Liquid crystal compound anti-ice surface
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ABSTRACT
In some cold areas/regions, ice accumulation is harmful to aircrafts, highways and power lines. To overcome this challenge, many researchers have focused on developing anti-icing surfaces. In this paper, liquid crystal compound Cholest-5-en-3-ol[(3β)-4-(2-propenyloxy)benzoate was synthesised, and a liquid crystal surface (LC surface) is prepared by heating the liquid crystal compound to 250°C and then cooling it. We determined ice-phobic properties of LC surface using differential scanning calorimetry (DSC) and polarised optical microscope (POM). A phenomenon that the freezing of water droplet on the LC surface is delayed was found. Compared with the two measurement methods, we obtained similar result that water freezing temperature was delayed nearly by 8° C on average on the LC surface. A process of ice/frost formation is observed using POM. The results displayed that the glass wafer without LC was covered completely by ice/frost, whereas on the LC surface at the same temperature no ice/frost was formed. Characteristics of LC surface were observed by field emission scanning electron microscope (FESEM) and Fourier transform infrared (FT-IR) imaging system. We suggest that the reason behind anti-ice surface is related to surface molecules and this is an important factor which may have an effect on anti-icing property.

1. Introduction
Ice on bare surfaces leads to high maintenance efforts for power transmission lines, aircrafts and other vehicles. In the past several decades, more and more researchers have focused on anti-icing surfaces by preventing ice formation or reducing ice adhesion.[1–13] Ice formation is inevitable at a low temperatures. Water droplet, in contact with ice, will freeze in dry surface as well as in wet surface.[4] Therefore, ideal anti-icing surfaces would be those in which water will be removed from the surface before it freezes. This means the water freezing temperature was delayed on the surface. In order to solve this problem, researchers have developed a variety of materials on the surface of which the freezing temperature of water droplet can be delayed, such as micro/nanostructure surfaces,[14] slippery liquid-infused porous surface[15] and so on.

Liquid crystal is an important material used in several domains.[16–22] For the past several decades, a blend of liquid crystalline polymer with the other polymers such as
polypropylene or polyethylene terephthalate has been a hot topic worldwide.[23,24] Mesogenic compounds also can improve the performance of the nanofiltration membranes. With the mesogenic compound-modified chitosan, an excellent high flux was obtained.[25,26] However, there is rarely any report that liquid crystal compounds are applied to the anti-ice field.

In this paper we find a special liquid crystal compound, that is Cholest-5-en-3-ol(3β)-4-(2-propenyloxy)benzoate. The compound was heated beyond the clearing point and then cooled to 0°C to obtain a liquid crystal surface (LC surface). We observed a phenomenon that the freezing of water on the surface is apparently delayed. This phenomenon is observed by differential scanning calorimetry (DSC) and polarised optical microscope (POM).

## 2. Experiment

### 2.1. Material

#### 2.1.1. Synthesis of Cholest-5-en-3-ol(3β)-4-(2-propenyloxy)benzoate (M1)

4-Hydroxy methyl benzoate (15.2 g) and 100 mL of N,N-dimethylformamide (DMF) were introduced in a 250 mL four-neck flask and heated to dissolve, and then 13.8 g of K₂CO₃ and 18 g of allyl bromide were added under a nitrogen atmosphere and heated at reflux temperature. The reaction was followed by thin-layer chromatography (ethyl acetate/hexane, 1:5) until the initial product disappeared (24 h). After cooling down to room temperature the DMF was removed under reduced pressure and the residue was treated with diethyl ether (150 mL) and water (100 mL). After separation of the organic phase, the aqueous phase was extracted two more times with diethyl ether (150 mL, respectively). The united organic phases were dried over sodium sulphate and after removal of the solvent were dried in vacuo. Then 300 mL of 15% NaOH solution and 150 mL of tetrahydrofuran were added into the flask. The mixture was heated to be a clear solution under reflux and continuous stirring for 1 h. The solution was acified with HCl to pH = 4. The raw product obtained by filtration was washed with water and re-crystallised from ethanol, then dried in vacuum at 60°C. The yield of M1 (Figure 1) is 88% (8.6 g) with Tₘ at 116°C.

Fourier transform infrared (FT-IR) images, nuclear magnetic resonance (NMR) images, thermogravimetry and elemental analyses are shown in supplemental material.

#### 2.2. Characterisation

##### 2.2.1. Differential scanning calorimetry (DSC)

The freezing temperature of water was characterised by DCS (Q2000; TA instrument, New Castle, DE, USA).

![Figure 1. Schematic of synthesis of M1.](image-url)
2.2.2. Polarised optical microscope (POM)
The freezing process of water was observed by POM (Scope A1; Carl Zeiss Instrument, Oberkochen, Germany) with a heating and cooling stage (THMSE-600; Linkam, Tadworth, UK).

2.2.3. Field emission scanning electron microscope (FESEM)
The features of LC surface were observed by FESEM (Zeiss Ultra Plus; Carl Zeiss Instrument, Oberkochen, Germany).

2.2.4. Fourier transform infrared imaging system (FT-IR imaging system)
The surface information of LC surfaces was collected by Fourier Transform Infrared Imaging System (spectrum spotlight 300; PerkinElmer Instrument, Waltham, MA, USA). The total functional group absorption map was obtained.

2.3. Method
To avoid impurity on the surface of aluminium pan or glass wafer, their surfaces were cleaned by ultrasonic rinsing in acetone for 30 min and then drying with nitrogen.

2.3.1. Determination of water freezing temperature by DSC
2.3.1.1. Preparation of LC surface. M1 was added into an aluminium pan. The pan is heated from 40°C to 250°C at rates 20°C/min. When the heated temperature reached 250°C, the temperature is maintained for 5 min and then the temperature is cooled down to −30°C at rates of 10°C/min. Then we obtained an LC surface in the aluminium pan.

2.3.1.2. Determination of water freezing temperature on LC surface by DSC. About 5 μL water was dropped on the LC surface in the aluminium pan, and the pan was operated close to linear cooling modes as shown in Figure 2. A schematic of the process is shown in Figure 2. As shown in Figure 2, temperature of the pan is cooled down to 0°C at rates 10°C/min (black curve) and thereafter is cooled at rates 5°C/min (blue curve) until water starts freezing. Then the pan is warmed at rates 10°C/min (red curve) to 40°C and maintained for 5 min at this temperature to ensure complete melting of ice before the next cycle.

2.3.2. Observation of water freezing temperature by POM
2.3.2.1. Preparation of LC surface. M1 was put on a glass wafer which was set on the heating and cooling stage. Then the glass wafer was heated from 40°C to 250°C at rates 20°C/min. When the heated temperature reached 250°C, the temperature is maintained for 5 min and then the temperature is cooled down to −30°C at rates of 10°C/min. Hence an LC surface on the glass wafer is obtained.

2.3.2.2. Determination of water freezing temperature on LC surface by POM. About 5 μL of water (the same bulk sample as that of determining water freezing temperature on LC surface) was dropped on the LC surface put on the glass wafer, and the pan was operated close to linear cooling modes as shown in Figure 2. As the process is similar to determination of water freezing temperature by DSC (Section 2.3.1.2), the details are omitted.

3. Result and discussion
3.1. Characterisation of M1
DSC curves of M1 are shown in Figure 3. The melting point is at 115.4°C and clearing point at 246.6°C. When M1 is cooled down, a crystallisation point was found (Figure 3).

The optical texture of M1 was determined by POM with a heating stage. Photographs of M1 are shown in Figure 4. M1 exhibited a cholesteric phase during the heating and cooling cycles. A typical cholesteric oily streak texture appeared at 116°C (Figure 4a), and the cholesteric phase was not in transition when heating M1 to 200°C (Figure 4b). When M1 was heated to 250°C (Figure 4c), an isotropic phase appeared. However, when M1 was cooled from 250°C to 230°C, the isotropic phase displayed a broken focal–conic texture (Figure 4d),
and the texture did not change at temperature of −30°C (Figure 4e). As shown in Figure 4, we found a special phenomenon that a broken focal–conic texture is maintained when M1 was cooled after heating to the cleaning point.

3.2. Phenomenon of delayed freezing on compound surface

The freezing temperatures of a water droplet on LC surface with upper processes were obtained by DSC at a continuous linear cooling. Through analysis of the blue curved line of the DSC curve, we found that compared with the aluminium pan surface (Figure 5), the LC surface (Figure 6) demonstrated lower freezing temperature. Freezing temperatures of water droplet on the surfaces of the aluminium pan and LC are −14.2°C and −24.2°C, respectively. The freezing temperature of water droplet on the LC surface is lower about 10.0°C than water droplet on the surface of the aluminium pan, and thus freezing of water was delayed on LC surface. The black curved lines in the figures are linear cooling curves, and we found that the curves were broke at the temperature of freezing. Such a phenomenon means water released that much of heat such that temperature of the system of DSC was changed. To provide a reliable data, we collected formed dataset in each of 20 runs on the same sample. A typical set is shown in Figure 7. Figure 7a is a set of freezing temperatures on the aluminium pan surface, and Figure 7b is a set on the LC surface.

Furthermore, we analysed a survival curve in which the data came from the cooling and heating cycles, as shown in Figure 7. The natural definition of the freezing temperature is a temperature at the 50% unfrozen mark of survival curve, and this temperature was called $T_{50}$ at which the water droplet has frozen up to its half quantity.

Figure 3. (colour online) DSC curve of M1.

Figure 4. (colour online) POM texture of M1. M1 heats up to 250°C, and then cools to −30°C: (a) 116°C (b) 200°C (c) 250°C (d) 230°C and (e) −30°C.

Figure 5. (colour online) DSC and cooling curve of water droplet on the aluminium pan surface.

Figure 6. (colour online) DSC and cooling curve of water droplet on the LC surface.
The results are shown in Figure 8. As shown in Figure 8, the proposed $T_{50}$ are $-14.8^\circ C$ and $-25.0^\circ C$ on aluminium pan surface (Figure 8a) and LC surface (Figure 8b), respectively.

3.3. Observation of water freezing temperature by POM

The water droplet freezing temperature was determined by using POM with heating and cooling stage. The experimental method is described earlier. The heating and cooling stage can control the temperature, and we can obtain information about surface temperature from the display of stage control software.

Surface of glass wafer is shown in Figure 9. Figure 9 is a photograph of top view of a sample which is water droplet on glass wafer surface. Figure 9a is a photograph taken at 0°C. Water droplet on glass wafer surface is transparent, and thus we can see the surface of glass through the water droplet (red frame in

![Figure 9](image-url)

**Figure 9.** (colour online) Photograph of water droplet on the surface of glass wafer: (a) before freeze at 0°C; (b) after freeze at $-16.8^\circ C$. 
The sample was cooled down on the stage. The water droplet clouded when the sample temperature was $-16.8$°C (red frame in Figure 9b). Surface of LC freezing process was the same as glass wafer surface. We also can see the LC surface in Figure 10a (red frame) at 0°C. This area clouded at $-23.8$°C (Figure 10b). These observations agree well with the result measured by DSC, as shown in Figures 5 and 6.

### 3.4. Observation process of ice/frost formation by POM

In order to consolidate the anti-ice effect of the LC surface, the in situ observations of ice/frost formation by POM are shown in Figure 11. In Figure 11a2, the glass wafer surface is covered almost completely with ice/frost ($-16.8$°C) and the water droplet was frozen. While there is nearly no ice/frost, the big liquid water droplet and small condensed water located nearby the water droplet (yellow region in Figure 11b2) co-exist on the LC surface ($-17$°C) at the same time. When the surface temperature was $-24$°C, the glass wafer without LC is covered completely with ice/frost (Figure 11a3). Comparing the same area (nearby the water droplet) on LC surface, at the identical temperature, shows the area without any ice/frost on the LC surface, instead some little condensed water droplet (yellow region in Figure 11b3). The phenomenon on the LC surface demonstrates an obvious contrast against the glass wafer surface.

### 3.5. Observation features of liquid crystal surface

Features of LC surface were observed by FESEM, and photograph is shown in Figure 12. The LC surface as shown in Figure 12 is smooth and clear, therefore we cannot find any special features on the surface through FESEM. Thus, we collect information of LC surface.

![Figure 10](image10.jpg)  (colour online) Photograph of water droplet on the surface LC: (a) before freeze at 0°C; (b) after freeze at $-23.8$°C.

![Figure 11](image11.jpg)  (colour online) Sequences image of formation ice/frost on: (a) glass wafer surface; (b) LC surface.
from FT-IR imaging system to observe functional group distribution on the LC surface. The result is shown in Figure 13. Figure 13 shows the total IR absorption of the LC surface. IR absorption peak is uniformly distributed on the surface and the feature is similar to the micro/nanostructure anti-ice surface. Micro/nanostructure surface is related to the solid contact density in three-phase contact lines which are key to generate anti-icing properties on a surface.[14] Thus, we suggest that each liquid crystal compound’s molecular structure should be abstracted to a micro/nanos-structure (as shown in Figure 14), and the reasons of delay in freezing are that the surface do not have any defects that may be ice-nucleation active sites. Even if, in our research, the structure is smaller than micro/ nanostructure, which can be observed directly, the phenomenon of delay in freezing is same.

**4. Conclusion**

In this paper, we synthesised liquid crystal compound Cholest-5-en-3-ol(3β)-4-(2-propenyoxy)benzoate, and a LC surface was obtained by heating this compound to 250°C and then cooling it down. We determined water droplet freezing temperature on the LC surface and aluminium pan surface by using DSC. Freezing temperatures of water droplet on the *aluminium pan surface* and *LC surface* are −14.2°C and −24.2°C, respectively. We found that water droplet freezing on the LC surface was delayed. To provide a reliable data, we determined the same sample on 20 runs. The data showed that the property of the surface was not changed. We analysed survival curve from collected data of 20 runs. $T_{50}$, which is a temperature at the 50% unfrozen mark of survival curve, was calculated. The values of $T_{50}$ are −25.0°C and −14.8°C on LC surface and aluminium pan surface, respectively. We utilised POM to observe the freezing process directly. The results are similar to the results of DSC. Freezing temperatures of water droplet on the LC surface and on glass wafer are −23.8°C and −16.8°C, respectively. The process of ice/frost formation is observed by POM. It was found that when the surface temperature was −24°C, the glass wafer without LC was covered completely with ice/frost, while at the same temperature the LC surface was not covered with ice/frost, instead some little condensed water droplets were found nearby the big water droplet. Compared with the two measurement methods, we obtained similar results that water freezing temperature was delayed nearly by 8°C on average on the LC surface and the liquid crystal compound surface has become ice-phobic. The features of LC surface were observed by FESEM and FT-IR imaging system. The photographs taken by FESEM give little information about surface, whereas those taken by FT-IR imaging system provide more details. LC surfaces are similar to anti-ice surface which have micro/ nanostructure. Hence, we suggest that the reason behind delay in freezing is also similar. The phenomenon we observed may inspire another researchers to discover further ice-phobic materials.
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Disclosure statement

No potential conflict of interest was reported by the authors.

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