Synthesis and Mesomorphism Study of Novel Carbohydrate-derived Liquid Crystals Containing Glucosyl and Chenodiolyl Residues

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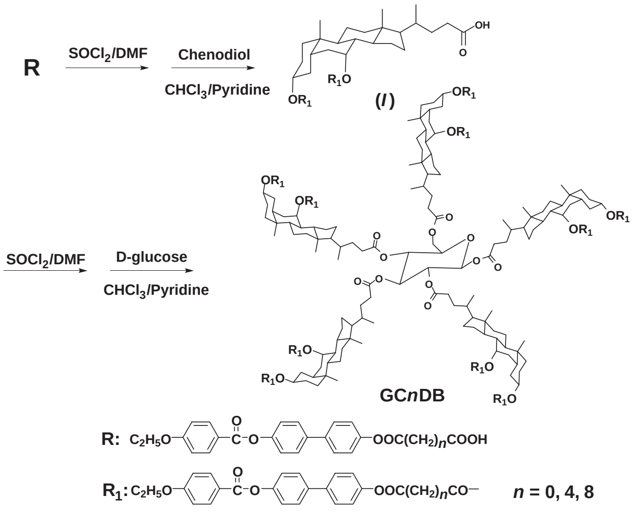
Synthesis of carbohydrate-derived liquid crystals by assembling D-(+)-glucose with mesogenic units containing chenodiolyl moieties and a flexible spacer is reported for first time and the thermal properties and liquid-crystalline behavior were carefully studied.

Carbohydrates are a new yet very promising source for liquid crystals synthesis. Not only because they could form various types mesomorphous materials, also because they are the very common core structure of glycolipids, which are important biological macromolecules exhibiting liquid-crystalline behavior.[1–5] Sugar systems containing cholesteryl residues[6,7] which show perfect liquid crystal textures, have been reported previously. Chenodeoxycholic acid has a similar molecular structure to cholesterol. In marked contrast to the extensive studies of carbohydrate-derived liquid crystals containing cholesteryl derivatives, carbohydrate-derived liquid crystals containing chenodeoxycholic acid were far less investigated. In order to gain more understanding and explore the possibility to apply chenodeoxycholic acid and carbohydrate compounds to form novel liquid-crystalline materials, we designed and synthesized a series of liquid crystals using glucose as the chiral core structure, mesogenic units containing chenodiolyl moieties. Those mesogenic moieties are introduced to the five hydroxy groups of glucose by direct esterfication. The obtained liquid crystals are termed as GC*n*DB, (Glucose-chenodiol-*n*-diacid-biphenyl, *n* denotes the number of methylene in diacid).

Chemical structures and synthetic route of the target compounds GC*n*DB were shown in Scheme 1. The compound *R* was transformed into its acid chloride and reacted with chenodeoxycholic acid to give compound *I*. Chenodeoxycholic acid derivative *I* was then transformed into acid chloride and reacted with anhydrous D-(+)-glucose in chloroform and pyridine under reflux for 36 h to give the crude product. The crude product was purified and recrystallized from ethanol. The detailed synthetic approach is described in supplementary material,[8] and the desired representative compound GC4DB was carefully identified by ^{1}H NMR, ^{13}C NMR, element analysis, and IR.[9]



Scheme 1. Synthetic route of GC*n*DB series.

The FT-IR of representative GC4DB showed characteristic bands at 1748 and 1729 cm^{-1} which correspond to two C=O stretching representing Ar–OOCR, Ar–COOR, respectively, 1605 cm^{-1} due to aromatic C=C stretching, and 1254 cm^{-1} due to C–O–C stretching. The ^{1}H NMR spectra of GC4DB showed a series of multiple peaks at δ 0.93–4.01, 7.14–8.15, 1.31, 1.58–4.09, and 4.11–6.66 corresponding to chenodiolyl, aromatic, methyl, methylene, and glucosyl groups, respectively. The concrete ^{13}C NMR spectra of glucose derivative GC4DB showed six peaks at δ 62.41, 69.10, 69.23, 70.66, 72.32, 91.21, these peaks indicated the existence of chiral core structure glucose; the typical five carbonyl carbon peaks at δ 174.12, 172.75, 172.42, 172.22, 171.72 were the characteristic peaks to indicate the perfect substitution on glucose. So the target compound GC4DB was obtained.

The thermal properties of GC*n*DB series were studied by differential scanning calorimetry (DSC) and summarized in Table 1. The representative DSC thermogram of GC4DB was shown in Figure 1 (Netzsch DSC 204, equipped with a liquid nitrogen cooling system. Scan rate: 10 °C/min). The DSC curves of GC4DB indicated that it did not crystallize during cooling from the isotropic melt. Furthermore, it was quite stable and

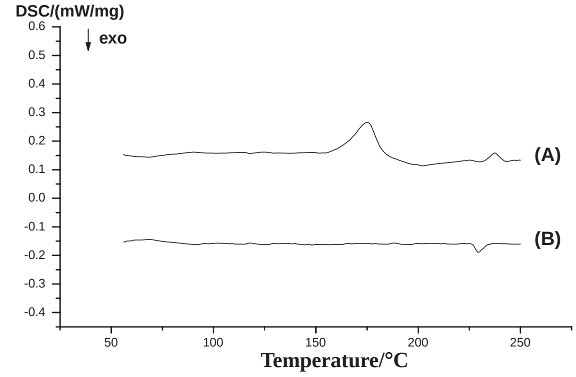


Figure 1. DSC thermograms of liquid crystal GC4DB. A: first heating; B: first cooling.

Table 1. Phase-transition temperatures and specific rotation of GC*n*DB

GC*n*DB (*n*)	T^{m}(/°C)^{a}	T^{i}(/°C)^{a}	ΔT(/°C)^{a}	T^{a}(/°C)^{a}	$[\alpha]_{589}^{20}$ (c 0.34, in $CHCl_3$)
0	203.3	235.0	31.7	252.0	−10.3
4	175.3	237.0	61.7	255.0	−23.9
8	170.1	234.0	63.9	251.0	−49.5

$^{a}T^{m}$: Temperature of melting point. T^{i}: Isotropic transition temperature. T^{a}: Temperature at which 5% weight loss occurred. $\Delta T = T^{i} - T^{m}$: Mesogenic region. $[\alpha]_{589}^{20}$: Specific rotation.

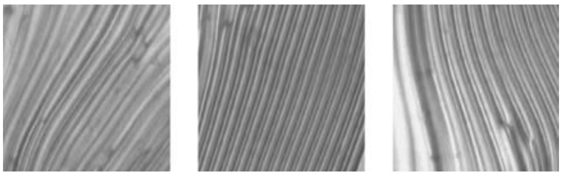

(a) (b) (c)

Figure 2. Optical textures of GC*n*DB series. (a) GC0DB, on heating to 205 °C. (b) GC4DB, on heating to 190 °C. (c) GC8DB, on heating to 200 °C.

no sharp melting peak was observed when it was reheated. This phenomenon is often observed with a small molecular weight polymer, but GC4DB is not a polymer. A similar phenomenon is observed in GC*n*DB series. The observations indicate that the crystallization of these molecules is hindered owing to steric effect.[10]

As summarized in Table 1, the GC*n*DB series all showed the enantiotropic behavior, the wide mesogenic region with their high clearing points. On heating, the melting points of GC*n*DB series decreased from 203.3, 175.3, to 170.1 °C with GC*n*DB from GC0DB to GC8DB. This is the result of increased molecular flexibility with the longer spacer group (*n* increased from 0 to 8). The results thermal gravimetric analysis (TGA) show that the temperatures when 5% weight loss occurred (T^{a}) are all higher than 250 °C, which reveals the GC*n*DB series have relative high thermal stabilities.

Furthermore, the specific rotations (SROT: $[\alpha]_{589}{}^{20}$, a Perkin-Elmer Polarimeter model 341, temperature: 20 °C, wavelength: 589 nm) of GC*n*DB series were measured and summarized in Table 1. There is a remarkable increase of SROT of GC*n*DB series from $[\alpha]_{589}{}^{20} - 10.3$ (c 0.34, in $CHCl_3$) to $[\alpha]_{589}{}^{20} - 49.5$ (c 0.34, in $CHCl_3$) with the flexible spacer chain extends (*n* increased from 0 to 8), which is due to the longer distance between the biphenyl unit and chenodiolyl. The more freedom the chain has, the less compact the molecular pack is.

The liquid crystal textures of GC*n*DB series were studied by polarizing optical microscopy (POM). The representative optical textures of GC*n*DB series were shown in Figure 2. Typical chiral nematic fingerprint textures[11] were observed in mesogenic region of GC*n*DB series and the length of flexible spacer group did not affect the mesogenic type and texture of GC*n*DB series.

The quenched samples of GC*n*DB series were identified by wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS), (XRD measurements are performed using a nickel-filtered Cu Kα radiation with a DMAX-3A Rigaku powder diffractometer), and the X-ray diffraction patterns of quenched GC*n*DB series were shown in Supporting Information.[8] No peak appeared in SAXS and broad peaks occurred at $2\theta \approx 20°$ ($d \approx 4.5$ Å) in WAXD. The broad peaks indicated that the GC*n*DB series were almost amorphous.

In conclusion, a series of novel glucose-derived liquid crystals GC*n*DB series were designed and synthesized. They demonstrate wide mesogenic region and high thermal stabilities, which could lead to potential applications. These compounds do not crystallize on cooling. The length of spacer group plays an important role to the SROT and melting point. The fingerprint textures were observed, which were typical characteristic of chiral nematic LC phase.

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8 Supporting Information is available: The synthetic route of GC4DB; the Synthesis and experimental details; the molecular structure of GC4DB and the X-ray diffraction patterns of quenched GC*n*DB series.

9 Selected physical data of GC4DB are as follows: ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ 1.31 (m, 30H, $-CH_3$), 4.09 (m, 20H, $-CH_2-O-$), 7.14 (d, 20H, $J = 5$ Hz, –O–Ar–COO–), 8.15 (d, 20H, $J = 1$ Hz, –O–Ar–COO–), 7.16–7.64 (m, 80H, –Ar–Ar–), 1.58–2.36 (m, 80H, $-OOC-(CH_2)_4-COO-$), 0.93–4.01 (m, 185H, H–chenodiolyl), 4.11 (d, 2H, $J = 0.67$ Hz, CH_2–glucosyl), 4.60–6.66 (m, 5H, CH–glucosyl); ^{13}C NMR (300 MHz; $CDCl_3$; Me_4Si) δ 14.61 (10 × q), 63.76 (10 × t), 114.24, 132.27 (40 × d), 121.82, 163.33, 164.89 (30 × s), 122.08, 128.08 (80 × d), 137.89, 150.09, 150.56 (40 × s), 24.17, 33.80, 33.96 (40 × d), 172.21, 173.21 (20 × s), 13.53, 13.36, 19.31 (15 × q), 20.77, 24.86, 28.03, 29.63, 31.23, 31.24, 31.57, 32.46, 35.81, 40.22 (50 × t), 34.75, 37.03, 42.64, 45.36, 49.11, 56.10, 71.35, 73.91 (40 × d), 35.02, 42.47, 174.12, 172.75, 172.42, 172.22, 171.72 (15 × s), 62.41 (t), 69.10, 69.23, 70.66, 72.32, 91.21 (5 × d). IR (KBr) ν 2936, 2849, 1748, 1729, 1605, 1254 cm^{-1}. Anal. Calcd for $C_{396}H_{442}O_{81}$: C, 73.20; H, 19.94%. Found: C, 72.90; H, 19.71%.

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