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Order Parameter and Elastic Constants Studies of Liquid Crystals

Khalid Al.Ammar[1], Naheda Humood Al.Garah[2]
[1]Physics Department – college of Education for pure science–Babylon University
[2]Physics Department – college of Dentistry –Babylon University

Abstract
This study focused on the smectogenic polysiloxane, PG296, and the nematogenic, PG375, Where noted the lower order parameter at higher molecular weight polymers, they do support the overall trend of an increased nematic range with increasing polymer concentration. The reduced solvent power of 5CB when used with the polymer PG375 might be associated with the lack of side groups of similar cyanobiphenyl structure in the polymer but could also be related to the strong dipolar anti-parallel associations that might be expected to form between the cyano terminated polymer side groups, thus locking in the backbone configuration. The elastic constants and S2 as a function of polymer concentration, where the constants decreases with increasing concentration of the solution.

 Keyword: liquid crystals, polysiloxane

I.   Introduction

The chemical structures of polysiloxane the smectogenic polysiloxane used in these studies, PG296, and the nematogenic, PG375, are presented for side-by-side comparison in figure 4. Both materials have a 52-unit polysiloxane backbone, flexibly coupled to the rigid aromatic groups by an aliphatic chain that contains four or six carbon atoms.

The side group elements in the homopolymer PG375 possess many of the features of the side group elements of the copolymer PG296. These similarities in chemical structure were selected to minimise the number of variables that might have been expected to influence the properties of the solutions formed as increasing concentrations of the polymer were added to the pentyl cyanobiphenyl, 5CB. The remaining differences in polymer structure, which were expected to be highlighted by experimental investigation of the solutions, were the similarity between PG296 biphenylsubstituentR(see figure4) and 5CB, expected to aid the solubility of the polymer in this solvent. The non-polar group R -, copolymerized with R in PG296, expectedto influence the anti-parallel ordering of the nematogenic elements and the ratio of bend to splay elastic constants [1,2]. The ester linkage in the homopolymer PG375 side group which, together with the methyl substituted benzene ring decreases the length to width ratio of the group. This was expected to more noticeably affect the order parameter of the solutions in the higher concentration of benzoate ester associated with the homopolymer solutions.

II.   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 6cm2 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 oC.

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 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 130oC [3].

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 [4]. 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 Geiger) 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 [5]. 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 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 [6, 7, 8] fig (1) shows the electro-optical cell construction.
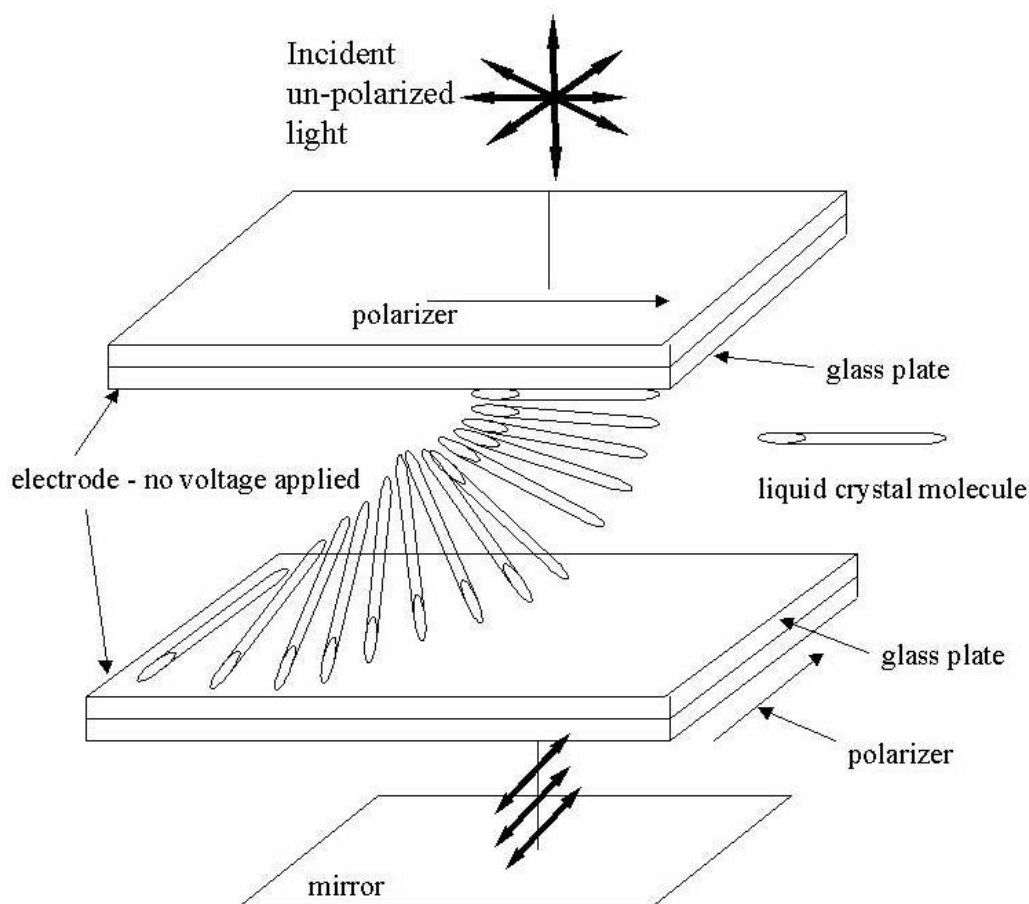

Figure (1) Electro – optic cell

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 that 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.

Place the mk1000 controller on a level clean surface with sample ventilation if the mk 1000 controller is equipped with a cooling fan. Make sure the vents on the sides are unobstructed the rear parallel of a standard mk 1000.

All connections to the mk 1000 use different types of ports eliminate the possibility of an incorrect connection a minimum configuration uses only the sensor / heater port for connecting the hot stage or hot chuck cable to, and the line power input port for connection the power cable to additional connection for communications and cooling accessories are available depending on the feature purchased do hot connect power cable and turn on the mk 1000 until all other connections have been made.

Temperature control system, which includes MK 1000 controller, nitrogen container nitrogen pump (LN2 - p), and hot – cooling stage. 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.

Features:
1-   Two operation modes, keypad operation using the front panel of the controller, or software control though PC.
2-   User adjustable ramp (rate of heating / cooling) to user set temperature point.
3-   Program able operation command set.
4-   Wide temperature range.
5-   Precisely controls temperature to 0.001 0C option save temperature data to the 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, $\square \parallel$, $\square \square$, $\Delta\square$;
- -   Elastic constants, K_{11} and K_{33};
- -   Threshold Voltage, V_{th};
- -   Polarization current, I_p;
- -   Viscosity, $\square 1$;
- •   Optical performance of LCD devices
- -   Voltage – transmittance curve;
- -   Switching speed, rise, falling time.
- •   Application software, WinLC, provides user an integrated tool 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;
- •   Light sealable working chamber shields a way the room lighting.
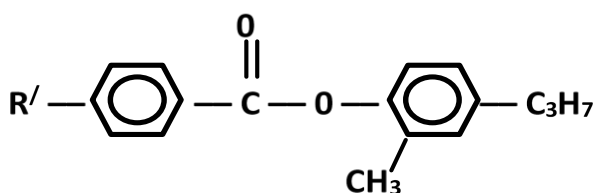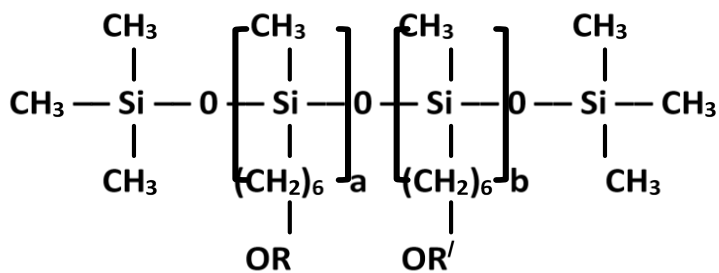

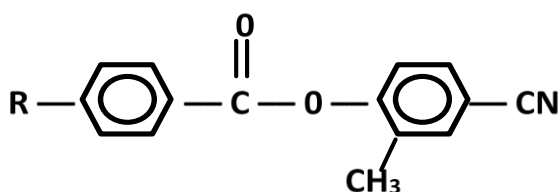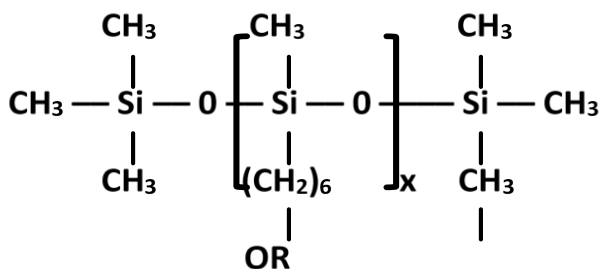Figure (2) picture of a device.

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

Materials and phase behavior:

PG296

PG375

Figure 4: The chemical structures of the side chain polysiloxane liquid crystal polymers used in this work. For the copolymer. PG296, a=b=26, and for the homopolymer, PG375, x = 52.

The phase diagrams determined for these polymers, in solution with 5CB, are presented in) figures5(a and b. Solutions of smectogenic PG296 exhibited a nematic mesophase in the solution concentrations studied. The nematic to isotropic transition of these solutions was characterized by a narrow stable, biphasic region in which the isotropic and nematic phases coexisted. The temperatures at which this transition occurred was monitored optically by microscopic observation of thin film samples and thermally by DSC for the 22.5 and 38.3% w/w solution concentration. Good agreement was found between the results of these techniques to within $O.5\square C$. The stability of the phase transition suggests that the solution itself was stable under the conditions in which it was stored and used. The biphasic region occurred at a steadily increasing temperature, with increasing polymer concentration and remained quite narrow at approximately $1\square C$ in comparison with the behaviour of the pure smectogenic polymer [9,10].

This behaviour may be capered with the nematic to isotropic transition behaviour observed for the solution of PG375 in 5CB, see figure5b. The results of the observation, of nematic to isotropic transitions in relaxed thin film samples or drop of solution on microscope slides are shown in the figure, that the solutions formed between PG375 and 5CB only produced repeatable behaviour at the nematic to isotropic transition if sufficient time had elasped since the last mechanical deformation of the system. This effect was suggested to be due to the changes in the polymer backbone conformation. The suggestion made, that the relaxed state of the polymer backbone might be a random walk conformation, dominated by attractive van der Waals interactions between the side chain groups, carries with it the implication that the solvent action provided by 5CB is not sufficiently strong to penetrate this conformation and hence oblige the polymer to adopt a more open structure. This behaviour is analogous to the results of studies on the chain conformation of non—mesogenic polymers in various isotropic solvents in which the configuration of the polymer chain may be controlled by the choice of solvents, strong solvents being better able to penetrate the convoluted chain and hence modify the structure. The reduced solvent power of 5CB when used with the polymer PG375 might be associated with the lack of side groups of similar cyanobiphenyl structure in the polymer but could also be related to the strong dipolar anti-parallel associations that might be expected to form between the cyano terminated polymer side groups, thus locking in the backbone configuration.
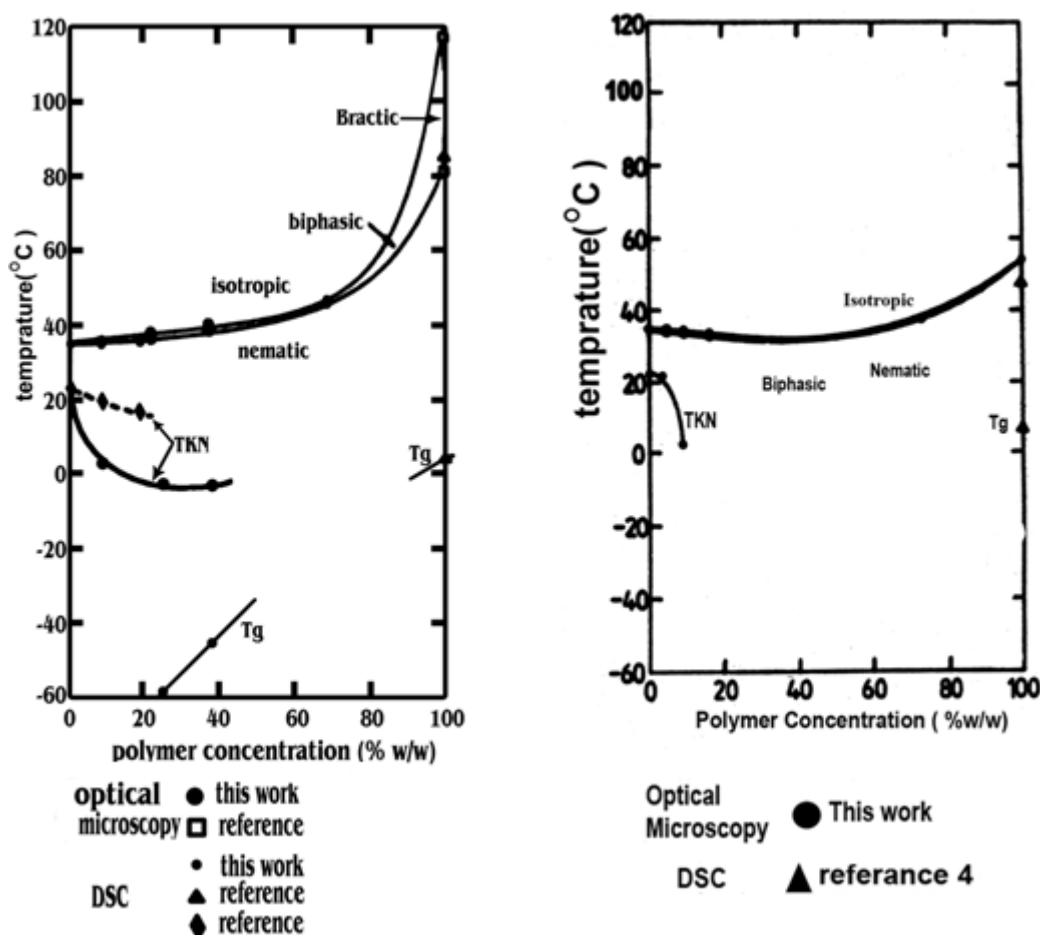
Figure 5: Phase diagrams showing the data presented in this work and other data from the literature, for the entire solution concentration range of both suites of solutions. The data collected from solutions of PG296 are presented in (a), and those from solutions of PG375 in (b).

Low temperature data is also summarized in figure5. For.PG296 solutions, the low temperature data, presented as part of this work, show the results of optical and DSC observations of TKN and Tg. The exhibition of both transitions in the DSC results for the 22.5 and 38.3% w/w solutions did not occur in the same measurement but depended upon the thermal history of the sample. The DSC results from reference 5 may be seen to lie somewhat high of the results reported herein, perhaps due to a different annealing procedure, but none the less, they do support the overall trend of an increased nematic range with increasing polymer concentration. The marked upward trend in Tg.

Order Parameter and Elastic Constants:
The order parameter and elastic constants of the PG296 and PG375 solutions are presented as a percentage of their values far 5CB at Tc-T=10□ C and as a function of polymer concentration in (figure 6) a and b, respectively. This value of reduced temperature was selected to allow the inclusion of K22 data from reference 5, and the values of K11 for

the PG296 solutions have been incremented to account for the Siox alignment used to evaluate K11 for the PG375 solution.

All parameters presented in figures 6 can be seen to decrease with increasing polymer concentration. This important feature of the addition of the polymers to 5CB was suggested to be the result of a dilution of the forces which create the nematic phase, due to an increased wean separation between nematogens caused by the presence of the non - mesomorphic polymer backbone.

The slight differences between the refractive index results for both polymer solution suite are enhanced in the values of S2 presented in the figures. For the PG375 solution, the reduced length to width ratio for all the polymer side chain groups say have contributed to the extra change in order parameter in comparison with the PG296 solutions' results. The effect on order parameter of the instability of the PG375 solutions, exhibited by the birefringence measurements. In figure 6a, is also evident in figure 6b.
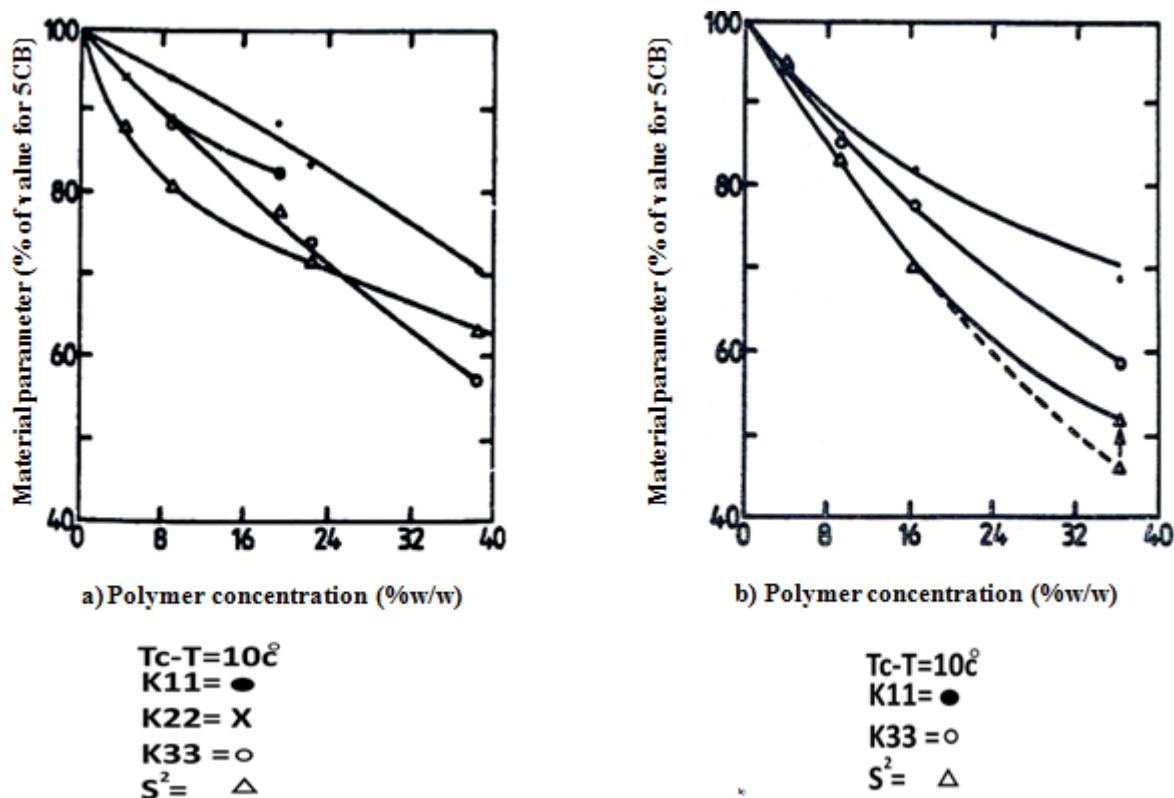
Figure 6: Order parameter and elastic constant data for solution of (a) PG296, and (b) PG375, presented as a percentage of their values for 5CB at Tc—T=10°C.

The splay and bend elastic constants for both solution suites can be seen to have decreased by approximately the same degree at the highest solution concentration. The twist elastic constants however, reported in reference 5 for some of the PG296 solution; appear to have more closely followed the parameter S2. Inspection of the other material parameters for the 19.5% w/w solution presented in this work reveals that they lie systematically high of the values that might be expected if the change in material parameters were a steady function of solution concentration. It is suggested, therefore, that the value of K22 at this concentration might also be slightly higher than should be expected, and that the behaviour of the twist elastic constant as a function of concentration might sore nearly follow that of the bend elastic constant.

The reduction of the bend relative to the splay elastic constant for low molar mass nematic mixtures have been discussed in terms of the reduction of anti—parallel ordering[1] and, more recently, an enhancement of the smectic—like local ordering[2,11]. The former explanation would seem unlikely to be responsible for the observed trends in this study as the solution. Show different anti—parallel ordering at a given concentration, but similar decreases in the ratio of the bend to splay elastic constants. The latter explanation would require X-ray scattering investigation to establish the possible correlation between any local smectic—like structure of the solutions and the reduced elastic constant ratio. What is remarkable in the results presented for these polymers is the similarity between their elastic constant behaviour. The overall reduction in their magnitudes was discussed in terms of the presence of the polymer backbone. Perhaps it is with respect to this restriction in side group motion and position imposed by their attachment to the backbone, that the relative changes observed should be discussed. In particular, for the splay deformation, when the mesogenic elements move to increase the distance separating their ends, the gap that develops must be filled with other molecules if the overall density of the material is to remain constant. For mesogenic elements attached to a polymer backbone, the increased separations of the ends of the flexible aliphatic group is hindered by the backbone, which may be considered as providing a resistive force. The increased force required to achieve this deformation in the solutions may account for the smaller decrease in K11 than K22. The preparation of solutions from a polymer with the same backbone length, but a reduced number of side groups, might allow experiments into the relative importance of the dilution or restriction mechanisms for the interaction of the polymer backbone with the nematogenic elements.

For the sake of completeness, figure 7 a and b show the change in the ratios of each elastic constant to the square of the order parameter as a function of solution concentration for polymer PG296 and PG375, respectively. The values of K22 are those presented in reference 5. The reader is reminded that the error in this ratio was estimated to be ±7%. Within the limits of this error, the ratio can be seen to be approximately constant as a function of polymer

concentration [12, 13]. The solution instability shown for the highest concentration sample of PG375 solution in figure 7b must still be regarded as significant, even with errors of this magnitude to take into account. The similarity in behaviour of the elastic constants and S2 as a function of polymer concentration supports the suggestion that a similar mechanism may be responsible for their reduction as a function of increasing solution concentration.
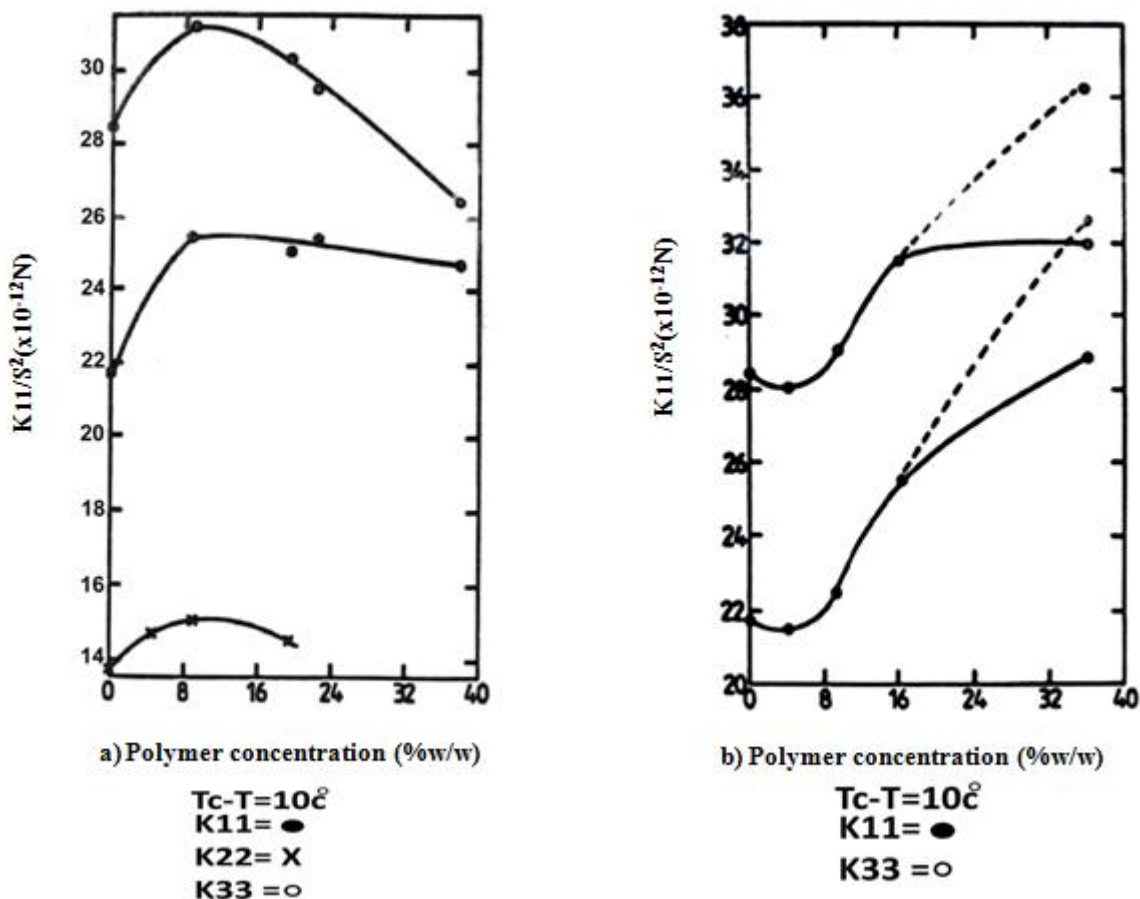

Figure 7: Variation of the ratio of each elastic constant to the square of the order parameter for (a) the PG296 solutions, and (b) the PG375 solutions. The data are presented as a function of solution concentration at Tc − T =10°C.

III. Conclusion

The differences and similarities in material parameters observed for solutions of smectogenic polysiloxane, PG296, and the nematogenic PG375 in pentyl cyanobiphenyl have been discussed in terms of the chemical structures of the solutes and solvent, and the physical interactions between the molecules. In particular, the relative stabilities of the solutions formed, and the permittivity components of the solutions were Contrasted in terms of the differences between the structure of the polymers' side groups and the chemical structure of the 5CB solvent.

The similarities in the remaining material parameters were associated with the incorporation of polymer backbone into the solutions as a function of

increasing polymer concentration, and the resulting dilution of the forces required for the formation of a well ordered nematic phase.

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