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Mesomorphic properties of chiral three-arm liquid crystals containing 1,2,4-butanetriol as core

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ABSTRACT

A series of symmetric and asymmetric three-arm liquid crystals (**TALCs**) of which the molecular structure with a central core of 1, 2, 4-butanetriol attached by three rod-like mesogenic moieties have successfully been synthesized. The rod-like mesogenic side arms are 4′-(4-(trifluoromethyl) benzoyloxy) biphenyl-4-carboxylic acid (TFBA) and 4′-(4-(allyloxy) benzoyloxy) biphenyl-4-carboxylic acid (AOBA), respectively. BTA0 and BTA3 are symmetric **TALCs** with three TFBA or three AOBA as LC side arms, respectively. BTA1 is an asymmetric **TALC** with one AOBA and two TFBA as side arms. BTA2 is an asymmetric **TALC** with two AOBA and one TFBA as side arms. The chemical structures and LC properties of the LC side arms and **TALCs** were characterised by FTIR, ^{1}H NMR, elemental analysis, DSC, TG, POM and X-ray diffractometer. TFBA displayed smectic B (S_mB) phase, AOBA exhibited nematic (N) phase. The **TALCs** all displayed chiral mesophase properties. BTA0 displayed chiral smectic C (S_mC^*) mesophase. BTA1, BTA2 and BTA3 exhibited cholesteric (*ch*) mesophase. In addition, a chiral smectic A (S_mA^*) mesophase was observed for BTA1. The results indicated that the 1, 2, 4-butanetriol is vital in inducing chiral mesophase of the **TALCs**. The side arms also played an important role in the mesophase type and mesogenic region. The **TALCs** displayed cholesteric mesophase when nematic LC side arm AOBA was introduced into the chiral core. The mesogenic region of the **TALCs** increased with the content of the wide-mesophase-region LC side arm AOBA introduced into the **TALCs** increasing. The melting temperature and the clear temperature of the **TALCs** were lower than those of the LC side arms (TFBA and AOBA). The mesophase regions of the **TALCs** were wider than those of the LC side arms.

1. Introduction

Cholesteric liquid crystal (LC) materials have attracted considerable interest because of their unique optical and electrical properties, which include selective reflection of light, thermochromism and potential applications such as optical-electro materials [1–8]. As one kind of unconventional LCs, star-shaped LC usually has a core and symmetric or asymmetric mesogens as the side arms. Currently, star-shaped LC has aroused a great deal of interest among chemists because of its symmetric molecular structure and interesting optical properties [9–18]. The common mesophase of star-shaped liquid crystals is columnar [10,13,19–21]. To the best of our knowledge, cholesteric star-shaped LCs have been described rarely in the past. Yao [15], Zhang [17] and Saezz [22] have introduced cholesteric mesomorphic arms into a core and obtained cholesteric star-shaped LCs. In these cases, the cholesteric mesomorphic phase of the star-shaped LC was mainly the result of cholesteric mesomorphic arms. We have tried other strategies to obtain cholesteric star-shaped LCs that nematic mesomorphic arms were introduced into chiral cores [23–25]. Glucose, maltose, melitose and sorbitol were adopted as chiral cores. These studies indicate that chiral core is prone to induce the cholesteric phase in the star-shaped LCs with nematic side arms. In these studies, star-shaped LCs are symmetric structure.

Recently Hird [26] summarized the properties and applications of fluorinated liquid crystals. The small size of the fluoro substituent enables its incorporation into all types of liquid crystal, including calamitic, discotic, banana, lyotropic and polymers, without destroying the liquid crystalline nature of the material.

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However, the fluoro substituent is larger than the hydrogen atom, and hence causes a significant steric effect, which combines with the high polarity, to confer many fascinating and often remarkable modifications to melting point, mesophase morphology and transition temperatures, as well as many other very important physical properties such as dielectric anisotropy, optical anisotropy and visco-elastic properties.

The introduction of trifluoromethyl terminal substituents to calamitic LC is prone to lead to smectic mesophase due to the stronger lateral force of the molecules [27–32], while star-shaped LCs containing trifluoromethyl terminal substituents have been seldom reported. The simultaneous introduction of nematic LC side-arm and smectic LC side-arm containing trifluoromethyl terminal substituents to a chiral core leads to new chiral asymmetric functional materials. It is necessary to know the effect of the chiral core and both LC side arms on behaviors of star-shaped LCs. In this article, we synthesized a series of symmetric or asymmetric three-arm LCs bearing nematic side arms or smectic side arms containing trifluoromethyl substituents or both the LC side arms based on 1,2,4-butanetriol.

2. Experimental procedures

2.1. Materials and methods

4-(Trifluoromethyl) benzoic acid, 4′-hydroxy-4-biphenylcarboxylic acid are obtained from Sigma-aldrich without any further purification. 1,2,4-Butanetriol (*BT*), is obtained from Chengdu Best-reagent Co. *BT* used in this manuscript is a mixture of *S* and *R* isomer, and its specific rotation (in THF) is −2.9°. Ltd. Allyl bromide is obtained from Yancheng Longgang chemical plant. *N,N′*-dicyclohexyl carbodiimide (DCC) and 4-dimethylamino pyridine (DMAP) are obtained from Shanghai Chemical Industry Company. Hydroxybenzoic acid is obtained from Beijing Reagent Factory. Tetrahydrofuran (THF) is dried over sodium metal and distilled. Pyridine is purified by distillation over KOH before using. Other analytical reagents are used as received.

2.2. Measurement

^{1}H NMR, ^{13}C NMR and FTIR are measured by Varian WH − 90PFT NMR Spectrometer (Varian Associates, Palo Alto, CA) and Perkinelmer instruments Spectrum One Spectrometer (Perkinelmer, Foster City, CA), respectively. Thermogravimetric analysis (TGA) and DSC measurements are carried out with a NETZSCH TGA 209C thermogravimetric analyzer, and a NETZSCH instruments DSC 204 (Netzsch, Wittelbacherstrasse, Germany) at a scanning rate of 10 °C min^{-1} under a flow of dry nitrogen. XRD measurements is performed with nickel-filtered Cu Kα ($\lambda = 1.54$ Å) radiation with a D8 ADVANCE XRD (Bruker, Karlsruhe, Germany). The X-ray measurements include wide-angle X-ray diffraction (WAXD) experiments and small-angle X-ray scattering (SAXS) measurements. Measurement of optical rotation (a) is carried out with a PerkinElmer instrument Model 341 Polarimeter at room temperatures using sodium light source ($\lambda = 589$ nm). The polarized optical microscopy (POM) study is performed using a Leica DMRX (Leica, Wetzlar, Germany) equipped with a Linkam THMSE − 600 (Linkam, Surrey, England) heating stage.

2.3. Synthesis

The synthetic routes to the mesogenic side arms, 4′-(4-(trifluoromethyl) benzoyloxy) biphenyl-4-carboxylic acid (TFBA) and 4′-(4-(allyloxy) benzoyloxy) biphenyl-4-carboxylic acid (AOBA) are shown in Scheme 1.

2.3.1. 4′-(4-(trifluoromethyl) benzoyloxy)biphenyl-4-carboxylic acid (TFBA)

A solution of 4-(trifluoromethyl) benzoic acid (40 g, 0.210 mol) and thionyl chloride (40 mL) was placed in a round flask equipped with a absorption apparatus to absorb hydrogen chloride. The mixture was stirred at room temperature for 3 h, and heated to 60 °C for 10 h to allow the reaction to proceed to completion. The excess thionyl chloride was distilled under reduced pressure. 4-(trifluoromethyl)benzoyl chloride (*TFB-C*) was obtained by distillation under reduced pressure (b.p.105 °C/38 mm Hg). Yield: 87%.

A sample of 4′-hydroxy-4-biphenylcarboxylic acid (38.5 g, 0.18 mol) was dissolved in 80 mL dry THF and 20 mL dry pyridine. The *TFB-C* (37.4 g, 0.18 mol) was dissolved in 20 mL dry THF. The THF solution of *TFB-C* was added dropwise into the solution of 4′-hydroxy-4-biphenylcarboxylic acid. The reaction mixture was refluxed until the result of FTIR analysis showed that the characteristic absorption bands of chloride and hydroxyl disappeared completely and then the solvent was partially removed under reduced pressure. After cooling to room temperature, the residue was poured into 600 mL ice water and neutralized with dilute hydrochloric acid. The crude product was obtained by filtration and washed with cold ethanol. The white powder 4′-(4-(trifluoromethyl) benzoyloxy) biphenyl-4-carboxylic acid (TFBA) was obtained after several re-crystallization from ethanol. Yield: 86%. m.p.: 253.5 °C. IR (KBr,cm^{-1}): 3063 − 2560 (−OH in Carboxylic acid dimer), 1739, 1674 (C═O), 1610,1515 (Ar). ^{1}H NMR ($CDCl_3$, d, ppm): 7.186 (s, 2H, Ar−$\underline{H}$); 7.553–7.562 (d, J = 5.4 Hz, 2H, Ar−$\underline{H}$); 7.784–7.837 (m, 4H, Ar−$\underline{H}$); 8.351–8.526 (m, 2H, Ar−$\underline{H}$); 8.708 (s, 2H, Ar−$\underline{H}$).

2.3.2. 4′-(4-(allyloxy) benzoyloxy) biphenyl-4-carboxylic acid (AOBA)

4-(allyloxy)benzoyl chloride (ABA-C) was prepared by 4-(allyloxy) benzoic acid (ABA was prepared according to ref. [33]) and thionyl chloride. A solution of ABA (20 g, 0.11 mol) and thionyl chloride (35 mL) was placed into a round flask equipped with a absorption apparatus to absorb hydrogen chloride. The mixture was stirred at room temperature for 4 h, and heated to 60 °C for 3 h. The excess thionyl chloride was distilled off under reduced pressure. ABA-C was obtained by distillation under reduced pressure. Yield: 82%.

A sample of ABA-C (27.5 g, 0.14 mol) was dissolved in 100 mL dry THF in a 500 mL round flask. 4′-Hydroxy-4-biphenylcarboxylic acid (30.0 g, 0.14 mol) was dissolved in 100 mL dry THF and 20 mL dry pyridine. The THF solution of ABA-C was added dropwise into the solution of 4′-hydroxy-4-biphenylcarboxylic acid. The reaction mixture was refluxed until the result of FTIR analysis showed that the characteristic absorption bands of chloride and hydroxyl disappeared completely and then the solvent was partially removed under reduced pressure. After cooling to room temperature, the mixture was poured into 800 mL ice water and neutralized with dilute hydrochloric acid. The crude product was obtained by filtration and washed with cold ethanol. The light yellow powder 4′-(4-(allyloxy) benzoyloxy) biphenyl-4-carboxylic acid (AOBA) was obtained after several re-crystallization from ethanol. Yield: 58%. m.p.: 198.7 °C. IR (KBr, cm^{-1}): 3070 − 2544 (−OH in Carboxylic acid dimer), 2997 − 2866 (−CH_2), 1729, 1686 (C═O), 1605, 1496 (Ar). ^{1}H NMR ($CDCl_3$, d, ppm): 4.405–4.472 (m, 2H, CH_2═$CHC\underline{H}_2O$); 5.349–5.366 (d, J = 10.2 Hz,1H, $C\underline{H}_2$═$CHCH_2O$); 5.449–5.480 (d, J = 18.6 Hz,1H, $C\underline{H}_2$═$CHCH_2O$); 6.055–6.125 (m, 1H, CH_2═$C\underline{H}CH_2O$); 7.018–7.032 (d, J = 8.4 Hz, 2H, Ar−$\underline{H}$); 7.270–7.330 (m, 2H, Ar−$\underline{H}$); 7.675–7.687 (d, J = 7.2 Hz, 4H, Ar−$\underline{H}$); 8.111–8.144 (d, J = 6.6 Hz, 2H, Ar−$\underline{H}$); 8.175–8.215 (d, J = 8.0 Hz, 2H, Ar−$\underline{H}$).