

The Influence of Non – Polar Group on the Properties of Poly-Siloxanes Side Chain Liquid Crystal Polymers

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Abstract

The purpose of this work is to know the effect of adding non-Polar group to a group of polymers based on the poly-siloxane backbone. It is found that adding the non-polar group would reduce the contribution of the dipole moment of the cyano - group parallel to the molecular long axis of the mesogenic unit and lead to a suppression of dielectric anisotropic ($\Delta\epsilon$) for the system. The five samples different molecular weight and equal flexible spacer have been prepared. The intensity coming out of the polarizer be high $E=0$ but when apply a little of the electric field reduced intensity. The complete switching voltage increases with increasing molecular weight. The increase in temperature leads to decrease in response times (τ^{on} , τ^{off}) which is due to the decrease in the viscosity of the polymer. The increases order parameter whenever decreases molecular weight, this was attributed to the degree of cross-link that get in the molecules of the material are few. The effect of the low molecular weight of the polymer reduces the threshold voltage and that it is possible to have relationship an increase flexible spacer of polymer.

Keyword: Non – Polar group, poly-siloxane, liquid crystal polymers.

الخلاصة

هدف العمل هو معرفة تأثير اضافة مجموعة غير-قطبية لمجموعة من البوليمرات اعتمادا على العمود الفقري لبوليمر البولي-سايلاكسين، ولقد وجد أن إضافة مجموعة غير قطبية يقلل من مساهمة عزم ثنائي القطب من مجموعة-سيانو موازية لمحور الجزيئة الطولي للوحدة الميزوجنية وهذا يؤدي إلى تقليل متباين الخواص العازلة ($\Delta\epsilon$) للنظام. لقد تم استخدام خمس نماذج مختلفة بالوزن الجزيئي ومتساوية بطول الفاصل، وضعت في خلية Planer تتحول فيما بعد إلى Homotropic عند تطبيق المجال الكهربائي عليها. ان الشدة النافذة من المستقطب تكون عالية عند عدم $E=0$ ولكن عند تطبيق مجال كهربائي بقدر قليل تنخفض الشدة وان الفولتية تزداد بزيادة الوزن الجزيئي. ان الزيادة في درجة الحرارة تؤدي الى نقصان في ازمان الاستجابة البصرية (τ^{on} , τ^{off}) وذلك يعود الى النقصان في لزوجة البوليمر. ان معامل التوجيه يزداد كلما قل الوزن الجزيئي وذلك يعزى الى ان درجة التشابك الحاصل للجزيئات المكونة للمادة تكون قليلة. ان تأثير انخفاض الوزن الجزيئي لبوليمر يقلل فولتية العتبة وهذا ومن الممكن ان يكون له علاقة بزيادة ثابت المرونة للبوليمر.

المفاتيح: مجموعة غير قطبية، بولي سايلاكسين، بوليمرات بلورية سائلة.

1. Introduction

Liquid crystalline polymers can be classified into main chain, side chain and combined. This classification is based on the place of the polymer where the mesogenic is inserted, i.e. within the main chain, as side groups, or both within the main chain and as side groups. [Percec *et al.*, (1992)] 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 synthesized and studied [Warner, (1989); Plate *et al.*, (1989)].

The order parameter (\bar{s}) in nematic liquid crystals is one among the most important physical parameters [De Gennes *et al.* (1993); Bahadur, (1991); Charandrasekhar *et al.*, (1977)], which dictate its performance in display devices. The material properties of liquid crystals, viz. the dielectric, optical and magnetic anisotropies depend on the order parameter. Thus, it is of great importance to study the temperature dependence of the orientation order parameters of liquid crystalline materials. Due to their distinctive shape nematic liquid crystal molecules undergo stronger attractive forces when arranged parallel to one another. The value \bar{s} for molecules fully orientation equal one while molecules randomly oriented equal zero, determines the director vector (\hat{n}) average direction or the preferred direction of the molecules and does not give degrees or force direction in the mesomorphic of the liquid crystal, and changes from one point to another within the phase, causing the emergence of turbid appearance of the phases [Chistyakov *et al.*, (1969)].

To measure the regularity in the liquid crystal molecules in relation to (\hat{n}) use orientational order parameters (\bar{s}), where Russian scientist Tsvetkovt 1942 [Eren San *et al.*, (2003)] enter this term and which can calculate using the following formula:

$$\bar{s} = \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle$$

Where θ is the angle between the director and the long axis of molecule and brackets, denote to range all of the molecules in the sample, as shown Fig. (1).

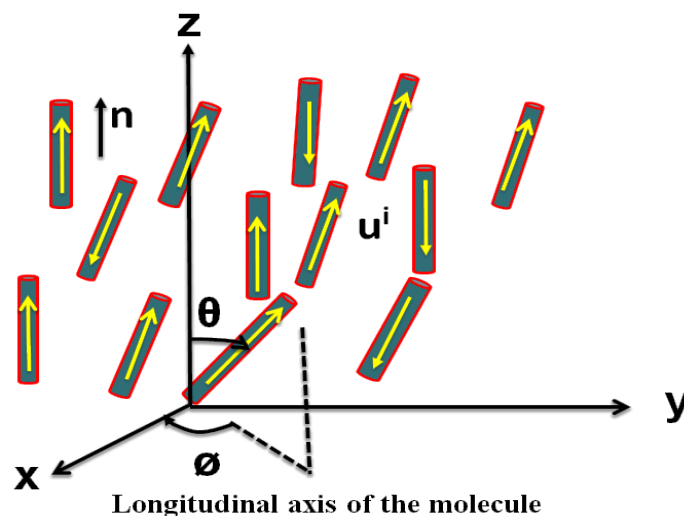


Figure (1): Orientation (θ, ϕ) relative to axes (x, y, z).

The influence of the electric field primarily to the rigid aromatic mesogenic unit, and so, and expect when the application of electric fields to side-chain liquid-crystal polymers to produce similar macroscopic alignment with the possibility of significant and interesting interactions between the various components of these molecular composites. However, with a conventional liquid polymer any applied electric field will rapidly relax at rates dependent on the viscosity of the material, and thus only flow fields followed by rapid cooling generally result in orientation. [AL-Amman *et al.*, (1996); Finkelmann *et al.*, (1984); Davis *et al.*, (1986)].

2. Experimental details

2.1 Fundamental Materials and Specification:

Synthesis and Chemical structures of polymer poly – siloxanes

A series of polymer poly-siloxane based side chain liquid crystalline copolymer of the repeat unit see Fig. (2) have been prepared by free radical polymerization. These materials have been prepared by Dr. M. J whitcombe at the department of chemistry, university of reading. The standard conditions used (initiation by AIBN in chlorobenzene at 55°C) have been modified to give a range of molecular weight by increasing the initiator concentration and by the addition of various amounts of dodecanethiol as a chain transfer agent [Moussa *et al.*, (1987)].

Both of this modification reduces the molecular weight of the polymer produced. There is no data yet reported in the literature relating to the electro – optic or orientation order of these material.

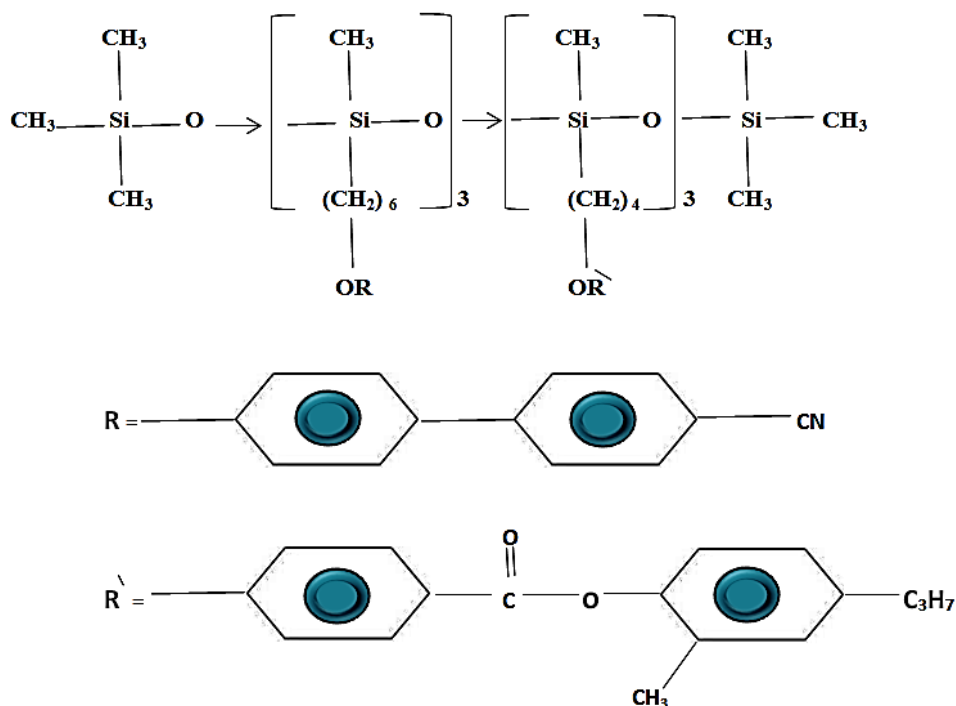


Figure (2): Structure of the polymer poly - siloxanes used in this work. [Moussa *et al.*, (1987)].

Table (1): Molecular weight and phase transition data determined by using Differential Scanning Calorimeter (D.S.C) in chemistry department, university of Reading, U.K

Polymer	M_w	Dp_n	T_g °C	T_{NI} °C
1	1.1×10^5	275	38	133
2	1.0×10^4	110	35	122
3	0.6×10^4	30	30	106
4	2.1×10^3	25	22	90
5	1.6×10^3	10	16	78

2.2 Samples preparation:

Blazers tin oxide coated glass slides used for all electro – optic cells constructed in this work. This was easily cut, and was sufficiently flat to allow the fabrication of cells with parallel plate separation to within a few seconds of arc. The glass was cut into plate of approximately 6 cm² area, and etched using HCl acid with zinc metal powder, as a catalyst, to give a 2cm² electrode surface. Each glass plate was washed, in soup water and cleaned in an ultrasonic bath for 30 minutes at 60 °C.

One technique was used to achieve uniform planer alignment of the liquid crystal director. The cell electrodes were coated with a thin layer of polyimide precursor [consisting of a 5% solution of Rodehftal 322 (Rh one Poulenc chemical Ltd.) in dimethylformaimed], using a spin – coater running at 4,500 r.p.m. The coated slides were heated in an oven for 30 min at 80°C and then rubbed at R.T in a single direction with a cloth using controlled repeatable procedure , heated again for 30 min at 130°C [Saengsuman *et al.*, (2007)].

As a consequence cell construction involved the following procedure a small portion of the selected polymer sample was carefully applied to one of the treated glass electrodes this was then heated for some time (typically 10-15 minutes) above the clearing point of the polymer in order to allow trapped air to escape [Zhang *et al.*, (2007)]. The second glass electrode was then mounted above the first electrode, and the complete assembly inserted into a homemade clamping frame. The electrodes were fixed permanently using (Araldite Rapid epoxy resin ciba Geigy) the majority of the cell used in this work were prepared using "kapton" sheet of nominal thickness 0.025 mm, as spacers, to separate the electrodes [Mitchell *et al.*, (2005)]. The thickness of the cells were measured using micro meter techniques, both gave similar results, with typical electrode separations in the range 0. 026 – 0.030 mm, the final step in the preparation of the electro – optic cell was the connection of the leads which carried the electric field from the power supply [Auriemma *et al.*, (2007); Channuau *et al.*, (2008)], Fig.(3) shown the electro-optical cell construction.

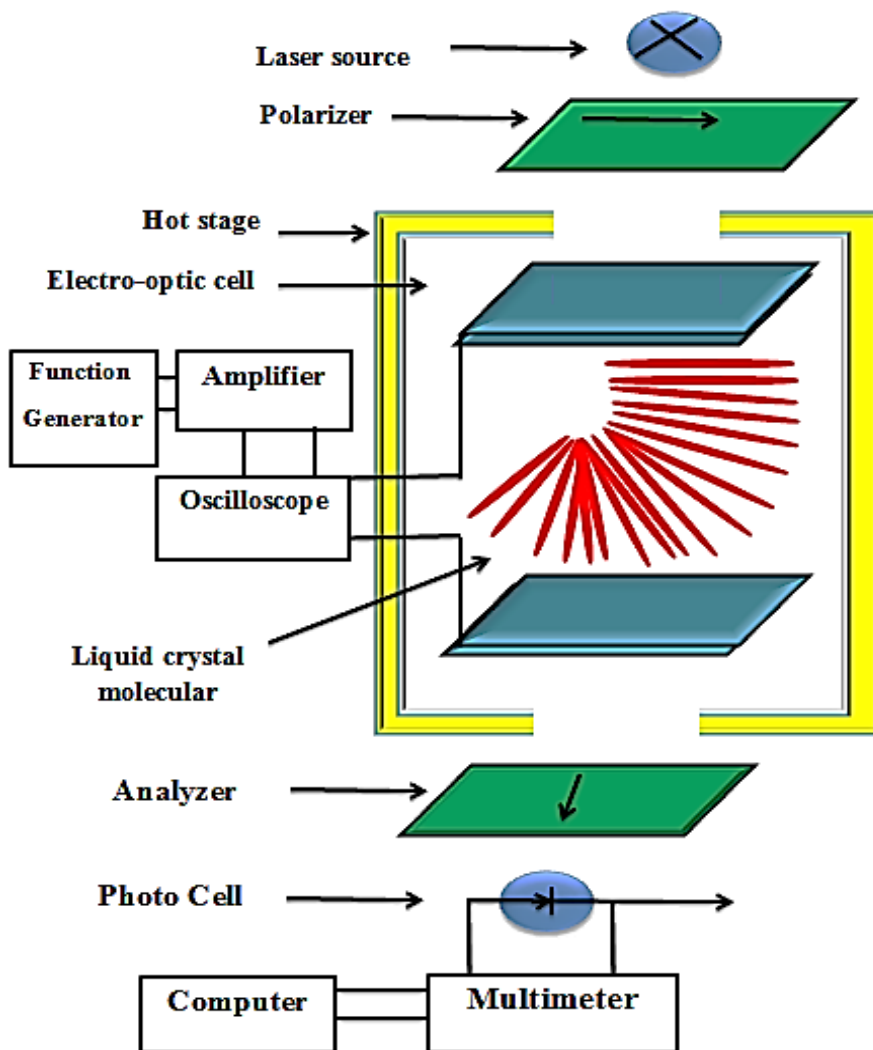


Fig. (3) Scheme of the work system

The most important three devices were used in this work for electro – optic measurement is: *Mk 1000 and Hcs 402 and ALCT*.

The ALCT - Automatic Liquid Crystal Property Tester: It is use software allows for the measurement of material parameters for both positive and negative dielectric nematic liquid crystals, and material parameters of FLC.

The ALCT can also be integrated with Instec's microscope hot and cold stages and temperature controllers, enabling the user to analyze the temperature dependence of the above parameters.

HCS 402 Microscope Hot/Cold Stag: The use of Dual-Heater Microscope Hot and Cold Stage for Increased Temperature Gradient Uniformity.

The MK1000 High Precision Temperature Controller: It provides temperature control resolution and precision to 0.001°C

3. Results and discussion

In Fig. (4), shown the variation of intensity with threshold voltage (U_c) for each polymers under study. All threshold voltage measurements were made after the sample had been held at the required temperature for a period of time at least three times longer than the relaxation time. The response time at low voltage is long, it determined the threshold voltage from a plot of the change in the transmitted optical intensity as a function of the applied small voltages. The experimental data shown in table (2).

By extrapolation, this method allow every the true threshold voltage to be excluded. To reach the steady state between each voltage step the samples were left for 3 – 5 hours and this was checked by monitory the transmitted light versus time. For the material [Nogales *et al.*, (2005)], the steady state reached within 3hours, at the most. Typically, at each stage the sample was held for a period of time ten times longer than the response time.

Figs. (5 - 9), shown the variation of switch – on time τ^{on} as a function of the time for which the field is switching τ^{off} , measured at constant temperature below T_{NI} for polymers 1,2,3,4,5. The viscosity of the polymer is relatively low the reproducible switching effect were observed at temperatures close to the nematic- isotropic transition temperature and measurement were made in the range of T_{NI} to $T_{NI}-3$ for polymers 1 & 2 and no response to the applied field had been observed for these polymers in the smatic phase but measurements were made for the polymers 3.4 and 5 in the range of T_{IN} to $T_{NI}-5$ at the same time reproducible switching effects were observed in the nematic phase for polymers 3.

Initially the τ^{on} is short, but this arises only from the insufficient time allowed for complete relaxation to the predefined surface alignment state. As the time for which the field is removed τ^{off} , increases, the following τ^{on} increases until a quasi-equilibrium is reached. From such curves, it can obtain values for τ^{on} and τ^{off} which represent switching between equilibrium conditions. Repetition of the cyclic experiment at different but fixed temperatures allows the temperature variation of τ^{on} and τ^{off} to be mapped out.

In Fig. (10), there is a marked reduction in the threshold voltage for both increasing temperature and reducing the molecular weight. In this series of polymers the chemical composition that has a backbone and spacers and group mesogenic considers end- groups of great significance therefore $\Delta\epsilon$ are important from this measured.

In Fig. (11), makes a direct comparison of the threshold voltages obtained in the nematic phase at a constant step below T_{NI} for the series of polymers prepared. It is clear that there is an increase in the threshold voltage with increasing molecular weight. Indeed the effect of the end – groups of the polymer chains are taken into account (these must reduce $\Delta\epsilon$) then the trend will be even more marked.

The marked increase of the threshold voltage with temperature follows similar dependence observed of the materials [Mitchell *et al.*, (2006)] in which the mesogenic density along the polymer backbone is changed.

In Fig. (12), shows even when the variation in order parameters in taken into account there remain substantial difference members of this molecular weight series, in other words if the increasing of the threshold voltage as a function of molecular weight as shown in Fig. (11), was due reduction in the order parameter alone than all five curves in Fig. (12), would superimposed. In general the chemical composition of the polymer chains affects the electro-optical properties of the material, which

contains three main parts the flexible spacer and the mesogenic groups and type the backbone the component of the chains.

The effect of each of the τ^{on} and τ^{off} are affected by temperature, molecular weights and the flexible spacer, it is note the flexible spacer equal to (3), which is a constant for all the polymers so it will get response times somewhat acceptable, where short the flexible spacer leads to times response is very large and because the strong couple between mesogenic groups and the backbone of the polymer.

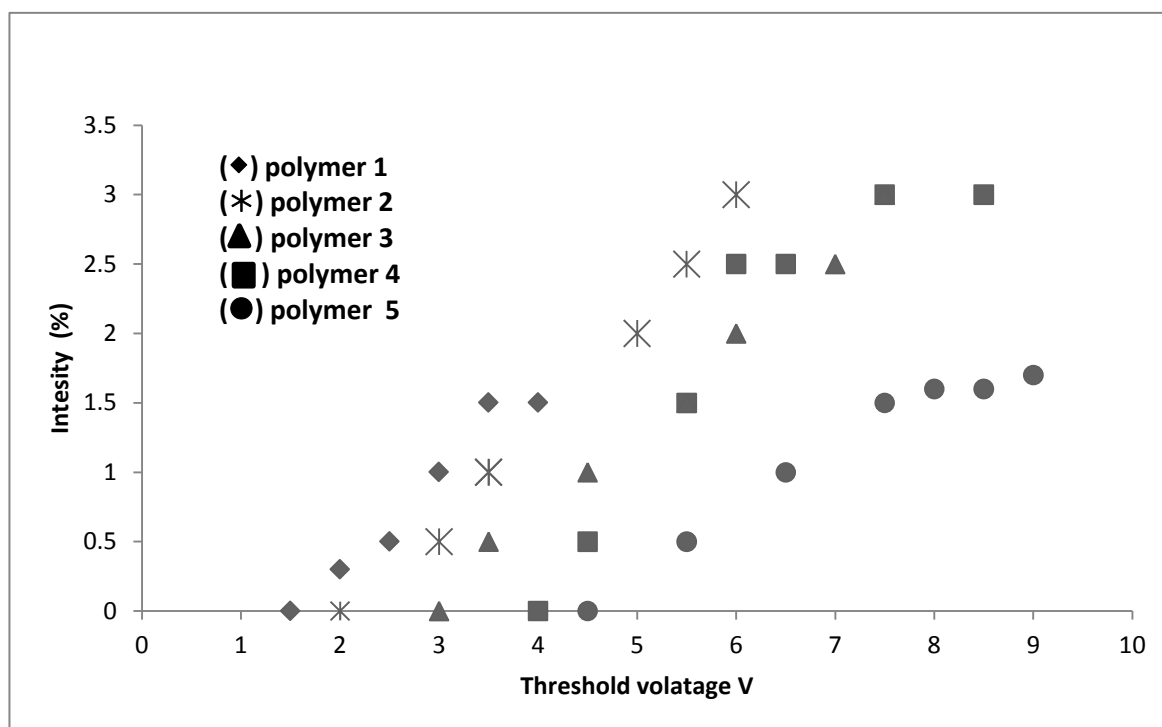
The increase in temperature leads to a decrease in response times and this is due to the decrease in the viscosity of the polymer out that it get stability (steady value for response time), the access to stability the different between mesogenic chains and the polymer chain and within the time scale of (τ^{off}). This was attributed to the mesogenic units related high response to the electric field applied within a certain period of time to get to the steady values for τ^{off} while backbone chain and because of the weak nature will need a longer period of time to get to the steady values for τ^{off} . When the side chains can relax independently of the polymer chain and this occur slight ahead of the polymer chain relaxation.

In this work the decrement of the response time of the material to the electric field can be explained in the following manner: the terminal cyano-substituted was selected because of interest in the electric properties that would be conferred on the polymers possibly making them suitable for specialty applications. However, the situation complicated by the antiparallel correlation of molecular dipoles, resulting from the overlap of adjacent cyano-substituted mesogenic units. Then adding the non-polar group would reduce the contribution of the dipole moment of the cyano-group parallel to the molecular long axis of the mesogenic unit and lead to a suppression of dielectric anisotropic ($\Delta\epsilon$) for the system.

The increasing of molecular weight leads to increase in threshold voltage $U_c = \sqrt{k_{ii}/\epsilon_o\Delta\epsilon}$ that indicates an increase in the elastic constant K_{ii} , if it is taking into account $\Delta\epsilon$ it decreases with increasing threshold voltage resulting from a change in molecular weight. That molecular chain lead to the emergence of curvature elastic constant by, the more directly from the coupling of mesogenic units to the polymer backbone, and by also the elasticity of interactions between the chains as might arise from entanglements where the threshold voltage increase in this case.

Table (2): between light intensity and Threshold voltages applied for all five polymers

first polymer		second polymer		third polymer		fourth Polymer		fifth Polymer	
Thresh old voltage(V)	Intens ity (%)	Thresh old voltage(V)	Intens ity (%)	Thresh old voltage(V)	Intens ity (%)	Thresh old voltage(V)	Intens ity (%)	Thresh old voltage(V)	Intens ity (%)
4.5	0	4	0	3	0	2	0	1.5	0
5.5	0.5	4.5	0.5	3.5	0.5	3	0.5	2	0.3
6.5	1	5.5	1.5	4.5	1	3.5	1	2.5	0.5
7.5	1.5	6	2.5	5.5	1.5	3.5	1	3	1
8	1.6	6.5	2.5	6	2	5	2	3.5	1.5
8.5	1.6	7.5	3	7	2.5	5.5	2.5	4	1.5
9	1.7	8.5	3	7.5	3	6	3		

**Fig. (4):** Variation of intensity with threshold voltage for polymers 1,2,3,4 and 5 at 73⁰C, 85⁰C, 101⁰C, 119⁰C and 130⁰C respectively.

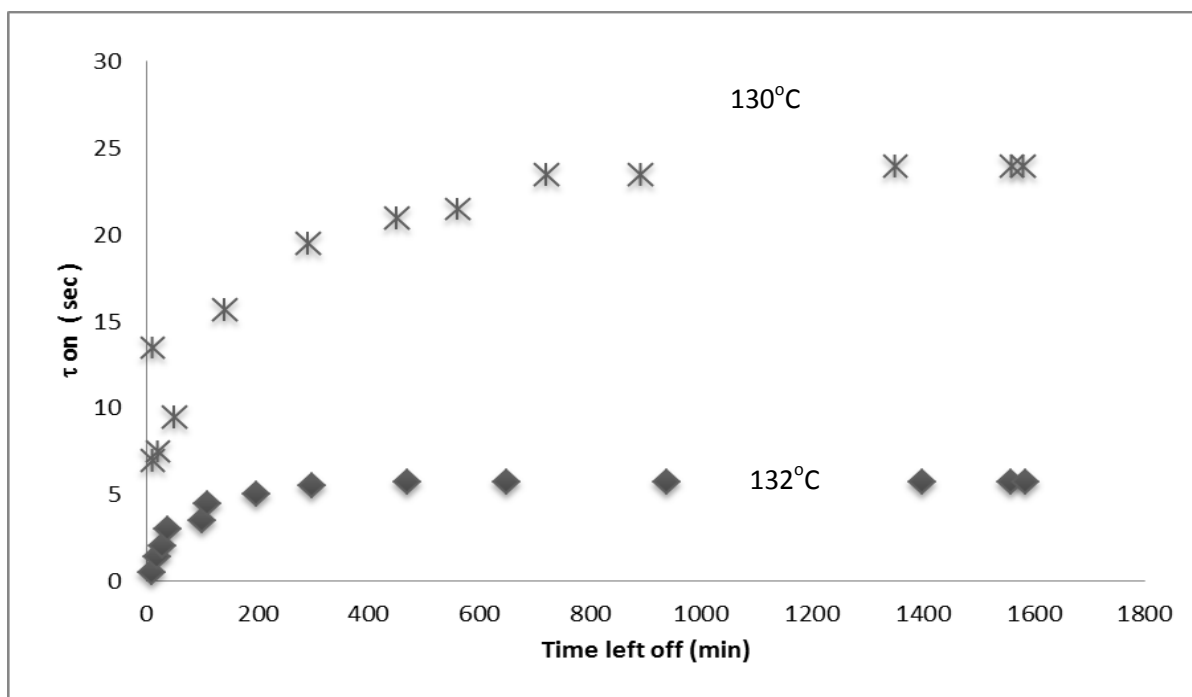


Fig. (5): τ_{on} versus time left off at constant temperature below T_{NI} for polymer 1.

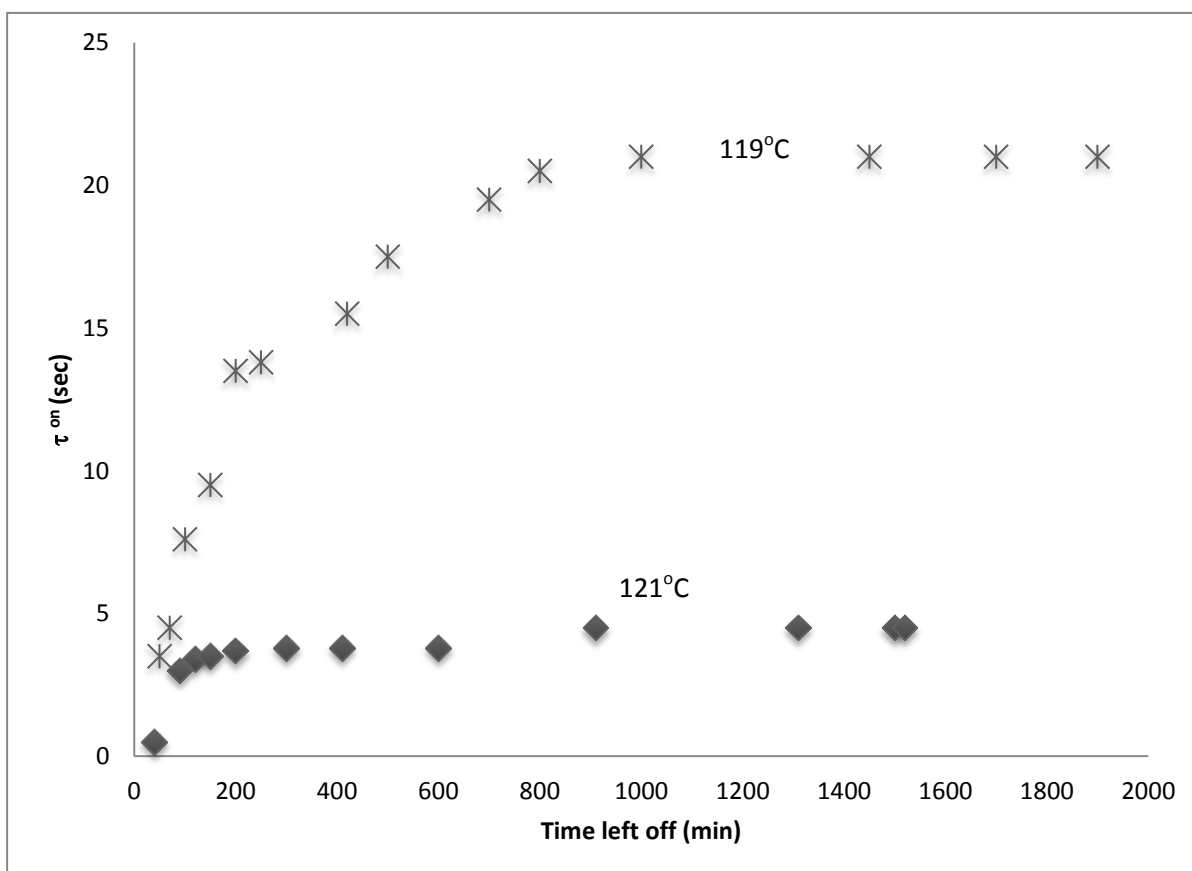


Fig. (6): τ_{on} versus time left off at constant temperature below T_{NI} for polymer 2.

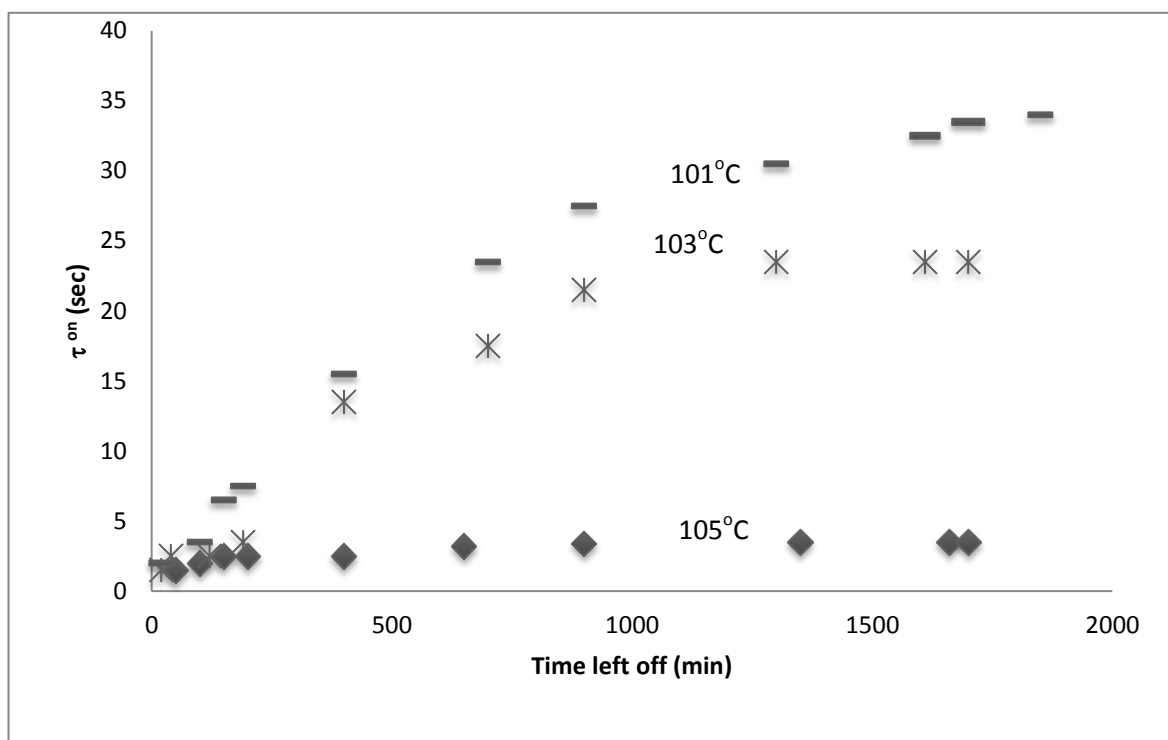


Fig. (7): τ_{on} versus time left off at constant temperature below T_{NI} for polymer 3.

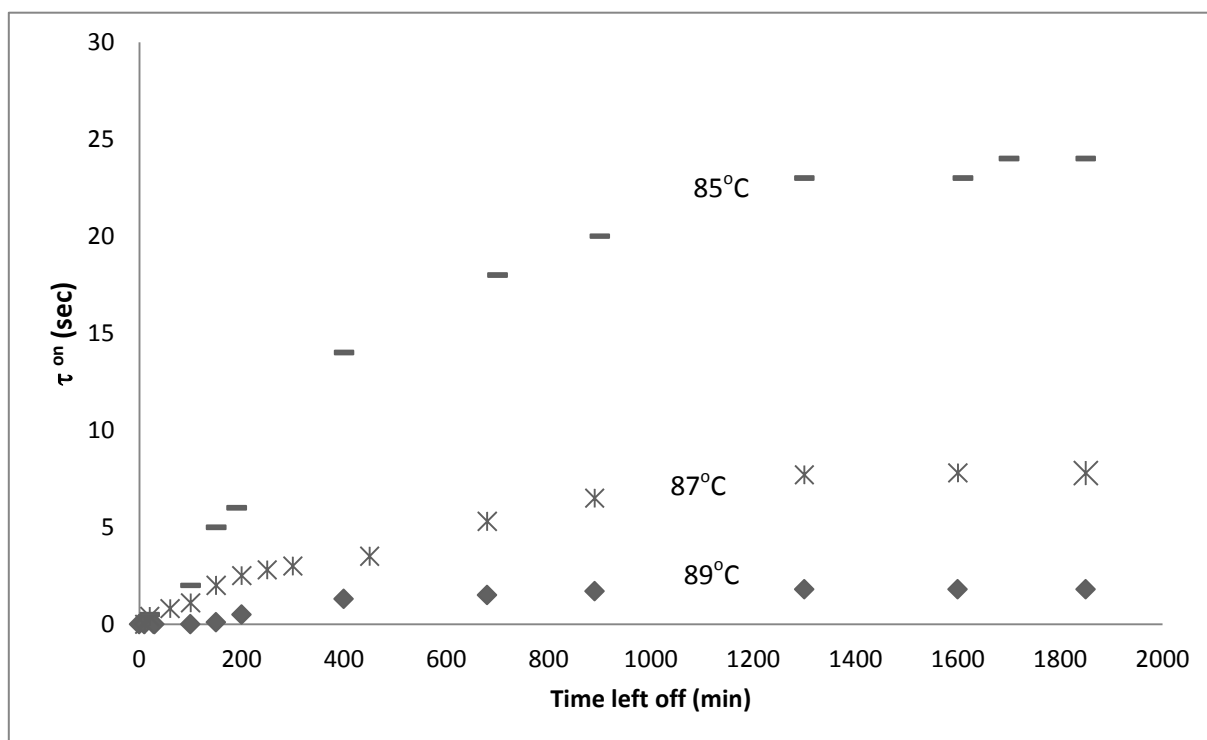


Fig. (8): τ_{on} versus time left off at constant temperature below T_{NI} for polymer 4.

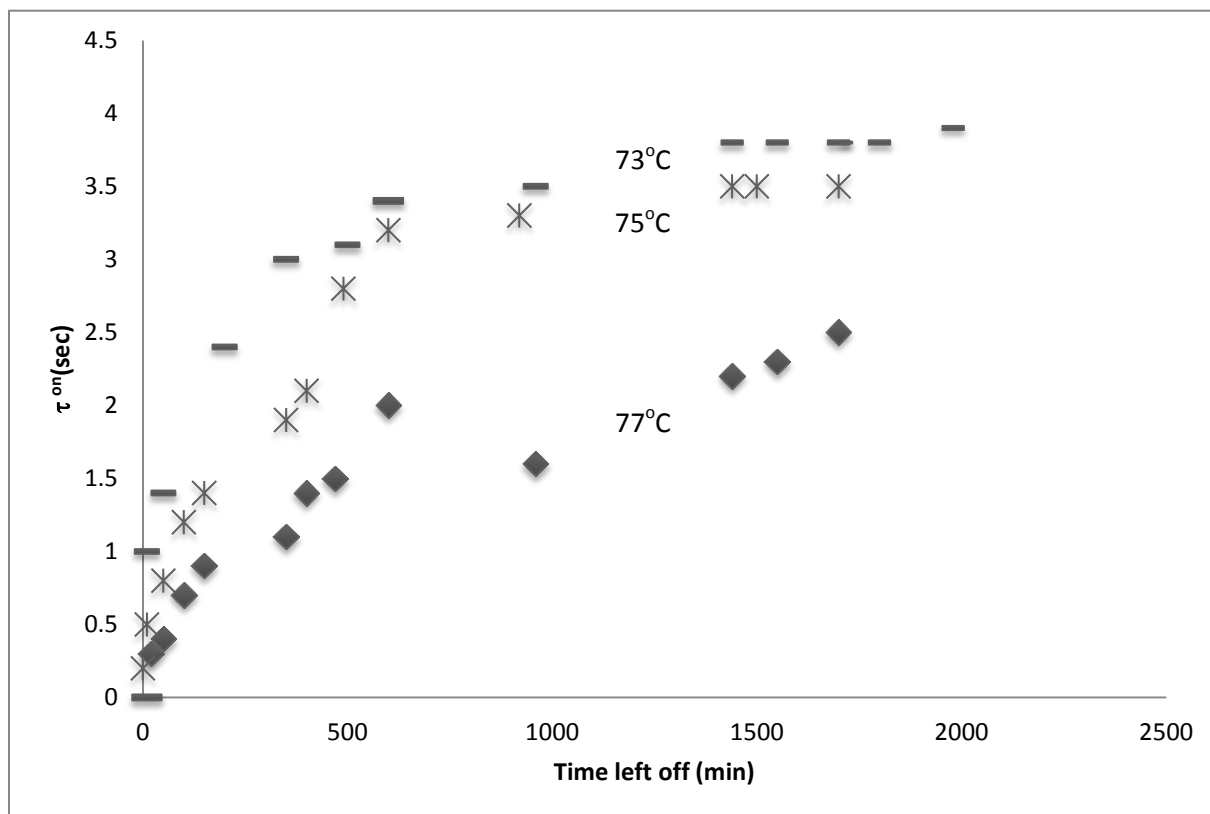


Fig. (9): τ_{on} versus time left off at constant temperature below T_{NI} for polymer 5.

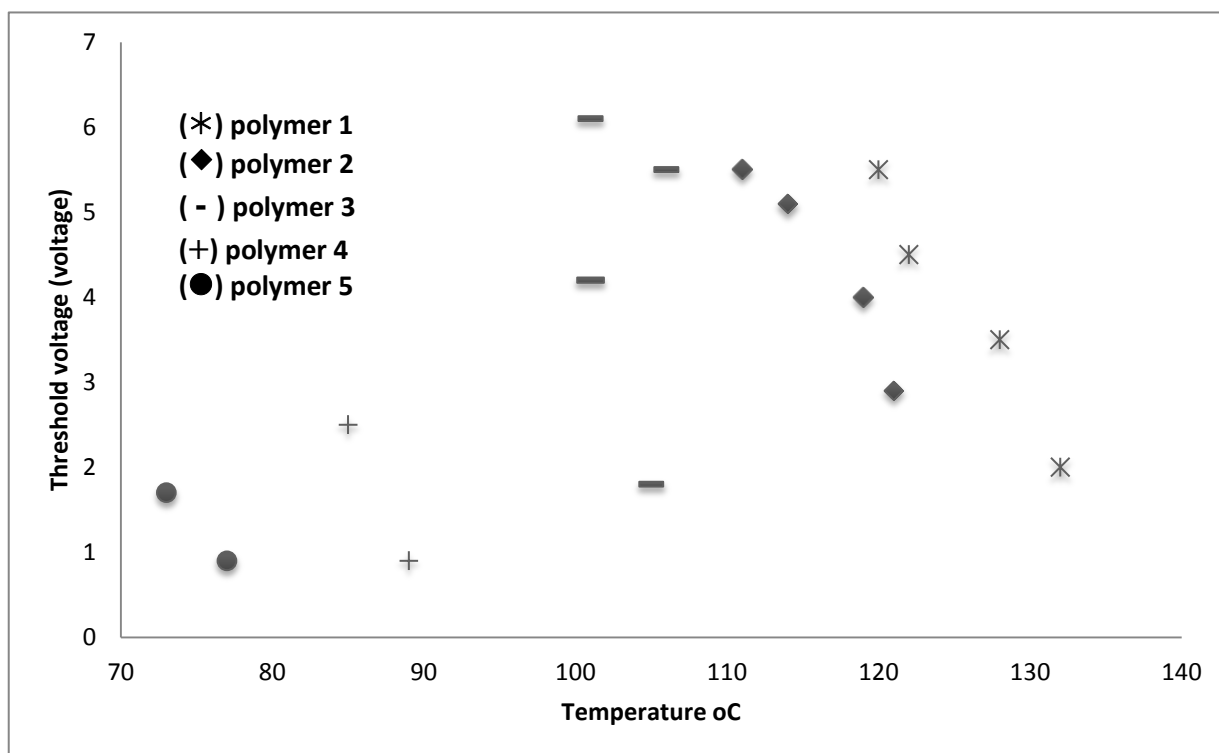


Fig. (10): Threshold voltages as a function of temperature for polymers poly-siloxanes.

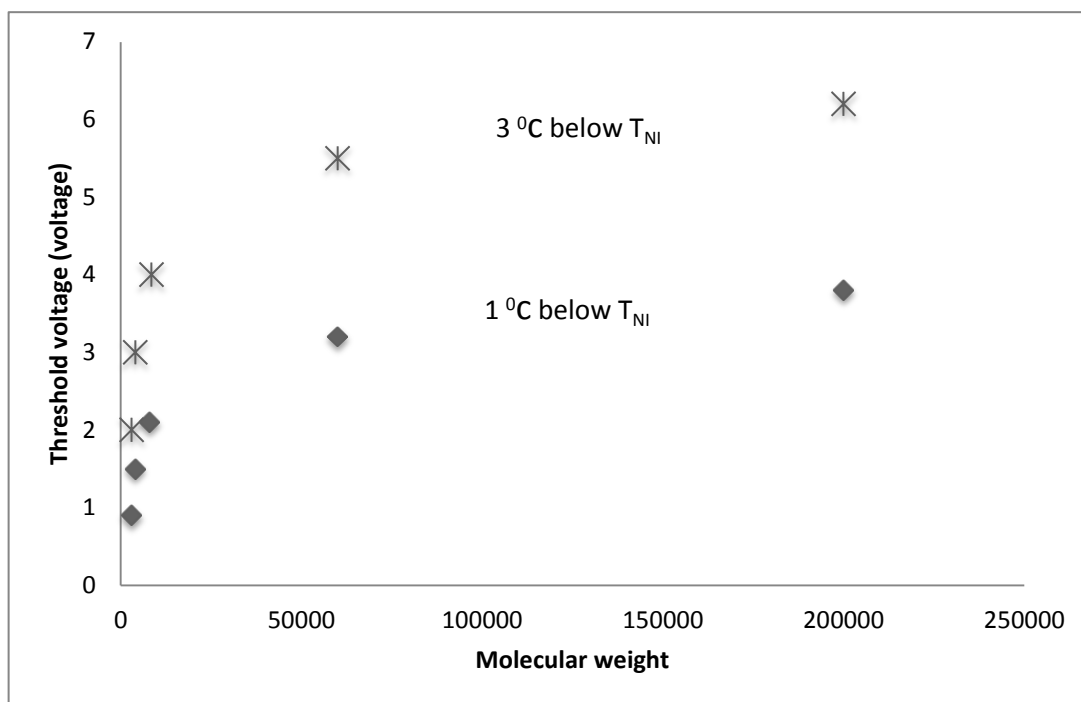


Fig (11): Threshold voltages as a function of molecular weight at 1 °C (♦) and 3 °C (*) below T_{NI} .

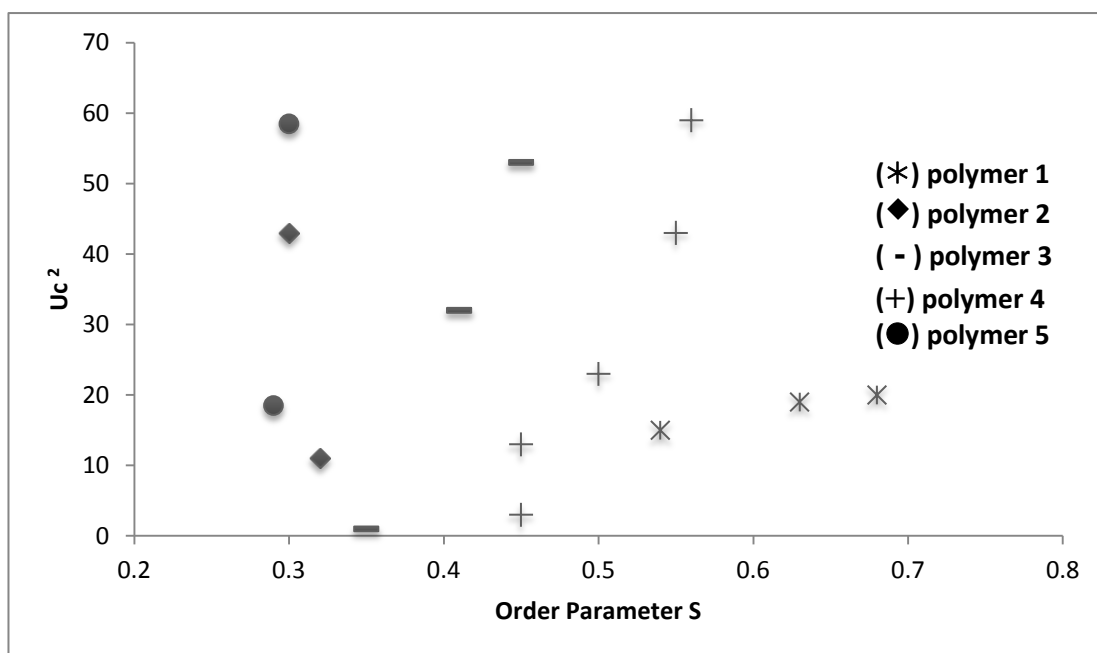


Fig. (12): square threshold voltages against the order parameter S .

4. Conclusions

- ❖ The chemical composition and molecular weight of the most influential factors on the behaviour of the polymer and speed peaks indicates that the material quickly changes.
- ❖ The performance of the electro - optical cells has improved after add the non-polar group would reduce the contribution of the dipole moment of the cyano - group parallel to the molecular long axis of the mesogenic unit and lead to a suppression of dielectric anisotropic ($\Delta\epsilon$) for the system.

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