

Rheological studies in *p*-*n*-Alkoxy Benzoic Acid Liquid Crystals

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Abstract— Rheological measurements are reported for thermotropic *p*-*n* alkoxy benzoic acid mesogens (*n* OBA, *n* = 3-9). All rheological properties measurements were performed using Rheometer. The existence and the extent of a linear viscoelastic range for the series was investigated. The mesogens display shear thinning (non-Newtonian) behaviour obeying the constitution equation of Carreau model with the power indices from 0.7 to 1.2. No shear-independent plateau (region II) is observed. dynamic mechanical experiments, are sufficient for describing the the non-spherical structure (rods) of molecules in the nematic and smectic phases which are oriented by the flow field by showing strong elastic nature at different frequencies and temperature studied in their linear viscoelastic region. Dynamic time sweeps indicate a constant relaxation behavior of the normal stress and dynamic moduli to thermal history (5rad/s) attributing no shift from equilibrium position which leads to no change in the molecular weights.

Keywords: Thermotropic Liquid crystals, Complex moduli, viscosity, Shear, Stress.

1. INTRODUCTION

As complex fluids, liquid crystals are distinguished microscopically by molecular alignment and long-range orientation order, and macroscopically by a liquid–solid duality in that they flow as anisotropic viscous fluids but resist orientational distortion as elastic solids. Calamitic (rod-like) liquid crystals based on *p*-alkoxy benzoic acid were investigated earlier for their liquid crystalline properties [1,2]; and have gained increased interest for the design of a variety of liquid crystalline compounds[3–6]. Further, the electric, magnetic, optical properties of liquid crystals were established[7].

Beside special electro-optical properties liquid crystals show intriguing mesoscopic structures and mechanical properties that suggest new applications. Now understanding of rheological behavior of these mesogens gained additional interest, since a significant number of product and processing properties depend to a large extent on flow-induced orientation [8].

Motong *et. al.* [9] observed that the low molar mass liquid crystals could act as a melt viscosity reduction like additives in different mixtures to improve the operating torque on the screw extruder [10-12]. The TLCs have attracted a great deal of interest because of their potential applications [13] and since they exhibit nematic-isotropic transitions at temperatures well below their decomposition temperature. It should be mentioned that the thermal and deformation histories of a thermotropic liquid crystals may greatly influence its morphological state as well as its orientational order, which in turn influences its rheological behavior. In the liquid crystal phase the viscosity of liquid crystals depends on the orientation of the director relatively to the flow. Thermotropic liquid crystals such as 8CB and 5CB, for example, possess an underlying order that can be controlled by varying the temperature and gives rise to their viscoelastic flow characteristics [14-15].

From the structural point of view, it is interesting to investigate the influence of shear and stress on the geometry of the benzene ring and how intra molecular arrangements affect the geometry of these molecules. These days such questions can be addressed by rheological investigations. The mechanical properties like flow under stress of the liquid crystalline materials are studied, since the LCs are used for nondestructive mechanical testing of materials under stress which is also used for the visualization of RF (radio frequency) waves in waveguides. 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. Many investigations on rheological behavior of liquid crystalline materials have been done in histories [16-18]. The existence and annihilation of defects in the presence and absence of flow is well documented [19-20]. The soft systems like, polymer solutions, gels and colloidal suspensions can 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 [21-22]. Although various lyotropic and thermotropic polymer liquid crystalline materials have been extensively researched, 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 [23-24].

The objective of this work is to examine the experimental measurements of thermotropic liquid crystals with variation in carbon chain length having nematic and smectic structures under various aspects like steady shearing, and strain deformations for signs of nonlinear viscoelastic behavior. The advantage of these measurements is that since the deformation is small the finer details of the structure remain intact. 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. These TLC's structures are not as complex and expensive as that of the typical polymers and mixtures from an economic point of view and industrial perspective. The complex moduli functions are strictly defined only within the linear response regime, and therefore an important practical experimental issue is the determination of its range of validity. 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. In view of above objectives the properties like viscosity, elasticity deformation behavior of the *p-n* alkoxy 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. EXPERIMENTAL DETAILS

Materials

p-n alkoxy benzoic acid thermotropic mesogens (*n*OBA, *n* = 3 to 9) were obtained from M/s Frinton Laboratories, USA. The rheological measurements were carried out using a controlled stress rheometer (ARG2, TA Instruments) 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 measurements are done repeatedly to gain the producible values. No edge fracture was observed in the range of shear rates investigated at different temperature. The steady state flow, dynamic moduli variation as a function of time, frequency and temperature are carried out.

The samples were allowed for the stress to relax and attain thermal equilibrium for 3 minutes. Prior to any measurements, the linear viscoelastic region (LVR) of the samples was determined. All rheological measurements were performed within the linear viscoelastic region. Steady-state flow procedure was performed to measure shear viscosities of the composite polymer aqueous solutions. The flow curves were obtained by increasing the shear rate from 10 to 200 s⁻¹.

III. RESULTS AND DISCUSSION

LCs have rich linear viscoelastic behavior. They both store and dissipate energy. This is due to the larger length scale of the structures inherent in them. These supramolecular structures endow complex fluids with their unique properties, and the interactions between, or within, them govern their dynamics.

Textures, phase transition temperatures and Variation of dynamic moduli by dynamic oscillation or frequency sweep for *p-n* alkoxy benzoic acid thermotropic mesogens was reported earlier. The angular frequency variation of viscosity was also 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 [25]. Further the rheological characterization is carried out by time, temperature, strain sweeps and also the steady state viscosity measurement.

3.1 Time sweep

Preliminary tests of the complex modulus with the time were performed on the mesogens to determine whether time effects could influence their viscoelastic response. The time sweep is simply going to analyze the sample under the described conditions for a specific length of time. The sample is said to be stable if the storage and loss modulus are parallel to each other and the x-axis.

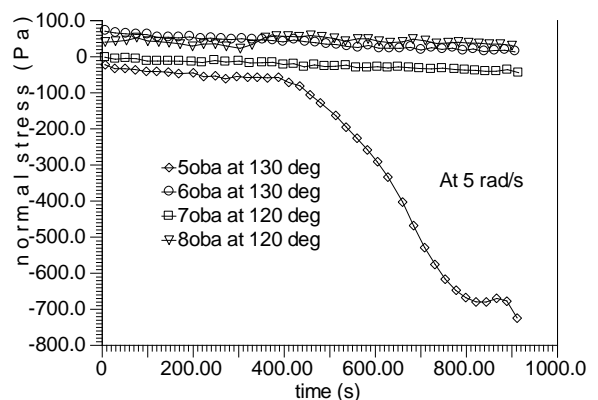


Fig.1. Normal stress vs time after 10 min of loading the samples in the nematic region.

Time dependence of normal stress (at 5rad/s) after 10min loading has been investigated in *n*OBA series and Representative plots showing the temporal evolution in the normal stress functions in nematic phase are shown in Fig. 1 ($n = 5$ to 8). For ($n=5$) 5OBA the normal stress shows negative value and decreases with increase in time after 400s indicating insufficient to allow the complete relaxation while for $n=6-8$ is positive and constant. The changes may be attributed to the squeezing flow applied in the loading and could also responsible for time effects [26-27].

Time dependence of complex moduli G^* at the frequency 5rad/s is performed to reflect the influence of viscoelastic parameter and is reported in Fig. 2. No significant changes of the G^* with time are recorded for $n=6,7,8$. The rheological experiments lasted not more than 10min after loading for about 10 min. For this same reason strain sweep was performed above 1rad/s so that the test should be completed before these were significant time effects.

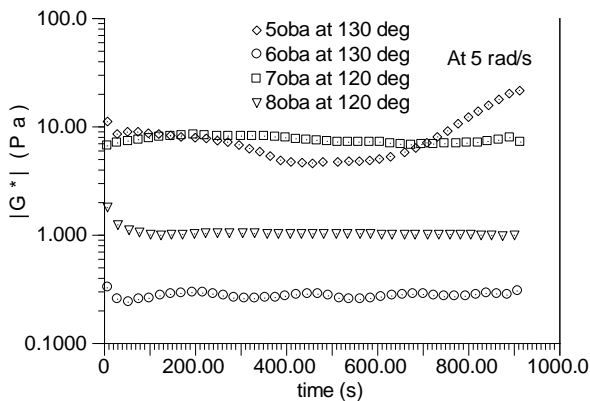


Fig.2. Complex moduli vs time at angular frequency of 5 rad/s .

For 5OBA, there is a variation of G^* in the nematic regime (after 10 min loading) which is not constant when compared with other mesogens. This may be said to the negative normal stress as shown in Fig 1. The data presented in the time sweep revealed that the sample is stable over the acquisition parameters. The conclusion is based on the fact that the storage and loss modulus are essentially constant and parallel with each other.

3.2. Strain sweep

In order to determine the strain amplitude range over which linear viscoelasticity prevails, strain sweep experiments were carried out at a frequency of 5 rad/s and 6.238 rad/s in the overall strain amplitude range of 0.01%–100%. The storage and loss moduli as a function of strain amplitude for the *n*OBA mesogens of carbon $n = 3$ to 9, are studied. The storage (G') and the loss (G'') moduli are sensitive to change in microstructure during the experiment and shows similar nature, hence complex moduli (G^*) with respect to the % strain are shown in Fig. 3 and Fig. 4 respectively

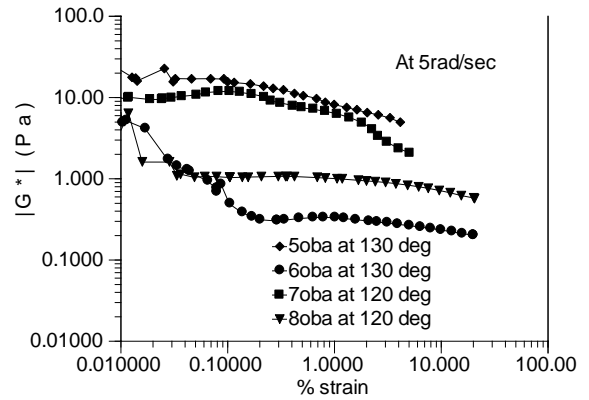


Fig.3. Variation of complex moduli with respect to strain amplitude at 5 rad/s in the nematic temperature regime.

The complex moduli (G^*) is constant up to a certain value of %strains, which can be identified as the limit strain amplitude (γ_c) for the onset of nonlinearity. The TLCs shows a linear viscoelastic behavior at small strain amplitudes with a general trend and the onset of nonlinearity is obtained at low % strains i.e. at 10% strain. Comparatively, the linear viscoelastic region is large for the samples exhibiting even carbon chain length, in which the butyloxy benzoic acid gives high value of complex moduli. This critical %strains helps us in observing the structural rearrangement nature and their relaxation times ($\sim 1/\omega_c$) at different frequencies.

The range of linear viscoelastic limit is similar to liquid crystal polymers and smaller as compared to conventional polymers. Liquid crystals exhibit low strain limit of linear viscoelastic region due to unique structure as well as rod like molecules.

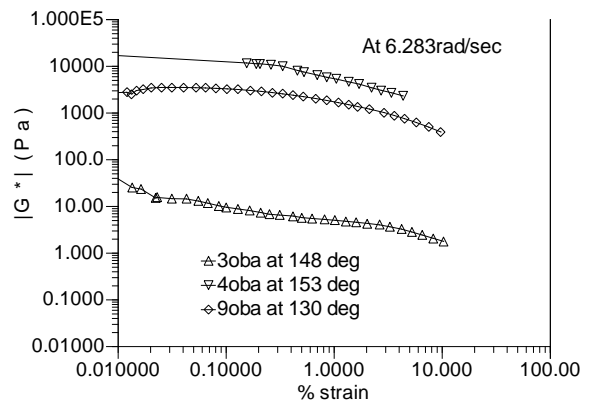


Fig.4. Variation of complex moduli with respect to strain amplitude at 6.283 rad/s in the nematic temperature regime.

the linear region is limited only to very small strain amplitudes, of $\gamma < 0.1\%$ for 7OBA. These strains are at the low end of the resolutions of the rheometer and the scatter in the data at these low deformation rates is observed in figure 3. represented by the increased breadth of the 95% confidence intervals of the Student's *t*-distribution at low deformation rates, testifies to this.

3.3. Temperature sweep

A temperature sweep is an experiment that attempts to gauge the effect of temperature on the sample. A temperature sweep will indicate at what temperature the material begins to readily exhibit liquid-like properties.

The temperature variation of complex moduli at different fixed frequencies is studied and the results of some samples are shown in Fig 5a to 5d for different frequencies. From Figures 5a and 5b it can be observed three regions for $n = 5$ and 6 respectively which are exhibiting nematic phase only. The viscosity of liquid crystals, like that of common fluids, decreases with temperature elevation. With the decrease of temperature, G^* decreases (region 1), constant G^* plateau (region 2) and G^* increases (region 3) is observed. The transition into the isotropic phase, i.e. the disordered system, is accompanied by an increase in the resistance of the material to shear that is consistent with the rise in the complex modulus. With the increase of frequency G^* constant plateau is dominating. The kinematic viscosity measured for Nematic liquid crystal of 4-pentyl 4'-cyanobiphenyl (5CB) has shown sharp rise in kinematic viscosity in nematic-isotropic transition region. This is related to intensive development of order parameter fluctuations in nematic phase and density fluctuations in isotropic phase. The viscosity increase may be caused by pre-transitional fluctuations of the order parameter [28].

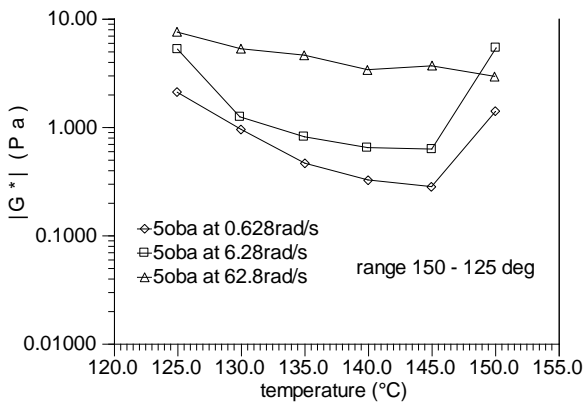


Fig.5a. Complex moduli vs temperature for 5OBA compound in full LC range (isotropic – nematic – solid).

A large jump in the shear viscosity is observed at the transition temperature of thermotropic 5CB due to the phase transition of the liquid crystal [29]. However, nematics and some cholesterics demonstrate a substantial viscosity variation at temperatures of the transition liquid crystal phase-isotropic fluid. In most cases the viscosity rises. The viscosity increment of nematics is insignificant [30-32].

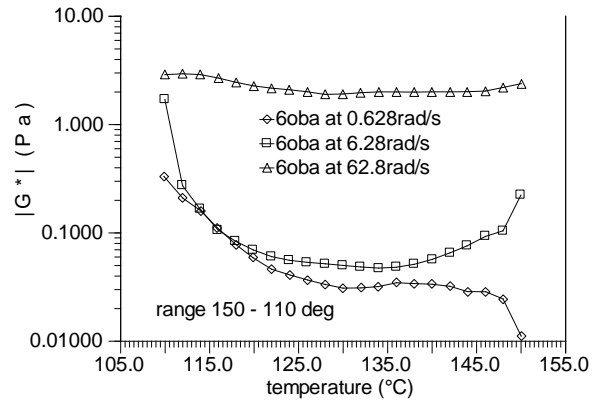


Fig.5b. Complex moduli vs temperature for 6OBA compound in full LC range (isotropic – nematic – solid)

In 7OBA and 8OBA which exhibits both nematic and smectic phases, two regions are observed, 1. constant G^* plateau and 2. increase of G^* with the decrease of temperature from isotropic, are observed as shown in Figures 5c and 5d respectively. For 7OBA, a steep rise is observed due to the transition of mesophase from nematic - smectic phase. A similar local maximum at this transition assumed as N_C -SmC transition is observed in the viscosity measurements for 7OBA. This is likely to be due to smectic phase clusters distributed in the nematic phase [33]. The evidence for existence of Nematic subphase Cybotactic nematic in 7OBA and two Smectic C sub phases SmC1, SmC2 is also presented. The temperature range of the nematic phase, however, can be divided into two regions by viscosity. Since the high temperature nematic (N subphase) is much less viscous than the low temperature one (N_C subphase). For 8OBA the starting increment of G^* is observed at the vicinity of 100°C where the transition of nematic - smectic phase takes place. The roughly irregularities of all the figures with complex moduli with the temperature variation corresponds to the boundaries of the biphasic region. Hence the incidence of an isotropic – nematic – smectic – transition is announced by an easily noticed rheological anomaly. Nevertheless it is prudent to confirm the existence of such a transition by inspecting the sample under Polarizing Optical Microscope.

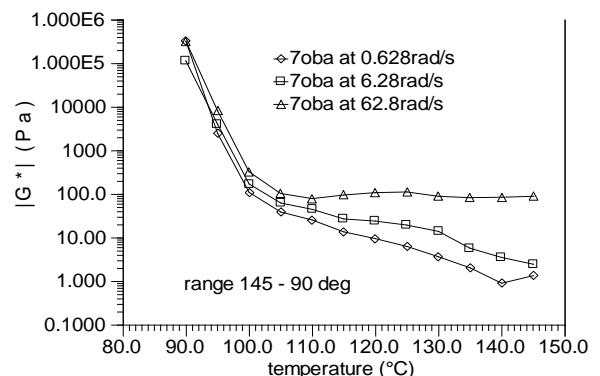


Fig.5c. Complex moduli vs temperature for 7OBA compound in full LC range (isotropic – nematic – smectic - solid).

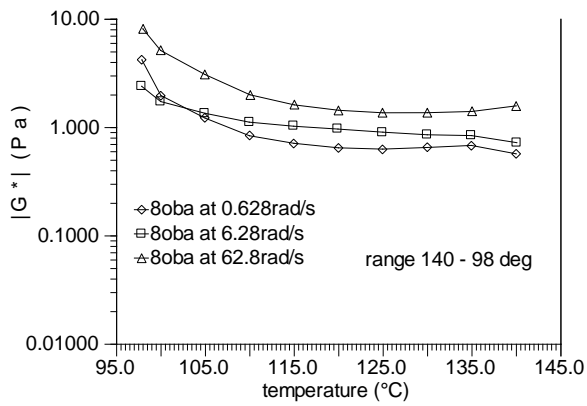


Fig.5d. Complex moduli vs temperature for 8OBA compound in full LC range (isotropic – nematic – smectic – solid)

3.4. Steady state flow

The rheological nature of liquid crystals changes depending on the shear rate. Fig. 6 and Fig. 7 shows the flow curves in nematic and smectic regions respectively. The steady shear viscosity, shown in figures 6, 7, exhibits the typical trend seen for low molecular weight liquid crystals. At shear rate up to 100s^{-1} the viscous nature decreases showing shear thinning fluids nature in both phases having a lower apparent viscosity at higher shear rates. The shear rate depends of viscosity occurs when the shear rate is high enough to disturb from equilibrium the distributions of inter particle spacing. There is no sudden shear thickening which is an important characteristic in application point of view which results no sudden tearing or breaking. This proves that liquid crystals possess the viscosity anisotropy. The viscosity is less if molecules are oriented along the flow. The viscosity anisotropy of liquid crystals appears only at a slow flow velocity.

A pseudo plastic fluid behavior was reported for liquid crystals with very low viscosities as these viscosities are low enough to allow liquid crystal pumping inside a conventional circuit [34]. The viscosity of lamellar liquid crystals also decreases with increasing shear rate according to power law. This suggests limited structural modifications, such as alignment of lamellar planes but not viscous component [35].

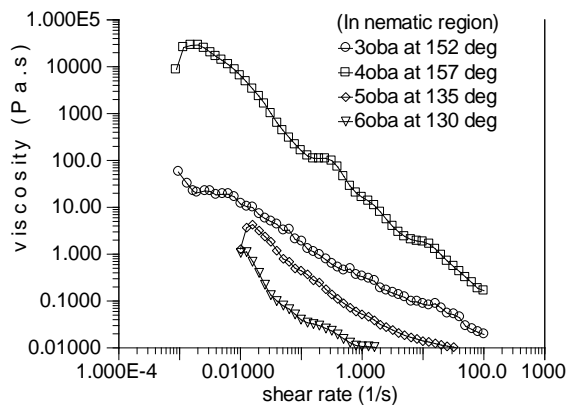


Fig. 6. Viscosity vs shear rate for all TLCs studied in the nematic region.

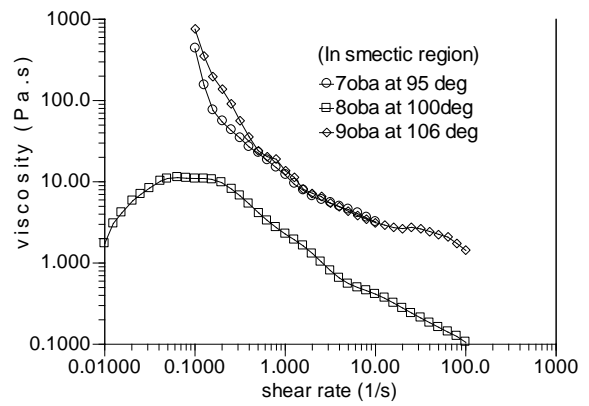


Fig.7. Viscosity vs shear rate for all TLCs studied in the smectic region.

The experimental data of shear vs viscosity fits to Carreau model [36] very well with the power index (n) from 0.7 to 1.2. The rod like molecules start to tumble with shear and they rotate from tumble to wagging after certain critical shear rate. With the increase of shear the wagging region transforms to flow aligning region. At the high shear rate region, the molecules start to move with flow aligning direction, which leads to strong shear thinning behaviour [37]. The shear thinning phenomenon can also be attributed to the slipping of layers past each other and at higher shear rates the loss of shear thickening shows that there is no breakdown of the sliding layer flow. There is no indication of Newtonian regime in either the high or low shear rate limit for these compounds and is attributed to immobilization of the molecules.

Fig.8 depicts viscosity vs strain in both nematic and smectic phases. In nematic region the shear thinning is observed at low strains and at high strains (>100) a start up of constant viscosity plateau region is observed, while for smectic phase there is no start up of viscosity plateau at high strains, and thereby exhibits a variation from that of nematic phase. η value for 8OBA consists of smectic phase at the lowest shear rate is comparable to materials which form strong gels [38]. For the all series of compounds studied the structure of a sheared thermotropic liquid crystals appears to be similar to that found in simulations of small molecule liquids [39] and hard sphere suspensions. The dramatic drop of viscosity shows that there is yield stress above which the partially ordered structure transforms into a layered structure [40].

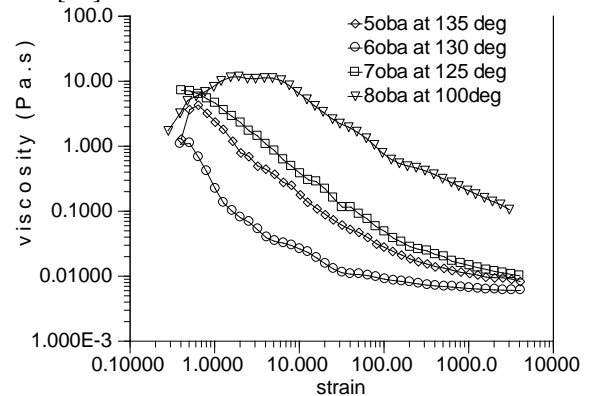


Fig.8. Viscosity vs strain for all TLCs studied in the nematic region ($n = 5,6,7$) and smectic region ($n = 8$).

The similar nature is observed in frequency experiment also. Therefore it may be emphasized that at a particular temperature in nematic and smectic phases by varying frequencies, two regions can be observed which may be due to different transitions from one phase to another. This may be endorsed to stiff rod-like molecules, aligned preferentially and the liquid molecules positionally disordered but orientationally ordered. According to Stokeian dynamics simulation results for the steady shear viscosity the samples studied exhibits the Brownian viscosity characteristic resulting a usual stiffness of the molecules and viscosity decreases with shear rate because of flow induced orientations.

IV. CONCLUSIONS

The linear viscoelasticity of *p*-n alkoxy benzoic acids mesogens was investigated in an attempt to define common trend of liquid crystal due to liquid-solid duality. The data presented in the time sweep revealed that the sample is stable over the acquisition parameters. A substantial change in the complex modulus is observed during phase transitions mesophase for every member of the series. Over the range of shear rate and strain at different temperatures investigated, the viscosity displays shear thinning region) and starting up of constant viscosity matrix, flow behavior typical of many liquid crystalline systems. Lowering the viscosity facilitates the filling of large or complex molds. 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 a particular liquid crystal phase is not found distinctive, but each phase has its unique typical rheological properties in itself. The distinguishing features of the mechanical behavior can be summarized by stating that the series exhibited different rheological properties of different unique compounds like strong gels, polymer liquid crystals. The reduction of viscosity at high shear rates and increase in the moduli of these TLC's can result in significant improvements in process ability.

VI. ACKNOWLEDGEMENTS

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REFERENCES

- [1] B.Jones, J. Chem. Soc.(1935), p.1874.
- [2] G.W Gray, B.Jones, J. Chem. Soc., (1954) p.2556–2562.
- [3] T.Ganicz, W.I.A.Stanczyk, N.K. Gladkova. I .Sledzinska, Macromolecules, 33, (2000), p.289–293.
- [4] Yao. N; Jamieson A.M., Macromolecules, 31, (1998) p.5399–5406.
- [5] Hsu C.-S.; Chu P.-H.; Chang H.-L.; Hsieh T.-H. ; J. Polym. Sci. A: Polym. Chem., 35, (1997) p.2793.
- [6] Inoue. A.; Maniwa.S.; Ide, V. , J. Appl. Polym. Sci., 64, (1997) p.303–310.
- [7] P. G. de Gennes, “The Physics of Liquid Crystals”, Clarendon Press, Oxford 1974
- [8] Alejandro D. Rey, Tomohiro Tsuji, Macromol. Theory Simul. 7, (1998) p.623–639.
- [9] Motong et.,al, journal of applied polymer science,107, (2008) p.1108 – 1115.
- [10] Leslie. F.M., “Theory of flow phenomena in liquid crystals”, in Advances in Liquid Crystals, Academic press, New York, 1, (1979).
- [11] Ernst. B., Navard. P, Macromolecules. 28, (1989) p. 1419,
- [12] Fischer. H., Keller.A., Windle.A. H. J , Non-Newtonian Fluid Mech. 67, (1996) p. 241.
- [13] Elvira.S., Nobile.M.R., J. Rheol. 48, (2004) p. 1407- 1423.
- [14] Gahwiller.Ch., Phys. Rev. Lett. 28, (1972) p. 1554.
- [15] Negita.K.; Inoue.M.; and Kondo.S. , Phys. Rev. E 74, (2006) p. 051708.
- [16] Porter.R.S.;Griffen.C., Mol. Cryst. Liq. Cryst., 25, (1974) p. 131.
- [17] Iizuka. E. Mol. Cryst. Liq. Cryst. 25, (1974) p. 287.
- [18] Meiboom.S.,Hewitt.R.C , Phys. Rev. A. 15:6, (1977) p. 2444 -2453.
- [19] Rey .A.D, Liq. Cryst. 7, (1990) p. 315.
- [20] Rey. A.D., Mol. Cryst. Liq. Cryst. 225, (1993) p. 313.,
- [21] Duke.R., Chapoy.W.L.L., Rheol. Acta 15, (1976) p. 548.
- [22] Kiss.G., Porter.R.S., Polymer Preprints 18:1, (1977) p. 185.
- [23] He. J., Bu. W., Polymer. 35, (1994) p. 5061.,
- [24] He. J., Bu. W., Zhang. H., Polym Eng Sci. 35, (1995) p. 1695.
- [25] S.Sreehari Sastry, R. Chandra Krishna, A. Bindu Madhavi, T.Vindya Kumari, Ha Sie-Tiong IJERT 3 (2014) 1731-1736
- [26] Romo-Urbe.A.,Lemmon.T.J., Windle.A.H., Rheol.J., 41, (1997) p. 1117– 1145.
- [27] Elvira. S., Ph.D. thesis, University of Salerno, edited by CUES (2003)
- [28] Yaroslav v. Sperkacha, volodymyr s. et.al.,Mol. Cryst. And liq. Cryst., 366(2001) p. 91-100,
- [29] benjamin d. Hamlington, benjamin steinhaus, james j., Liquid Crystals, 34,(2007), p. 861–870
- [30] Tsvetkov.V.N., Mikhailov.G.M., J. Exp. Tech. Phys. 7, (1939) p. 1399–1408.
- [31] Babaev.A.S., Temaev.B.G., Stafeev.V.I., J. Phys. Chem. 52(6), (1978) p. 1412–1415.,
- [32] Johnson.J.F., Porter.R.S.,” Liquid Crystals and Ordered Fluids,” vol. 2 (London, Plenum Press, New York, (1974) p. p. 342,
- [33] Sergey Olegovich Ilyin and Ivan Ivanovich Konstantinov , liquid crystals, 43, (2015)369–380.
- [34] Rocio Bayón, Silverio Coco, María Barcenilla , et.al., Appl. Sci., 6, (2016) p.121
- [35] J.Zhao, Z.N. Wang, Indian journal of chemistry,50 , (2011) p 641-649.
- [36] Carreau. P. J. Trans. Soc. Rheol, 16, (1972) p. 99.
- [37] Muir , M. C. & Porter , R. S. Processing rheology of liquid crystal polymers: a Review, Mol. Cryst. Liq. Cryst.,169, (1989) p.83-95.
- [38] Krishna Prasad.S., Geetha G. Nair, Bhargavi.R., Jayalakshmi.V., Shanker.G., Yelamaggad.C.V., J. Phys. Chem. B, 114, (2010) p. 697–704.,
- [39] Hanley. H. J. M., Rainwater.J., Clark. N. A., Ackerson. B. J., J. Chem Phys 79, (1983) p.4448,
- [40] Ackerson. B. J., Pusey. P. N., Phys Rev Lett, 61, (1988) p.1033 – 1036.