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Mesomorphic properties of multi-arm liquid crystals containing glucose and sorbitol as cores

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ABSTRACT

Six thermotropic cholesteric multi-arm liquid crystals (MALCs) were synthesized with glucose and sorbitol as chiral cores. ***b0***, ***b1*** and ***b2*** were introduced into hydroxy groups of the chiral cores as the mesogenic units in the arm scaffold. The roles played by the chiral cores and the terminal chain length of the mesogenic units to the mesomorphic behavior of the MALCs were studied. ***b0***, ***b1*** and ***b2*** displayed nematic phase. ***c0***, ***c1***, ***c2***, ***d0***, ***d1*** and ***d2*** exhibited cholesteric phases and wide mesogenic regions. The results indicated that the chiral cores played an important effect on inducing the cholesteric phase and an obvious effect on the melting temperature, clear point and mesophase region of the MALCs. The corresponding melting temperature and the clear point of ***d0***, ***d1*** and ***d2***, were lower than those of the ***c0***, ***c1*** and ***c2***. The mesophase regions of the formers were narrower than those of the latters. The terminal chain length of the mesogenic units played an important effect on mesogenic region, too. The mesogenic region increased as the terminal chain length increasing for the MALCs containing the same chiral core.

1. Introduction

Cholesteric liquid crystals (ChLCs) with the unique property of selective reflection, high optical rotation power and circular dichroism have presented large potential for various optical applications [1–12]. The optical properties result from chiral molecules in the nematic state that induce a twist in the director of adjacent molecules thereby forming a super molecular helical structure with a pitch p corresponding to a 2π twist of the nematic director [13]. Generally, ChLCs can be divided into low molecular mass compounds and polymers. However, the liquid crystalline polymers synthesized sometimes exhibit not only a cholesteric mesophase, but also a smectic one [14–22]. Compared with the polymers, the main advantages of the low molecular mass compounds are the lower viscosity and superior chemical purity. To the best of our knowledge, among the low molecular mass ChLCs, multi-arm LCs (MALCs), whose molecular structures deviate greatly from the conventional rod-like shape, have been few synthesized. As one kind of unconventional LCs, MALC usually has a core and a few mesogenic units as the side-chain liquid crystal arms. It has a higher molecular weight than the conventional low molecular mass compounds. MALC has attracted much attention for their symmetrical molecular structures and interesting properties [23–48]. Derivatives of benzene [23–26,29–40], condensed aromatic rings [41,42], cyclotriphosphazene [43–46], tetrachlorosilane [27] and pentaerythritol [47,48] are often taken as cores of the multi-arm compounds. To obtain cholesteric multi-arm liquid crystals (ChMALCs), chiral cores and arms should be constructed into the molecular structures. But to our knowledge, sugar has seldom been taken as cores in synthesizing MALCs [49,50].

Some researches have been carried in this laboratory in the field of ChMALCs. They were obtained by introducing cholesteric mesogenic units into the chiral core or non-chiral core. Yao and Zhang [23] introduced cholesteric mesogenic units into phloroglucinol. Zhang and Xiao [49,50] introduced cholesteric mesogenic units into glucose. For latter, the cholesteric mesogenic phases of the MALCs were induced by not only chiral core but also cholesteric mesogenic arms. To study the effect of chiral cores on inducing cholesteric mesogenic phase, nematic mesogenic units were chosen to introduce into the chiral cores. In this paper, ring-form glucose and chain-shape sorbitol were chosen as chiral cores to synthesize ChMALCs ***c*** and ***d***. ***b0***, ***b1*** and ***b2*** were conveniently introduced into the chiral cores by esterification with DCC as dehydration agent and DMAP as catalytic agent in the present study. The influence of the chiral cores and the mesogenic arms on the mesomorphic properties of the MALCs was carefully studied and discussed here.

2. Experimental procedures

2.1. Materials

Benzoic acid, metoxybenzoic acid, ethoxybenzoic acid, biphenol, sorbitol and anhydrous α-D-(+)-glucose were obtained from

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Beijing Chemical Industry Company (China). Sebacic acid, thionyl chloride, pyridine and tetrahydrofuran were bought from Shenyang Chemical Industry Company (China). DCC and DMAP were bought from Shanghai Chemical Industry Company (China). All solvents were purified by standard methods.

2.2. Measurement

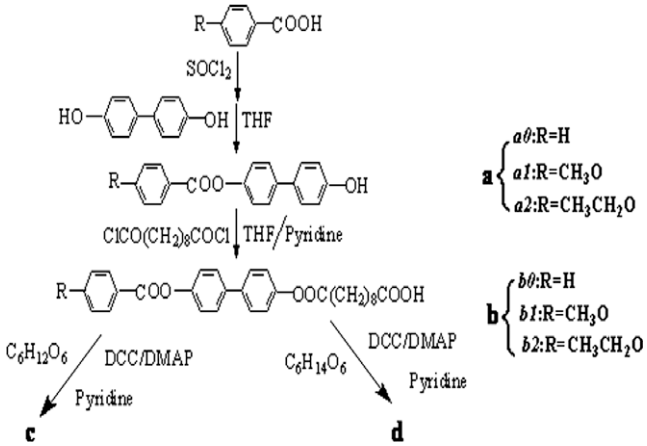
FT-IR spectra were measured on a Spectrum One (**B**) spectrometer (Perkin-Elmer, Foster City, CA, USA). Proton nuclear magnetic resonance (^{1}H NMR) spectra (300 MHz) were obtained with a Gemini 300 spectrometer (Varian Associates, Palo Alto, CA). The elemental analyses were carried out with Elementar Vario EL III (Elementar, Hanau, Germany). Phase-transition temperatures and thermodynamic parameters were determined with a DSC 204 (Netzsch, Wittelsbacherstr, Germany) equipped with a liquid nitrogen cooling system. The heating and cooling rates were 10 °C min^{-1} under nitrogen atmosphere. The reported thermal transition temperatures were collected during the first heating and cooling cycle. The thermal stability of the MALCs was measured with a Netzsch TGA 209C thermogravimetric analyzer in nitrogen atmosphere. A DMRX POM instrument (Leica, Wetzlar, Germany) equipped with a THMSE-600 hot stage (Linkam, Surrey, England) was used under an atmosphere to observe the phase-transition temperatures and analyze the LC properties for the MALCs through the observation of optical textures. XRD measurements were performed with nickel-filtered Cu Kα (λ = 1.52 Å) radiation with a DMAX-3A powder diffractmeter (Rigaku, Tokyo, Japan). The optical activities for the compounds were determined with a Perkin-Elmer Model 341 Polarimeter. All optical activity measurements of the MALCs were carried out in tetrahydrofuran (THF) with 2 ml cuvette of 100 mm length using light of a Na-lamp at λ = 589 nm.

2.3. Synthesis

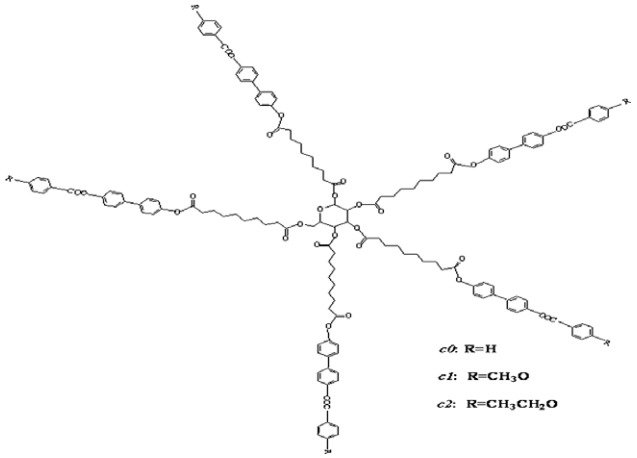
The synthetic route of the mesogenic arms and the MALCs was shown in Scheme 1, and the structures of ***c*** and ***d*** were shown in Schemes 2 and 3. Benzoic acid, metoxybenzoic acid and ethoxybenzoic acids are written as *4-R*-benzoic acid, where *R* denotes the para-substituent on benzene ring.

2.3.1. 4′-Hydroxy-4-(4-R-benzoyloxy]biphenyl (***a0***–***a2***)

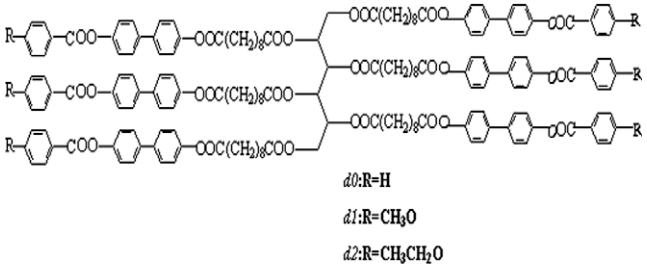
a0–***a2*** were prepared by the same synthetic method. The synthesis of ***a2*** was given as an example. The mixture of *4*-ethoxybenzoic acid (16.6 g, 0.1 mol) and thionyl chloride (47.6 g, 0.4 mol) in a 250 ml round-bottom flask was stirred for 2 h at room temperature, and then was refluxed for 4 h. The excess thionyl chloride was removed to give the corresponding acid chloride. The acid chloride (18.4 g, 0.1 mol) was dissolved in THF (20 ml). The solution was then added drop wise into the solution of 4,4′-dihydroxybiphenyl (74.7 g, 0.4 mol) in THF (180 ml) and Pyridine (20 ml) under quick stirring. The reaction mixture was refluxed for 18 h and poured into 1000 ml ice water and neutralized with dilute hydrochloric acid. The crude product was obtained by filtration and washed with 5% dilute sodium hydroxide solution, dilute hydrochloric acid and water. The white powder ***a2*** was obtained by recrystallization from ethanol. Yield 56%.



Scheme 1. The synthesis of multi-arm liquid crystals.



Scheme 2. The structure of multi-arm liquid crystals ***c***.



Scheme 3. The structure of multi-arm liquid crystals ***d***.

2.3.2. 8-[4-(4-R-Benzoyloxy)biphenyl-4′-yloxycarbonyl]pelargonic acid (***b0***–***b2***)

b0–***b2*** were prepared by the same synthetic method. The synthesis of ***b2*** was given as an example. Compound ***a2*** (10.02 g, 0.03 mol) was dissolved in the solution of THF (100 ml) and dry pyridine (20 ml). The solution was then added drop wise to solution of sebacic chloride (21.5 g, 0.09 mol) in THF (50 ml). The reaction mixture was then refluxed for 15 h and poured into ice water. The crude product was obtained by filtration and washed with water and cold ethanol. The white powder ***b2*** was obtained by recrystallization from ethanol. Yield 60%.

2.3.3. Penta {8-[4-(4-R-benzoyloxy)biphenyl-4′-yloxycarbonyl] pelargonic acid} glucose ester (***c0***–***c2***)

c0–***c2*** were prepared by the same synthetic method. The synthesis of ***c2*** was given as an example. The anhydrous α-D-(+)-glucose (0.594 g, 3.3 mmol) solution in dry pyridine (20 ml) was added drop wise to the solution of ***b2*** (8.55 g,16.5 mmol) in dry