Pyroelectricity in Synthetic Amphitropic Glycolipid for Potential Application of IR Sensor Device

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Pyroelectricity in Synthetic Amphitropic Glycolipid for Potential Application of IR Sensor Device

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Synthetic pure β-anomer glycolipid with large pyroelectric coefficient (∼80 μC/m²K under zero applied bias field) is reported. The pyroelectric and dielectric properties of glycolipid prepared in thin films, annealed at various temperatures have been investigated. The induced polarization in the glycolipid thin films systems remains stable up to 100°C, thus this material is appropriate for sensor materials for pyroelectric application. The real part of the dielectric constant is also low as compared to that of the other ferroelectric ceramic materials used in pyroelectric devices; therefore these new materials have significant potential application for infrared sensing devices.

Keywords Glycolipids; pyroelectric; amphiphilic liquid crystals

I. Introduction

The discovery of pyroelectricity in liquid crystal (LC) materials ignited considerable interest for application in uncooled IR ferroelectric sensors. This is because, currently uncooled IR detectors are made by ceramic materials, which use a device configuration, wherein the active pixel is thermally isolated from silicon substrate by using polyimide and cannot withstand very high temperature (∼600°C). On the other hand, LC material can be prepared at or close to the room temperature (RT) and thus from processing viewpoint, these material are very attractive. Pyroelectricity in liquid crystalline (LC) materials typically occurs for chiral substituted systems.

Members of glycolipid family, glycosides can be found naturally in biomembrane [1]. Although present as minorities, these natural products were found with diverse structures, which seem to suggest that they can be as important as the other natural phospholipids. Glycosides are amphitropic [2], meaning that they are capable to self-assemble in dry as well as when solvated [3]. In nanotechnology, synthetic glycosides such as alkyl polyglucosides (APGs) are important as surfactants and stabilizers. Interest in thermotropic behaviours of

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glycosides is recent [4]; hence much less understood and investigation for possible thermotropic application is underexploited. However, they have drawn much attention in recent years, for example, the sugar headgroup being chiral imply possible ferroelectric behaviour and tilted structures (like S C) in the lipid organization [5, 6]. Moreover, temperature dependent current, suggesting pyroelectric effect [7] and membranes response to an applied voltage implying piezoelectricity have been demonstrated [8].

In our earlier works, we have reported the pyroelectric properties of a β-dominant mixture glycolipid ((2-n-decyl-n-tetradecyl)-4-O-maltoside (C14–10G2) with 9:1 ratio of β:α anomers. This system exhibits high pyroelectric coefficient at RT [9]. In the current investigation, we are focusing on the same system but highly pure β-anomer with purity above 99% to study the phase properties and pyroelectric behaviour at various annealing temperature.

II. Experimental

Figure 1(a) shows the molecular structure of β-anomer of C14–10G2. It consists of a hydrophilic polar headgroup with two glucose sugar units. The headgroup is connected through a glucosidic linkage to a long branched hydrophobic apolar alkyl chain (-C14C10) and its overall structure mimic closely to those of natural lipids such as phospholipids and glyco-glycerol lipids. Thermotropic phase transition temperatures of the samples were obtained by repeated heating and cooling by optical polarizing microscope (OPM) and differential scanning calorimeter (DSC). The results are presented in Table 1. C14–10G2 exhibits LC behaviour over a wide temperature range of 23° C to 233° C. The α-anomer of C14–10G2 has its hydrophobic alkyl chain link to the glycosidic oxygen axially (Fig. 1c) instead of equatorially (Fig. 1b) as in the β-C14–10G2.

The glycolipid thin films were prepared by dissolving it in ethanol and ultra-sonicated at 60° C for 40 mins to form 0.5 g/ml concentration. The solution was spin coated (thickness of 2.97 ± 0.05 μm) onto a glass substrate deposited with bottom and top Al electrode to form metal-insulator-metal structure.

![Figure 1](image-url)
Table 1

Summary of measured pyroelectric coefficient and FOM of the glycolipid samples

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>ε′ (at 100 Hz)</th>
<th>p (μC/m²K)</th>
<th>FOM (μC/m²K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>10.26</td>
<td>25.99</td>
<td>13.40</td>
</tr>
<tr>
<td>60</td>
<td>8.10</td>
<td>62.83</td>
<td>45.58</td>
</tr>
<tr>
<td>100</td>
<td>6.12</td>
<td>76.46</td>
<td>74.89</td>
</tr>
<tr>
<td>140</td>
<td>5.58</td>
<td>59.40</td>
<td>62.66</td>
</tr>
<tr>
<td>β-dominant mixture C₁₄₋₁₀G₂ with 9:1 ratio of β:α anomers at RT</td>
<td>16</td>
<td>105</td>
<td>88</td>
</tr>
</tbody>
</table>

Dielectric measurements were performed at the frequency range of 100 Hz to 10 MHz using impedance analyser HP4294A (Agilent) at various temperature. The β-C₁₄₋₁₀G₂ samples were annealed at 60°C, 100°C and 140°C for 1 hour. Quasi-static pyroelectric measurement on the annealed sample was conducted to study the pyroelectric property of the thin films. This technique has been revealed to give highly accurate measurement of the pyroelectric coefficients [10].

III. Results and Discussion

Real and imaginary permittivity data for β-C₁₄₋₁₀G₂ at heating for RT, 60°C, 100°C and 140°C is presented in Fig. 2(a)i–ii. The relatively large value of dielectric permittivity at the low frequency and high temperature indicates that the molecular reorientation is a cooperative process. At low frequency range the loss seems to be quite large, a feature that is quite common with the existence of hydroxyl group (OH) in the glycolipid molecules [6]. The dielectric profiles obtained for RT and 60°C contains no peak corresponding to the dispersion region, but at 140°C and ~1 kHz, a relaxation peak appears, due to the presence of the polar molecule reorientation process in the columnar phase. Furthermore, this relaxation has a broad absorption because of fluctuations of molecular dipoles. The coupling between the orientational fluctuations of the molecules and the extended hydrogen bond network is quite strong in the glycolipid molecules [6]. Due to the limitation of the equipment the peak below (<100 Hz) was not measured. However, at 100°C, an absorption peak is expected.

Real and imaginary permittivity of the annealed sampled measured at RT is presented in Fig. 2(b)i–ii. The dielectric profiles of the samples are quite similar to each other at all the annealed samples. After annealing the samples, the dielectric constant and loss are reduced in values and consequently boosting the figure of merit (FOM) of the material (see later for more discussion).

The short-circuited pyroelectric current of the films, I_p, represented by the rate change of polarization, see Equation (1):

\[ I_p = pA \frac{dT}{dt} \] (1)
where $p$ is the pyroelectric coefficient, $A$ is the effective area of the sample and $dT/dt$ is the rate change of temperature. In this paper, our discussion is mainly focused on the pyroelectric properties of the glycolipid treated under different annealing temperature on the pure glycolipid. The annealing temperatures were chosen according to the phases investigated which are $\text{SmA}$ ($60^\circ\text{C}$), cubic ($100^\circ\text{C}$) and columnar ($140^\circ\text{C}$). Pyroelectric properties of the annealed sample were measured at RT. A square waveform of pyroelectric current was observed, when a triangular waveform temperature was applied to the glycolipid thin film as shown Fig. 3(a). Pyroelectric coefficient calculated for the pure $\beta$-$\text{C}_{14-10}$-$\text{G}_2$ is shown in Fig. 3(b).

The results suggests that when glycolipid thin films experience a temperature gradient, a short circuit pyroelectric current due to the change of the electric dipole moment is produced. Table 1 gives the magnitudes of pyroelectric coefficient of samples at different annealing temperature. It also provides the value of FOM ($= p/\sqrt{\epsilon' \tan \delta}$) for each variation. The pyroelectric FOM reflects the voltage responsivity of a pyroelectric material and its high value is desirable for the detection of pyroelectricity.

The result shows that thin films of pure $\beta$-$\text{C}_{14-10}$-$\text{G}_2$ annealed at $100^\circ\text{C}$ exhibits the best performance of pyroelectric activity followed by that at $60^\circ\text{C}$ and $140^\circ\text{C}$. When the solution of glycolipid is being spin casted on the glass substrates, the sugar heads (hydroxyl groups) of the glycolipid presumably tend to attach on the surface of the glass substrates and develop hydrogen bonds between the adjacent sugar heads. Thus, the sugar heads form...
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Figure 3. (a) Pyroelectric current waveform with respect to temperature variation at rate of 0.05°C/s for pure $\beta$-C$_{14-10}$G$_2$ (b) Annealing effect on the pyroelectric coefficient for pure $\beta$-C$_{14-10}$G$_2$.

a hydrogen bonded network within the same layer, thus limiting the headgroup motion. It is suggested that the apolar flexible alkyl chains form a homeotropic alignment as shown in Fig. 4(a) as a result of repulsion from the polar headgroup region.

At 60°C, within the annealed sample, the apolar alkyl chain are more flexible, i.e., has a higher degree of freedom to move randomly, since the glycolipid molecules has less rotational freedom due to the hydrogen bonding network of the headgroup. In addition, the flexible tail groups have a larger movement than head groups and a higher possibility of overlapping to form interdigitated smectic A$_d$ bilayers. At 60°C, the glycolipid ($\beta$-C$_{14-10}$G$_2$) molecules were found to be slightly tilted with respect to the layer normal and a larger tilted angle compare to the molecular arrangement at RT (refer to Fig. 4(b)). Consequently, a larger resultant dipole moment along the normal plane was observed in the absence of the electric field. Hence, the pyroelectric coefficient values of the glycolipid thin films rapidly increased to 62.8 $\mu$Cm$^{-2}$ K$^{-1}$ as the annealing temperature increased to 60°C.

Further increase of the annealing temperature on the glycolipid thin films above 85°C will lead to a phase transition from the SmA phase to a cubic phase, as confirmed by OPM studies. When the annealing temperature increased to 100°C, the thermal energy weakened the hydrogen bonds network between the polar sugar head groups. Subsequently, the polar sugar head gained some degree of freedom for a phase transition from an interdigitated smectic A$_d$ phase to a complicated highly ordered, but optically isotropic, cubic bicontinuous phase [1]. On the other hand, the apolar alkyl chains moves more freely with higher energy resulting the polar sugar heads curve slightly as shown in Fig. 4(c) and 4(d). In the bicontinuous cubic phase, the glycolipid thin films exhibited highest value of pyroelectric coefficient after being treated at 100°C, due to an unexpected large resultant dipole moment per unit volume in this phase.

When the annealing temperature increased further to 140°C, apolar alkyl tail groups occupied greatest flexibility for random orientation to force the polar sugar head groups closely packed together to form a hexagonal columnar phase as shown in Fig. 4(e). The molecular arrangement in this columnar phase might lead to the total net dipole moment per unit volume to decrease because parts of the dipole of each glycolipid molecule are now heading in the opposite direction. Consequently, the dipoles heading in the opposite direction will cancel off the resultant dipole moment per unit volume resulting in deterioration of the pyroelectric activity in the films which were annealed at 140°C.
Pyroelectric values of the previous report [9] were much larger than the current results. This is because the previous glycolipid was a mixture consisted of some percentage (~10%) of \( \alpha \)-anomer (i.e., \( \alpha \)-C\(_{14-10}\)G\(_2\)) that led to different self-assembly structure (especially in the chain region) compare to the pure \( \beta \)-structure glycolipid thin films (as shown in Fig. 4(f)). The \( \alpha \)-anomer have the apolar alkyl chain axially linked to the headgroup, altering the chain organization further apart from each other causing some degree of distortion which may have led to a higher net dipole moment per unit volume and pyroelectric coefficient.

IV. Conclusion

A few possible comprehensive models of molecular organization have been proposed for the glycolipid C\(_{14-10}\)G\(_2\) with respect to the effect of the annealing temperature on the pyroelectric activity. The proposed models are supported by our OPM studies. In this study, the pure \( \beta \)-C\(_{14-10}\)G\(_2\) treated at 100\(^\circ\)C exhibits the strongest pyroelectric activity.
The pyroelectric activity is enhanced in the bicontinuous cubic phase. Furthermore, it is found that the orientation (of $\alpha/\beta$) of the apolar alkyl chains attached to the glycosidic oxygen affects the molecular organization, hence its resultant dipole. Thus, a 90% mixture of $\beta$-dominant C$_{14-10}$G$_2$ gave higher pyroelectricity compare to that of the pure $\beta$-anomer.

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