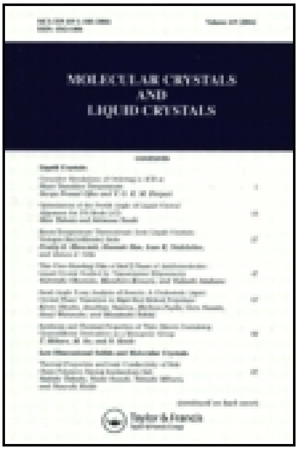

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Poluri A. Kumar [a] & Venkata G. K. M. Pisipati [a]

[a] Centre for Liquid Crystal Research and Education (CLCRE), Faculty of Physical Sciences, Nagarjuna University, Nagarjuna Nagar, 522 510, India

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Synthesis of a Novel Antiferroelectric Liquid Crystal: Influence of Biphenyl Ester Linkages on Magnitude of Spontaneous Polarization

POLURI A. KUMAR and VENKATA G. K. M. PISIPATI*

Centre for Liquid Crystal Research and Education (CLCRE), Faculty of Physical Sciences Nagarjuna University, Nagarjuna Nagar 522 510, India

A novel AFLC compound, (S)-4-dodecyloxyphenyl-4-(2-methyl)-butyloxybiphenyldicarboxylate (DPMBBD), has been synthesized and its liquid crystalline behaviour is studied by thermal microscopy (TM), Diffrential Scanning Calorimetry (DSC), spontaneous polarization (P_S) and response times (τ) measurements. The preliminary investigations on the ferroelectric properties of the present material imply the presence of an antiferroelectric phase (Sm-C_A*) with a high magnitude of spontaneous polarization. Further, the molecular contributions towards the magnitude of spontaneous polarization in the antiferroelectric phase are discussed in the light of ester linkages of biphenyl moiety.

Keywords: DPMBBD; AFLC; spontaneous polarization; Sm-C_A*

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* Corresponding author.

INTRODUCTION

The tristable antiferroelectric liquid crystal (AFLC) materials have attracted much attention in recent years due to their technical importance 'in the memory devices. Since the discovery[1] of the first ever AFLC compound, MHPOBC the quest for these interesting materials has become an important aspect among the material chemists. Considering the significance of spontaneous polarization as one of the important parameters of these antiferroelectric materials, many research groups are now actively involved in the isolation of AFLC materials exhibiting high magnitude of spontaneous polarization[2].

In continuation of our previous efforts[3-5] to generate ferroelectric materials with high P_S, the present communication deals with a novel synthetic route along with some important molecular contributions towards the appearance of antiferroelectric ordering and high magnitude of spontaneous polarization in the present compound. The molecular skeleton of *4-dodecyloxyphenyl-4-(2-methyl)-butyloxy-biphenyl-dicarboxylate* (DPMBBD) (Fig. 1) contains **(a)** two transverse dipoles on either side of the biphenyl moiety, **(b)** methyl spacer between the biphenyl core and asymmetric carbon, and **(c)** asymmetric configuration in the end chain.

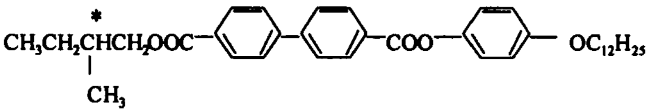


FIGURE 1 Molecular structure of DPMBBD.

EXPERIMENTAL

Materials and Methods

Optical textural observations[6] were made with Hertel & Reuss polarizing microscope, the temperature is monitored and controlled by an Instec milli Kelvin temperature controller interfaced to a computer with an accuracy of ± 0.01 K. DSC thermograms were recorded on a DSC-7 Perkin Elmer and Mettler Toledo DSC equipped with FP90 central processor (for simultaneous textural observation), with a scan rate of 5 °C/min. For the measurement of ferroelectric properties, the compound was filled in a polyimide buffed 10 microns spacer cell (Display Tech., USA) by capillary action in its isotropic state.

Spontaneous polarization was measured by field reversal method[7] with an automated set-up where the resulting polarizing current profiles observed on a 500 MHz digital storage oscilloscope (Hewlett Packard 54610B). The profiles were digitized and analyzed by a HPIB, which was interfaced to a computer. Response times were simultaneously determined[8] with spontaneous polarization measurements. The PMR spectra were run on a Joel GSX-400 (400 MHz) multinuclear NMR spectrometer.

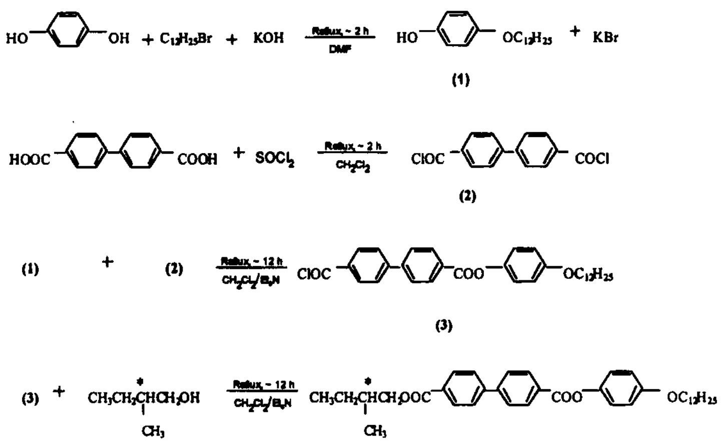
The chiral ingredient, (S)-2-methyl-butanol was obtained from Aldrich, USA and 4,4'-biphenyldicarboxylic acid was supplied by Sigma Chemical Company, USA. All other chemicals and solvents used in the present study were of BDH or E.Merck grade. The organic solvents were purified by standard literature methods[9].

A step-wise synthetic route of DPMBBD is illustrated in Scheme 1 while the experimental details of the synthesis are presented as follows :

p-alkoxyphenol **(1)** was prepared by mixing together DMF solutions of *p*-hydroxyphenol (hydroquinone) (2.2 g/ 20.0 mmol in 20 mL of DMF) and 1-bromododecane (2.5 mL/ 10.0 mmol in 15 mL of DMF). After stirring the reaction mixture at room temperature for ~ 0.5 h, 0.56 g/ 10.0 mmol of KOH was added and refluxed at 75 °C for ~ 2h. The KBr precipitate was suction filtered and washed repeatedly with DMF solution. The resultant solution was then extracted from diethylether and the etherial layer was dried over anhydrous sodium sulphate for ~ 12h. A white coloured crude product was suction filtered, washed repeatedly with methanol and dried in $CaCl_2$ desiccator. The crude product was then recrystallized from hot dichloromethane solution to get an yield of 3.7 g (66.7 %).

4,4'-biphenyldicarboxylic acid dichloride **(2)** was synthesized by the magnetic stirring of dichloromethane solution containing 6.05 g/ 25.0 mmol of 4,4'-biphenyldicarboxylic acid and 3.0 mL/ 25.0 mmol of thionylchloride solution. The resultant reaction mixture was then refluxed at ~ 70 °C for 2 h. After the evolution of SO_2 was ceased, the volume of the reaction medium was reduced to ~ 10 mL by vacuum distillation to get an yellow oily product which was then extracted twice with diethylether and the final desired product was dried in *vaccuo*. The yield obtained was 4.4 g (63.3 %).

4-dodecyloxyphenyl-4'-carbonylchloro-biphenylcarboxylate **(3)** : A dichloromethane solution (40 ml) containing 2 (5.5 g/ 20.0 mmol) and 1



SCHEME 1 Synthetic route of DPMBBD

(2.75 g/ 10.0 mmol) was magnetically stirred at ambient temperature for 2 h. 0.5 ml (9.0 mmol) of triethylamine was then added to the reaction mixture dropwise and refluxed at 60 ^{o}C with constant stirring for 10 - 12 h. The resultant solution, after cooling to room temperature, was poured into a beaker containing ~ 50 ml of cold water. The product, separated as a white solid, was then extracted with petroleum ether and dried over anhydrous Na_2SO_4 for 6h. The white crude product obtained on removing the excess ether, followed by repeated washings with cold methanol, was recrystallized from hot benzene to get an yield of 2.7 g (56.1 %).

4-dodecyloxyphenyl-4-(2-methyl)-butyloxy-biphenyldicarboxylate (DPMBBD) was obtained by the esterification of carbonylchloride moiety of compound **3** (4.85 g/ 10.0 mmol) with (S)-2-methyl-1-butanol

(0.5 mL/ 6.0 mmol) in 40 mL of dichloromethane solution following the method as described in step 3. The crude ester was purified by recrystallization from hot methanol solution to get an yield of 2.68 g (45.4 %), melting point 121.4 °C.

^{1}H NMR (δ ppm in $CDCl_3$): 1.02 (t, 3H, $-CH_2-C\underline{H}_3$); 1.48 (q, 2H, $-C\underline{H}_2-CH_3$); 4.01 (t, 2H, $OC\underline{H}_2-$); 1.32 (m, 20H, $OCH_2-(C\underline{H}_2)_{10}-CH_3$); 1.76 (t, 1H, $-C\underline{H}-CH_2-$); 0.91 (t, 3H, $-CH-C\underline{H}_3-$); 1.83 (d, 2H, $-CH-C\underline{H}_2-$); 7.92 - 8.06 (m, 8H, biphenyl ring); 6.88 - 6.93 (m, 4H, phenyl ring).

RESULTS AND DISCUSSION

Thermal Studies (TM and DSC)

DPMBBD is stable at room temperature and also showed a high degree of thermal stability when subjected to repeated thermal scans for TM, DSC and P_s measurements.

The phase variants and their transition temperatures are determined[6] from the characteristic textural observations under a polarized microscope. On cooling the isotropic liquid, DPMBBD exhibits yellow coloured focal conic fan texture in smectic-A phase, appearance of transient bars with concentric striations across these focal conic fans in smectic-C* phase and broken focal conic texture in smectic-F* phase. The existence of smectic-C_A^* phases is confirmed by spontaneous polarization studies. Further, the transition temperatures obtained by TM are found to be in good agreement with DSC thermograms.

Ferroelectric characterization

Polarizing current peaks at different temperatures are analyzed to obtain the magnitude of spontaneous polarization. From the individual profiles of the polarizing current peaks (10 Hz, 2 volts per micron) Sm-C* and Sm-C_A* phases are clearly identified. The magnitude of P_s (Fig. 2) was found to increase with decreasing temperature and attained a saturated value in Sm-C_A^* phase. The present compound showed a high magnitude of P_s (~ 150 nC.cm^{-2}) at 80.0 ^{o}C in antiferroelectric phase. The high P_s value in Sm-C_A^* phase may be attributed to the strong dipolar and electrostatic interactions between each molecule in the adjacent layers[2,10].

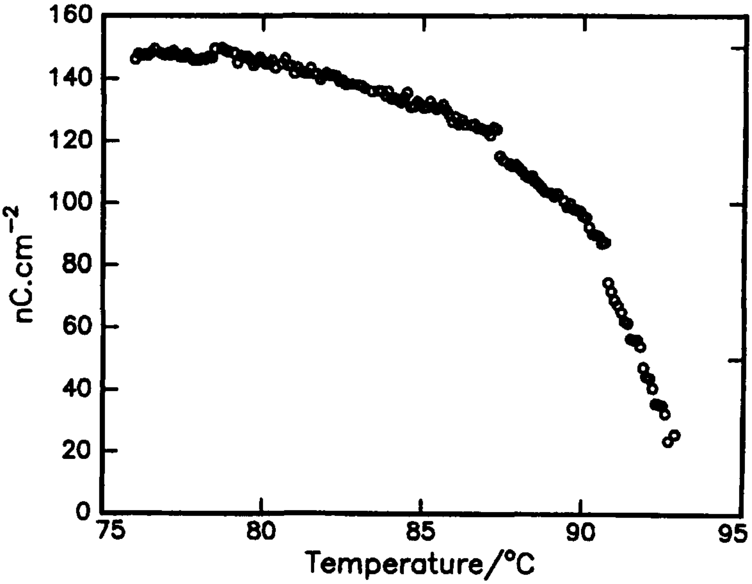


FIGURE 2 Temperature variation of spontaneous polarization (nC.cm-2) of DPMBBD

The micro second response times (τ) in Sm-C* and Sm-C$_A$* phases are found to be 168 and 251 respectively. Further, the trend in the magnitude of τ is similar to that of spontaneous polarization.

Based on thermal (TM and DSC) and ferroelectric (P_s and τ) studies, DPMBBD is found to exhibit the following phase sequence. The transition temperatures are given in degree centigrade while the enthalpy values (in J/g) for well resolved transition peaks are represented in parentheses.

$$\text{Iso} \xrightarrow[(3.78)]{121.4} \text{Sm-A} \xrightarrow[(-)]{92.8} \text{Sm-C}^* \xrightarrow[(0.15)]{90.7} \text{Sm-C}_A^* \xrightarrow[(4.51)]{75.7} \text{Sm-F} \xrightarrow[(20.2)]{46.1} \text{K}$$

Molecular contributions towards high magnitude of spontaneous polarization and origin of antiferroelectric ordering

(a) Presence of transverse dipoles on either side of the biphenyl moiety has a pronounced influence on the magnitude of spontaneous polarization. This can be justified by comparing the present molecule with the analogous ferroelectric materials[11] (Fig. 3), where the transverse dipoles are separated from the biphenyl moiety by oxygen atoms, show comparatively low magnitudes of spontaneous polarization (~ 120 n.C/cm^2). Further, the role of these two dipoles can best be interpreted in terms of elongated delocalized electron cloud achieved through conjugation.

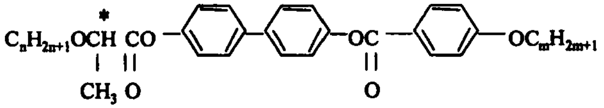


FIGURE 3 Molecular structure of analogous FLC compounds

(b) The conjugation play an important role on the appearance of antiferroelectric ordering by means of dipolar interactions between the adjacent layers which intern enhances the inherent stabilization of the antiferroelectric phase. The resultant pairing of the transverse dipoles in the neighbouring layers is supposed to be the origin of the antiferroelectricity [2,12].

(c) Presence of methyl group as a spacer unit between the chiral centre and the biphenyl core may further enhance the stabilization of antiferroelectric ordering[2].

Further detailed investigations on other physical parameters are now in progress.

Acknowledgements

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