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RAPID DETECTION AND IDENTIFICATION OF LIQUID CRYSTAL STATES BY LIGHT SCATTERING

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Thermotropic mesophases can be detected by the light scattering properties of these phases. This article deals with a rapid scan technique for the detection and characterization of these mesophases by measuring light scattering as a function of temperature. From the number of compounds studied it is apparent that the method allows for a rapid and reasonably precise determination of transition temperatures. In addition, the method is found to be useful in the characterization of mesophases, in particular the nematic phase.

Historically, the discovery of mesophases is intimately associated with the light scattering properties of mesophases [1–5]. Early investigators observed that melting, as determined by the fluid properties of the substance, often yielded a definitely opaque or turbid fluid state. On increasing the temperature the opacity or turbidity abruptly disappears yielding a true isotropic liquid. These turbid or opaque states were shown later to be true mesophases. By careful observation of changes in turbidity as a function of temperature one can determine mesomorphic transition temperatures with a fair degree of accuracy. However, there are several limitations connected with the visual determination of mesomorphic transition temperatures amongst which is the considerable eye strain involved in such determinations.

With the advent of modern electronic temperature programmers, the automatic determination of transition temperatures has now become feasible. The principle of these methods involves the recording as a function of temperature of any physical property which undergoes an abrupt change at the transition temperature. Examples of this are the techniques of differential thermal analysis and differential scanning calorimetry where one essentially measures the enthalpy changes occurring at each transition.

In this paper, we will describe a new automated rapid scanning technique involving the measurement of light scattering.

Description of technique

The apparatus that we have used utilizes the Mettler Model FP2 melting point apparatus with linear cooling mode capability, but any apparatus of similar design can be used. Essentially, the apparatus consists of a linear temperature

programmer and a furnace with a built-in tungsten light source and a solid state photodetector (see Fig. 1). An output from the photodetector is available for direct connection to the y axis of any $x - y$ 10 mV recorder. The sample is contained in capillaries, available from the Mettler Co., which are 1 mm in diameter and 9 cm in length, Again, any similar thin walled capillary can be used. A thin

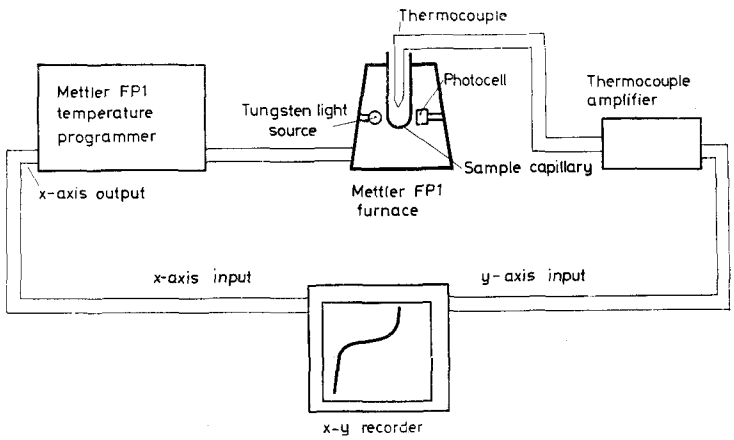

Fig. 1. Block diagram of light scattering apparatus

chromel–alumel thermocouple is inserted in the sample tube along with the sample and the entire assembly then placed in the furnace between the light source and photodetector. The thermocouple signal is then amplified and connected to the x-axis of the $x - y$ recorder. We, therefore, have the capability of monitoring the intensity of light transmitted by the sample as a function of the temperature of the sample. It should be pointed out that the change in intensity of transmitted light is a function of the light scattering properties of the sample and not its light absorbing properties. The apparatus has the capability of monitoring light transmission in both the heating and cooling mode.

Sample handling is quite important in this technique and a detailed description of this procedure follows. The capillary is filled to a depth of 6 mm by the usual techniques, and then the fine chromel–alumel thermocouple inserted such that the tip of thermocouple is 4 mm from the bottom of the capillary. The capillary tube is then warmed, by a flow of hot air, until the sample is just molten and fills the lower portion of the tube. At this point, the sample tube is cooled slowly to room temperature and allowed to stand for at least one hour, so as to minimize any supercooling effects. It is absolutely essential during this warming and cooling process that air bubbles be not trapped in the sample. We have found that gentle tapping of the tube while the sample is in the molten state easily removes any trapped gases. The final capillary-thermocouple assembly will have an appearance

similar to that shown in Fig. 2. Note that the thermocouple is in contact with the sample yet there is an unobstructed path 4 mm in height for the light beam to pass.

At times, one encounters samples of such high absorptivity that insufficient light is transmitted to detect the phase transition. The obvious solution to this problem is to decrease the total path length of the sample. This is accomplished easily by inserting, along with the sample, a glass rod 4 mm in height.

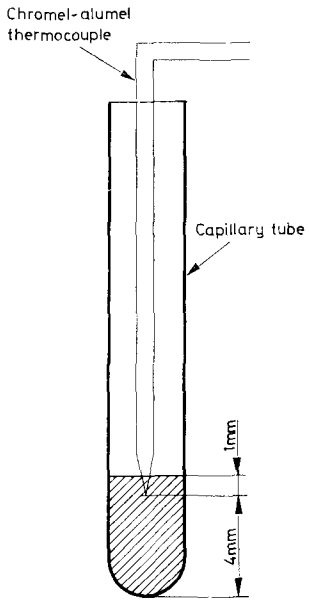

Fig. 2. Detail of thermocouple placement

It is occasionally desirable to exclude oxygen from the sample capillary. In such cases the sample is degassed and sealed in the capillary tube. This obviously necessitates placing the thermocouple in a cavity adjacent to the sample and would, therefore, lead to some error in the transition temperature. Such error can be minimized, however, by using heating rates of 0.2°/min in the immediate vicinity of the transition. The optimum heating rate was found to be 2°/min.

Examples

This technique has been applied to a variety of different liquid crystals and examples of recording traces in both the heating and cooling modes are shown in Figs 3 – 5.

Some rather interesting features of these light transmission curves should be pointed out. In general, the onset of the solid-nematic, solid-smectic, solid-

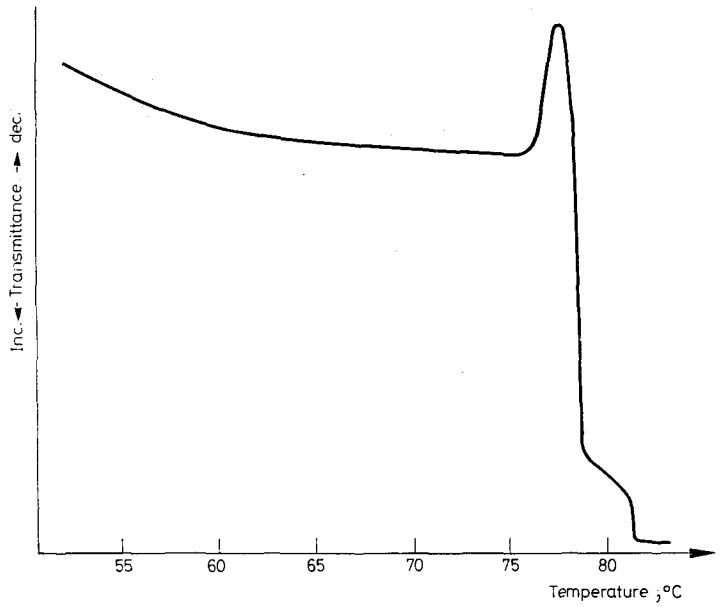

Fig. 3. Cholesteryl palmitate — heating mode

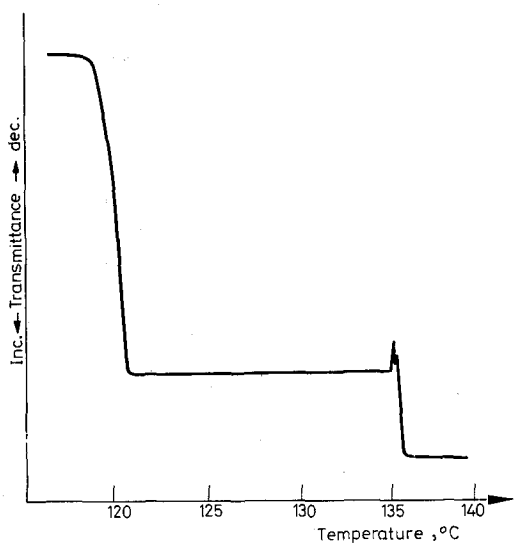

Fig. 4. 4,4¹-Bis(methoxy)azoxy benzene — heating mode

cholesteric, smectic-nematic and cholesteric-isotropic liquid transitions are accompanied by a continuous and rapid increase in light transmission. On the other hand, the onset of the nematic-isotropic liquid transition is accompanied by a rather dramatic decrease in light transmission followed immediately by an equally dramatic increase in transmission. This behavior is probably associated with the character-

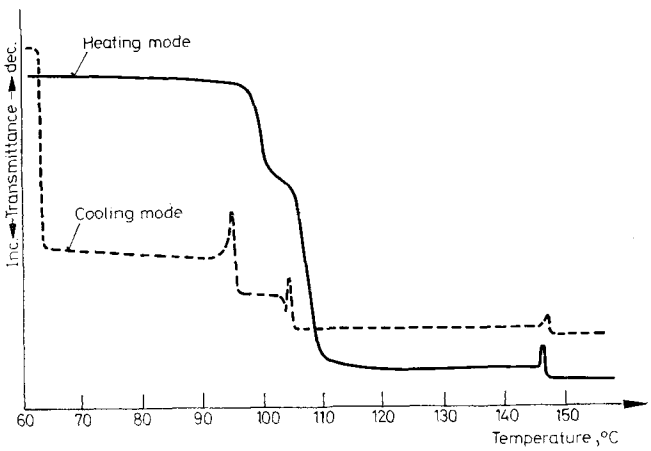

Fig. 5. p-n-Octyloxybenzoic acid — heating and cooling mode

Table 1

Compound	Light scattering			Literature [6—8]		
	T_1	T_2	T_3	T_1	T_2	T_3
p-n-propoxybenzoic acid	144.6	—	155.6	145	—	154
p-n-butoxybenzoic acid	143.0	—	161.0	147	—	160
p-n-pentoxybenzoic acid	125.0	—	150.8	124	—	151
p-n-hexyoxybenzoic acid	105.5	—	152.0	105	—	153
p-n-heptyloxybenzoic acid	92.6	105.6	143.4	92	98	146
p-m-octyloxybenzoic acid	99.5	106.3	146.9	101	108	147
4,4¹-Bis(methoxy)azoxy benzene	119.2	—	135.9	118	—	135
4,4¹-Bis(ethoxy)azoxy benzene	133.6	—	165.5	137	—	168
4,4¹-Bis(propoxy)azoxy benzene	115.0	—	123.2	115	—	124
4,4¹-Bis(butoxy)azoxy benzene	105.2	—	129.7	102	—	137
4,4¹-Bis(pentoxy)azoxy benzene	99.4	—	111.6	76	—	123
4,4¹-Bis(hexyloxy)azoxy benzene	85.4	—	120.8	81	—	129
4,4¹-Bis(heptyloxy)azoxy benzene	70.8	90.4	121.9	74	95	124
p-methoxycinnamic acid	170.8	—	188.4	170	—	186
Cholesteryl benzoate	147.0	—	173.9	146	—	178.5
Cholesteryl palmitate	77.5	—	81.4	77	—	81

T_1 = lowest transition; T_2 = intermediate transition; T_3 = transition to isotropic liquid.

istic way in which the nematic phase separates from the isotropic liquid. As the temperature increases the nematic phase forms spherical droplets separated by isotropic liquid. If the refractive index of the two phases are quite different scattering should be large and the transmitted light intensity should decrease. As the process continues the bulk of the sample is eventually transformed into the isotropic liquid and the light transmission should again increase. This behavior is so general that its appearance can be taken as good evidence for the existence of a nematic mesophase.

Fig. 5 illustrates the complex type of behavior which sometimes appears in the cooling mode. It is obvious that such behavior is not conducive to simple interpretation and would necessitate further studies to completely elucidate this behaviour. Fortunately, complex curves of this sort do not seem to appear in the heating mode.

Table 1, which lists the transition temperatures measured by this technique, indicates fairly good agreement with literature values. The average deviation from the literature values is $\pm 2.9°$.

Conclusions

While only a small number of systems have as yet been studied by this technique it will be apparent to the reader that the method allows for a rapid and reasonably precise determination of transition temperatures. In addition nematic mesophases can be detected with good reliability.

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RÉSUMÉ — On peut déceler les mésophases thermotropiques par leurs propriétés diffusantes vis-à-vis de la lumière. L'article présente une technique de balayage rapide pour déceler et caractériser ces mésophases en mesurant la diffusion de la lumière en fonction de la température. A partir des composés étudiés, on a trouvé que la méthode permettait une détermination rapide et suffisamment exacte des températures de transition. On a trouvé aussi qu'elle pouvait servir à caractériser les mésophases, en particulier les phases nématiques.

ZUSAMMENFASSUNG — Thermotrope Mesophasen können an Hand der Lichtstreuungs-Eigenschaften dieser Phasen nachgewiesen werden. Die vorliegende Arbeit beschreibt eine schnelle Abtast-Methode zum Nachweis und zur Charakterisierung dieser Mesophasen durch Lichtstreuungsmessungen als Funktion der Temperatur. Aus der Zahl der untersuchten Verbindungen geht hervor, daß die Methode eine schnelle und ziemlich genaue Bestimmung von Übergangstemperaturen ermöglicht. Ferner ist die Methode zur Charakterisierung von Mesophasen, besonders der nematischen Phase geeignet.

Резюме — Термотропные мезофазы можно детектировать на основании свойств светорассеяния этих фаз. В статье описана методика обнаружения и характеристики этих мезофаз путем измерения светорассеяния как функции температуры. Судя по ряду исследованных соединений, этот метод является пригодным для быстрого и надежного определения температур переходов. Кроме того, метод полезен при характеристике мезофаз, в частности, нематической фазы.