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The role of temperature on dielectric relaxation and conductivity mechanism of dark conglomerate liquid crystal phase

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ABSTRACT

In this study, dielectric properties and ac conductivity mechanism of the bent-core liquid crystal *3′-{4-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-[6-(1,1,3,3,5,5,5-heptamethyltrisiloxan-1yl)hex-1-yloxy]benzoyloxy]benzoyloxy}biphenyl* (**DBB**) have been analyzed by impedance spectroscopy measurements at different temperatures. According to the polarizing microscopy results, **DBB** liquid crystal compound exhibits a dark conglomerate mesophase ($DC^{[*]}$ phase) which can be identified by the occurrence of a conglomerate of domains with opposite chirality. The chiral domains of this low-birefringent mesophase become more visible by rotating the polarizer. The variation of the real (ε') and imaginary (ε'') parts of dielectric constant with angular frequency and Cole–Cole curves of **DBB** have been analyzed. The fitting results for dispersion curves at different temperatures revealed that **DBB** system exhibits nearly Debye-type relaxation except for 125 °C. Moreover, it has been determined that while the relaxation frequencies shift to higher frequencies as the temperature increases from 25 °C to 125 °C, the peak intensities remarkably decrease with increasing temperature. According to Cole–Cole plot and phase angle versus frequency curve, it has been determined that **DBB** LC may have a possibility of utilizing as a super-capacitor at room temperature. Furthermore, it has been found that the conductivity mechanism of the **DBB** alters from Correlated Barrier Hoping (CBH) model to Quantum Tunneling Model (QMT) with in increasing temperature at high frequency region. In terms of CBH model, optical band gaps at 25 °C and 75 °C temperatures have also been calculated. Finally, activation energies for some selected angular frequencies have also been calculated.

1. Introduction

Liquid crystals which exhibit the fluidity of liquids and the anisotropy of crystals are the advanced technological materials which have significant interest for applications in mobile data processing and communication tools in the last decades [1–3]. Until 1996, liquid crystal research had been mainly focused on the synthesis of rod like or disc like molecules because of their appropriate LC phases such as nematic phase in display applications [3–11]. Although some researchers synthesized several bent-core liquid crystals and reported their some properties [12–15], their importance was not been realized until 1996. It was known that molecular chirality has been necessary to produce a chiral liquid-crystalline phase [16]. After the discovery of electro-optical switching in LC phases exhibited by the achiral bent-core liquid crystals [17], the liquid crystal studies comprising achiral bent-core compounds had a great deal of interest due to their outstanding physical properties which differ significantly from mesophases of calamitic and disc-like compounds. Numerous systematic studies have been done in order to obtain unique LC phases of these achiral molecules showing macroscopic polar order and superstructural chirality to date 1,2,3, [18–22]. The remarkable behavior of this new class of thermotropic liquid crystals is the presence of superstructural chirality which results from the combination of tilt and polar order of the molecules in successive layers. This leads to LC phases showing anti-ferroelectric and ferroelectric switching 1,18.

Bent-core liquid crystals are known to exhibit optically isotropic phases, for example: the dark conglomerate (DC) phases with a sponge-like structure [23,24], and B4-type helical filament phases [25,26]. The DC phases have no birefringence or low-

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birefringence. In the DC phases, layers are strongly deformed and organized in a sponge-like structure. Due to the special organization of the layers, the mesophases appear optically isotropic between crossed polarizers on cooling from the isotropic liquid. Dark and bright domains can be observed by the rotation of the polarizer by a small angle and the brightness of these chiral domains exchange on rotation of the polarizer in the opposite direction. The optical activity in the DC phase of achiral bent-core mesogens is attributed to the layer chirality or to the coupling of molecular conformational chirality to the layer chirality 1 [27,28].

Due to their attractive functional properties, DC phases based materials are of significant interest for a variety of application such as organic semiconductors, thin film transistors ands solar cells [29,30], NLO materials [31,32] and thin film polarizers [33]. Here we investigated the influence of temperature on dielectric properties and conductivity mechanisms of the dark conglomerate (DC) phase formed by a silylated achiral bent-core molecule with a branched alkyl chain.

2. Experimental

2.1. Mesomorphic properties of DBB liquid crystal

The synthesis of bent-core liquid crystal molecule, *3′-{4-[4-(3,7-Dimethyloctyloxy) benzoyloxy] benzoyloxy} -4-{4-[4-[6-(1,1,3,3,5,5,5- heptamethyltrisiloxan-1yl) hex-1-yloxy] benzoyloxy] benzoyloxy} biphenyl* (DBB) has been carried out by the procedure in our previous work [34]. Firstly, *4-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoic acid* has been attached to *4′-benzyloxybiphenyl-3-ol* [35] by esterification using dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) as catalysts to yield *4′-Benzyloxy-3-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxybiphenyl.*

After hydrogenolytic debenzylation (H_2, 10% Pd/C in THF) of the benzylated intermediate and DCC esterification with *4-[4-(5-hexenyloxy)benzoyloxy]benzoic acid* [36], olefine terminated bent-core compound, *3′-{4-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-(5-hexenyloxy)benzoyloxy]benzoyloxy}biphenyl,* has been obtained. In the final step, 1,1,1,3,3,5,5-heptamethyltrisiloxane has been attached to the olefinic precursor by a hydrosilylation reaction using Karstedt's catalyst to yield the target siloxane substituted compound **DBB** [34] (Scheme 1).

Compound **DBB** was characterized ^{1}H-, ^{13}C-NMR and ^{29}Si-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in $CDCl_3$ solutions, with tetramethylsilane as internal standard). Microanalysis was performed using a Leco CHNS-932 elemental analyzer.

Compound DBB [34]: **^{1}H-NMR:** δ (ppm)=8.29 (d; $J\approx8.7$ Hz; 2 Ar–H), 8.28 (d; $J\approx8.7$ Hz; 2 Ar–H), 8.15 (d; $J\approx8.9$ Hz; 2 Ar–H), 8.14 (d; $J\approx8.9$ Hz; 2 Ar–H), 7.66 (d; $J\approx8.7$ Hz; 2 Ar–H), 7.51–7.50 (m; 2 Ar–H), 7.45 (broad s; 1 Ar–H), 7.37 (d; $J\approx8.7$ Hz; 2 Ar–H), 7.36 (d; $J\approx8.7$ Hz; 2 Ar–H), 7.30 (d; $J\approx8.7$ Hz; 2 Ar–H), 7.23–7.19 (m, 1 Ar–H), 6.98 (d; $J\approx8.9$ Hz; 2 Ar–H), 6.97 (d; $J\approx8.9$ Hz; 2 Ar–H), 4.11–4.08 (m; 2H OCH_2), 4.04 (t; $J\approx6.5$ Hz; 2 H, OCH_2), 1.85–1.79 (m; 3H, CH_2, CH), 1.66–1.47, 1.39–1.15 (2m; 15H, CH, 7 CH_2), 0.95 (d; $J\approx6.4$ Hz; 3H, CH_3), 0.87 (d; $J\approx6.6$ Hz; 6H, 2 CH_3), 0.57–0.53 (m; 2H, $SiCH_2$), 0.08 [s; 9H, Si–$(CH_3)_3$], 0.06 [s; 6H, Si–$(CH_3)_2$], 0.02 [s; 6H, Si–$(CH_3)_2$]. **^{13}C-NMR:** δ (ppm)=164.45, 164.43, 164.31, 164.30 (CO), 164.16, 163.69, 155.34, 151.26, 150.58, 141.99, 137.95, 126.86, 126.82, 121.99, 120.97 (Ar–C), 132.32, 131.74, 129.77, 128.24, 124.60, 122.08, 122.03, 120.62, 120.38, 114.42, 114.41 (Ar–CH), 68.45, 66.81 (OCH_2), 39.31 (CH_2), 37.35, 36.10 (CH), 33.15, 29.96, 29.13, 28.07, 25.80, 24.75, 23.26 (CH_2), 22.78, 22.69, 19.76 (CH_3), 18.35 ($SiCH_2$), 1.95, 1.41, 0.34 (CH_3). **^{29}Si-NMR:** δ (ppm)=7.37, 7.09, -20.97. **$C_{63}H_{78}O_{12}Si_3$** (1111.56); Anal. Calc.: C, 68.07; H, 7.07. Found: C, 68.36; H, 6.76%.

Transition temperatures were measured using a Mettler FP-82 HT hot stage and control unit in conjuction with a Leica polarizing microscope. The associated enthalpies were obtained from DSC-thermograms which were recorded on a Perkin-Elmer DSC-7, heating and cooling rate: 10 °C $\min^{-1}$.

Spectroscopic data and mesomorphic properties for the target material **DBB** had already been given in Ocak et al. [34]. The phase transition temperatures and chemical structure of **DBB** are shown in Fig. 1.

Siloxane substituted bent-core compound **DBB** exhibits dark conglomerate phase with ferroelectric switching 34. On cooling from the isotropic liquid, dark and bright domains have been observed by rotating the polarizer by a small angle. The brightness of these domains is exchanged on rotation of the polarizer in the opposite direction. If the sample was rotated between the slightly decrossed polarizers, the brightness of the chiral domains was not changed. This indicates a conglomerate of domains with opposite chirality as typical for dark conglomerate phases. Polarized light optical photomicrographs on cooling are shown in Fig. 2.

2.2. Preparation of liquid crystal cell

Empty cell has been prepared by indium–tin-oxide (ITO) coated glass plates purchased by Instec Colorada Inc. The thickness of the empty cell was set at $d=9\pm0.2$ μm by Mylar spacer. The ITO cell has been filled with **DBB** by capillary action.

3. Results and discussions

3.1. Analysis of temperature effect on frequency dependent dielectric parameters

The dielectric properties of **DBB** Liquid crystal have been analyzed by HP 4192A Impedance Analyzer within the frequency interval of 5 Hz–15 MHz at various temperatures varying from 25 °C to 150 °C.

The variations of the real part of the dielectric constant with angular frequency at these temperatures are shown in Fig. 3.

As shown in Fig. 3, regardless of the operating temperature, the real component of dielectric constant has a characteristic saturation region and sharp decrease behavior as the angular frequency increases from 10^4 to 10^8 rad/s. It has been observed that as the temperature increases, the maximum value of ε' remarkably decreases.

In order to define the effect of temperature on dielectric relaxation type of **DBB**, the dispersion curves for each temperature have been fitted by Origin Lab 8.5. The equation of fitting function has been given in Eq. (1)

$$\varepsilon'(\omega)=\left[\varepsilon'_{\text{high freq.}}+(\varepsilon'_{\text{low freq.}}-\varepsilon'_{\text{high freq.}})\frac{1+(\omega\tau)^{1-\alpha}\sin\frac{1}{2}\alpha\pi}{1+2(\omega\tau)^{1-\alpha}\sin\frac{1}{2}\alpha\pi+(\omega\tau)^{2(1-\alpha)}}\right] \quad (1)$$

where α and τ are absorption coefficient and relaxation time. As is known, absorption coefficient parameter, α takes values between zero and one ($0<\alpha\le1$). When α equals to zero, it corresponds to Debye type relaxation. The non-Debye type occurs when the value of absorption coefficient varies between; $0<\alpha<1$ region [37].

Dielectric relaxation parameters $\varepsilon'_{\text{low freq.}}$, $\varepsilon'_{\text{high freq.}}$, α, τ, f_c and dielectric strength, $\Delta\varepsilon_s$ are given in Table 1. Since absorption coefficient values for 25 °C, 75 °C and 150 °C temperatures are very close to zero, the relaxation type has been considered as nearly-Debye. On the other hand, since α has been determined as far from zero for 125 °C temperature, the relaxation mechanism has been determined as non-Debye type. The effect of temperature on absorption coefficient are also shown in Fig. 4.