The Influence of Fluorinated Alkyl Chains on the Stabilization of Hydrogen Bonded Liquid Crystals

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Perfluorinated alkyl chains were introduced into hydrogen bonded associates. Both, mesophase induction and stabilization were observed.

Perfluorinated alkyl chains became very interesting for liquid crystal research during the last few years because of their chemical stability, reduced flexibility and the possibility to introduce additional dipole moments.[1,2] A further specialty is the tendency of phase separation between hydrogenated and fluorinated alkanes.[3] In this paper we try to connect these properties and the behavior of carboxylic acids to form hydrogen bonded associates.[4-7] Therefore, mixtures of partially perfluorinated carboxylic acids and derivatives of pyridine were investigated.

Figure 1 presents the phase diagram of 4-n-butyloxybenzoic acid (Cr 151 N 162 I) as proton donor D and 4-(4-n-hexyloxyphenyl)pyridine (Cr 62 I) as acceptor A. A hydrogen bonded associate at equimolar concentration can be recognized by the existence of two eutectic points. The associate DA shows the polymorphism Cr 87 S_A 133 N 138 I.

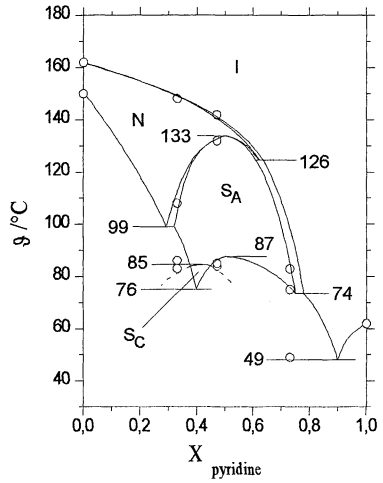
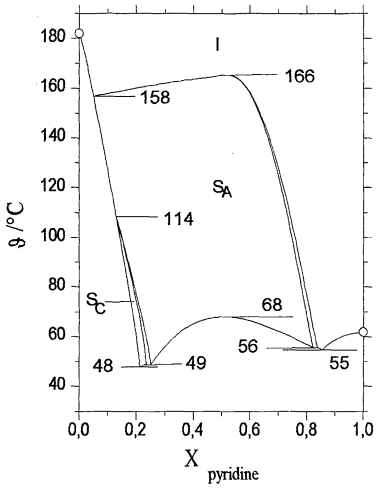


Figure 1. Associate of the type DA containing only hydrocarbon chains.

The respective phase diagram with the partially fluorinated 4-n-(1H,1H-perfluorobutyloxy)benzoic acid (Cr 182 I) in Figure 2 demonstrates a clear extension of the liquid crystalline phase range (Cr 68 S_A 166 I). The high vapor pressure of the fluorinated acid did not allow the preparation of single concentrations like those in the phase diagram of Figure 1. Therefore, only contact preparations could be investigated under a heating stage microscope using polarized light.



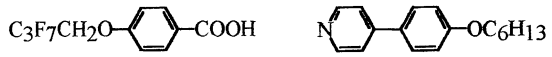


Figure 2. Typical phase diagram the type DA using a perfluoroalkyloxybenzoic acid.

An elongation of the fluorinated alkyl chain to 4-n-(1H,1H,2H,2H-perfluorooctyloxy)benzoic acid in the mixture with the same proton acceptor results in increasing of the clearing temperature to 198 °C. An extension of the fluorinated part to 4-n-(1H,1H,2H,2H-perfluorodecyloxy)benzoic acid results in a further increase of the clearing temperature to 209 °C.

Symmetrical associates of the type D_2A with a pronounced maximum in the mesophase stability at 230 °C are formed with the bifunctional 4,4-bispyridylethylene as demonstrated in Figure 3. It is necessary to point out that the microscopic investigation is very difficult because the fluorinated benzoic acid is sublimating at this temperature range. The respective associate containing normal alkyl chains has a clearing point of 177 °C.[8]

Another interesting version is the associate DA_2 observed in the binary system of hexafluoroglutaric acid and 4-(3,4,5-tri-n-dodecyloxy)benzoyloxypyridine. A columnar phase is obtained at the respective concentration range as shown in Figure 4. Furthermore a mixing gap in the isotropic state was found. Unfortunately both components undergo decomposition at about 100 °C. That's why the type of mesophase was classified only by microscopic observation. The formation of this mesophase is of special interest, because the corresponding associate containing glutaric acid shows no liquid crystalline properties (Cr 86 I). So,

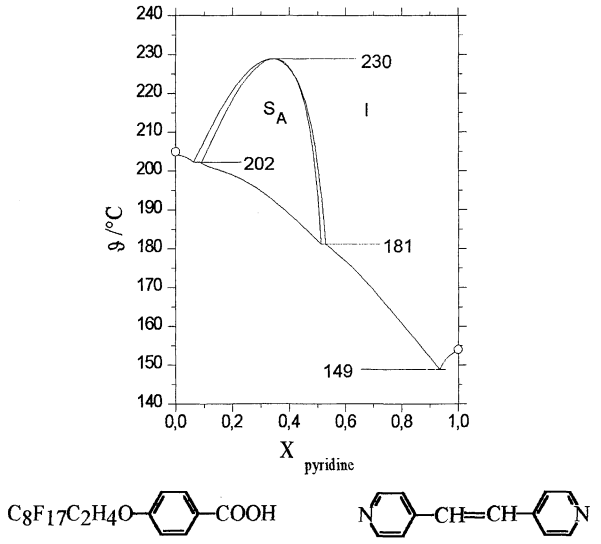


Figure 3. Phase diagram of the type D_2A.

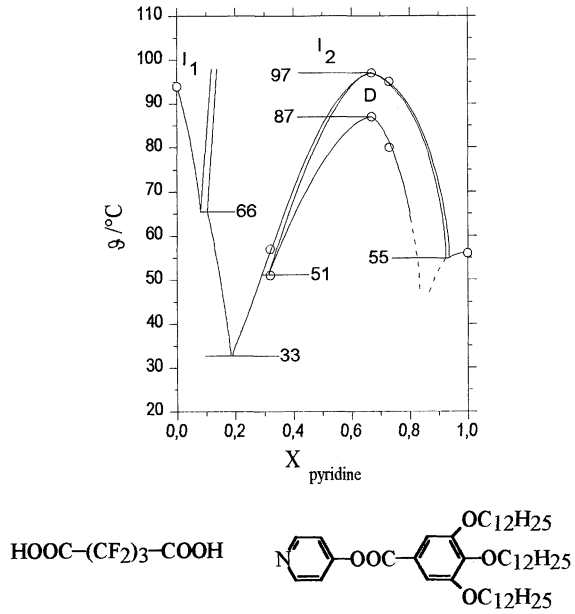


Figure 4. Columnar mesophase in a binary system DA_2.

an additional fact is given, that underlines the significant influence of fluorinated alkyl chains on the mesophase behavior.

The former results are in good agreement with tendencies known from liquid crystals containing perfluorinated alkyl chains. Tendencies of demixing on molecular level based on steric effects and on the stiffness of perfluoroalkyl chains lead to higher clearing temperatures and to the stabilization of smectic phases. In accordance to Bernhardt et al. [9] the transition temperatures of hydrogen bonded associates are lower than those of comparable covalent compounds. So, the stabilify of the associate DA_2 in Figure 4 allows to predict the existence of a columnar mesophase at the respective covalent equivalent if the hydrogen bonds are replaced by ester groups. According to our knowledge such mesogens are not known yet. In that way the prediction of liquid crystalline properties of new molecular structures seems to be an interesting approach of hydrogen bonded associates. This new application offers the possibility to check reasonable structures, and non-conventional shapes too, by simple mixing of commercially available substances or standard building units.

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