

## Electro-optic Properties of Siloxane Based Liquid Crystal Polymers

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### Abstract

A series of siloxane based side chain liquid crystal polymers have been prepared with a systematic variation in spacer length. All the polymer exhibited a smectic phase, for which the smectic-isotropic transition temperature increased as the spacer length increased. Infrared dichroism and x-ray scattering procedures have been utilized to determine the orientational order parameters for this series of polymers and these are related to the measured electrooptical properties. It is found that with increasing spacer length ( $n$ ) of polymer the threshold voltage is lowered with a functional form of  $n^{-2}$  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 origin of the effects observed which appear to arise from the constraints offered by the coupling of the mesogenic units to the polymer backbone.

### الخلاصة

تم تحضير سلسلة من البوليمرات السايكلوكسانية تختلف عن بعضها البعض بتغير طول الفاصل ، كافة هذه البوليمرات أظهرت الطور السمكتي و أن درجة حرارة الطور السمكتي إلى الايزوتروبي تزداد مع زيادة طول الفاصل. تم استخدام طريقة التلون لاشعة تحت الحمراء و تشتت الأشعة السينية لأيجاد عامل الاتجاهية للبوليمرات وتم توضيح علاقتها بالخصائص الكهرو بصرية المقاسة . وجد انه بزيادة طول الفاصل ( $n$ ) للبوليمر يؤدي الى خفض فولتية العتبة و بدلالة  $(n^{-2})$  و ان التغير الحاصل بفولتية العتبة يؤدي إلى التغير الحاصل في معامل المطاطية و كذلك اختلاف عامل الاتجاهية. تم استخدام موديل ليوضح أصل هذه الظواهر و التي تنشأ بسبب قوة الربط بين المجموعة النهائية للبوليمر إلى عموده الفقري بواسطة الفاصل.

## 1-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]. Fundamental to understanding such materials is a quantitative knowledge of the interactions between those three normally incompatible components for which the inherent connectivity of the polymer system inhibits large scale segregation. 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 [3,4], 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 [5] and negative coupling [6] are possible, although the level of coupling in either case is relatively small. Studied involving cross-linked systems [7] and fibres [8] 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 [9,11] 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. The state of orientational in these homopolymers is obtained through the use of infra-red spectroscopy and x-ray scattering techniques. Carefully programmed electro-optic measurements are used to evaluate the threshold voltages for this series of polymers. Comparison is made with existing models of curvature deformation in low molar mass liquid crystal systems.

## 2-Material

Scheme 1 shows the material used in this study. Monomers with ( $n=2,3$  and  $6$ ) were prepared by the method of Potugal et. Al. [12]. For the preparation of the monomer with  $n=5$  and  $n=4$  were detaled elsewhere [13] and [14] respectively. 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 smectic phases with well defined smectic-isotropic transition temperatures. The collected polymer characteristics are shown in table 1. This table also shows the variation of the sign of the coupling between the mesogenic units and the polymer chain in which +ve represents alignment parallel to the polymer backbone and -ve a perpendicular arrangement. These data have been taken from previous work on copolymers [7,8]. It is not expected that the small variation in composition between these materials and the homopolymers of this study will effect the overall nature of the coupling in the polymers. The variation in sign of the coupling appears to be essentially the well-known odd-even effect displayed in many of the properties of both low molar mass [15] and polymeric liquid crystalline materials [16]. This would also appear to be the case with the values of  $T_{SI}$  listed in Table 1.

### 3-Experimental

An electro-optic experiment involves the measurement of changes in the optical properties of thin film of liquid crystal polymer induced through the application of an electric field. The experimental arrangement used for these electro-optic cell (described below ) was held inside a temperature controlled stage providing a uniform temperature environment within fluctuations of  $0.25^{\circ}\text{C}$ . The optical system consisted of a 5mW helium-neon laser with

crossed polarizer and analyzer configuration and a photodiode with amplifier for light intensity measurements. Electric fields were provided by means of a power amplifier (HP 6827A) driven by a function generator (Thandar TG501), an arrangement which could provide waveforms in the frequency rang 0.05 to 30 KHz with peak to peak voltages in the range 0 to 240 volts. In this study a fixed frequency of 500 Hz was used throughout. The intensity of transmitted light through this optical system was recorded as a function of time using a microcomputer system based around an IBM compatible PC. Through the use of a specially written software system,EOCS, sophisticated electro-optical experiments could be performed on a continuous or cyclic basis, involving temperature control, data recording, field switching and analysis [17]. 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 dimethylformamide 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  $1^{\circ}\text{C}$  below the measured clearing point for 10-24 hours. This technique was successful in inducing 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 using infra-red dichroism employing a Perkin-Elmer 580B spectrometer fitted with a wire grid polarizer and heating stage [18]. The order parameter measurements were made at a variety of temperatures using monodomain samples prepared as prealigned cells similar to those used for the electro-optic measurements but using crystals of potassium bromide as the cell windows [18]. For each measurement care was taken that the prealigned cell had sufficient time to reach equilibrium and successive measurements over a time period were taken to ensure this was the case. The orientational order parameter for the polymer CBZ3 was measured using x-ray scattering techniques [19,20]. The measurements were made using monodomain samples prepared by holding in a magnetic field (0.6T) at a variety of temperatures. The x-ray scattering measurements were made at room temperature on quenched glassy samples using a computer controlled 3- circle diffractometer [19]. It was not possible to

prepare monodomain samples of polymer CBZ2 using either the prealignment on potassium bromide discs or by means of the available magnetic fields. As an alternative approach an estimate of the order parameter as a function of temperature was made by utilizing data obtained from a similar cross-linked liquid crystal system based on a copolymer with  $n=2$  and  $4$  mol% hydroxyethylacrylate [7]. For this liquid crystal elastomer, monodomain samples can be prepared using a stress field, and the orientation measurements were made using x-ray scattering techniques [19].

## 4-Results

### 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. 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  $K_{11}$  for small deformations. The threshold voltage  $U_{th}$  is related to the curvature elasticity, assuming strong anchoring by [21]

$$U_{th} = \sqrt{\frac{K_{11}}{\epsilon_0 \Delta \epsilon}}$$

1

Where  $\Delta \epsilon$  is the anisotropy of the dielectric permittivity, Equation (1) suggests that evaluation of  $K_{11}$  should be a relatively straightforward procedure. However for a polymer system there are a number of particular problems involved in the evaluation of  $U_{th}$ , 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 [17,18]. 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 [17]. 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 ensure 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. The nature of the anchorage may be assessed by measuring the threshold voltage for a series of equivalent cells with differing cell thicknesses. A plot of the reciprocal of the threshold electric field  $E_{th}$  against the cell thickness should be linear and pass through the origin only if the surface anchorage is strong and hence Equation 1 applies. Figure 2 shows the results of such an investigation, this is the case for CBZ6, and it is clear that the conditions for strong anchorage have been met.

Figure 3 shows the experimentally determined threshold voltages for the series of polymers described in Table 1 measured as a function of temperature. It was not possible to make reliable measurements at temperature lower than those reported in the figure. 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  $n=6$  [18]. The increase in the threshold voltage with decreasing spacer length is shown more clearly in figure 4.

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 [8,22-24].

## 5-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 figure 4 may be mapped onto a universal function of the form:

$$U_{th} = \frac{\alpha(T_{NI} - T) + \beta}{n^4}$$

2

Where  $\alpha, \beta$  and  $q$  are constants. A fit to the experimental data gives  $\alpha=12$ ,  $\beta=103$  and  $q=2$ , in which the correlation coefficients obtained are ; 0.97 ( $n=6,5,4$ ), 0.96 ( $n=3$ ) and 0.9 ( $n=2$ ). In terms of the applicability of this to interpretation of the curvature elastic constants, it is reasonable to take the dielectric anisotropy  $\Delta\epsilon$  as constant across the series of polymers with differing coupling chain length. Of course there will be a slight increase (15% from  $n=6$  to  $n=2$ ) 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 a small approximation would allow us to make direct comparison between the different polymers in term 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.

## 6-Order Parameter

Figure 5 shows the measured order parameter for the range of polymers shown in Table 1 . The reader is reminded that the data shown for CBZ2 was in fact obtained for a cross-linked version of the same basic polymer. Each of the curves shows the expected form for  $S$  versus temperature typical of a liquid crystal system. The values obtained for CBZ6 are broadly similar to those in the literature [25] although some care is necessary in making direct comparisons since the molecular weight of the polymers may be different. Orientational order parameters for the other polymers have not been reported previously.

## 7-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 [26-28] or developed from the Landau-De Gennes expansion of free energy as a function of the order parameter [26;29,30]. Each of these routes leads to a similar conclusion since in both cases higher order orientational parameters than  $S$  or indeed higher dependency on  $S$  than  $S^2$  are neglected. Saupe and Nehring use the Maier Saupe approach to establish the relationship [27,28]:

$$K_{ii} = \frac{C_{ii} S^2}{V_m^{7/3}} \quad 3$$

Where  $V_m$  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 the tie temperature dependence into  $S^2$  and  $V_m$  although the latter term varies only slightly over the temperature range considered in this study. We can think of  $C_{ii}$  as an intrinsic curvature elastic constant. If we take account of the dependence of  $\Delta\epsilon$  on  $S$ . We may combine equations (1) and (3) to give [18]:

$$U_{th}^2 = \frac{C_{ii} S}{V_m^{7/3} \Delta\epsilon^0 \epsilon_a} \quad 4$$

Where  $\Delta\epsilon$  is an intrinsic dielectric anisotropy i.e, that for a perfectly aligned system. The purpose of this restructuring is to allow the temperature / order parameter variations on

$K_{11}$  to be considered a independently of the effect of those variables on the dielectric properties. Figure 6 shows a plot of  $U_{th}^2$  against the measured orientational order parameter  $S$  for each of the polymers considered in this study. From the experimental data there is a clear trend between the  $U_{th}^2$  and the order parameter, but any reasonable fit to the data allowing the curve to pass through  $U^2=S=0$ , would require a non-linear relationship at variance with the general prediction described above in Equation 4. The divergence between Equation 4 and the experimental data increases as the spacer length decreases for example in Figure 6b for the polymer CBZ2. The approximation involved in the model of Saupe and Nehring (Equation 3) is most easily demonstrated through the approach based on the Landau-De Gennes expansion. For the relationship  $K \propto S^2$  it is necessary to discard all terms other than the first and it is clear from many studies that the higher order terms are essential for a complete description of the behavior of a liquid crystal phase [30]. Such a simplification may only be appropriate for consideration in the isotropic phase as originally proposed by De Gennes [29].

If the variation in the threshold voltage with coupling chain length was due to differences in the level of orientational ordering then each set of data shown in Figure 6 would superimpose. This is clearly not the case. We may relate the slope for each set of points in Figure 4 to the intrinsic elastic constant  $C_{ii}$  Figure 7 shows a plot of these slopes against the coupling chain length  $n$  or more strictly the number of alkyl groups in the spacer units.

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. 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. The monotonic variation suggests that the sign of such coupling (Table 1) is not an important factor in relationship to the electro-optic response. The curvature for the plots in Figure 6 is similar to those observed for previous studies of other polysiloxane and polymethacrylate based polymers [18,31] and indicates that the non-linearity of the data in terms of  $S$  is a more general feature of both side-chain liquid crystal polymers and some low molar mass system [32,33].

## 8-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 smectic-isotropic transition temperature with increasing spacer length mirrors similar behavior found in homologous series of low molar mass liquid crystalline materials [15]. 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. In terms of the variation of the smectic-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 [15] and in main –chain liquid crystal polymers [16]. 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. If we make any correction for the slight increase in the dielectric anisotropy with



decreasing spacer length, then this will simply enhance the rapidly increasing threshold voltage at low values of  $n$ . Figure 6 shows that this rapidly rising threshold voltage with changing coupling chain length arises in part from factors beyond those related to the varying order parameter. In the spirit of the approach of Nehring and Saupe [27,28] we may relate this to some increase in the intrinsic curvature elasticity of the system. Of course this type of model only fits the data in the most general way and it is inappropriate to attempt to extract quantitative information from this approach. It seems reasonable to attribute the increase of the intrinsic elastic constant to reducing the spacer length to changing levels of interactions between the mesogenic units and the polymer backbone. In Figure 7 we have plotted the slope of  $U_{th}^2$  versus  $S$  against the coupling chain length. This slope is related to the intrinsic elastic curvature elasticity  $C_{ii}$ . We have also plotted this factor corrected for the change in the number density of the highly anisotropic polarisable groups which provide the major contribution to the dielectric anisotropy. The general trend is the same and the modification is small. In addition to the systematic variation in the coupling chain there is also some variation in the degree of polymerization 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 data shown in Table 1. We have previously reported some threshold voltage measurements for a series

of polysiloxane based side chain liquid crystal polymers with differing molecular weights  $s$  [31]. There was a distinct variation in the threshold voltage but 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 polymerization from 50 to 300 resulted in an increase of the threshold voltage of only less than 10% [17]. 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.

A microscopic model of curvature elasticity must take account of the additional constraints imposed by the coupling chain and the polymer backbone. A curvature to the director must involve the angular deviation of one volume element with respect to another as shown in Figure 8 within the format of a side-chain liquid crystal polymer. Any variation in the alignment of unit  $A$  must involve not only work against the smectic field, but also changes to the conformation of the coupling chain and/or the polymer backbone. The fact that the variation of the intrinsic curvature elasticity is very directly dependent upon the length of the coupling chain suggests that the length of the polymer backbone between the units  $A$  and  $B$  is not important. This probably arises from the fact that for small distortions the polymer chain is not required to move. Essentially the side-groups are tethered to fixed points. This view is supported by electro-optic measurements made on a series of random copolymers with  $n=2$  [8]. At a suitable copolymer composition the positive coupling for the side-groups with  $n=2$

cancels the negative coupling of the side – chains with  $n=3$  [8]. Although there is no preferential coupling between the mesogenic side-chains and the polymer backbone, there is no particular reduction in the threshold voltage [34]. This suggests that it is the constraints of attachment to the polymer chain which is important rather than the geometry of the coupling. This is in accord with the observation made in this work that the sign of the coupling does not appear to be significant in determining the electro-optic response.

If we cause a small distortion  $\Delta\beta$  to the angular alignment between units of the polymer then this will require some modification to the conformation of the coupling chain. This modification must be distributed over the length of the coupling chain. For small distortions ( $\Delta\gamma$ ). The variation in energy with skeletal bond rotation angle in the coupling chain is of the form  $(\Delta\gamma)^P$  where  $P$  is typically in the range 3 to 4. The latter assessment was made through the use of molecular modeling techniques using standard semi-empirical potentials on a representative portion of the CBZ6 polymer [35]. Such calculations did not include intermolecular terms. If the distortion  $\Delta\beta$  transforms to a skeletal bond rotation  $\Delta\gamma$  then for a minimum energy increase this will be distributed over the  $m$  bonds for which bond rotation is possible at these temperatures. This gives an energy contribution of the form:

$$\Delta E = m \left[ \frac{\Delta\gamma}{m} \right]$$

5

From Equation 5 we can see that the intrinsic curvature elasticity coefficient should scale as  $0000$  with  $P$  typically 4. In addition there will be the essential contribution arising from the smectic field which for the range of polymers considered here, should be largely constant. We could take as this constant term the behavior of the polymer CBZ6 since this approaches that observed for the equivalent non-polymeric liquid crystal systems [21]. The experimental data shown in Figure 7 suggests for the variable term a relationship of the form  $n^{-q}$  where  $q$  is in the range of 4.4 to 4.9 dependent upon the weighting given to the data for the polymer CBZ2. This compares to the exponent found in the model of  $= 3$ . The differences between the experimental result and the model are not surprising given the simplicity of the approach. Clearly the model does not take account of the constraints offered by the neighbouring tethered mesogenic units and the fact that any distortions of the coupling chain may be localized rather than distributed over the complete chain. However the basic thrust, that the coupling to the polymer chain acts as an additional constraints which add to the elasticity appears to be correct.

## 9- Summary

This study has focused on the properties of a series of siloxane based liquid crystal polymers with identical mesogenic units but with differing lengths of the coupling chain. Distinct and significant trends are observed in both the phase transition behavior and in the static electro-optic properties. These trends support the concept that an increasing spacer chain length decouples to a certain extent the motions of the mesogenic side-groups from those of the polymer backbone. The variations in the threshold voltage with changing spacer length arise from factors over and above the minor variations observed in the orientational order. These additional factors are related to the constraints on the alignment of the mesogenic units arising from the relatively close coupling to the polymer chain.

## 10-References

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## 11-Figure Captions

1. 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.
2. A plot of the reciprocal of the threshold electric field against cell thickness for a series of surface aligned electro-optic cells prepared using the polymer CBZ6. The measurements were made at  $T-I_{SI}=10^{\circ}\text{C}$  with a 500Hz waveform. The line represents a least squares fit to data.
3. The measured threshold voltages for the series of polymers examined (CBZ6-00, Cbz5 - 00, CBZ4-00, CBZ3-00, CBZ2-00) plotted as a function of the temperature. Note the threshold data are plotted on a logarithmic scale.
4. The measured threshold voltages for the series of polymers shown in Table 1, plotted against the number of alkyl units in the coupling chain. The experiments were performed at the temperature shifts below the  $T_{SI}$  for each polymer.
5. The orientational order parameter  $S$  plotted against the measurement temperature for the series of polymers CBZ6-00, CBZ5-00, CBZ5-00, CBZ4-00, CBZ3-00, CBZ2-00.
6. The square of the measured threshold voltage plotted against the measured orientational order parameter  $S$  at the same temperature for the series of polymers (a) CBZ6-00,CBZ5-00,CBZ4-00, CBZ3-00, and (b) CBZ2-00.
7. The slope of the curves shown in Figure 6 plotted against the number of the alkyl units in the coupling chain. The slopes are proportional to the intrinsic curvature elasticity in the approach of Nehring and Saupe [27,28] shown in Equation (4). 00 represent the slopes taken from Figure 6. 00 represent the slope corrected for the varying number density of mesogenic units and scaled to the point for CBZ6, as discussed in the text.
8. A Schematic showing the components of the model described in the text.

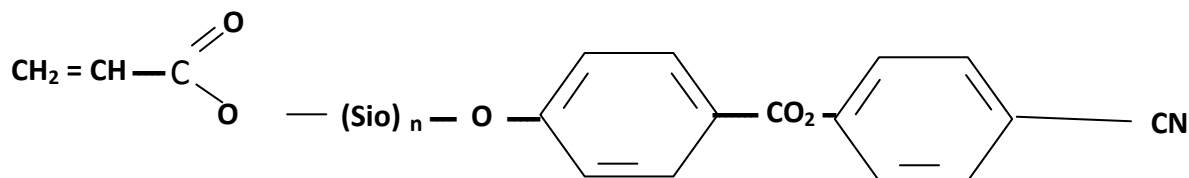
**Table 1**  
**Polymer Characteristics**

| Polymer | n | $M_a^a$           | $D_p^a$ | $T_g^b$<br>°C | $T_{SI}^b$<br>°C | Sing of<br>Coupling |
|---------|---|-------------------|---------|---------------|------------------|---------------------|
| CBZ6    | 6 | $4.7 \times 10^5$ | 160     | 44            | 138              | +                   |
| CBZ5    | 5 | $3.1 \times 10^5$ | 250     | 50            | 124              | -                   |
| CBZ4    | 4 | $4.4 \times 10^5$ | 260     | 53            | 116              | +                   |
| CBZ3    | 3 | $4 \times 10^4$   | 100     | 60            | 111              | -                   |
| CBZ2    | 2 | $4.5 \times 10^4$ | 130     | 68            | 109              | +                   |

<sup>a</sup>Obtained from g.p.c. measurements

<sup>b</sup>obtained using a Perkin Elmer DSC-2 with a scan-speed of  $10^\circ \text{Cmin}^{-1}$

<sup>c</sup>The sign of coupling indicates the preferential alignment of mesogenic units parallel ( + ve ) or perpendicular ( -ve ) with respect to the polymer chain as show figer 1 . Data taken from reference ( 7,8 ) .



**Scheme 1**

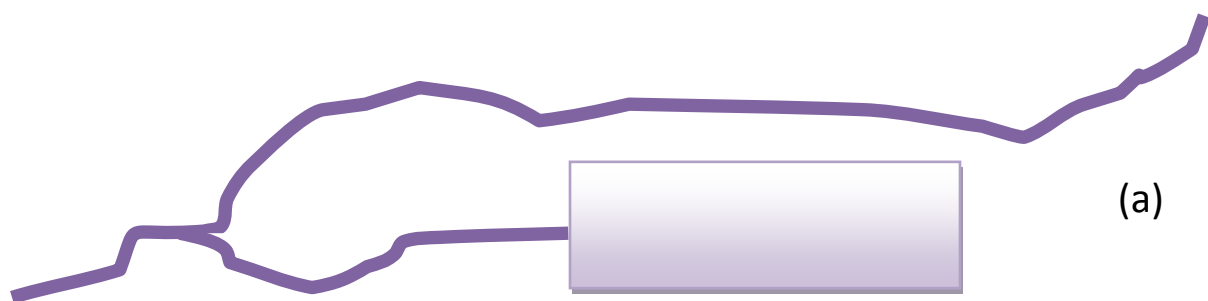
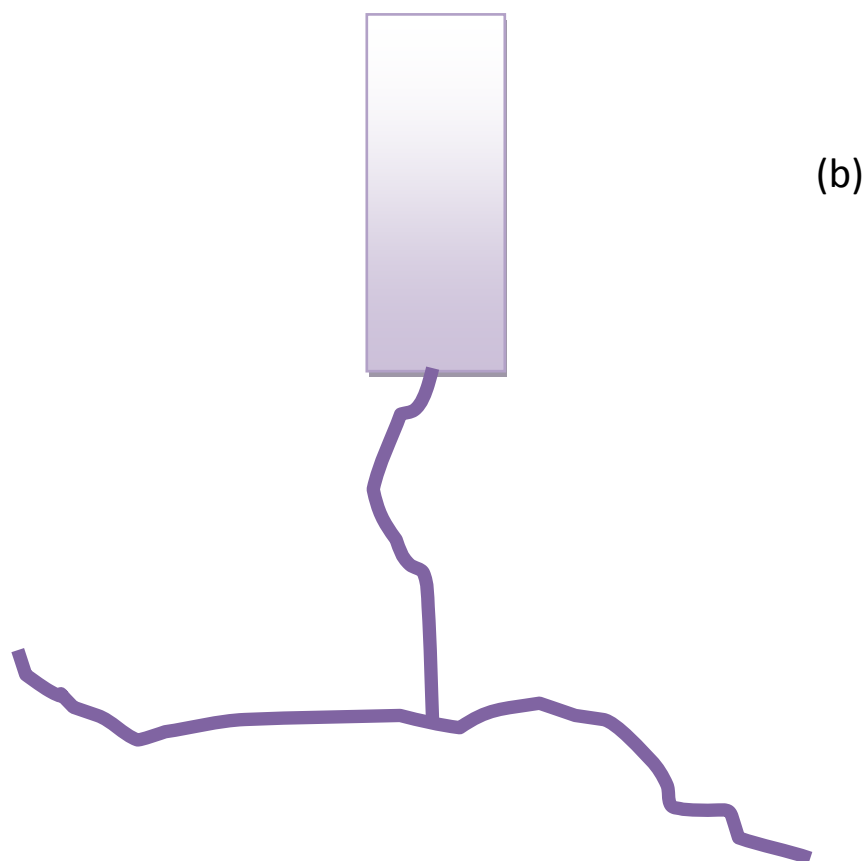


Fig -1 -



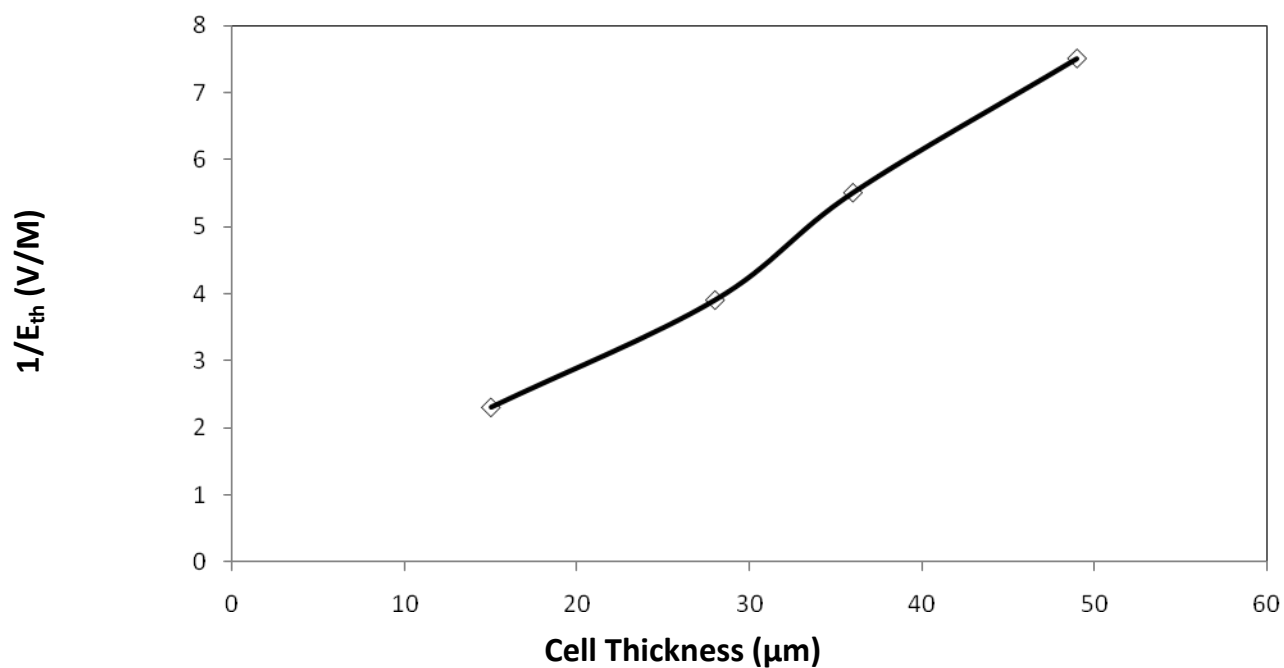


Fig.2

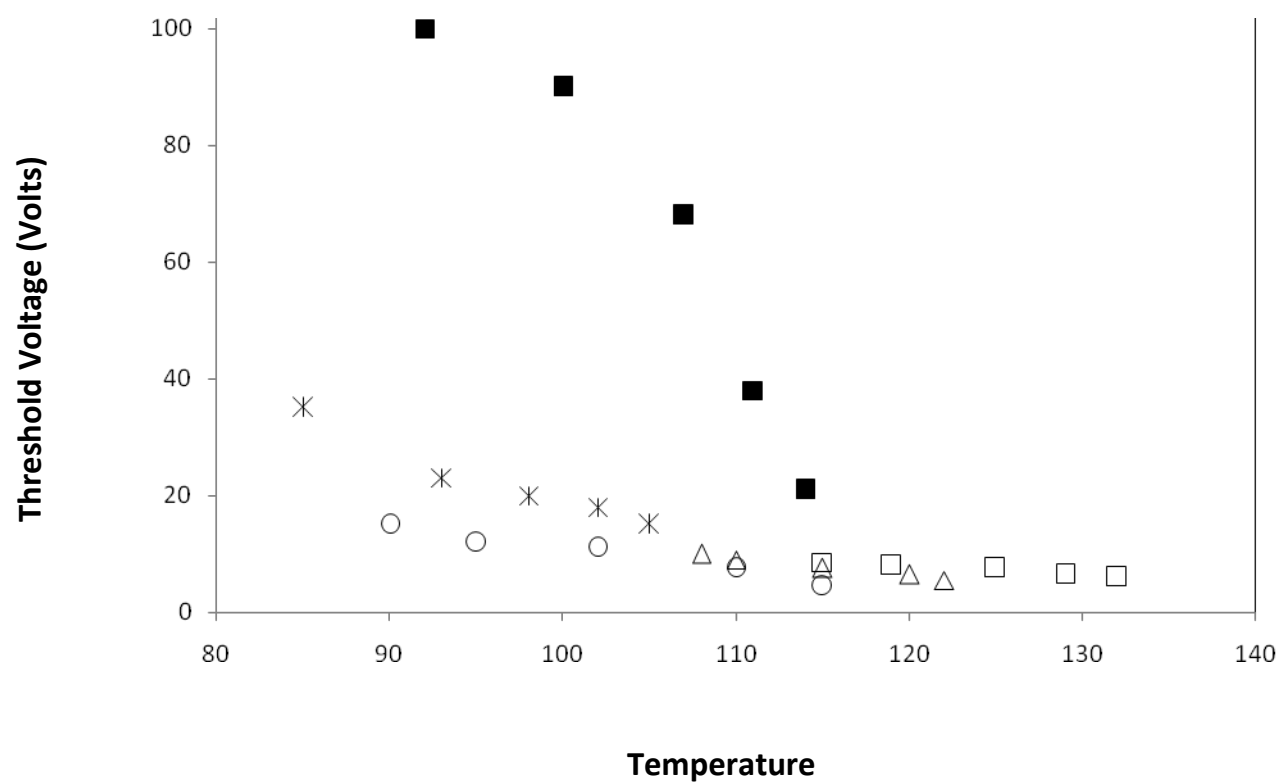


Fig.3



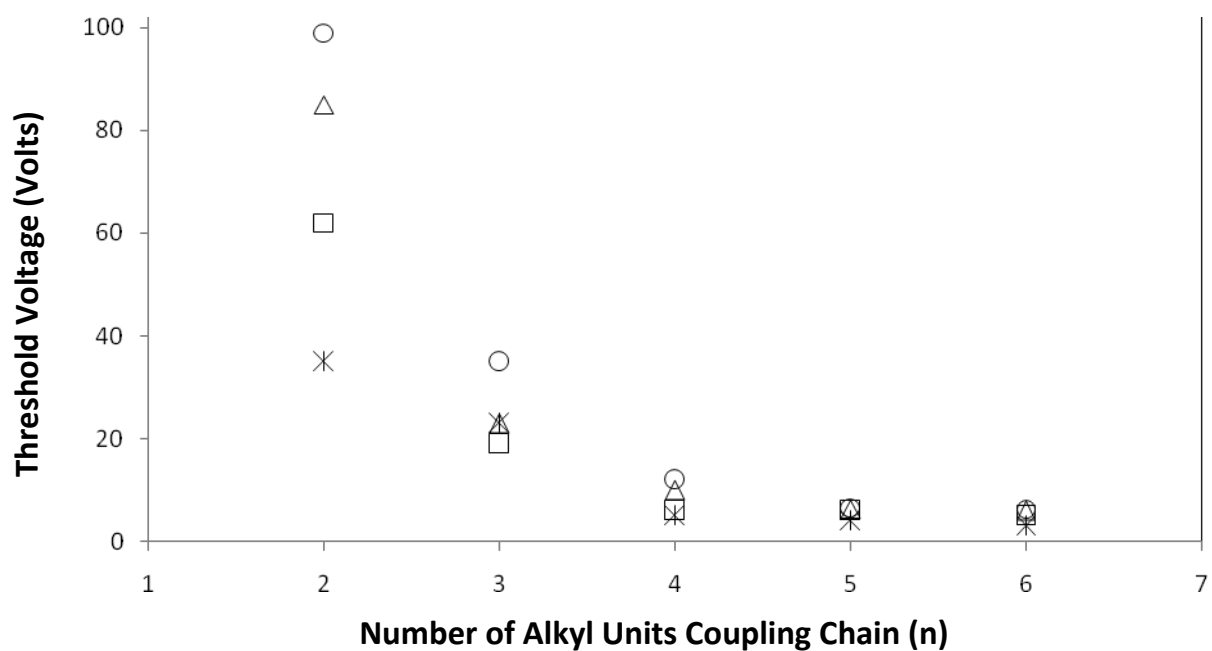


Fig. 4

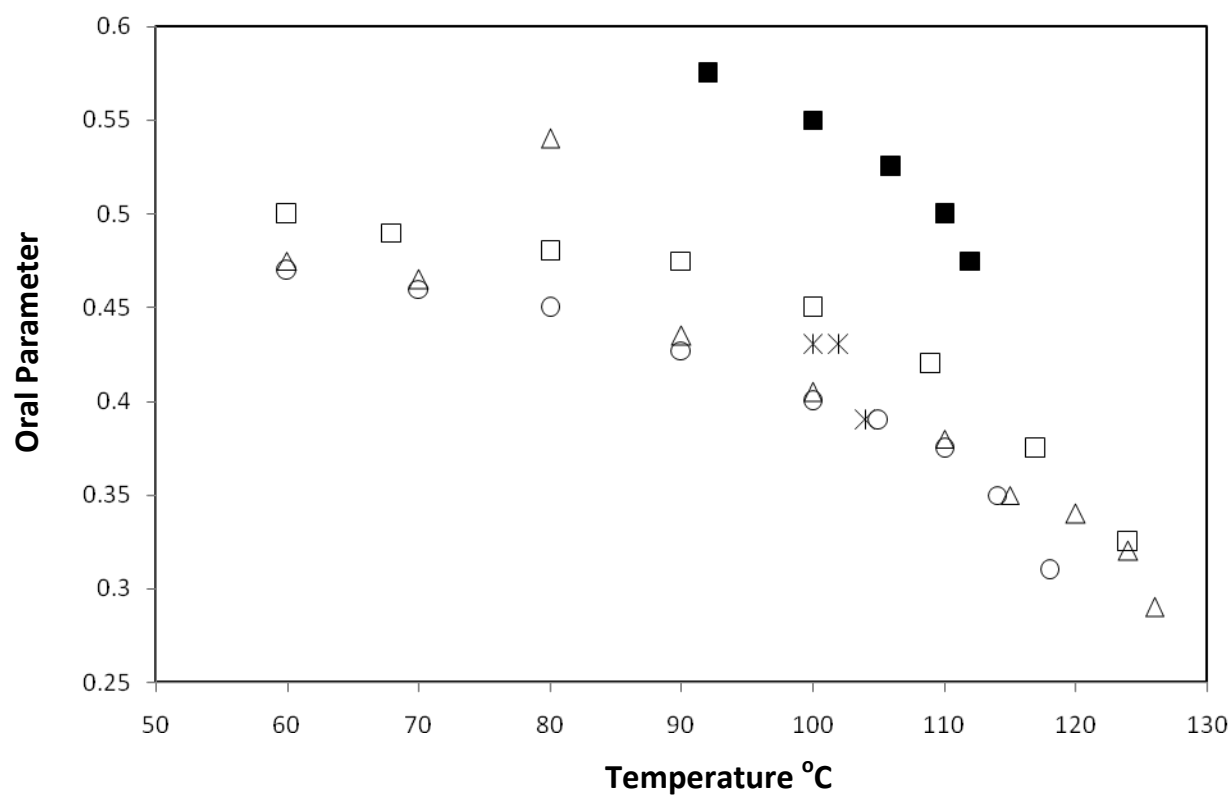


Fig.5

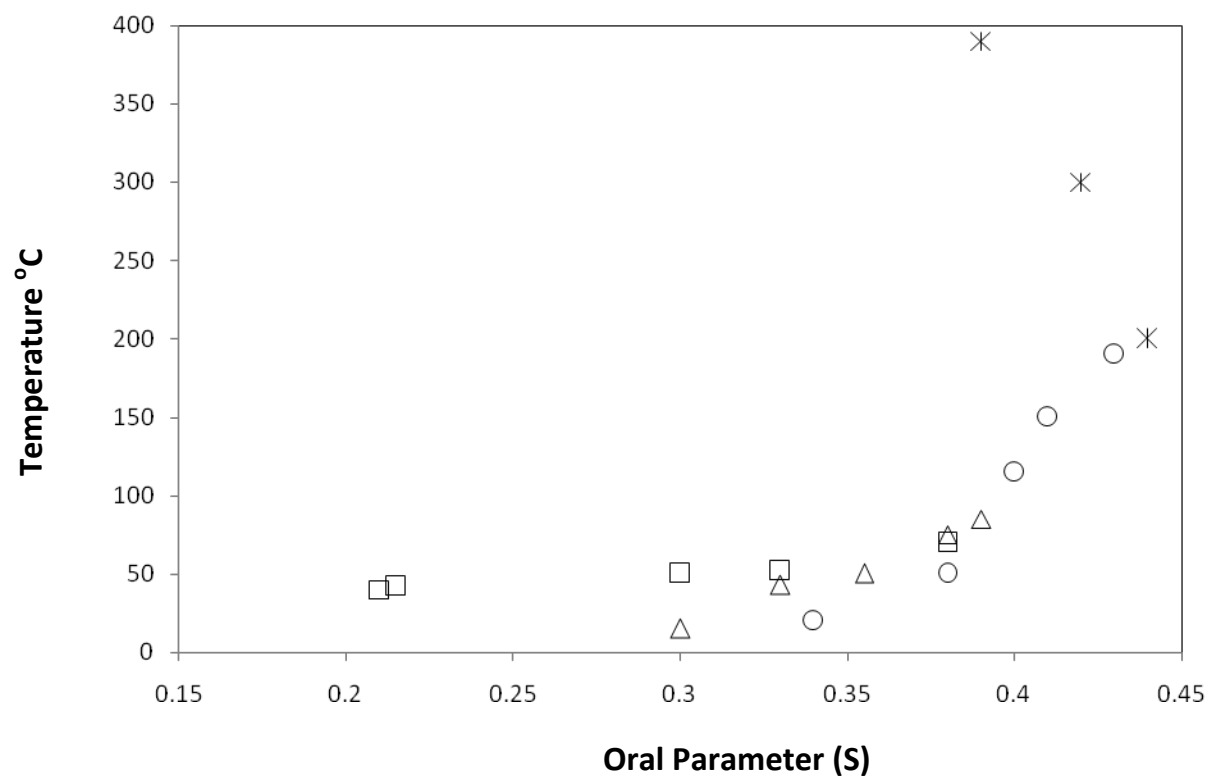


Fig.6a

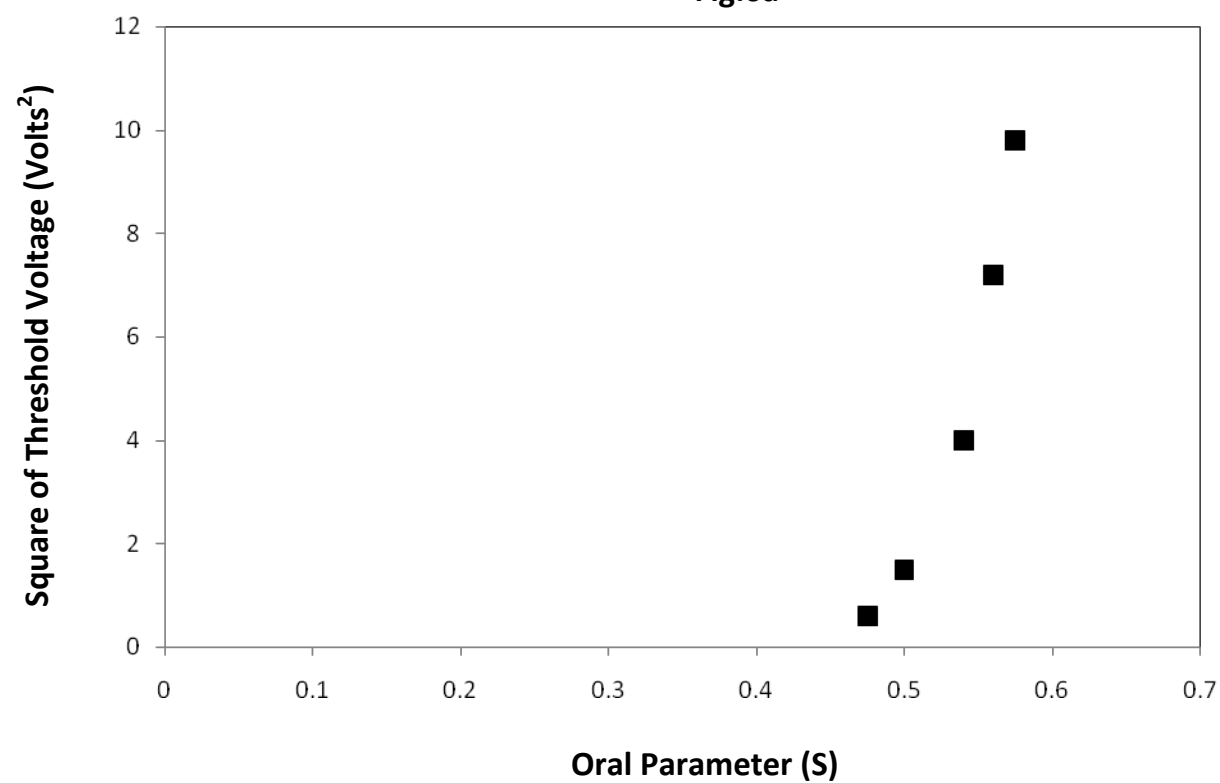
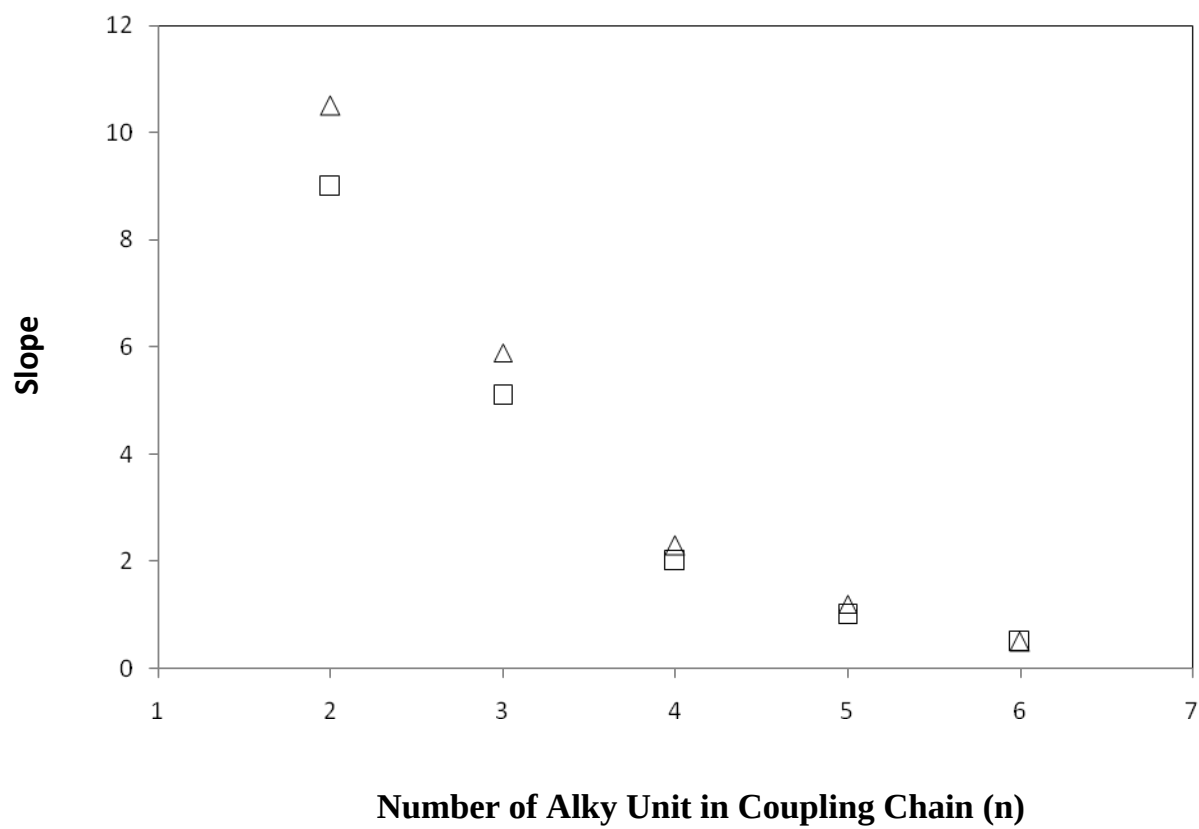
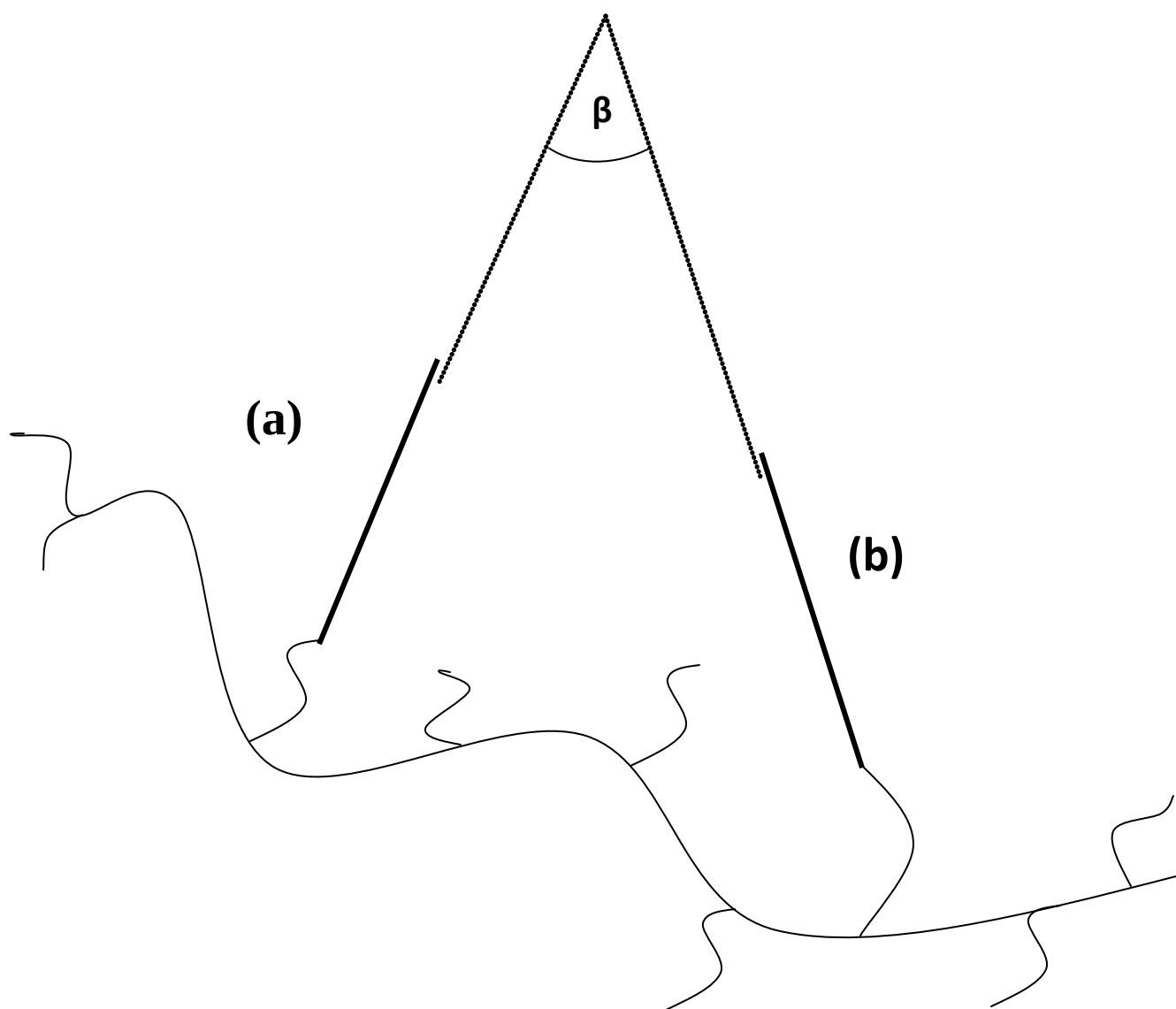


Fig.6b



**Fig.7**



**Fig.8**