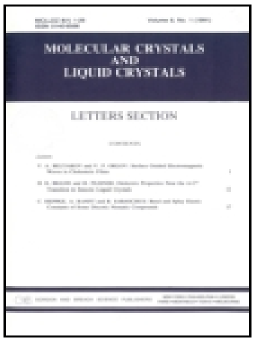

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Biphenyl-based liquid crystal precursors with alkanoate and hydroxyl group

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ABSTRACT
We synthesized a series of 4′-hydroxy-[1,1′-biphenyl]-4-yl alkanoate with a potentially reactive functional hydroxyl group as a LC precursor, which facilitates reaction with other chemical groups to tailor biphenyl-based liquid crystals (LCs) for specific applications. Several liquid crystalline materials were also synthesized based on these LC precursors to show high probability to generate various potential LCs. With increasing chain length, the melting point decreased and R_f (retardation factor: migration distance of substance ÷ migration distance of solvent front) of the synthesized LC precursor increased. This LC precursor series provides a useful first synthesis step to design tunable biphenyl/ester-based LCs.

KEYWORDS
Liquid crystals; Biphenyl derivatives; Liquid crystal precursor; Ester; Odd-even effect

Introduction

Liquid crystals (LCs) have been widely used in various areas ranging from display technology to biomedical sciences [1–3]. Biphenyl LC derivatives are one of the commonest LCs [2,3]. A linker between the two aromatic groups of typical thermotropic LCs determines the chemical, thermal and light stability of these LCs [4]. For example, ester linkages show chemical stability, but susceptibility to moisture, temperature and ultraviolet (UV) radiation [4,5]. In contrast, biphenyl-based LCs without a central linkage between the benzene units exhibit the highest thermal, chemical and UV stability [4,5]. Biphenyl-based LCs derived from this mesogen are widely used in the synthesis of LC epoxies, elastomers and polysiloxanes as well as side-chain liquid crystal polymers [1–3,6–12]. Ester end groups are commonly incorporated, due to their high thermal stability and ease of synthesis [6–12]. Biphenyl-4-yl monoalkanoates derivatives (Y-biphenyl-O-CO-C_nH_{2n+1}) are particularly useful and have been demonstrated to yield a wide range of LC behavior and are easily adapted in a wide range of synthetic schemes [8–12], and thus, have been extensively examined for specific applications such as elastomers and gelators [8–12]. Specifically, with –OH as a Y group, the 4′-hydroxy-[1,1′-biphenyl]-4-yl alkanoate (HO-biphenyl-O-CO-CnH_{2n+1}) offers several pathways to synthesize various LCs, such as alkyl halide, ester, alkyl sulfonate, aldehyde, ketone and carboxylic acid formations. To the best of the author's knowledge, there has been no report highlighting the synthesis of

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biphenyl-4-yl monoalkanoates precursor with a reactive hydroxyl group for a further reaction to obtain LCs with a specific required structure, such as monomers for a polymerization for side-chain liquid crystalline polymers, copolymers, elastomers, liquid crystalline benzoxazines and polysiloxanes [2,3,6,8].

In this study, a facile method to synthesize 4′-hydroxy-[1,1′-biphenyl]-4-yl alkanoate with a reactive hydroxyl group was developed. The melting point, yield and R_f (retardation factor in thin layer chromatography: migration distance of substance ÷ migration distance of solvent front) were determined as a function of the aliphatic chain length. Due to the hydroxyl functional group (-OH), the 4′-hydroxy-[1,1′-biphenyl]-4-yl alkanoate precursor can be easily reacted with other functional compounds, affording an opportunity to incorporate thermally stable LC mesogens into a variety of hybrid systems. This synthetic approach is adaptable and high yielding, producing high purity of ester biphenyl-based liquid crystalline precursor compounds suitable for further reaction. In addition, LC compounds with a hydroxyl head and a long aliphatic tail may find use as hydrogen bonding additives for use in applications, such as supramolecular nanostructures and biological applications [15,16].

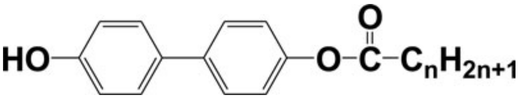
Experimental

The main chemicals used in this study were 4,4′-dihydroxybiphenyl (Sigma, 97%), a series of carboxylic acids (pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid and hexadecanoic acid), N,N′-Diisopropylcarbodiimide (DIC, Sigma, 99%), 4-(Dimethylamino) pyridine (DMAP, Sigma, 99%) and THF (Anhydrous, Sigma, 99.9%). All the chemicals were used without further purification. Cholesteryl chloroformate, pyridine, dichloromethane, triethylamine, K_2CO_3 and acetonitrile were obtained from Sigma for production of liquid crystalline materials.

To a stirred solution of 1.86 g (10 mmol) of 4,4′-dihydroxybiphenyl (biphenol) in 10 ml THF, 50 mg (0.4 mmol) of DMAP and 10 mmol of carboxylic acid were added. After the mixture was stirred for 5 min, 1.26 g (10 mmol) of DIC was added into the mixture, and then, the final reaction mixture was stirred under nitrogen purge for 3 h at room temperature through Steglich esterification. Insoluble solids, primarily precipitated urea, were then filtered off, and the filtrate was concentrated by a rotary evaporator until complete solvent removal. The residue was dissolved in a small amount of $CHCl_3$ and purified by a silica gel column, using $CHCl_3$ as an eluent to remove residual reactants and side reaction compounds.

C9EsBP-Chol and C9EsBP-PEG were synthesized as an example to generate liquid crystalline materials based on the LC precursor. 204 mg (0.6 mmol) of C9EsBP-OH and 224 mg (0.5 mmol) of cholesteryl chloroformate in 5 ml of dichloromethane were stirred under nitrogen at 200 rpm for 30 min. 39.6 mg (0.5 mmol) of pyridine was added into the mixture and stirred under reflux for 24 h through amine-catalyzed reaction, producing C9EsBP-Chol. To synthesize C9EsBP-PEG, polyethylene glycol (0.5 mmnol) and 4-toluenesulfonyl chloride (0.5 mmnol) were mixed with trimethylamine (0.5 mmnol) and 4-dimethylaminopyridine (0.02 mmol) in dichloromethane at room temperature for 24 h. Meanwhile, K_2CO_3 and acetonitrile were mixed at 60°C for 2 h. Subsequently, the two mixtures were mixed together at 60°C for 24 h.

^1H and ^{13}C NMR spectra were acquired in $CDCl_3$ using a Varian 600-MHz spectrometer. Differential scanning calorimetry (DSC) measurements were performed with a TA DSC Q2000 at the scanning rate of 10°C min^{-1} under nitrogen. The second heating/cooling cycle



Scheme 1. Structure of 4′-hydroxy-[1,1′-biphenyl]-4-yl alkanoate.

was used to identify the transition temperatures. A polarized optical microscope (POM, Leica) equipped with a hot stage was used to observe the transition temperatures under two crossed polarizers. All POM images were obtained under a cooling condition at 3°C min^{-1} with magnification objective of 50×. Thin layer chromatograph (TLC) was utilized to determine R_f (retardation factor in thin layer chromatography).

Results and discussion

Biphenyl esters have been widely used as the building blocks of mesogenic compounds, due to their structural simplicity and ease of derivatization. Scheme 1 shows the hydroxyl biphenyl ester studied in this paper. The biphenyl esters are generally composed of a rigid biphenyl group, long hydrocarbon tails and one or two polar ester bonds [8–11].

Yields for the synthetic approach for each compound varied between 38% and 65%. This variation in yield was due to the two hydroxyl (HO-) groups on the biphenol resulting in further side reaction; $H_{2n+1}C_n$-CO-O-biphenyl-O-CO-C_nH_{2n+1}. In the reaction, the stoichiometric ratio between biphenol and carboxylic acid was 1:1. It was expected that the theoretical yield would be lower than anticipated because the two carboxylic acid end groups may react with two HO- groups on the biphenol via further Steglich esterification in spite of anticipating the reaction of only one hydroxyl group on a biphenol with one carboxylic acid. It is difficult to control the reaction in such a way that only one carboxylic acid is attached to each biphenol. We utilized column chromatography to purify the monofunctional product by removing the difunctional compound deprived of both hydroxyl groups.

Depending on the length of the hydrocarbon tail, tunable properties were expected [13]. Indeed, Table 1 indicates that liquid crystalline transition temperatures, melting points and R_f were changed, depending upon the chain length. The transition temperatures were determined based on polarized optical microscopy. As seen in Fig. S1, the melting point decreased, in general, with increasing chain length, due to the longer flexible chain spacers coupled with the biphenyl units [13]. The typical odd–even effect [12] was also observed with respect to the melting point. The odd–even effect informs information on a molecular shape. For

Table 1. Melting points (T_m: from crystal to LC or liquid phase), clearing points ($T_{LC\text{-to-iso}}$: from LC to liquid phase) upon heating, R_f, Yield, and purification method for synthesized products in this study.

n	T_m (°C)	$T_{LC\text{-to-iso}}$ (°C)	R_f	Yield (%)	Purification
4	122.1	X	0.13	61	Column, recrystallization
5	120.4	X	0.14	57	Column, recrystallization
6	121.5	X	0.14	60	Column, recrystallization
7	120.5	X	0.15	53	Column
8	120.5	X	0.15	48	Column, recrystallization
9	119.8	X	0.17	65	Column, recrystallization
10	120.1	X	0.17	58	Column
11	119.4	X	0.18	57	Column, recrystallization
12	119.4	X	0.19	61	Column, recrystallization
13	118.0	X	0.19	38	Column, recrystallization
14	118.7	123.5	0.21	62	Column, recrystallization
15	118.1	X	0.21	45	Column, recrystallization

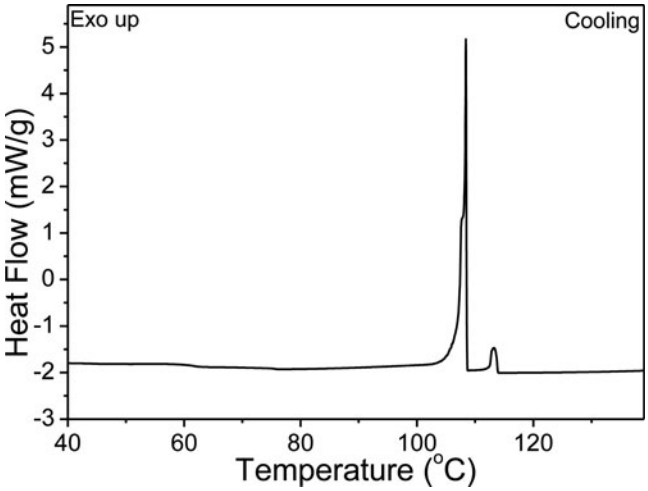


Figure 1. DSC scan of HO-biphenyl-O-CO-$C_{14}H_{29}$ upon cooling. Cooling rate is 10°C min^{-1}.

alkyl chains in all-trans conformation, the even homologs have a stretched elongated shape, whereas molecules with an odd number of atoms in the aliphatic tails are bent-shaped, which influences various properties [14]. Using thin layer chromatography (TLC), we observed that R_f increased with increasing chain length, due to the relatively hydrophobic longer aliphatic chains moving faster on the hydrophilic TLC.

DSC confirms the thermal properties of this series of 4′-hydroxy-[1,1′-biphenyl]-4-yl alkanoate (HO-biphenyl-O-CO-C_nH_{2n+1}). Only HO-biphenyl-O-CO-$C_{14}H_{29}$ among the series exhibited two transition temperatures upon cooling in Fig. 1. A melting temperature was only observed in the other LC precursors. The melting points of each compound are highlighted in Table 1 and Fig. S1. Polarized optical microscopy (POM) gives a visual interpretation of the liquid crystalline textures of HO-biphenyl-O-CO-$C_{14}H_{29}$ to confirm the liquid crystalline phases. As seen in Fig. 2, fan-type liquid crystalline textures for HO-biphenyl-O-CO-$C_{14}H_{29}$ were observed after 113.5°C (B), upon cooling, while an isotropic phase was observed above 124.0°C (A). As it was further cooled down, the liquid crystalline phase disappeared, and transitioned to a crystalline phase below 105.5°C (C).

Based on this LC precursor, liquid crystalline materials were synthesized to evaluate a potential application and approach for next steps. Figures 3(A) and (B) indicate liquid crystalline behavior of C9EsBP-Chol (C_9H_{19}-CO-O-biphenyl-cholesteryl) and C9EsBP-PEG (C_9H_{19}-CO-O-biphenyl-PEG), respectively. A small peak from isotropic to liquid crystalline phase was observed at 213°C upon cooling for C9EsBP-Chol in Fig. 3(A) where the POM image showed an ordered structure. It became a crystal at 69°C. C9EsBP-PEG also showed

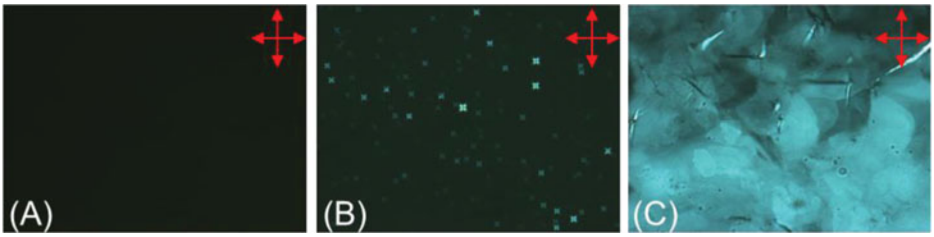


Figure 2. POM images of HO-biphenyl-O-CO-$C_{14}H_{29}$ at 124.0°C (A), 113.5°C (B), and 105.5°C (C). Cooling rate is 3°C min^{-1} with magnification objective of 50×.

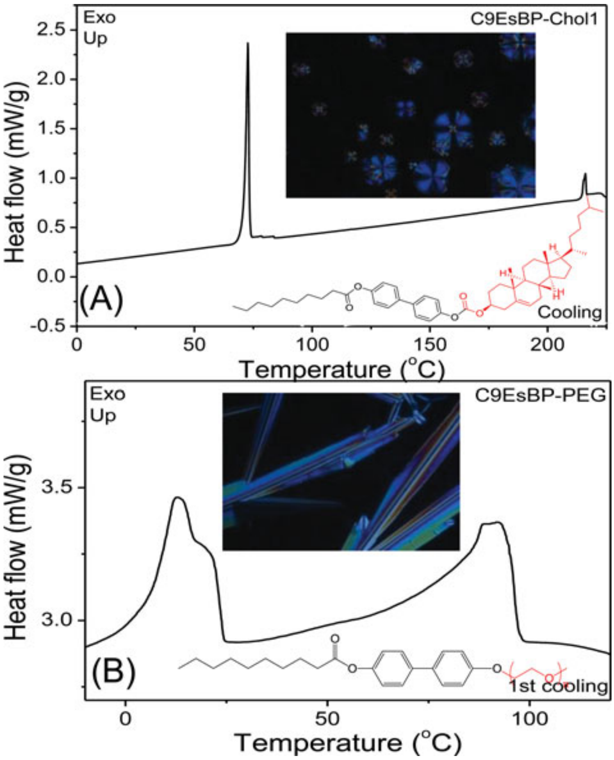


Figure 3. Dynamic DSC scan upon cooling for C9EsBP-Chol (A) and C9EsBP-PEG (B). Insets are POM images in LC phase and chemical structure.

two broad transition temperatures due to the large PDI of the PEG starting material, which was demonstrated in Fig. S4 in supplementary information.

Conclusion

The monoalkoxycarbonyl hydroxyl-biphenyl precursors were successfully synthesized. A liquid crystalline phase was also observed for the synthesized precursor; HO-biphenyl-O-CO-$C_{14}H_{29}$, whereas only a melting point was observed for the other precursor compounds. An odd–even effect on the melting point was also observed. The melting point of the synthesized LC precursor decreased with increasing aliphatic chain length. R_f increased as a function of aliphatic chain length. C_9H_{19}-CO-O-biphenyl-cholesteryl and C_9H_{19}-CO-O-biphenyl-PEG showed liquid crystalline behavior by reacting the LC precursors with cholesteryl chloroformate and PEG, respectively, to show high probability of various potential LCs. It is suggested that the monoalkoxycarbonyl hydroxyl-biphenyl precursors could be utilized as a starting material to synthesize a specific liquid crystal, by attaching a required functional group to the biphenyl containing an ester group.

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