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Tilted supramolecular structures of amphiphilic glycolipids in straight-core smectic C liquid crystals

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Optical microscopic and the electric polarization studies show that amphiphilic glycolipids form tilted supramolecular structures in straight-core tilted smectic liquid crystals. Glycolipid and chiral smectic C (SmC) structures show spontaneous polarization while glycolipid and non-chiral SmC structures show no spontaneous polarization. We deduce from these observations that glycolipid molecules in chiral SmC structures nano-segregate in tilted double layers sandwiched between layers of straight-core liquid crystal molecules. In non-chiral SmC structures, tilted glycolipid molecules are nano-segregated in the layers of straight-core liquid crystal molecules. This indicates that, in contrast to the currently accepted interdigitated model, amphiphilic glycolipids may already have a tilted structure.

1. Introduction

Amphiphilic glycolipid molecules consist of polar (hydrophilic) head groups and apolar (hydrophobic) alkyl chains. Due to their polar asymmetry, the head groups and the alkyl chains self-aggregate into microscopic regions forming liquid crystalline (LC) phases. They are also amphotropic due to their polar asymmetry. They form LC phases in their pure form as the temperature is varied, and in solvents as the concentration is varied. The LC phases formed in an aqueous medium are of great interest, in particular because of the role they play in biological cell membranes [1]. The LC properties of glycolipids in the lyotropic form have been rigorously studied in the last decade, but have been little studied in their thermotropic form.

Glycolipids can be isolated from living materials such as marine sponges [2], or can be synthesized chemically or enzymatically [3]. Thermotropic LC phases of glycolipids were first observed in alkyl glucopyronosoids, for example, hexadecyl-β-D-glucopyronosoids [4]. They are known to from smectic, columnar and cubic phases. The smectic phase is believed to be similar or identical to the lamellar (L_α) phase they form in an aqueous medium; the columnar hexagonal (Col_h) phase is believed to resemble the inverted hexagonal phase they form in an aqueous medium [5]. In the cubic phase, rod-like, spherical or lamellar-shaped aggregates form three dimensional lattices [6]. The smectic and columnar phases are optically anisotropic while the cubic phase is optically isotropic. In spite of being chiral, only a few amphiphilic glycolipids are known to exhibit a cholesteric phase in the lyotropic form. The role of chirality in the thermotropic phase of these materials is largely unknown.

The structure of the glycolipid bilayers was studied by powder diffraction measurements, which showed diffuse rings of scattering commonly associated with smectic A and C phases. In all such materials, the measured layer spacing was larger than the length of one molecule, indicating the formation of double layers. However, the length of the double layers was less than the length of two molecules. It is generally accepted that the hydrogen bond-forming ability of the polar moiety is crucial to the formation of mesophases in amphiphilic derivatives [7]. Therefore, it was concluded that polar moieties overlap to produce an interdigitated smectic A phase known as smectic A_d [8, 9]. Later it was suggested that the stability of the hydrogen bonds of hydroxyl groups is particularly sensitive to temperature, due to their orientational freedom [10]. This observation led to the now widely accepted structure in which the alkyl chains partially overlap to form the core of the smectic A_d bilayers and polar moieties are on the outside [11]. However, alkyl chains are not known to overlap in other LC systems.

Recently it was found that the glycolipid dodecyl-β-D-glucopyranoside ($C_{12}G_1$) forms double layers sandwiched between antiferroelectric bent-core ('banana-shape') LC layers [12]. X-ray and polarization measurements revealed that in the bent-core environment the

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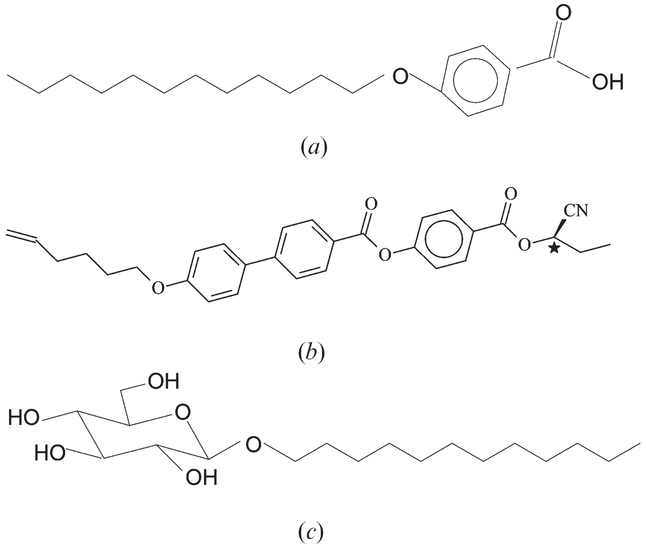


(*a*)

(*b*)

(*c*)

Figure 1. Chemical structure of (*a*) C_{12}, (*b*) 9B and (*c*) $C_{12}G_1$.

glycolipid double layers exhibit a tilted configuration in which the chiral glycolipid molecules are tilted with respect to the layer normal, giving rise to spontaneous polarization. In its pure form, however, $C_{12}G_1$ does not show macroscopic polarization. In order to determine whether the tilt of the glycolipid is due to the influence of the bent core molecules, or they already have a tilted structure, we investigated the optical microscopic and electrical properties of glycolipids in mixtures with straight-core tilted smectic LCs.

2. Experimental results

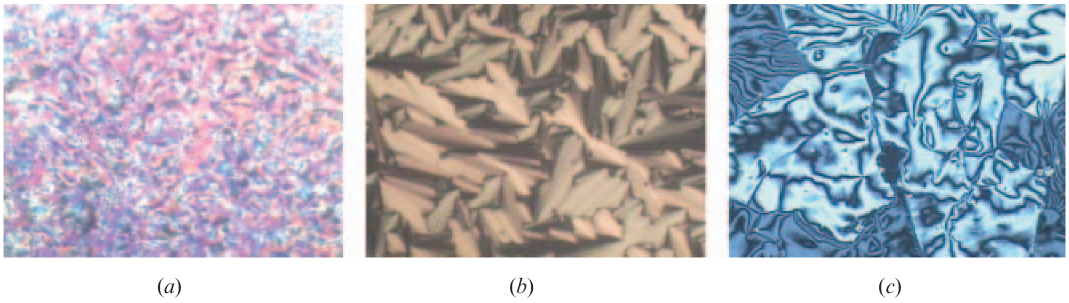
We prepared two sets of homogeneous binary mixtures of straight-core smectic C (SmC) LCs and dodecyl-β-D-glucopyranoside ($C_{12}G_1$) which has one glucose head group and one alkyl chain of 12 carbon atoms:

(a) 4-dodecyloxybenzoic acid (denoted C_{12}) and $C_{12}G_1$ containing 20, 40, 60 ± 0.4 wt % of $C_{12}G_1$;
(b) Liquid crystal 9B and $C_{12}G_1$ containing 20, 40, 60 ± 0.4 wt % of $C_{12}G_1$

The chemical structures of the materials studied are shown in figure 1. The mixtures were prepared in the isotropic phase and filled into 4 μm cells from Displaytech Inc. The cells were coated with transparent ITO electrodes and over-coated with polyimide layers rubbed in anti-parallel directions. The LC phases were identified by polarizing microscopy. The temperature of the samples was controlled using an Instec hot stage HS 2000. Microscopic textures formed by the mixtures were homogenous, as they were cooled to LC phases at the rate of $0.5^\circ\mathrm{C\,min^{-1}}$. The samples were held at 3°C above the transition in the isotropic phase, and also in the LC phase of the mixtures, for more than 24 h to verify the uniform miscibility of the two compounds.

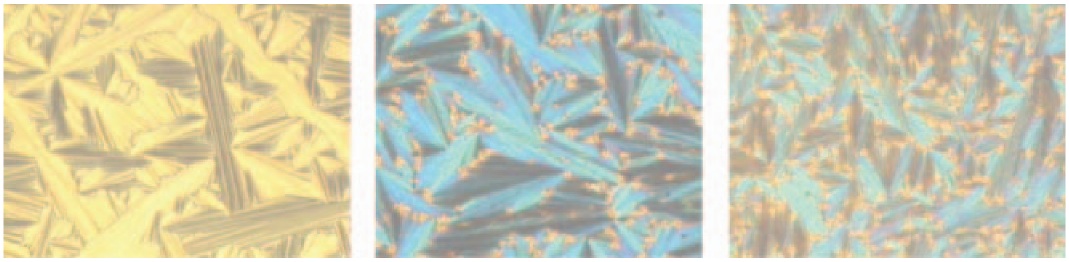
$C_{12}G_1$ has a smectic phase in the range 80–142°C. 4-Dodecyloxybenzoic acid has the following phase sequence: crystalline below 90.5°C, SmC phase between 90.5 and 132°C, N phase between 132 and 140°C. These two compounds were uniformly miscible up to more than 2/3 $C_{12}/C_{12}G_1$. The isotropic transition of the mixtures of 20, 40 and 60 % wt samples were at 130, 128 and 122°C respectively. The textures of thin films of C_{12}, $C_{12}G_1$ and C_{12}–$C_{12}G_1$ mixture at 120°C are shown in figure 2. The textures of pure $C_{12}G_1$ has a grey focal-conic fan texture while the textures of pure C_{12} have focal-conic fan texture with bright birefringent colours, both typical of the smectic phase; the mixtures show schlieren textures. All the mixtures crystallized at 90°C which is the crystallization temperature of C_{12}. This is about 10°C above the crystallization temperature of $C_{12}G_1$.

Liquid crystal 9B has the following phase sequence: crystalline below 90°C, SmC* between 90 and 144.5°C, SmA* phase between 144.5 and 154°C, N* phase between 154 and 156°C on heating. It crystallized at 116°C on cooling. The two compounds are uniformly miscible up to more than 2/3 9B/$C_{12}G_1$, with textures similar to that of pure 9B. At about 132°C, some areas of all the samples because isotropic. Bâtonnets existed in the isotropic areas until the whole sample became isotropic. The crystal to LC transition was at 90°C on heating, which is the same as the pure 9B transition



(*a*) (*b*) (*c*)

Figure 2. Textures of (*a*) pure C_{12}, (*b*) pure $C_{12}G_1$ and (*c*) C_{12} with 40 wt % $C_{12}G_1$ at 120°C.



(*a*) (*b*) (*c*)

Figure 3. Textures of (*a*) pure 9B, (*b*) 9B with 20%, (*c*) 9B with 40% $C_{12}G_1$ at 120°C.

temperature. The textures of various concentrations at 120°C are shown in figure 3; they did not changed significantly on addition of $C_{12}G_1$, but the size of the focal-conic domains became smaller and less bright.

Using the triangular wave form technique [13], all the samples were examined for spontaneous polarization. None was observed in the mixtures of C_{12}–$C_{12}G_1$ samples. For 9B–$C_{12}G_1$ samples with less than 70 wt% $C_{12}G_1$, the time dependence of the electric current under triangular voltage excitation revealed ferroelectric-type polarization switching. The temperature dependences of polarization, as determined from the area under the polarization current peaks, are shown in figure 4. The polarization appears to decrease above 120°C for all the samples, which is due to the lowering of the SmC* phase transition. The polarization is almost independent of the $C_{12}G_1$ concentration (about 10% difference is within the error limits of the polarization measurements) far from the transition.

3. Discussion

We have observed that glycolipids can be mixed with straight-core chiral smectic LCs without affecting the spontaneous polarization with over 60% of glycolipids.

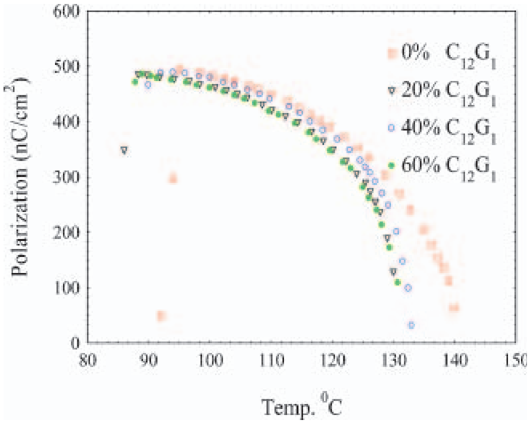


Figure 4. Polarization vs temperature for 9B and 9B–$C_{12}G_1$ on heating.

These glycolopids can also be mixed with straight-core non-chiral smectic LCs but then do not show spontaneous polarization. In all such mixtures, the transition temperatures of the LC phases were similar to those of straight-core LCs, and the textures of thin films were similar to those of straight-core LCs. These are similar to previous observations with a glycolipid in mixtures with bent-core LCs, in which the phase structure of glycolipid was dominated by bent-core LCs [12].

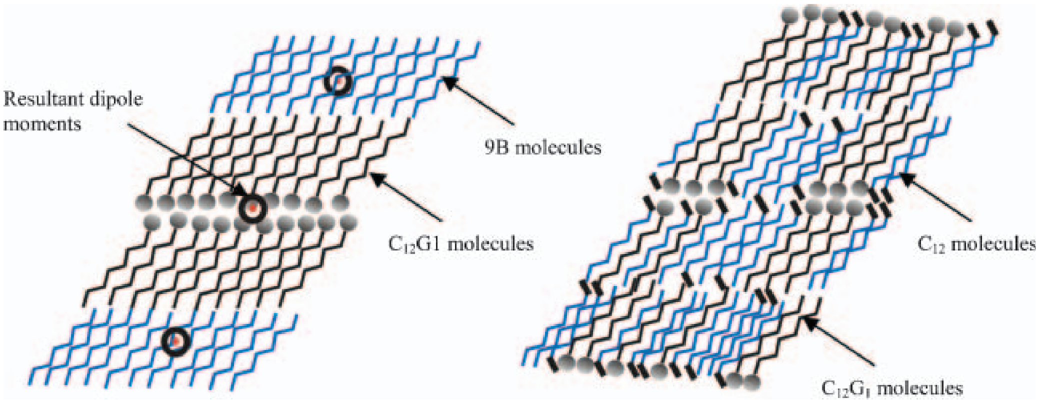
Optical microscopic textures of 9B consisted of small (5–10 µm diameter) focal-conic fan-shaped domains with hyperbolic and elliptical defect lines typical of smectic liquid crystals. The textures of pure C_{12} also consisted of smaller (diameter 5 µm or less) focal-conic fan-shaped domains with bright birefringent colours. The textures of $C_{12}G_1$ consisted of similar focal-conic fan-shaped domains but appeared much darker and their birefringence was as low as 0.05. Amphiphilic glycolipids prefer homeotropic alignment on clean glass surfaces. This is mainly because of the polar asymmetry of the glycolipid molecules. They show a mixture of homeotropic and focal-conic fan texture in polyimide-treated cells, because polar (hence hydrophilic) sugar head groups tend to avoid the hydrophobic polyimide surface; while apolar (hence hydrophobic) alkyl chains tend to lie preferably along the polyimide surface, leading to a mixture of both planar and homeotropic alignments.

The textures of C_{12}–$C_{12}G_1$ samples were quite different from the textures of both pure C_{12} and $C_{12}G_1$. They consisted of schlieren-type textures with birefringent colours as bright as those of pure C_{12}. Schlieren texture is typical of SmC LCs when placed between untreated glass plates. Uniform colour away from the defects indicated planar alignment. This was quite different from almost all other binary mixtures of calamitic LCs and glycolipids, in which the birefringent colours were less and textures were darker due to the addition of the glycolipids. The textures of 9B–$C_{12}G_1$ samples consisted of focal-conic fans similar to those of a pure 9B sample, but they became darker and the focal conic domains became smaller as the glycolipid concentration was increased. Change in the size of focal conic domains may be due to the influence of chiral glycolipid molecules on the helical pitch of 9B. The characteristics of 9B–$C_{12}G_1$ textures are quite similar to those of bent-core LCs and glycolipid mixtures [12]. These microscopy observations indicate that C_{12}–$C_{12}G_1$ mixtures may have a structure different from that of 9B–$C_{12}G_1$ mixtures.

Macroscopic polarization of 9B–$C_{12}G_1$ samples is unaffected by the addition of even over 60 wt% of glycolipid $C_{12}G_1$, which indicates that $C_{12}G_1$ molecules themselves contribute to the electrical polarization in a similar manner to $C_{12}G_1$ molecules in bent-core LCs [12]. X-ray measurements of $C_{12}G_1$ in bent-core LCs samples revealed that two double layers of glycolipid molecules were sandwiched between layers of bent-core molecules, preserving the antiferroelectric order of the bent-core LCs [12]. It is unfavourable for bent-core LC molecules to be dispersed in the glycolipid bilayers because hydrophobic–hydrophilic interactions prevent alkyl chains of the bent-core LC molecules from being in the vicinity of polar headgroups of the glycolipid molecules. The same scenario exists for 9B molecules in relation to glycolipid molecules. It is also important to note that X-ray measurements consistently show the bilayer thickness of $C_{12}G_1$ to be much less than the length of two fully stretched $C_{12}G_1$ molecules. Therefore, we propose that $C_{12}G_1$ molecules form tilted and electrically polarized bilayers sandwiched between layers of 9B as shown in figure 5 (*a*). In this configuration, glycolipid bilayers are head to head and the alkyl chains are outside, where only those alkyl chains of glycolipid molecules come into contact with 9B molecules. Such packing indicates that glycolipid bilayers form nanostructures in the host medium.

By symmetry, chiral glycolipid molecules tilted with respect to the layer normal result in permanent dipole moments perpendicular to the plane of the tilt, as was pointed out by Meyer *et al.* for smectic C* liquid crystals [14]. But when the molecules are amphiphilic, the rotation of molecules around a two-fold axis is prevented due to hydrophobic–hydrophilic interactions, and the symmetry is further reduced. Therefore the direction of the permanent dipole moment is not determined by the symmetry itself but by the conformation of the molecules. However the formation of double layers introduces a situation similar to the rotation of molecules around the two-fold axis. The existence of a two-fold symmetry axis enables the molecules with permanent dipole moments to have two degenerate minimum energy states in a monoclinic environment. In double layers, these two states are shifted perpendicular to the two-fold axis, and molecules corresponding to those two states lie in two separate layers. So the double layer structure establishes permanent dipole moments directed perpendicular to the tilt direction in the plane of the double layers. In chiral smectic liquid crystals and glycolipid mixtures, the glycolipid molecules are tilted in the same direction in their own layers as the straight core chiral smectic molecules.

Unlike glycolipds in both ferroelectric straight-core LCs and antiferroelectric bent-core LCs, glycolipids in non-chiral straight-core LCs do not show macroscopic polarization. There is also no evidence of the formation of helical structure in these mixtures. Amphiphlic glycolipids are, however, known to be excellent dopants for induced chirality in achiral lyotropic LCs [15]. Usually, the chirality can be induced in a non-chiral mesogenic host phase by adding a small amount, even less than 3%, of mesogenic or non-mesogenic chiral dopant [16]. The textures of C_{12}–$C_{12}G_1$ samples show



(*a*) (*b*)

Figure 5. Proposed models: (*a*) ferroelectric structure, (*b*) non-ferroelectric structure. Headgroups of the glycolipid molecules are shown as spheres while COOH groups of the C_{12} molecules are shown as rods.

tilted structure and complete uniform macroscopic miscibility, indicating that both liquid crystals, C_{12} and $C_{12}G_1$, have the same type of LC structure. It is apparent from these observations that in order for C_{12}–$C_{12}G_1$ mixtures to show no electric polarization, the molecules must be packed in such a way that net macroscopic polarization is zero. Therefore we propose that $C_{12}G_1$ molecules are tilted and nano-segregated in C_{12} layers, meaning that C_{12} and $C_{12}G_1$ are not uniformly mixed at a microscopic level. How this is possible is evident from the molecular structure of C_{12} (see figure 1). The COOH group at one end of the C_{12} molecules can be in the vicinity of the polar headgroups of the glycolipid molecules, enabling the C_{12} molecules to accommodate $C_{12}G_1$ molecules in the same layer. These COOH groups may enable C_{12} molecules to make hydrogen bonds with headgroups of the glycolipid molecules. However, the glycolipid molecules may nano-segregate because polar headgroups prefer not to be in the vicinity of the alkyl chains of C_{12} molecules, and still have to make bilayers as shown in figure 5 (*b*). This nano-segregation of chiral glycolipid molecules may prevent transfer of the chirality into the entire system. Nano-segregated regions of tilted chiral $C_{12}G_1$ molecules must be electrically polarized. Since the C_{12} molecules are achiral, they have a mirror plane and a centre of inversion in the monoclinic environment. Therefore the C_{12} molecules have rotational degrees of freedom. Therefore some C_{12} molecules may reorient so that the net macroscopic polarization of C_{12}–$C_{12}G_1$ mixtures is zero or very small in the bulk.

In summary, optical microscopy and polarization measurements show that amphiphilic glycolipid as guest forms tilted supramolecular structures in straight-core tilted smectic liquid crystals which play the role of the host. In these superstructures, the phase behaviour of glycolipids is dominated by the host calamitic LCs. The amphiphilic glycolipids appear to adopt the phase behaviour of the host monophilic LCs. In a chiral SmC phase, glycolipid molecules nano-segregate into pairs of tilted and ferroelectric layers sandwiched between chiral SmC layers. In a non-chirial SmC, glycolipid molecules are nano-segregated in the layers of C_{12} molecules and no chirality transfer occurs. These results indicate that, in contrast to the currently accepted interdigitated model, glycolipid bilayers may already have a tilted structure. Tilted glycolipid bilayers are electrically polarized. However, the tilted structures have not been observed in pure amphiphilic glycolipids. This may be because the tilt is not correlated between the bilayers. The glycolipid molecules have more than one chiral centre and modelling and/or simulation may be required to determine how they organize in a tilted smectic, i.e. which way the net dipole will point relative to the tilt plane. Other chiral amphiphilic lipids may also have a tilted structure. Since the biological cell membrane consists of amphiphilic lipid bilayers, tilted structure and the electric polarization of lipids may play an important role in the activities of the cell membrane.

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