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Investigations on liquid crystalline partially fluorinated 'one-chain' and 'two-chain' benzoic acids

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The mesomorphic properties of perfluoroalkyl alkyloxy-substituted benzoic acids with one (**K1S**) and two (**K2S**) partially fluorinated alkyl chains are presented. These classes of compound were investigated by means of differential scanning calorimetry, polarizing optical microscopy, X-ray diffraction of non-oriented samples and, in one case, temperature-dependent IR spectroscopy. Because of dimerization via H-bonding, the presence of carboxy groups leads to an enhanced thermodynamic mesophase stability with respect to the corresponding alkyl esters. The 'one-chain' acids **K1S** form SmC phases, while the 'two-chain' acids **K2S** exhibit hexagonal columnar phases (Col_h). In the case of one-chain compounds, fluorination leads to the suppression of nematic phases. Furthermore, elongation of the fluorinated chain segments causes a reduction of the mesophase range, due to an increased crystallization tendency of these chains. In the case of two-chain acids **K2S**, an increased thermodynamic stability of the columnar phases can be observed on increasing the length of the perfluoroalkyl segments. Here the thermal behaviour of the compounds is also sensitive to the non-fluorinated alkyl chain length.

1. Introduction

It is well known that not only *anisometry*, but also *aggregation* by strong interactions such as H-bonding [1–4], Coulomb [5], charge-transfer [6, 7], π-π [8, 9] or coordinative forces [10] can be responsible for the mesomorphic properties of liquid crystalline compounds. The third driving force is *segregation* between incompatible moieties [11–18], and in this respect, the introduction of perfluoroalkyl chains into either mesogenic or non-mesogenic compounds plays a major role, and has been investigated since the late 70s [19–21, and references therein]. In general, nematic phases are depressed while segregated phases, such as smectic phases, are favoured and sometimes even new mesophase types are generated. Normally, short perfluoroalkyl groups (CF_3 and C_2F_5) lower the melting points by some 20 to 50°C with respect to the non-fluorinated analogues. Longer perfluoroalkyl segments ($>C_4F_9$) tend to increase the transition temperatures [22–24], sometimes by 17 to 20°C per difluoromethylene unit [25].

With respect to anisometry of molecules, it is known that the molecular shape strongly determines the morphology of the mesophase. Linear mesogens mostly lead to nematic or smectic mesophases. Increasing the wedge-like character of a mesogen, i.e. building taper-shaped or cone-shaped structures, leads in principle first to bicontinous cubic (Cub_{bi}), then to columnar (Col) and finally to spheroidic cubic phases (Cub_s) [3, 14, 26, 27]. One example of such behaviour is shown by the terminally alkyloxy-substituted D-glucitol derivatives (see figure 1) [27]. Both, elongation *and* increasing the substitution number of the alkyl chains enhance the wedge-like character of the compounds. Hence, the given phase sequence is a consequence of these changings.

In the first paper of this series [28], we discussed the influence of the terminal substitution of methyl, ethyl and succinimidyl alkoxybenzoic esters with perfluoroalkyl chains on the mesomorphic behaviour (see figure 2). For the 'one-chain' methyl esters ($R_1 = F(CF_2)_n$–$(CH_2)_m$–O, $R_2, R_3 = H$, **K1E**), the introduction of perfluoroalkyl chain segments led to monotropic SmA phases. For the succinimidyl esters, enantiotropic SmA phases have been observed in the case of one-chain derivatives (**K1NS**) and Col_h phases in the case of the 'two'- and 'three-chain' compounds (**K2NS** and **K3NS**). Thus the generation of mesomorphism by segregation of the fluorinated segments was found for these compounds, as well as the formation of mesophases with curved interfaces on enhancing the wedge-like character of the systems.

In this paper, we present the mesomorphic properties of the corresponding partially fluorinated one- and

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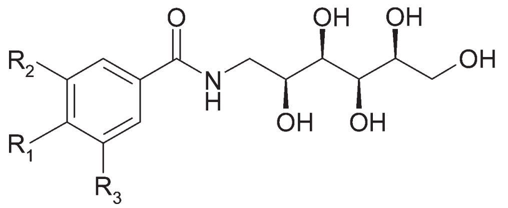
two-chain acids. The hydrolysis of the esters leads to carboxyl groups, which are capable of forming hydrogen bonds. As mentioned already, H-bonding has a strong influence on liquid crystalline phases. Here, we discuss aggregation via H-bonding, segregation by the fluorophobic effect, and the influence of molecular shape (anisometry) on the mesomorphism of these compounds. The results of investigations on the corresponding 'three-chain' acids **K3S** will be presented in the third paper of this series [29].

2. Results

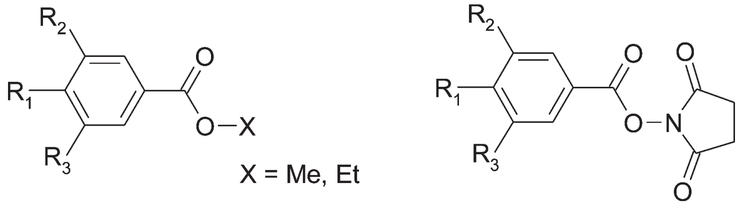
The synthesis of the compounds has been reported earlier in detail [28]. The structure of the investigated perfluoroalkyl alkyloxy-substituted benzoic acids is shown in figure 3. The acronym used to refer to the compounds contains the number of chains (**K1** or **K2**), the type of the compound (**S** for acid) and the chain length [***n*,*m***] (***n*** for the perfluoroalkyl chain and ***m*** for the alkyl chain). The mesomorphic behaviour of some one-chain acids **K1S** has already been described [4, 22, 24, 30–35], as has the behaviour of some members of the **K2S** series with shorter chain lengths forming monotropic $\mathrm{Col_h}$ phases [20]. Here, we describe the behaviour of new members of these homologous series.

The acids were investigated by means of differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD) of non-oriented samples. Additionally, temperature-dependent IR spectroscopy has been performed with the one-chain acid **K1S[6,5]**, in order to investigate the influence of H-bonding on the mesomorphism of this compound. The thermal data of the one-chain acids **K1S** are given in table 1, and the data of the two-chain acids **K2S** can be found in table 2. Both classes of compound exhibit liquid crystalline phases. In the case of the one-chain compounds SmC phases are observed. With two-chain acids, hexagonal columnar phases ($\mathrm{Col_h}$, space group *P6mm*) appear. All the mesophases are enantiotropic, although the columnar phases of the two-chain acids **K2S[8,11]** and **K2S[10,11]** appear only after careful annealing (see later). Mesophases were identified by their optical textures under POM and by XRD diffractograms of non-oriented samples. The X-ray



$R_1 = C_{12}H_{25}O$ $R_2,R_3 = H$ Cr 182 SmA 250 I
$R_1,R_2 = C_6H_{13}O$ R_3=H Cr 172 $\mathrm{Cub_{bi}}$ 185 I
$R_1,R_2 = C_{12}H_{25}O$ R_3=H Cr 162 $\mathrm{Col_h}$ 254 I
$R_1,R_2,R_3 = C_{12}H_{25}O$ Cr 94 $\mathrm{Cub_s}$ 227 I

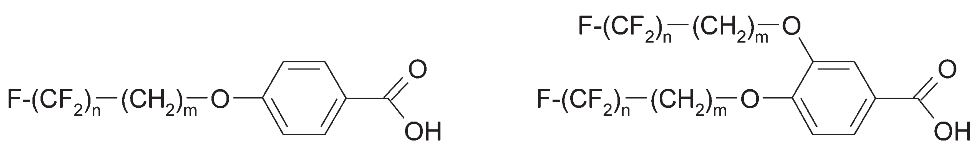
Figure 1. Example of the influence of the length and number of alkyl chain substituents on the phase type [27].



KxE[n,m] **KxNS[n,m]**

R_1, R_2, R_3:
H, $F\text{-}(CF_2)_n\text{-}(CH_2)_m\text{-}O$
x = 1,2,3

Figure 2. Partially fluorinated alkyl- and N-succinimidyl-benzoates **K*x*E[*n*,*m*]** and **K*x*NS[*n*,*m*]**.



K1S[n,m] **K2S[n,m]**

Figure 3. The one- and two-chain acids **K1S[*n*,*m*]** and **K2S[*n*,*m*]**.

Table 1. Transition temperatures T and enthalpies ΔH for the one-chain acids **K1S[*n,m*]**.

n,m	Cr	T/°C (ΔH/kJ mol^{-1})	SmC	T/°C (ΔH/kJ mol^{-1})	I	Lit.
12,4	●	212	—	—	●	[34]
10,10	●	172.0 (24.3)	●	178.0 (4.3)	●	
10,8[a]	●	183.0 (25.0)	●	190.0 (14.7)	●	
10,6[a]	●	195.5 (37.5)	—	—	●	
10,5[a]	●	195.5 (23.0)	●	200.0 (10.7)	●	
10,4	●	200	●	202	●	[34]
8,11[a]	●	148.5 (23.8)	●	171.0 (15.6)	●	
8,8[a]	●	158.0 (17.5)	●	175.0 (11.4)	●	
8,5[a]	●	175.5 (24.0)	●	186.5 (2.5)	●	
8,4	●	178.0 (3.4)	●	190.0 (2.8)	●	[34, 35]
8,2	●	209	—	—	●	[31]
7,4	●	168	●	187	●	[34]
6,11	●	129.5 (18.0)	●	162.0 (9.2)	●	
6,8	●	146.5 (15.7)	●	173.0 (7.2)	●	
6,6	●	160	●	178	●	[32]
6,5[a]	●	155.0 (12.4)	●	181.5 (10.7)	●	
6,4	●	162	●	183	●	[34]
6,2	●	198	—	—	●	[31]
4,4	●	146	●	170	●	[34]
2,4	●	134	●	153	●	[34]

[a]Before melting, several crystalline phases could be detected.

Table 3. X-ray data for the SmC phases of the one-chain acids **K1S[*n,m*]**. n,m = length of the perfluoroalkyl and the alkyl chain; T = measuring temperature, θ = angle of reflection with the indexation hkl = 001/002/003.

n,m	T/°C	Lattice constants/Å	θ/° measured *θ/° calculated*
6,5	170	c = 33.8 halo: d = 5.3	1.30/2.62/— *1.31/2.61*
6,8	167	c = 39.8 halo: d = 5.4	1.11/—/— *1.11/2.22*
6,11	160	c = 42.8 halo: d = 5.2	1.03/—/— *1.03/2.06*
8,5	180	c = 36.3 halo: d = 5.5	1.22/2.43/— *1.22/2.43*
8,8	171	c = 41.7 halo: d = 5.4	1.06/2.11/— *1.06/2.12*
8,11	165	c = 45.3 halo: d = 5.3	0.98/—/2.92 *0.97/1.95/2.92*
10,5	195	c = 42.0 halo: —[a]	1.05/—/— *1.05/2.10*
10,8	187	c = 45.0 halo: d = 5.5	0.98/—/— *0.98/1.96*
10,10	174	c = 46.8 halo: —[a]	0.95/1.87/— *0.94/1.89*

[a]Small angle measurement only with $\theta < 3°$.

results are listed in table 3 for the SmC phases and in table 4 for the columnar phases.

In the following discussion, only the behaviour of the annealed samples will be described. For **K1S** (figure 4) and **K2S** (figure 5), 3D bar diagrams with transition temperatures and phase types are shown. The comparison of the two plots shows that the influence of the perfluoroalkyl chain length n on the thermodynamic stability (higher transition temperatures) and the mesophase range is not the same for the two classes of acids. For one-chain acids **K1S[*n,m*]**, the thermodynamically most stable mesophase is observed with large n and small m. On the other hand, the broadest mesophase range can be found for short perfluoroalkyl chains (small n) and long alkyl segments (large m). Here, the influence of n and m on thermodynamic stability and mesophase range are opposite. In most cases in the literature, perfluoroalkyl chains are considered to stabilize LC phases and also to broaden them. However, these results have been found mostly for compounds with rather short perfluoroalkyl chains ($n < 8$). In the case of one-chain acids **K1S**, the fluoro content is still responsible for the suppression of nematic phases, as the non-fluorinated acids form both nematic and SmC phases [36]. On elongation of the fluorinated chain, the melting points increase faster than the clearing points, and hence the mesophase range becomes smaller.

Table 2. Transition temperatures T and enthalpies ΔH for the two-chain acids **K2S[*n,m*]**.

n,m	Annealing	Cr	T/°C (ΔH/kJ mol^{-1})	M	T/°C (ΔH/kJ mol^{-1})	I
6,8	—	●	88.0 (33.6)	—	—	●
6,11	without + with	●	102[a]	—	—	●
8,8[c]	—	●	98.0 (33.8)	Col$_h$	124.5 (1.5)	●
8,11	without	●	121.5 (62.3)	—	—	●
	with	●[b]	111.5 (35.1)	Col$_h$	140.0 (1.2)	●
10,8[c]	—	●	117.5 (45.0)	Col$_h$	151.0 (1.7)	●
10,11	without	●	138[a]	—	—	●
	with	●	128[a]	Col$_h$	161[a]	●

[a]Data from polarizing microscopy.
[b]T_g at 95°C.
[c]Before melting, several crystalline phases could be detected.

Table 4. X-ray data for the two-chain acids **K2S[*n*,*m*]**. *n*,*m* = length of the perfluoroalkyl and the alkyl chain; *T* = measuring temperature, θ = angle of reflection with the indexation *hk* = 10/11/20/21.

n,*m*	Phase	*T*/°C	Lattice constants/Å	θ/° measured θ/° *calculated*
8,8	Col_h	116	*a* = 42.6 halo: *d* = 5.5	1.20/2.07/2.39/— *1.20/2.07/2.39*
8,11[a]	Col_h	130	*a* = 45.3 halo: *d* = 5.5	1.12/1.96/2.26/— *1.13/1.95/2.25*
10,8	Col_h	140	*a* = 46.3 halo: *d* = 5.5	1.10/1.89/2.21/2.89 *1.10/1.91/2.20/2.91*
10,11[a]	Col_h	140	*a* = 48.0 halo: *d* = 5.5	1.06/1.85/2.13/— *1.06/1.84/2.12*

[a]annealed samples.

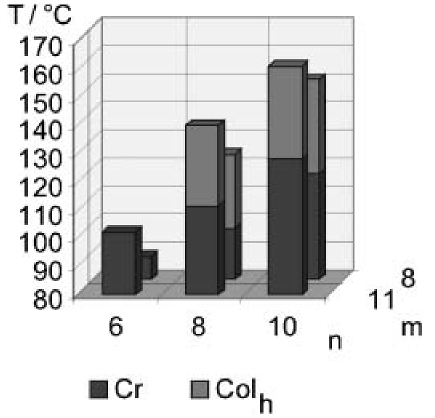


Figure 5. 3D bar plot of the mesophase behaviour of the two-chain acids **K2S[*n*,*m*]**. *n*,*m*: length of the perfluoroalkyl and the alkyl chain, respectively; data from table 2.

For the two-chain acids **K2S**, a slight stabilization of the mesophase on elongation of the perfluoroalkyl chains is also observed. Here, the analogous non-fluorinated acids do not form liquid crystalline phases [37]. Apparently, the segregation of the fluorinated chains is essential for the formation of mesophases. However, compared with the corresponding non-mesogenic fluorinated ethyl esters [28], it is obvious that both the segregative force and the aggregation via H-bonding are necessary for the mesomorphic behaviour. Furthermore, the two-chain acids **K2S** with their Col_h phases show that perfluoroalkyl chains can induce not only lamellar, but also mesophases with curved interfaces.

The one-chain acids **K1S** known from the literature and cited already form SmC phases. This has been confirmed for our additional homologues. The textures show characteristic marbled, schlieren and 'crocodile leather' areas (figure 6). The X-ray diffractograms exhibit equidistant reflections, indicating a layered morphology (figure 7). The tilt angle of the mesogens against the layer normal has been measured by two-dimensional XRD of oriented samples to be 40°.

In order to investigate the influence of H-bonding on the mesophase, we performed temperature-dependent IR spectroscopy with **K1S[6,5]** (figure 8). On increasing the temperature, small bands associated with free OH- and CO-groups appear above the melting point. Hence, a small amount of free acid is present already in the mesophase. The same result has been found by Babkov *et al.* for 4-perfluoroalkylcyclohexane carboxylic acids

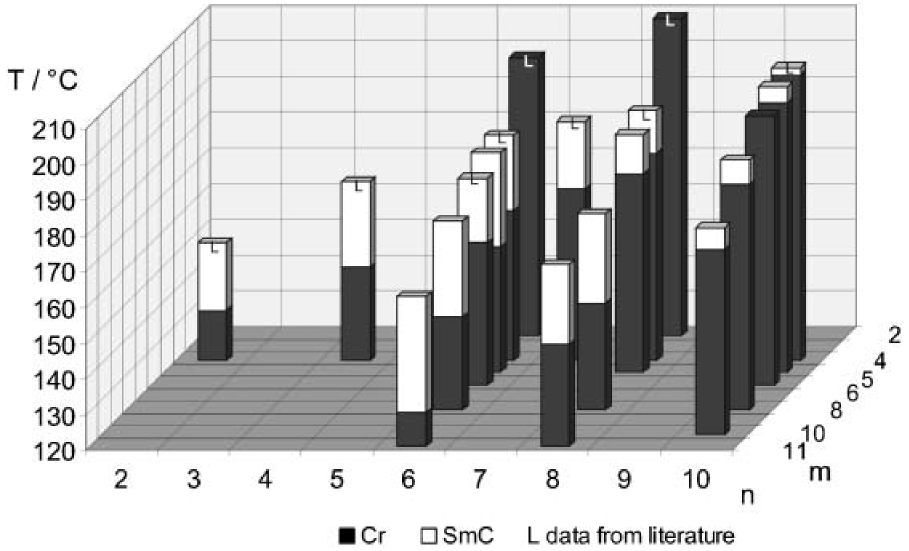


Figure 4. 3D bar plot of the mesophase behaviour of the one-chain acids **K1S[*n*,*m*]**. *n*,*m*: length of the perfluoroalkyl and the alkyl chain, respectively; data from table 1.

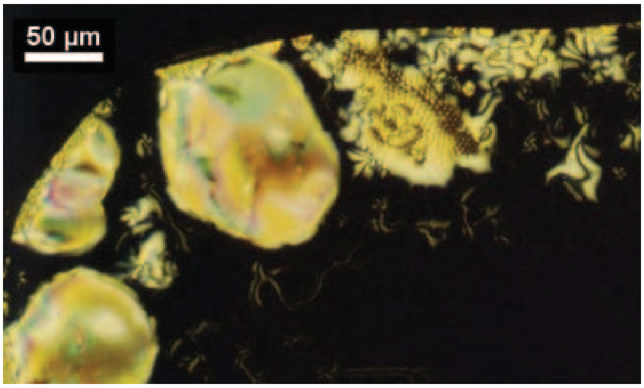


Figure 6. Marbled, schlieren and 'crocodile-leather' texture of the SmC phase of the one-chain acid **K1S[6,11]** at 160°C.

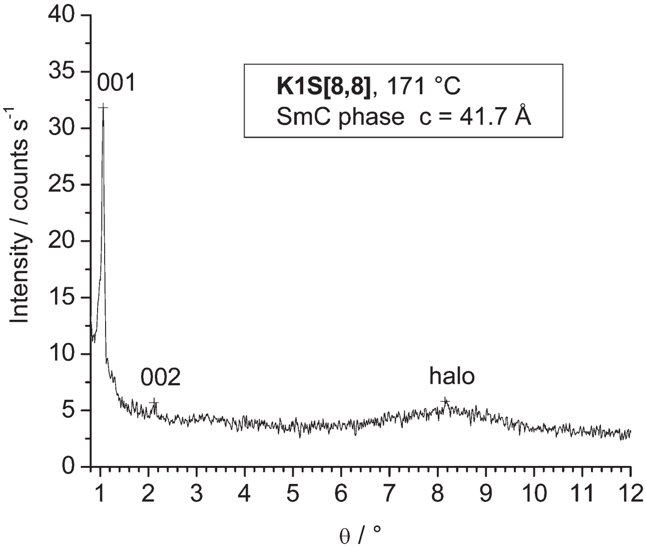
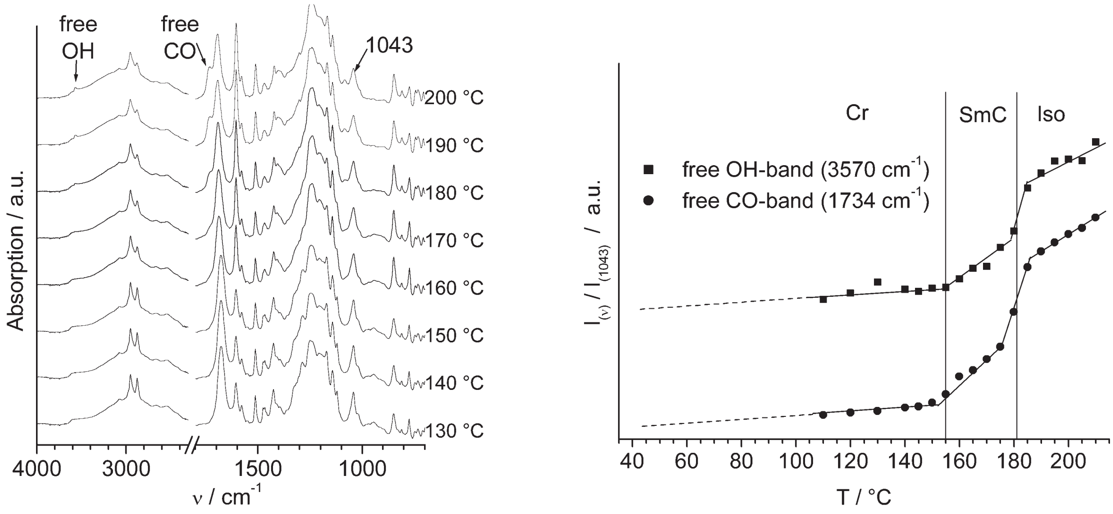


Figure 7. X-ray diffractogram of a non-oriented sample of the partially fluorinated acid **K1S[8,8]**.

[33]. The existence of monomeric acid may lead to a high intermolecular exchange of H-bonds within the double layer and consequently a sufficient mobility in the mesophase. On clearing, the intensity of these bands increases to a large extent, i.e. a large number of H-bonds disappear in the isotropic phase.

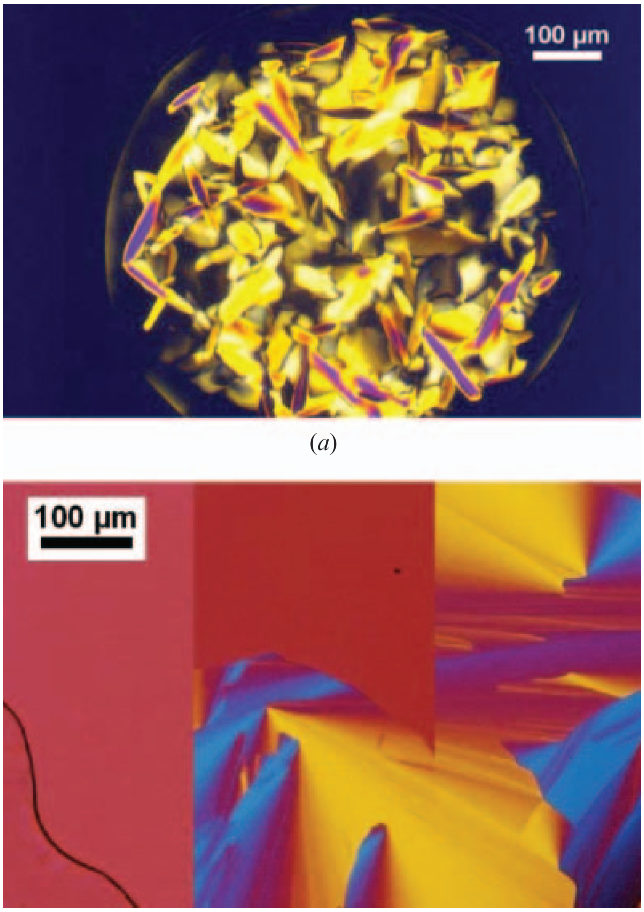
After increasing the wedge-shaped character of the compounds going from the one-chain acids **K1S** to the two-chain acids **K2S**, lamellar phases were no longer detected. The textures under POM consist either of smooth and large, or broken and lancet-like spherulitic structures (see figure 9). The diffractograms show reflections, which correspond to ratios of the layer distances d_{hk0} of $1:\frac{1}{\sqrt{3}}:\frac{1}{2}:\frac{1}{\sqrt{7}}$, cf. figures 10 and 13 (*b*), indicating a hexagonal columnar phase $\mathrm{Col_h}$ of the space group *P6mm*.

The LC phase of the two-chain acids **K2S[8,11]** and **K2S[10,11]** showed some peculiarities with respect to their thermal behaviour, as mentioned already. First, standard measurements in DSC (heating and cooling at 10°C min^{-1} without annealing) and POM exhibited only a melting of the crystalline phase Cr I into the isotropic liquid. Only annealing at 5 to 10°C *above* these melting points allowed the slow growth of the



(*a*) (*b*)

Figure 8. Temperature-dependent IR spectroscopy of the one-chain acid **K1S[6,5]**. (*a*) Spectra at different temperatures; normalization to the band at 1043 cm^{-1}. The most significant changes take place with the occurrence of free OH- and CO-groups. 130–150°C: Cr; 160–180°C: SmC; 190–200°C: I (*b*) Change in intensity of the bands of the free OH- and CO-group.



(*a*)

(*b*)

Figure 9. (*a*) Broken spherulitic texture of the Col_h phase of the two-chain acid **K2S[10,8]** at 149°C. (*b*) Development of a spherulitic texture (Col_r phase) of the two-chain acid **K2S[8,11]** on annealing at 123°C. From left to right: beginning, after 3 h, after 15 h.

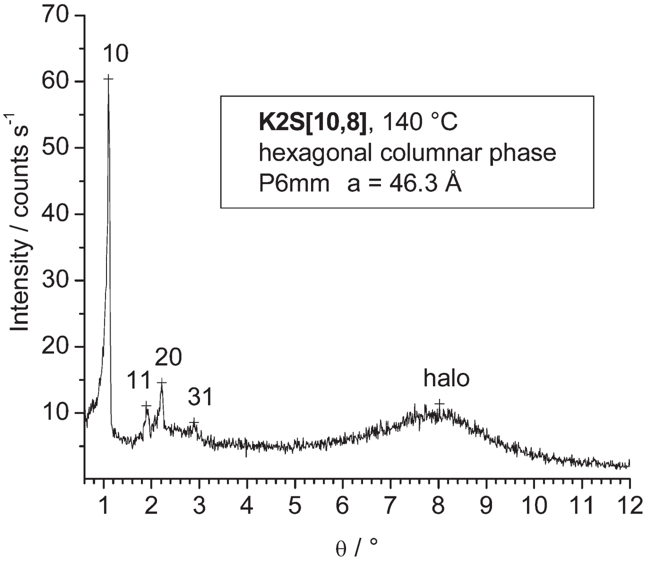


Figure 10. X-ray diffractogram of a non-oriented sample of the partially fluorinated acid **K2S[10,8]**.

columnar phase (see § 5). This development is shown in figure 9 (*b*) for the Col_h phase of **K2S[8,11]**. Complete transformation into this phase can be observed no earlier than after one day of annealing under these conditions. After the conversion, further heating and cooling cycles reveal a melting from the crystalline phase Cr II to the LC phase at a lower temperature, and a clearing to the isotropic phase at higher temperatures, than the previously detected melting point of Cr I. The NMR spectra of both the annealed and non-annealed samples of **K2S[10,11]** are identical, as shown in figure 11. Thus, the possibility of chemical reaction or degradation during the annealing process can be excluded. The DSC thermograms of the annealed samples were completely different from those of the non-annealed samples (see figure 12). After annealing, the transition temperatures were fully reproducible, even if the samples were heated to 50°C above the clearing temperature or stored at room temperature for several months.

Upon annealing, the X-ray diffractograms also show these changes (see figure 13). Before annealing, only an isotropic liquid phase is present, while after annealing, the typical pattern of the 10-, 11- and 20-reflections and the halo of a hexagonal columnar phase can be detected. However, the differences between the two crystalline phases do not seem to be very large.

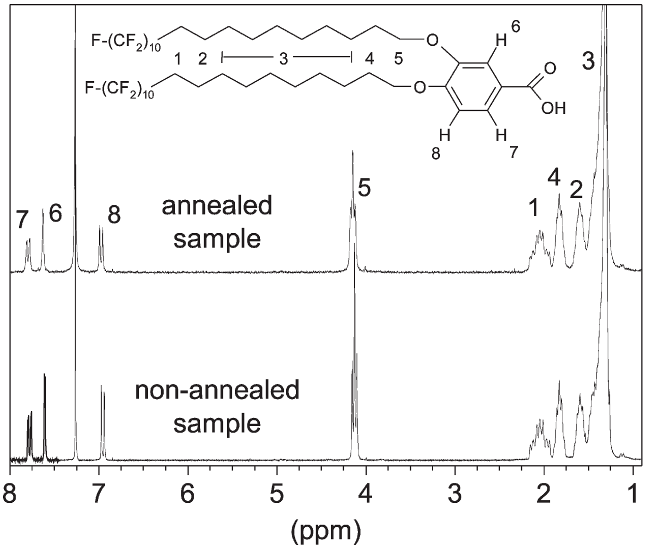


Figure 11. Comparison of the ^{1}H NMR spectra of the two-chain acid **K2S[10,11]** before and after annealing ($CDCl_3$/CF_3COOD = 10/1).

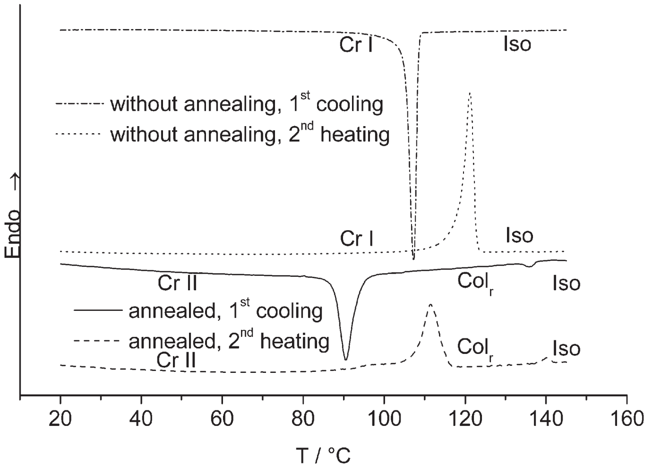


Figure 12. DSC thermograms (2nd heating and cooling at 10°C min^{-1}) of the two-chain acid **K2S[8,11]** before and after annealing.

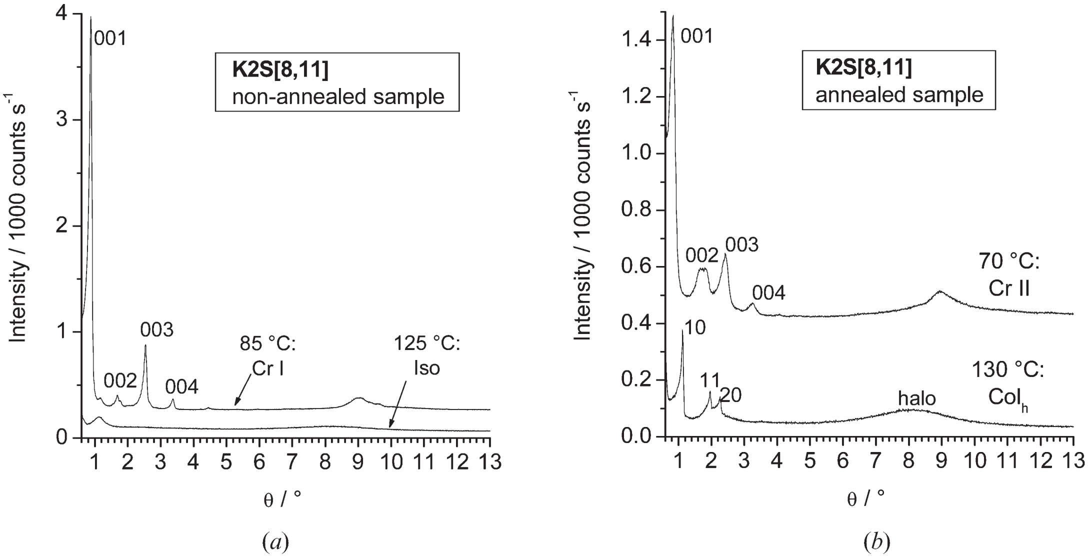
3. Discussion

The results from X-ray measurements and temperature-dependent IR spectroscopy of the one-chain acids **K1S** led to the modelling of a tilted arrangement of H-bonded dimers in the SmC phase. Molecular modelling (Cerius 2) of the acids with extended, all-*trans* alkyl and perfluoroalkyl chains gave the molecular length l_{Mol}. Assuming dimerization, and using the measured tilt angle of 40° of the aggregates with respect to the layer normal, the layer thickness L is given by the equation $L = 2l_{\mathrm{Mol}} \cos 40°$ (see table 5). These calculated values are slightly larger than the measured layer constants c. In reality, the alkyl chains are not in an all-*trans* conformation, but will exhibit several *gauche* defects. Consequently both, the modelled molecular length l_{Mol} and the modelled layer thickness L must be reduced to a certain extent, depending on the length of the alkyl chains. This can explain the differences between c and L. The resulting model is shown in figure 14.

Table 5. Modelling of the SmC phases of the one-chain acids **K1S[*n*,*m*]**. c = layer distance from measurement; l_{Mol} = molecular length from molecular modelling; L = calculated layer thickness with assumed dimerization and a tilt angle of 40°, $L = 2l_{\mathrm{Mol}} \cos 40°$.

n,*m*	c/Å	l_{Mol}/Å	L/Å
6,5	33.8	22.6	34.6
6,8	39.8	26.5	40.6
6,11	42.8	30.3	46.4
8,5	36.3	25.2	38.6
8,8	41.7	29.0	44.4
8,11	45.3	32.9	50.4
10,5	42.0	27.8	42.6
10,8	45.0	31.6	48.4
10,10	46.8	34.1	52.2

Thus, the fluorinated one-chain acids **K1S** behave comparably to the analogous non-fluorinated 4-alkyloxybenzoic acids [36]. One driving force for the generation of the mesophases (SmC and nematic) is the formation of anisometric dimers via H-bonding. Additionally, the fluorination of the alkyl chains leads to the suppression of the nematic phases and, mostly, to increased transition temperatures. Due to the layered morphology, the fluorinated chains lie parallel to each other, leading to an enhanced crystallization tendency. In consequence, on elongation of the perfluoroalkyl chains the melting points increase faster than do the clearing points. The mesophase range decreases with



(*a*) (*b*)

Figure 13. Comparison of the X-ray diffractograms of the two-chain acid **K2S[8,11]**; (*a*) before annealing, (*b*) after annealing.

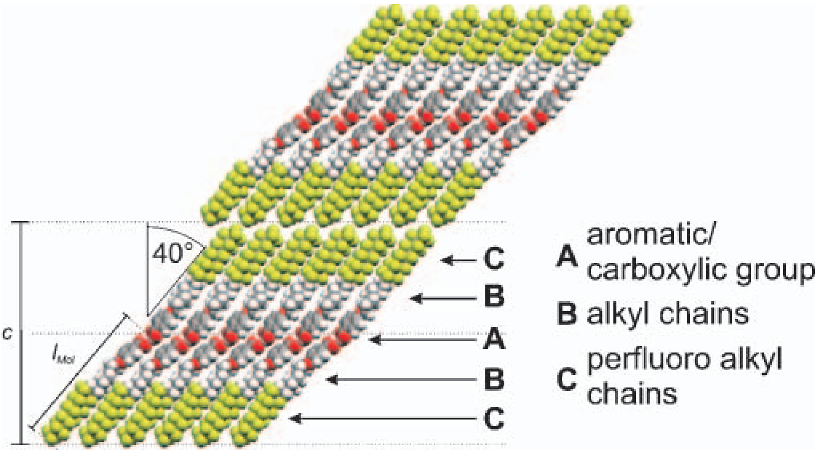


Figure 14. Model of the layer arrangement of the SmC phase of the one-chain acids **K1S**.

increasing perfluoroalkyl chain length, as described already.

In the case of the fluorinated one-chain methyl esters **K1E** (see figure 2), which exhibit monotropic SmA phases [28], only the segregation of the fluorinated chains remains as the driving force for their mesomorphism. Thus, in the case of all one-chain benzoic compounds, only one of the two principles is necessary for the generation of a LC phase: either aggregation via H-bonding *or* segregation by perfluoroalkyl chains.

Modelling of the columnar phases of the two-chain acids **K2S** had to be done in a different way. The knowledge of either the density ρ and the molecular mass M or the molecular volume V_{Mol} together with assuming the thickness of a lattice element (cross-section through the column) to be 4 Å, allows the calculation of N, the number of molecules per unit cell or per lattice element. The density ρ has been generally set to $1\,\mathrm{g\,cm^{-3}}$: density measurements with **K2S[8,11]** revealed this value. A hexagonal columnar unit cell consists of one lattice element. The method of calculation is described in detail in the preceding paper for the corresponding alkyl and succinimidyl esters [28]. The results of the calculation are listed in table 6.

The calculation of N_{M} and $N_{\Delta V}$ yields values between 3 and 4. These values allow a rounding off to $N=3$ or up to $N=4$. But as the well known dimer formation of carboxylic acids seems not to favour an odd number of molecules in a lattice element, the presence of four molecules — i.e. two dimers ($N=4$) — is probable. In the case of a hexagonal cell, the columnar shape is circular and the molecules have on average to be distributed radially around a centre. The resulting model for the two-chain acids **K2S** is shown in figure 15.

The fact that the $\mathrm{Col_h}$ phase of the two-chain acids **K2S[8,11]** and **K2S[10,11]** appears only after annealing in the isotropic phase just above the melting point, is unusual. From the X-ray diffractograms we can conclude that the phases Cr I and Cr II are not very different. Nevertheless, the $\mathrm{Col_h}$ phase apparently does not easily appear from the 'virgin' phase Cr I. Only after long annealing (one day 5–10°C above T_{m} of Cr I) or directly on heating from the Cr II phase (with T_{m} around 10°C lower than that of Cr I), the hexagonal columnar phase is formed. The reason must be kinetic and not thermodynamic. Because the transition peaks in DSC are rather narrow, the need to annealing cannot arise from a slow liquid crystal growth from the isotropic phase above the virgin phase Cr I, but only by a considerably slower rate of formation of the first hexagonal columnar nuclei, at a temperature that is, on the other hand, around 10–15°C lower than the clearing temperature of the $\mathrm{Col_h}$ phase, once formed. By contrast, the transition on heating from the crystalline phase Cr II to $\mathrm{Col_h}$ is realized with no hindrance. Apparently, nuclei for the $\mathrm{Col_h}$ phase are much more easily and quickly formed from the Cr II phase than in the isotropic phase after melting of Cr I, at a

Table 6. Number of molecules N per motif in the columnar phases of the two-chain acids **K2S[*n*,*m*]**. a,b = measured lattice constants; N_{M} and $N_{\Delta V}$ = calculated number of molecules per lattice unit. N_M has been calculated using the molecular mass M and the density ρ. Volume increments ΔV and the molecular volume V_{Mol} have been used for $N_{\Delta V}$. N is the rounded average of N_{M} and $N_{\Delta V}$.

n,*m*	Phase	a/Å	$M/\mathrm{g\,mol^{-1}}$	N_M	$V_{\mathrm{Mol}}/\mathrm{Å^3}$	$N_{\Delta V}$	N
8,8	$\mathrm{Col_h}$	42.6	1214	3.1	934	3.7	4
8,11	$\mathrm{Col_h}$	45.3	1298	3.3	1037	3.8	4
10,8	$\mathrm{Col_h}$	46.3	1414	3.2	1064	3.5	4
10,11	$\mathrm{Col_h}$	48.0	1498	3.2	1166	3.8	4

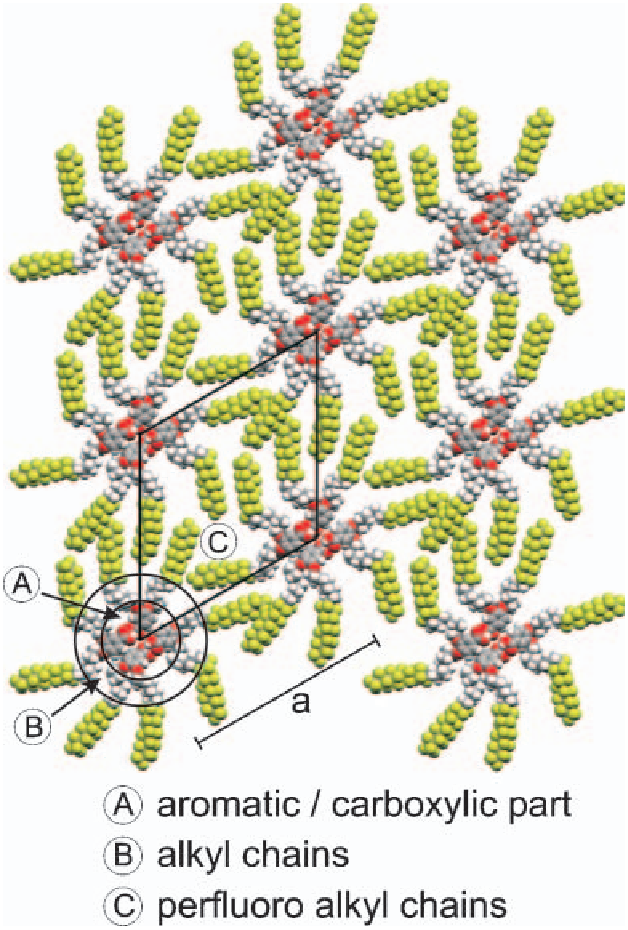


Figure 15. Model of the radial arrangement of two-chain acids **K2S** to one lattice element of the hexagonal columnar unit cell.

temperature 10–15°C lower than the 'regular' transition at around 137°C after the annealing procedure.

The slow appearance of the columnar phase of the two-chain acids **K2S[8,11]** and **K2S[10,11]** on annealing could only be observed in preparations with high interfacial forces, i. e. in thin layers between two glass plates. Here, at 5 to 10°C *above* their melting points with respect to Cr I a sufficiently high annealing rate was achieved. Attempts to obtain the hexagonal columnar phase after similar annealing in, for example, DSC pans were unsuccessful. This again supports the assumption of the unusual importance of a nucleation process for the formation of the $\mathrm{Col_h}$ from the isotropic phase after the virgin crystal phase Cr I.

4. Conclusion

With the presented perfluoroalkyl alkyloxy-substituted one- and two-chain benzoic acids **K1S** and **K2S**, the different possibilities of perfluoroalkyl chains in generation and stabilization of microsegregated liquid crystalline phases are shown. In layered morphologies, longer perfluoroalkyl chains decrease the mesophase range due to an enhanced crystallization tendency [31]. Temperature-dependent IR spectroscopy, as well as modelling of the SmC phase of the one-chain acids **K1S**, reveal a similarity with their non-fluorinated analogous 4-alkoxybenzoic acids: the H-bonded dimers play the major role in stabilizing the smectic phase. The perfluoroalkyl chains mainly suppress nematic phases.

Although the perfluoroalkyl chains are known to be rather stiff, the columnar phases of the two-chain acids **K2S**, with their highly curved interface, are thermodynamically reasonably stable. This is due to the strong segregative force of the fluorinated segments with respect to the apolar alkyl and the polar carboxylic segments. This strong segregation is not present in the non-mesomorphic analogous compounds: fluorinated ethyl esters (no strong polar unit) and the simple two-chain alkoxybenzoic acids (no fluorinated part). With a wedge-like shape of the molecules in the two-chain acids **K2S**, the microsegregation leads to hexagonal columnar phases of the space group *P*6*mm* ($\mathrm{Col_h}$).

Hence, perfluoroalkyl chains demonstrate two concurrent properties: the crystallization tendency lowers the mesophase range (**K1S**), while the fluorophobic effect enhances it by segregation (**K2S**).

5. Experimental methods

The synthesis and chemical characterization of the one-chain and two-chain acids **K1S[*n*,*m*]** and **K2S[*n*,*m*]** was described in the previous paper of this series [28].

Temperature-dependent infrared spectra were recorded with a Bio-Rad FTS 40 FTIR spectrometer at a resolution of $4\,\mathrm{cm^{-1}}$. The samples were prepared by melting a small portion of compound upon a silicon wafer, and covering the wafer with a pellet of KBr. Then, the samples were heated under inert atmosphere (nitrogen) with a heating device from Specac Ltd, England, with a resolution of ±2°C. The spectra were evaluated by a parabolic base-line correction and normalized to an indifferent band.

^{1}H NMR spectra were measured from solution in a mixture of chloroform-*d*/trifluoroacetic acid-*d* (10/1) on a Bruker AC 250 spectrometer (250 MHz) with TMS (tetramethyl silane) as an internal standard.

A Perkin Elmer DSC 7 was used for thermal analysis (DSC), standard heating rate was $10^\circ\mathrm{C\,min^{-1}}$. Polarising microscopy was performed on a Nikon Diaphot 300 with hot stage Mettler FP82. Photographs were taken with a Nikon F4 camera.

X-ray diffractograms were obtained with a Guinier diffractometer from Huber with a scintillation counter. The standard resolution was 0.01° with 20 s data collection per step. The X-ray tube contained a copper anode with a quartz crystal as monochromator ($CuK_{\alpha1}$ radiation, $\lambda = 1.54051$ Å) from Seifert. The samples were prepared in glass capillaries of 1 mm diameter. The 2D-diffractogram was registered together with S. Diele, Institut f. Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, Germany, with a 'HI-STAR-Flächendetektor' from Siemens (method: proportional counting ionization chamber). The samples were oriented on a germanium wafer.

Molecular modelling was performed with the software 'Cerius 2' from msi.

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