Effect of Coupling Chain Length on the Electric –Optic Properties of Siloxane Based Side Chain Liquid Crystal Polymers

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Abstract: *A series of siloxane based side chain liquid crystal polymers have been prepared with asysematic variation in spacer length. Nematic liquid crystal polymers possess large optical nonlinearities owing to their large refractive index anisotropy coupled with the collective molecular reorientation. All the polymer exhibited a smectic phase, for which the Nematic -isotropic transition temperature increased as the spacer length increased. Electro-optic measurements are used to evaluate the threshold voltages for this series of polymers. It is found that with increasing spacer length (n) of polymer the threshold voltage is lowered and that the variation of the threshold voltage arises from changes to the intrinsic curvature elasticity rather than to differences in orientational order. A simple model is used to indicate the origion of the effects observed which appear to arise from the constraints offered by the coupling of the mesogenic units to the polymer backbone.*

Keywords: *The spacer length polysiloxane , liquid crystal polymers, electro – optic properties .*

I. INTRODUCTION

Side chain liquid crystal polymers are a composite from of macromolecule built up from three basic types of molecular unit. These are the polymer backbone, the mesogenic units, and the coupling chains which link the mesogenic unit to the polymer chain. A large number of side chain polymers in which the nature of these three components and their interconnection are varied have been synthesised and studied [1.2]. They are classified as main-chain LCP where mesogenic groups are part of the polymer backbone. Another approach was to link the rigid group to a polymer backbone as side chains (side-chain LCP)[3].it was necessary to give the mesogens some more freedom of movement as they were already very restricted while being part of a polymer. It is now clear that the relatively short length of coupling chains will result in some interaction between the mesogenic unit and the polymer backbone chains. A variety of nematic phases have been proposed [4.5], in which the sign of the coupling may favour a positive or parallel arrangement simply because of the nematic field, or the bias may be to a perpendicular or negative arrangement of the side group and the polymer chain due to the particular geometry of the coupling chain. Small angle neutron scattering experiments have shown that for polyacrylate and polysiloxane based side chain liquid crystal polymers both positive [6].and negative coupling [7] are possible, although the level of coupling in either case is relatively small. Studied involving cross-linked systems [8] and fibres [9] have shown that there is a regular alternation in the sign of the coupling for a particular polyacrylate and polysiloxane based systems as the length of the coupling chain is increased. This contribution focuses on the influence of this coupling between the mesogenic side-group and the polymer backbone on the resultant electro-optic properties of such materials. In particular we centre our attention on the influence of the coupling chain upon the curvature elasticity which determines the ease with which the director pattern may be modified using external electric fields .A number of contributions concerned with these properties have appeared, for example [10.11] although none has considered the systematic variation of properties with changing coupling chain length for a series of polymers. We shall considered a series of polysiloxane based side-chain liquid crystal homopolymers in which the coupling chain length is systematically varied. Electro-optic measurements are used to evaluate the threshold voltages for this series of polymers. Although the variation of threshold voltage with systematically changing coupling chain length correlates with spares variety of values for similar polysiloxane based polymers [12.13]. Comparsion is made with existing models of curvature deformation in low molar mass liquid crystal systems. Where A more modern approach is the elastic continuum theory [14] the LC is considered as a continuum and molecular details are ignored.

II. MATERAIALS

Monomers of type [1] (where n=2,3 and 6) were prepared by the method Portugal et al. [15] as shown in Scheme 1. For the preparation of the monomer with n=5, 5-chloropentanol was prepared via reduction of the appropriate acid chloride with LiAIH4 [16]. The use of this route for the preparation of the monomer with n4 results in cyclisation of the 4-chiorobutanol and hence gives poor yields for the first step. An alternative procedure to prepare the 4-(4-hydroxybutoxy) benzoic acid was used as detailed elsewhere [17]. Polymerization

of these monomers was performed in deoxygenated chlorobenzene solutions under reduced pressure at 55°C with 1 mol % AIBN as the initiator. After 24 hours, the resulting polymers were collected by precipitation into methanol and purified by repeated precipitation into diethyl ether, followed by drying under reduced pressure for 48 hours at 100 C. The molecular weight data were obtained by g.p.c. (RAPRA Ltd) at room temperature with tetrahydrofuran as the eluent. All of these polymers show nematic phases with well defined nematic-isotropic transition temperatures.

III. EXPERIMENTAL WORK

1. Cell preparation

Good alignment is necessary in polymer layers before electro – optic properties can be measured. If this is not achieved, then the freederricksz transition is observed over arrange of applied field and meaningless data results. Therefore, efforts have been spent to achieve high quality fabricated electro-optic cells [18]. The typical construction of an electro – optic cell used experimentally in these investigations is shown in Fig (1). Electro-optic cells with predefined director orientation were constructed from patterned tin oxide coated glass slides (Baltracon Z20). The cell electrodes, after cleaning in an ultrasonic bath and drying, were coated with a thin layer of a polyimide precursor consisting of a 5% solution of Rodehftal 322 in dimethyl formamide using a spin coater. These coated slides were then subjected to thermal cycles and a mechanical treatment using a cloth.

The selected polymer sample was carefully applied onto one of the treated glass electrodes and the complete assembly was heated above the clearing point of the polymer in order to allow the trapped air to escape. The second glass electrode was then mounted above the first electrode using 0.025 mm thickness Kapton sheet as spacers . The quality of the prealignment treatment was confirmed through examination of each cell with a polarizing microscope. Complete and uniform director alignment was obtained by holding the completed electro-optic cell at a temperature 1 0C below the measured clearing point for 10-24 hours. This technique was successful in inducting a uniform director alignment within the electro-optic cells prepared for all the materials used in this work. In all cases the predefined director alignment was parallel to the electrode surface and to the direction of rubbing. The orientational order parameter S for the polymers in the series with n=4,5,6 was measured as a function of temperature [19].

2. Electro-optic systems

The most important three devices were used in this work for electro – optic measurement are Mk 100, ALCT, and HCS 402 shown in Fig (2).The Mk 1000 series temperature controller offers precision, accuracy, and stability for temperature measurement and control. When coupled with heating / cooling equipment from instc, the Mk 1000 can provide temperature control, which is accurate to 0.001oC. Two operation modes, keypad operation using the front panel of the controller, or software control though pc as well as. Adjustable ramp (rate of heating / cooling) to user set temperature point. Programmable operation command set. Precisely controls temperature to 0.001oC option save temperature data to the computer. RTD thermistor or thermocouple, LC cell holders for many types of LC cells. ,and ALCT Liquid Crystal measuring subsystem, which includes ALCT- EO1 (referred as ALCT after), test cell holder, photo detector head, and connecting cables. Using this system with well prepared LC test cell and proper method, user can measure - Liquid crystal mixture physical parameters- Optical performance of LCD devices- Application software, WinLC, and Optical test bench subsystem, which includes light source, polarizer, rotatable hot – cooling stage holder analyzer, and photo detector holder. This test bench allows user to:- Arrange polarizer and analyzer perpendicular and parallel to each other.- Test cell in side of the hot-cooling stage can be rotated in full 360 o range. - Light source, polarizer and analyzer are installed in sealed dark sections to prevent the contamination of optical components. - Light sealable working chamber shields a way the room lighting. and   Hot and cold stages Instec was founded over two de eades ago by a group of pioneering liquid crystal researchers therefore ourm heating and cooling stage system are designed specifically with liquid crystal applications in mind. We used the device the Hcs402 hot and cold stage is designed to give superior performance in sample temperature control and other applications. While the Hcs402 provides excellent temperature uniformity, which is more than sufficient for most applications, there will always be a small vertical temperature gradient between the bottom heat plate and the sample. The Hcs402is equipped with cable heaters: one located underneath the sample chamber and other is part of the cover, above the sample chamber. This configuration provides. Thermally uniform "sample oven" the Hcs402 upper heating element compensates for the temperature gradient by providing and additional heat source above the sample this is a highly desirable feature when dealing with thicker sample and when spacers are used to increase the sample chamber height.

IV. RESULTS

1. Static electro-optic properties

This study is concerned with evaluating the static electro-optic properties for the range of liquid crystal polymers shown in Table 1 as a function of temperature. By using the experimental arrangement described in the previous section it was possible to determine the threshold electric field required to distort the surface prealigned director orientation .In order to achieve complete switching we typically applied 147 to 240 volts (peak to peak) at a frequency of 500 Hz. Figs.(4a , 4b, 4c, 4d, 4e).show the variation of the transmitted light intensity as a function of the applied voltage and the required voltage for each material in this work for complete switching. For all polymers the dielectric anisotropy is positive. The electric field deforms an initial planar surface alignment and in this case of the geometry is dominated by the splay component of the curvature elasticity K11 for small deformations. The threshold voltage V_{th} is related to the curvature elasticity, assuming strong anchoring by [20]:

2. $V_{th}=\pi (K11/ \varepsilon^0 .\Delta\varepsilon)^{1/2}$ ……………..…(1)

where is the anisotropy of the dielectric permittivity, Equation (1). suggests that evaluation of K11 should be a relatively straightforward procedure. However for a polymer system there are a number of particular problems involved in the evaluation of V_{th} , each of which relates to the high viscosity of the polymer. The most important of which is ensuring that before starting any measurements the sample is in a complete equilibrium state. For each of the samples considered and for each temperature of measurement we have establish the real relaxation time of the polymer system through the use of a cyclic electro-optic procedure [21] shown more clearly in Fig. (6) This type of experiment ensures that the relaxation times measured relate to response of the complete system by using a probe, the response time following the application of an electric field [14]. All threshold voltage measurements were made after the sample had been held at required temperature for a period of time at least three times the relaxation time. As the response time following the application of small voltages is particularly long we determined the threshold from a plot of the change in the transmitted optical intensity as a function of the applied small voltage. By extrapolation this method allowed both the true threshold voltage to be estimated and any dynamic effects to be excluded. To ensure that a steady state was reached following each voltage step the sample was left for a period between 3 and 5 hours. During this time the transmitted light intensity was monitored to ensured that the steady state had been achieved. Typically at each stage the sample was held for a period of time ten times longer than the response time. The threshold voltages obtained in this manner may be related to the curvature elastic constant only if it is valid to assume strong anchoring of the director at the cell wall. There is a marked reduction in the threshold voltage for both increasing temperature and spacer length. A similar trend in terms of the of temperature behavior has been observed in the study of a series of copolymers with n=6 .The increase in the threshold voltage with decreasing spacer length is shown more clearly in fig.(7) .The variation of the threshold voltage with systematically changing coupling chain length correlates with spares variety of values for similar polysiloxane based polymers reported in the literature [4,7,8].
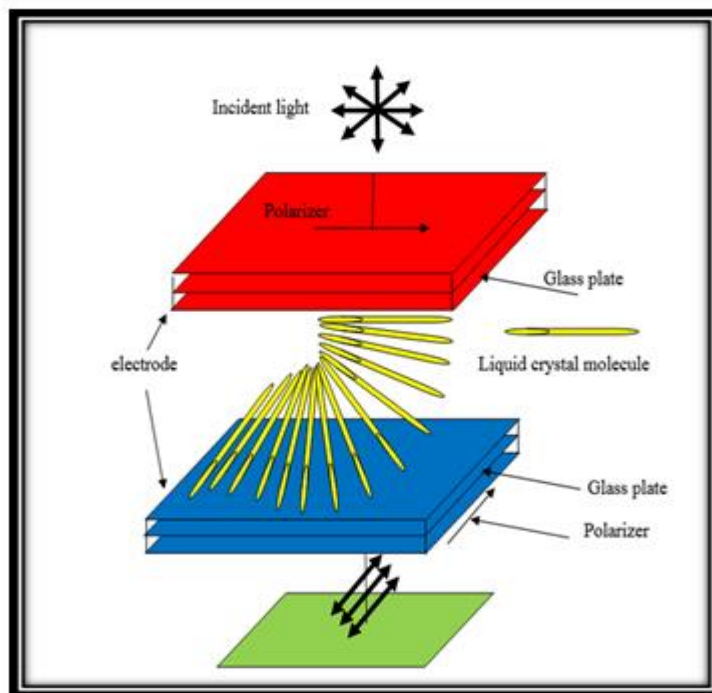

Fig. (1). Electro-optic cell.

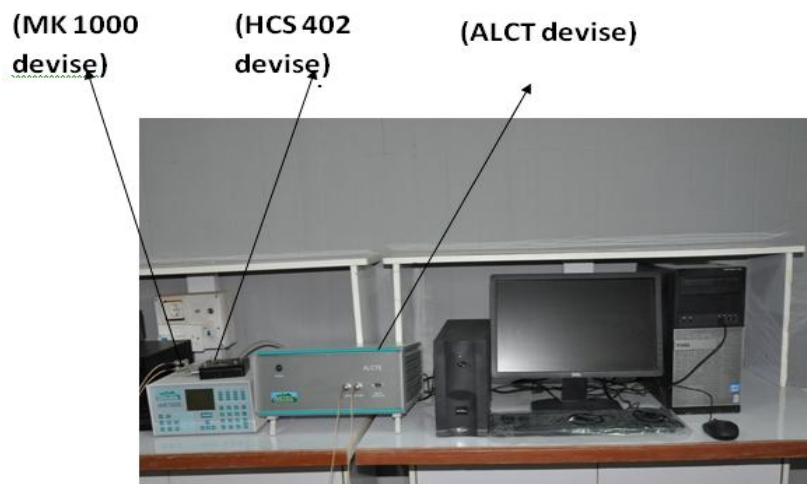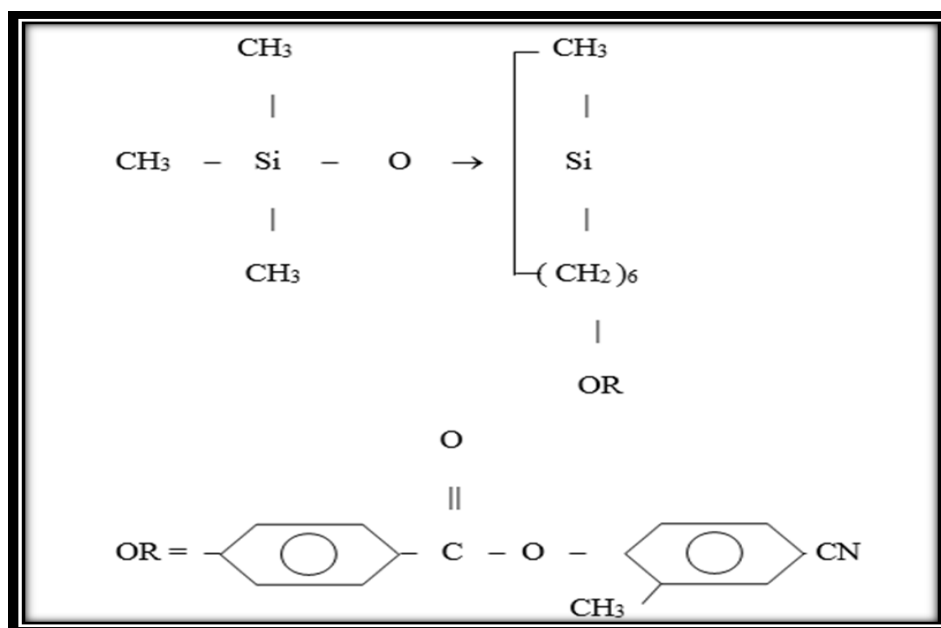(MK 1000 devise)   (HCS 402 devise)   (ALCT devise)

Fig. (2). Picture of devices.

Table . (1) Molecular weight and phase transition data determined by using D.S.C∗ in Chemistry department, university of Reading, U.K

Polymer	n	Mn	Dp	Tg^{0}c	Tni^{0}c
1	6	5.1×10^5	180	39	**135**
2	5	2.0×10^5	100	40	**130**
3	4	2×10^5	60	45	**120**
4	3	3.2×10^5	50	52	**100**
5	2	1.0×10^5	40	62	**85**

Scheme. (3) A schematic representation of the two basic geometries of coupling between the polymer backbone and the mesogenic side- chain. (a) a parallel or positive coupling, (b) a perpendicular or negative coupling.
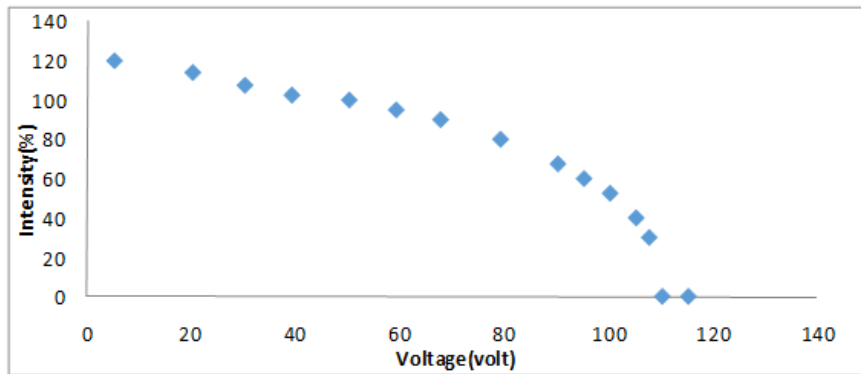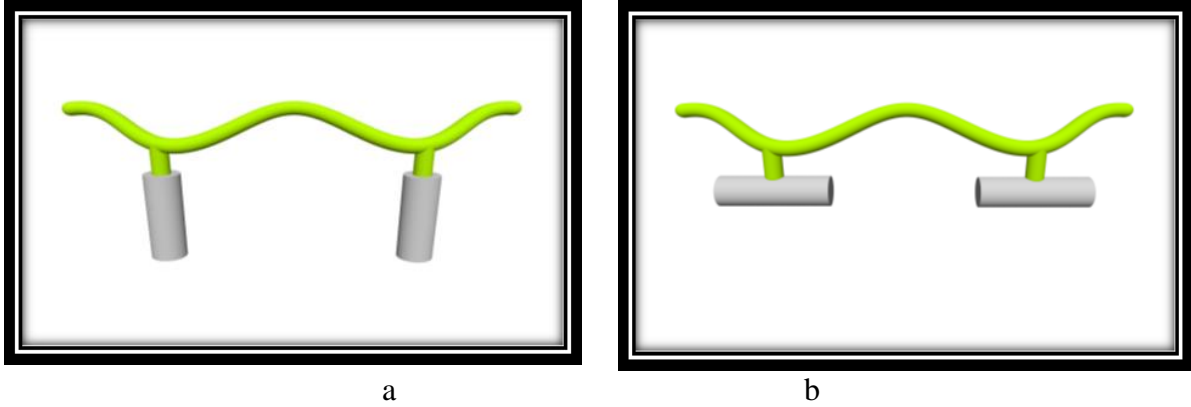
a

b

Fig. (4a)

Figs (4a,4b,4c,4d,4e) shows the variation of the transmitted light intensity as a function of the applied voltage and the required voltage for each material in this chapter for complete switching. For The Polymeres (P.2, P.3, P.4, P.5, P.6).
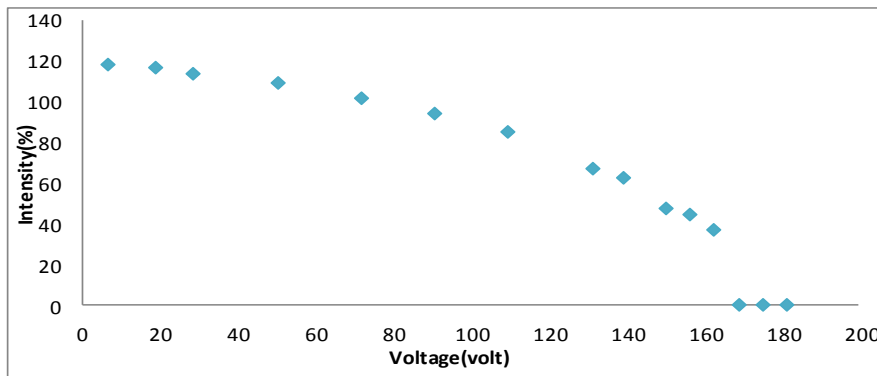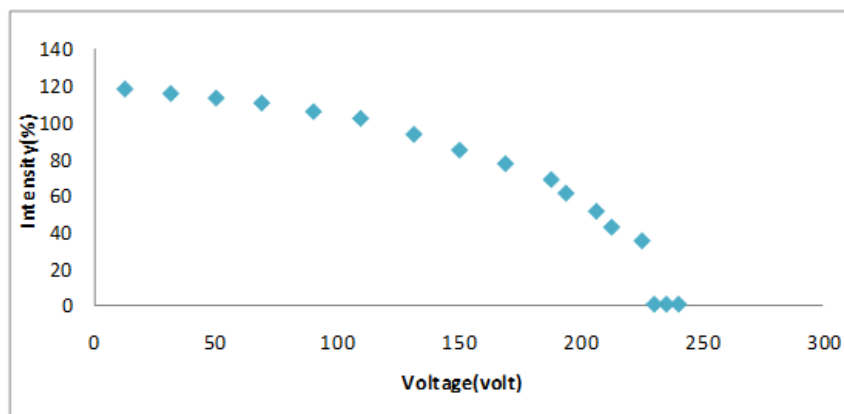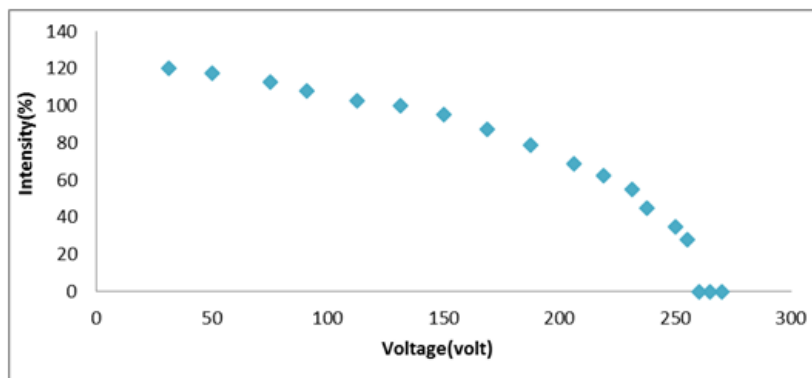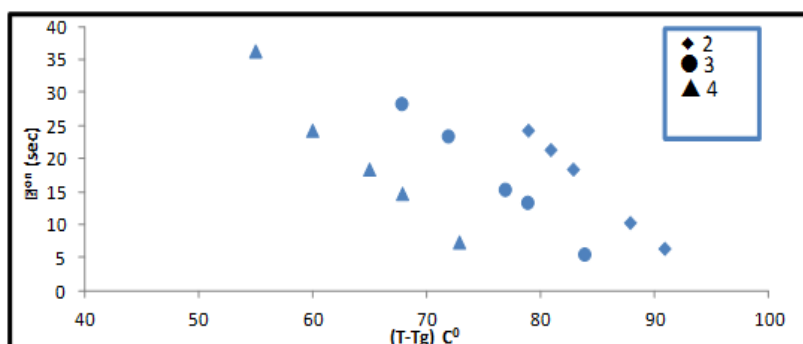

Fig (4b)

Fig (4c)

Fig (4d)

(5) shows the τ^{on} values as a function of the (T – Tg) obtained by the method involving the cyclic type.
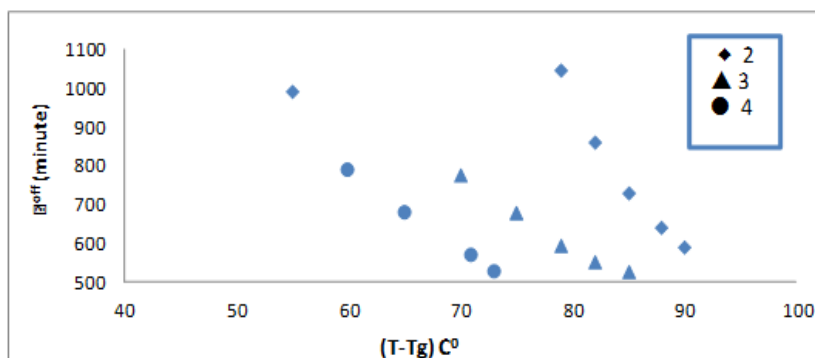

Fig (6) shows the τ^{off} values as a function of the (T – Tg) obtained by the method involving the cyclic type.
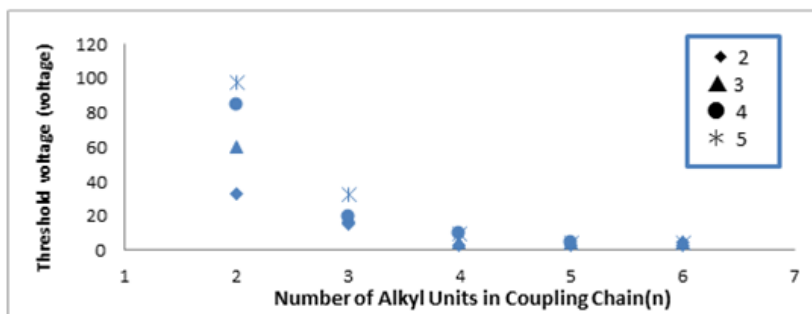

Fig **(7)** the measured threshold Voltages for the series of polymers shown in Table I, plotted against the number of alkyl units in the coupling chain.

2 Relationship between threshold voltage and the spacer length

In order to examine the role of the spacer length it is useful to eliminate the effects on the threshold voltage versus temperature curve of the differing transition temperatures. For this purpose the data shown in Fig **(7).**may be mapped onto a universal function of the form:

$$V_{th} = \frac{\alpha(T_{NI} - T) + \beta}{n^a} \qquad \text{……………..(2)}$$

where α, β and q are constants .A fit is reasonable to take the dielectric anisotropy & as constant across the of polymers with differing coupling chain length. Of course there will be a slight increase (— 15% from n6 to n2) due to the increasing number density of the mesogenic units and the fact that the remaining two components, namely the polymer backbone and the coupling chain probably make only an isotropic contribution. Such small approximation would allow us to make direct comparison between the different polymers in terms of the measured threshold voltages. If we make the correction for the change in number density of the highly polarisable groups then this will enhance the trend of increasing threshold voltage with decreasing spacer length.

3. Order parameter

Measurements were made for each sample over a range of temperatures to include both nematic phases, the resultant order parameter are displayed in Fig. (8).The variation of the polymer space length leads to distinctive trends in the order parameter versus temperature plots however; each individual curve has the same basic form.

4. Curvature elasticity

A microscopic understanding of curvature elasticity remains a considerable challenge even in the area of low molar mass liquid crystalline materials. Existing approaches in the literature are very much first order relating either to the Maier-Saupe mean field theory [22-23] or developed from the Landau-De Gennes expansion of free energy as a function of the order parameter [22,24,25].Saupe and Nebring use the Maier-Saupc approach to establish the relationship [26,23]:

$$K_u = \frac{c_{ii} S^2}{V_m^{7/3}} \qquad \text{…………………(3)}$$

where Vm is the molar volume and c_{ii} is temperature independent constant which is a function of the particular molecule or mesogenic unit. In essence this approach groups all of tie temperature dependence into S2 and Vm although the latter term varies only slightly over the temperature range considered in this study. We can think of c,1 as an intrinsic curvature elastic constant. If we take account of the dependence of b.c on S we may combine Equations (1) and (3) to give [27]:

$$V_{th}^2 = \frac{c_{ii} S}{V_m^{7/3} \Delta \varepsilon . \varepsilon \circ} \qquad \text{…………………(4)}$$

where $\Delta \varepsilon$ is an intrinsic dielectric anisotropy i.e. that for a perfectly aligned system.If the variation in the threshold voltage with coupling chain length was due to differences in the level of orientational ordering . This is clearly not the case, We may relate the slope for each set of points in Fig (7) to the intrinsic elastic constant c_{ii} Fig (9) shows a plot of these slopes against the coupling chain length n or more strictly the number of alkyl - groups in the spacer unit. The fact that there is a variation in the slope indicates that the coupling chain has a significant role in determining the curvature elastic constant. If we partition the slope into a component which is independent of n and a variable component, it is clear that the n independent term is small in comparison to the variable component. The strong variation in slope would appear to indicate that there is significant and changing coupling between the mesogenic side groups and the polymer backbone.

V. DISCUSSION

The variation of the coupling chain length in this series of siloxane based side chain liquid crystal polymers has impact upon both the phase behavior and upon the electro-optic properties. The increase in the nematic-isotropic transition temperature with increasing spacer length mirrors similar behavior found in homologous series of low molar mass liquid crystalline materials [28].In these cases the increase is attributed, at least in a first approach, to the increasing degree of anisotropy of the mesogenic unit. Of course this is also true of side-chain liquid crystal polymers, but for such materials there is the added complications arising from the constraints and interactions provided by the polymer chain. It would be reasonable to assume that as the coupling chain shortened, so the coupling between the mesogenic unit and the polymer chain would increase. If ordering increases as a result of this coupling, it is natural to expect the transitions to rise. In practice as shown in (Table 1).the opposite is observed. This suggests that the emphasis on the role of the polymer chain should be one of constraint than enhanced ordering through coupling. Clearly there is a subtle balance between these possibilities and small variation can lead to marked effects. as shown in Fig. (5) there is a strong temperature dependence of the switching times. In terms of the variation of the nematic-isotropic, variation transition temperature with spacer length, this appears to have some element of the well-known odd-even effect observed

in low molar mass liquid crystalline materials and in main –chain liquid crystal polymers [29]. The increase in the glass transition temperature with decreasing spacer length follows expectations based on the restricted motions of the polymer backbone segments. Clear trends are observed in the threshold voltage variation as a function of both temperature and spacer length. It is emphasized that considerable care and effort has been taken to exclude from these experiments the time dependent effects of the high viscosities associated with polymeric liquid crystal systems. In part the increase of the threshold voltage with decreasing temperature is expected on the basis of an increasing order parameter. The origin of the variation of the threshold voltage with spacer length is not so clear. It seems reasonable to attribute the increase of the intrinsic elastic constant to reducmg the spacer length to changing levels of interactions between the mesogenic units and the polymer backbone. In addition to the systematic variation in the coupling chain there is also some variation in the degree of polymerisation of this polymer series (Table 1). This could be thought to have some influence on the electro-optic properties, although there appears to be no pattern in the threshold voltages which matches the rather random fluctuation of the molecular weight data shown in Table I. We have previously reported some threshold voltage measurements for a series of methylmcthacrylatce based side-chain liquid crystal polymers with differing molecular weights [30]. There was a distinct variation in the threshold voltage hut this was only really significant for materials with a degree of polymerisation of less than 50. For the CBZ6 polymer a variation of the degree of polymerisation from 50 to 300 resulted in an increase of the threshold voltage of only < 10% [23]. We can safely conclude therefore that the trends seen in the data reported here are truly a reflection of the role of the length of the spacer chain.

VI. CONCLUSION

A conclusion section must be included and should indicate clearly the advantages, limitations, and possible applications of the paper. Although a conclusion may review the main points of the paper, do not replicate the abstract as the conclusion. A conclusion might elaborate on the importance of the work or suggest applications and extensions.

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