

## Thermo-optical studies of nematic liquid crystal mixtures

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**Abstract** Integrated optical transmittance (IOT) and differential scanning calorimeter (DSC) studies of two nematic liquid crystal mixtures (ZLI-3497-100 and ZLI-3741) were made for phase transition measurements, during both heating and cooling cycles. Transition temperatures, transition enthalpies ( $\Delta H$ ) and entropies ( $\Delta S$ ) have been determined using DSC technique.

The IOT and DSC studies indicated good agreement for the transition temperatures for the both mesogens, which exhibited broad nematic – isotropic phase transition. The different peaks observed in IOT studies during phase transitions seems to correspond to different constituents of the mesogens.

**Keywords** IOT, DSC, phase transition, liquid crystal mixtures

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### Introduction

Differential scanning calorimetry (DSC) [1, 2] has been a major tool to study the phase transition and thermodynamical properties of liquid crystals (LC). The transition phenomenon severely limits the useful range of liquid crystals for use in various device applications [3, 4]. The integrated optical transmittance (IOT) is also used to localize the phase transition points. Various studies on phase transition behaviour of liquid crystals have been made [5-9] to understand the transition phenomenon. In the present work, we report the experimental measurements of IOT and DSC on two nematic mixtures ZLI-3497-100 and ZLI-3741. Using DSC data, transition temperature, transition enthalpies ( $\Delta H$ ) and entropies ( $\Delta S$ ) have been estimated. The white light optical transmission study has provided the dynamic change in its percentage transmittance as a function of continuous change in temperature during both

heating and cooling runs. The mixtures under study, were procured from M/s E-Merck, Germany. These LCs contain multi-component systems having molecules of different structures viz. cyano-biphenyls (CB), biphenylcyclohexane (BCH), phenylcyclohexane (PCH), cyclohexyl cyclohexanes (CCH), aromatic esters (AE) etc.

### 2. Experimental details

#### 2.1. IOT:

The nematic-isotropic transition temperature of the mixtures were determined using a polarizing microscope fitted with a hot stage arrangement in which a shielded light dependent resistance (LDR) monitors transmitted light [7]. Sample holder consists of a glass-slide and cover slip combination, the temperature of which is regulated by keeping it in an electrically powered hot stage, driven by a variac. Both cover-slip and glass-slide are

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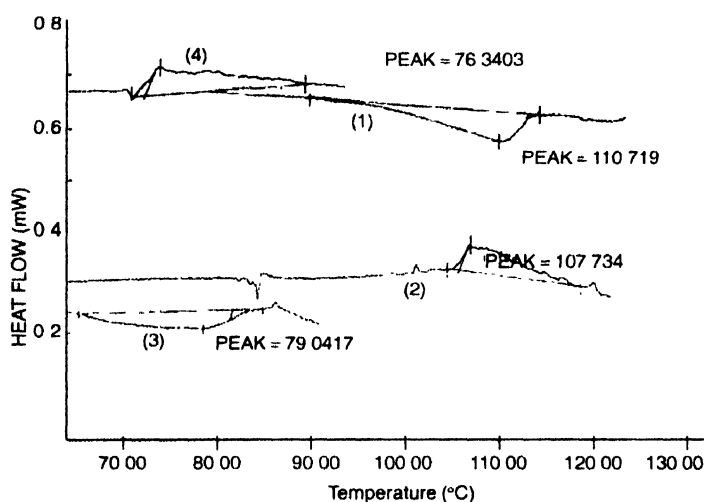
unidirectionally PVA (Polyvinyl alcohol) aligned to induce homogeneous alignment of sample. Temperature of the sample is measured, by a copper-constantan thermocouple. Temperature was stable to an accuracy of  $\pm 0.1^\circ\text{C}$  as controlled by Shimaden micro-controller (SR 7 1B/8Y 1/10).

## 2.2 DSC :

Thermodynamical study of the samples were made using a Perkin- Elmer Differential Scanning Calorimeter (model DSC-7) which has a built-in soft-ware 'PEAK' to determine the peak transition temperature, the onset temperature and the transition enthalpy ( $\Delta H$ ). The calorimeter was allowed to run at the scanning rate of  $5^\circ\text{C}/\text{min}$ . in the temperature range  $70^\circ\text{C} - 125^\circ\text{C}$ . Maximum accuracy in the transition temperature is  $\pm 0.1^\circ\text{C}$ .

## 3. Results and discussion

Figure 1 shows typical DSC plots of heat flow in mW with temperature in  $^\circ\text{C}$  in both heating and cooling runs of ZLI-3497-100 and ZLI-3741 respectively at the scanning rate (SR) of  $5^\circ\text{C}/\text{min}$ .



**Figure 1.** Variation of heat flow (mW) with temperature ( $^\circ\text{C}$ ) for ZLI-3497-100 curve (1) for cooling and (2) for heating run; for ZLI-3741 curve (3) for cooling and (4) for heating run

min. The peak transition temperature ( $T_p$ ), the differences of ending ( $T_e$ ) and starting temperatures ( $T_s$ ), transition enthalpies

( $\Delta H$ ) and transition entropies ( $\Delta S$ ) in heating and cooling runs are given in Table 1.

The DSC study on ZLI-3497-100 has clearly identified the transition peaks at  $107.73^\circ\text{C}$  for heating run and  $110.71^\circ\text{C}$  for cooling run with transition enthalpies 0.6834 and 1.1923 J/gm and entropies 0.001795 and 0.00310 J/gm  $^\circ\text{K}$  respectively in heating and cooling cycles. For ZLI-3741, the transition peaks are at  $76.34^\circ\text{C}$  for heating run and  $79.04^\circ\text{C}$  for cooling run exhibiting the enthalpies 0.6690 and 1.3774 J/gm and entropies 0.00191 and 0.00390 J/gm  $^\circ\text{K}$  for heating and cooling cycle respectively. During heating, the peak transition temperatures agree quite well with the literature values [10].

Figure 2 shows optical transmission (rate of change of light resistance  $dR/dT$ ) versus temperature of the samples. Here the scanning rate was  $<1^\circ\text{C}$  and temperature was measured to an accuracy of  $\pm 0.1^\circ\text{C}$ . Measurements were taken for heating and cooling cycles. The transition temperatures of the mixture ZLI-3497-100 and ZLI-3741 were not as sharp as in a single component such as EBBA [7]. The breadth of nematic-isotropic phase transitions in ZLI-3497-100 was found to vary between  $96 - 109^\circ\text{C}$  for heating cycle, and between  $99^\circ\text{C} - 110^\circ\text{C}$  for cooling cycle; while in ZLI-3741 this breadth was  $75^\circ\text{C} - 85^\circ\text{C}$  for heating cycle and  $74^\circ\text{C} - 84^\circ\text{C}$  for cooling cycle.

Such a behaviour of phase transition over a temperature width in a mixture, has also been observed earlier in many mixtures [9, 11- 14]. Demus *et al* [12] concluded that the breadth of transition depends upon purity of the substance and increases with lower purity. The different peaks in Figure 2 might correspond to different components present in the mixtures. The preliminary data sheet of the mixtures indicate that ZLI-3497-100 contains five components: PCH/BCH/CCH/CBC/AE while ZLI-3741 contains PCH/BCH/CBC only three components. Thus, the five peaks observed in ZLI-3497-100 and three peaks in ZLI-3741 seem to correspond to their components. Different components in the mixture may behave as impurities with respect to each other and thus cause a broad phase transition (multiphase region). The N-I transition temperatures using IOT (given in Table 1) agree fairly well with the peak transition temperatures using DSC.

**Table 1.** Transition temperature by IOT and thermodynamical data of samples from DSC measurements.

Sample	Cycle	DSC					IOT		Literature values (16) $^\circ\text{C}$
		$T_s$ (Tstart) $^\circ\text{C}$	$T_p$ (T peak) $^\circ\text{C}$	$T_e$ (Tending) $^\circ\text{C}$	$\Delta H$ (J/gm)	$\Delta S$ (J/gm $^\circ\text{K}$ )	$T_s - T_e$ $^\circ\text{C}$	N-I Transition $^\circ\text{C}$	
ZLI-3497-100	Heating	105.38	107.73	119.42	0.6834	0.001795	96-109	109	107
	Cooling	88.50	110.71	115.41	1.1923	0.00310	99-110	110	
ZLI-3741	Heating	74.93	76.34	83.87	0.6690	0.00191	75-85	85	73
	Cooling	66.72	79.04	84.86	1.3774	0.00390	74-84	85	

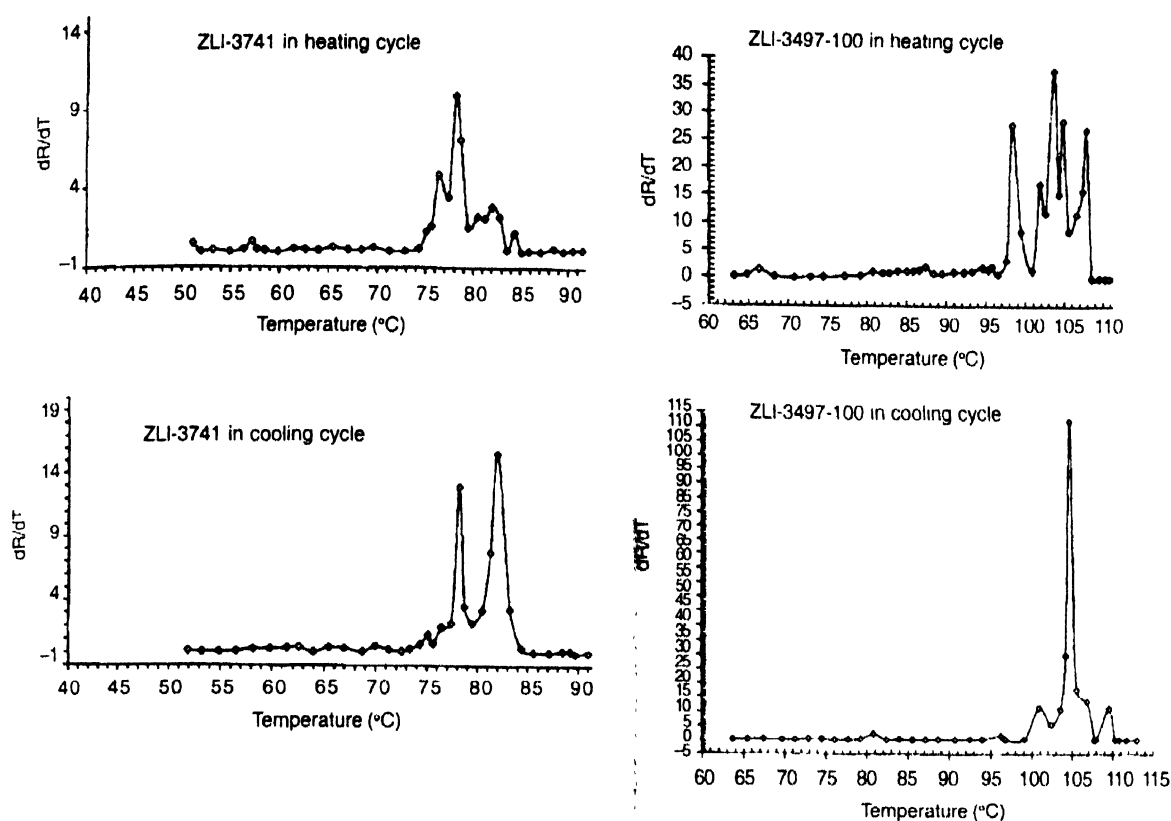


Figure 2. Temperature  $T$  ( $^{\circ}\text{C}$ ) dependence of rate of change of LDR resistance ( $dR/dT$ ) for ZLI-3497-100 and ZLI-3741 in heating and cooling cycle.

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