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Effect of Gold nanoparticle on Electro _ Optical Properties of Polysiloxane Liquid Crystal Polymer

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ABSTRACT

We investigate the nonlinearity of a liquid crystal cell doped with gold nanoparticles by considering their selective absorption. Such nonlinearities are promising for optical processing applications and optical limiters. Systems displaying thermal nonlinearities are particularly attractive as the maximum nonlinearity may occur in the absence of an applied field and additionally this nonlinearity can be controlled by the reorientation of the liquid crystal. This study focuses on the electro-optic properties of polymers with a different molecular weights based on the polysiloxane backbone. It is found that there is a strong coupling between the mesogenic side chain groups and the polymer chain that the elasticity of the polymer chain plays a strong role even in the static electro – optic properties. The switching times (on) and (off) have been measured through the period between planer and homotropic alignment which happens under the electrical field effect. Additionally, it is found that adding gold nanoparticles moieties will decrease the phase transition temperatures and thus decreasing of switching times. The variation of the threshold voltage is measured at constant steps below nematic – isotropic transition temperature (TNI) for series of polymers. It is found that the high molecular weights of polymers have great threshold voltage of the electro-optic response and this is related to the intrinsic elastic constant of the liquid crystal polymers. The performance of the electro_optical cells has improved after add the gold would reduce the contribution of the dibole moment of the cyano _groub baralle to the molecular long axis of the mesogenic unit and thus reduce density of the mesogenic unit attached to polymer chaine and lead to a Increases of dielectric anisotropic ($\Delta\epsilon$) and thus enhanced backbone mobility for the system.

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INTRODUCTION

To work with nanoscale matter (10^{-9} m) every day is more important in both scientific and technological activities ,a typical example is the case of metal nanoparticles which are an important part of this broad field of study .Metallic nanoparticles are very interesting because of the high diversity of applications that are based on their magnetic [1–2] .[Due to their small size, metallic nanoparticles have a large surface area per volume unit and therefore a high number of atoms at the surface [3] The doping of liquid crystals Polymer) LCps (with nanoparticles has become a common method of improving their optical ,magnetic, electrical and physical properties [4] For example ,ferroelectric nanoparticles have been shown to decrease the Fr'eedericksz threshold and increase the birefringence of nematics [5-6] Hybrid nanostructures can be conceptualized from the combination of gold nanoparticles with organic molecules ,dendrimers [7] polymers [8] polypeptides [9] proteins [10] oligonucleotides [11] The gold in nanoparticle form has been known from the very beginning of human civilization, e.g. in ancient Egypt and Rome, [12] but systematic scientific investigations and first colloidal synthesis were performed much later in 1857 by Michal Faraday [13]. Ever since, the metal nanoparticles have found various applications in industry, medicine and pharmacy and they have framed an entire new field in nanoscience concerned with the nanoparticles' synthesis, their chemical modifications and investigation of their properties [14–15] gold nanoparticles) AuNPs (obtain much more attention than the others. AuNPs are the most stable metal nanoparticles presenting fascinating aspects, such as assembly of multiple types involving material science, behavior of the individual particles, size-related electronic, magnetic, optical properties, and applications to catalysis and biology [16-17]. Given the fact that the colloidal gold particles

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played a central role in the development and understanding of the basic colloidal chemistry and physics [18–19], we will draw upon our understanding of colloidal dispersions to cite examples and theoretical insight relevant to our system. The perusal of this classic literature also demonstrates how the pioneers recognized that various observations, for example, color of colloidal gold solutions, could be attributed to the presence of rod-like nanoparticles. The recent interest in gold nanoparticles is propelled by both the advances in our scientific understanding of their synthesis and physical properties [20–21]

Experimental:

The procedures followed for the construction of electro – optic cells with predefined director orientation in these investigations were similar to those developed for low molecular weight liquid crystal [90, 91]. Blazers Z20 tin oxide-coated glass slides were 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 6cm² area, and etched using HCl acid with zinc metal powder as a catalyst to give a 2 cm² electrode surface. Each glass plate was then washed hand-by-hand in soap and water and cleaned in an ultrasonic bath for 30 minutes at 65 °C. The plates were then rinsed in distilled water and dried in an oven for 20 minutes at 60 °C. This treatment produced plates sufficiently clean for the surface treatment procedure, which is the subject of the next section. In this work 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 dimethyl formaimed] in dimethylformaimed], using a spin – coater running at 4,500 r.p.m these coated slides were heated in an oven for 30 minutes at 80°C they were then rubbed at room temperature in a single direction with a cloth using controlled repeatable procedure , heated again for 30 minutes at 130°C , finally it will be putted for one hour at 200°C in the oven.

Cell filling by means of capillary effects are widely used for low molar mass liquid crystal compounds. However, these methods cannot readily be applied to polymeric system due to their intrinsic high viscosity . oven. 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 . 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. The thickness of the cells were measured using micro meter techniques, both gave similar results, with typical electrode separations in the range 26 – 30 µm. 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, A silver conductive adhesive (A-500 Johnson matthey chemical Ltd.) with (500-1000) µohm / cm³ resistivity was used to connect a thin PTFE coated wire to the electrodes of the cell care was taken not to allow the conducting adhesive to stray on to the opposite plate since the resulting short circuit would render the cell inoperative. To avoid a further possible short circuit, between the cell holder and the area connecting the wires to the cell, the area was covered with a piece of "kapton" In general structure of the polymer (poly-siloxane) studied in this search is shown in Fig. (3.2).This polymers were synthesized in the chemistry department, university of Reading by Whitcombe. The polysiloxane contains on backbone with side chain mesogenic moieties and non-mesogenic units attached via alkyl spacer units, compounds have been synthesized with a repeat units in the backbone. Composites consisting of nematic liquid crystal (Polysiloxane) and gold nanorods have been elaborated and investigated with a polarizing microscope, It was detected that the nanorods form inside the oriented liquid crystal matrix their own self-assembling well-ordered structures, The gold nanorods were inserted into liquid-crystal Polymer (LCp) matrixes in very small amount (0.07 vol.%). In order to obtain the composites based on gold nanorods and nematic LC, the latter was dissolved in ethanol, after this, water suspension of nanoparticles covered by surfactant was added, and then the solvents were removed in vacuum. The obtained nanocomposites (NC) were treated by ultrasound before the insertion into the cell.fig. (1) shows the electro-optical cell construction.

Experimental Set-up:

The most important three devices were used in this work for electro – optic measurement are :

1. Mk 1000
2. Hcs 402
3. ALCT

The mk 1000 series temperature controller offers precision, accuracy , and stability for temperature measurement and control. It provides temperature control resolution and precision to 0.001°C, accommodates both Platinum RTD and individually calibrated thermistors as temperature sen, and can optionally control up to four (4) instec hot and cold stages, plates, or chucks. Two operation modes, keypad operation using the front

panel of the controller, or software control through pc as well as. Adjustable ramp (rate of heating/cooling) to user set temperature point. Programmable operation command set. Precisely controls temperature to 0.001°C option save temperature data to the computer. RTD thermistor or thermocouple, LC cell holders for many types of LC cells.

Features:

- 1- Two operation modes, keypad operation using the front panel of the controller, or software control through PC.
- 2- User adjustable ramp (rate of heating / cooling) to user set temperature point.
- 3- Fully programmable without host computer.
- 4- Wide temperature range
- 5- Accurate to (0.001°C) temperature resolution and precision.

Precisely controls temperature to 0.001°C option save temperature data to the computer. RTD thermistor or thermocouple, LC cell holders for many types of LC cells.

Temperature control system, which includes MK 1000 controller, nitrogen container nitrogen pump (LN₂ - p), and hot – cooling stage. It features, Large viewing Aperture. Dual pane window for better thermal isolation. Integrated Aperture window defrost system. Gas purge sample chamber. Inner lid for improved sample temperature uniformity. Vertical and horizontal mounting. Optional precision X – Y micropositioner for sample positioning. Application software, wintemp, allows remote control from host computer.

ALCT Liquid Crystal measuring subsystem:

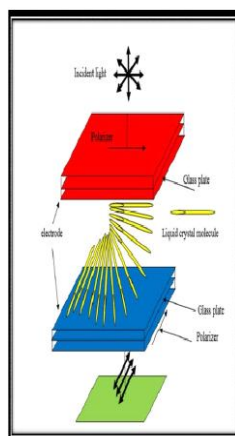
The automatic liquid crystal measurement systems (ALCT) are USB based instruments which can be connected conveniently to both desktop and laptop computers. Using this system with well-prepared LC test cell and proper method, user can measure:

- Liquid crystal mixture physical parameters :
 - Threshold Voltage V_{th} .
 - Polarization current I_p .
 - Viscosity .
 - Elastic constants K_{11} and K_{33} .
 - Dielectric constants $\epsilon_{||}$, ϵ_{\perp} , ϵ_{Δ} .
- Optical performance of LCD devices:
 - Voltage – transmittance curve.
 - Switching speed, rise, falling time.
- Application software, WinLC, provides user an integrated tools to configure measurement setup, data collection, analysis and visualization.

Optical test bench subsystem:

This includes light source, polarizer, rotatable hot – cooling stage holder analyzer, and photo detector holder. This test bench allows user to:

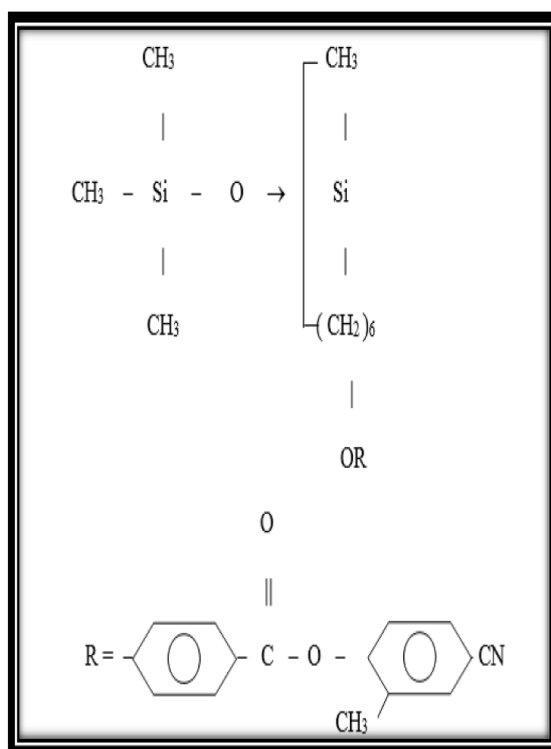
- Test cell in side of the hot-cooling stage can be rotated in full 360° range
- Arrange polarizer and analyzer perpendicular and parallel to each other.
- Light sealable working chamber shields a way the room lighting.
- Light source , polarizer and analyzer are installed in sealed dark sections to prevent the contamination of optical components.
- Light sealable working chamber shields a way the room lighting.



(1) Electro – optic cell



(2)A photograph of the work system.



(3) materials chemical structures

Table 1: Molecular weight and phase transition data polysiloxane

TNI C	T _g C	Dp	M _w	polymer
130	48	320	1.7×10 ⁶	1
125	40	102	8.1×10 ⁵	2
104	26	15	7.2×10 ⁴	3
77	16	7	4.5×10 ³	4
61	4	4	3.1×10 ³	5

Results:

Figures (4-8) defined by which voltages necessary to make a complete switching, and from these Figures it can be seen is the variation of the transmitted light intensity as a function of the applied voltage and the required voltage for each material. For getting on the switching voltage must be the transmitted light intensity decrement with increasing of the required voltage, so it can be determined to complete switching. The required voltage is increased with increasing of molecular weight M_w this is due to viscosity η and the degree of entanglement between the molecules are high. The same behavior was observed for the poly-siloxane liquid crystal, although there are some differences in the required voltage. The voltages for the complete orientation are identified, applied to the cell, and calculates the required time to the occurrence of complete orientation. Where Fig. (9-13)

show switch on - time on as a function of the time for which the field is switched off before the ^{off} measurement. Using the system and the method described in work, we have implemented a cyclic experiment in which we use the values of τ^{on} to determine when a steady state is reach. As mentioned in work the approach allows both 'on and 'off to be evaluated. in order to achieve complete switching we typically applied(147 to 240) volt (peak to peak) at a frequency of 500 Hz. 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. By reducing the temperature TNI the saturation states showed in these figures shifted, the required voltage for complete switching was increased in this case. The same behavior was observed for the materials in work although the materials in this work show larger differences between the required voltages for each material compared with the materials in work. Reproducible switching effect were Observed at temperatures close to the nematic-isotropic transition temperature where the viscosity of the polymer is relatively low and measurement were made in the range of TNI to TNI -4 for materials no.1 and 2 and no response to the applied field had been observed for these materials in the smectic phase but measurements were made for the materials no.3.4 and 5 in the range of TNI to. TNI -5 at the same time reproducible switching effects were observed in the smectic phase no.3 show τ^{on} as a function of the time for respectively , each set of experiment were made at constant temperature. The experimental arrangement used for the static electro properties is similarly used for the dynamic electro-optic effects. Fields with a frequency of 500Hz were employed for measurements. The static electric – optic properties are important because they contain important experiments between the threshold voltage U_c and curvature elastic constants K_{ij} and their relationship to composition and temperature for the liquid crystal copolymers. The results obtained for the material in this study are presented in Fig. (14). There is a marked reduction in the threshold voltage for both increasing temperature and reducing the molecular weight. In this series of polymers, Fig. (15) makes a direct comparison of the threshold voltages obtained in the nematic phase at a constant step below TNI for the series of polymers prepared. It is clear that there is an increase in the threshold voltage with increasing molecular weight.Indeed if the effect of the end – groups of the polymer chains are taken into account then the trend will be even more marked. It is emphasized that any dynamic effects arising from changing viscosity have been eliminated in the procedures outlined above. A few contributions ,have dealt with measuring the threshold voltage for polysiloxan polymers. Unfortunately, molecular weight data were not given , however the threshold voltages reported are broadly similar to those found here. The marked increase of the threshold voltage with temperature follows similar dependence observed of the materials ,in which the mesogenic density along the polymer backbone is changed. It is noticeable that there is no sudden step in the threshold voltage at the transition from nematic to smectic phases for polymers 3. From a smectic phases the value of K11 is usually similar to that observed for the nematic phase ,since layer deformation is a relatively facile process.

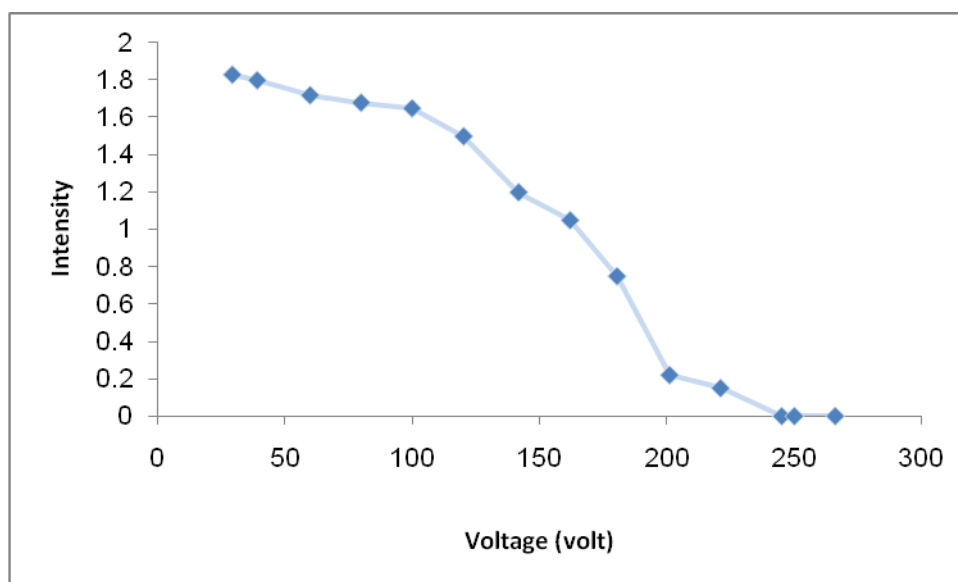


Fig. 4: The relation between voltage and intensity for Polymer 1.

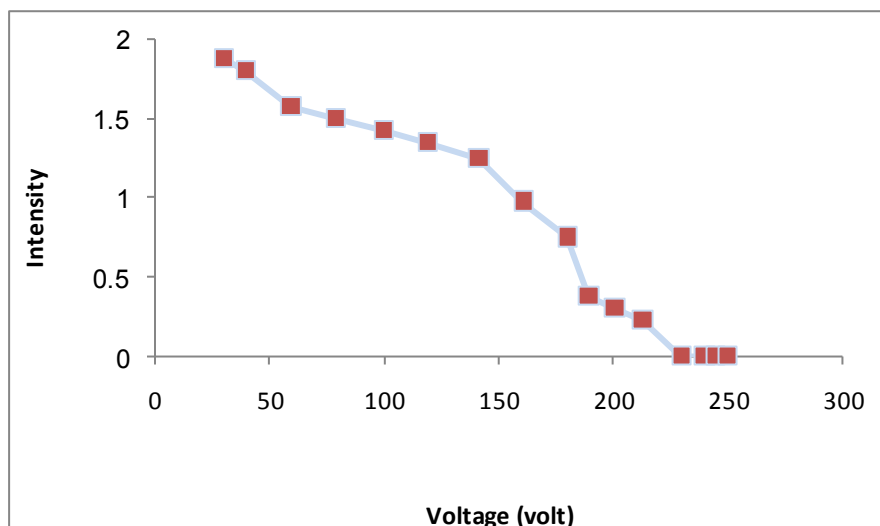


Fig. 5: The relation between voltage and intensity for Polymer 2.

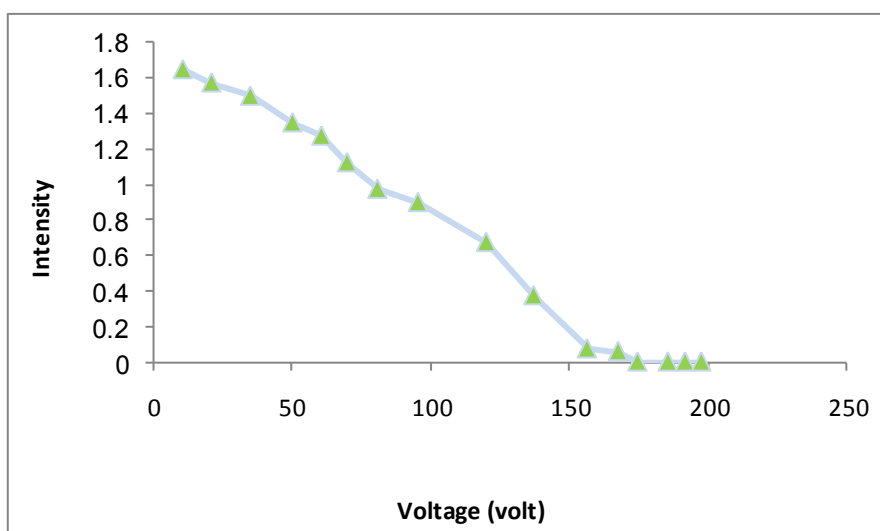


Fig. 6: The relation between voltage and intensity for Polymer 3.

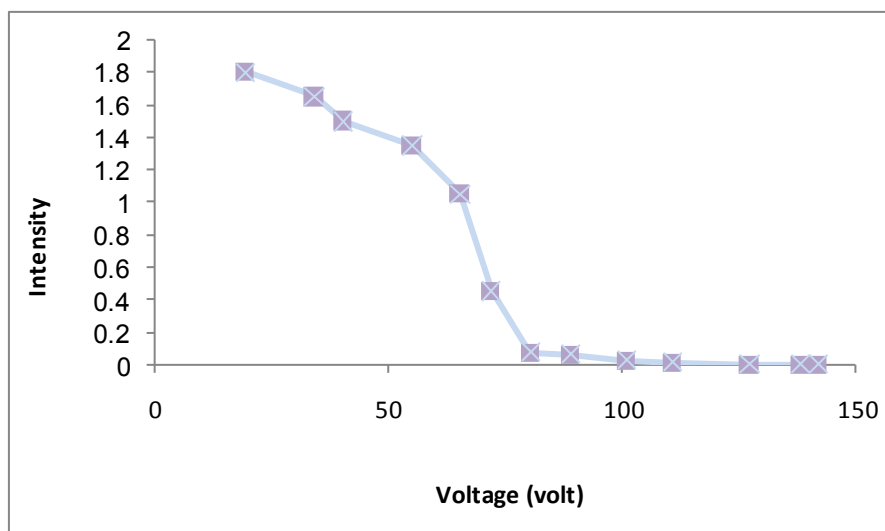


Fig. 7: The relation between voltage and intensity for Polymer 4.

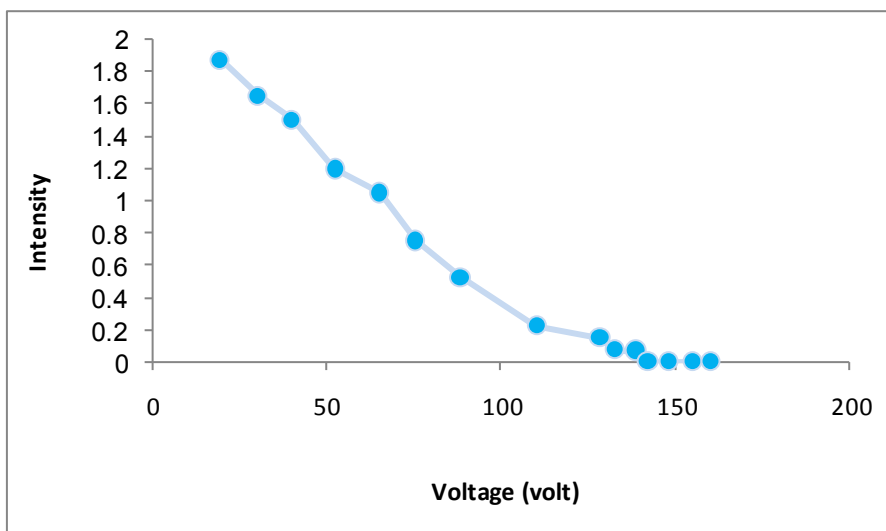


Fig. 8: The relation between voltage and intensity for Polymer 5.

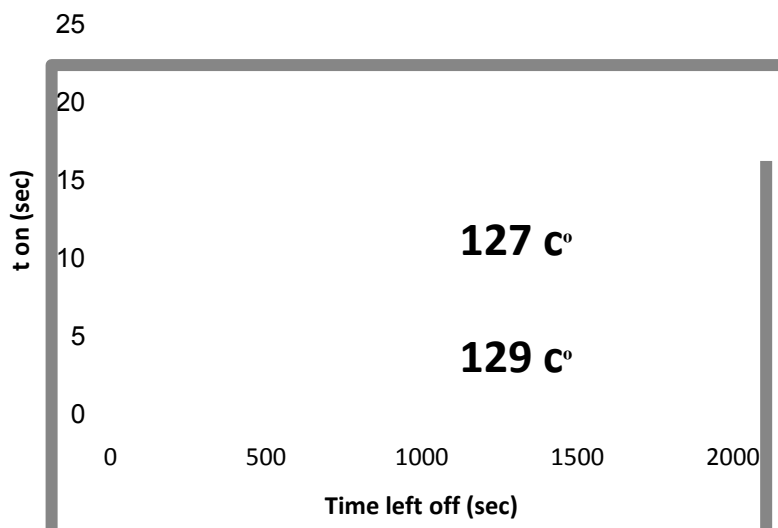


Fig. 9: The relation between t on and time left off for polymer 1

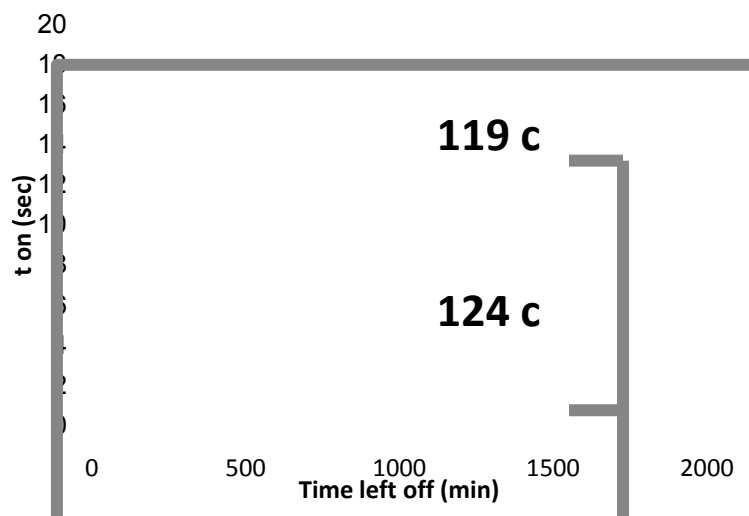


Fig. 10: The relation between t on and time left off for polymer 2.

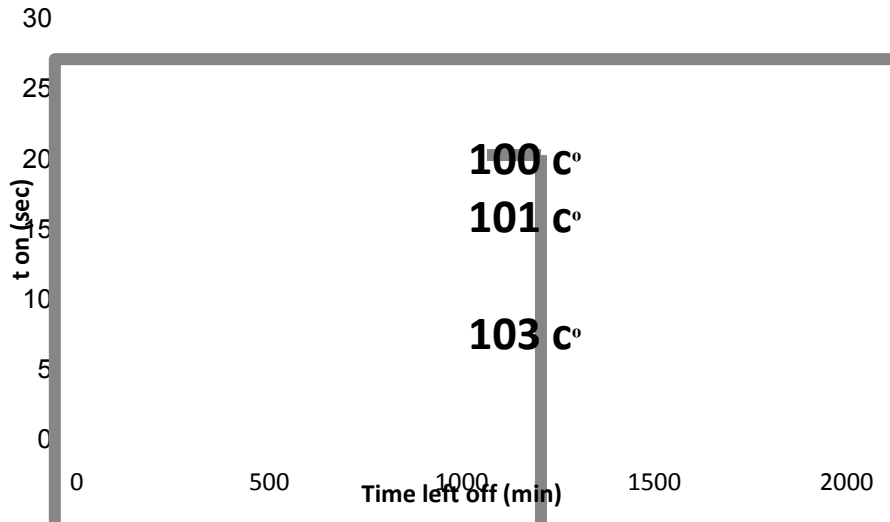


Fig. 11: The relation between t_{on} and time left off for polymer 3.

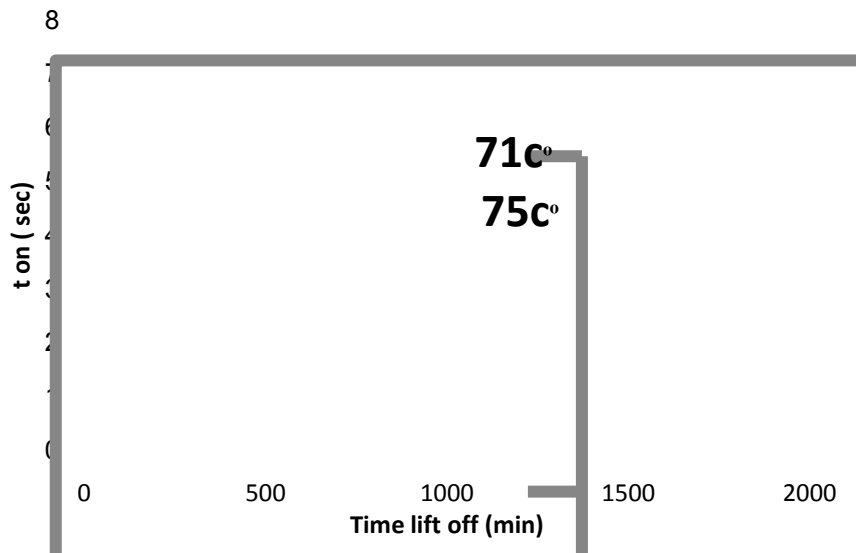


Fig. 12: The relation between t_{on} and time left off for polymer 4.

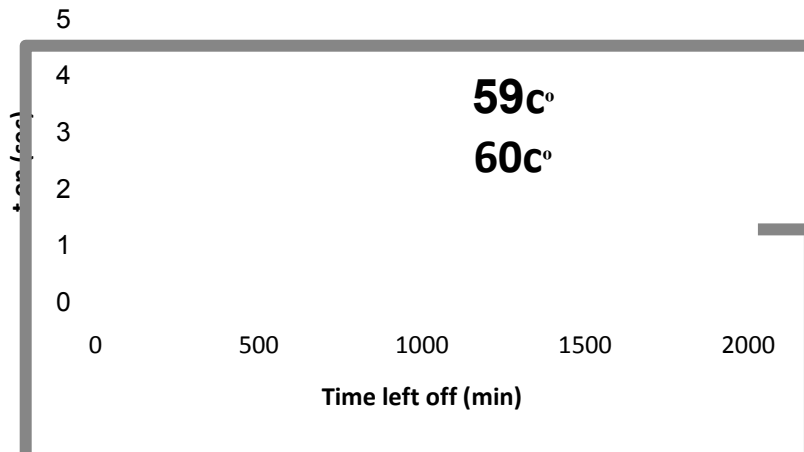


Fig. 13: The relation between t_{on} and time left off for polymer 5.

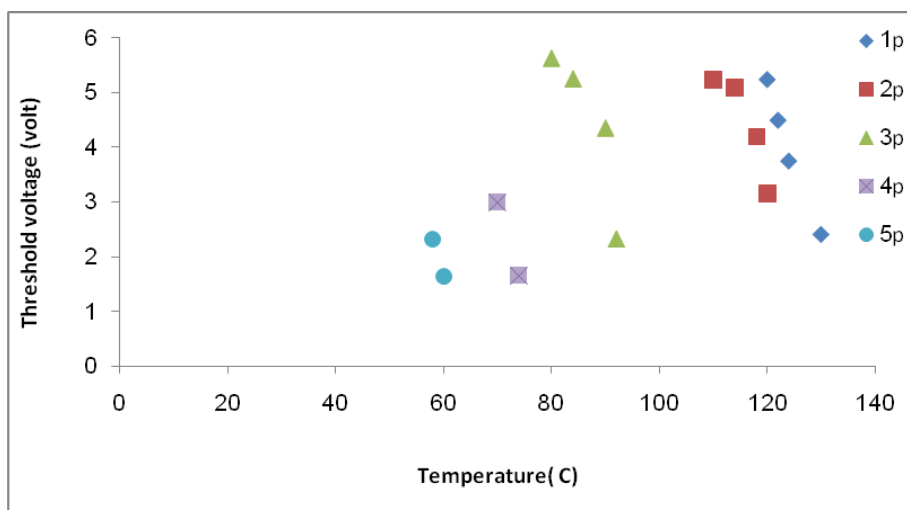


Fig. 14: Plots of the measured threshold voltages a function of temperature.

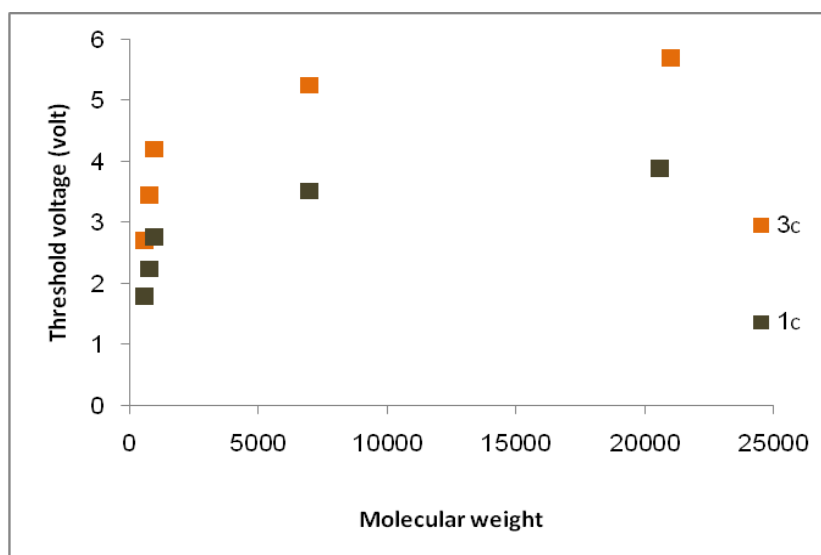


Fig. 15: A plots of the measured threshold voltages as a function of the molecular at (1 and 3) $^{\circ}\text{C}$ below TNI.

Discussion:

Variation of the degree of polymerization in this series of polysiloxan based side chain liquid crystal polymers has impact upon the phase behavior, the order parameter and upon the electro-optic properties. it is found that decreasing the molecular weight lower, the phase transition temperature for high molecular weight polymers (material no.1,2 and 3) a smectic phase is observed with very narrow nematic range however at low molecular weight (material no.4 and 5) only the nematic phase is observed. complementary to the reduction of the phase transition temperature with decreasing the molecular weight of the polymers there is a marked lowering of the glass transition temperature of value of the glass transition is found to increase as the molecular weight of the polymer is increased. Changing the molecular weight has a marked impact upon the switching times and the threshold voltage comparison of those results for \square off as a function of temperature with those measured using conventional optical relaxation techniques shows a significant difference which increases as the temperature is lowered, a similar trend was observed for a series of siloxane based side chain liquid crystal polymers figure shows that reorientation in an electric field results in electrical energy coupling to the mesogenic units. Since the polymer chain is coupled to the mesogenic side chain then this well also under go motion. However, the response of the mesogenic units and that of the polymer need not be on the same time scale. The polymer chain may take much longer to reach equilibrium and because of the week nature of the coupling this need not be evidenced by the orientation of the side chains on removal of the electric field, the side chains can relax independently of the polymer chain and this occur slightly ahead of the polymer chain relaxation. This slower relaxation of the polymer chain is only detected since it influences the subsequent

response to the electric field. The range of homo polymers behaved in a similar manner to many other reported liquid crystal polymers for example the switch on time decreased as the temperature was increased above the glass transition, such effects are related to the reduction polymer viscosity. In this study it is found that the higher molecular weight has the lower switch off times, this is attributed to the contribution from limited segment lengths of the polymer back bone in work of this these is a suggestion has been made that the differences in the molecular weight of the polymers.

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