Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THE THERMAL ANALYSES OF MESOPHASES*

JULIAN F. JOHNSON

Department of Chemistry and Institute of Material Science, University of Connecticut, Storrs, Connecticut 06268 (U. S. A.)

AND GERALD W. MILLER

Instrument & Equipment Division, Photo Products Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898 (U. S. A.)

(Received February 26th, 1970)

ABSTRACT

This paper illustrates the use of some of the techniques of thermal analysis, namely, differential thermal analysis, pressure differential thermal analysis, and thermomechanical analysis, to study mesomorphic compounds or liquid crystals. The desirability of covering wide temperature ranges and use of multiple methods is stressed as an aid in interpreting the nature of the transformations. Transition temperatures and enthalpic changes are very important for studying structure–property effects in these materials.

INTRODUCTION

The increasing amount of research on mesophases or liquid crystals attests to their growing importance. This class of compounds exhibits one or more first order transitions between the crystalline solid and the isotropic liquid state transition, as well as with other solid-state transitions below the change from crystalline solid to mesomorphic state. Typically, the intermediate liquid crystal state has some order characteristic of crystalline solids, but the flow properties corresponds to those of liquids. A textbook[1] and a review article[2] have been published which cover the technical aspects of liquid crystals to 1960.

Thermal analysis plays a very important role in the characterization of these compounds. Temperatures of transition, heats of transition, volumetric changes, changes in polarized light intensity, and the influence of pressure on transition temperatures aid in characterizing the structure and physical behavior of mesomorphic compounds. Several works[3–6] have been published on the thermal characteristics of selected mesomorphic compounds. Two other publications[7,8] have dealt with the thermodynamic aspects of the transition phenomena in mesophases. This paper illustrates several aspects of thermal analysis for the characterization of mesomorphic

---

*Presented at the Symposium on Recent Advances in Thermal analysis, American Chemical Society Meeting, Houston, Texas, U. S. A., February 23–27, 1970.

compounds as well as the detail to which attention must be paid in measuring these properties.

EXPERIMENTAL

Materials

The 4,4'-azoxyanisole, cholesteryl caprylate, and cholesteryl propionate were used as received from the Aldrich Chemical Company.

Methods

The Du Pont DSC cell was used for determining all of the calorimetric changes of the materials in this study. The dilatometric data were measured with the use of a fused quartz cylinder and piston arrangement on the stage of the Du Pont 941 Thermomechanical Analyzer. The material under examination was mixed with a proprietary silica filling medium so that as the material under study expanded in volume, it raised the quartz piston in the vial. The volumetric change from this measurement was calculated by taking the average internal diameter of the piston times the height of displacement as the total volume changed at any point in a given run. The DC output from the 941 TMA was fed through a derivative circuit into the 900 Thermal Analyzer so as to record the $\mathrm{d}V/\mathrm{d}T$ curve shown in Fig. 6. The operation of the dilatometric attachment has been described previously[9].

The response of the DSC cell as a function of pressure was measured on the DuPont Pressure DSC cell illustrated in Fig. 1. A standard DSC cell is housed in a

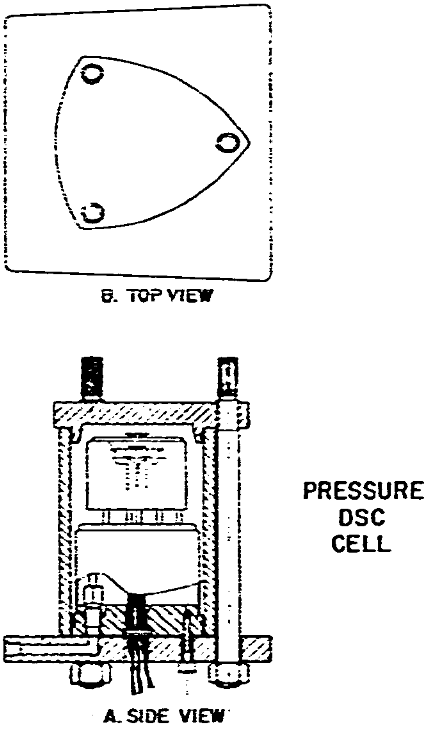


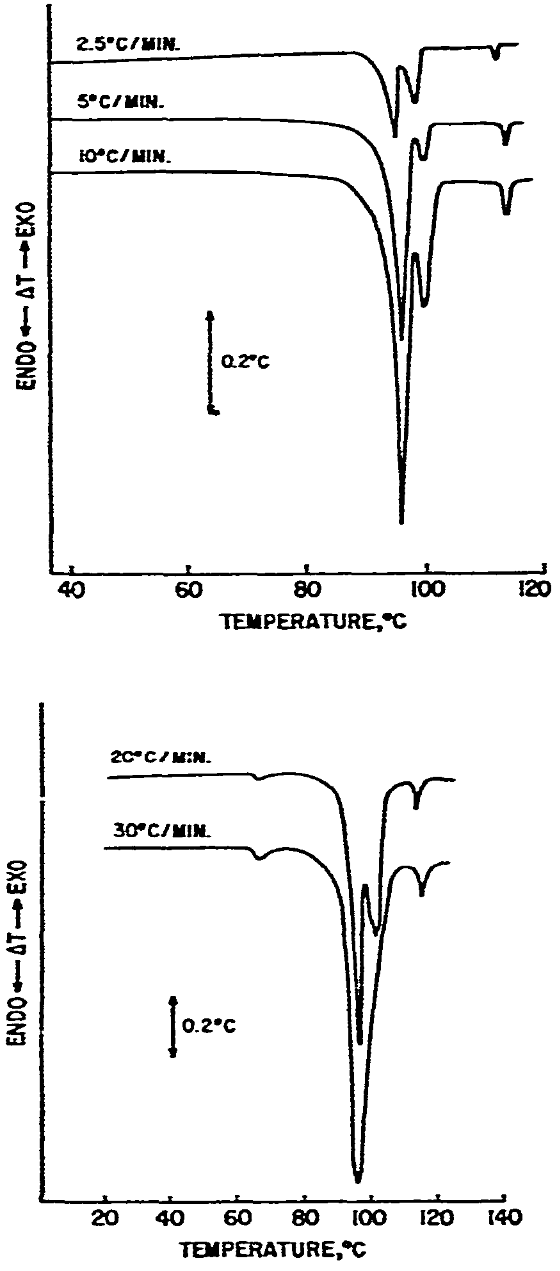
Fig. 1. Schematic of pressure DSC cell.

steel pressure vessel consisting of a bottom pressure plate with appropriate thermoelectric feed-throughs and air channels for pressurization of the vessel. The vessel is a steel cylinder which fits atop a pressure plate and is capped by a second pressure plate, the whole of which is held together by three large steel bolts. The pressure seal is made through "O" rings around the top cap and around the base plate to the DSC cell at the top and bottom, respectively, of the detachable steel cylinder (Fig. 1). A valve is provided for pressurizing the vessel with both a leak and exit valves for the function of introducing a pressure leak if necessary and releasing the pressure from the cell after the run is finished. Other than the pressure capability and the piping necessary for this function, the operation of the DSC cell is the same as that described previously for the DuPont 900 DSC cell[10]. Heating rates up to 20°C/min are easily accomplished with this cell, and it can be pressurized to 1000 psi. Vacuum operation is also possible with a lower pressure limit of about 25 microns. Temperature accuracy of the cell under pressure is identical to that of the DSC cell at ambient pressures. There is, however, some small loss in sensitivity as the pressure is increased, and this is to be expected from the changes in heat transfer characteristics that accompany the use of pressure.

RESULTS AND DISCUSSION

As mesophases, by definition, exhibit multiple transitions, the determination of these temperatures of transition is of primary importance. Originally, this was done visually using melting point capillaries. A variety of other methods, including temperature programmed microscopes[11] and gas chromatographic columns[12], have also been used to measure transition temperatures. Differential thermal analysis, however, because of its precise temperature measurement and ease of operation, is the method now in most frequent use. However, operating conditions must be carefully selected to obtain the maximum amount of information. Fig. 2a shows, for example, the DSC measurements on cholesteryl propionate at three typical heating rates of 2.5, 5, and 10°C/min. Three transitions are easily observed: the crystal–smectic at 99°C, smectic–cholesteric at 110°C and chlolesteric–isotropic liquid at 115°C. These are characteristics of a number of cholesteryl esters that have been previously reported[5,8]. However, should we increase the heating rate to 20 or 30°C/min as shown in Fig. 2b, more information becomes available while experiencing the increased areas of the three observed endotherms with increased rate of heating. This is the typical behavior of any compound when the heating rate is increased using differential thermal analysis. At more rapid heating rates, however, differential thermal analysis can record even very small calorimetric events. Hence, a transition at 64°C can now be detected. While no explanation of the nature of this event is currently available and it has not been previously reported in the literature, the figure serves to illustrate a method for determining phase changes that are accompanied by very small calorimetric changes.

A major advantage of differential thermal analysis is that its operation is automatic, requiring no attention once the measurement is started, and it is feasible to routinely cover wide temperature ranges even though no transitions are anticipated at low temperatures. Figs. 3 and 4 illustrate calorimetric measurements over a large temperature range. For 4,4'-azoxyanisole no transitions are observed until 48 °C, and only the 116 and 135.5 °C phase changes have been recorded in the literature. There are no transitions occurring between −100 and 48 °C as shown in Fig. 3. However, for cholesteryl caprylate shown in Fig. 4, a previously unreported transition exists at



Figs. 2a and b. Heating-rate effects on the DSC response of cholesteryl propionate.

−112°C as well as a reported change from the solid to cholesteric mesophase at 109°C. It's not the purpose of this paper to discuss the nature of the transitions in detail, but rather to illustrate the utility of thermal analysis in providing basic information about mesomorphic compounds.

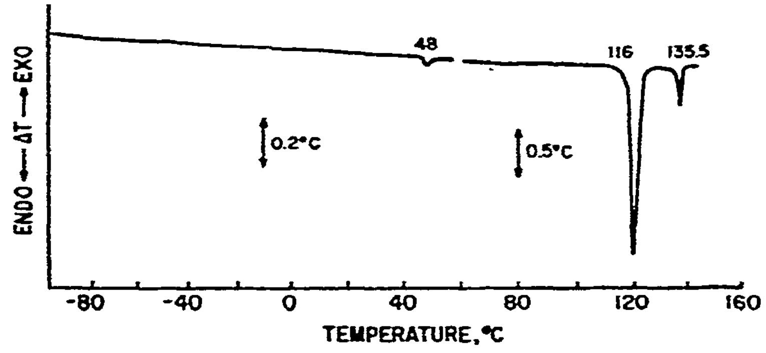


Fig. 3. DSC behavior of 4,4'-azoxyanisole.

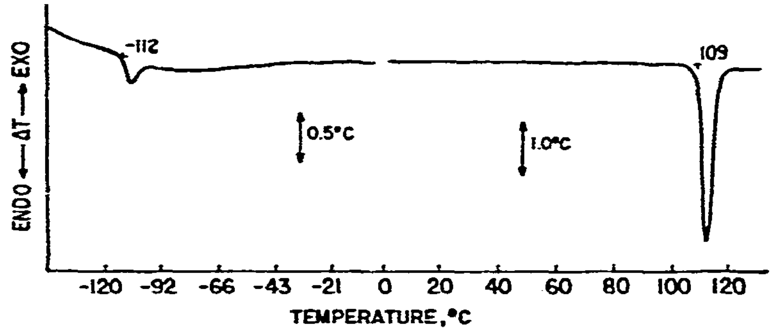


Fig. 4. DSC behavior of cholesteryl caprylate.

In determining the calorimetric aspects of any new compound, it is necessary that the compound is either subjected to a regime of thermal history or the thermal history in the manufacture or processing of the material should be known to properly assess results from the DSC scan. This is illustrated in Fig. 5 wherein the effect of thermal history is shown on the location and very existence of transitions in cholesteryl propionate. Hence, for the material which is slowly cooled[4], there is apparently only one major endotherm with two minor endotherms occurring, whereas when rapidly quenching in liquid nitrogen from the melt, a fourth transition appears in the DSC trace. Note also that the major transition in slowly cooling cholesteryl propionate is of much smaller intensity than when cholesteryl propionate is quenched, and the fourth induced transition appears to represent a major temperature transition at 101°C.

Another method of detection of first order transitions can be shown by the determination of changes in density of mesomorphic compounds as a function of temperature. Direct recording of thermal expansion data provides a convenient experimental technique for determining these properties. Fig. 6 shows a plot of volume and the first derivative ($\mathrm{d}V/\mathrm{d}T$) as a function of temperature. Recording the volumetric behavior as a function of temperature shows a change in the volumetric coefficient of expansion at 7 as well as one at 96 °C. However, the first derivative curve is much more emphatic in its definition of these transitions, showing clearly first order transition phenomena occurring at both temperatures with two minor first order transition phenomena occurring at 108 and 118 °C. Here, clearly, the derivative mode resolves more accurately than the integral mode of volume measurements. The deriva-

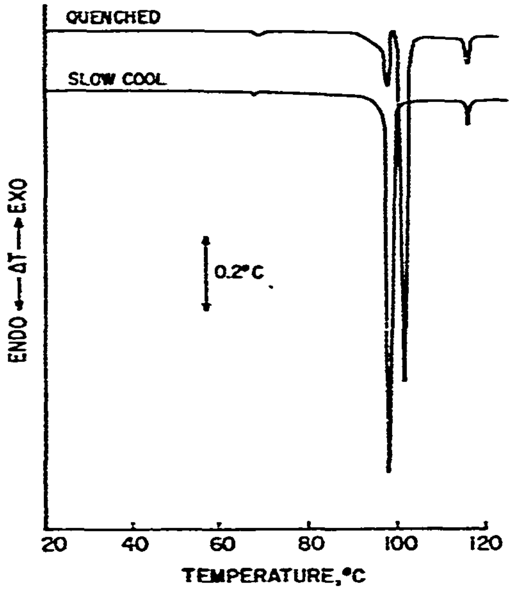


Fig. 5. Thermal-history effects on the DSC response of cholesteryl propionate.

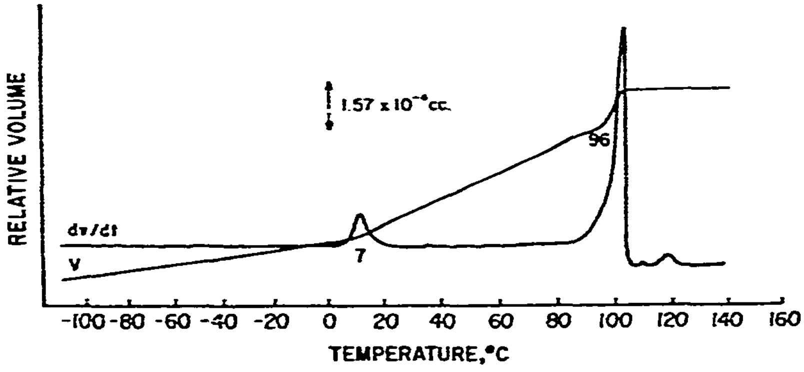


Fig. 6. Volumetric response with temperature for cholesteryl propionate.

tive mode also tends to clearly illustrate first and second order transitions and to differentiate objectively between the two. Second order transitions appear as baseline shifts, whereas first order transitions appear as peaks when using the derivative mode with volume expansion curves. Changes such as those shown in Fig. 6 may be used for

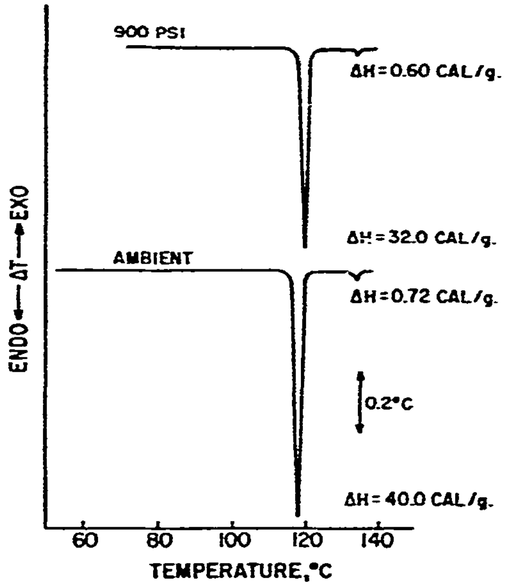


Fig. 7. Pressure effects on the DSC response of 4,4'-azoxyanisole.

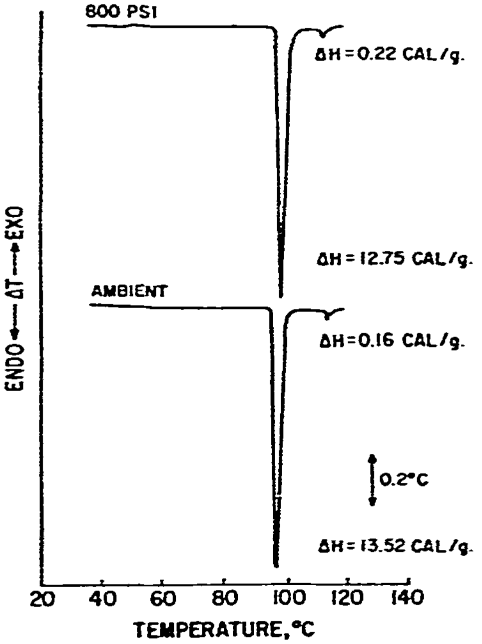


Fig. 8. Pressure effects on the DSC response of cholesteryl propionate.

the quantitative interpretation of pre- and post-transition phenomena. Actually, the more modes of thermal analysis which are employed in the characterization of a mesomorphic state, the greater the information and ease of interpretation. Another method for studying mesomorphic behavior is through the use of differential thermal analysis as a function of pressure. The minor modifications necessary to accomplish this are the design of an appropriate pressure vessel and the use of a good DTA cell. Only minor plumbing changes are necessary to accomplish pressurized measurements in the Du Pont DSC cell. Figs. 7 and 8 illustrate the effect of pressure on both the temperature transition and the calorimetric quantity of each transition. In Fig. 7 it is noteworthy that there is about a 20% decrease in the enthalpy value for the major transition, whereas there is about the same percent enthalpy change for the minor transition at 135°C.

However, in determining the enthalpy response of cholesteryl propionate as a function of temperature, Fig. 8 illustrates a decrease in enthalpy in going from ambient to 800 psi for the major transition, whereas the reverse is true for the minor transition at 116°C where the ΔH-value increases from 0.16 calories per gram to to 0.22 cal/g. The inverted effect here for the minor transition may be attributed to the ease with which cholesteryl esters can sublime. Consequently, some small amount of the cholesteryl esters sublimes during the 116°C transition, and it might appear that in order to determine a more accurate change in the enthalpy value, cholesteryl propionate should be run under pressure. The ΔH-value for the major endotherm should be about 20% less than the ΔH observed at the ambient for the same transition. There appears to be no straightforward explanation for observing only a very small decrease in the ΔH of the major transition, whereas the 4,4′-azoxyanisole behaves according to what might be expected at that pressure. In determining the calorimetric response under pressure, some small change in the temperature of the cholesteric to isotropic transition occurs; there is an increase of about 3°C. A change of about 2.5°C in the nematic to isotropic transition for 4,4′-azoxyanisole also occurred.

The results described in this study illustrate that: several methods of thermal analysis should be used for characterization of mesomorphic compounds; broad temperature ranges should be scanned within a given measurement; heating rates and thermal histories can change the thermal response of a compound under study; and the quantitative aspects of thermal analysis can aid in interpreting more accurately the physical behavior of these mesomorphic transitions.

REFERENCES

1 G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, New York, 1962.
2 G. H. Brown and W. G. Shaw, *Chem. Rev.*, 57 (1957) 1049.
3 R. S. Porter and J. F. Johnson, *J. Phys. Chem.*, 66 (1962) 1826.
4 R. S. Porter and J. F. Johnson, *J. Appl. Phys.*, 34 (1963) 51.
5 E. M. Barrall II, R. S. Porter, and J. F. Johnson, *J. Phys. Chem.*, 70 (1966) 385.
6 E. M. Barrall II, R. S. Porter, and J. F. Johnson, *Mol. Cryst.*, 3 (1967) 103.
7 E. M. Barrall II, R. S. Porter, and J. F. Johnson, *J. Phys. Chem.*, 71 (1967) 895.

8 E. M. Barrall II, R. S. Porter, and J. F. Johnson, in R. F. Schwenker and P. D. Garn (Eds.), *Thermal Analysis*, Vol. II, Academic Press, New York, 1969, p. 555.
9 G. W. Miller, in R. L. Patrick (Ed.), *Treatise on Adhesion and Adhesives*, Vol. III, M. Dekker, New York, 1970.
10 G. W. Miller, *Appl. Polym. Symp.*, 10 (1969) 35.
11 E. M. Barrall II and M. A. Sweeney, *Mol. Cryst.*, 5 (1969) 257.
12 E. M. Barrall II, R. S. Porter, and J. F. Johnson, *J. Chromatogr.*, 21 (1966) 392.

Thermochim. Acta, 1 (1970) 373–381