

Effect of Molecular Weight on The Static Electro – Optic Properties of Polysiloxane Liquid Crystal Polymers

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Abstract :

This study focused on the electro - optic properties of a total or a series of polymers that have different molecular weights and are based on the polymer backbone. It is found that low molecular weights reduces the transition temperature and eventually leads to a destabilisation of the nematic phase, the effect of reducing the molecular weight of the polymer is to lower the observed threshold voltage. This may be related to an increase in the intrinsic elastic constant of the liquid crystal polymers. It is found that there is a strong coupling between the mesogenic side chain groups and the polymer chain and that the elasticity of the polymer chain plays a strong role in the static electro – optic properties .

Keyword : polysiloxane , electro – optic properties

الخلاصة

هذه الدراسة ركزت على الخواص لمجموعة أو سلسلة من البوليمرات التي تمتلك أوزان جزيئية مختلفة و مبنية على عمود فقري لبوليمر البولي سايلوكسين . وجدت ان الاوزان الجزيئية المنخفضة تقلل من درجة حرارة انتقال الطور وفي النهاية تسبب عدم استقرار في الطور النيماتي، وتأثير انخفاض الوزن الجزيئي للبوليمر تقلل فولتية العتبة. وهذا من الممكن أن يكون له علاقة بزيادة ثابت المرونة للبوليمر . وجد إن هنالك ارتباط قوي بين الجانب الميزوجيني في البوليمر ولذلك فان مرونة البوليمر تلعب دور قوي في الخواص الكهرو بصرية .

الكلمات المفتاحية: polysiloxane ، والكهربائية – الخصائص البصرية

Introduction

Material that exhibit liquid crystalline phases have been recognized for almost a century (RENTZER,1888) yet it is only over the last two decades that such materials have evolved from the laboratory curiosity stage to become the basis of a new science. Liquid crystalline phases have recently been called the fourth state of matter. (SAEVA,1979) however, such a definition belies the richness of structural properties that characterizes the many different liquid crystalline phases and leads to the immense interest in their behavior.

A liquid crystalline phase is generally defined in terms of the long – range intermolecular order exhibited by its constituent molecules in a crystalline phase there are three degrees of long – range positional order. In a liquid crystalline phase at least one of their in on long – range positional order. There may, however, exist short range rotation or orientational order between the molecules if they exhibited a shape a anisotropy, so that a true isotropic liquid phase is only exhibited when neither positional long – range nor orientational short – range order exist. Thus, if one or more of these degrees of positional or rotation order are manifest by the anisotropy molecules, then we have a useful definition of the crystalline phases

(HILSUM, 1983). As shape anisotropy is a prerequisites in this definition we might expect macroscopic properties such as refractive index, electric conductivity, viscosity and elasticity also to be anisotropic. since liquid crystalline phases are also fluid, external fluids (magnetic, electrical, optical, mechanical and thermal) may be used to Induce changes these properties . it was the interdependence of the optical and electrical properties and the quest for new electro – optic devices that led to the recent resurgence of interest in liquid crystalline phases(HILSUM, 1983).

Experimental :

Blazers 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 6cm^2 area, and etched using HCL acid with zinc metal powder, as a catalyst, to give a 2 cm square electrode surface. Each glass plate was then washed by hand, in soup and water and cleaned in an ultrasonic bath for 30 minutes at $60\text{ }^\circ\text{C}$. 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 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 .(Saemgsuman , 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, 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 , 2005). The thickness of the cells were measured using micro meter techniques, both gave similar results, with typical electrode separations in the range $0.0026 - 0.030\text{ mm}$ 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, 2007),(Channuau, 2008),(Wangsonb, 2008) fig(1) shows the electro-optical cell construction.

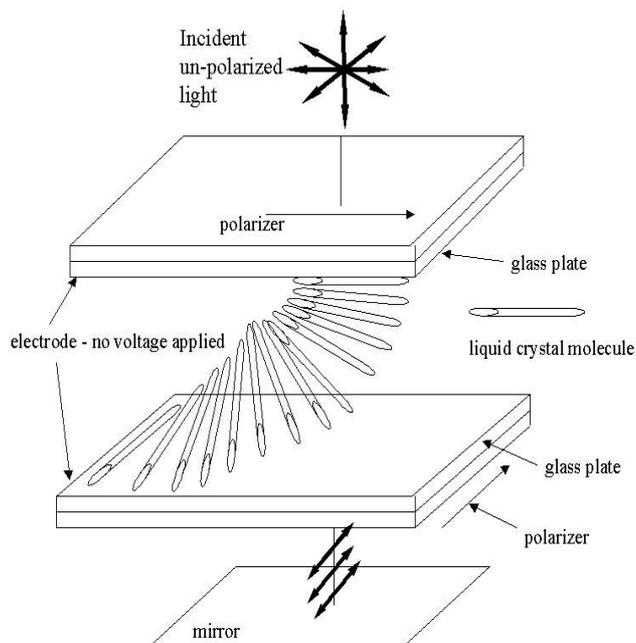


Figure (1) Electro – optic cell

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. when coupled with heating / cooling equipment from instc , the mk 1000 can provide temperature control which is accryate to 0.001°C. 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 0.001°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 micropositionar for sample positioning

Application software, wintemp, allows remote control from host 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

• Liquid crystal mixture physical parameters :

- Dielectric constants, $\epsilon_{||}$, ϵ_{\perp} , $\Delta \epsilon$;

- Elastic constants, K_{11} and K_{33} ;

- Threshold Voltage, V_{th} ;

- Polarization current, I_p ;

- 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° range;
- Light source, polarizer and analyzer are installed in sealed dark sections to prevent the contamination of optical components;
- Light sealable working chamber shields a way the room lighting.



Figure (2) picture of a device .



Figure (3) picture of a device with optical test bench subsystem .

Materials :

Chemical structures

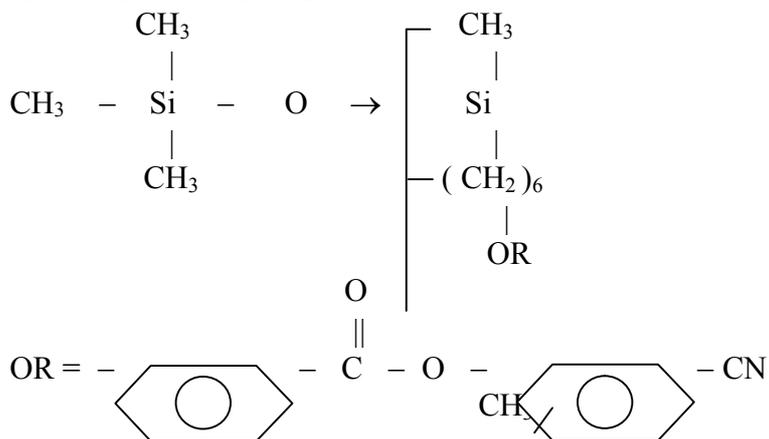


Table (1): Molecular weight and phase transition data polysiloxane

polymer	mW	Dp	T _g °C	T° C	T _{Ni} °C
1	1.7×10 ⁶	320	48	126	130
2	8.1×10 ⁵	102	40	121	125
3	7.2×10 ⁴	15	26	99	104
4	4.5×10 ³	7	16	72	77
5	3.1×10 ³	4	4	56	61

Results

Static electro-optic properties

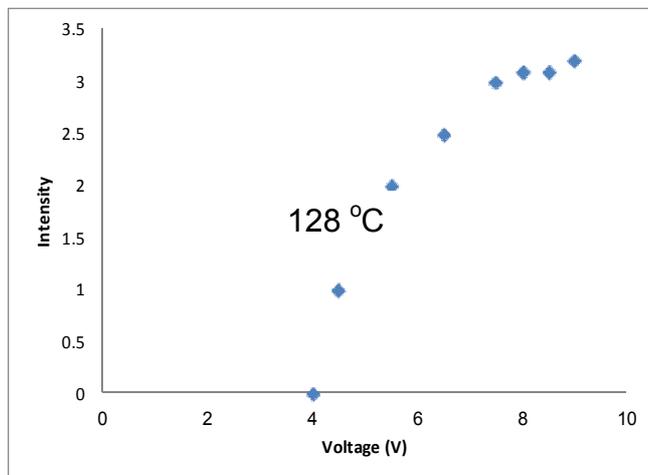
We have used the experimental arrangement described above to evaluate the static electro-optic properties for each member of the molecular weight series of the side chain liquid crystal polymers shown in Table 1. In these experiments, we determine the minimum or threshold electric field required to distort the surface predefined director orientation. In this geometry, the electric field perturbs an initial planar surface alignment and this mode of deformation is dominated by the splay component of the curvature elasticity K_{11} for small deformations. The threshold voltage is related to the curvature elasticity.

$$U_c = \sqrt{\frac{K_{11}}{\epsilon \Delta \epsilon}}$$

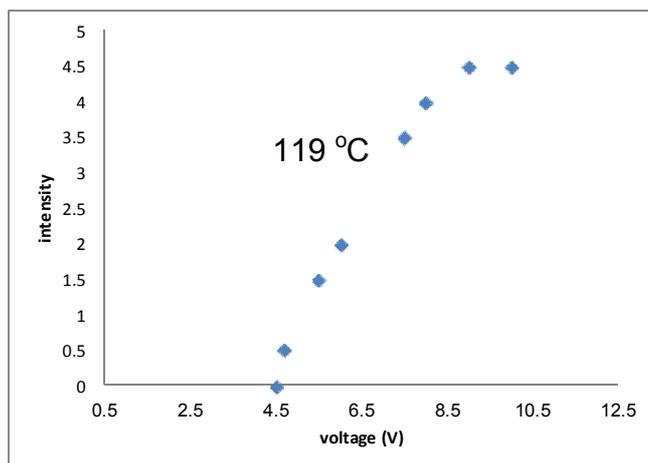
where $\Delta \epsilon$ is the anisotropy of the dielectric permittivity and U_c the threshold voltage. From this equation it can be seen that the evaluation of K_{11} should be straight forward procedure through the measurement of U_c , however for a polymer system there are a number of particular problems of evaluating U_c , each of which relates to the high viscosity of the polymer. The most important is to ensure 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 established the real relaxation of the polymer system through use of cyclic electro-optic. 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. As the response time at low voltages is long we determined the threshold voltage 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 each the steady state between each voltage step the samples were left for about 3-5 hours and this was checked by monitoring the transmitted light versus time.

Typically at each stage the sample was held for period of time ten times longer than the response time. The results obtained for the materials in this study are presented in Fig(6). There is marked reduction in the threshold voltage for both increasing temperature and reducing molecular weight. In this series of polymers, the chemical composition other than the proportion of end-groups, is unchanged and hence, should be unchanged and therefore the observed variations in threshold, voltages must arise as a consequence of the differing degrees of polymerisation.

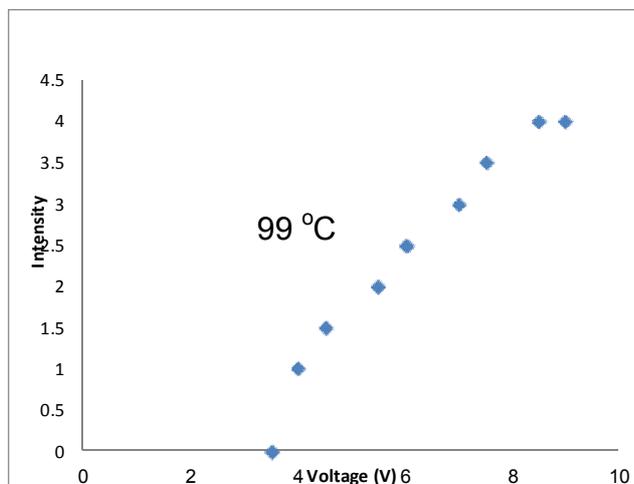
Fig(7) marks a direct comparison of the threshold voltages obtained in the nematic phase at constant step below T_{NI} for the series of polymers prepared. It is clear that there is an increase the threshold voltage with increasing molecular weight .



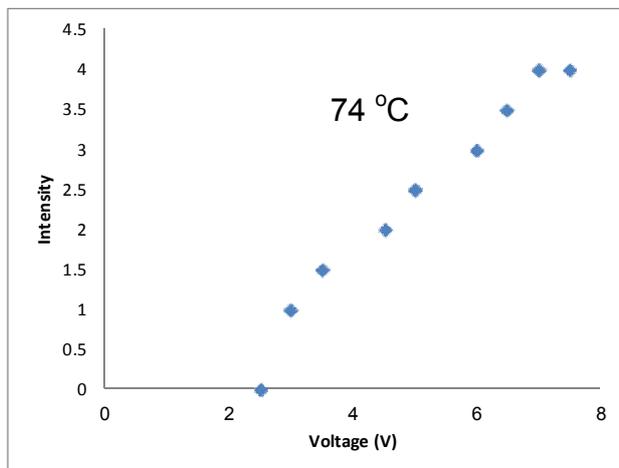
Figure(4): the relation between voltage and intensity for polymer 1.



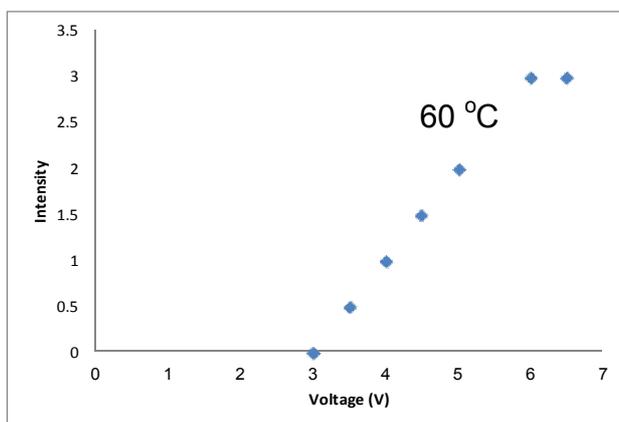
Figure(5): the relation between voltage and intensity for polymer2.



Figure(6): the relation between voltage and intensity for polymer3.



Figure(7): the relation between voltage and intensity for polymer4.



Figure(8): the relation between voltage and intensity for polymer5.

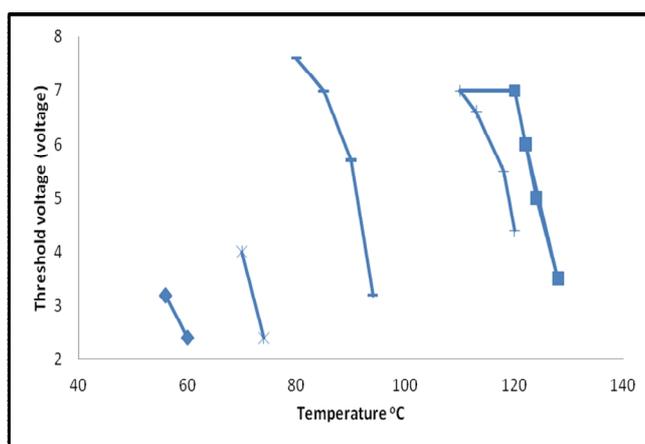
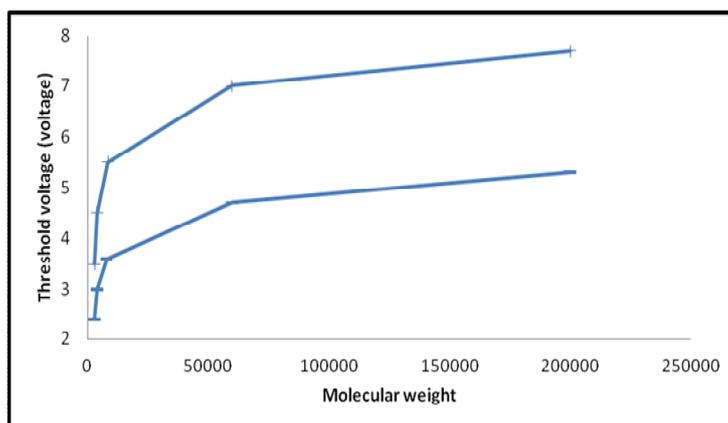


Figure (9):plots of threshold voltages as a function of temperature .

1 (■) , 2 (+) , 3 (-) , 4 (*) , 5 (◇)



Figure(10): Plots of threshold voltages as a function of the molecular weight at 1°C (-) and 3°C (+) below T_{NI} .

Discussion :

It is clear that increasing the molecular weight will not change the magnitude of $\Delta \epsilon$ and hence if the curvature elastic constant is unaffected by the degree of polymerisation the threshold voltage should be constant the observation that U_c increases with increasing molecular weight indicates an increase in the elastic constant K_{11} the increase of the intrinsic elastic constant may be attributed to changing levels of interaction between the mesogenic units and the polymer backbone . There is evidence for this from small angle neutron scattering experiments carried out by hardouin *et.al.* (Mohan, 2011). On different molecular weight polysiloxane based polymers. They found that the anisotropy of the radius of gyration increased by (30-40)% on an approximate doubling of the molecular weight it is possible to divide the contribution of the molecular chain to the apparent curvature elasticity into two components . The first arises from the elasticity of interactions between the chains as might arise from entanglements such effect have been observed in the electro-optic properties of cross – linked side chain liquid crystal polymers (Mohan, 2011) and the increase in the threshold voltage was substantial . It would perhaps be expected that the threshold voltage would be much lower when the molecular weight falls below. That critical weight required for entanglements and this additional elasticity would increase with increasing temperature the second contribution arises more directly from the coupling of the mesogenic units to the polymer backbone and is perhaps typified by the increase in the threshold voltage which arise as the coupling chain is shortened (Mohan, 2011). It is not clear here which is the dominant factor.

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