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Effect of $BaTiO_3$ Nanoparticles Amount Addition on Electro-Optical Properties of Side Chain Liquid Crystal Polymer

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Abstract : In this paper of this studies the synthesis and characterization of liquid crystalline side chain polymers with mesogenic groups laterally attached to the polymer main chain are described by variation of the terminal group ,moiety ,a change in the glass transition temperature, the nonlinearity of liquid crystal cell doped different molecular weights with Barium Titanate nanoparticles $BaTio_3$ by considering their selective absorption This study focuses on the electro – optic properties of polymers with a different molecular weights based on the polysiloxane backbone. Additionally, it is found that adding barium titanate nanoparticles moieties will decrease the phase transition temperatures and thus decreasing of switching times , and which is due to in the viscosity of the polymer which is product from 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 . 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 .when decreases molecular weight The increases order parameter cause by 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. The application of a stress field to the elastomer while in the nematic phase result in a stress –induced alignment of the mesogenic units in the direction of the extension .The performance of the electro – optical cells has improved after add the barium titanate would reduce the contribution of the dipole moment of the cyano – group parallel to the molecular long axis of the mesogenic unit and thus reduce density of the mesognic unit attached to polymer chain and lead to a Increases of dielectric anisotropic ($\Delta\varepsilon$) and thus enhanced backbone mobility for the system.

Key word : Barium Titanate nanoparticales, Polysiloxane, electro-optic properties.

Introduction:

Studies being accomplished during the last few years show that the formation of liquid crystalline (LC) phases in polymers with mesogenic side groups follows mainly the regularities known for low molecular weight liquid crystals .These regularities concern the organization of structure in such systems[1,2] while the orientation of the polymers in magnetic and electric fields which became possible after the synthesis of some new nematic polymers with CN- containing mesogenic groups[3,4].

Mesomorephic side chain polymers made of mesogenic cores linked by one end to a polymeric backbone via flexible spacers have been known for a long time[5] Liquid crystalline polymers can be ordered into main chain, side chain and combined. This arrangement is based on the place of the polymer where the mesogenic is put in, the main chain, as side groups, or both within the main chain and as side groups[6] Sidechain liquid crystal polymers contain three basic types of molecular unit. These are the polymer backbone, the mesogenic or liquid crystal forming unit[7,8] This design principle of side –chain liquid crystal polymers are now well established[9] Polymers consist of large organic molecules (macromolecules) of repeating small structural units(monomers) connected together in a process called polymerization[10]. Each molecule is composed of thousands of atoms connected by covalent chemical bonds , molecules in polymer attract each other by forces that depend on the type of the polymer. As polymers consist of huge, combined molecules which are hard to polymer[11] Although the terms nanomaterial and nanocomposite represent new and thrilling fields in materials science, such materials have A nanocomposite is defined as a composite material where at least one of the dimensions of one of its constituents is on the nanometre size measure[12] liquid crystalline phases have recently been called the fourth state of matter[13] The order parameter ($\bar{S}$) in nematic liquid crystals is one between the most important physical parameters[14].The diectric ,optical and magnetic anisotropies depend on the order parameter vie the martial properties of liquid crystals .The orientation order parameters of liquid crystalline martials dependence of the temperature since their distinctive shape nematic liquid crystal molecules suffer stronger attractive forces when arranged parallel to one another. The value $\bar{S}$ for molecules completely orientation equal one although molecules randomly oriented equal zero, limits the director vector ($\hat{n}$) average direction or the chosen direction of the molecules and does not give degrees or force direction in the monomorphic of the liquid crystal, and variations from one point to another within the phase, producing the emergence of unclear appearance of the phases[14] in the liquid crystal molecules in relation to ($\hat{n}$) use orientation order parameters ($\bar{S}$) come into this term and which can calculate using the following formula[15]

$$\bar{S}=\langle\frac{3}{2}Cos^{2}\theta-\frac{1}{2}\rangle$$

Wherever 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)

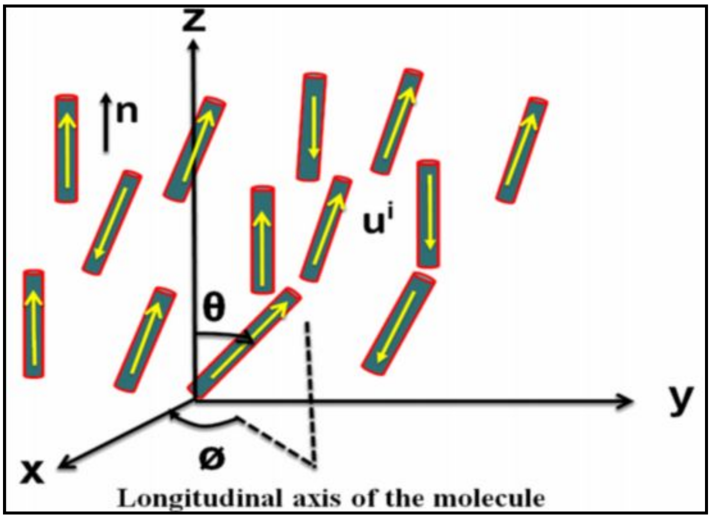

Figure (1): Orientation (θ, ø) relative to axes (x, y, z).

An electro –optic experiment involves the measurement of changes in the optical properties of thin films of the liquid crystal polymers induced through the to within a few seconds of arc. The glass was cut into plate of approximately 6 cm^2area, and etched using HCl acid with zinc metal powder, as a catalyst, to give a 2cm^2electrode application of electric fields. The experimental arrangement used for these electro –optic measurements has been described previously in detail elsewhere[16] 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 surface. Each glass plate was washed, in soup water and cleaned in an ultrasonic bath for 30 minutes at 60 °C. the optical system consisted on a 5 m W helium – neon laser with crossed polarizer and a analyzer system and a photodiode with amplifier for intensity measurements 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 form aimed], using a spin – coater running at 4,500 r.p.m these coated slides were heated in an oven for 30 minutes at 80oC 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[17]

Electric fields were provided by means of a power amplifier (Hewlett Packard 6827 A) driven by a function generator (Thunder TG 501) this arrangement provided waveforms in the range 0.05 to 30 KHz with peak to peak voltages in the range 0 to 240 volts . The intensity of the transmitted light through this optical was recorded as a function of time using a microcomputer system based around a 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. The elector – optic cells with predefined director orientation were constructed from patterned tin oxide coated glass slides . After cleaning in an ultrasonic bath and drying, the cell electrodes were coated with a thin layer of a polyimide precursor consisting of a 5% solution of Rodehftal 322 in dimethyl form amide using a spin-coater[18].

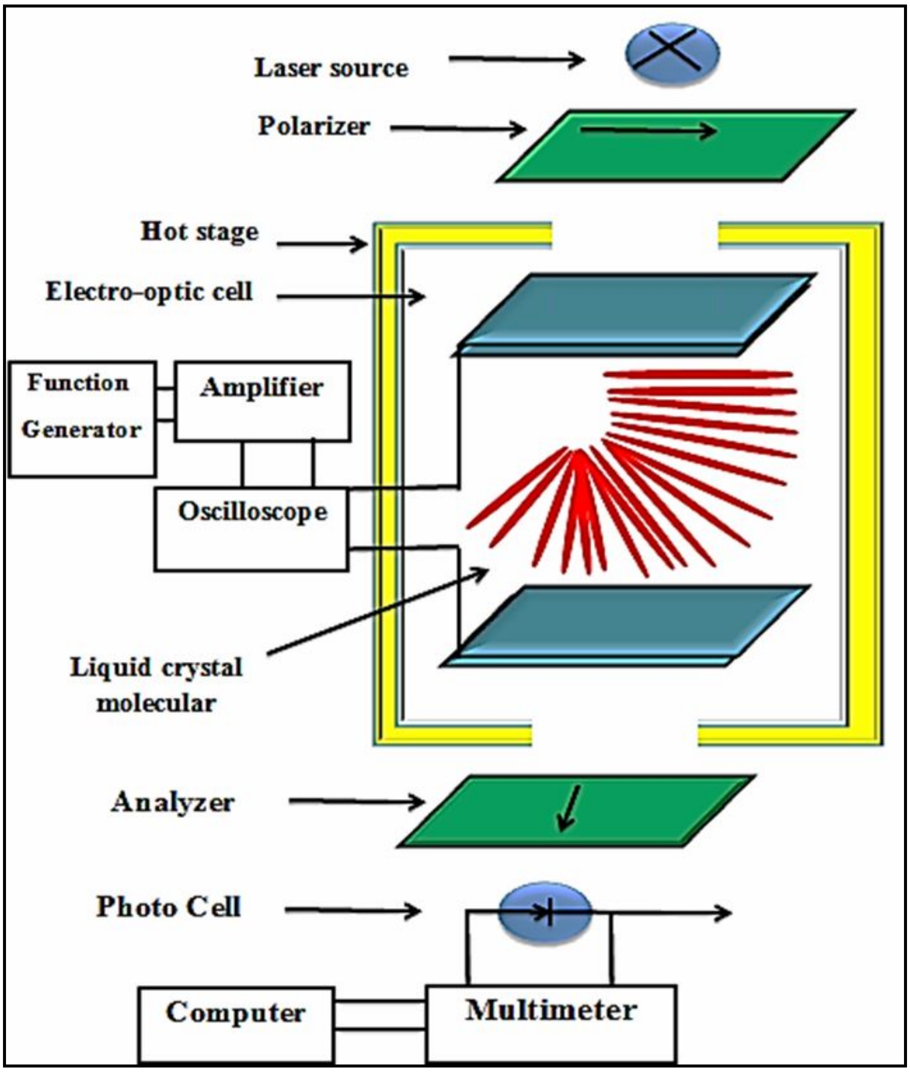

Fig (2) scheme of the work system

Experimental Set- up : (Mk 1000; Hcs 402; ALCT)

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 accyrate 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.

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 micropositionar for sample positioning Application software, wintemp, allows remote control from computer.

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 mixture.

- **Liquid crystal mixture physical parameters :**

- Dielectric constants, $\varepsilon \parallel$, $\varepsilon\perp$,$\Delta \varepsilon$

- Elastic constants, K11 and K 33
- Threshold Voltage, Vth
- Polarization current, IP
- Viscosity γ_1

- **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, which includes white LCD 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

1. Light sealable working chamber shields a way the room lighting.

Fig (3) picture of a device

Materials :

Chemical structures : used in this work.

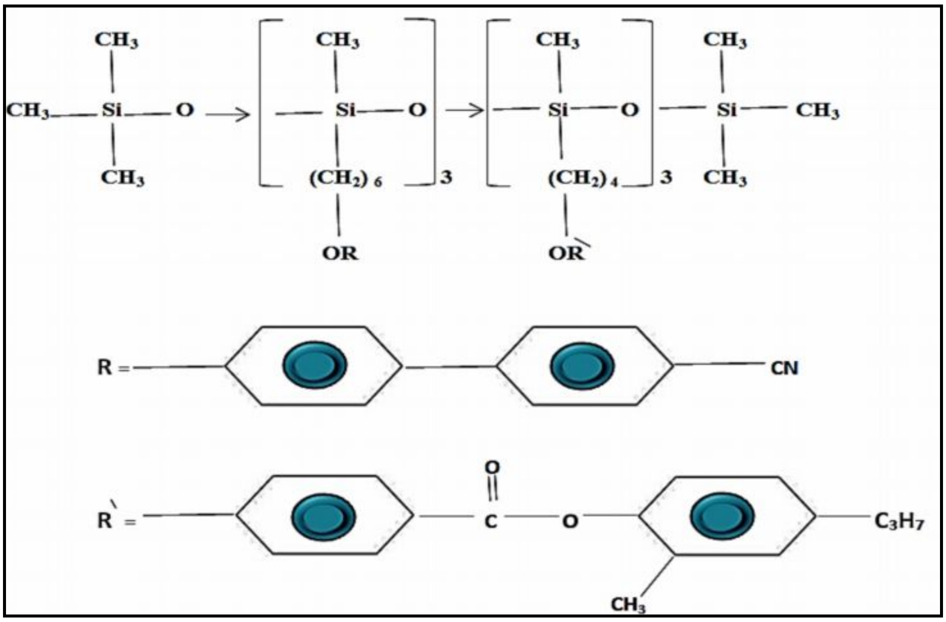

Figure (4): Structure of the polymer poly - siloxanes

Results:

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 and using one molecular weight with different addition from BaTio3. The required voltage is increased with increasing of molecular weight MW this is due to viscosity 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 voltage for the complete orientation are identified, applied to the cell, and calculates the required time to the occurrence of complete orientation. Where Fig (5) show switch on – time on as function of the time for which the field is switched off before the measurement. Using the system and the method described in work, we have implemented a cyclic experiment in which we use the values of to determine when a steady state is reach. As mentioned in work the approach allows both and to be evaluated. in order to achieve complete switching we typically applied (147-250) 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 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 electro – optic properties are important because they contain important experiments between the threshold voltage Uc and curvature elastic constants Kii 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 (4). There is a marked reduction in the threshold voltage for both increasing temperature and reducing the molecular weight. In this series of polymers, Fig (11) makes a direct comparison of the threshold voltage 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 polysiloxane 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. In the present study, using infrared dichroism to analyze the orientation ordering of the liquid crystalline side-chain polymers on prealigned cells, Also using the different molecular weights to obtain information about the orientation order of the head part, by observing the bands corresponding to the vibrations of the relevant functional groups, where the major vibration absorption band C≡N occur in the 2235 cm-1 region. The dependence of temperature with different molecular weight Mw .Where of these liquid crystals. It is evident that the polymers with the highest Mw exhibit the lowest reflect an incomplete monodomain formation due high viscosity, there was no experimental evidence to suggest that the measurements were anything other than true steady state values.

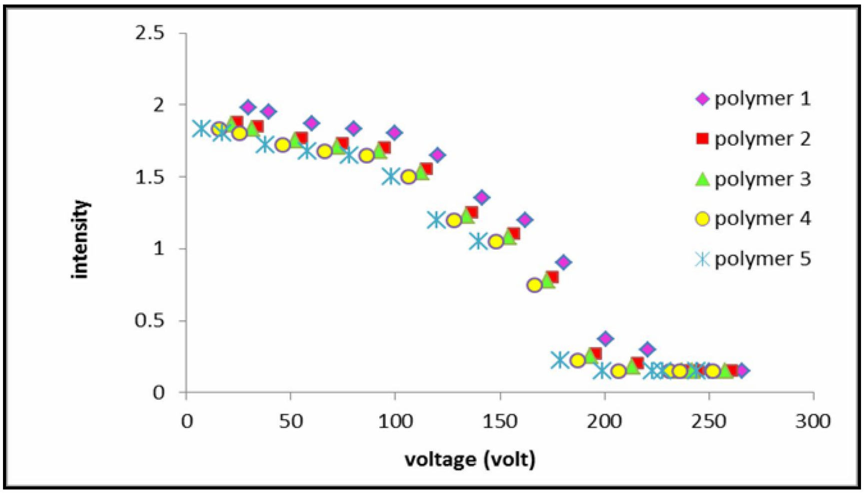

Fig. (5): Variation of the normalized intensity with voltage for polymer (1,2,3,4&5)

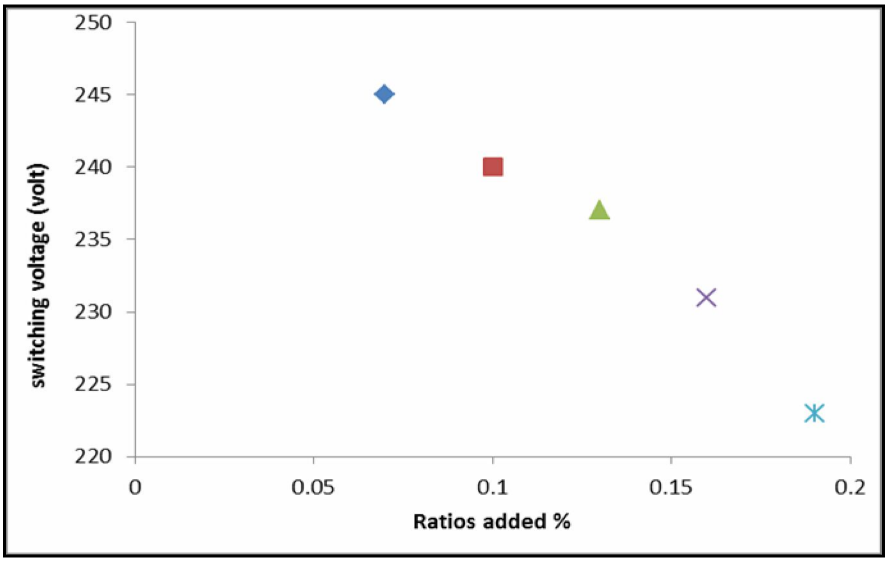

Fig. (6): Switching voltages as a function of gold additives ratios of polymers.

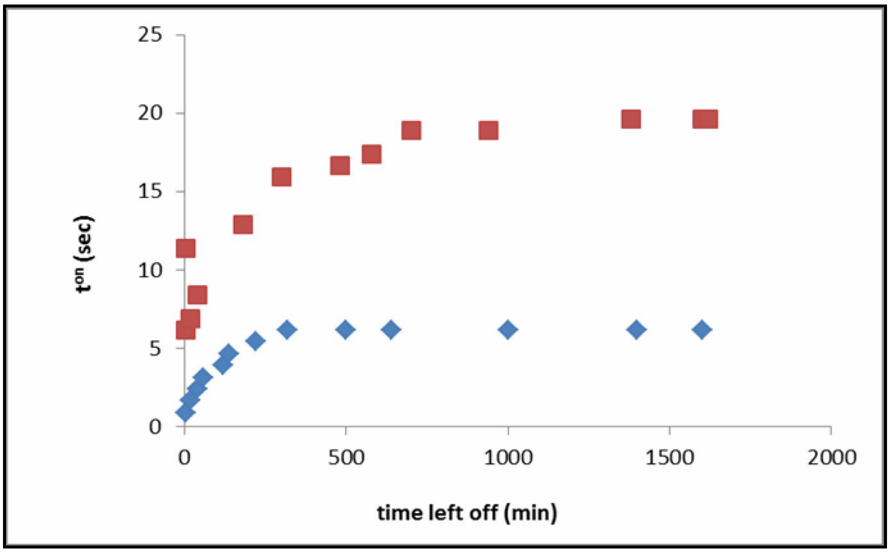

Fig. (7): Switching – on (t^{on}) and time left off (t^{off}) at constant temperature below TNI for polymer 1.

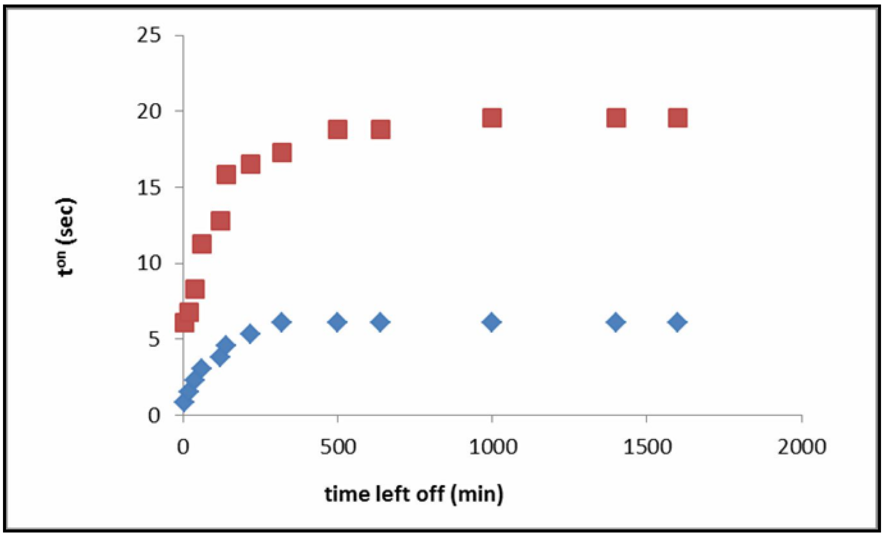

Fig. (8): Switching – on (t^{on}) and time left off (t^{off}) at constant temperature below TNI for polymer 2.

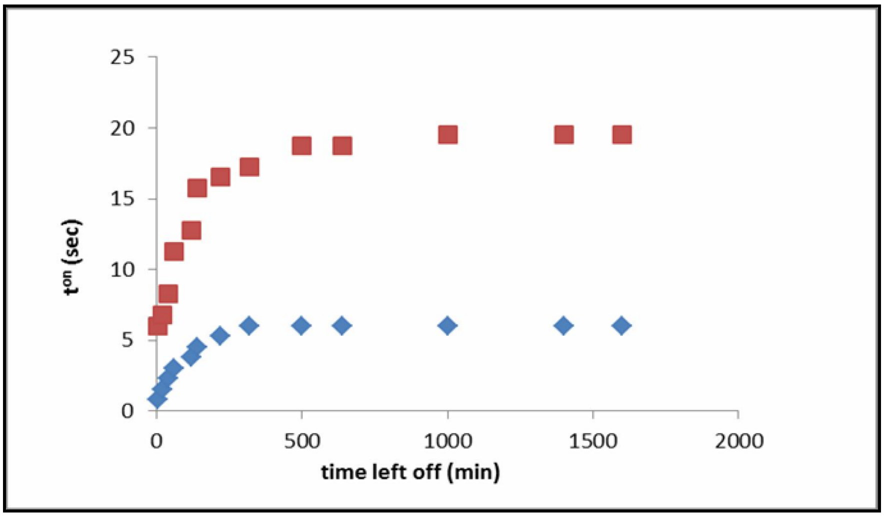

Fig. (9): Switching – on (t^{on}) and time left off (t^{off}) at constant temperature below TNI for polymer 3.

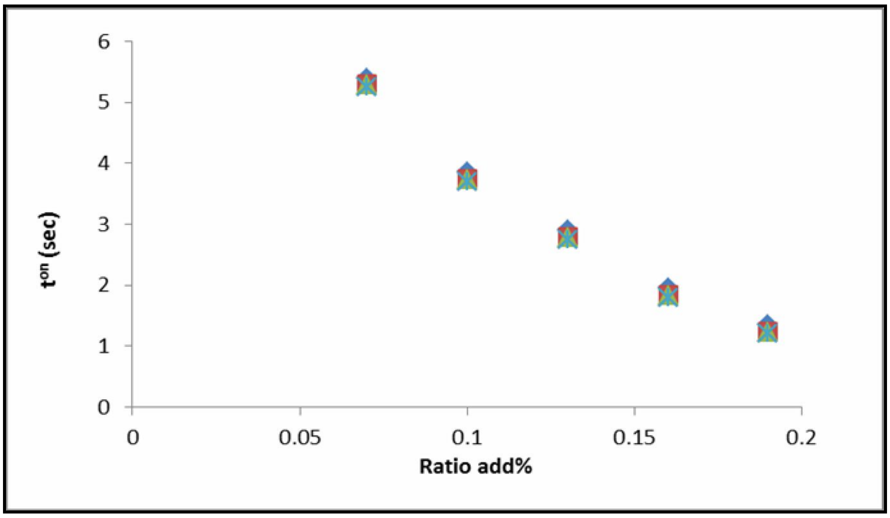

Fig (10): Switching – on (t^{on}) as a function of the ratios added for polymer poly-siloxanes.

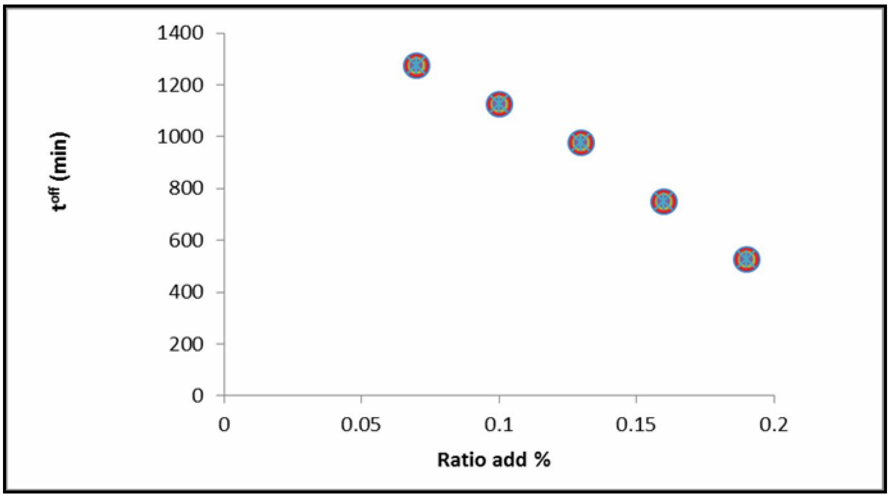

Fig. (11): Switching – off (t^{off}) as a function of gold additives ratios using the method exponential decay of the transmitted light signal.

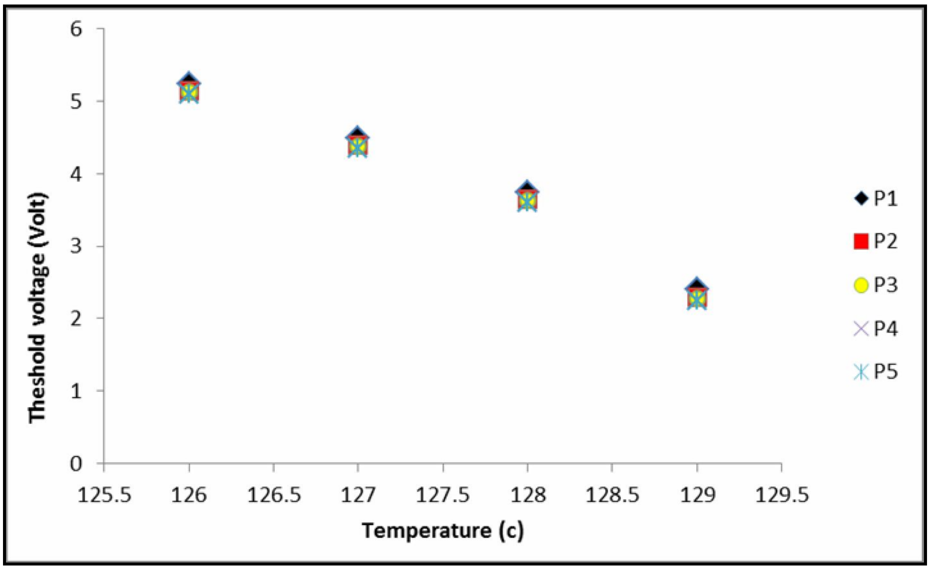

Fig. (12): Threshold voltages a function of temperature for polymer poly - siloxanes.

Discussion:

In this study, research on the impact of the BaTiO3 nanoparticles on electro-optical properties of liquid crystals polymer polysiloxan with side chain used different molecular weight, and when adding BaTiO3 nanoparticles which is equal (0.07) to the polymer polysiloxane with side chain will work to increase the viscosity of the polymer, as well as the works of these nanoparticles added to increase connectivity polymer shed when an electric field, and working to reduce the degree phase transition of polymer, this leads to reduce the switching times (9).

Finally redeeming range Syano was chosen because of the interest in electrical characteristics of the polymer could make it particularly suitable for applications, and in any case add BaTiO3 possible particles increase the density mesogen units which are connected with a series polymer to increase the contribution of dual-electrode parallel group Syano molecules torque along the axis mesogen Group this in turn increases the dielectric anisotropy Δε. It is found that decreasing the molecular weight lower, the phase transition temperature for high molecular weight polymers (materials no.1,2 and 3) a smectic phase is observed with very narrow nematic range however at low molecular weight (material no.4and 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 market 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.

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