Synthesis and Characterization of a Novel Ferroelectric Liquid Crystal Compound Derived from L-tyrosine

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A novel ferroelectric liquid crystal compound, (S)-4-(2-chloro-3-(4-*n*-dodecyloxy)phenylpropionato)-4′-(2-methyl)butyloxy-biphenylcarboxylate(CDPMBB) has been synthesized using L-thyrosine as chiral ingredient. The thermal and phase behaviour of the compound is studied by thermal microscopy (TM) and differential scanning calorimetry (DSC). The ferroelectric characterization is performed in terms of spontaneous polarization (P_S), which reveals that CDPMBB show high magnitude spontaneous polarization.

Keywords: CDPMBB; FLC; Spontaneous Polarization; Smectic-C*.

Introduction

Great interest has been directed towards novel ferroelectric liquid crystals (FLC) with high spontaneous polarization that ensures high switching speed. Since the first high speed electro-optic FLC device was discovered [1], a number of FLC compounds with extremely large spontaneous polarization were developed using amino acids as chiral ingredients [2, 3]. In search of materials with high spontaneous polarization we have made a successful attempt to isolate a FLC molecule possessing two asymmetric centres. The molecular skeleton of CDPMBB is designed in such a way that: **(a)** two asymmetric centres are incorporated along the long molecular axis using L-tyrosine and (S)-2-methyl-butanol as chiral ingredients, **(b)** highly electronegative chlorine atom is introduced on the α-carbon of the amino acid by nucleophilic substitution with retention of the asymmetric configuration [4, 5] and **(c)** the number of transverse dipoles and phenyl rings (biphenyl moiety) are increased along the long molecular axis. In continuation of our previous efforts [6 – 15] to generate ferroelectric materials with high P_S, this communication deals with a novel route of synthesis and also summarizes some important physical parameters which make the present compound most suitable for future application demands.

Experimental

The two chiral centres introduced in the present compound were derived from a chiral ingredient, (S)-2-amino-3-(4-hydroxy)phenyl propionic acid (L-tyrosine), available commercially (CDH, India) in high enantiomeric purity. The synthetic route for the preparation of CDPMBB along with the reaction conditions are illustrated in Scheme 1 while a detailed synthetic procedure including various intermediates is presented in the following.

(S)-2-chloro-3-(4-hydroxy)phenyl propionic acid (**1**) is prepared by dissolving (S)-2-amino-3(4-hydroxy)phenyl propionic aicd (5.43 g, 30.0 mmol) in

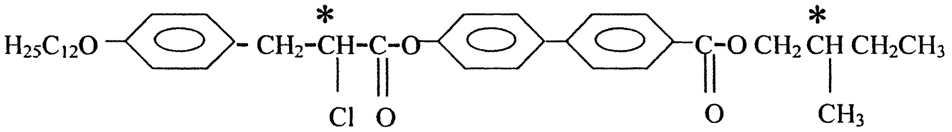
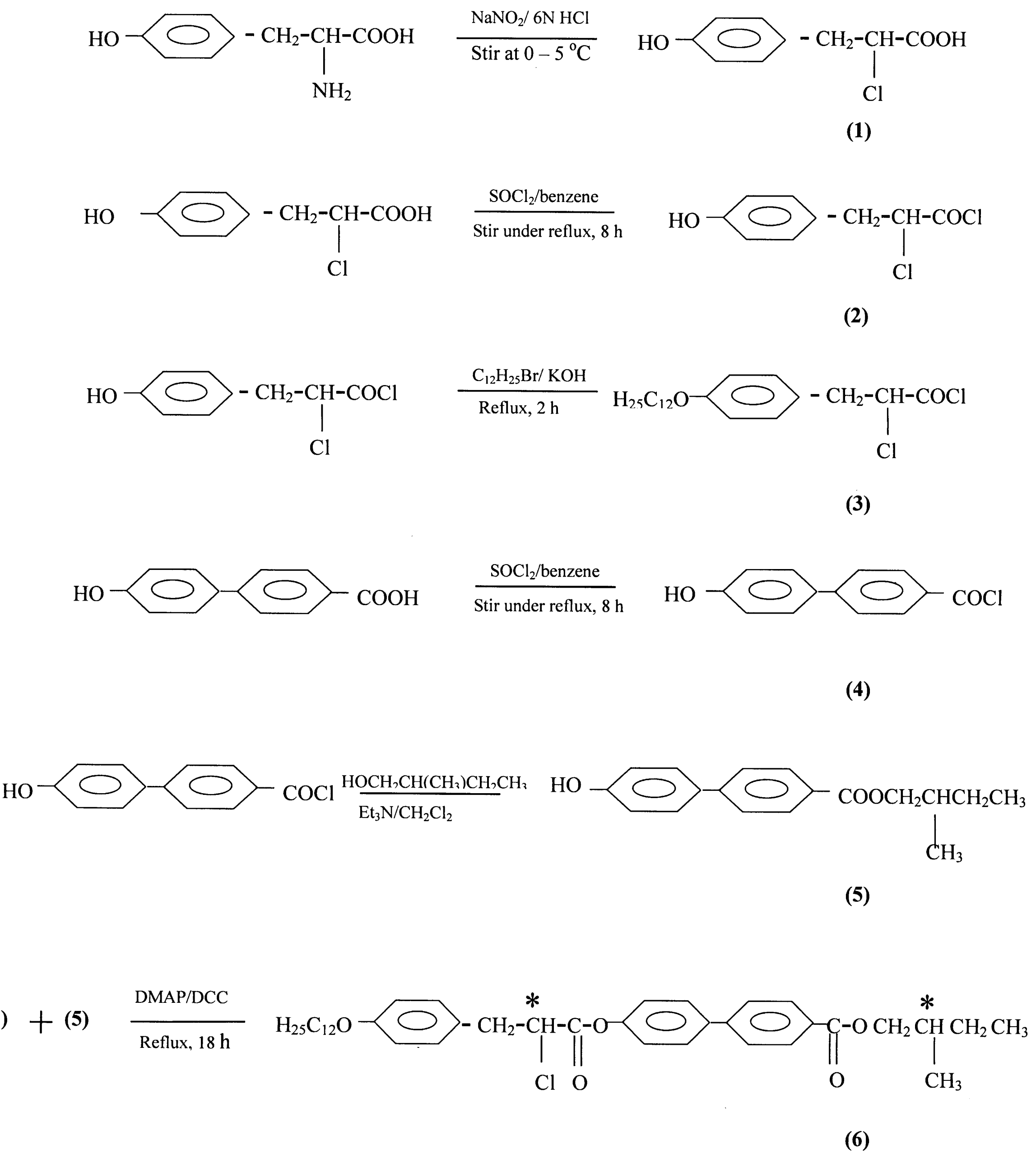


Fig. 1. Molecular structure of CDPMBB.



Scheme 1. Synthetic route for CDPMBB.

20 cm^3 of 6 N HCl and bringing the solution to 0 °C. Freshly pulverized sodium nitrite (2.72 g, 32.0 mmol) is added to the solution in small portions with vigorous stirring while maintaining the reaction temperatures between 0 and 5 °C. The reaction mixture is stirred for 14 – 16 h and then extracted with 40 cm^3 of diethylether. The etherial layer is dried over anhydrous sodium sulphate for 12 h. The crude

product, obtained as a yellow product on removing the excess solvent by distillation under reduced pressure, is washed repeatedly with cold EtOH and finally recrystallized from hot dichloromethane to get a 53.2% yield.

(S)-1,2-dichloro-3-(4-hydroxy)phenyl propionic acid **(2)** is synthesized by mixing **1** (25.0 mmol) with *$SOCl_2$* (40 mmol) in 40 cm^3 of dry benzene under nitrogen atmosphere and keeping the reaction mixture under reflux with continuous stirring at 75 °C for 8 h. After the evolution of SO_2 gas has ceased, the volume of the resulting solution is reduced by vacuum distillation to get a yellow product which was suction filtered, washed several times with cold methanol and recrystallized from hot benzene solution to get a yield of 53.1%.

(S)-1,2-dichloro-3-(4-dodecyloxy)phenyl propionic acid **(3)**: A dichloromethane solution (40 cm^3) containing **2** (20 mmol), 1-bromododecane (25 mmol) and KOH (30 mmol) is magnetically stirred under reflux for 2 h. The resultant yellow precipitate (KBr) is suction-filtered and washed repeatedly with dichloromethane. The resulting yellow solution is extracted with diethyl ether and dried over anhydrous sodium sulphate for $\sim$12 h. A yellow oily product of **3** with a yield of 42.1% is obtained by removing the excess dichloromethane by distillation under reduced pressure.

4′-hydroxy-4-biphenylcarboxylic chloride **(4)** is synthesized by mixing 4′-hydroxy-4-biphenylcarboxylic acid (25.0 mmol) with *$SOCl_2$* (40.00 mmol) in 40 cm^3 of dry benzene under nitrogen atmosphere and keeping the reaction mixture under reflux with continuous stirring at 72 °C for 8 h. After the evolution of SO_2 gas has ceased, the volume of the resulting solution is reduced by vacuum distillation to get a yellow solid product which is suction-filtered, washed several times with cold methanol and recrystallized from hot benzene to get a yield of 48.6%.

(S)-4-hydroxy-(2-methyl)butyloxy-biphenylcarboxylate **(5)** is prepared by refluxing **4** (25 mmol) with (S)-2-methylbutanol (27 mmol) in 40 cm^3 of dichloromethane solution for $\sim$4 h. Triethylamine (4.0 mmol) is then added drop wise, and the mixture is refluxed at 60 °C with constant stirring for 10 – 12 h. The resultant solution, after cooling to room temperature, is poured into a beaker containing $\sim$50 cm^3 of cold water. The product, separated as a white solid, is then extracted with petroleum ether and dried over Na_2SO_4 for 6 h. The white crude product obtained on removing the excess ether and followed by repeated washings with cold methanol, is recrystallized from hot benzene to get 41.8% yield.

The final desired product, CDPMBB **(6)** is obtained by stirring together dry dichloromethane solutions (40 cm^3) of **3** (6.0 mmol) and **5** (6.0 mmol) for 6 h at room temperature under inert atmosphere. To the resulting reaction-mixture 0.38 g (3.1 mmol) of 4-dimethylaminopyridine (DMAP) and 0,82 g (4.0 mmol) of N,N′-dicyclohexylcarbodiimide (DCC) are added drop wise under constant stirring. The mixture is then refluxed for 15 – 18 h at 75 °C. The volume of the resultant yellow solution is reduced by vacuum distillation to get an oily product. This oily residue is then extracted twice sith diethylether, and the etherial layer is dried over anhydrous Na_2SO_4 for 12 h. The crude product obtained on slow evaporation of ether is washed repeatedly with cold acetonitrile solution, which is finally recrystallized from hot benzene solution to get a yield of 31.2%.

All the intermediate products including the desired product thus obtained are purified by passing through silica gel columns using appropriate eluent mixtures, and their structures are confirmed by IR and NMR spectral analyses. CPCDBD is highly stable at room temperature and also shows a high degree of thermal stability when subjected to repeated thermal scans for differential scanning calorimetry and spontaneous polarization measurements.

Results and Discussion

The phase variants and transition temperatures of CDPMBB are determined [16] from the characteristic textural observations under a polarizing thermal microscope (Olympus BX 50) equipped with an optical display (DP-10) at a scan rate of 0.1 °C per minute. On cooling the isotropic melt, CDPMBB exhibits focal conic fans (smectic-A), concentric striations across focal conic fans (smectic-C*) and broken focal conic fans (smectic-F*). The phase transition temperatures observed through thermal microscopy are found to be in reasonable agreement with DSC data (Perkin-Elmer DSC-7). The phase sequence and transition temperatures (°C) of the present compound are:

Iso (120.3) Sm-A (91.5) Sm-C* (59.2) Sm-F* (52.4) Cryst.

The spontaneous polarization is measured in a 10 μ polyimide buffed cell (Display Tech., USA) by the field reversal method with a modified integrator part. Polarizing current peaks at different temperatures are analyzed to obtain the magnitude of spontaneous polarization. The temperature variation of the spontaneous polarization is represented in Figure 2. The magnitude of spontaneous polarization is found to increase with decreasing temperature and to attain a saturated value in the Sm-C* phase. The present compound shows a high P_S (~ 57 nC · cm^2) at 65 °C in the ferroelectric phase. The structural contribution towards the magnitude of spontaneous polarization in the present material can be realized from the presence of two highly polar asymmetric carbons. The effective role of these asymmetric configurations can best be accounted for on the basis of the existence of an elongated delocalized electron cloud *via* biphenyl moiety as spacer unit.

Detailed investigations relating to other physical parameters, *viz.* response times, viscosity, dielectric constant, tilt angle, etc. are in progress.

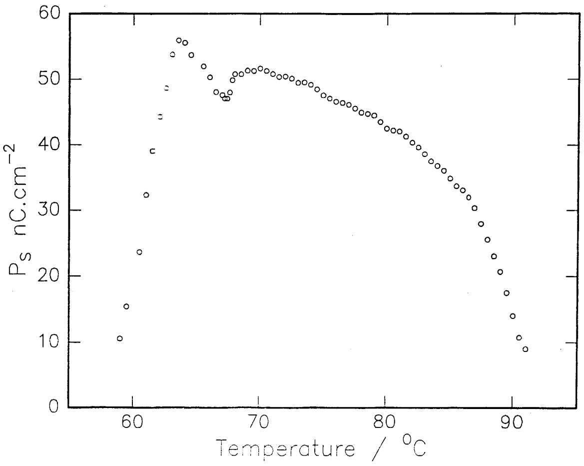


Fig. 2. Temperature variation of spontaneous polarization.

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