

Visco-Elastic Properties of Low Molar Mass P-N- Alkoxy Benzoic Acid Mesogens

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Abstract—Textures, Phase transitions, flow and dynamic rheological studies on low molar mass thermotropic p-n alkoxy benzoic acid mesogens (nOBA, n = 3-9) were carried out using polarizing optical microscope and rheometer.. This paper describes the rod like structure of molecules in the nematic and smectic phases which are oriented by the flow field by showing strong elastic nature $G^1 > G^{11}$ at different frequencies and temperature studied in their linear viscoelastic region. The angular frequency variation of viscosity also had been carried out showing an irregular distribution of viscosity at the transitions from one mesophase to another, to reduce the applied strain or pressure. An odd-even effect has been observed when loss angle is measured in the nematic region of the mesogens.

Keywords---Thermotropic, mesogens, viscoelastic, dynamic moduli.

1.INTRODUCTION

The phase behavior of liquid crystals is governed by the shape and size of their molecular constituents [1] in which rod-shaped (lower molar mass) mesogens can form nematic and smectic phases, the former characterized by orientational order but an absence of the translational order observed in smectics. Liquid crystals are the synthetic biological anisotropic viscoelastic textured materials [2 - 4]. They are used as precursor materials in the manufacturing of fibers, films, blends and as functional materials in sensors, electro optical devices, lubricants, actuators, reactive media [3,5,6]. Liquid crystalline materials contain different elasto-magneto-optical properties [7] which depend to a large extent on flow-induced orientations. Low molar mass liquid crystals (LMMLC's) are most widely used materials for electro-optical applications including erasable optical disks, full color "electronic slides" for computer-aided drawing (CAD), and light modulators for color electronic imaging [8] observed that the LMMLC's could act as a melt viscosity reduction like additives in different mixtures to improve the operating torque on the screw extruder [9]. The TLCs have attracted a great deal of interest because of their potential applications [10] and since they exhibit nematic-isotropic transitions at temperatures well below their decomposition temperature. The ability to orient during flow and then develop extended structures during thermal treatment allows mesophase exhibit excellent thermal properties. For this excellent thermal properties one must control the flow of

mesophase, in turn, requires an understanding of the rheology of these complex fluid. Oscillatory shear is used widely in characterization of viscoelastic materials.[11]. Dynamic oscillation testing is much more powerful tool to reveal the secrets of microscopic structure of the viscoelastic material. There fore it is more attractive and useful from a practical point of view[12]

Measurement and characterization of viscoelastic behaviour of liquid crystal mesogens serve multiple purposes. They help understanding a fluid response to deformations; knowledge essential in developing critical specifications in handling, transportation, application, and in determining the optimum conditions for the efficient operation of possessing equipment.

Many investigations on rheological behavior of liquid crystalline materials have been done in histories [13-15]. Lyotropic liquid crystals, polymer solutions, gels exhibit viscoelastic properties on application of a strain amplitude oscillation, they can respond both solid-like by storing the energy and also liquid-like by dissipating the energy. The solid like response of the system is determined by the elasticity while the fluid like response is set by the viscosity. Mostly rheological properties of lyotropic liquid crystal systems have been reported with reminiscent behavior on concentrated suspensions [16 17]. A little research and development have been performed on the thermotropic liquid crystalline materials. The deformation of the TLC's under shear or frequency (strain) is influenced by various factors, such as the thermal behaviors, the characteristics of viscosity components, the flow mode, processing conditions of the TLC's [18 19].

The objective of this paper is to determine that whether these thermotropic liquid crystals show any peculiar observations like lyotropic LCs or not. and reproduce and examine the experimental measurements of thermotropic liquid crystals with variation in carbon chain length having nematic and smectic structures under small amplitude oscillatory shear frequency for signs of nonlinear viscoelastic behavior. The advantage of these measurements is that the finer details of the structure remain intact since the deformation is small. The results of rheological studies give

the background for formulation of boundary problems in solid state mechanics as well as dynamics of fluids. The rheology of these intermediate mesophases between fluid and solid are not only scientifically interesting, but also are technologically important making them sticky and tacky [20]. The unique anisotropic viscoelastic nature of liquid crystals where the orientation dependence of viscosity is manipulated by boundary surfaces leads to an additional functionality such as lubrication.[21] In view of above objectives the properties like viscosity, elasticity deformation behavior of the *p-n* alkoxy thermotropic benzoic acids (*n*OBA, *n* = 3, 4, 5, 6, 7, 8, 9) which exhibits both nematic and smectic phases results are analyzed and discussed for getting an opportunity to modeling the compounds with respect to the applications point of view.

II. MATERIALS AND EXPERIMENTS

p-n alkoxy benzoic acid thermotropic mesogens (*n*OBA, *n* = 3 to 9) were obtained from M/s Frinton Laboratories, USA. The phase transition temperatures and textures were measured using a Meopta optical polarizing microscope with hot-stage, as described by Gray [22]. The viscoelastic measurements were carried out using a controlled stress rheometer ARG2 provided with a magnetic thrust bearing for ultralow, nanotorque control and temperature varying peltier plate. The rheological tests have been performed using 40 mm parallel plate configuration which will allow a more defect free ordering of the liquid crystal between the peltier plate and geometry. Small thin amount of samples are used for shearing which produces low thermal fluctuations and any disturbances created by the anisotropic energetic interactions and then align perfectly in the flow direction. Before loading the sample the zero gap is made at test temperatures. The samples were first heated up to their clearing temperature and kept at that temperature for 5 minutes to eliminate the influence of any thermal history fluctuations. The measured values are the average value of the experiment.. No edge fracture was observed in the range of shear rates investigated at different temperature. The variation of dynamic moduli, loss angle and viscosity as a function of frequency are carried out. Three different types of oscillatory rheology tests were carried out on i) variation of complex moduli with respect to angular frequency, ii) measurement of loss angle with respect to angular frequency, and iii) viscosity variation with variation in angular frequency.

III. RESULTS AND DISCUSSION

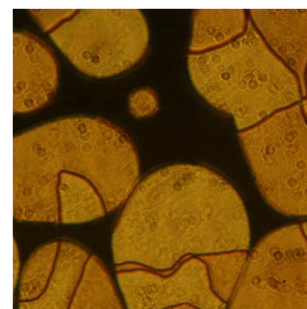
3.1. Phase transition temperatures

The phase transition temperatures and textures were observed with using a Meopta optical polarizing microscope. The transition temperatures are measured with 0.1°C accuracy and are shown in Table 1 which in good agreement with the literature values [23].

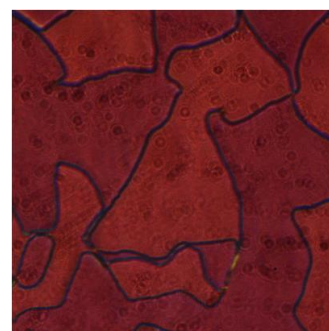
Table I. Phase transition temperatures of *p-n* alkoxy benzoic acids for *n* = 3 to 9.

Compounds	Mesomorphic range (°C)			
3OBA	143	-----N-----	153	
4OBA	145	-----N-----	157	
5OBA	21.6	-----N-----	146.5	
6OBA	101.9	-----N-----	150.5	
7OBA	89.8	----sc----	97.5	-----N----- 144
8OBA	95.1	----sc----	102.4	-----N----- 136.2
9OBA	86.3	----sc----	116.5	-----N----- 135.2

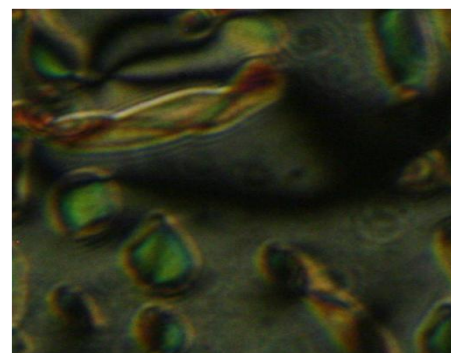
The textures of series of alkoxy benzoic acids also have been observed while heating and cooling as these are enantiotropic. The compounds with *n*=3-6 have shown Nematic schlieren textures and with *n*=7-8 have shown smecticC schlieren texture before going to crystal structure during cooling. The texture of series in different phases are shown in Fig 1.



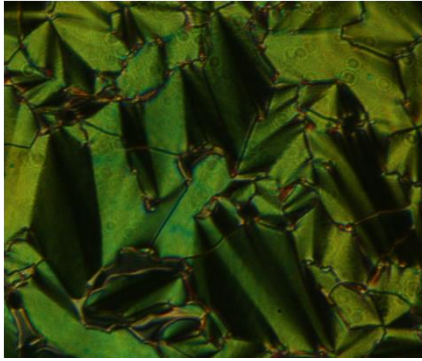
Transition from Isotropic to Nematic



Nematic phase



Transition from Nematic to SmecticC



Smectic C phase

Fig.1. Textures of nOBA in their phases

3.2. Viscoelastic measurements: The viscoelastic parameters are strictly defined within the linear viscoelastic regime as to know where to start the oscillatory tests. The results of oscillatory shear tests are presented in different ways for analyzing the data such plots of G'' , G' vs angular frequencies, angular frequency variation of loss angle to analyze the property variation.

a) Variation of dynamic moduli: After the compounds linear viscoelastic region has been defined by a strain sweep, its structure is further characterized by using a dynamic oscillation or frequency sweep. Variation of dynamic moduli is observed by dynamic oscillation or frequency sweep at a strain below the critical strain as determined by strain sweep test. During the frequency sweep the frequency is varied while the amplitude of the deformation - or alternatively the amplitude strain is kept constant. For the analysis, the storage and loss moduli are plotted against the frequency. The data at low frequencies describe the behaviour of the samples at slow changes of stress. Oppositional the behaviour at fast load is expressed at high frequencies. A frequency sweep records a fingerprint spectrum of the material.

Figure 2 (a-g) shows the frequency dependence of storage modulus (G') and loss modulus (G'') at different temperatures in the nematic and smectic phases. The angular frequency increased from 0.1–100 rad/s in the linear viscoelastic region at low %strains. From the figures it is depicted that the viscous and elastic properties of orientable molecules in the liquid crystalline materials are sensitive to particle orientation.

At low frequencies, a frequency-independent plateau (region 1) is observed suggesting that the material contains cooperative rearrangements as in rubber polymers [24]. Above low frequencies, frequency dependent region (region 2) is seen for both the moduli (rapid increment); noticeable is the fact that G' remains greater than G'' until the highest frequency of measurement. For all the samples, plateau region (G^1) extends over the entire range of frequencies since the materials studying here exhibits non-spherical nature The variation of complex moduli as a function of angular

frequency in the smectic phase is shown in Fig 1e, 1f and 1g for $n = 7, 8$ and 9 respectively interpreting the large storage moduli when compared it in the nematic phase.

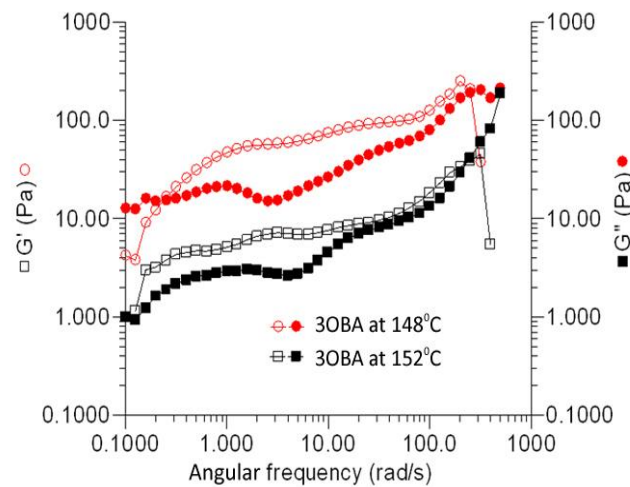


Fig.2(a)

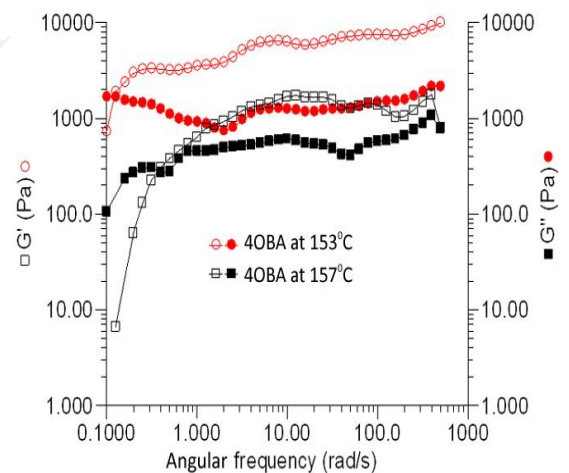


Fig. 2(b)

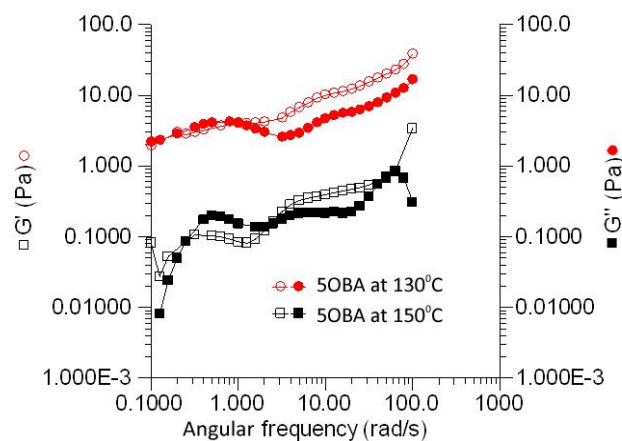


Fig. 2(c)

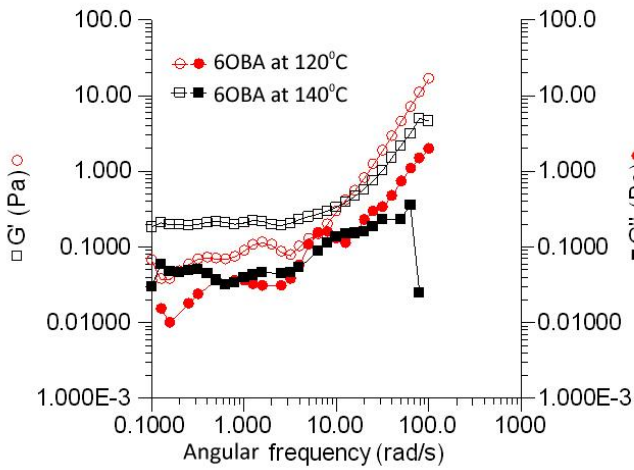


Fig. 2(d)

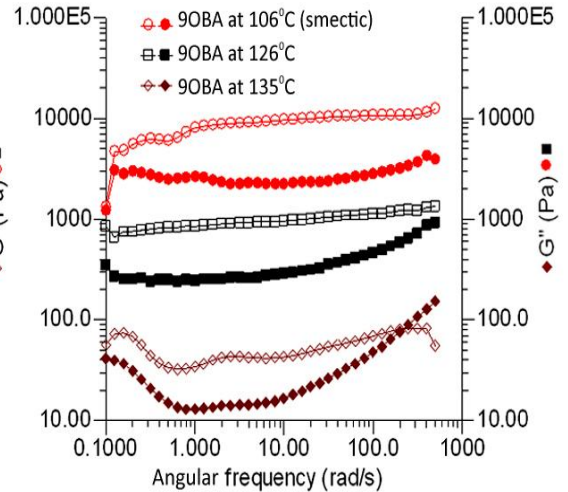


Fig. 2(g)

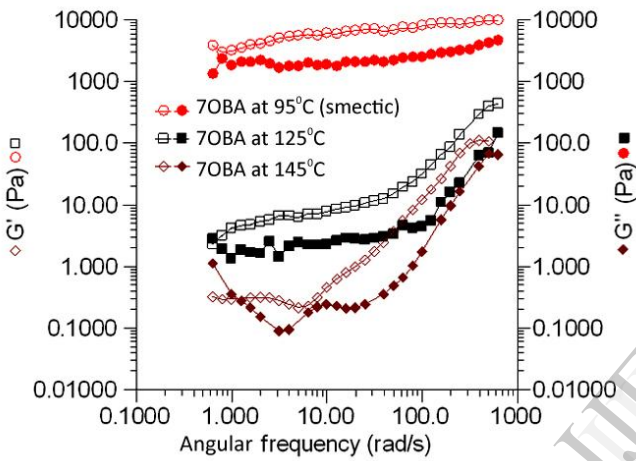


Fig. 2(e)

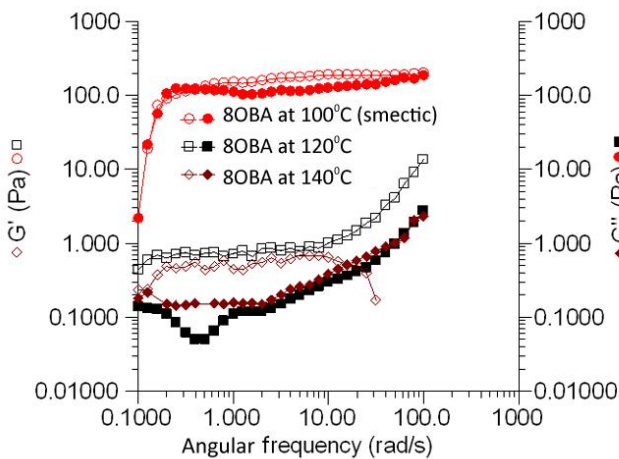


Fig. 2(f)

Fig.2 G^I and G^{II} of the samples studied as a function of angular frequency at different temperatures.

G' and G'' are independent of frequency over the entire range showing the high stability of rigidity even at high deformations. The characteristic relaxation time ($\tau \sim \omega_c^{-1}$) is calculated. At higher frequencies the relaxation times exhibit low values suggesting that the structural relaxation becomes lower with increasing frequency and temperature. The figures produced of G^I and G^{II} with respect to the variation of frequency shows roughly independent of molecular length and the crossover frequencies (or relaxation times) are mostly seen and repeated in the nematic textures than smectic may be due to the absence of translation order (presence of flexibility) in the nematic phase. Therefore, in *p-n* alkoxy benzoic acid mesogens the carbon chain number consists of $n = 3,4,5$ exhibits different relaxation times than compared with other alkoxy benzoic acids.

b) Measurement of loss angle δ : The loss angle δ which is the ratio of G^{II} and G^I , has been shown in Fig. 6 in the nematic region. From Fig.3 it is observed that the minimum and maximum loss angle (in degrees) for thermotropic LCs is higher than 90° when compared to thermotropic LCPs [25]. If $\delta = 90^\circ$ indicates a pure viscous, and $\delta = 0^\circ$ shows a pure elastic. δ is greater than 90° indicating more pure viscous nature due to the unique anisotropic properties of mesogens. In flexible polymers, a viscous behavior in the low frequency region and an elastic in the high frequency region is expected. Fig. 2 shows an odd-even effect such that the odd numbered carbon chain exhibits a viscous response in the low frequency range and at high frequency range a transition from viscous to elastic behavior takes which is reverse for the even number of carbon chainlength. Hence *p-n* alkoxy benzoic acid (*n*OBA) mesogens can be utilized in both ways in which even numbered alkoxy gives transition from elastic to viscous while odd numbered alkoxy gives transition from viscous to elastic even at high temperatures and frequencies.

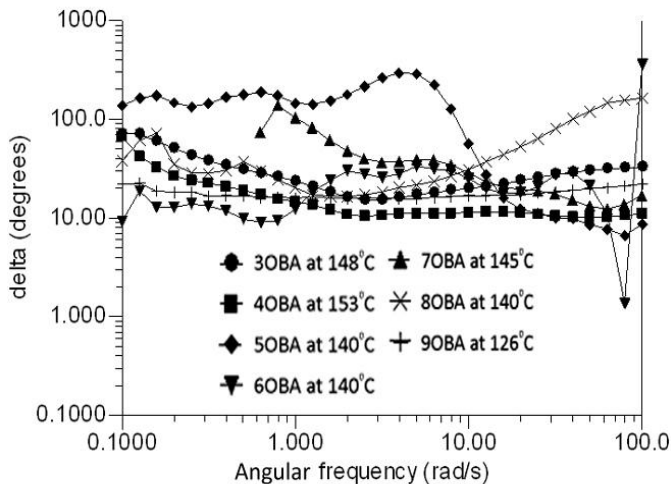


Fig. 3 Mechanical loss vs frequency for all the TLCs samples in nematic temperature region.

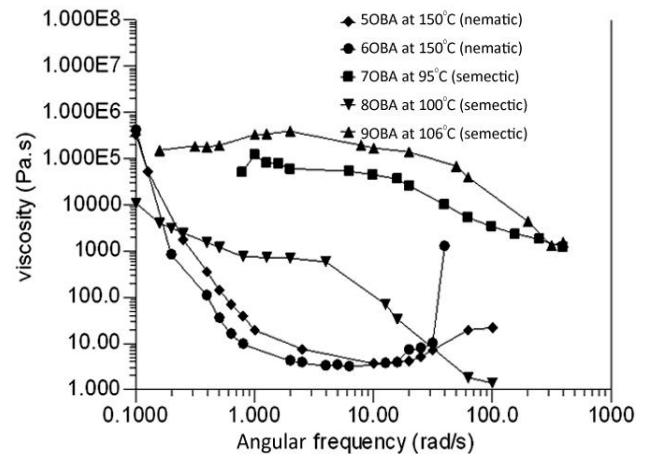


Fig. 4. Viscosity vs frequency for all the TLCs samples in nematic and smectic temperature region.

c) *Variation of viscosity:* Fig. 4 presents the variation of viscosity with angular frequency. Three different regions are observed for nematic mesophases. ($n=5,6$). A typical decrement of viscosity at frequencies less than 1 rad/s (region 1), a constant viscosity plateau at frequencies greater than 1 rad/s (region 2) and increment is observed on further increase of frequency (region 3). The decrease in viscosity at lower frequencies is understood as the alignment of rod shaped molecules in the shear direction and it is orientationally ordered. We can also use shear induced effect to explain this phenomenon. [25] These behaviours mostly observed in the viscosity vs shear rates plot [26 27] and viscosity-temperature plots in thermotropic liquid crystalline polymers [28] But for smectics ($n=7,8,9$), only two regions are observed constant plateau (at low frequencies) and decrement of viscosity with frequency variation at smectic transition temperature.

IV. CONCLUSIONS

An irregular distribution of viscosity investigated, over the range of angular frequency at different temperatures which is typical of many liquid crystalline systems. Lowering the viscosity facilitates the filling of large or complex molds. The variation of complex moduli crossovers with increase in frequency and temperature suggests that the structural relaxation becomes slow. The frequency behavior of these

TLCs has been studied in their linear viscoelastic regime that appears to be predominantly in plateau zone ($G^1 > G^{11}$). This type of behavior can be attributed due to the non-spherical structure (rods) of molecules in the nematic and smectic phases which are oriented by the flow field. Hence the nematic and smectic of different orientational degree and shapes can be oriented by a flow field producing much stronger elastic effects with large normal stress differences. In the series of *p-n* alkoxy benzoic acid mesogens we observed different rheological properties of different unique compounds like strong gels, polymer LCs. These LMM TLC's structures are not as complex and expensive as that of the typical polymers and mixtures from an economic point of view and Benzoic acid related compounds containing different activating groups like alkoxy are the most commonly used chemical standard, cheap and highly available organic substances without any complexity and mixtures in it structures having good application abilities in food preservative, biology etc. The anisotropic viscoelastic nature of these compounds may lead to additional industrial perspective such as lubrication.

V. ACKNOWLEDGEMENTS

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