Synthesis and Properties of Perfluoroalkylalkoxy Substituted Benzoic Acid Derivatives

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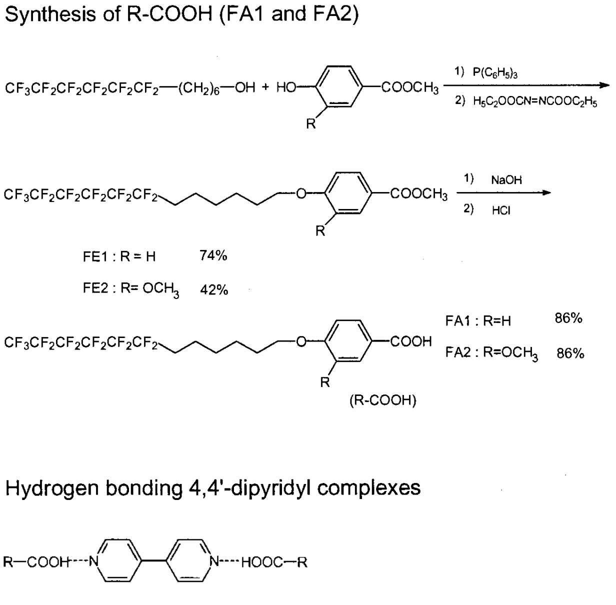
Several benzoic acid derivatives having long perfluoroalkyl substituents are synthesized, which form dimers through hydrogen bonding or complexes with bases. These materials are expected to organize nano-phase separated liquid crystalline structure, for instance, a cubic phase, due to the incompatibility between perfluoroalkyl groups and hydrocarbon moieties.

Recently thermotropic cubic liquid crystalline phases have attracted much attention.[1] Structure of the cubic phases of well known 4'-*n*-alkoxy-3'-nitrobiphenyl-4-carboxylic acids have been intensively investigated.[2] Several new compounds organizing cubic phases have been synthesized.[3] For instance, hydrogen (H-) bonded mesogens based on siloxane-containing benzoic acid derivatives and 4,4'-dipyridyl are found to show a cubic phase at a moderate temperature range around 100 °C.[4] In these acid/base H-bonded complexes, it is thought that the high incompatibility (insolubility) between flexible, bulky, non-polar siloxane moieties and H-bonded, polar, aromatic hard cores is one of the important factors to organize thermotropic cubic phase. Similar to siloxane substituents, it is well known that perfluorinated alkyl segments also exhibit incompatibility with aromatic cores and even alkyl groups.[5] However the rigidity significantly differs between these segments. Fluorinated alkyl segments are relatively rigid unlike the flexible siloxane groups. In this note we have synthesized benzoic acid derivatives having perfluorinated long alkyl segments as shown in Scheme 1, and investigated phase behavior of these organic acids and their H-bonded complexes with 4,4'-dipyridyl, namely, whether these materials organize cubic structure. The prerequisite of chemical structure for realizing thermotropic cubic phases will be discussed.

Two benzoic acid derivatives with a linear perfluorinated alkyl segment FA1 and FA2 were synthesized as shown in Scheme 1. Starting from perfluoroalkylalkyl alcohol and methyl 4-hydroxybenzoate derivative, the methyl esters FE1 and FE2 were prepared by Mitsunobu reaction. The esters were hydrolyzed to yield corresponding organic acids FA1 and FA2. These materials are analogues of previously studied siloxane-acids.[4] The phase behavior of the esters, the neat acids forming dimer through H-bonding and their acid/base complexes with 4,4'-dipyridyl (DiPy) are summarized in Table 1, which was determined with differential scanning calorimetry (DSC), polarized optical microscope (POM) and X-ray scattering technique.[6]



Scheme 1. Synthesis and chemical structure of the neat acids under investigation and the 4,4'-dipyridyl complexes.

Table 1. Phase behavior of the esters, the neat acids and their 4,4'-dipyridyl (DiPy) complexes

Acid	Base	Phase behavior/°C
FA1	-	Cr_1^a 132 Cr_2^a 156 S_C^b 177 i^d
FA1	DiPy	----
FA2	-	Cr^a 104 i^d
FA2	DiPy	Cr_1^a 99 Cr_2^a 114 S_C^b 117 S_A^c 41 i^d
FE1	-	Cr_1^a 43 S_A^c 48 i^d
FE2	-	Cr_1^a 7.5 i^d

The phase transformation temperatures were obtained from DSC data in the first cooling process at the rate of 5 K/min; [a]crystalline. [b]SmecticC. [c]SmecticA. [d]Isotropic.

The neat acid FA1 shows a smectic C (S_C) phase between 156 °C and 177 °C. FA2 has a methoxy group at the meta position to the carboxylic acid group. Due to this substituent the isotropization temperature of FA2 decreases by 60 degrees compared to FA1. This acid, however, exhibits no liquid-crystalline phases. Phase behavior of the DiPy complex of FA1 is not determined because the temperature range of liquid crystalline phases is relatively high so that thermal decomposition occurs during observation. The DiPy complex of FA2 melts at 114 °C and then transforms to S_C-phase showing Schlieren texture. Interestingly director fluctuation in this phase seems to be a similar extent to nematic phase. Thereafter S_A-phase exists from 117 °C to 141 °C. In this phase the entire field under POM becomes optically extinct, indicating a tendency to align homeotropically when sandwiched between two parallel glass plates. Using polyimide coated glass plates focal-conic texture is observed. With X-ray scattering technique, small-angle reflection corresponding to a periodicity of 43 Å is detected. Then S_A to isotropic phase transformation occurs at 141 °C with enthalpy change of 4.6 KJ/mol. A picture of the phase transition under POM (out of cross nicol ≈ 50°) sandwiched non-coated two parallel glass plates is shown in Figure 1. Two optically extinct phases (isotropic and an S_A-phase) are observed. The discontinuous region grows when the temperature increases, which corresponds to the isotropic phase. This phase transformation seems to take place like two-phase separation.

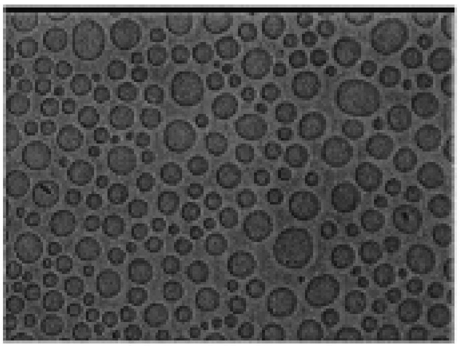


Figure 1. A picture of FA2-DiPy complex showing a S_A-i phase transition

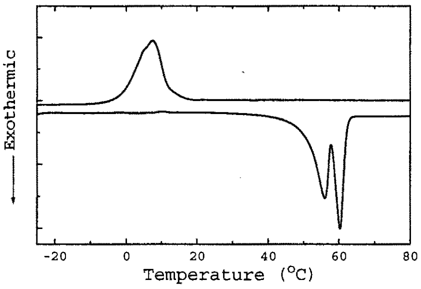
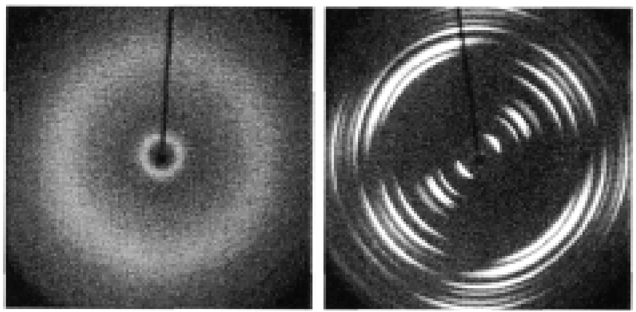


Figure 2. DSC trace of the ester FE2 at a cooling/heating rate of 5 K/min.

The ester FE1 shows monotropic S_A-phase at 48 °C, which is followed by crystallization at 43 °C. The phase behavior of FE2 is unique. On heating the compound melts in two steps at 56 °C and 60 °C accompanying with enthalpy change of 23 KJ/mol and 14 KJ/mol, respectively. On cooling crystallization occurs at 7.5 °C. Figure 2 shows the DSC trace. X-ray investigation of this compound was performed. As shown in Figure 3a, in the isotropic phase reflection at small angle is observed, which indicates that even in the isotropic phase a kind of aggregate exists. Figure 3b shows the X-ray pattern around 30 °C dramatically changed, which exhibits without external fields highly aligned structure. Although the small-angle reflections indicate oriented lamella phase, we have not understood this structure now.

As mentioned above, the dipyridyl-complexes of the benzoic acid derivatives having perfluorinated alkyl segment do not organize a thermotropic cubic phase. The chemical architecture of these materials is similar to the siloxane containing organic acids previously studied. Both substituents (perfluoroalkyl and siloxane segment) show some similar properties, incompatible with aromatic moieties. However the rigidity significantly differs. This point might be one of the crucial factors to organize thermotropic cubic phase. We are now synthesizing materials with relatively flexible fluorinated moieties to investigate chemical prerequisite for forming thermotropic cubic phases.



(a) (b)

Figure 3. X-ray pattern of FE2 (a) at 35 °C and (b) at 25 °C.

References and Notes

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6 DSC 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 experiments were performed with Bruker D8 DISCOVER using a power of 1.6KW and a wavelength of 1.54 Å (Cu Kα) with two-dimensional detector HI-STAR.