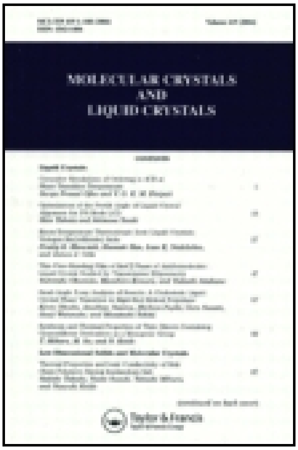

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New Mesogenes Forming Nanophase Separated Liquid Crystalline Structure - Cubic Phase -

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New Mesogenes Forming Nanophase Separated Liquid Crystalline Structure – Cubic Phase –

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Hydrogen bonded complexes between 4-(oligodimethylsiloxyl)alkoxy benzoic acids and 4,4'-dipyridyl were found to exhibit a thermotropic liquid crystalline cubic phase. One of the important factors to realize the cubic structure could be the incompatibility between the flexible, bulky siloxane moiety and the rigid mesogenic core, which probably causes nanophase separation. We have investigated benzoic acid derivatives having a polar, relatively rigid perfluorinated alkyl segment that also exhibits incompatibility with hydrocarbon parts. The neat acids and their hydrogen bonded complexes with 4,4'-dipyridyl does, however, not show thermotropic liguid crystalline cubic phase, but a smectic *A* phase. In this paper we will consider the chemical prerequisite to realize a thermotropic cubic phase.

Keywords: Cubic phase; Siloxane moiety; Perfluorinated moiety; Nanophase separation; H-bonded complex

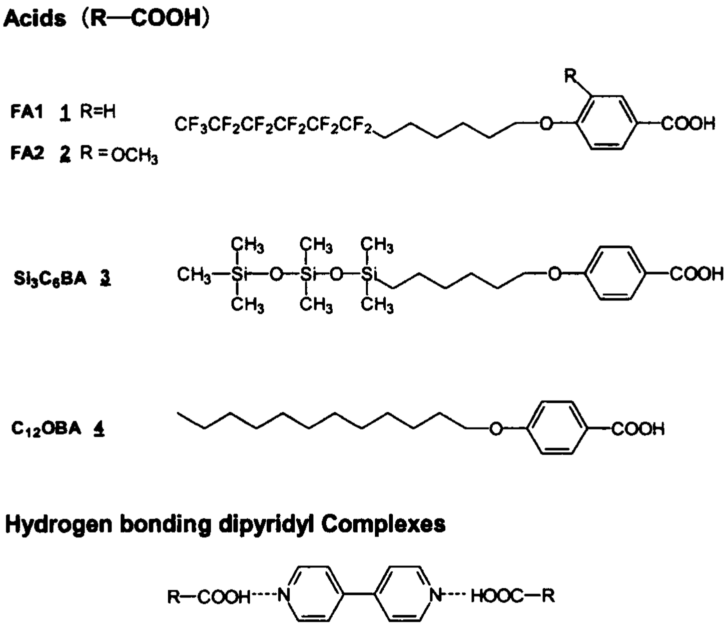
INTRODUCTION

Recently cubic thermotropic liquid crystalline (l.c.) phases have been investigated intensively. New hydrogen-bonded mesogenes based on 4-(oligodimethylsiloxyl)alkoxybenzoic acids and 4,4'-dipyridyl were found to show thermotropic cubic phases[1,2]. In these complexes it is thought that the high incompatibility between flexible, bulky and nonpolar siloxane moieties and H-bonded, polar aromatic mesogenic cores is one of the important factors to realize cubic structure.

Perfluorinated alkyl segments also exhibit incompatibility with aromatic mesogenic cores and even with alkyl hydrocarbon groups. However the high rigidity of the segments significantly differs from siloxane substituents. We synthesized some benzoic acid derivatives with perfluorinated alkyl groups and investigated phase behavior of these organic acids and their hydrogen bonding complexes with 4,4'-dipyridyl to know whether in these compounds a cubic thermotropic l.c. phase is formed. Chemical structure prerequisite to organize cubic structure will be considered in this paper.

EXPERIMENTAL

The chemical structure of the compounds under investigation is shown in Scheme 1. The synthesis of the siloxane-acid **3** refers to the previous paper[1] and that of the fluorinated-acids **1** and **2** will be described elsewhere. 4-Dodecyloxybenzoic acid **4** was bought from Kanto Chemical and used without further purification. Differential scanning calorimetry data were recorded with a MAC Science DSC-3100 at a heating/cooling rate of 5 K/min. Texture observation was performed using an Olympus BX-50 polarizing microscope equipped with crossed polarizers and a Linkam LK-600PH hot stage. X-ray scattering measurements were carried out with monochromatic CuK_α radiation using a Bruker X-ray machine with a two-dimentional HiSTAR detector.



SCHEME 1 The chemical structure of investigated organic acids and their 4,4'-dipyridyl complexes through hydrogen bonding

RESULTS AND DISCUSSION

In Table 1 the phase behavior of neat acids **1** – **4** and their 4,4'-dipyridyl complexes are summarized. All of the acids form an elongated, dimeric structure through cyclic hydrogen bonding. On comparing **1** with **4** the rigid perfluorinated alkyl segment affects the isotropic phase transformation temperature to become higher. Interestingly **1** shows only a smectic *C* phase while **4** has a nematic phase. This result indicates that the incompatibility of the perfluorinated alkyl moiety with the hydrocarbon segments could cause nanophase separation, preferentially leading to

TABLE 1 Phase behavior of the neat acids and 2:1 acid/base complexes with 4,4'-dipyridyl (DIPy). The phase transformation temperatures were obtained from DSC data in the first cooling process at the rate of 5 K/min.

Acid	Base	Phase behavior (°C)
FA1	1	Cr_1 132 Cr_2 156 S_C 177 *i*
FA1	1c DIPy	----
FA2	2	*Cr* 104 *i*
FA2	2c DIPy	Cr_1 98 Cr_2 113 S_A 141 *i*
Si_3C_6BA	3	Cr_1 33 Cr_2 67 *i*
Si_3C_6BA	3c DIPy	Cr_1 42 Cr_2 96 ***Cub*** 100[a] S_A 103 i_1 115 i_2
$C_{12}OBA$	4	*Cr* 88 S_C 130 *n* 137 *i*
$C_{12}OBA$	4c DIPy	*Cr* 89 S_C 153 *i*

Cr_1, Cr_2 = crystalline; S_C = smectic *C*; S_A = smectic *A*; *i*, i_1, i_2 = isotropic, ***Cub*** = cubic
[a]The smectic *A* phase is observed only on cooling.

segregated lamellar structure. The acid 2 has a methoxy group at the meta position to the carboxylic acid group. Owing to this substituent the isotropization temperature of 2 decreases by about 70 degrees compared to 1. The neat acid 2 exhibits no l.c. phases. The siloxane-containing acid 3 exhibits an isotropic phase transformation temperature at 67°C with a transient smectic *C* phase on cooling the melt. This temperature is much lower than that of the other three acids, which is caused by reduction of the packing efficiency due to the bulkiness and flexibility of the siloxane moiety.

The determination of phase sequence of the 4,4'-dipyridyl complex of **FA1** (1c) is difficult because the temperature range of l.c. phases are high so that thermal decomposition of the complex occurs during observation. We could observe the phase behavior of 2c. This complex shows a smectic *A* phase between 141 and 113°C, with a tendency to align perfectly homeotropically between glass plates. Then crystallization occurs at 113°C.

As already described in the previous papers the 4,4'-dipyridyl complex of **Si_3C_6BA** (**3c**) shows a cubic phase from 100 to 96°C below the temperature range of a smectic *A* phase[1]. The textures observed with polarized optical microscope are reported in Figure 1. We recognize that dark areas gradually develop in the focal conic texture of a smectic *A* phase and the entire areas eventually become completely optically extinct that is a cubic phase. The structure investigation of the cubic phase was described in the previous paper by means of X-ray and Deuterium NMR[2].

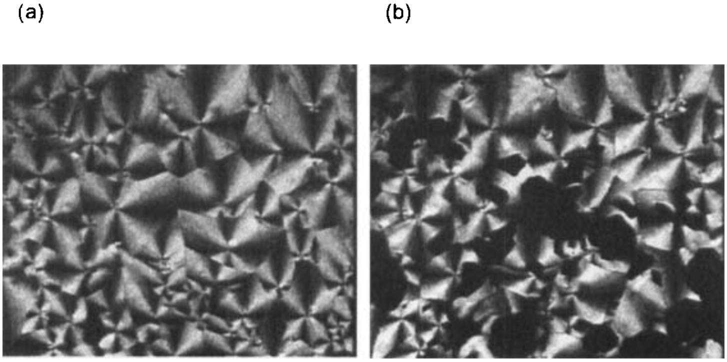


FIGURE 1 Textures of (a) the smectic *A* phase and (b) the phase transformation from the smectic *A* to the cubic phase

The new H-bonded mesogenes composed of siloxane-containing benzoic acids and 4,4'-dipyridyl do exhibit a cubic mesophase. However we have not found cubic thermotropic l.c. phase in the benzoic acid derivatives with perfluorinated alkyl segments we synthesized until now. One of the reasons to the findings could be that the perfluorinated alkyl chain of the compounds be short to affect nanophase separation organizing a cubic structure. The other reason would be that the rigidity of the perfluorinated moiety is high, preventing from realizing a cubic structure. Now we will try to synthesize some benzoic acids derivatives with a relatively longer, branched perfluorinated alkyl segment or a flexible fluorinated segment, which could give further information of prerequisite of chemical structure to form a cubic thermotropic l.c. phase.

CONCLUSIONS

We found new hydrogen-bonded mesogenes based on 4-(oligodimethylsiloxyl)alkoxybenzoic acids and 4,4'-dipyridyl, which show cubic thermotropic liquid crystalline phase. However the H-bonded complexes between benzoic acid derivatives having perfluorinated alkyl segments and 4,4'-dipyridyl exhibit only smectic phases. One of the important differences between the perfluorinated alkyl groups and siloxane segments is the rigidity, which might prevent forming a cubic phase. Investigation of other benzoic acid derivatives e.g. with a flexible fluorinated moiety or longer, branched perfluorinated alkyl segment could give more information about chemical structure prerequisite to organize a cubic thermotropic l.c. phase.

References

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[2] E. Nishikawa and E. T. Samulski, *ibid.*