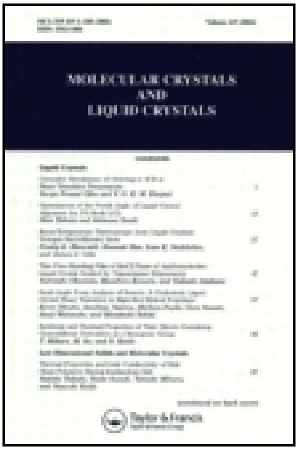

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Phase Transition Temperatures of LCs using Fabry-Perot Etalon

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Phase Transition Temperatures of LCs using Fabry-Perot Etalon

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A spectroscopic technique using the Fabry-Perot etalon coupled with a spectrometer has been used to determine most accurately the phase transition temperatures of a wide range of liquid crystals viz. nematic, smectic and cholesteric. Using this technique *new mesophase transitions* have been detected and classified for the cholesteric liquid crystals(13). These findings have been corroborated by the analysis of the thermal runs of the same samples using Differential Scanning Calorimetery. The technique has been applied successfully to determine the *PTTs* of FLCs and AFLCs too. A comparison of the results obtained by us with those reported by others clearly indicates the success of the Fabry-Perot technique in determining the **PTTs** with greater sensitivity.

Keywords: 1. Phase Transition Temperatures; 2. Phase Transitions using Fabry-Perot Etalon; 3. Liquid Crystal Mesophases; 4. FLC and AFLC phases; 5. Phase Transitions by Optical method

Because so many polymorphs are known in different liquid crystals, several techniques are used in conjunction with each other to identify the various mesophases. Let us consider the major methods of LC phase characterisation and identification. viz. 1)mutual miscibility(1) of known mesogen; 2) x-ray diffraction (XRD)(2); 3)differential scanning calorimetery (DSC)(3); 4) polarized light microscopy (PMS)(4,5).
We have now added the Fabry-Perot Etalon method(13) of analysing the laser light scattered from a LC sample to determine their phase transition temperatures. The difference between the many different LC phases and mesophases is generally minimal. Such minimal differences in structure mean that the precise classification of LCs often requires the use of sensitive analytical techniques. Each individual LC phase has been characterised as a distinct phase of matter by a number of different physical techniques and new LC

phases continue to be discovered as the identification techniques improve.

One of the important manifestations of LCs is their melting or softening behaviour. When heating a crystalline solid that is not mesomorphic, it changes from the solid phase directly into an isotropic liquid phase at its melting point T_m. In liquid crystalline materials, several different mesophases(6,7,8) may form before the isotropic melt phase occurs at the clearing temperature. The mesophases are differentiated from each other by the different ways in which the molecules pack. At the clearing point this may give rise to a disordering of the molecules, either a positional disordering, an orientational disordering or a conformational disordering. An explanation by Brostow(9) involves a description of the melting behaviour of the homologue series of n-paraffins. When methane melts, the regular spacing of the molecules is lost, giving positional disordering, with an attendant contribution to the entropy of fusion. When the next member in series (ethane) melts, positional disordering occurs, but because two ethane molecules may be parallel to or perpendicular to each other, as well as a host of intermediate conditions, there can be a loss of orientation as well. This gives an additional degree of freedom: orientational disorder. N-decane, a longer paraffin molecule, has many more configurations due to rotations about single bonds. This permits another kind of disorder: conformational disordering. Each of these disorderings contribute to the entropy of fusion. Camphor, which contains 10 carbonations as does n-decane, has rigid and almost spherical molecules, and no orientational or conformational effects can occur. As a result, the entropy of fusion of camphor is much less than that of n-decane. Thus, liquid crystallinity depends on molecular anisotropy and the manner in which the molecules pack. The long range ordering in the formation of Bravais lattices in crystalline solids is completely absent in gases, but a degree of long-range order occurs in liquid crystals. When a liquid crystal goes from a solid through various mesophases to the isotropic liquid phase, the degree of long-range order decreases and this is expressed by a decrease in the order parameter S in the case of orientational disorder. In research and commercial manufacture, it is vitally important to be able to identify the types of LC phases that are exhibited by a compound or a mixture of compounds. It is impossible to discern with any degree of certainty what type of LC phase is present by just looking at a sample or by manipulating the sample. However, a good deal of information can be obtained by this simple and cost effective method. It is very easy to see if a material possesses any liquid crystal phase by simply looking at a sample as it is being heated and cooled. LC samples appear opaque because of director fluctuations in the bulk, non-aligned sample. Accordingly, the opaque appearance combined with some degree of fluidity signifies the presence of LC phase in a pure sample. It is possible to see changes between different LC phases on heating and cooling from the sweeping change across the opaque texture. The nematic (N) phase is close in order to the isotropic liquid and is a very fluid, non-viscous LC phase that is lightly opaque. Smectic phases are much more viscous and appear less transparent than the nematic phase. Accordingly, it would be easy to detect the presence of a nematic phase and a smectic phase (e.g. S_A) in the same compound. The nematic phase could be identified as such but of course the smectic phase could just be one of several possibilities. The more ordered crystal smectic mesophase (e.g. crystal B) appears very much like waxy solids and accordingly can sometimes be distinguished from the true smectic liquid crystal phases. Chiral liquid crystal phases often have helical pitch lengths of the order of the wavelength of visible light at some temperature and so selectively reflect visible light. Accordingly, a colored appearance would signify a chiral liquid crystal phase (eg. N^*, S_C^*, S_I^*). For example, a relatively fluid, non-viscous opaque phase that reflects red light at a relatively low temperature and blue light at a higher temperature could be classified as a chiral nematic phase. Some liquid crystal phases can be identified quite simply by using just one technique. However, to be more certain of the liquid crystal phase type, several different techniques are often employed. The most widely used experimental technique of liquid crystal phase identification is optical polarising microscopy[PMS] which reveals that each different liquid crystal phase has a distinct optical texture. However, the identification of liquid crystal phases through PMS is often difficult and requires a lot of experience. Differential scanning calorimetry[DSC] is nearly always employed as a complimentary tool to optical microscopy and reveals the presence of mesophases and liquid crystal phases by detecting the enthalpy change that is associated with a phase transition. However, this technique cannot identify the type of liquid crystal phase but the level of enthalpy change does give some information about the degree of molecular ordering within a mesophase. The Debye-Scherrer technique of unoriented powder samples is used for the identification and classification of mesophases by X-rays [XRD].

Liquid crystal phases present in novel compounds can also be identified and classified by miscibility studies. The material with unknown mesophases is mixed with a known material that possesses mesophases that have already been identified ultimately. If a particular mesophase of the unknown material is completely miscible with a known mesophase of the known material, then it can be concluded that the two phases of each compound are identical and belong to the same miscibility group.

Other techniques used to identify the structure of mesophases and liquid crystalline mesophases include neutron scattering studies[NSS](usually of partially deuteriated samples) and nuclear magnetic resonance[NMR] studies (particularly useful for analysing lyotropic liquid crystal phases).

We have introduced the simple spectroscopic technique(10,11,12,13) of studying the laser light scattered by the liquid crystal using a Fabry-Perot etalon coupled to a spectrometer[FPSS] to determine most accurately; the mesophase transition temperatures for the first time in the field of liquid crystals. The angle at which a coherent beam of monochromatic laser light is scattered from the liquid crystal compound is a function of the structural arrangement of the molecules in it and also the orientational order and/or the positional order. The angular diameter of the FP rings formed in turn depend upon (a) the wavelength λ of light incident, (b) the spacing d between the FP plates; and (c) the angle θ at which light incident on it. If (a) and (b) are unchanged, then the diameter of FP rings would remain constant so long as the liquid crystal compound maintains its phase. When a phase transition occurs, the orientational order and/or the positional order changes which in turn scatters the incident laser light and changes the angle of incidence of the light falling on the FP etalon. This changes the diameter of the FP rings. The change in the diameter thus occurs at the phase transition temperature and signals a mesophase transition.

In our experiment the laser light which is scattered from the liquid crystals is incident on the Fabry-Perot etalon at angles (θ) depending on the orientation of the molecules of the LCs. Hence whenever a phase transition occurs, there is a significant change in the angle (θ) at which the laser light is incident on the FP plates. This in turn, leads to a significant change in the diameter of the Fabry-Perot fringes at the phase transition temperatures.

EXPERIMENTAL WORK

Fabry Perot Scattering Studies [FPSS] : The following samples

i) MHPOBC(R) [(R)4-(1-Methylheptyloxycarbonyl)phenyl-4'-octyloxybiphenyl-4-carboxylate)],

ii) K15 [4-n-Pentyl-4'-cyano-biphenyl],

iii) ZLI-3488 [**MERCK** Ferroelectric Smectic Liquid Crystal].

have been studied using a low power He-Ne laser as the optical source. A Fabry-Perot etalon coupled with a spectrometer telescope forms the rest of the system. The liquid crystal sample was heated by an indigenous electric heater. The laser light scattered by the liquid crystal sample at 90° to the incident beam was allowed to fall on the FP Etalon and the FP rings were obtained. The diameters of the rings were measured at various temperatures. The temperatures were measured accurately using a Remote Sensing Infra-red thermometer having a resolution of 0.1^{0}C.

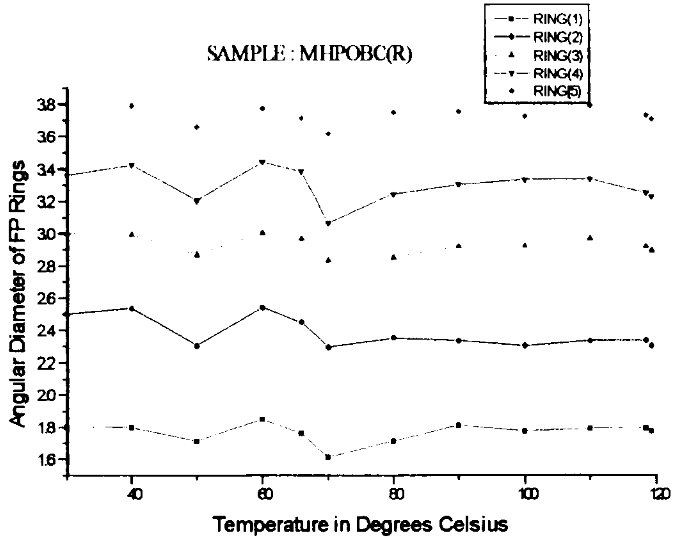

FIGURE 1 Temp. vs. Angular Diameter of the FP rings [Sample (i)].

The observations of the Scattering experiment can be summed up as follows:-The graphical mappings [figs.1,2,3] of Temp. vs. Angular Diameter of the FP rings show an abrupt variation (with a spectrometer of least count = 30") at the phase transition temps. of the LC.

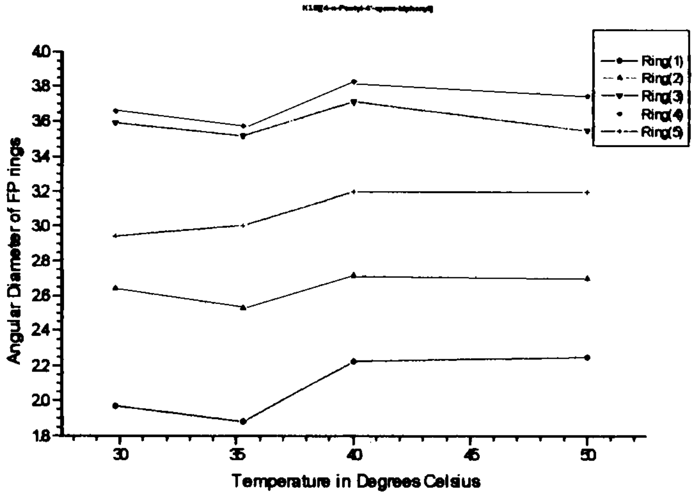

FIGURE 2 Temp. vs. Angular Diameter of the FP rings [Sample (ii)].

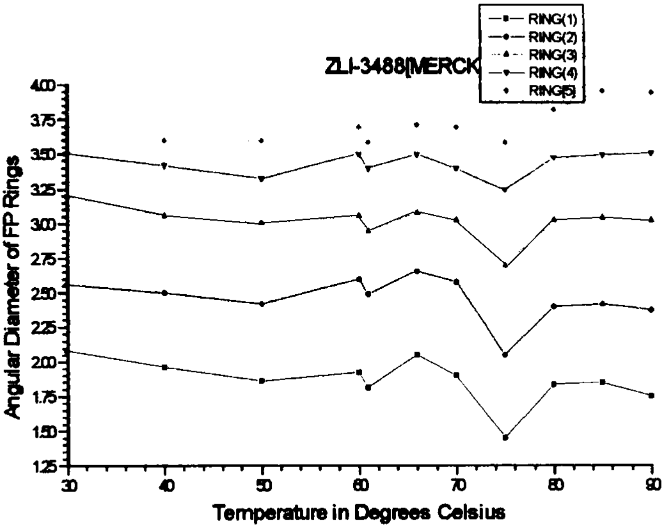

FIGURE 3 Temp. vs. Angular Diameter of the FP rings [Sample (iii)] .

The different PTTs of the above liquid crystals ***[Table below]*** have been determined here by the simple spectroscopic technique(13) with precision. These compare well with those reported earlier by other workers. We have been able to identify **additional mesophase transitions** at the temperatures of 50°C, 60°C, 100°C for MHPOBC(R) and at the temperatures of 50°C and 70°C for ZLI 3488.

FINAL RESULTS AT A GLANCE :

NAME OF THE SAMPLE	IDENTIFIED PTTS. °CELSIUS	STD. PTTS. °CELSIUS
MHPOBC(R)	30	30
	50	NOT REPORTED
	60	NOT REPORTED
	66	66
	100	NOT REPORTED
	118	118
K15	----	24
	35.3	35.3
ZLI - 3488	50	NOT REPORTED
	61	61
	65	65
	70	NOT REPORTED
	85	85

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