Viscoelastic Properties of *p-n* Alkyl Benzoic Acid Mesogens

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Abstract: Dynamic rheological behaviour, such as storage modulus (G') and loss modulus (G") are measured as a function of frequency at different temperatures in nematic region and also studied linear viscoelastic behaviour of *p-n* alkyl benzoic acid (*n*BA) mesogens. Different zones are exhibited by the samples, - a plateau zone at low frequencies, a transition zone at high frequencies and a zone entire plateau showing for crossover frequencies and relaxation times. The dependence of the elastic (G′) and loss (G″) moduli on frequency is strong. The observed crossover points of G′, G″ in the study of frequency range is indicating that nematic phase of *n*BA has behaved like both viscoelastic solid and liquid for small deformations (<1% strain). A typical shear thinning behaviour of viscosity has been displayed when the samples are subjected to shearing at a constant temperature. This typical shear thinning has approached slowly moving to Newtonian viscosity at high shear rates showing progressive development of nematic molecular orientation along flow direction on increasing shear rate. Rheological behaviour of the *n*BA nematic phases is in general consistent like the other reported compounds except the one thermotropic liquid crystals. The higher shear force and lower viscosity ratio is observed in these compounds in which pentyl benzoic acid has high ratio indicating the high molecular orientation may be due to low chain entanglement.

Keywords: Thermotropic liquid crystals; viscoelastic; shear thinning; deformation.

I. INTRODUCTION

Rheological study will enhance the understanding better about deformation of mechanical and viscoelastic properties of complex fluids when these are subjected to stress. A Rheometer measures rheological properties of complex fluids as a function of shear rate or frequency of deformation. The mechanical properties like flow under stress of the liquid crystalline materials are studied. Though liquid crystals are preferred for non destructive mechanical testing under stress, these are also used for the visualization of radio frequency (RF) waves in waveguides. Flow properties of liquid crystal compounds are essential for many applications at different temperatures [1]. Many investigations are carried out on rheological behaviour of liquid crystalline materials, polymers, gels etc [2-4]. The soft systems like polymer solutions, gels and colloidal suspensions use to can exhibit viscoelastic properties on application of strain amplitude oscillation. Those respond in both ways like solid by storing the energy and liquid on dissipating energy. Solid like response of a system is determined by elasticity while fluid like response is set by viscosity. A few works on thermotropic mesogens are reported [5-6] however, an extensive work is done on lyotropic liquid crystal systems to study reminiscent behaviour on concentrated suspensions [7-9]. The work on disclinations and molecular structure during flow in mesophases is made [10-11]. The flow mechanics of liquid crystalline systems is relatively complicated than that of isotropic fluids due to coupling of molecular orientation and flow. Benzoic acid related compounds having different activating groups like alkyl are important precursor for synthesis of many other organic substances. The study in present paper is on shear (G[1]) and loss (G[11]) moduli as a function of frequency in the linear viscoelastic region on thermotropic *p-n* alkyl benzoic acid mesogens where $n = 5$ to 8 for modeling.

II. EXPERIMENTAL

A. Materials:

   p-n alkyl benzoic acid mesogens (*n*BA) were obtained from M/s Frinton Laboratories, USA. Molecular structure of the compound is shown in Fig.1.

Fig.1 Molecular structure of *n* BA

B.Methods:

The phase transition temperatures were measured using a Meopta optical polarizing microscope (POM) with hot-stage, as described by Gray [12]. The rheological measurements were carried out using a controlled stress Rheometer (ARG2, TA Instruments) which is provided with accessories- a magnetic thrust bearing for ultralow, nanotorque control and temperature varying Peltier plate. The rheological tests for shearing had been performed on small amount of samples using 40 mm parallel plate configuration that produces low thermal fluctuations. For achieving a perfect alignment in flow direction, caution was taken for not having any disturbances due to anisotropic energetic interactions. Before loading The zero gap is made at test temperatures before loading the samples. The average values of measurements were represented here for the repeatedly made individual experiments. There was no edge fracture in the range of shear rates investigated at different temperatures for these samples. At small strain amplitude sweep of different frequencies, frequency sweeping in the linear viscoelastic regime, and steady state shearing viscosity the properties are measured for *p-n* alkyl benzoic acid mesogens (*n*BA) where *n* = 5 to 8.
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III. RESULTS AND DISCUSSION

A. Phase Transition Studies:

   The phases and their transition temperatures (^{o}C) obtained from POM measurements on *p-n* alkyl benzoic acid mesogens (*n*BA) which are exhibiting enantiotropic nematic mesophase. The phase transition temperatures are shown below and found to be in good agreement with the literature values.

For   *p*-pentyl benzoic acid (5BA)   **82**   **Cr** **117**   **N**   ↔   **Iso**

For   *p*-hexyl benzoic acid (6BA)   **Cr** ↔   **N**   ↔   **Iso**
                                    95.2   **112.5**

For   *p*-heptyl benzoic acid (7BA)   **Cr** ↔   **N**   ↔   **Iso**
                                    102.8   **117.5**

For   *p*-octtyl benzoic acid (8BA)   **Cr** ↔   **N**   ↔   **Iso**
                                    99.1   **109.6**

(Note: Cr= Crystal , N=Nematic, Iso = Isotropic,)

B. Rheological Studies:
I. The strain sweep behaviour:

The linear viscoelastic range (LVR) for the 5BA, 6BA, 7BA and 8BA has been investigated at different frequencies, however, the range made at 1Hz frequency is taken to represent the case. Storage and loss moduli in the range between 0.01% and 100% as a function of the strain amplitude are measured. Figure 1 shows the storage modulus (elastic nature) of the samples with the applied strain amplitude. It is inferred from Fig.1 the onset of nonlinearity (γ_c) is independent of carbon chain length. This independence of γ_c on the molecular structure is also reported by Elvira Somma [13]. The peculiar behaviour of 7BA for not showing any LVR even in G^1 and G^{11} is due to strain amplitude that might overcome the limit of linear viscoelasticity. The low strain used here (0.01%), the oscillation does not significantly perturb the microstructure of the compounds, rather act as a passive probe to the evolving fluid microstructure 8BA. At high strain amplitudes, 5BA, 6BA, and 8BA there is a constant value of linear viscoelastic region noticed at high frequencies.
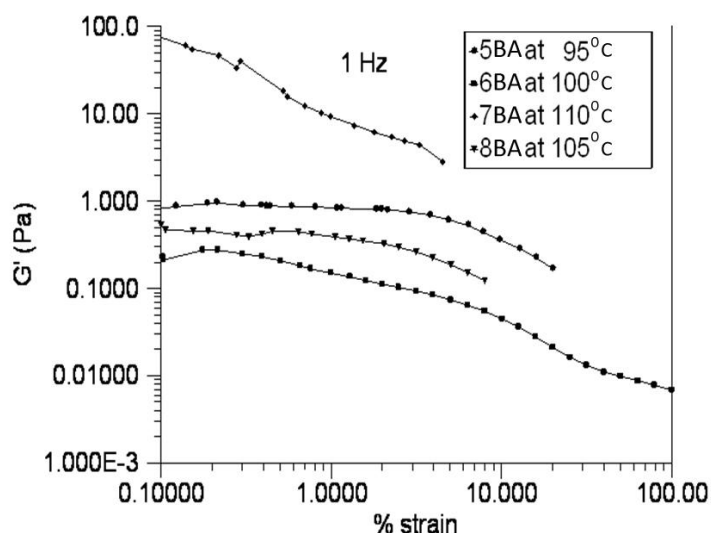

Fig.1. Strain amplitude dependence of Dynamic elastic modulus, G^1 of 5BA,6BA,7BA,8BA
in the nematic regime at 1Hz frequency.

II. The frequency sweep behaviour

The frequency sweep study has been done in the nematic region. The rheological characterization of these compounds has shown that the response at high frequencies changes predominantly from viscous to elastic. This behaviour is also observed earlier on polymer liquid crystals [14]. The data in Table 1 have shown the two crossover frequencies ($\acute{\omega}_c$) and relaxation times of these mesogens. The viscoelastic properties of these mesogens are in the range of 10 – 1000 Pa. Enhancement of elastic character called as a plateau regime in the storage modulus at low frequency is observed in 7BA and 8BA which is shown in different materials other than TLC in earlier studies [15]. Hence from the data in Table 2 it is noticed that the transition at solid –liquid or liquid – solid status in the alkyl benzoic acids both at low and high frequencies.

Table 2**:** Crossover frequencies ($\acute{\omega}_c$) and relaxation time (τ) p-n Alkoxy Benzoic acids .

S.no	Compound	Crossover frequency $\acute{\omega}_c(\tau)$ in rad/sec	
		I	II
1	5 BA	3.14(0.31)	396(0.002)
2	6 BA	6.28(0.15)	1235(0.008)
3	7 BA	1.25(0.8)	500(0.002)
4	8 BA	5(0.2)	250(0.004)

Figures 2. and 3. Have shown $G^1(\acute{\omega})$ and $G^{11}(\acute{\omega})$ as a function of frequency in which 1% strain is applied for 5BA and 6BA and is 0.01% for 7BA and 8BA i.e. in linear viscoelastic region. 5BA and 6BA compounds have shown the plateau zone at low frequencies, that is moving into a transition zone at high frequencies. Relatively rigidness of 6BA has decreased than of 5BA. The terminal to plateau zone behaviour has been observed for a thermotrpic liquid crystal polymer with kinked linkages [16]. It is observed that the orientational properties of liquid crystal phases are not disturbed by the oscillatory deformation at low strain amplitude (0.01%) and frequency. The figures produced for G^1 and G^{11} with respect to frequency variation have shown roughly independent molecular length. The molecular flexibility is high for the butyloxy and nonyloxy benzoic acid when compared to other carbon chain lengths, that is perhaps those no longer behave as rigid rods.
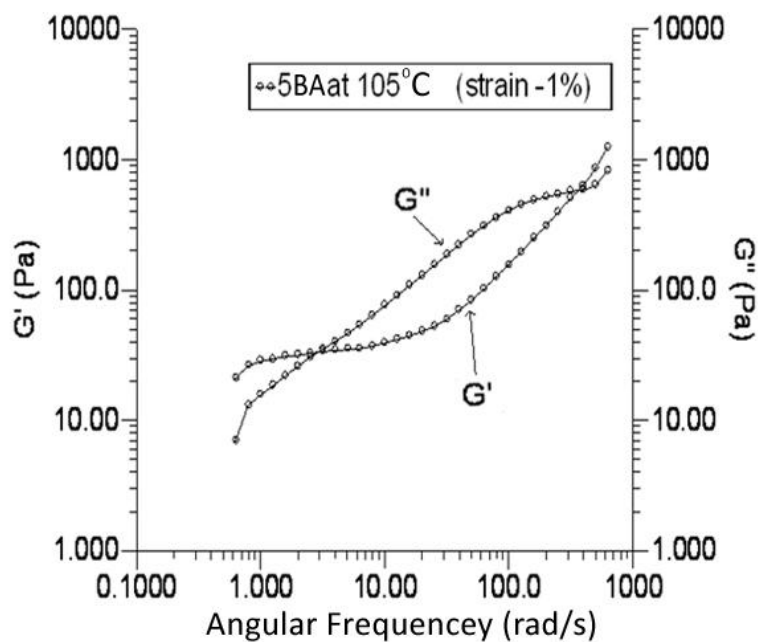

(a)
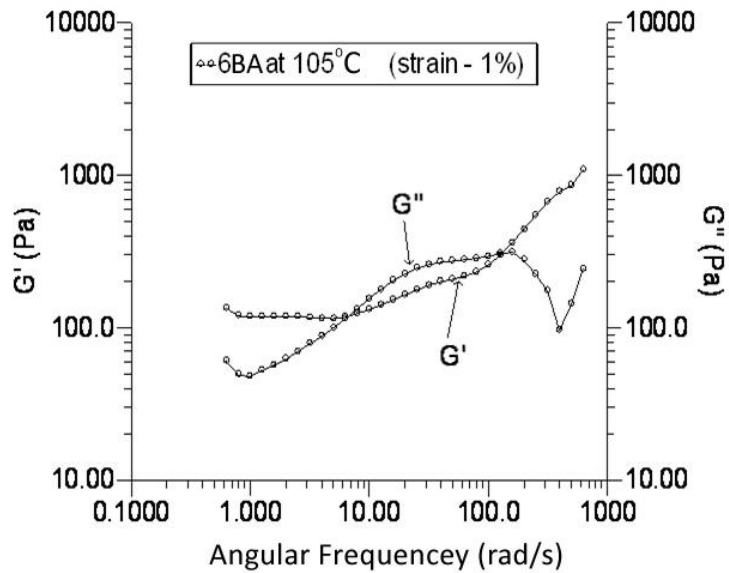
(b)

Fig 2: Frequency dependence of Storage modulus G^1 and viscous modulus G^{11} for (a) 5BA (b) 6BA

For 7BA and 8BA the storage of elastic energy has dominated the viscous dissipation energy. This zone behaviour has shown lowering in rigidity (increasing the flexibility) of molecules orientation rather than effecting deformation which is perhaps due to increase in molecular chain length.
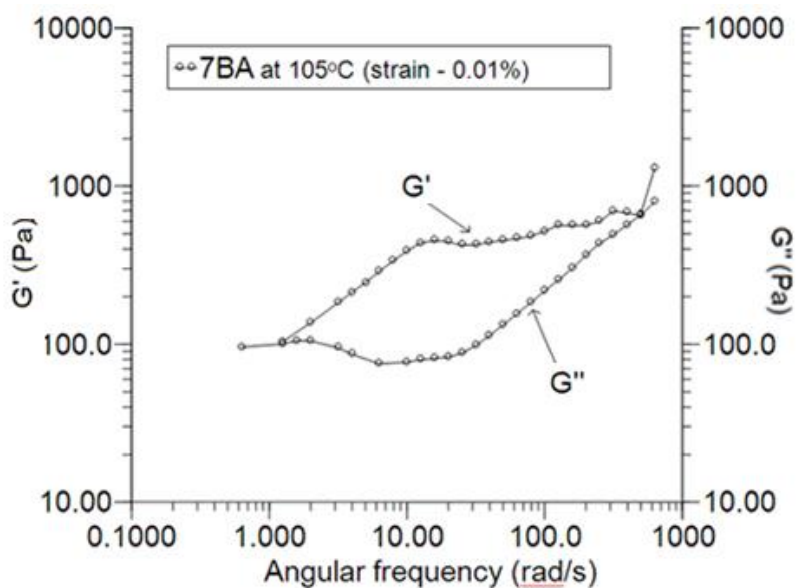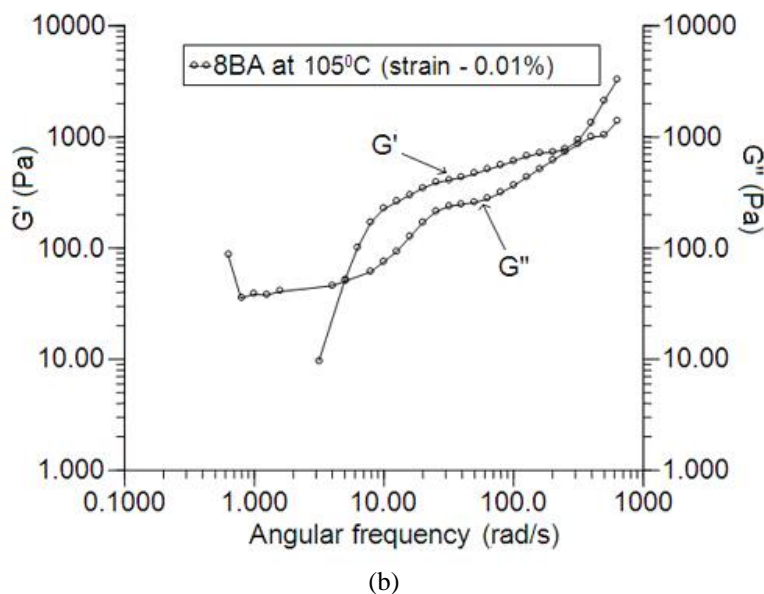

(a)

(b)

Fig 3: Frequency dependence of Storage modulus G^1 and viscous modulus G^{11} for (a) 7BA (b) 8BA

III. Steady state shearing

Figure 4 has represented for shear rate dependence of steady shear viscosity for the mesogens. The higher shear force and lower viscosity ratios are observed in these compounds among them pentyl benzoic acid (5BA)has high ratio indicating the high molecular orientation for its low chain entanglement. The shear thinning region appeared at low shear rates is a distinct feature in the flow curve of liquid crystalline compounds than of isotropic liquids. The viscosity as presented in Fig. 4 has shown shear thinning at lower shear rates and it has reached to a value at higher shear rates that are greater than 1 s-[1]. This trend has continued for Onogi and Asada's three-region flow curve (consists of regions I,II and III) made for small molecule liquid crystals and polymeric liquid crystals. At low shear rates there is slightly dependence of viscosity (region II) on molecular structure whereas the deformation dominated the rigidity of molecular chain length at high shear rates and then after a constant viscosity (region III) is maintained. However, the behaviour seen in regions II and III is always reproducible. The shape of the flow curve is in good agreement qualitatively with the data obtained for other mesophases [17-18]. This indicates that high shear rates would enhance alignment of LC materials resulting the difference in viscosity. The molecular packing, is causing it to vanish at higher shear rates. Marrucci and Maffettone [19-20] developed a two-dimensional model for polydomain flow for tumbling rod-like liquid crystals. The liquid crystal model predicted shear thinning viscosity in the presence of a kink that corresponds to the transition taking place from tumbling behaviour to the oscillating regime. This type of tumbling is observed during high shear rates. This has occurred when a molecule rotation under applied shear. The phenomenon has been observed for both low molecular weight liquid crystals and some lyotropic liquid crystals. This observation would support the viscosity growth as depicted in Figure 4 reflecting partial reformation of the orientation at lower rates in which structure remains intact more. With the tumbling effect in TLC's it is confirmed that these compounds consist of slightly flexible molecules than perfectly stiff ones.
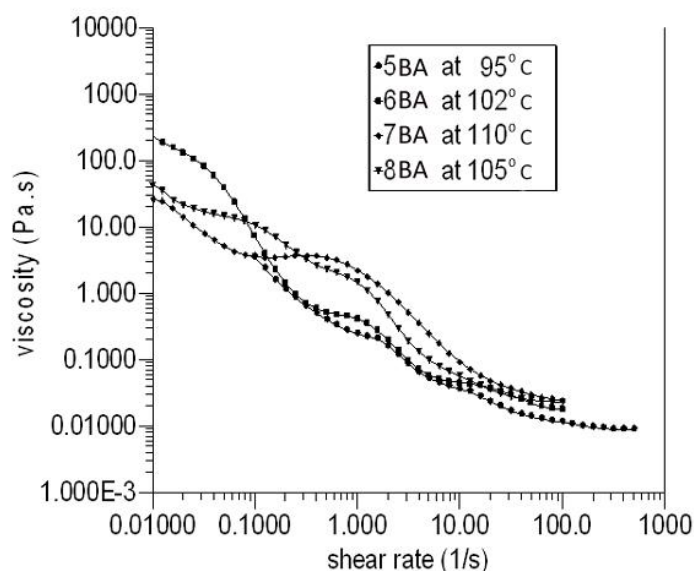
Fig. 4: Shear rate dependence of Viscosity of 5BA, 6BA, 7BA and 8BA
at temperatures in the nematic region.

IV. CONCLUSIONS

Thermotropic *p-n* alkyl benzoic acid mesophase behaviour in terms of rheological properties and effect of possible oscillation and shearing on the nematic phase is pertinently noted down. Rheology measurements performed on these compounds has revealed that the effect of alkyl chain length on viscosity is negligible. These compounds, however, did exhibit shear thinning, when either the viscosity decreased as the frequency, or strain rate, increased. The strain sweep experiments have certified the behaviour that the linear viscoelasticity is independent for molecular chain length because of dissimilarity in the molecular packing. The frequency sweep test conducted, at high frequencies, for the effect of deformation on Thermotropic liquid crystals has indicted the deformation of loss moduli dominating under high strain amplitude, and storage moduli at low strain amplitude. The domination of deformation on the rigidity of molecular chain length at higher shear rates has shown the viscosity has shear thinning at lower shear rates and at higher shear rates. The relative insensitivity of the steady-state viscosity on chain length has indicated that the deformation and relaxation between the original state and shearing are different.

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