cholesteric mesophase and two mesophases (cholesteric and smectic) monotropically on cooling, respectively, but the p=1 and 3 compounds had no mesophase. The dielectric data indicated the existence of one relaxation below 200 K in the polycrystalline state of all compounds. The mechanisms for the mesomorphisms and relaxations were discussed from the chemical structure.

INTRODUCTION

Phase transitions of various ester derivatives of cholesterol have been extensively studied to understand the relation of structural characterization with the mesogenicity.[1,2] Mesomorphisms of homologous series of cholesteryl *n*-alkylcarbonates[2] are known to change rather unusually by the length of alkyl groups, being similar to those of cholesteryl *n*-alkanoates.[1] Recently, we found that the mesogenicity of cholesteryl fluoroalkanoates were strikingly decreased by the substituted F atoms in the alkanoate groups.[3,4] In the homologues of cholesteryl [ω-monohydrofluoroalkanoates [$C_{27}H_{45}OC(O)(CF_2)_n CF_2H$, n=1,3,5,7] (CHFA) and cholesteryl perfluoroalkanoates [$C_{27}H_{45}OC(O)(CF_2)_mCF_3$, m=1,2,6] (CPFA), only the n=7 and m=6 compounds show one and two monotropic mesophases on cooling, respectively.[4]

The purpose of this work is to clarify phase transitions of a homologous series of cholesteryl α,α,ω-trihydrofluoroalkyl-carbonates [$C_{27}H_{45}OC(O)OCH_2(CF_2)_pCF_2H$, p=1,3,5,7] (CTHFAC).

EXPERIMENTAL

CTHFAC was prepared by a dehydrogenchloride reaction of cholesteryl chloroformate and α,α,ω-trihydrofluoroalcohol in the presence of pyridine.[5] The crude samples contained a minute amount of di-cholesteryl carbonate.[5] They were purified by several recrystalizations from acetone-chloroform(3:1) and ligroin solutions alternately, and finally recrystallized from acetone solution. The samples were identified to be the object compounds and judged to be thoroughly purified by TLC, DSC and NMR.

Phase transitions were measured with a differential scanning calorimeter (Perkin Elmer, DSC-II) at a heating/cooling rate of 5 K min^{-1}. The textures of each phase were observed by a polarizing microscope (Nikon, Optiphoto-pol XTP-11) equipped with a Mettler FP-2 hot stage at a heating/cooling rate of 1 K min^{-1} under a crossed polarizer. Dielectric measurements were carried out with a Multi-frequency LCR Meter (YHP, Type4274A) connected with a personal computer at several frequencies between 100 Hz and 100 kHz. The electrodes consist of two parallel gold plated glass plates separated by a 100-μm Teflon spacer.[6]

RESULTS

Figure 1 shows DSC curves for all the samples. The p = 1 and 3 compounds have no mesophase. However, the other longer carbonates exhibit monotropic mesophases. In the p = 5 compound, one cholesteric liquid crystalline state appears monotropically on cooling; on the optical observation on cooling from the isotropic phase, a cholesteric focal conic texture with spherulitic domains appeared in the mesophase and this phase also showed a cholesteric color. The endothermic peaks for the freezing were very broad. These phenomena suggest that the α,α,ω-trihydrofluoroheptylcarbonate group (p = 5) is the shortest alkyl chain to form a mesophase in CTHFAC. The p = 7 compound shows two monotropic mesophases on cooling. On the optical observation on cooling from the isotropic state, there was seen a cholesteric focal conic texture with spherulitic domains similar to that in the p = 5 compound, and a broken fan shaped texture appeared at the subsequent mesophase, which may be assigned to be a smectic phase. On the first heating from the as-grown crystals, one endothermic peak appears, corresponding to the melting point, T_m, but a very small peak and a couple of large peaks appear on the more than

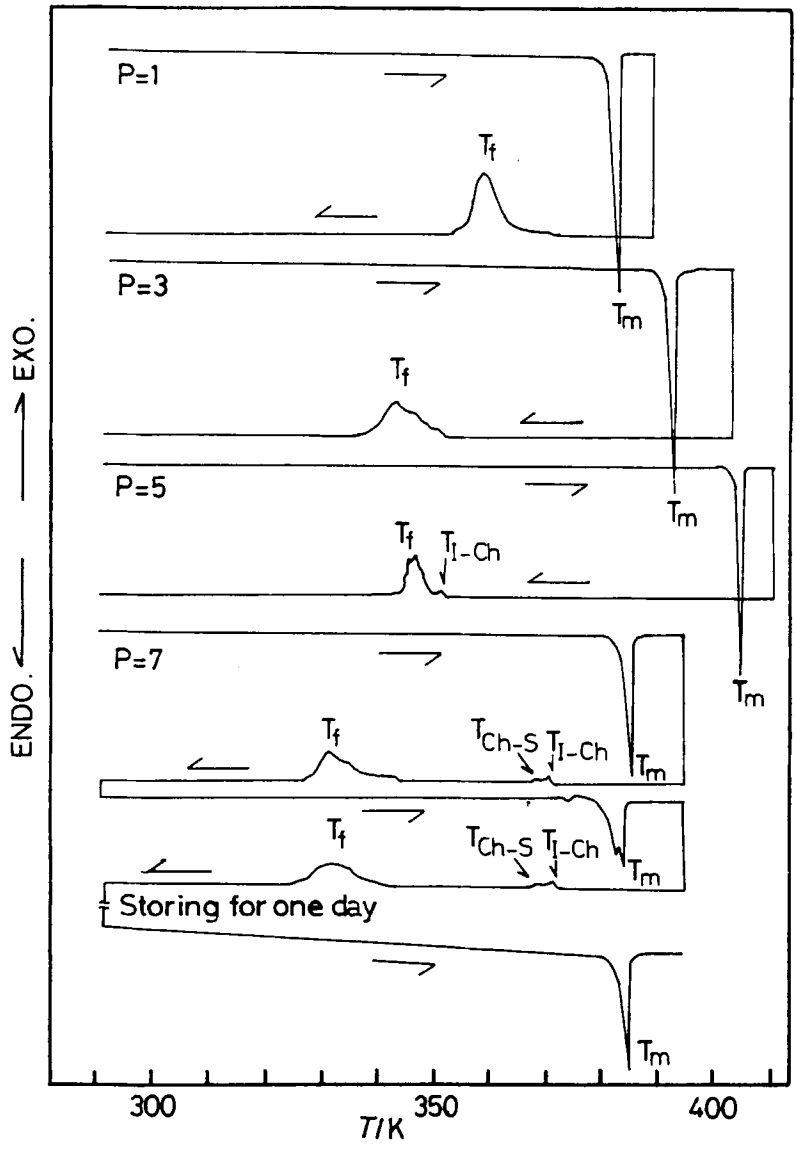

FIGURE 1 DSC curves for CTHFAC [$C_{27}H_{45}OC(O)OCH_2(CF_2)_pCF_2H$]. T_m: melting point, T_f: freezing point, $T_{I\text{-}Ch}$: transition temperature from isotropic to cholesteric, $T_{Ch\text{-}S}$: transition temperature from cholesteric to smectic.

TABLE I

Phase transition parameters for CTHFAC homologues [$C_{27}H_{45}OC(O)OCH_2(CF_2)_pCF_2H$]

p		T_m K	ΔH_m kJmol^{-1}	ΔS_m JK^{-1}mol^{-1}		$T_{I\text{-}Ch}$ K	$T_{Ch\text{-}S}$ K	T_f K	$\Delta H_{I\text{-}Ch}$ kJmol^{-1}	$\Delta H_{Ch\text{-}S}$ kJmol^{-1}	ΔH_f kJmol^{-1}	$\Delta S_{I\text{-}Ch}$ JK^{-1}mol^{-1}	$\Delta S_{Ch\text{-}S}$ JK^{-1}mol^{-1}	ΔS_f JK^{-1}mol^{-1}
1	1h	380	23.8	62.7	1c			364			21.7			60.4
	2h	380	21.5	56.5	2c			364			20.2			56.3
	3h	380	21.5	56.7	3c			364			20.1			55.8
3	1h	390	29.3	75.0	1c			350			22.4			65.0
	2h	390	27.4	70.2	2c			351			22.7			66.1
	3h	390	26.6	68.1	3c			351			22.5			65.1
5	1h	403	35.6	88.3	1c	351		350	1.1		28.5	3.0		82.1
	2h	403	35.0	86.9	2c	352		350	1.2		28.8	2.2		82.8
	3h	403	36.0	89.3	3c	352		350	1.0		28.1	3.0		80.7
7	1h	383	36.4	95.0	1c	370	365	348	1.5	<0.1	29.8	3.6	<0.1	90.2
	2h	382	34.8	90.8	2c	370	365	348	1.3	<0.1	29.4	3.6	<0.1	89.0
	3h	382	34.7	90.9	3c	370	365	348	1.2	<0.1	28.7	3.1	<0.1	87.1

nh: on the nth heating, T_m: melting point, ΔH_m: heat of fusion, ΔS_m: entropy of fusion, nc: on the nth cooling, $T_{I\text{-}Ch}$: phase transition temperature from isotropic to cholesteric, $T_{Ch\text{-}S}$: phase transition temperature from cholesteric to smectic, T_f: freezing point, $\Delta H_{I\text{-}Ch}$: enthalpy of I-Ch transition, $\Delta H_{Ch\text{-}S}$: enthalpy of Ch-S transition, ΔH_f: heat of freezing, $\Delta S_{I\text{-}Ch}$: entropy of I-Ch transition, $\Delta S_{Ch\text{-}S}$: entropy of Ch-S transition, ΔS_f: entropy of freezing.

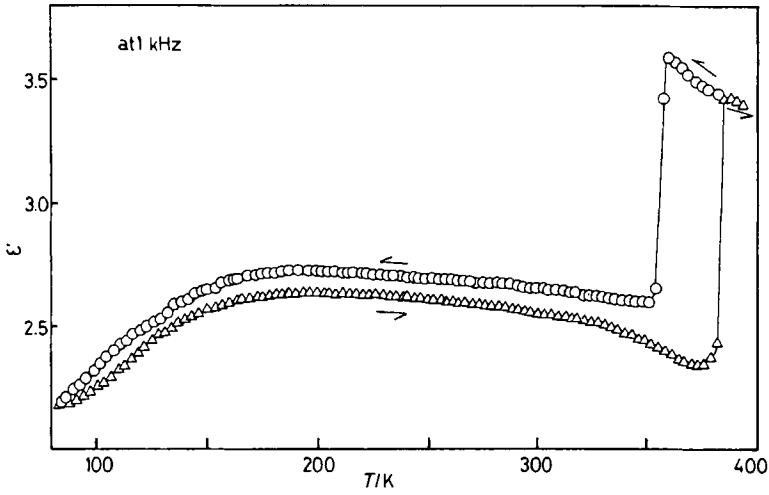

FIGURE 2 Temperature dependence of dielectric constant, ϵ', in polycrystalline state of the p = 1 compound. ○: on the first cooling, △: on the first heating.

2nd heating processes. The existence of the latter peaks suggests that the crystals frozen from the molten state contain metastable phases, since the crystals stored for one day at room temperature revert to the as-grown crystals on the DSC curve as seen in Figure 1. Phase transition parameters for all the samples are listed in Table I. Figure

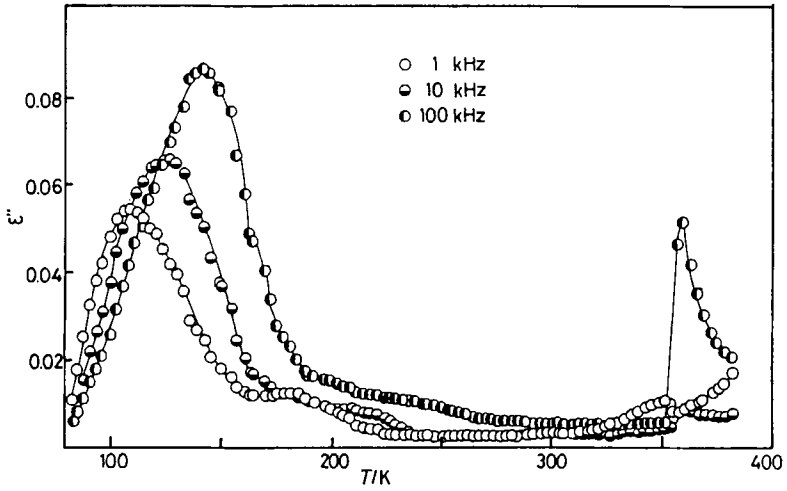

FIGURE 3 Temperature dependence of dielectric loss, ϵ'', in polycrystalline state of the p = 1 compound on the first cooling.

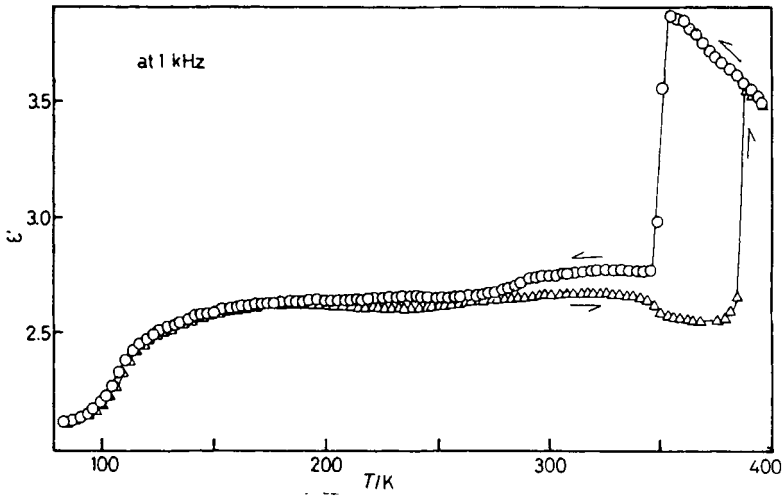

FIGURE 4 Temperature dependence of dielectric constant, ϵ', in polycrystalline state of the p=3 compound. ○: on the first cooling, △: on the first heating.

2 shows temperature dependence of dielectric constant, ϵ', in polycrystalline state of the p=1 compound. The abrupt changes of ϵ' appear near 360 K on the first cooling and near 380 K on the first heating, which corresponds to T_f and T_m, respectively. The gradual change of ϵ' with temperature below 200 K suggests the existence of relaxation. Figure 3 shows temperature dependence of dielectric loss,

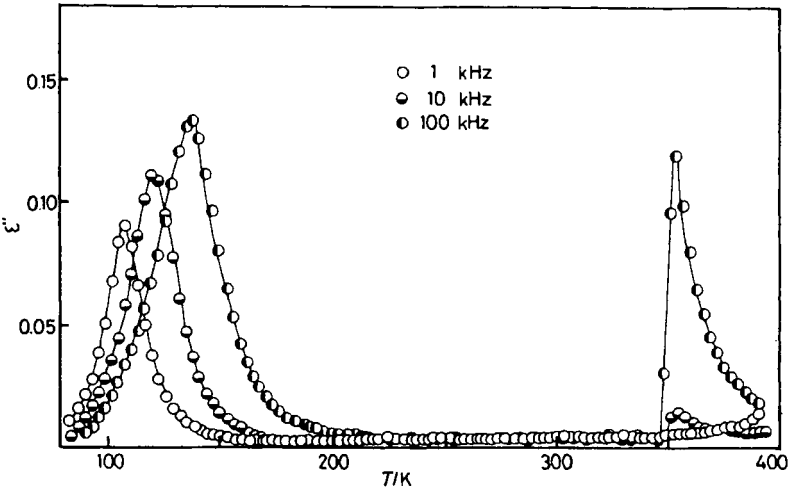

FIGURE 5 Temperature dependence of dielectric loss, ϵ'', in polycrystalline state of the p=3 compound on the first cooling.

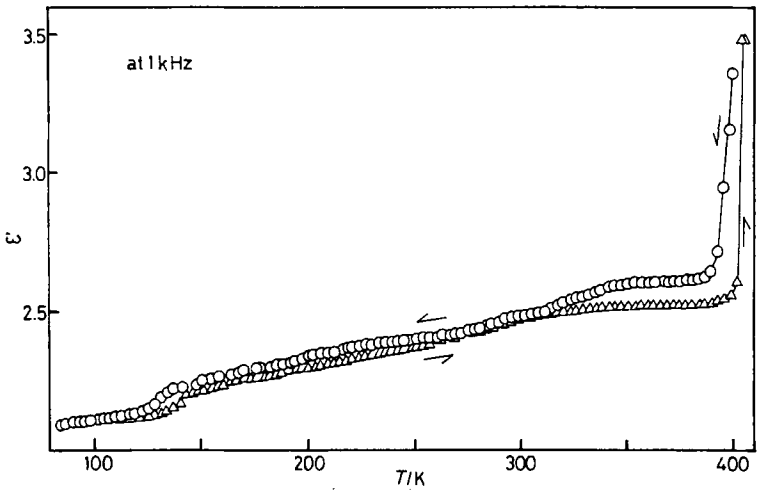

FIGURE 6 Temperature dependence of dielectric constant, ϵ', in polycrystalline state of the p = 5 compound. ○: on the first cooling, △: on the first heating.

ϵ'', on the first cooling for the p = 1 compound. One relaxation is seen below 200 K, and the abrupt change of ϵ'' near 360 K is due to the freezing. Dielectric data of the p = 3 compound are shown in Figures 4 and 5 and are essentially similar to those of the p = 1 compound. The abrupt changes of ϵ' are seen near 385 K on heating and near

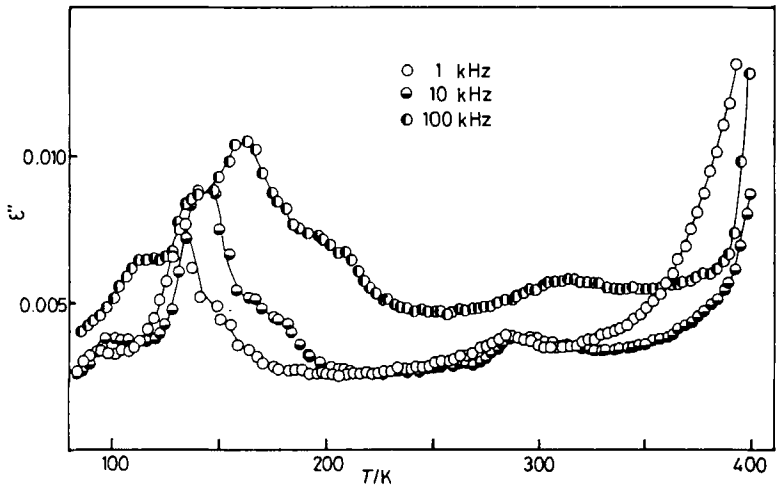

FIGURE 7 Temperature dependence of dielectric loss, ϵ'', in polycrystalline state of the p = 5 compound on the first cooling.

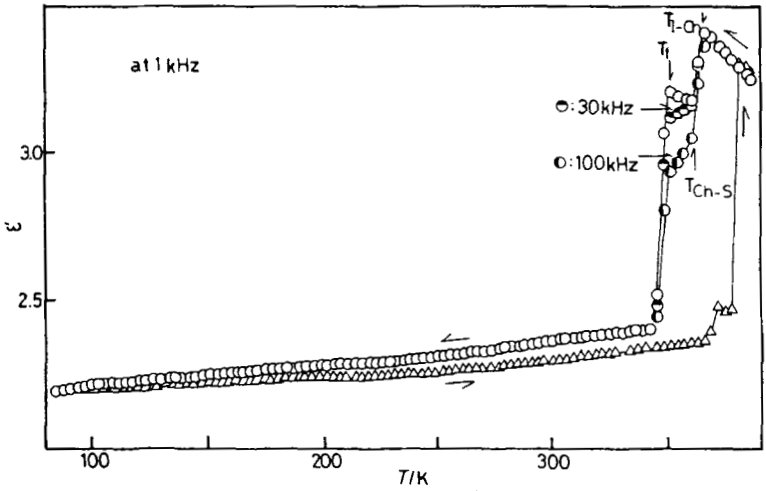

FIGURE 8 Temperature dependence of dielectric constant, ϵ', in polycrystalline state of the p=7 compound. ○: on the first cooling, △: on the first heating.

355 K on cooling, which correspond to T_m and T_f, respectively. One relaxation is seen below 200 K. The other dielectric data are shown in Figures 6 and 7 for the p=5 and in Figures 8 and 9 for the p=7. In the p=5, the value of ϵ' shows discontinuous changes near 390 K on cooling and near 403 K on heating, corresponding to T_f and T_m. However, the freezing point is higher by about 40 K in the dielectric measurements than that in the DSC measurements (T_f=350 K), and

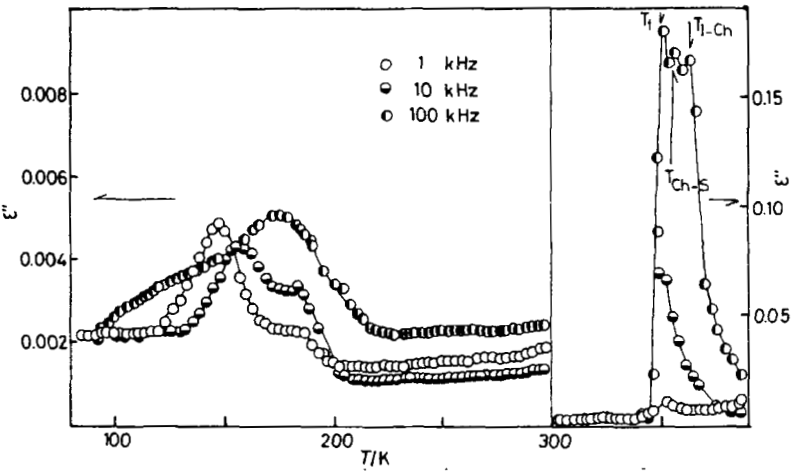

FIGURE 9 Temperature dependence of dielectric loss, ϵ'', in polycrystalline state of the p=7 compound on the first cooling.

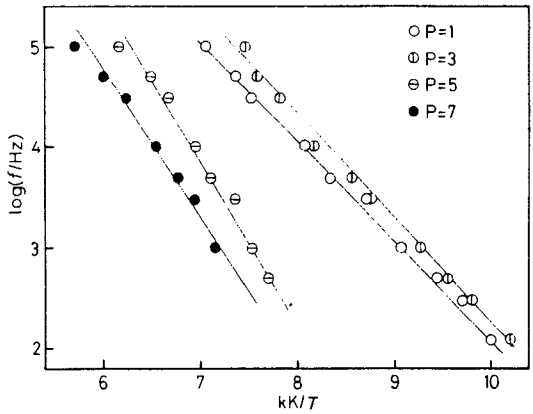

FIGURE 10 Arrhenius plots for the relaxations in the polycrystalline state of CTHFAC homologues.

hence, change of ϵ' corresponding to $T_{I\text{-}Ch}$ is concealed. As seen in Figure 7, one dielectric relaxation is observed below 200 K, but rapid changes of ϵ' and ϵ'' are observed near 140 K regardless of frequency. These rapid changes suggest the existence of one phase transition in the crystalline state. Plots of ϵ' and ϵ'' versus temperature for the $p=7$ shows the two mesophases only on cooling. In the cholesteric state, the value of ϵ' decreases rapidly as temperature is decreased, but shows no dependence on frequency in the present frequency range. In the smectic state, the value of ϵ' decreases as frequency is increased above 10 kHz, which suggests that the orientation of dipoles towards the applied field begins to be hindered above 10 kHz. In the polycrystalline state, one very small relaxation is also observed below 200 K in Figure 9. The Arrhenius plots for the relaxations are shown in Figure 10 for all the compounds. The relaxation temperature shifts to higher temperatures as p is increased. The relaxation parameters obtained from the plots are listed in Table II.

TABLE II

Relaxation temperature, T_{max}, activation enthalpies, ΔH, and activation entropies, ΔS, for the relaxations in CTHFAC

p	T_{max} at 1 kHz / K	ΔH / kJ mol^{-1}	ΔS / JK^{-1} mol^{-1}
1	108	18	1
3	108	18	1
5	133	29	55
7	140	30	−1

DISCUSSION

Plots of phase transition temperatures and the entropies of fusion against the length of alkyl chain in the CTHFAC homologues are shown in Figure 11 with those for CHFA homologues. The figure suggests that the length of alkyl chain for CTHFAC are longer by —OCH_2— than that for CHFA in the chemical formula, where p for CTHFAC is equivalent to n-2 for CHFA. However, the phase transition parameters appear to be reasonable by assuming that p is equivalent to n-1; T_m shows a somewhat odd-even effect except for n = 1, and both changes of $T_{I\text{-}Ch}$ and ΔS_m by p/n-1 seems to be reasonable. The above results suggest that the oxygen atom attached to the alkyl group does not behave as a member of the alkyl chain and C(O)—O bond has nature of double bond partially by the adjacent carbonyl

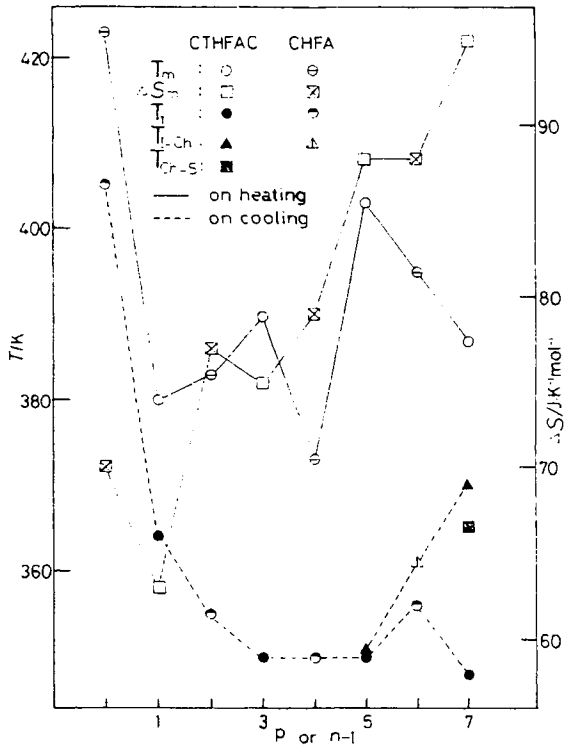

FIGURE 11 Change of phase transition parameters with the length of alkyl chain for CTHFAC [$C_{27}H_{45}OC(O)OCH_2(CF_2)_pCF_2H$] and CHFA [$C_{27}H_{45}OC(O)$-$(CF_2)_nCF_2H$].

group. In the previous work on phase transitions of cholesteryl monobromopropionate and monochloropropionate,[3] we found that the substitution of halogen atom at α position in the propionate decrease much the ability for the formation of mesophase. On the other hand, the halogen atom at β position little affected the mesogenicity of cholesteryl propionates. The above rule succeeded in both homologues of CHFA and CPFA. Our recent X-ray work[7] indicated that the pentanoate group of cholesteryl δ-monohydrofluoropentanoate bends out of the lath-like cholesteryl group in the crystals. This bending was concluded to cause the decrease of mesogenicity. Apparently, the mesogenicities of CTHFAC homologues are also much decreased by the substituted F atoms, compared with those of the corresponding cholesteryl alkylcarbonates, although the F atoms are not substituted at α position in the alkylcarbonate groups. Therefore, some conformations of the fluoroalkylcarbonate chains are presumed to cause the decrease of mesogenicity in CTHFAC.

Our previous dielectric work[8] reveals that CHFA shows one dielectric relaxation at low temperatures below 200 K in the crystalline state. This relaxation was concluded to be related to a local molecular motion of terminal —CF_2H group, from the facts that the activation enthalpies, ΔH, for the relaxation lay between 14 and 28 kJ mol^{-1} and CPFA homologues had no relaxation in the crystalline state. This local molecular motion responsible for the relaxation was not connected with the phase transitions in the crystalline state. Figure 12

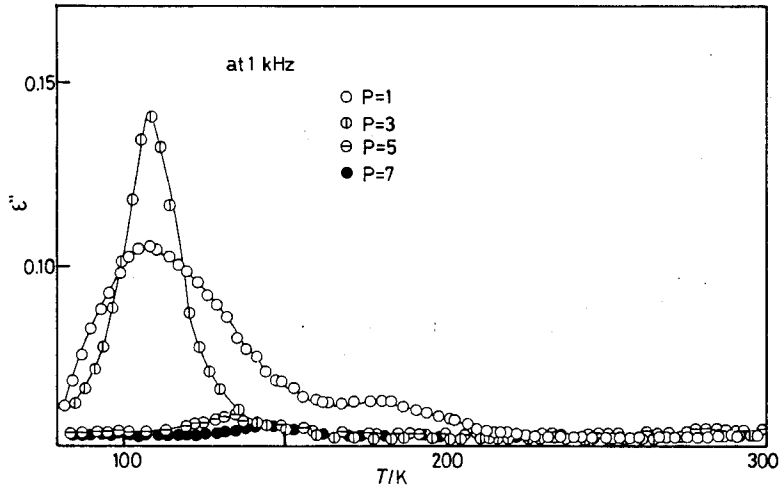

FIGURE 12 Temperature dependence of dielectric loss, ε″, in polycrystalline state of CTHFAC [$C_{27}H_{45}OC(O)OCH_2(CF_2)_pCF_2H$] on the first cooling.

shows comparison of the relaxations in the polycrystalline state of CTHFAC homologues. As seen in the figure, the relaxations are observed in all the crystals, being akin to those for CHFA crystals; all the relaxations appear at lower temperatures below 200 K, and the values of ΔH are small values between 18 and 30 kJ mol^{-1}. Therefore, the relaxations may be related to a local molecular motion of terminal —CF_2H group. The magnitudes of relaxation for the p = 1 and 3 crystals, however, are larger by about one factor than those for the p = 5 and 7 crystals. This difference might be explained by the molecular packing, especially the environment around the terminal —CF_2H group in the crystals.[8]

In conclusion, this work indicates that the mesogenicity of CTHFAC homologues are much more decreased by the substituted F atoms compared with that of the corresponding cholesteryl alkylcarbonate homologues, and that the mesomorphic behavior is essentially similar to that of CHFA. Since the finding of the successive phase transitions in the n = 1 crystal of CHFA,[9] our interest has been more increased on phase transition in the crystalline state of various fluorinated derivatives of cholesterol. We plan to study the structure of CTHFAC crystals in order to clarify the phase transitions and the mesomorphism, and to understand the more detailed mechanisms of molecular motion (the relaxation).

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