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Evidence of re-entrant ferroelectric ordering in an achiral AFLC: a detailed study by spontaneous polarization

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A winged achiral antiferroelectric liquid crystalline compound, 1,3-phenylene bis-[phenylene-1-(biphenyldicarboxylato)-3-(4-*n*-tetradecyloxybenzoyl)biphenyldicarboxylate] (PBPBTB), having 1,3-phenylene [4-biphenyldicarboxylate-(4-*n*-tetradecyloxy benzoate)] units as wings, has been synthesized. Its mesogenic properties were characterized by thermal microscopy, differential scanning calorimetry, response time and spontaneous polarization measurements, and dielectric studies, suggesting the presence of new achiral phases. An interesting enantiotropic cyclic sequence among ferro- and antiferro-electric ordering was confirmed by the polarizing current profiles. The occurrence of re-entrant ferroelectric phenomena in the present compound was confirmed by detailed spontaneous polarization and preliminary dielectric studies.

1. Introduction

Following the recent trend of inducing chirality into liquid crystals, which is largely associated with the molecular structure possessing C_{2v} symmetry [1], many research groups [2–4] are now engaged in the isolation of achiral molecules. In such achiral molecules, the influence of chirality on the macroscopic properties is solely dependent on the direction of polar ordering with respect to the tilt and plane of the molecule. The recent depolarized reflected light microscopy (DRLM) studies by Link *et al.* [4], on bow-shaped molecules provide strong evidence for the impact of such polar ordering in adjacent layers, substantiating the origin of ferro-/antiferro-electric orderings. Nevertheless, the alignment of bent molecules in smectic layers (either synclinic or anticlinic) is a rather crucial factor for deciding the class of ordering. Recently, many research groups [2–6] have adopted such assumptions to account for experimental observations with various possible molecular arrangements. However, their views are confined to ferro- and antiferro-electric orderings and may lead to many limitations when the molecule possesses a new ordering. Based on recent views [2–6] relating to intra- and inter-layer molecular interactions, and with our previous experience [7–10] on ferro- and antiferro-electric materials, we have made for the first time in the class of achiral molecules a successful attempt to design and synthesize an antiferroelectric compound, of a kind which exhibits re-entrant ferroelectric ordering (figure 1). This achiral mesogen is named *Suparna* (Sanskrit word denoting *Su* as good and *parna* as possessing wings). The molecular skeleton of PBPBTB has been designed as the combination of a central core comprising 1,3-phenylene bis(biphenyldicarboxylate) with two lateral wings of 1,3-phenylene [4-biphenyldicarboxylate-(4-*n*-tetradecyloxy benzoate)] via ester linkages.

2. Experimental

Optical observations were made with a Hertel & Reuss polarizing microscope, with the temperature controlled to an accuracy of ± 0.01 K by an Instec milli Kelvin temperature controller interfaced to a computer. DSC thermograms were recorded on a Perkin Elmer DSC-7 instrument with a scan rate of $5°\mathrm{C\,min^{-1}}$. The spontaneous polarization of PBPBTB filled into a polyimide buffed cell with a 10 μm spacer (Display Tech., USA), was measured by the field reversal method [11], applying a field of $12.5\,\mathrm{V\,\mu m^{-1}}$ at a frequency of 8 Hz; the resulting polarizing current profiles were recorded using a 500 MHz digital storage oscilloscope (Hewlett Packard 54610B). Response times were measured from the polarizing current profiles by calculating the full width at half height [11]. While measuring the spontaneous polarization, simultaneous phase identification and switching behaviour were observed through the polarizing microscope. Dielectric studies were carried out on a HP 4192A LF impedance analyser. The phase

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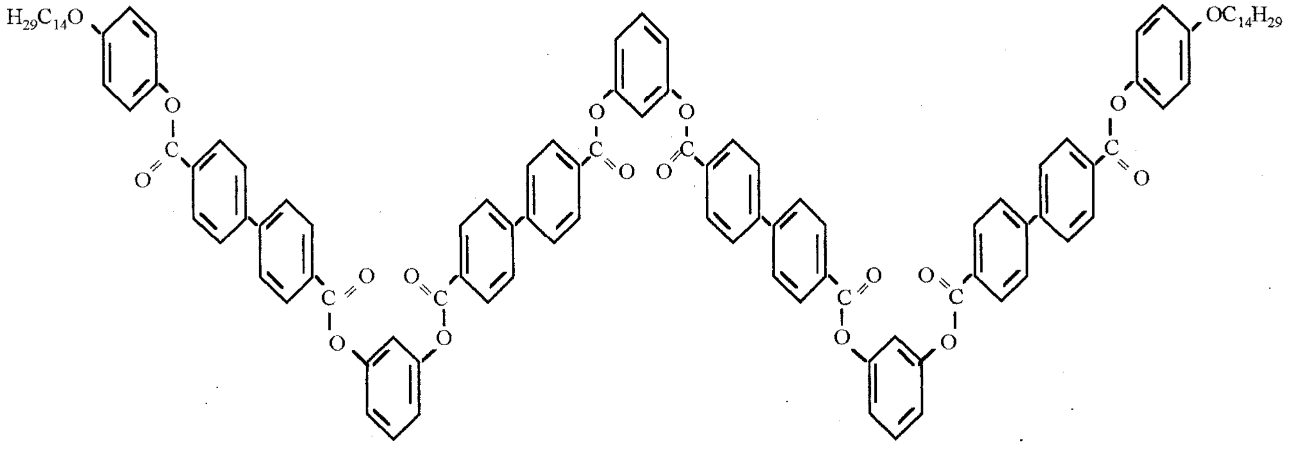

Figure 1. Molecular structure of PBPBTB.

variants and their transition temperatures were determined by comparison with the characteristic textures of traditional liquid crystals [12], while the identification of subphases was confirmed by spontaneous polarization studies. PBPBTB was synthesized by using 1,3-dihydroxybenzene units as central bent moieties. A detailed procedure for the synthesis along with ^{1}H NMR data are reported elsewhere [13].

3. Results and discussion

3.1. *Thermal studies (TM and DSC)*

On cooling the isotropic melt, and compound exhibits yellow focal-conic fans of SmA-like texture at 148°C; this phase is designated as S_1. On further cooling to 131.8°C, concentric striations are developed over the focal conic fans with a simultaneous colour change from yellow to green, indicating the onset of an S_3 phase which is similar to the SmC* phase of chiral molecules. It is interesting to note that a distinct colour change (green to red) over the entire region of arced focal-conic texture at 126.1°C implies the existence of a ferro- to antiferro-electric (S_3–S_4) transition. However, on further cooling, the reappearance of a green arced focal-conic texture at 120.1°C is critical in the sense that this texture (S_5) resembles the S_3 observed at 131.8°C. This observation, however, provides substantial evidence for the re-entrant ferroelectric phase (S_5) established in the foregoing discussion on spontaneous polarization. Further decrease of temperature to 100.4°C, results in the formation of broken focal-conic fans of SmF-like texture and is assigned as S_6. The phase transition temperatures observed through the thermal microscope are found to be in good agreement with the DSC thermograms. The corresponding thermal ranges of the observed phases are further confirmed by the characteristic individual profiles of the polarizing current peaks (figure 2).

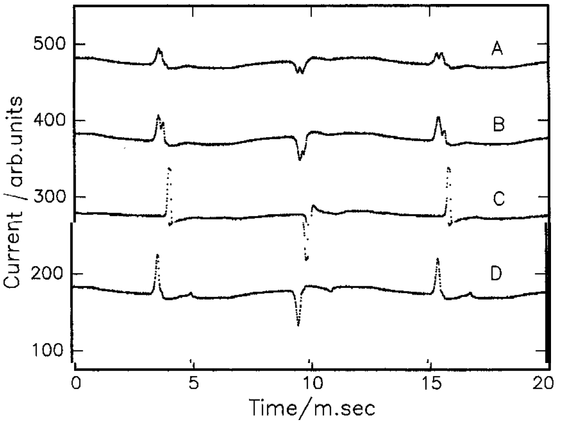

Figure 2. Polarizing current profiles in different phases: (A) onset of S_2 phase at 131.8°C; (B) phase transition from S_2 to S_3 at 128.8°C; (C) S_3 phase at 127.2°C; (D) S_4 phase at 120°C.

3.2. *Spontaneous polarization*

From the individual profiles of the polarizing current peaks, ferro- and antiferro-electric orderings are clearly identified. Polarizing current peaks at different temperatures were analysed to obtain the magnitude of spontaneous polarization. Figures 2 and 3 illustrate polarizing current profiles in different phases while the variation of spontaneous polarization with temperature is shown in figure 4.

3.3. *Ferroelectric phases*

The observation of double polarizing current peaks (figure 2A) at 131.8°C confirms the onset of a ferroelectric subphase. Since the shape of the polarizing current peak resembles that for the SmC_α phase of traditional ferroelectric liquid crystals, this phase is designated as S_2. These two peaks persist without much change in

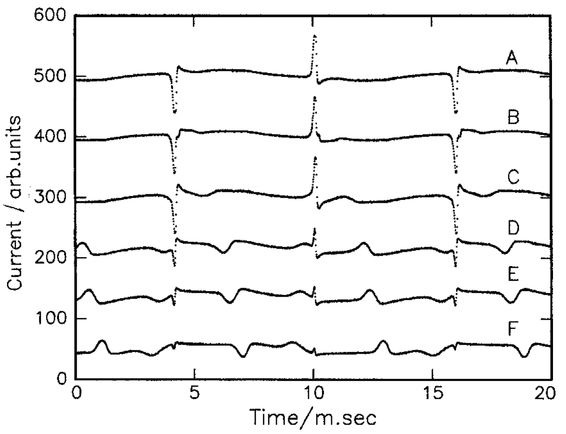

Figure 3. Polarizing current profiles showing re-entrant ferroelectric S_5 phase: (A) S_3 phase at 127.1°C; (b) S_4 phase at 121.1°C; (C) onset of re-entrant ferroelectric S_5 phase at 119.6°C; (D), (E) and (F) stabilization of re-entrant ferroelectric S_5 phase at 113.1, 110.1 and 102.1°C, respectively.

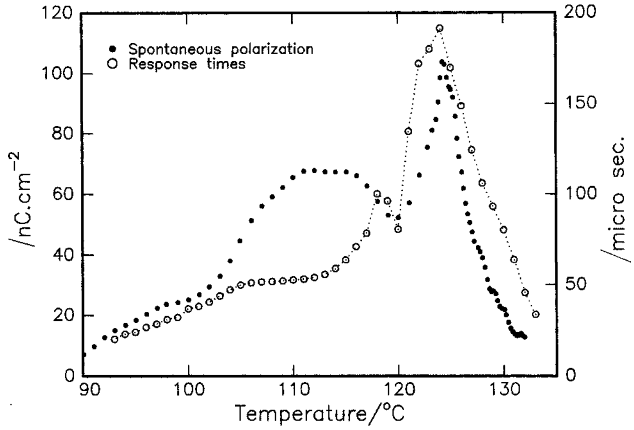

Figure 4. Variation of spontaneous polarization and response time with temperature in different phases.

shape throughout their thermal range (~ 2.6°C). Further, it is clear from figure 4 that the magnitude of spontaneous polarization (~ 14 nC cm^{-2}) is unaltered in its entire thermal span, indicating the stability of this phase.

The phase transition from S_2 to S_3 at 129.2°C is manifested by the coalescence of the double current peak. When the transition takes place, it is observed that one of the S_2 peaks diminishes to become a shoulder then, in S_3 phase, merges with the other peak, as illustrated in figure 2 B. This may be attributed to the co-existence of the phases. Further, the shoulder merges into a single predominant peak (figure 2 C) with the onset of the S_3 phase. The thermal range of the phase S_3 and its $\mathbf{P}_s$ are measured to 2.7°C and ~ 20 nC cm^{-2}, respectively.

3.4. *Antiferroelectric phase*

The occurrence of double polarizing current peaks at 126.5°C confirms the onset of an antiferroelectric phase, designated as the S_4 phase. The current polarizing profile consists of two characteristic peaks (figure 2 D) which are different from those observed in the case of the S_2 phase (figure 2 A). The thermal range of this phase is ~ 6°C. Figure 4 illustrates the expected trend of the proportional increase of spontaneous polarization. The stabilization of antiferroelectric ordering can be observed with the gradual increase of spontaneous polarization and the simultaneous persistence of this polarizing current profile throughout the thermal range of this phase. The saturated value of spontaneous polarization attained in this phase at 124.2°C (110 nC cm^{-2}) is nearly five-fold the value obtained in the S_3 phase (~ 20 nC cm^{-2}). This trend of increasing spontaneous polarization may be explained in terms of the reorientation of dipolar interactions in adjacent molecular layers, as shown in figure 5.

3.5. *The re-entrant phenomenon in ferroelectric ordering*

With further decrease of temperature from the antiferroelectric phase (figure 3 B), a new polarization current peak emerges (figure 3 C) at 120.1°C and grows as broad peak. This broad peak is unaltered in the entire thermal span (~ 20°C) with the simultaneous quenching of polarizing current peaks corresponding to the antiferroelectric phase. The corresponding saturated $\mathbf{P}_s$ value at ~ 113°C is found to be 70 nC cm^{-2} which strongly suggests the existence of an entirely new phase (S_5). It is further in evidence from figure 4 where a sudden fall of $\mathbf{P}_s$ from 110 (S_4) to ~ 60 nC cm^{-2}, then reaching a saturated value of 70 nC cm^{-2} at 113°C, manifests the antiferroelectric at a new phase transition. In this new phase, a gradual increase in the magnitude of $\mathbf{P}_s$ (figure 4) is observed; it finally attains a saturated value (70 nC cm^{-2}) with decreasing temperature indicating the

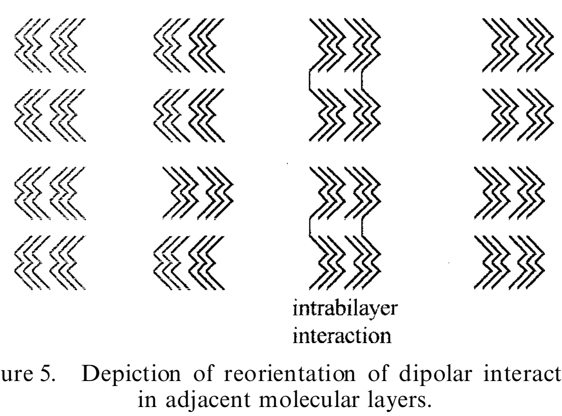

Figure 5. Depiction of reorientation of dipolar interactions in adjacent molecular layers.

stabilization of the phase. Owing to its relative high $\mathbf{P}_s$ value (70 nC cm^{-2}) over a wide thermal range (~ 20°C), it is reasonable to assign this new peak to the re-appearance of the ferroelectric phase, S_5. The polarizing current profiles associated with this re-entrant phenomenon of antiferro- to ferro-electric transitions are represented in figure 3 A–F. Although, a few instances are reported of chiral molecules showing the re-emergence of modifications in SmC* subphases in a very narrow thermal range [14, 15], for the first time in the study of achiral ferroelectric liquid crystals, we have realized the re-appearance of ferroelectric ordering; this leads to an interesting enantiotropic cyclic sequence among ferro- and antiferroelectric orderings (ferroelectric–antiferroelectric–ferroelectric). The profiles of figure 3 illustrates the presence of re-entrant S_5 along with the simultaneous quenching of the antiferroelectric phase.

3.6. *Response times*

The microsecond response times (τ) in the different phases have been simultaneously measured with the spontaneous polarization studies. Figure 4 illustrates the temperature variation of response times for the present compound. As expected, the response time temperature profile is similar to that for spontaneous polarization in the entire antiferro-, ferro-electric thermal ranges. In the ferroelectric phase τ increases with decreasing temperature and attains a value of ~ 200 µs in the antiferroelectric phase. A glance at the trend in the response times profile (figure 4) clearly shows a steep fall followed by a sharp well resolved peak at ~ 120°C. At this juncture, it is reasonable to recall the discussed results of the spontaneous polarization experiment, wherein a similar trend in temperature variation (figure 4) and disappearance of double polarizing current peaks (figure 3) at the same temperature, strongly suggest the transition from antiferroelectric to re-entrant ferroelectric phase. The response time remained unaltered with a saturated value of ~ 50 µs between 115 and 103°C, indicating the stabilization of the re-entrant ferroelectric phase. Further decrease of temperature beyond 100°C perturbs this saturated value, leading to a fall in response time which indicates the culmination of the re-entrant ferroelectric phase.

The existence of re-entrant ferroelectric ordering is also seen from preliminary studies on dielectric behaviour. The temperature variation of permittivity (ε') and dielectric loss (ε'') at 10 KHz are represented in figure 6. The dielectric spectrum shows a well resolved peak at ~ 126°C manifesting the transition from ferroelectric (S_3) to antiferroelectric phase (S_4), while the transition from antiferroelectric (S_4) to re-entrant ferroelectric phase (S_5) is observed as a sharp peak at ~ 120°C. Interestingly, in both the permittivity and dielectric loss profiles all other mesogenic transitions may also be identified.

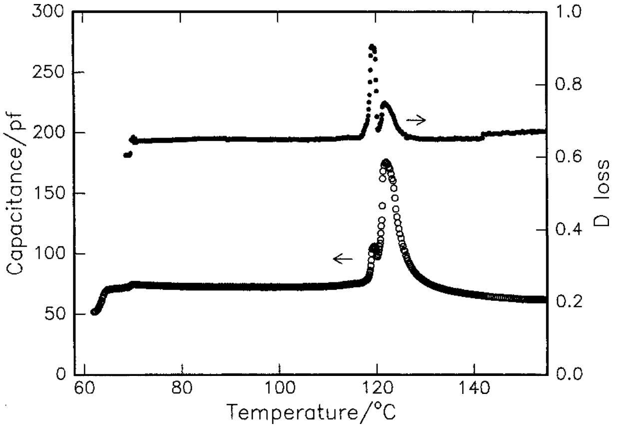

Figure 6. Variation of permittivity and dielectric loss with temperature in different phases.

The transition temperatures and thermal ranges of the different achiral phases obtained by this technique are in good agreement with the TM and DSC data, and spontaneous polarization studies. Further detailed dielectric investigations on the re-entrant ferroelectric phenomenon are in progress.

3.7. *Contributions from chemical constitution*

The origin of antiferroelectric ordering in the PBPBTB molecule can be correlated with the following chemical structural contributions.

(i) Conjugation, which is maintained throughout the molecule, has a pronounced influence on the appearance of antiferroelectric ordering through the dipolar interactions (via ester moieties) between adjacent layers; this in turn enhances the inherent stabilization of the antiferroelectric phase. The resulting pairing of transverse dipoles in neighbouring layers is supposed to be the origin of antiferroelectric ordering [1, 9].

(ii) Our previous studies [8] on antiferroelectric materials revealed the presence of biphenyl rings as spacer units which facilitates the extension of conjugation and promotes the occurrence and stabilization of antiferroelectric ordering.

(iii) The presence of long alkyl end chains also favours the appearance of antiferroelectric ordering [5].

5. Conclusions

TM, DSC and spontaneous polarization studies reveal that the compound PBPBTB exhibits the following enantiotropic liquid crystalline phases. Transition temperatures are given in degree centigrade while the well resolved enthalpy values (J g^{-1}) are shown in parentheses.

$$\mathrm{I}\ \underset{(4.22)}{\overset{148.0}{\quad}}\ S_1\ \underset{(0.01)}{\overset{131.8}{\quad}}\ S_2\ \underset{(-)}{\overset{129.2}{\quad}}\ S_3\ \underset{(0.25)}{\overset{126.1}{\quad}}\ S_4\ \underset{(-)}{\overset{120.1}{\quad}}\ S_5\ \underset{(0.10)}{\overset{100.4}{\quad}}\ S_6\ \underset{(20.21)}{\overset{65.3}{\quad}}\ \mathrm{Cr}$$

It is now well established that the sequence between the various molecular orderings leads to a 'cyclic' process in which the complete liquid crystalline thermal range is sandwiched between high and low temperature ferroelectric orderings. This significant dual ferroelectric thermal selectivity makes PBPBTB a promising pioneer candidate to contribute both to fundamental and applicational aspects of liquid crystal science.

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