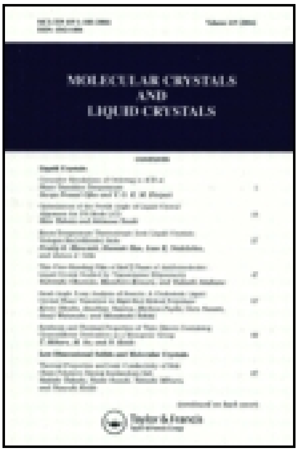

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Synthesis and Characterization of a Novel Dimeric Liquid Crystalline Dendrimer

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A liquid crystalline aryl ester dendrimer containing 1,4-bis(4-hydroxybenzoyloxy) butane as the core moiety was successfully synthesized through an efficient convergent synthetic approach. The polyester fragment was synthesized through a process involving the condensation of 4-(dodecyloxy) benzoic acid with 2,2,2-trichloroethyl-3,5-dihydroxybenzoate. The coupling step was followed by removal of the 2,2,2-trichloroethyl ester group with zinc acetic acid. Characterization of all the synthesized compounds was carried out using spectroscopy methods. The thermal behavior of the acid dendritic wedges and the aryl ester dendrimer was investigated by differential scanning calorimetery and polarizing optical microscopy. Optical microscopy showed a focal-conic texture characteristic of the smectic A phase for novel dimeric dendrimer.

Keywords Aryl ester dendrimer; convergent approach; liquid crystal dimer; mesomorphism

Introduction

Dendrimers are relatively new materials with a highly controlled molecular structure in several space orientations [1,2]. Liquid crystal dendrimers are an exciting development that combines mesomorphism and directional properties. In recent years, there has been an increasing interest in the field of liquid crystalline dendrimers [3,4]. The induction and the control of the mesomorphic properties (phase type and stability) in dendrimers can be achieved by a dedicated molecular design which depends on the chemical nature and structure of both the functional groups and the dendritic matrix [5]. In consequence, dendrimers have become an extraordinary tool to study the structure–activity relationships in the field of liquid crystals because they are able to adopt different conformations, provided that the chemical nature of the dendritic core allows for such deformations, to obtain the most stable structures.

Liquid crystal dimers have been the subject of intense research since the first example was reported in 1927 [6]. Initial interest in these materials stemmed from their ability to act as model compounds for semi-flexible main chain liquid crystal polymers, but are now of fundamental interest in their own right because their behavior is significantly different to that of conventional low molar mass liquid crystals [7]. Normally the mesophase behavior of such dimeric compounds is influenced by the length and structure of mesogenic units,

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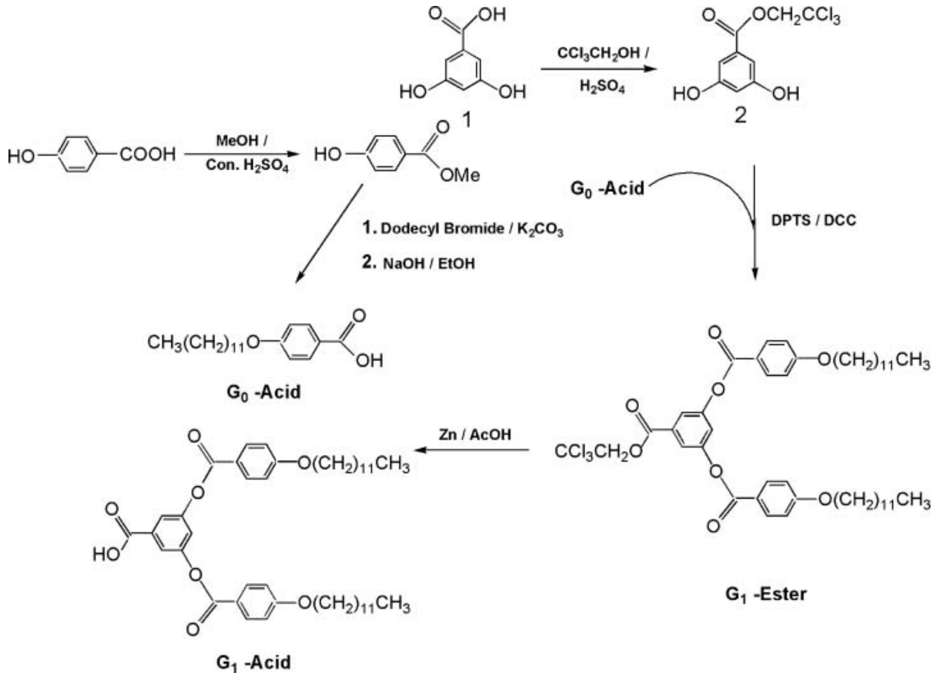
*Address correspondence to Massoumeh Bagheri, Chemistry Department, Science Faculty, Azarbaijan Shahid Madani University, Tabriz Postal Code: 5375171379, P.O. Box: 53714-161, Iran. Tel.: +98-412-4327500; Fax: +98-412-4327541. E-mail: massoumehbagheri@yahoo.com the nature and length of the spacer and terminal chains, the existence of lateral groups, and by the structure, position, and direction of the linking groups. Until now a great number of dimeric mesogens have been synthesized and characterized [8,9]. Therefore, we have designed and synthesized the first-generation aryl ester dendrimer as a new liquid crystal dimer. This molecule has two substituted bent-shaped mesogenic units with four ring structures and dodecyloxy terminal chains ($-C_{12}H_{25}$) linked symmetrically as a dimer through a flexible spacer [$-COO(CH_2)_4OOC-$]. This mesogenic twin differs from the other reported liquid crystal dimers in view of the structure of mesogenic units.

Experimental

Materials

The purification and drying of compounds and solvents was carried out according to the common procedures. 4-Hydroxybenzoic acid; 3,5-dihydroxybenzoic acid; 1-bromododecane; zinc dust; glacial acetic acid; 2,2,2-trichloroethanol; dicyclohexylcarbodiimide (DCC); N,N-dimethylaminopyridine (DMAP), and *p*-toluenesulphonic acid (PTSA) were purchased from Merck and used as received. 4-(Dimethylamino)pyridinium *p*-toluenesulphonate (DPTS) [10], 4-(dodecyloxy)benzoic acid (G0-acid) [11], and 2, 2, 2-trichloroethyl-3,5-dihydroxybenzoate (2) [12] were synthesized according to the literature procedure (Scheme 1). 1,4-Bis(4-hydroxybenzylcarbonyloxy) butane (3) was synthesized by the method reported in our previous publication [13].



Scheme 1. Synthesis of G1-acid dendron.

Synthetic Procedures

2, 2, 2-Trichloroethyl-3,5-di(1-(4-(n-dodecyloxy)benzylcarbonyloxy))benzoate (G1-ester). To a solution of G0-acid (5.64 g, 18.43 mmol) and compound **2** (1.75 g, 6.14 mmol) in dry dichloromethane (25 mL) was added DPTS (1.08 g, 3.68 mmol), and the mixture was stirred at room temperature under nitrogen atmosphere for 15 min. DCC (3.80 g, 18.43 mmol) was then added and stirring continued at room temperature until the reaction had reached completion (2 h), a precipitate of dicyclohexylurea appeared during this time. The reaction mixture was filtered and the filtrate was evaporated to dryness under reduced pressure. The crude product was then purified by column chromatography with CH_2Cl_2/hexane (2:3 v/v) to give product in 60% yield, m.p. 59–61°C. FT-IR (KBr): $\bar{\upsilon}$ 2917-2850 (aliphatic C-H), 1738 (C=O), 1607, and 1580 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.88 (t, 3H, 2 × $-CH_2CH_3$, J = 7.12 Hz), 1.27 (overlapped m, 36H, 2 × $-(CH_2)_9-$), 1.80 (m, 4H, 2 × $\underline{-CH_2}CH_2OAr$, J = 6.56 Hz), 4.04 (t, 4H, 2 × $-CH_2OAr$, J = 6.50 Hz), 4.9 (s, 2H, $-CH_2CCl_3$), 6.98 (d, 4H, ArH meta to –COOAr, J = 8.92 Hz), 7.30 (t, 1H, ArH para to $-COOCH_2CCl_3$, J = 2.2 Hz), 7.96 (d, 2H, ArH ortho to $-COOCH_2CCl_3$, J = 2.16 Hz), 7.99 (d, 2H, ArH, ortho to –COOAr, J = 8.92 Hz) ppm.

3, 5-Di(1-(4-(n-dodecyloxy)benzyl carbonyloxy)) benzoic acid (G1-acid). To the solution of G1-ester (3 g, 3.48 mmol) in THF (25 mL) was added glacial acetic acid (5 mL), and the solution was stirred at room temperature for 15 min under nitrogen atmosphere. Zinc dust (0.95 g, 14.53 mmol) was then added and the contents were stirred vigorously at room temperature for 20 h. The reaction mixture was filtered and the filtrate poured into water (100 mL) and extracted with diethyl ether (2 × 100 mL). The combined extracts were washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness under reduced pressure. The crude product was purified by recrystallization from petroleum ether, resulting in 81% yield of white solid, m.p. 87–89°C; FT-IR: $\bar{\upsilon}$ 2920-2851 (aliphatic C-H), 1733 (C=O, ester), 1699 (C=O, carboxylic acid), 1607-1509 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.88 (t, 6H, 2 × $-CH_3$, J = 7.04 Hz), 1.27 (overlapped m, 36H, 2 × $-(CH_2)_9-$), 1.80 (m, 4H, 2 × $-\underline{CH_2}CH_2OAr$, J = 6.56 Hz), 4.04 (t, 4H, 2 × $-CH_2OAr$, J = 6.56 Hz), 6.98 (d, 4H, ArH meta to –COOAr, J = 8.92 Hz), 7.42 (t, 1H, ArH para to $-COOH$, J = 2.2 Hz), 7.86 (d, 2H, ArH ortho to –COOH, J = 2.16 Hz), 8.13 (d, 4H, ArH ortho to –COOAr, J = 8.92 Hz) ppm. ^{13}CNMR ($CDCl_3$): δ 13.12, 21.67, 24.99, 28.65, 30.90, 67.37, 113.41, 119.80, 119.95, 120.50, 130.16, 131.42, 150.52, 162.82, 163.31, and 168.15 ppm.

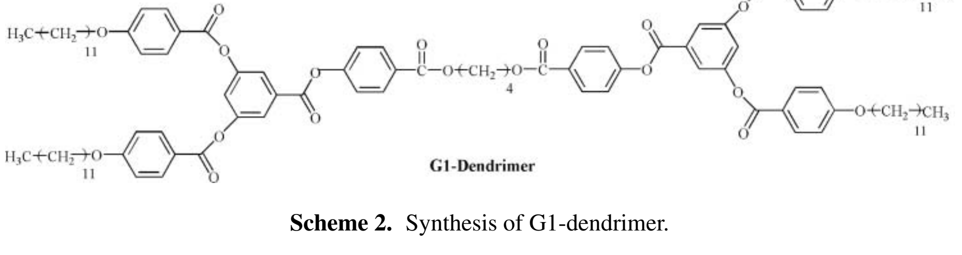
Arylc Ester Dendrimer (G1-dendrimer). To a solution of G1-acid (3.60 g, 4.9 mmol) and compound **3** (0.53 g, 1.63 mmol) in dry dichloromethane (25 mL) was added DPTS (0.03 g, 0.1 mmol). The mixture was stirred at room temperature under nitrogen atmosphere for 15 min. DCC (1.03 g, 4.9 mmol) was then added and stirring continued at room temperature for 24 h, during this time the filtrate was evaporated to dryness under reduced pressure, the crude product, a precipitate of dicyclohexylurea, appeared. The reaction mixture was filtered and purified by column chromatography with 4:1 hexane/ethyl acetate to give polyarylester dendrimer as a white solid in 81% yield. FT-IR (KBr): $\bar{\upsilon}$ 2923-2853 (aliphatic C-H), 1733 (C=O), 1606 and 1540 (C=C) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.88 (t, 12H, 4 × $-CH_2\underline{CH_3}$, J = 7.04 Hz), 1.27 (overlapped m, 72H, 4 × $-(CH_2)_9-$), 1.70 (m, 4H, 2 × $-\underline{CH_2}CH_2OCOAr$), 1.82 (m, 8H, 4 × $\underline{-CH_2}CH_2OAr$, J = 6.56 Hz), 4.02 (t, 8H, 4 × $-CH_2OAr$, J = 6.56 Hz), 4.21 (t, 4H, 2 × $-CH_2\underline{CH_2}OCOAr$, J = 4.72 Hz), 6.98 (d, 8H, ArH ortho to –OR, J = 8.88 Hz), 7.29 (d, 4H, d, 4H, ArH meta to –OCOAr, J = 3.12 Hz), 7.47 (t, 2H, ArH para to $-COOAr$, J = 2.09 Hz), 7.60 (m, 4H, ArH meta to –OCOAr, J = 3.12 Hz), 7.96 (d, 4H, ArH ortho to –COOAr, J = 2.16 Hz), 8.13 (d, 8H, ArH meta to –OR, J = 8.88 Hz) ppm. ^{13}CNMR ($CDCl_3$): δ 13.12, 21.67, 24.99, 27.91, 28.65, 30.90, 67.13, 67.37, 113.42, 119.80, 119.96, 119.81, 119.96, 120.51, 121.3, 127.19, 129.29, 130.17, 131.42, 155.52, 162.82, 163.31, and 166.13 ppm.

Methods

Melting points were recorded with an electrothermal 9100 apparatus. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker PS-15 spectrometer. Proton Nuclear Magnetic Resonance (^{1}H-NMR) spectra were taken on a 400 MHz-Bruker SP-400 AVANC spectrometer using deuterated chloroform as solvent with tetramethylsilane as internal standard. A differential scanning calorimeter Mettler 822 was used to determine phase transition temperatures at the heating and cooling rate of 10°C/min. The instrument was calibrated with indium regarding temperature and enthalpy. An optical Zeiss polarizing microscope equipped with long working distance objective was also used to observe phase transitions. The samples were heated and cooled with a TMS94 hot stage and associated temperature controller.

Results and Discussion

The synthetic pathways are summarized in Schemes 1 and 2. By implementing a convergent approach, the synthesis of the first-generation of aryl ester dendrimer was accomplished on the basis of diol (3) as a core. To begin the synthesis, trichloroethylester (2) was condensed with G0-acid using DPTS/DCC to afford the G1-ester dendritic wedge in 60% yield (Scheme 1). The trichloroester was then removed selectively in the presence of other ester groups using zinc and acetic acid to provide the acid wedge (G1-acid) in 81% yield. A key step in the synthesis of dendritic structures is the coupling step, in this case an esterification reaction. DCC and DMAP/DMF are commonly used as a catalyst/solvent in the esterification process of a carboxyl group for the reaction with hydroxyl mesogenic compound [14] with a significant amount of the rearranged urea. As the formation of urea is known to be favored at high pH, DMAP was replaced by its *p*-toluenesulfonic acid salt, as described by Moore and Stupp [15]. The reaction of the G1-acid dendritic wedge (dendron) with diol (3) in the presence of DPTS/DCC in CH_2Cl_2 gave the target first-generation dendrimer in 81% yield after chromatographic purification (Scheme 2); however, no trace of urea as side product was observed.



Scheme 2. Synthesis of G1-dendrimer.

The reason for the election of such a core is the presence of two hydroxyl groups on benzene rings that react with the carboxylic group of G1-acid to induce the mesogenic behavior of dendrimeric structure as a liquid crystal dimer. The ester linkages contribute to the linearity and the overall polarizability, while the terminal alkyloxy chains induce flexibility to the molecule. The dendrimer was soluble in all common solvents at room temperature. The solubility of the dendrimer is attributed to the presence of terminal flexible alkyl chains in spite of the presence of polar ester linkages.

The structure of the synthesized compounds G0-acid, G1-ester, G1-acid, and G1-dendrimer were characterized using FT-IR and ^{1}H-NMR spectroscopy techniques. The ^{1}H-NMR is consistent with structural assignments. To establish the extent of reaction from the ^{1}H-NMR spectra, the integration of resonances due to methylene hydrogen of the core (δ: 1.7 and 4.21) was compared with the resonances arising from aromatic hydrogen (δ: 8.13).

The thermal behaviors of these compounds were investigated by Differential scanning calorimetry (DSC) and polarizing optical microscope (POM) with a heating rate 10°C/min. Ambrožič [11] previously reported the mesogenic properties of 4-(n-alkyloxy)benzoic acids. The determined thermal transitions of G0-acid by DSC and POM are in good accord with the previously reported values [11]. No mesomorphic behavior is observed for G1-acid. This compound exhibits a melting temperature at 99°C directly into the isotropic liquid phase. The DSC thermogram obtained for G1-dendrimer is presented in Fig. 1 for the second heating cycle. As listed in Fig. 1, the heating process of the dendrimer showed two endothermic peaks at 39.5 (ΔH = 21.42 J/g) and 78°C (ΔH = 4.14 J/g) corresponding to the crystal-mesophase and mesophase-isotropization respectively.

Furthermore, POM observations confirm the presence of a smectic A (SmA) liquid crystalline phase for G1-dendrimer in the temperature region between two DSC peaks on heating process. The focal conic texture formation of the SmA phase is shown in Fig. 2.

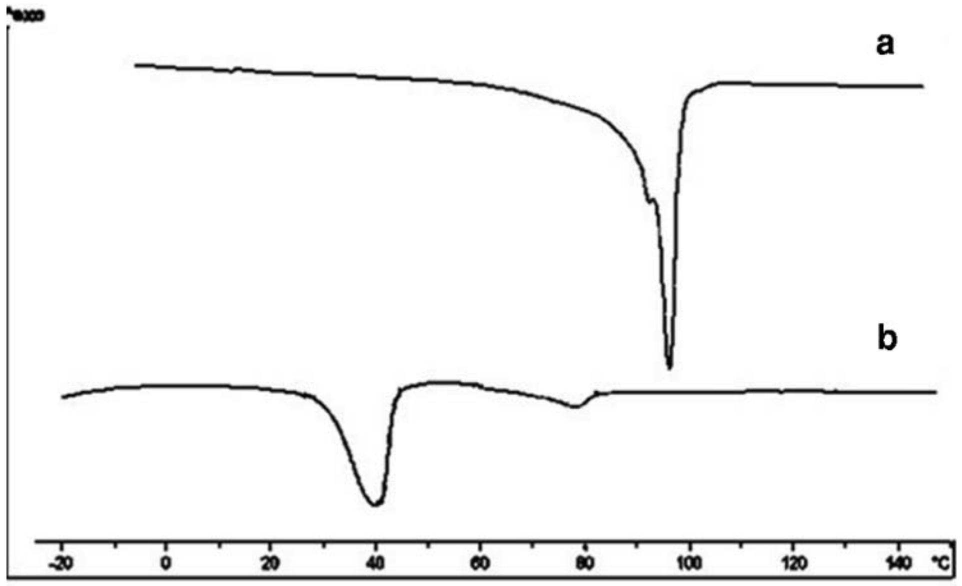


Figure 1. DSC thermogram of (a) G1-acid, and (b) G1-dendrimer.

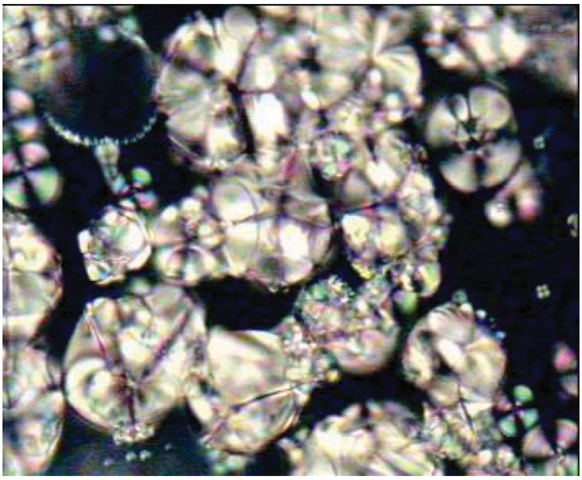


Figure 2. Optical polarized micrographs for G1-dendrimer on heating at 66°C (×200).

Conclusion

We have designed a novel liquid crystal dimer using the first-generation aryl ester based on a dendrimer. This compound was synthesized through an efficient convergent synthetic approach and exhibits a SmA phase. Therefore, the use of bent-shaped mesogens could be appealing to liquid crystal dimers.

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