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The determination of the phase transition temperatures of a semifluorinated liquid crystalline biphenyl ester by impedance spectroscopy as an alternative method

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ABSTRACT

Dielectric spectroscopy (DS) is a very powerful and important for better understanding of the molecular dynamics and relaxation phenomena in liquid crystals. The dielectric and impedance characteristics Ethyl 4-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)biphenyl-4′-carboxylate (**ENBC**) liquid crystal have been analyzed over the frequency range of 100 Hz to MHz in the temperature region from room temperature to 180 °C. The compound ENBC shows enantiotropic a smectic mesophase in a wide temperature range. The phase transition temperatures T (°C) of the liquid crystal **ENBC**, which were characterized by Differential Scanning Calorimetry (DSC), have been verified by the dielectric measurements and conductivity mechanisms of the **ENBC**. The activation energies for some selected angular frequencies have also been calculated.

1. Introduction

Liquid crystals (LC) are intermediate states between crystals and isotropic liquids. They have both mobility of liquids and anisotropy of crystals. These two properties enable liquid crystals to be used in technological applications [1–6]. Fluorinated liquid crystals are also of interest for applications. In fluorinated liquid crystals, fluorine atoms can replace H atoms in different parts of the molecule; at rigid core, central core or at flexible tails, etc. Fluorination of terminal chains usually supresses the nematic phases and induces smectic ones [7–9]. Smectic LC phases are the fluid layer structures combining long range orientational order and 1D positional order [10]. The molecules are free to rotate and they can move from one layer to the next. Although there are many type of smectic phases, the most important ones are Smectic A, Smectic B and Smectic C. In Smectic A, the molecules are on the average perpendicular to the layers and their axes have the same orientation. [11,12].

In this study, phase transition temperatures and electronic properties of Ethyl 4-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)biphenyl-4′-carboxylate (ENBC) liquid crystal [13], which exhibits enantiotropic SmA mesophase as high temperature phase in a wide temperature range and another mesophase M with unknown structure, have been analyzed by means of dielectric and impedance spectroscopy measurements. The complete characterization of these properties requires the use of variety techniques. In addition to the importance of Differential Scanning Calorimetry (DSC) on determining of the phase transition temperatures of liquid crystals, the advantages of Dielectric Spectroscopy (DS) as a useful method was presented in this work.

2. Experimental

2.1. Synthesis of and liquid crystalline properties of the ENBC

As reported previously [13] by our group, the compound ENBC was prepared by the etherification reaction of Ethyl 4-hydroxy-4-biphenylcarboxylate with 7,7,8,8,9,9,10,10,10-nonafluorodecyl bromide [8] and purified by recrystallization from ethanol. The chemical structure, transition temperatures and corresponding enthalpy values for ENBC have been given in Fig. 1. ENBC shows an enantiotropic SmA phase as high temperature phase and M mesophase with unknown structure below the temperatures of SmA mesophase. SmA mesophase displays a fan-shaped texture which is characteristic for the nontilted smectic phase as shown in Fig. 2. Both mesophases were detected by a calorimetric peak in the DSC heating and cooling scans (see Fig. 2).

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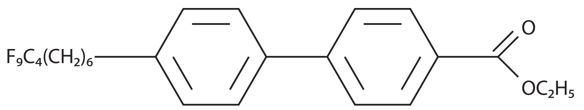

Compound	T/°C [ΔH/kJ mol^{-1}]
ENBC	Cr 102.3 [2.6] M 107.4 [0.7] SmA 160.6 [11.1] Iso

[a] Perkin-Elmer Pyris 6-DSC; heating rates 10 K min-1 for the melting and clearing process; enthalpy values are given behind the phase transition temperatures in italics in square parentheses; abbreviations: Cr: crystalline, SmA: nontilted smectic, M: low temperature mesophase with unknown structure and Iso: isotropic phase.

Fig. 1. Phase transition temperatures and transition enthalpies of compound ENBC[α].

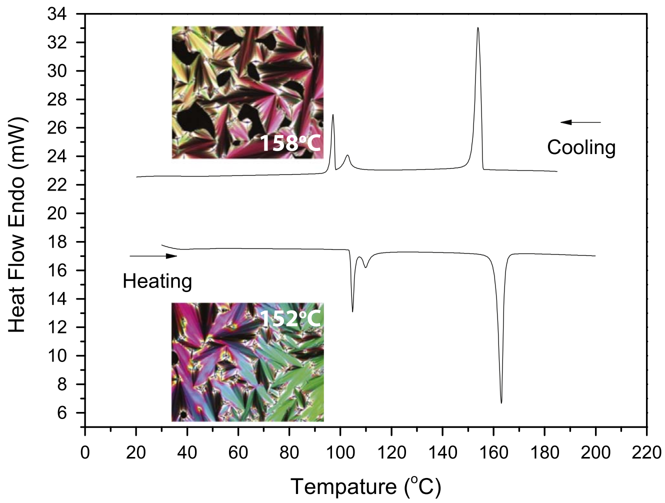

Fig. 2. DSC scan (second heating and second cooling) and polarised light optical photomicrographs of the SmA mesophase of the compound ENBC on heating at 152 °C and cooling at 158 °C.

2.2. Methods

The dielectric parameters of ENBC have been calculated by the capacitance method via HP 4192A LF Impedance Analyzer within the frequency range of 5 Hz–13 MHz within the temperature interval of 25–180 °C. The LC cells were screened any electric field effects by Faraday cage. The transition temperatures were measured using a Linkam THMS 600 hot stage and a Linkam TMS 93 temperature control unit in conjunction with a Leitz Laborlux 12 Pol. polarizing microscope.

Sandwich type cells have been prepared by indium-tin-oxide (ITO) coated glass plates purchased by Instec Colorada Inc. The inner surfaces of the glasses have been coated with the polyimide layers which shows different alignment. In this work, planar aligned cell has been used. Thickness of the empty sandwich cell was 9 ± 0.1 μm by Mylar spacer. The ITO cells have been filled with the LC by capillary action.

3. Results and discussions

3.1. The study of temperature effect on dielectric parameters of the ENBC

The dielectric parameters of ENBC have been measured by HP 4192A Impedance Analyzer within the frequency interval of 100 Hz–13 MHz at various temperatures varying from 25 °C to 180 °C. The frequency dependences of the real and imaginary parts of the dielectric constant of ENBC have been given in Fig. 3a and b, respectively. As shown in Fig. 3a, the real part of dielectric constant decreases while the frequency increases. On the other hand, the real part of dielectric constant has its maximum value at low frequencies. As seen in Fig. 3a and b, the real and imaginary part of dielectric constant of the LC decrease with temperatures. As shown in the inset of Fig. 3b, it has been observed that while the temperature increases from 25 °C to 180 °C, the relaxation frequencies increase and the peak intensities decrease. The increase in relaxation frequency and the sharply decrease of the imaginer part at 100 °C may be associated with the phase change of the material from crystal phase to mesophase. This temperature data has also verified with DSC method.

In order to define the effect of temperature on dielectric relaxation type of ENBC, the dispersion curves for each temperature have been fitted by Origin Lab 8.5. The equation of fitting function has been given in [14]. Dielectric relaxation parameters α, τ, and dielectric strength, $\Delta\varepsilon$ have been given in Table 1. Since absorption coefficient values for all temperatures are very close to zero, the relaxation type has been considered as nearly-Debye. The effect of temperature on absorption coefficient has also been given in Fig. 4.

According to Fig. 3 a and Table 1, the dielectric strengths $(\Delta\varepsilon=\varepsilon_s-\varepsilon_\infty)$ of **ENBC** have been increased as the temperature increases from 25 °C to 50 °C then this data decrease from 50 °C to 95 °C. However, the dielectric strength sharply decreased in the phase transition temperature of **ENBC** at 100 °C (see Fig. 4). The decrease in the value of dielectric strength, $\Delta\varepsilon$ after the phase transition temperature may be due to the reorientation of molecules in **ENBC** in this region.

In order to analyze dielectric relaxation mechanism of the ENBC, we have plotted Cole-Cole graphics (Fig. 5). As seen in Fig. 5 the diameters of the semi-circles have sharply decreased after phase transition temperature 100 °C.

The variation of the real parts of the dielectric constant of ENBC with temperatures in different frequency regions have also drawn in

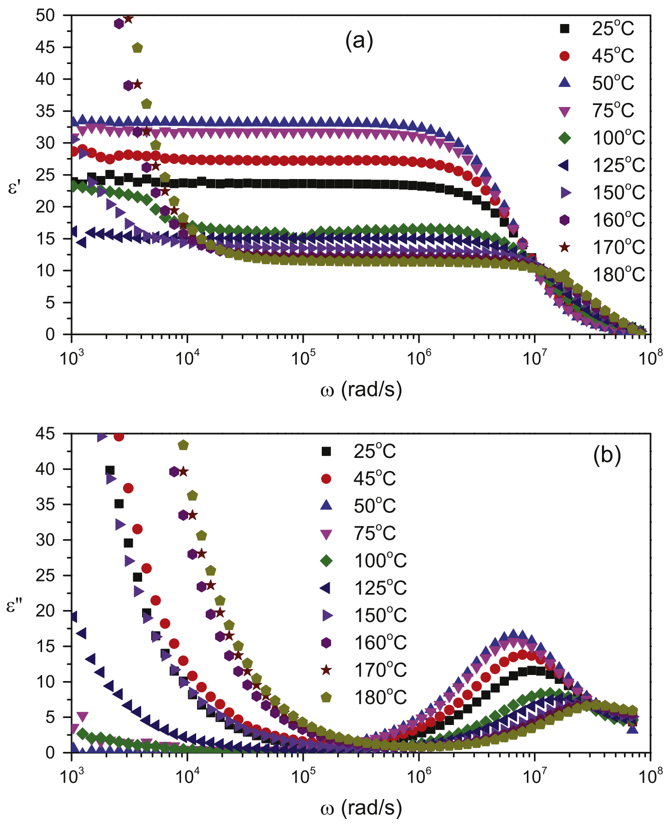

Fig. 3. The angular frequency dependence of (a) the real and (b) the imaginary parts of the dielectric constant of ENBC at different temperatures.