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TEMPERATURE CALIBRATION OF A POWER COMPENSATION DSC ON COOLING *

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ABSTRACT

The temperature calibration of a Perkin–Elmer DSC7 has been performed on cooling using the isotropic to nematic or cholesteric transitions of thermally stable liquid crystals. Correspondence has been established between the actual temperature and the temperature indicated by the instrument at different cooling rates for most heating rate calibrations used in practice. It has been shown that the indicated temperature at any heating rate calibration up to 20 °C min^{-1}, and cooling rates up to 20 °C min^{-1}, does not differ from the actual temperature by more than 2 °C. Therefore, uncorrected results can be used at the heating and cooling rates mentioned. Greater differences were observed at higher heating and cooling rates.

INTRODUCTION

There are several papers dealing with temperature calibration of DSCs (see, for example, refs. 1–3), but in these works the calibrations were always performed on heating. The solid to liquid transition (melting) of high purity materials is used for this purpose. The reason that only heating calibration is usually performed is that only the melting point has a definite value for pure substances. Calibration on cooling cannot be performed on crystalline materials, since supercooling is a common phenomenon during crystallization.

The calibration standards in most cases are metals, since their purity is considerably higher than that of organic substances and they do not exhibit any decomposition during melting. For example, the purity of the indium and lead used in the present work was at least 99.999%. In these cases the extrapolated onset of the melting can be used as the melting point. Organic substances are rarely used in practice because their purity cannot be raised

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to the abovementioned purity of metals, and also the heat conductance of metals is considerably higher than that of organic compounds.

The widespread use of liquid crystals has finally made possible calibration of DSCs on cooling. It is well known that the nematic (or cholesteric) to isotropic transition (T_{cl}, clearing point) does not exhibit a hysteresis on cooling. In other words, the transition occurs at the same temperature on cooling as on heating. The reason for this is that no nucleation is required for the isotropic to nematic (or cholesteric) transition, as the nuclei of a nematic (or cholesteric) phase are always present in the isotropic liquid owing to density fluctuations.

Cooling calibration can be very important for polymer crystallization studies, since processing conditions require high cooling rates (see, for example, ref. 4), and as will be seen in the present work, the temperature of the sample holder during high cooling rates can differ significantly from the indicated temperature. (It can be intuitively understood that the thermal lag will be increased at higher cooling rates.) Also, for calculations of the non-isothermal kinetics using the Avrami equation, a difference of only several degrees can be important owing to the rapid change in the rate constant with temperature.

In the present paper the calibration of a Perkin–Elmer DSC7 during cooling is reported, but the method used here can be easily applied for any other type of DSC.

EXPERIMENTAL

The DSC measurements were performed on a Perkin–Elmer DSC7 connected to a 7700 computer. The sample holder was cooled using an Intracooler II mechanical cooling accessory with a head temperature of about −100 °C.

The recording method used provided for the fastest possible data rate. This was necessary owing to the very narrow temperature range of the isotropic to nematic (or cholesteric) and the nematic (or cholesteric) to smectic transitions at low cooling rates. In this system this can be assured by selecting the "maximum data size".

The transition temperatures in the DSC experiments were determined as follows. For the metal standards (In, Pb and Sn), the smectic to nematic, the nematic to isotropic, the chiral to cholesteric and the cholesteric to isotropic transitions, it was taken as the onset temperature of the peak. For the crystal to smectic (or chiral) phase it was taken as the peak temperature (owing to impurities in the samples, see Results section). Finally, the transition temperature of the isotropic to nematic or cholesteric phases was accepted as the onset temperature of "crystallization".

The purity determinations were performed on a Du Pont 910 DSC connected to a 1090 analyzer at a heating rate of 0.5 ° C min^{-1}.

The optical textures of the liquid crystals used in this work were observed on a Leitz Laborlux 12 Pol polarizing microscope fitted with long working distance objectives and a Mettler FP80/82 controller microfurnace assembly. The controller was set to heat at 1 ° C min^{-1} and controlled to 0.1 ° C using the handset.

In the optical microscopy experiments, the crystal to smectic phase transition temperature was recorded as the temperature where the oven temperature could be held constant and the sample continued to melt. A fresh sample was used every time to ensure that the results were consistent. The smectic to nematic and the nematic to isotropic phase transitions were recorded as follows. The FP82 microfurnace has a slightly lower temperature in the center of the observation hole than near the edges since the glass slide is not in contact with the heater and is heated only by convection. Therefore, one can find a temperature where the lower temperature phase can be seen in the center of the observation hole completely surrounded by the higher temperature phase near the edges. This is the temperature that was recorded for the phase transitions.

Two liquid crystals were used in this work for calibration purposes.

(1) *N*-(4-*n*-octyloxy-2-hydroxybenzal)-4′-*n*-butylaniline (in this paper designated by LC1) was prepared at our Technical Center as described in Appendix A.

(2) (+)-4-*n*-hexyloxyphenyl-4′-(2″-methylbutyl)-biphenyl-4-carboxylate having the commercial name CE-3 (#59302 3C) was purchased from BDH Chemicals Ltd., Poole, Gt. Britain. The original synthesis of this liquid crystal is described in ref. 5, and the textures are reported in ref. 6.

Prior to the cooling calibration experiments, the DSC7 was calibrated on heating using high purity 99.999% indium (12790A) and 99.9999% lead (12450A) from Johnson Matthey Inc., Seabrook, New Hampshire. The heating calibration was carried out at every heating rate of interest (i.e. 2, 5, 10, 20, 40 and 80 ° C min^{-1}) with a reproducibility of ±0.1 ° C. The linearity of the calibration was checked by the melting point of tin being intermediate to the melting point of indium and lead.

RESULTS AND DISCUSSION

The temperature calibration of a Perkin–Elmer DSC-2 on heating can be described by the following equation [7]

$$T_{\text{real}} = T_{\text{disp}} - C_1(\mathrm{d}T/\mathrm{d}t) + C_2 \qquad (1)$$

where T_{real} is the actual temperature during a heating or isothermal run, T_{disp} is the temperature displayed by the instrument, C_1 is a thermal lag constant which depends on the type of capsule used and C_2 is the offset which depends on which heating rate has been used to calibrate the analyzer. For example, if the heating calibration is performed at a rate of 10 °C min^{-1},

$$T_{\text{real}} = T_{\text{disp}} - 0.085(\mathrm{d}T/\mathrm{d}t) + 0.85 \tag{2}$$

since C_1 is approximately 0.085 [7] for commonly used aluminum capsules. This equation should apply for both heating and cooling rates (for cooling rates $\mathrm{d}T/\mathrm{d}t$ would be negative), and the data in the present paper allow confirmation of this.

The sample holder of a DSC7 does not differ from a sample holder of a DSC-2, and therefore the same equation may be applied to the DSC7. This equation was verified when calibrating the DSC7 at different heating rates.

For a good cooling calibration, the DSC7 was at first calibrated at the heating rates of interest (2, 5, 10, 20, 40 and 80 °C min^{-1}) using In and Pb. Rerunning In and Pb on the calibrated instrument always gave melting points within ± 0.1 °C, and checking with Sn also gave results within ± 0.2 °C. Of course, temperature calibration on heating with such accuracy requires several precautions, which are detailed below.

(a) Even for calibration runs with high purity metal standards, the instrumental baseline must be good. This means that a baseline run should be made separately and subtracted from the actual calibration run.

(b) For high precision temperature measurements with DSC, the environment temperature must be constant (at least the fluctuation of the room temperature should be less than ± 2 °C).

(c) The cooling head temperature must be constant, i.e. a full equilibrium of the Intracooler head temperature must be reached before the calibration can be performed. According to our experience, a 2 h warming-up of the Intracooler is necessary after switching on.

(d) The standard iris-entry dry box purchased with the DSC7 was found to be insufficiently dry to avoid condensation. An air-tight glove entry dry box was used instead in order to prevent condensation on the cold parts of the sample holder.

(e) The bottom of the sample holder pan must be flat in order to ensure good contact with the sample holder surface (minimizing the external thermal resistance).

(f) The position of the sample holder cover should be constant. This is especially important when sample holder covers with two holes are used, because a change in position of the holes changes the instrumental baseline.

(g) When preparing the metal standard samples, the surfaces of the metal pieces which were in contact with air were cut off, and only the "inside" parts of the metals were used in order to prevent contamination of the metal standards by metal oxides formed in air. It was observed that this is extremely important for lead, where the melting point of a piece taken from

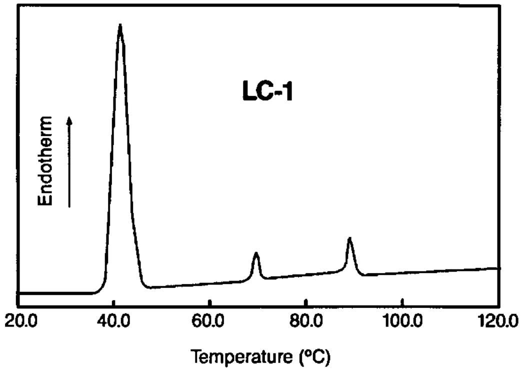

Fig. 1. DSC curve on heating at 10 °C min^{-1} of the liquid crystal LC1. The transitions are as follows: crystal to smectic C, smectic C to nematic and nematic to isotropic.

the surface can be lower than the true melting point of lead by one or two degrees.

(h) The metal standards were melted, then crystallized, and reheated. The melting point results were taken only from the second heating. This ensured that the maximum contact area of the metal piece with the sample pan bottom was obtained.

(i) High (and constant) purity purge gas.

(j) Constant, ca. 10 mg, weight for the metal standard samples.

Use of zinc is not recommended because the melting curve of zinc does not always give a straight leading edge, and a 1–2 °C variation in T_m was observed.

The DSC curves of the CE-3 and LC1 liquid crystals on heating are shown in Figs. 1 and 2. The DSC results on heating the CE-3 liquid crystal (at 5 °C min^{-1}, since at higher heating rates the crystal to chiral C transition is overlapped by the chiral C to cholesteric transition) are as follows: crystal

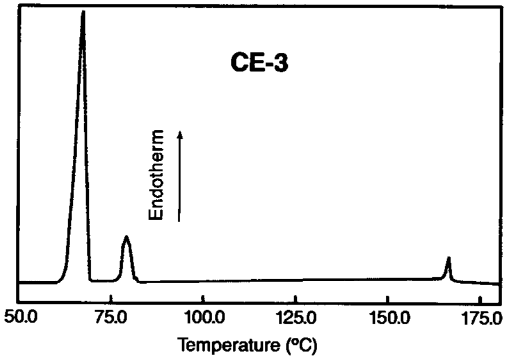

Fig. 2. DSC curve on heating at 5 °C min^{-1} of the liquid crystal CE-3. The transitions are as follows: crystal to chiral C, chiral C to cholesteric and cholesteric to isotropic.

to chiral C transition at 68.2° C ($\Delta H_f = 47.5$ J g^{-1}), then a chiral C to cholesteric transition at 77.9° C with a heat of transition of 3.32 J g^{-1}, and finally a cholesteric to isotropic transition at 165.4° C (the heat of this transition was 1.36 J g^{-1}). The phase transition temperatures shown by optical microscopy were: 68.5, 77.5 and 165.2° C. These results are slightly different than those reported by BDH Chemicals [8], but the good agreement between our DSC and microscopy results (rerun many times) support our data. Also, the transition temperatures reported by BDH Chemicals were determined using a Mettler FP5 capillary melting point apparatus, the accuracy of which is obviously lower than the temperature accuracy of our DSC calibrated to ±0.1° C. The DSC purity was 98.0% on the basis of the crystal to chiral C transition.

The LC1 liquid crystal has the following transitions checked by DSC at 10 ° C $\min^{-1}$: crystal to smectic C at 41.5 ° C, $\Delta H_f = 77.8$ J g^{-1}; smectic C to nematic at 68.6 ° C, $\Delta H = 2.49$ J g^{-1}; and nematic to isotropic at 88.4° C, $\Delta H = 4.54$ J g^{-1}. Results of the optical microscopy observations: crystal to smectic at 38.3° C; smectic to nematic at 69.1° C; and nematic to isotropic at 88.9 ° C. The purity was 99.0% on the basis of the crystal to smectic transition.

A precondition of using a liquid crystal for calibrating a DSC is that the isotropic to nematic transition should have the same temperature during at least two subsequent heatings, i.e. the liquid crystal should be thermally stable for at least two meltings. This condition was fulfilled with the liquid crystals mentioned. The cholesteric to isotropic transition of the CE-3 liquid crystal decreased only 0.1° C in two subsequent meltings, and the nematic to isotropic transition of the LC1 liquid crystal decreased only 0.2° C in two subsequent meltings. The lowering of the isotropic to cholesteric and the isotropic to nematic transition temperatures in two subsequent coolings was 0.2–0.3° C, obviously due to some negligible decomposition of the liquid crystals.

In the cooling calibration experiments, the samples were melted, then cooled in order to record the isotropic to nematic (or cholesteric) and the nematic (or cholesteric) to smectic transitions, and finally reheated to check the transition temperatures on heating again. The transition temperatures obtained during the cooling and the second heating were always used in this work. Fresh samples were used for each calibration.

The results were evaluated using the following equation

$$T_{\text{real}} = T_{\text{ind}} + \Delta T \tag{3}$$

Since T_{real} was obtained as T_{cl} (the clearing point), and T_{cr} is the isotropic to nematic transition temperature,

$$T_{\text{cl}} = T_{\text{cr}} + \Delta T \tag{4}$$

enables calculation of ΔT.

The results obtained were close for both CE-3 and LC1, although a systematic 1–1.5 °C difference was observed between the ΔT values obtained with using the two liquid crystals. The value of ΔT was smaller for CE-3, and this obviously means that a slight supercooling occurs for the transitions of LC1. Therefore, the results obtained with CE-3 are reported in this work. At very high cooling rates the isotropic to cholesteric and the cholesteric to chiral C transitions overlap. But at lower cooling rates it was noticed that the ΔT values obtained for the isotropic to cholesteric and the cholesteric to chiral C transitions were virtually identical, the standard deviation of the difference between the two being ca. ±0.2 °C. The results of the cooling calibration are therefore reported to an accuracy of ±0.2 °C.

T_{cl} values for CE-3 were 165.2–165.6 °C at all heating rates used. This indicates that at the sample weights used, and at all the heating and cooling rates applied in this work, the temperature gradient within the sample must be negligible.

With the weights of liquid crystals used in this work (ca. 4 mg), and considering that the radius of the sample pan is 0.3 cm, the liquid crystal film should cover the bottom of the sample pan by a film having thickness of about 0.15 mm. Therefore, the temperature gradient within the sample should be less than 0.5 °C, so the data should be meaningful even at 160 °C min^{-1} [9].

The results in Table 1 indicate that ΔT increases with increasing cooling rate at any heating rate calibration. Also, the difference between the indicated and the real temperature at heating calibrations equal to or less than 20 °C min^{-1} never exceeds 2 °C, provided that the cooling rate does not exceed 20 °C min^{-1}. Therefore, the indicated temperature during crystallization runs at moderate rates can be approximated by the indicated temperature for most practical applications. Naturally, higher differences could be observed at higher heating or cooling rates.

TABLE 1

ΔT in eqn. (4) for different cooling rates at different heating rate calibrations of a Perkin–Elmer DSC7

Heating rate (°C min^{-1})	Cooling rate (°C min^{-1})							
	1	2	5	10	20	40	80	160
2	−1.6	−1.2	−1.4	−1.0	−0.2	0.5	2.6	8.4
5	−1.0	−1.0	−0.4	−0.4	0.4	1.4	4.0	10.0
10	−0.8	−0.6	0.2	−0.2	1.2	2.2	5.2	11.0
20	−0.4	−0.2	0.6	1.0	1.8	2.8	5.2	11.8
40	−0.2	0	1.6	2.2	2.6	3.8	7.0	14.0
80	0.6	0.4	2.4	3.0	3.6	5.4	8.0	16.4

In order to take full advantage of the temperature precision indicated by these data, it is necessary to calibrate the analyzer at the heating or cooling rate to be used, or to correct the data after the fact, using eqn. (2). The above data demonstrate the precision which can be achieved with care in the cooling mode.

APPENDIX A

Preparation of 4-alkoxy-2-hydroxy benzaldehydes

This example is specific for 4-octyloxy-2-hydroxybenzaldehyde. Compounds with other chain lengths can be made using this method by substituting the appropriate alkyl bromide.

5.6 g (0.1 mol) of potassium hydroxide was dissolved in 125 ml of methanol. Once all the potassium hydroxide had dissolved, 13.8 g (0.1 mol) of 2,4-dihydroxybenzaldehyde was added to the solution. The resulting dark solution was heated to reflux for 1 h. All at once, 19.3 g (0.1 mol) of 1-octylbromide dissolved in 40 ml of methanol and 20 ml of *p*-dioxane were poured down the condenser into the boiling solution. Heating was continued under reflux for 16 h. The solution was allowed to cool to room temperature, 150 ml of water was added and the pH was brought to neutrality with dilute (10 : 1) HCl. The product was extracted from the solution with three or four 200 ml portions of hexane. The resulting hexane solution contained the 4-alkylated product and a small amount of 2,4-dialkylated product. The solution was dried over anhydrous magnesium sulfate and the hexane was removed under reduced pressure on a Rotovap. The product was sufficiently pure for the next step. If necessary, the product was distilled under reduced pressure with the product distilling at 147 °C/0.1 mm.

The anil was synthesized by dissolving 7.5 g (0.03 mol) of 4-octyloxy-2-hydroxybenzaldehyde in 300 ml of absolute ethanol and adding 4.5 g (0.03 mol) of 4-*n*-butylaniline. 6 g (0.05 mole) of anhydrous magnesium sulfate was added and the resulting solution was stirred vigorously and heated to reflux for 2 h. After this time, the solution was hot filtered to remove the magnesium sulfate and was allowed to cool to room temperature. Upon cooling, yellow crystals were expected form. If not, crystallization was forced by cooling in ice and scratching the flask. The yellow product was collected by vacuum filtration and washed with a small amount of cold absolute ethanol. The crude product was dissolved in hexane at room temperature, filtered through a fluted filter paper and the flask tightly sealed. It was then placed in crushed dry ice and allowed to recrystallize. The product was again collected by vacuum filtration, this time as fast as possible so that water did not condense onto the cold crystals. The product was then recrystallized from absolute ethanol.

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