

Chapter 4

Viscoelastic coefficient of novel thiol terminated alkoxy-cyanobiphenyl liquid crystals

4.1 Introduction

In the previous chapters, we have described our studies on the viscoelastic response of lyotropic liquid crystals. In this chapter we report our experiments on the viscoelastic modes of thermotropic liquid crystals. Thermotropic liquid crystals are the main constituents of liquid crystal mixtures used in display technology. The physical properties of thermotropic liquid crystals need to be investigated and understood in order to improve the characteristics of liquid crystal displays. Elastic constants and viscosity coefficients are important because they determine the response time of a display. In particular for the inplane switching mode, the twist elastic constant (K_{22}) is the predominant elastic constant since the switch on response time (τ_{ON}) and switch off response time (τ_{OFF}) are given by: [1]

$$\tau_{ON} = \frac{\eta d^2}{\epsilon_0 \epsilon_a V^2 - \pi^2 K_{22}} \quad (4.1)$$

$$\tau_{OFF} = \frac{\eta d^2}{\pi^2 K_{22}} \quad (4.2)$$

Here, η is the twist viscosity coefficient, ϵ_a is dielectric anisotropy, V is the applied voltage and d is the sample thickness. In order to improve the response time, the values of η should be small and ϵ_a should be large. The ratio of K_{22} and η which is known as the viscoelastic

coefficient is important for all practical purposes. Viscoelastic coefficients of thermotropic liquid crystals have been measured by NMR and rheology experiments [2,3]. Dynamic light scattering (DLS) has been employed to measure the viscoelastic coefficients of classical rod-like nematics [4–10]. Polymer stabilized liquid crystals have been studied using DLS [11]. The *in situ* formation of polymer network was found to increase the twist elastic constant and viscosity coefficient due to a coupling between elasticity of nematic and that of polymer network. Mixtures of side chain liquid crystal polymers and nematic (5OCB) have been studied as a function of applied electric field by Liu *et.al* [12]. Here, the twist relaxation frequency, on the addition of polymer, was found to decrease mainly due to an increase in twist viscosity. The effect of dopants on the viscoelastic coefficient of a thermotropic liquid crystal have been studied by Coles *et.al.* [13].

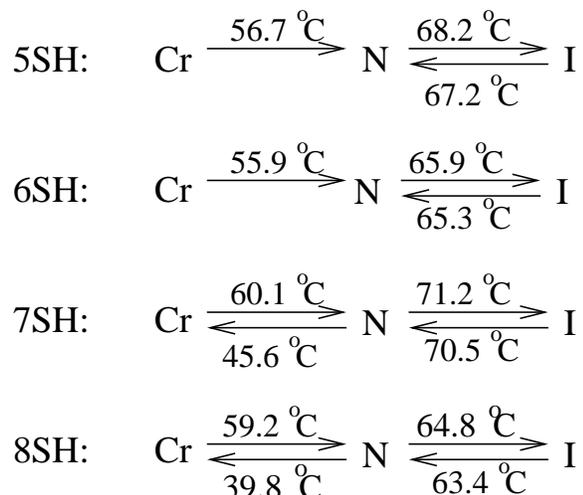
Ordinary alkyl- and alkoxy-cyanobiphenyls are well known and well studied systems [14,15]. In order to prepare dimers, oligomers and polymers, from these molecules, numerous terminally functionalized alkoxy-cyanobiphenyls have been synthesized [16]. But, terminally thiol functionalized cyanobiphenyls were synthesized very recently [17]. Thiol group has very good affinity to gold and these molecules have been found to form a highly ordered self assembled monolayer on gold coated substrates [18].

We discuss in this chapter, the studies of refractive indices and twist viscoelastic coefficient of the homologous series of thiol-terminated alkoxy-cyanobiphenyl liquid crystal as a function of temperature in nematic phase and compare it with alkoxy-cyanobiphenyl system. We also describe dynamic light scattering experiments carried out on these materials with applied electric field.

4.2 Experimental

The preparation of materials was carried out in our laboratory by Prof. Sandeep Kumar [17]. The structure of the molecule, with 5 carbon atoms in the alkoxy chain, is shown in Fig. 4.1. The thermal behavior of the materials was investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). We have studied the lower homologous

of the terminally thiol substituted alkoxy cyanobiphenyl series having 5 to 8 carbons in the chains. All these compounds showed distinct crystal-nematic and nematic-isotropic peaks in DSC. The phase sequence of these compounds are as follows:



Higher homologous of this series did not show a stable nematic phase. Hereafter we refer the compounds as nSH where n is the number of carbon atoms in alkoxy chain. The DSC for the compound having 7 carbon atoms in the alkoxy chain (7SH) is shown in Fig 4.2.

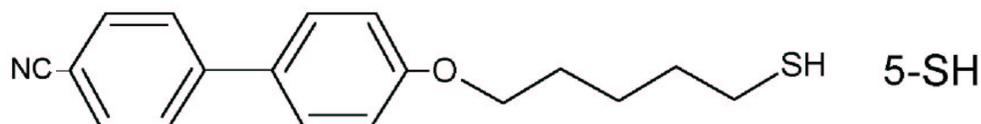


Figure 4.1: Structure of thiol terminated alkoxy-cyanobiphenyl molecule.

4.2.1 Sample cell preparation

For achieving the homeotropic alignment of molecules, two clean glass plates of $1\text{cm} \times 1\text{cm}$ dimension were coated with a surfactant, octadecyl triethoxy silane (ODSE) and then cured at 150°C for about two hours. ODSE is a long chain amphiphilic molecule having a polar group and an aliphatic chain. Polar end group is attracted to the glass plate and long

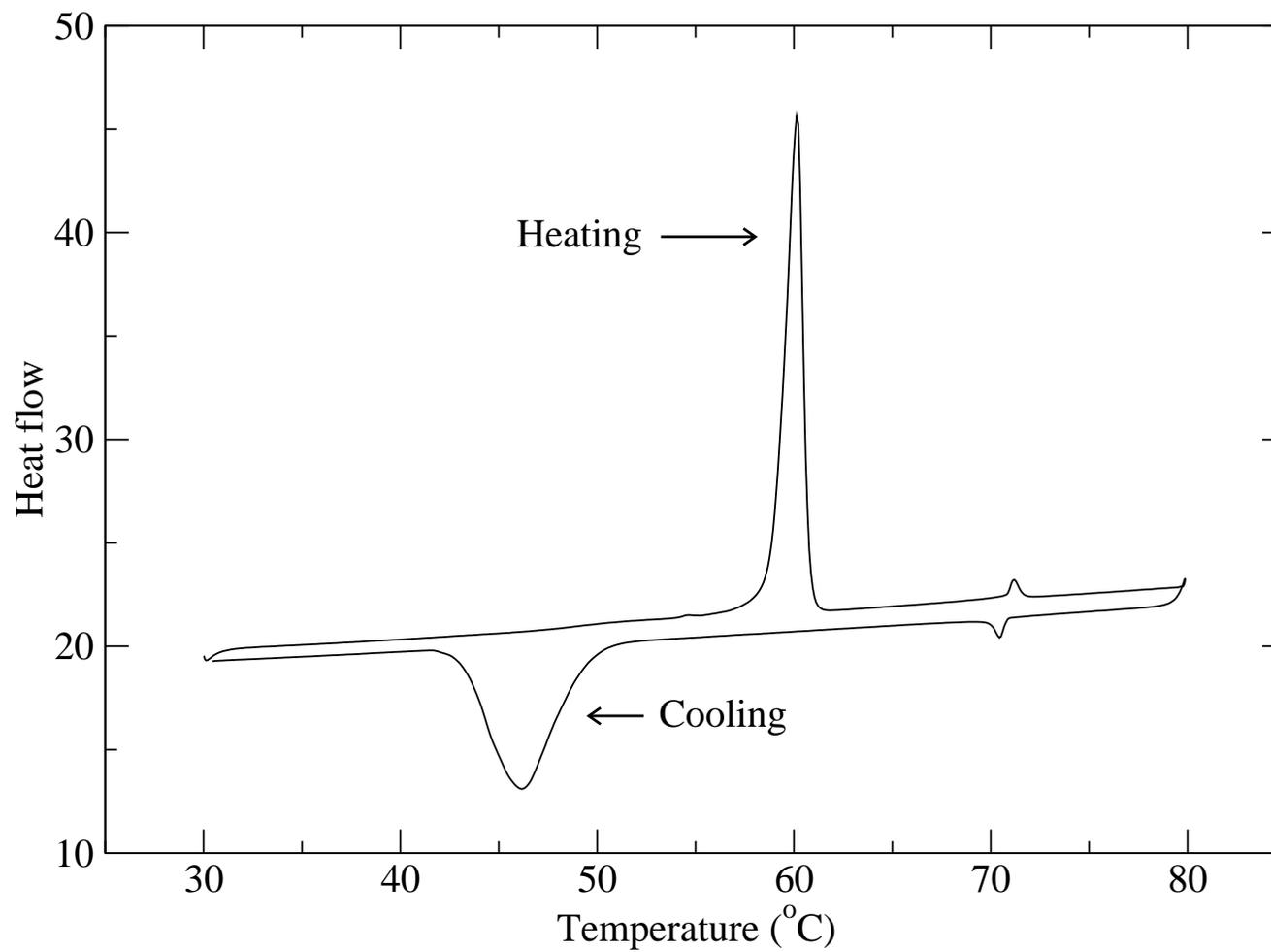


Figure 4.2: A DSC thermogram of 7SH. The heating and cooling rate was 5.0°C per minute. Nematic range is around 10°C on heating.

chain interacts with the alkoxy chain of the liquid crystalline molecules. This gives rise to perpendicular orientation of molecule with respect to the glass plates. Sample cells were made by keeping these treated glass plates one above the other with treated surfaces facing each other. The sides were sealed by using an epoxy glue and the thickness was fixed using glass beads of $12\ \mu\text{m}$. Sealed cells were cured at 150°C for about an hour. The thickness of these empty cells was measured using interferometric technique. A spectrometer (Ocean Optics S2000) was used to display the interference pattern of light reflected from the upper and lower glass plates. From the interferogram the cell thickness was measured. The sample was heated to isotropic phase and then filled in the cell by capillary method. Because of the surface treatment, the liquid crystalline molecules align homeotropically.

For dynamic light scattering experiments with the applied electric field, we have used ITO coated glass plates. Apart from this modification, the procedure to fabricate the cells, is similar to that described above. We used the oscillator output of lock-in amplifier (EG&G 5302) to apply an AC voltage to the cell.

4.2.2 Instrumentation and experimental geometry

The sample temperature was controlled using a commercially available heater (Instec MK1). The temperature stability of this heater was $10\ \text{mK}$. The hot stage was modified in our workshop in order to keep it vertical with respect to the scattering plane during the experiment. The sample cell was stuck to the heater wall using a high temperature Teflon tape. The heater was enclosed by a Teflon jacket to minimize heat loss. All other instrumentation was similar to that described in the previous chapters.

An Abbe refractometer was used to measure the n_e and n_o as a function of temperature. We have described the working of this refractometer in the previous chapter. The sample was put in the powder form in between the prisms and then heated to isotropic phase. The measurements were carried out while slowly cooling the sample, which leads to the homeotropic alignment of liquid crystal.

The experimental geometry, to obtain the twist fluctuations was similar to that described

in previous chapters. The incident laser light was parallel to the director with polarization perpendicular to the scattering plane. The scattered light was analyzed in the plane of scattering. The experiments were performed in the V-H geometry.

4.3 Results

We have carried out the experiments to measure the ordinary and extraordinary refractive indices and twist viscoelastic coefficient of thiol terminated cyanobiphenyl liquid crystals.

4.3.1 Refractive index measurement

We have shown the refractive indices of thiol terminated cyanobiphenyl liquid crystals, on slow cooling in Fig. 4.3. We have measured the refractive index upto a value of 1.7 due to the limitation of the refractometer. The value of n_e decreased while the value of n_o increased as we increased the temperature. We have also measured the values of n_e and n_o for 4'-(hexyloxy)-4-biphenyl-carbonitrile (6OCB) compound. The structure of 6OCB is same as that of thiol terminated alkoxy-cyanobiphenyl but it does not have a thiol group at the end. The values of n_e and n_o are lower in the case of 6OCB. These values increased to some extent by substitution of a thiol group at the end of alkoxy chain. Refractive indices were nearly independent of the length of alkoxy chain. It can be seen in Fig. 4.3 that n_e and n_o increase only by a small amount if the number of carbon atoms in the chain are decreased. We point out here that the values of birefringence remain almost same in all the cases.

4.3.2 Twist viscoelastic coefficient

As described in the previous chapters the auto correlation function from our experiments corresponds to twist fluctuations in the appropriate geometry. We fit the auto correlation function to a single exponential decay. A typical auto correlation function is shown in Fig. 4.4. The decay time of $g_2(\tau)$ corresponds to the twist relaxation of the director. The relaxation frequencies are a function of scattering wave vector given by Eqn. (2.3) in the geometry selected by us. In Fig. 4.5 we have presented the variation of relaxation frequencies as a

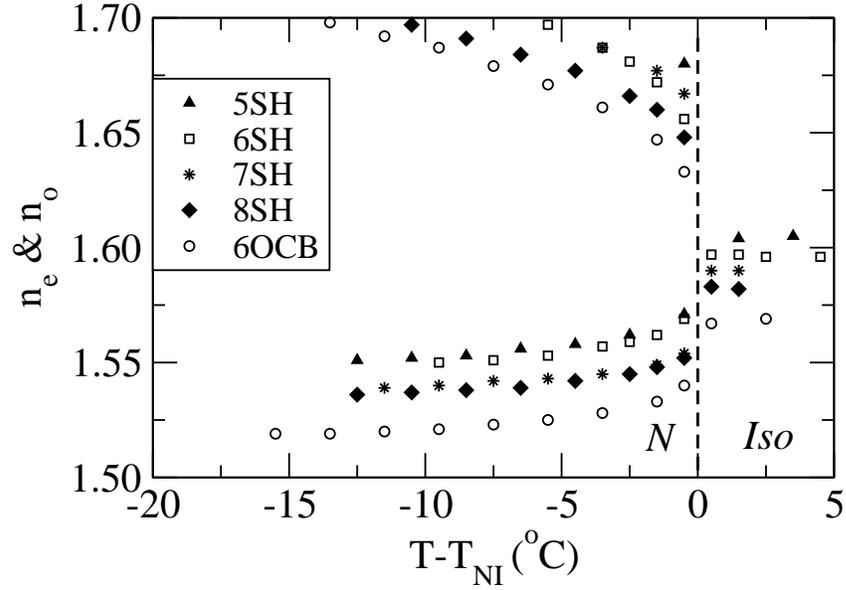


Figure 4.3: The variation of n_e and n_o for thiol-terminated alkoxy-cyanobiphenyl molecules as a function of temperature for different lengths of alkoxy chains. For comparison we have also plotted the values of n_e and n_o for 6OCB (open circles).

function of scattering wave vector for 6SH compound at various temperatures. The data were fitted to the straight lines. The slopes of various straight lines give the value of K_{22}/η . The variation of K_{22}/η as a function of temperature for 5SH, 6SH, 7SH and 8SH are shown in Fig. 4.6. We find that the twist viscoelastic coefficient increases as we increase the temperature in the nematic phase. We find that the values of K_{22}/η are slightly higher for odd number of carbon atoms in the alkoxy chain.

We have also performed dynamic light scattering experiments with applied electric field for 6SH. A sinusoidal (AC) electric field of intensity $4.65 \times 10^5 \text{Vm}^{-1}$ and of frequency 4.157KHz was applied using a lock-in amplifier. When an external electric field is applied in a homeotropically aligned nematic along the director, the twist relaxation frequency modifies (in comparison with the Eqn. (2.3)) according to the following relation [8]:

$$\Gamma = \frac{K_{22}}{\eta}q^2 + \frac{\epsilon_0\epsilon_a E_{app}^2}{\eta} \quad (4.3)$$

Here, ϵ_a is the dielectric anisotropy and E_{app} is the applied electric field. It is clear that the relaxation time ($\tau_r = 1/\Gamma$) does not diverge at zero wave vector in the presence of external

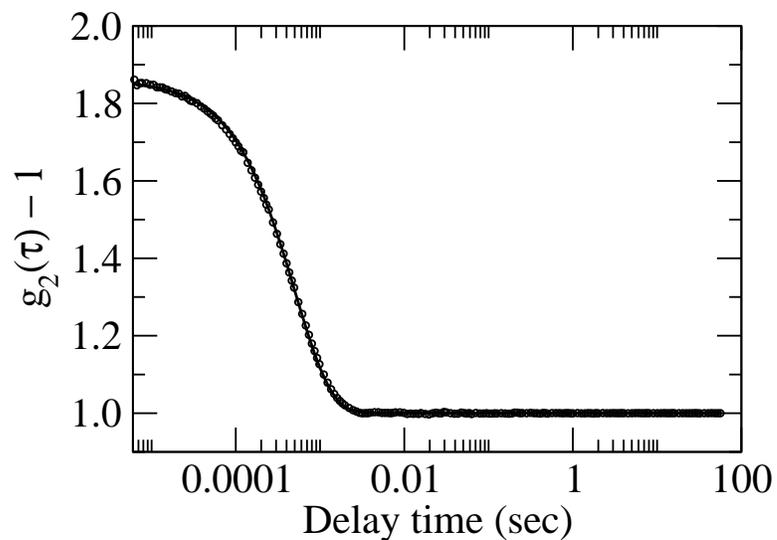


Figure 4.4: A typical auto correlation function from our experiment on the compound 6SH. The data were collected at 62°C at a scattering angle of 14° . The solid line is a single exponential fit to the experimental data points.

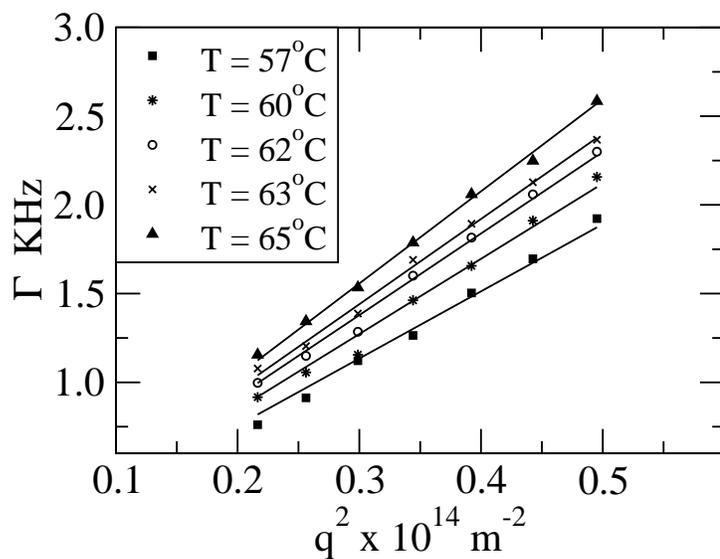


Figure 4.5: The variation of relaxation frequency with wave vector squared at different temperatures for 6SH sample. Solid lines are fits to Eqn. (2.3).

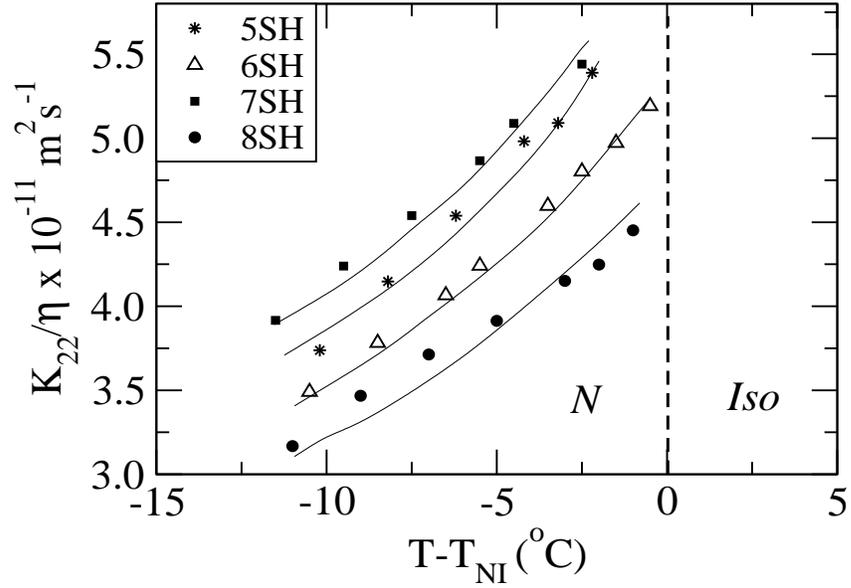


Figure 4.6: Twist viscoelastic coefficient of the homologous series of thiol terminated alkoxy-cyanobiphenyl in nematic phase as a function of reduced temperature. Solid lines are cue to the eyes.

electric field. We can expect the relaxation frequency to be higher in the presence of external electric field for nematics having positive dielectric anisotropy.

We have compared in Fig. 4.7 our results at different temperatures for 6SH compound with and without electric field. Open circles show the relaxation frequencies in the presence of applied electric field while stars show the relaxation frequencies in the absence of the field. We obtain the values of K_{22}/η from the zero field experiment and then substitute these values in Eqn. (4.3) and again fit it. From this fitting we calculate the values of $\epsilon_0\epsilon_a/\eta$ as a function of temperature.

Finally, to compare our results with standard alkoxy-cyanobiphenyl compounds, we have also performed an experiment to find the viscoelastic coefficient of 6OCB as a function of temperature. In Fig. 4.8 we have compared the values of K_{22}/η for 6OCB and 6SH. The values of K_{22}/η for 6OCB are approximately 3 – 4 times higher than that of 6SH.

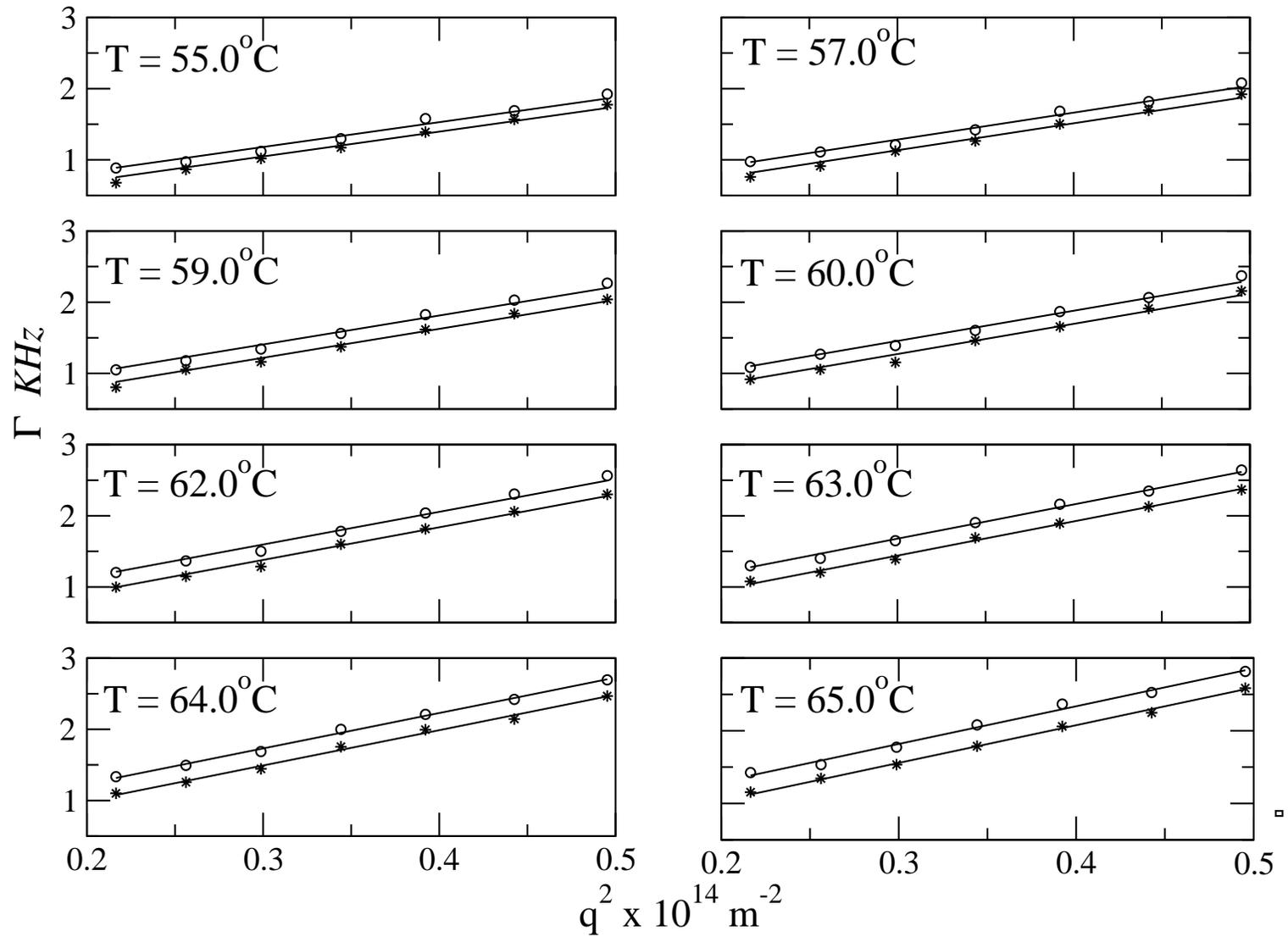


Figure 4.7: The comparison of relaxation frequency for 6SH compound with and without applied field. Different plots are at different temperatures. Circles represent the data with applied electric field and stars represent the data without field. Applied field is $4.65 \times 10^5 \text{ Vm}^{-1}$.

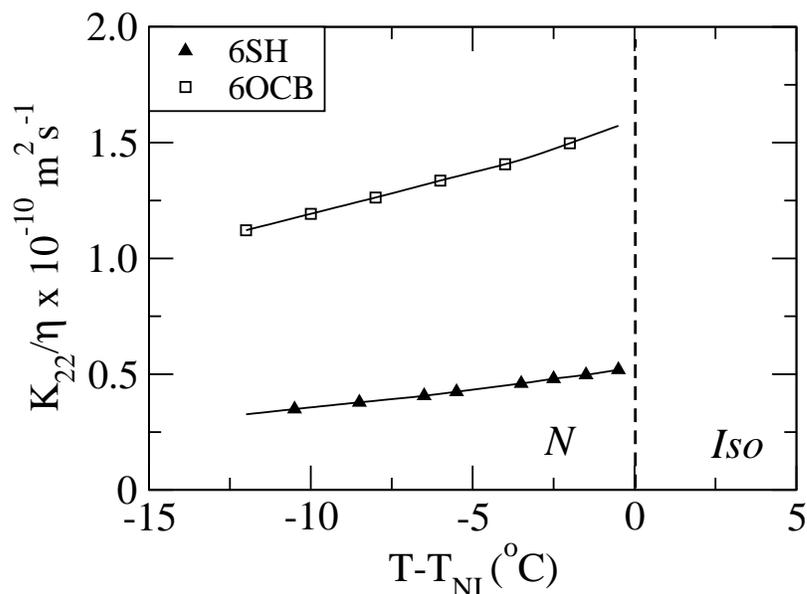


Figure 4.8: The twist viscoelastic coefficient of 6OCB (empty squares) and 6SH (filled triangle) as a function of reduced temperature. The values of K_{22}/η are 3 – 4 times higher in case of 6OCB. Solid lines are cue to the eyes.

4.4 Discussion

The ordinary and extraordinary refractive indices of liquid crystals are of importance as far as display properties are concerned. We have employed a technique where one can measure both the refractive indices in the same setup. We have used a polarizer in between the sample and eyepiece of Abbe refractometer to decouple the ordinary and extraordinary rays from the sample. There are two refractions from the sample and the two boundaries can be clearly distinguished by rotating the polarizer. This allows us to obtain the values of n_e and n_o simultaneously. The values of refractive indices of 6OCB are in agreement with the values reported [14]. These values are found to be slightly lower compared to the values of thiol terminated alkoxy-cyanobiphenyl compounds. The values of birefringence are almost same for all the compounds with different chain lengths.

There have been many experiments to measure the values of K_{22}/η for thermotropic nematic liquid crystals [5,7–9,12]. The typical values of K_{22}/η for some well known systems in literature are shown in Table 4.1. The values of K_{22}/η for our compounds are nearer

to those reported for other thermotropic nematic systems. For a Schiff's base thermotropic nematic [7] the values are comparatively high. For MBBA [5] and 5CB [8], twist viscoelastic coefficient is close to that of 6SH. In the case of 5OCB, it is surprisingly about twice of 5CB [12]. We have measured the values of K_{22}/η for 6OCB which again was found to be 3 – 4 times larger than that of thiol terminated alkoxy-cyanobiphenyl compounds.

We suggest that the presence of a big terminal group at the end of alkoxy chain makes the director relaxation slower and hence the values of twist viscoelastic coefficient turn out to be smaller.

Table 4.1: A comparison of the values of twist viscoelastic coefficient for various thermotropic nematic systems reported in literature.

Sample	$T - T_{NI}$	$K_{22}/\eta(m^2 s^{-1})$	Ref.
6SH	$-3.50^\circ C$	4.6×10^{-11}	our work
Nematic Schiff's Base	$-4.20^\circ C$	11.4×10^{-11}	[7]
MBBA	$-1.88^\circ C$	4.76×10^{-11}	[5]
5CB	$-4.00^\circ C$	5.9×10^{-11}	[8]
5OCB	$-5.00^\circ C$	9.6×10^{-11}	[12]

The dynamic light scattering experiments on liquid crystals, in the presence of an applied electric field, have also been reported in literature [4, 8, 12]. The main advantage of these experiments is that one can get the information about the viscosity coefficient separately in the same setup. In our setup we have carried out experiments on dynamic light scattering with applied electric field for 6SH sample. As expected, we find that the relaxation frequency to be higher when the field is applied (Fig. 4.7). The intercepts of fitted straight lines on the y - axis yield the values of $\epsilon_0 \epsilon_a E_{app}^2 / \eta$. We have shown ϵ_a / η as a function of absolute temperature in Fig. 4.9. From these data we have estimated the approximate value of twist viscosity (η) by assuming the values of dielectric anisotropy to be same as that of ordinary rod-like nematics. We find that the twist viscosity for $T - T_{NI} = 5$ is $0.12 Pa \text{ sec}$, which is nearly 5 times larger than that of 5OCB [12]. We suggest that the presence of thiol group at

the end of the terminal chain may increase the twist viscosity.

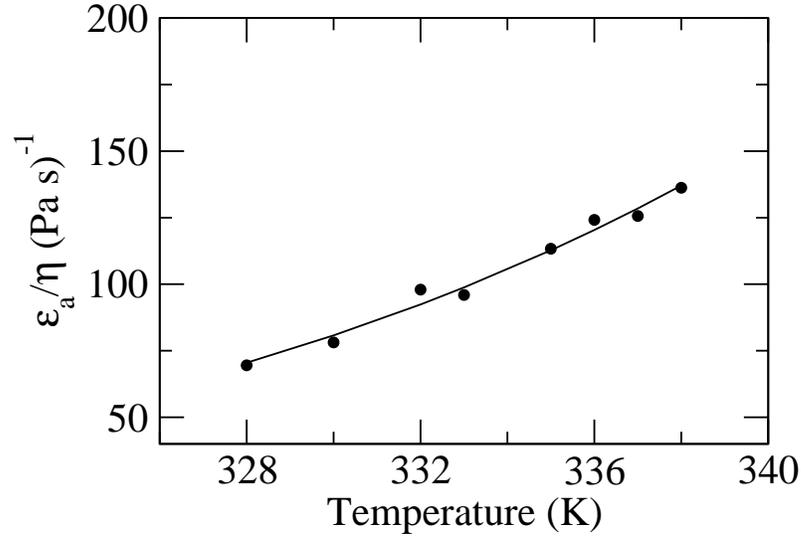


Figure 4.9: The variation of ϵ_a/η as a function of absolute temperature for 6SH under the applied electric field.

4.4.1 Estimation of activation energy

As we have described in the previous chapters, the activation energy can be estimated from the data on twist viscoelastic coefficient. We have taken the temperature dependence of η and K_{22} given by Eqn. (2.8) and Eqn. (2.9), respectively. It is known that [19] the order parameter of a liquid crystal is proportional to the optical birefringence. Therefore, we have used our refractive indices data (Fig. 4.3) of 6OCB, since there is not much change in the values of birefringence (δn) between 6OCB and nSH. We fit the values of $\ln(K_{22}/\eta\delta n)$ as a function of temperature to Eqn. (2.10). The fit is shown as a solid line in Fig. 4.10. We find that the value of E_a for 5SH is $18.6 \pm 0.6 \text{Kcal/mole}$, for 6SH is $17.9 \pm 1.0 \text{Kcal/mole}$, for 7SH is $16.0 \pm 0.8 \text{Kcal/mole}$ and for 8SH is $15.5 \pm 0.6 \text{Kcal/mole}$. Activation energy for MBBA is reported [20] to be around 12Kcal/mole . Thus, we find that the value of E_a is comparable to other rod-like thermotropic liquid crystals whereas it is smaller when compared to discotic liquid crystals as discussed in the previous chapter.

In this chapter, we have studied the refractive indices and viscoelastic modes of the homologous series of a novel thiol terminated alkoxy-cyanobiphenyl liquid crystal. We find that

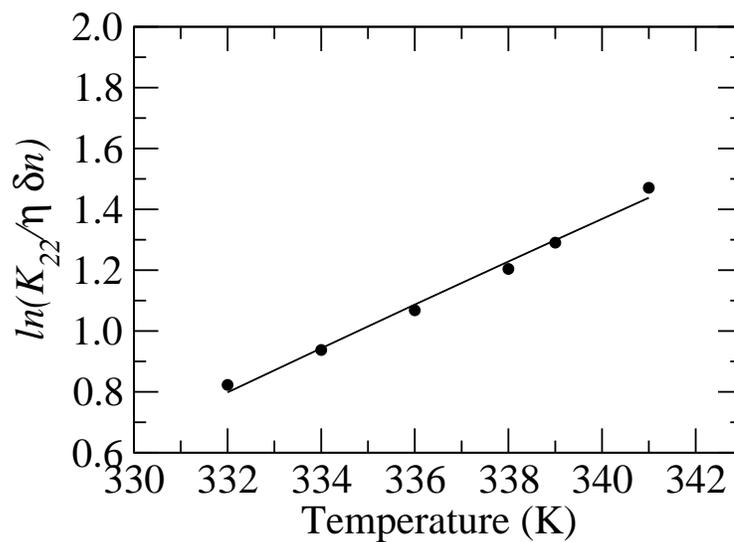


Figure 4.10: The calculation of activation energy from the data on viscoelastic coefficient for 7SH. Solid line is a fit to Eqn.(2.10). The estimated value of activation energy is $16.0 \pm 0.8 \text{Kcal/mole}$.

the values of twist viscoelastic coefficient are smaller than those of alkoxy-cyanobiphenyl system. We have done experiments on DLS with applied electric field. Such experiments are useful to find the values of viscosity and elasticity separately.

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