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Thermotropic liquid crystalline properties of amphiphilic branched chain glycolipids

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Glycolipids are amphotropic liquid crystals forming lyotropic liquid crystals in aqueous solutions and thermotropic liquid crystals in their dry form. We report studies on the thermotropic properties of seven different neat glycolipids: four maltoside, two glucoside and one pyranoside lipids. Optical birefringence, electrical conductivity, differential scanning calorimetry, and dielectric spectroscopy measurements were employed to characterize the phase structures of the materials. In general, they exhibit a wide (>100°C) mesophase (smectic, columnar) range with low (0.01–0.04) birefringence. They have large (60–120) dielectric susceptibility basically proportional to the number of polar sugar heads. Depending on the temperature the relaxation frequency of the susceptibility varies between <100 Hz and >1 MHz, mainly determined by the hydrogen bonding between the polar sugar heads.

1. Introduction

Glycolipids are one of the three lipids found in biological cell membranes. They contain polar (hydrophilic) sugar head groups and apolar (hydrophobic) alkyl chains. Glycolipids can be isolated from living materials, such as marine sponges [1], or can be synthesized chemically or enzymatically [2]. Some have immune-stimulating activity, making them candidates for anti-cancer drugs [3]; they play a role in cell fusion [4, 5] and in cell surface recognition processes [6].

Lyotropic properties of synthetic glycolipids have been extensively studied in the last decade but studies of their thermotropic states are scarce [7, 8]. Their thermotropic mesophases are stabilized by the hydrogen bond-forming ability of the polar moiety [2], which is highly sensitive to temperature. In their thermotropic form they often exhibit a smectic A phase with fluid bilayers [9], where the double layer spacing is consistently found to be smaller than two molecular lengths [10]. These observations lead to the now widely accepted structure in which the alkyl chains partially overlap to form interdigitated smectic A_d bilayers [11]. However, the layer periodicity can also be explained by a locally tilted layer structure, where the tilt direction of the different layers is uncorrelated, resulting in the orthogonal smectic appearance, similar to the de Vries smectic A phase of thermotropic liquid crystals with aromatic cores [12].

Other than their phase structures, very little is known about the macroscopic physical properties of thermotropic lipids, which justifies our study of their optical and dielectric properties in sandwich cell geometries. We compare their observed physical properties with those of typical thermotropic liquid crystals with aromatic cores, and explain most of the differences in terms of their molecular structures.

2. Structures and phase properties

We have studied six branched chain sugar lipids; four of them have one sugar head (glucosides) and two have two sugar heads (maltosides). In naming these materials we used the notation $C_{m\text{-}n}$,G_k, where m and n give the number of carbon atoms in the longer and shorter chains of their tails, respectively, and k is the number of sugar heads (k=1 corresponds to glucosides, k=2 denotes the maltosides). The synthesis and purification method of the materials, among other similar branched lipids, is published elsewhere [13]. As a control material we also have studied dodecyl-β-D-glucopyranoside ($C_{12}G_1$), purchased from Sigma Aldrich. It has a single

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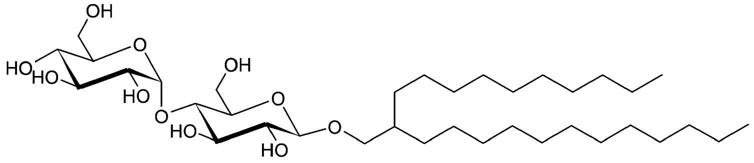
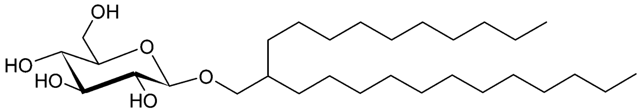
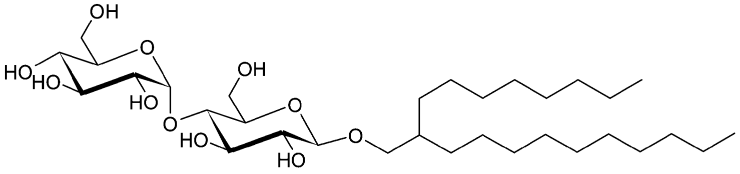
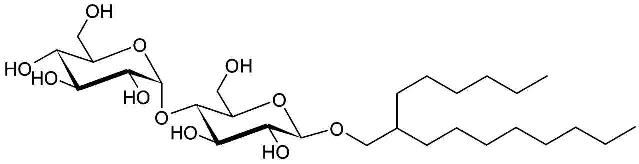
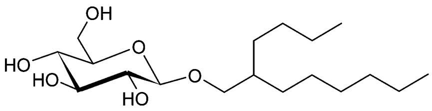
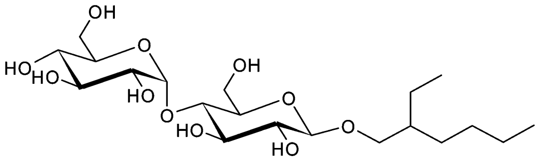
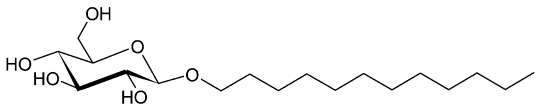
hydrocarbon chain with 12 carbons. The materials are hygroscopic, and their phase sequences are very sensitive to humidity. For this reason special care was taken to dry the materials before measurements.

Differential scanning calorimetry (DSC) and electrical conductivity measurements were used only to identify a phase transition; the phase assignments were mainly based on polarizing optical microscopy (POM) studies. The names, molecular structures and phase sequences above room temperature during heating and cooling, as determined from the combination of DSC, POM and electrical conductivity measurements, are listed in table 1.

All the branched chain materials had very wide mesophase ranges from below room temperature to above 100°C, with clearing temperatures increasing with increasing molecular mass. The materials with the shortest branched chains ($C_{8\text{-}4}G_1$ and $C_{6\text{-}2}G_2$), and the single chain $C_{12}G_1$, exhibit only one broad smectic phase, whereas those with longer branched chains show transitions between columnar and smectic phases. The textures on cooling typically consist of much larger

Table 1. Materials studied and their phase sequence (transition temperatures in °C) based on DSC, polarizing microscopy and electrical conductivity measurements. The phase sequence is given above room temperature during heating (upper rows) and cooling (lower rows) at 2°C min^{-1} heating/cooling rates.

Compound	Structure	Phase sequence
$C_{14\text{-}10}G_2$		Cr <23 SmA 85 Q 135 Col 233 I I 230 Col 80 SmA <23 Cr
$C_{14\text{-}10}G_1$		Cr <23 SmA (69 Q) 91 Col 173 I I 172 Col 50 SmA <23 Cr
$C_{12\text{-}8}G_2$		Cr <23 SmA 142 Q 203 I I 200 Q 140 SmA <23 Cr
$C_{10\text{-}6}G_2$		Cr <23 SmA 92 Col 191 I I 190 Col 90 SmA <23Cr
$C_{8\text{-}4}G_1$		Cr <23 SmA 131 I I 131 SmA <23Cr
$C_{6\text{-}2}G_2$		Cr <23 SmA 135 I I 133 SmA <23 Cr
$C_{12}G_1$		Cr 80 SmA 143 I I 140 SmA 75 Cr

domains than on heating, facilitating a better phase assignment. We found that at the transition to the mesophase sword-like domains form, the fully developed textures typically consisting of leaf-type fan-shaped domains resembling thermotropic columnar phases. This texture is clearly different from that found in the single chain $C_{12}G_1$, which forms classical fans typical for SmA and SmC materials in bookshelf geometry. The lower temperature phases of the first four materials resemble the smectic A phase in bookshelf alignment.

In the case of the longest tail materials, during heating between 85°C and 135°C (for $C_{14\text{-}10}G_2$) or between 69°C and 91°C (for $C_{14\text{-}10}G_1$), the texture becomes dark between crossed polarizers (in fact for $C_{14\text{-}10}G_2$ the texture is completely optically isotropic, see figure 1). This optically isotropic phase can be identified as cubic [8, 13]. The cubic phase does not appear on cooling, which represents another unusual feature of these materials, since other thermotropic liquid crystals always display fewer phases on heating than on cooling. The cubic phase is kinetically hindered and often fails to appear. In $C_{12\text{-}8}G_2$, the cubic phase appears just below the fluid isotropic phase, see figure 2 (*e*) and (*f*). In this case the transition to the isotropic fluid phase is in visible in POM, but is clearly seen in DSC and by the sudden change in the fluidity [13].

From the colour of the films placed between crossed polarizers (in comparison with the Michael–Levi colour chart), we deduce that all of the studied glycolipids have birefringences smaller than 0.05, which is several times smaller than is usual for calamitic materials. Because of the weak birefringence, in addition to thin films of 5–20 μm thickness, we also studied the materials in rectangular capillaries of 0.5 mm internal thickness. The birefringences are particularly small for molecules with longer tails, indicating more disorder of the hydrophobic chains than of the polar heads. Partly due to the lack of the nematic phase, these materials typically do not form aligned textures between rubbed polymer surfaces, (see example in indicating the weak influence of the surface alignment layer on the material, see figures 2 (*a*, *b*, *e*)). This is probably due to the hydrophobic nature of the polymer coating, which leads to preferred contact with the more disordered hydrophobic tails. This argument could also explain why $C_{8\text{-}4}G_1$, which has a short branched tail, becomes aligned in rubbed polyimide surfaces, see figures 2 (*c*, *d*).

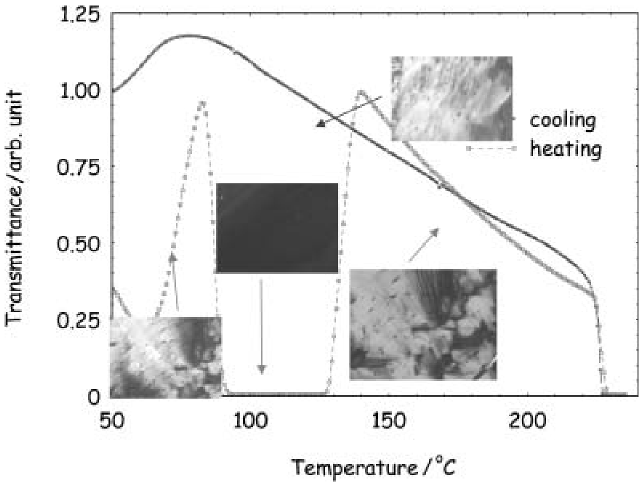


Figure 1. Transmittance vs. temperature for $C_{14\text{-}10}G_2$ in a 0.5 mm thick rectangular capillary.

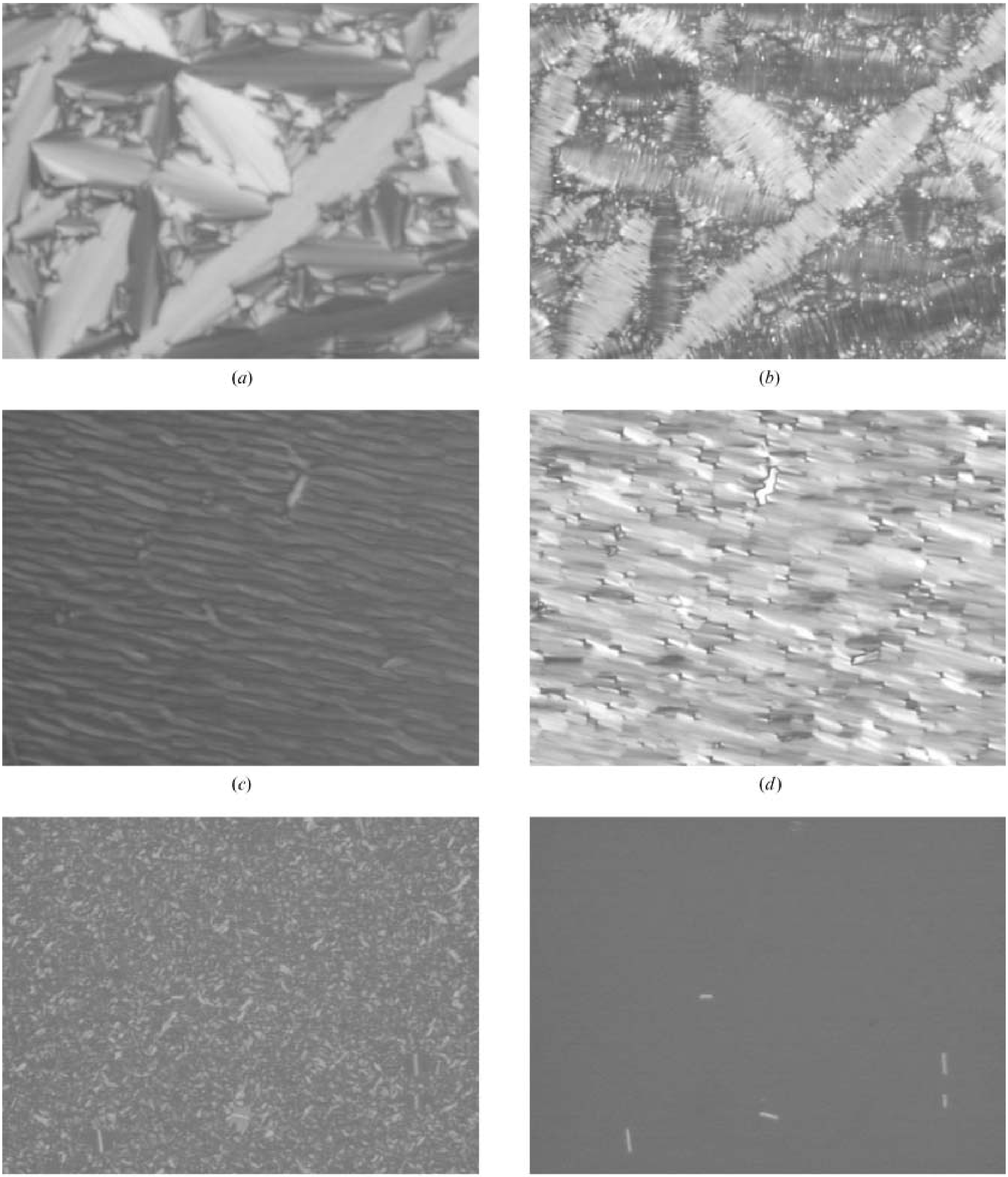
We tested the textures under the application of up to 30 V μm^{-1} low frequency electric fields across the films. No linear electro-optical switching could be observed, which indicates that the smectic A phase is not of the de Vries type, otherwise an electro-clinic effect would be seen.

3. Dielectric properties

Dielectric measurements were carried out in 5 μm cells with polyimide substrates on all the materials listed in table 1, except for $C_{14\text{-}2}G_2$ which could not be filled into cells without the formation of air bubbles. All the materials studied exhibit much larger static dielectric susceptibilities than conventional calamitic dielectric liquid crystalline materials. The susceptibilities are correlated to the number of sugar head groups: the dielectric susceptibilities of glucosides (1 sugar head) are about 55–60, while those of the maltose compounds (2 sugar heads) are in the range 90–110.

Figure 3 shows the frequency dependence of the real part of the dielectric permittivity at 30°C below their clearing points for all the materials studied. These results show that the static susceptibility is primarily determined by the number of sugar head groups, although the effect of the chains is also noticeable. Representative dispersion curves for a glucoside and a maltoside compound are shown in figure 4. The relaxation processes in the glucosides become more distributed at lower temperatures, whereas for the maltosides the height and the width of the peaks are almost temperature-independent.

The temperature dependences of the relaxation frequencies are plotted in figure 5. The relaxation frequencies strongly depend on temperature, and on the structure of the phase. Typically maltosides have an order of magnitude lower relaxation frequencies than the glucosides. Comparing the activation energies in the columnar phases, we see that they are approximately 2 kcal mol^{-1} in glucosides and 5 kcal mol^{-1} in



(a) (b)

(c) (d)

(e) (f)

Figure 2. Polarizing microscopic textures of 5 μm cells with inner surfaces coated with antiparallel rubbed polyimide alignment layer. $C_{14\text{-}10}G_1$ at (*a*) 90°C and (*b*) 46°C; $C_{8\text{-}4}G_1$ at (*c*) 126°C and (*d*) 40°C. $C_{12\text{-}8}G_2$ at (*e*) 90°C and (*f*) 143°C.

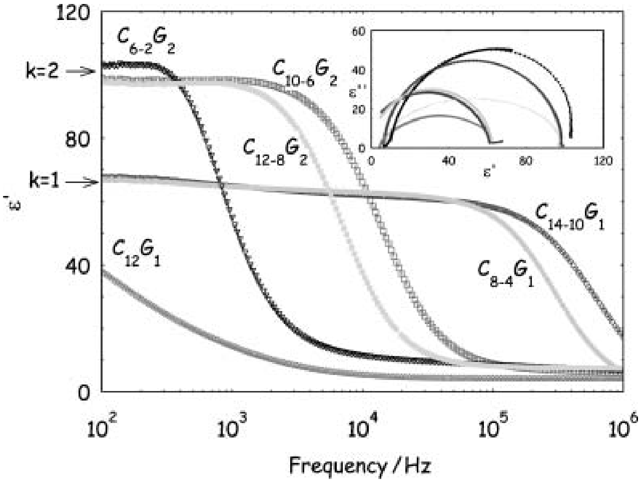


Figure 3. Dielectric dispersions of the materials studied at 30°C below their clearing points. The insert shows the corresponding Cole–Cole plots. (sample thickness 5 µm, bookshelf alignment).

maltosides. This again correlates with the number of sugar heads. However, in the smectic phases they are approximately 10 kcal mol^{-1} (except for $C_{14\text{-}10}G_1$, where it is 17 kcal mol^{-1}) independent of the number of heads, or branching. The activation energy is smallest in the isotropic phase, larger in the columnar phase and largest in the smectic mesophase. In a given phase the activation energy decreases with increasing chain length, and appears to be smaller in the branched chain than in the single chain substances (compare $C_{12}G_1$ with $C_{12\text{-}8}G_1$).

4. Discussion

The thermotropic liquid crystalline properties of the amphiphilic sugar lipids differ in a number of respects from the properties of conventional thermotropic liquid crystals. They have lower birefringence and show a tendency to align homeotropically on rubbed polymer surfaces, which for conventional thermotropics tend to promote planar alignment. This is due to the amphiphilic nature of the sugar lipids, where the polar heads tend to avoid contact with the hydrophobic polymer surface. The sugar lipids with branched chains have a very wide mesophase range, with a tendency to form a columnar phase at higher, and a smectic A phase at lower temperatures. Note that in contrast to normal calamitic thermotropic liquid crystals, in sugar lipids the smectic A phase is more ordered than the columnar phase. This is due to the random orientation and greater flexibility of the tail groups at higher temperatures. In this way the tails occupy a larger space than the polar heads, thus stabilizing the columnar phase. Such model structures of the molecular arrangements in the SmA and columnar phase with hexatic columnar packing are illustrated in figure 6.

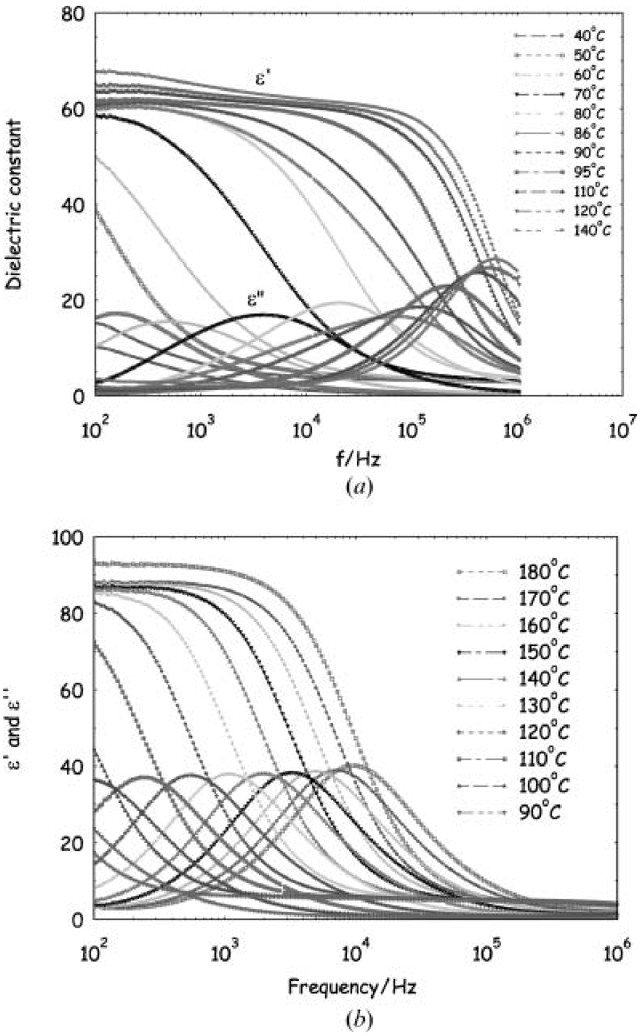


Figure 4. Dielectric spectra of (*a*) $C_{14\text{-}10}G_1$ and (*b*) $C_{12\text{-}8}G_2$. The data were obtained during heating.

The appearance of quasi-isotropic textures during the heating of $C_{4\text{-}10}G_2$ and $C_{14\text{-}10}G_1$ is due to a cubic structure, which is quite common in lyotropic materials, but rather unusual for thermotropic liquid crystals.

The dielectric susceptibility of amphiphilic sugar lipids is much higher than that of thermotropic dielectric smectic and columnar liquid crystals with aromatic cores [14]. The strong correlation between the number of sugar heads and the magnitude of the susceptibility shows that polar head groups are very important for the field-induced polarization. This relationship is only slightly modified by the non-polar hydrocarbon chains. We note that such high susceptibilities are observed only in connection with the so-called Goldstone mode of helical ferroelectric SmC* liquid crystals [15], suggesting that these materials may

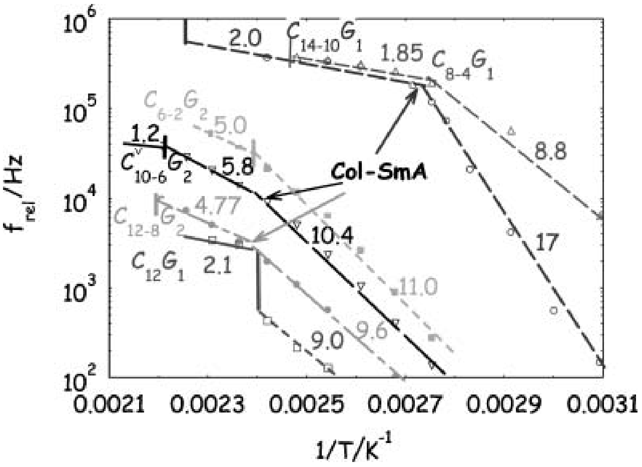


Figure 5. Relaxation frequency in logarithmic scale as a function of 1/*T*. Linear slopes correspond to Arrhenius behaviour. Vertical bars indicate the isotropic to mesophase transition (clearing point). The numbers above the lines give the corresponding activation energy, which is determined by the slope of the relaxation frequency, in logarithmic scale as a function of inverse absolute temperature, in kcal mol^{-1}.

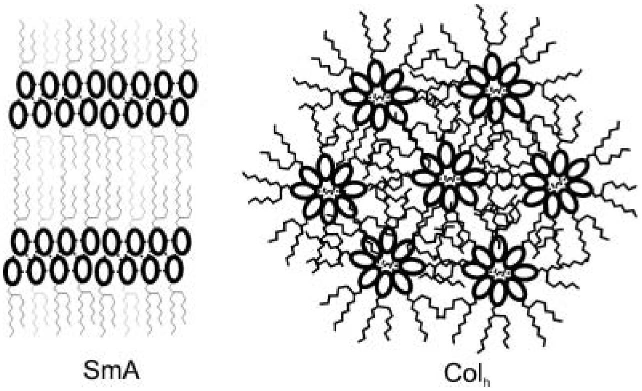


Figure 6. Model structure of molecular packing in the SmA and Col$_h$ (columnar structure with hexagonal lattice) phase. Ellipses represent the polar sugar head(s) and the zigzag lines illustrate the hydrocarbon tails. Dashed lines qualitatively illustrate the hydrogen bonding between polar heads.

also have tilted chiral smectic structures instead of orthogonal smectic or columnar phases. (Indeed our previous studies [14] suggested that $C_{12}G_1$ may have a locally tilted smectic structure, where the tilt direction of the different layers is not correlated.) The observation that in these materials the magnitude of the quasi-static dielectric constant is basically independent of the phase transitions, and persists even in their isotropic phase, shows that it is related to the molecular properties (such as polarity of head groups) rather than to phase structures. The temperature dependence of the relaxation times also differs from that of the Goldstone modes in SmC* materials: there it is almost temperature independent; here a strong temperature dependence is seen, that can be described by Arrhenius behaviour (see figure 5). We propose that strongly temperature-dependent low relaxation frequencies are due to hydrogen bonding between the head groups. Among the branched tail materials the relaxation frequency is larger for the glucosides, indicating that the size of the hydrogen bonds is smaller than for the maltosides. This is understandable, since the maltosides have twice as many bonds which can be linked to other heads. The activation energy generally increases with increasing order. In sugar lipids the smectic phase is more ordered than the columnar phase; we anticipate that the activation energy increases and the relaxation frequency decreases through transitions from the isotropic to the columnar, and then to the smectic phase. This is indeed seen in figure 5.

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