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Domenico Grasso[a]
[a] Dipartimento di Scienze Chimiche, University of Catania, Viale A. Doria, 6, 95125, Catania, Italy

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A new fast dilatometric method for locating phase transitions in liquid crystals

by DOMENICO GRASSO

Dipartimento di Scienze Chimiche, University of Catania, Viale A. Doria, 6,
95125 Catania, Italy

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A fast method for locating phase transitions by dynamic dilatometric measurements is described. 4-(Trans-4′-*n*-propylcyclohexyl)-benzoic-acid-trans-4″-*n*-propylcyclohexylester and the 4-*n*-octyloxybenzyliden-4′-bromoaniline were used to test the method. The results are in good agreement with those obtained by differential scanning calorimetry.

In general, dilatometric measurements are used to an increasing extent in different scientific fields as a complementary technique to others, in particular calorimetric measurements. Dilatometric measurements were performed, for example, in the study of drug/DNA interactions [1], in the study of the subtransition in dipalmitoylphosphatidylcholine [2], in crystallization kinetics [3], in protein reactions [4] and as criterion of site binding [5]. In all these cases, the measurements are obtained using devices consisting of a glass 'body' of suitable form attached to which is a straight capillary tube in which the movement of the meniscus of the liquid phase indicates the change of volume [4]. The height of the meniscus is measured with a cathetometer or by some automatic device. The measurements are performed at constant temperature in a thermostated bath with a very high stability and very low temperature fluctuations.

In the past few years the investigations by dilatometry of thermotropic liquid crystals, in order to obtain relations between the molecular structure and mesomorphic properties, have interested several scientists [6–8]. Here we propose a dynamic dilatometric method in order to obtain information about phase transitions in thermotropic liquid crystals.

The dilatometric method generally employed is that described by Guillon and Skoulios [6] which uses a dilatometer of the Bekkedahl type immersed in a large oil bath at a strictly regulated temperature. The measurements are made at thermal equilibrium and a long time for each measurement as well as many measurements for each sample are required. So, several work days are required to obtain an entire dilatometric curve. The method proposed here, uses a Mettler TA 3000 thermomechanical analysis unit and new technology in the preparation of the sample. This method obtains results with a reproducibility within 1 per cent. Working at a scan rate below 3°C min^{-1} and with small samples, the phase transitions occur in a relatively long time with respect to the time constant of the sample holder, so that the system is not too far from equilibrium. The present method was tested by characterizing the nature of the various phase transitions of 4-(trans-4′-*n*-propylcyclohexyl)-benzoic-acid-trans-4″-*n*-propylcyclohexylester (compound A) and of 4-*n*-octyloxybenzyliden-4′-bromoaniline (compound B) and by comparing the results with the data obtained by differential scanning calorimetry (D.S.C.).

Compound A used in the present study was obtained from Merck and was used after recrystallization from anhydrous ethanol. Compound B was synthetized and purified following standard methods [9].

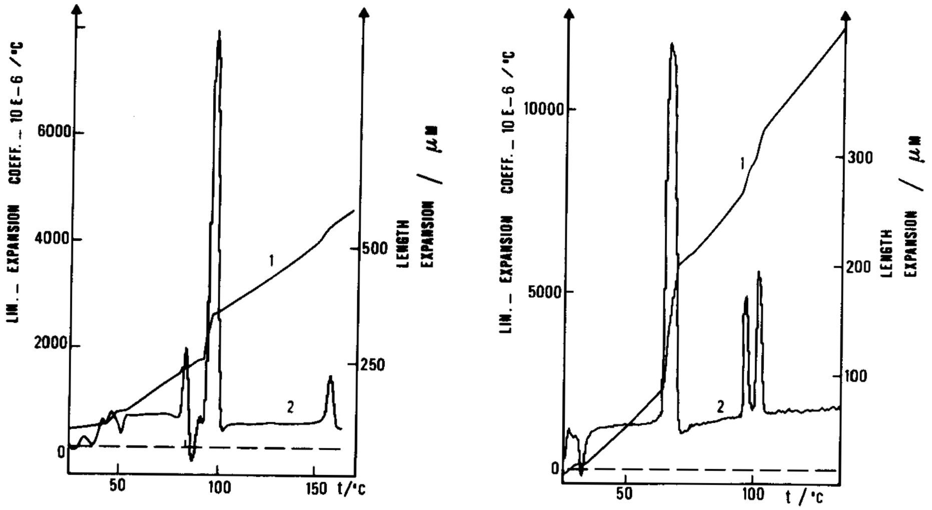
A Mettler TA processor equipped with a D.S.C.-20 measuring cell, previously calibrated for temperature and energy, using indium as standard, was used for the D.S.C. measurements. The transition temperatures were determined using a Galileo polarizing microscope with a 20 × 0·22 objective and a Mettler FP 52 microfurnace for sample-temperature control. The sample was mounted on a glass slide and covered with a glass cover slip.

A Mettler TA processor equipped with a TMA 40 thermomechanical analyser previously calibrated for temperature and length was used in order to obtain measures of length as a function of temperature at constant pressure. A quartz cylinder with a tight but freely movable piston was used as a sample holder. The movement of the piston is measured as a length change (ΔL) of the cylindrically shaped sample. Neglecting the radial expansion of the vial (which is relatively small) the mean volumetric expansion coefficient is calculated using the equation

$$\begin{aligned}\bar{\beta} &= \Delta V/V\Delta T,\\ &\approx \Delta L/L\Delta T,\end{aligned}$$

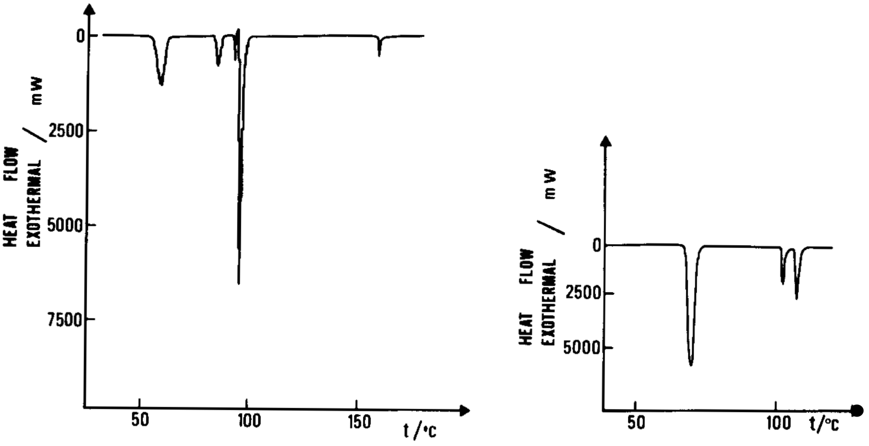
where ΔL is the movement of the piston caused by the temperature increase ΔT, and L is the axial thickness of the enclosed sample. The error due to neglecting the expansion of the piston and the vial is less than 5 per cent.

About 0·2 g of the sample was melted in the sample holder, then degassed in order to avoid porosity, and finally cooled until a compact solid was formed at the bottom of the cylinder. The sample was then covered with a small quantity of mercury of known mass, and finally sealed by a plug greased with silicon. When filling the vial, care was taken not to entrap small air bubbles. To ensure this, the piston has a small recess to collect the air bubbles and the wall of the cylinder has a small hole, through which air and excess mercury can be vented. After that, the piston is rotated to close the vial. Before each measuring scan, a blank curve was recorded in the same range of temperature, using the same sensitivity, parameters as heating rate, probe force, and the same sample holder with the same quantity of mercury, in order to obtain the highest precision in absolute measurements. The preparation of the sample is the most delicate step of the measurement and care is needed for good reproducibility of the results. Being a dynamic measurement, particular attention must be paid to the calibration of the time function for the temperature equilibration between the furnace and the sample. A preliminary measurement calibrated the temperature scale to the values of the transition temperature obtained from thermal microscopy. For our measurement the value of 3°C min^{-1} was chosen for the scan rate to achieve a small temperature gradient within the sample, and a short time for the measurement (about half an hour for a complete scan). The apparatus gives at the same time the curves relating to the lengthening of the sample and the corresponding linear expansion coefficient. The latter curve shows phenomena which are not very clear in the former.



(*a*) (*b*)

Figure 1. Sample lengthening as a function of the temperature (curve 1). Linear expansion coefficient as a function of temperature (curve 2). (*a*) Compound A and (*b*) compound B.



(*a*) (*b*)

Figure 2. D.S.C. thermogram obtained at a scan rate of 4°C min^{-1}. (*a*) Compound A and (*b*) compound B.

Figure 1 reports the dilatograms of compounds A and B. Figure 2 shows the corresponding D.S.C. thermograms determined by heating at 3°C min^{-1}. A comparison of the figures 1 (*a*) and 2 (*a*) for compound A, and 1 (*b*) and 2 (*b*) for compound B shows perfect correspondence between dilatometric and calorimetric thermograms. In particular the curves showing the linear expansion coefficient as a function of temperature are very similar to those for the D.S.C. For compound A five peaks corresponding to five first order phase transitions are evident (cf. figure 1 (*a*)). Moreover a negative peak is observed at about 85°C; this seems to be due to the annealing of the solid phase just formed. The high sensitivity of the present dilatometric method also demonstrates the solid–solid transition occurring in the D.S.C. thermogram at 91°C. It would have been very difficult to see this transition with the traditional dilatometric

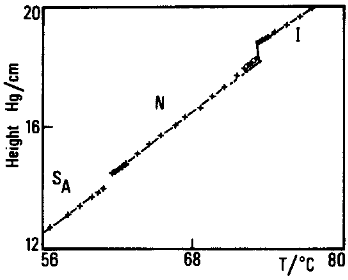


Figure 3. Volume as function of temperature of *N*-(4-*n*-pentyloxybenzylidene)-4-*n*-hexylaniline as reported [7].

method, which gives a series of points corresponding to an equilibrium state in the volume/temperature diagram. Figure 3 shows a typical traditional dilatogram reported from [7].

For compound B, the D.S.C. thermogram shows three peaks corresponding to first order phase transitions, while the dilatogram shows a further transition, evidenced from a negative peak at about 35°C. The experimental data allows us to propose the phase sequences for the compounds:

$$K_0\text{–}K_1\text{–}K_2\text{–}K_3\text{–N–I} \quad \text{compound A},$$

$$K_0\text{–}K_1\text{–}S_1\text{–}S_2\text{–I} \quad \text{compound B}.$$

Even though quantitative measurements have not been performed, from curves showing the length expansion of the samples (cf. figure 1), it is evident that in the transitions which involve solid–smectic or solid–nematic phases, the increase of volume due to the breakdown of the lattice is several times larger than for other transitions. A quantitative study of a homologous series of compounds is now in progress, in order to correlate the specific change of volume with the kind of transition and of the phases involved. In conclusion, the high resolution of the volumetric measurements obtained by the proposed dilatometric dynamic method gives detailed information about the phase transitions that occur in thermotropic liquid crystals and allow us to propose this method as additional to other calorimetric methods in the location of phase transitions.

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