

Synthesis and Characterization of A Novel Cholesteric Liquid Crystalline Containing Carboxyl Group

Jing MA^{1,2}, Ying Nan XUAN¹, Yong HUANG^{1,3*}

¹Key Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650

²Graduate School of the Chinese Academy of Sciences, Beijing 100039

³State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080

Abstract: A novel liquid crystal compound with a carboxyl group at one end, cholest-5-en-3-ol-(3 β) hydrogen decanedioate (**1**) was successfully prepared by the reaction of cholesterol with sebacoyl chloride. Its chemical structure and liquid crystalline properties were characterized by FTIR, ¹³CNMR, ¹HNMR, POM and DSC. The compound with an active carboxyl group shows thermotropic liquid crystalline behaviour.

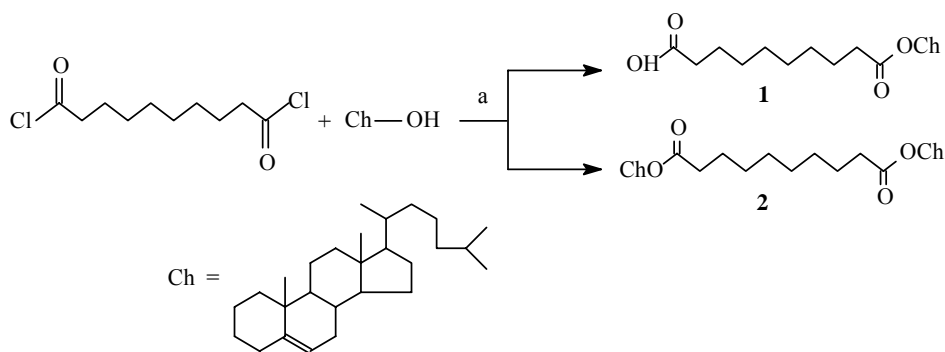
Keywords: Liquid crystal, cholesterol, thermotropic, texture.

Since Reinitzer¹ first reported in 1888 that cholesteryl benzoate displays liquid crystalline behaviour, the liquid crystalline properties of cholesteryl derivatives have been extensively researched. In the past, a range of liquid crystalline cholesteryl derivatives, such as halide, carboxylic ester and carbonic acid esters of cholesterol have been prepared, which mainly demonstrated cholesteric phase^{2,3}. Compared with other liquid crystals, cholesteric phase liquid crystals have aroused much interest because of their special optical properties, such as circular dichroism, selective reflection, intensively rotary polarization and rotary dispersion *et al.*^{4,5}, they would be applied in optical information storage, optical switching, nonlinear optics and liquid crystals display device(LCD) with other liquid crystals^{5,6}. However, very few publications have been reported dealing with liquid crystalline cholesteryl derivatives containing active group up to now, which provide an easy access to obtain main chain or side chain polymeric liquid crystals. In this paper, a novel cholesteryl derivative with a terminal carboxyl group was synthesized, showing thermotropic liquid crystalline behavior.

Experimental

Sebacoyl chloride⁷ 2 mL (7.8 mmol) and benzene 10 mL were placed in a three-necked flask equipped with a reflux condenser, calcium chloride guarding tube and magnetic stirrer. A solution of cholesterol 2.5 g (6.5 mmol), 30 mL benzene and 2 drops pyridine

* E-mail: yhuang@cashq.ac.cn

Scheme 1 Synthesis route of compound **1**a) Py / H₂O

were added dropwise under vigorous stirring at reflux temperature for 5 h (**Scheme 1**). The reaction mixture was stirred for another 2 h. At the end of the reaction, the excess benzene was removed under reduced pressure. The reaction mixture was then poured into distilled water. The precipitate was filtered, dried in air and recrystallized twice from acetic acid. Finally, 1.78 g of faint yellow powder was obtained in 48% yield.

Results and Discussion

Cholest-5-en-3-ol-(3 β) hydrogen decanedioate (**1**) was prepared *via* reacting cholesterol with sebacoyl chloride under mild conditions. Cholesterol is difficult to react directly with long chain acid because of its low reactivity. N, N'-Dicyclohexyl- carbodiimide (DCC)/4-dimethylaminopyridine (DMAP) is an efficient catalyst system, but the yield is very low (16%). Furthermore, the column chromatography is necessary in the post treatment. We use sebacoyl chloride as reagent and pyridine as catalyst for preparation of **1**. Two products **1** and **2** were obtained. The ratio of **1** to **2** is related to the ratio of cholesterol to sebacoyl chloride and the addition speed of cholesterol/benzene solution. In order to increase the yield of **1**, the excess sebacoyl chloride was used and the addition speed of the cholesterol/benzene solution should be slow.

The chemical structure of **1** was characterized by FT-IR, NMR and elemental microanalysis (calcd. for C₃₇H₆₂O₄: C, 77.89, H, 10.88. Found: C, 77.47; H, 9.91). In FT-IR spectrum, the absorb bands at 1733.7 cm⁻¹ and 1708.6 cm⁻¹ represent the ester group and carboxyl group, respectively. In ¹³CNMR spectrum, the signals at 179.7 ppm and 173.3 ppm stand for the carbon atom of carboxyl group and the carbon of ester group, respectively. Whereas, in the ¹HNMR the sharp peak at 5.35 ppm (s, 1H) is assigned to the hydrogen atom of -CH=C group, and the signal at 4.58 ppm (m, 2H) is the hydrogens adjacent to the oxygen; the peaks between 0.65 ppm and 2.34 ppm (m, 59H) are the hydrogens of alkyl groups including linear paraffin and cyclanes.

The thermal behavior of **1** is measured by DSC at the heating and the cooling rate of 5°C/min in nitrogen atmosphere and the liquid crystalline texture is investigated under crossed polars by POM with hot-stage. Results show that **1** can exhibit thermotropic

liquid crystalline behavior. **Figure 1-a** is the third heating run of **1**, it can be found that there are two endothermic peak appearing at 117.91°C and 120.49°C, that indicated the sample was in solid state-mesophase and mesophase-isotropic phase transition, respectively. In the third cooling run (**Figure 1-b**), the isotropic phase-mesophase transition begins at 122.43°C and the mesophasesolid state transition begins at 110.09°C, correspondingly.

The observations made by POM are in good agreement with the results of DSC experiments. The birefringence can be observed at room temperature. When the sample was heated to 112°C, it started to melt. The birefringence was observed again when heated to 119°C. When the sample was heated to 121°C, the birefringence disappeared, that indicated the mesophase transferred to the isotropic phase. The birefringence can also be observed when the sample was cooled at 118°C, which is similar to the fan texture of cholesteric phase(**Figure 2-a**). At 109°C it can be observed that the spherocrystal become growing in the fan texture (**Figure 2-b**). At 103°C the growth of spherocrystal stoped and the texture can be retained till room temperature (**Figure 2-c**). After keeping this temperature for about 30 min, the emergence in the edge of spherocrystal can be observed (**Figure 2-d**).

Different from other cholesteric derivatives, such as cholesteric decaneate, cholesteric lauricate⁴, **1** with end-carboxyl group does not display the instable, monotropic liquid crystalline phase during the heating process. Moreover, the mesophase transition interval becomes wider ($\Delta T=12^\circ\text{C}$). It might be expected that the introduction of active carboxyl group can result in an increase in both intermolecular force and the degree of order.

Figure 1 The DSC curves of **1** in the third heating and cooling mode

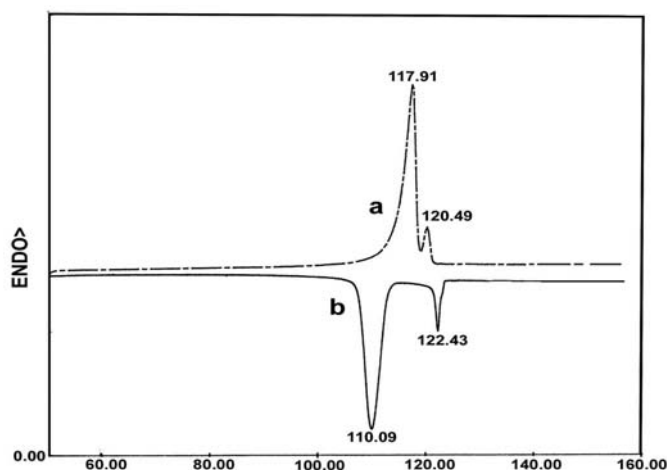
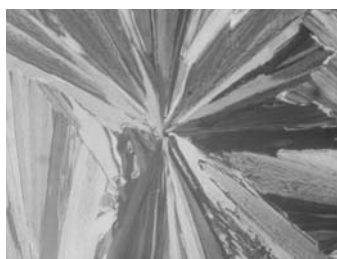


Figure 2 Photomicrograph (crossed polars, x 150, cooling)**a** (T=118°C, cholesteric fan texture)**b** (T=109°C, spherulitic growth)**c** (T=103°C, spherocrystal)**d** (T=30°C, after 30 min, emergence)

Acknowledgments

The financial support by the National Natural Science Foundation of China (Grant No. 29925411) and the Key Laboratory of Cellulose and Lignocellulosics Chemistry (LCLC-2003-142) are gratefully appreciated.

References

1. F. Reinitzer, *Wiener Monatsch*, **1888**, (9), 421.
2. G. W. Gray, *et al.*, *Mol. Cryst. and Liq. Cryst.*, **1976**, 37, 189.
3. J. A. Castellano, *et al.*, *Angew. Chem.*, **1970**, 82, 984.
4. L. Y. Wang, S. S. Liao, *Liquid Crystal Chemistry*, Science publication, Beijing, **1985**.
5. X. J. Wang, *WuLi (Physics, in Chinese)*, **1990**, 19(11), 685; 19(12), 743.
6. C. S. Hsu, L. J. Shin, *Macromolecules*, **1993**, 26 (12), 3162.
7. S. Hünig, E. Lükke, W. Brenninger, *Org. Syn. Coll.*, **1973**, 5, 536.

Received 3 November, 2003