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TEMPERATURE CALIBRATION OF AN ELECTRICAL COMPENSATION DSC ON COOLING USING THERMALLY STABLE HIGH PURITY LIQUID CRYSTALS

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Temperature calibration of DSCs is usually carried out on heating. In order to accurately control the temperature during cooling experiments, the calibration has to be carried out on cooling. Therefore, three high-purity, thermally stable liquid crystals were used to perform a temperature calibration of an electrcial compensation DSC on cooling. All three liquid crystals have several liquid crystalline phases, and they all were purified to a 99.9% level. Temperatures of the isotropic to nematic or cholesteric and the mesophase to mesophase transitions were used. It was verified that these liquid crystals have sufficient thermal stability for carrying out the calibration on cooling. The dependence of the real temperature on the indicated temperature has been established for all the combinations of the heating and cooling rates of practical interest. It is also shown that the van't Hoff equation can only be applied to the crystal to a liquid crystal transition, but not to the liquid crystal to liquid crystal or liquid crystal to isotropic transitions.

Keywords: DSC, liquid crystal, temperature calibration

Introduction

The first high-precision cooling calibration of a power compensation DSC was reported by Menczel and Leslie [1]. There it was mentioned that the calibration of differential scanning calorimeters is always carried out on heating [2–8] due to the fact that only the melting point has a definite value for pure substances. Earlier the calibration on cooling could not be performed, since the crystallization temperature of crystalline substances is always lower than the melting point due to common supercooling phenomena. In the first reported cooling calibration work [1] we used the isotropic to nematic and isotropic to cholesteric transition for the cooling calibration, but mentioned that the cholesteric to chiral

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smectic C transition can also be used, since it appeared not to have supercooling. Later Schick and Hohne reported another cooling calibration [9], but no systematic data were reported about the precision of the calibration in that work.

Knowledge of the exact sample temperature during cooling DSC runs can be very important especially in polymer crystallization studies. For example, it has been suggested that the crystallization temperature of certain polyesters is a linear function of the cube root of cooling [10]. Uncorrected temperature values were used in that work, and it is questionable that the linear relationship would still exist when the temperature values are corrected by calibration on cooling. Knowledge of the temperature during cooling runs is also important for calculations of crystallization kinetics using the non-isothermal Avrami equation, because a small temperature difference can cause considerable changes in the rate constant of crystallization [1].

In this paper, calibration during cooling runs is performed using three high-purity thermally stable liquid crystals. Each of these liquid crystals has several liquid crystal transitions and, as will be seen, all these transitions were used, thus greatly improving the precision of the calibration.

Experimental

Materials

Three liquid crystals were used for the cooling calibration.

(1) N-(4-n-octyloxy-2-hydroxybenzal)-4'-n-butylaniline (designated as LC-1); its preparation is described in [1].

(2) (+)-4-n-hexyloxyphenyl-4'-(2"-methylbutyl)-biphenyl-4-carboxylate with a commercial name of CE-3 (#59302 3C) purchased from BDH Chemicals Ltd., Poole, Gt. Britain [11]. Preparation is described in [12], and the textures are described in [13].

(3) (+)-(4-(2'-methylbutyl)phenyl-4'-n-octylbiphenyl-4-carboxylate) with a commercial name of CE-8 (#59307 3M), also purchased from BDH Chemicals Ltd., Poole, Gt. Britain [11]. Preparation and textures are described in [14].

Purification of these liquid crystals was conducted in our laboratory as described in Appendix 1. The purity of the liquid crystals used for calibration was 99.9% on the basis of the crystal to first liquid crystal transition.

Methods

A Perkin Elmer DSC7 connected to a DEC station 325°C computer was calibrated in this work, and purity determinations were also performed on this instrument at a heating rate of 1 or 0.5 deg·min^{-1}. An Intracooler II mechanical cooling accessory with a constant head temperature of about –100°C was used to cool the sample holder. Due to the very narrow temperature range of the liquid crystalline transitions, a data point had to be recorded at least every 0.05°C in order to achieve reasonable accuracy of calibration.

In the DSC experiments, the transition temperatures were determined as described in [1], i.e.

– for the metal standards (In, Pb and Sn) the transition temperature was taken as the onset temperature of the melting peak;

– for the crystal to smectic *C* (LC-1), the crystal to chiral smectic *C* (CE-3), and the crystal to S_J^* (CE-8) transitions it was taken as the extrapolated onset of the peak due to the high purity of the liquid crystals used;

– for the S_C to nematic, and the nematic to isotropic (LC-1), the chiral smectic *C* to cholesteric, and the cholesteric to isotropic transitions (CE-3), the S_J^* to S_I^*, the S_I^*, to S_C^*, the S_C^* to S_A, the S_A to cholesteric, and the cholesteric to isotropic transitions (CE-8) the transition temperature was taken as the extrapolated onset of the endothermic peaks (due to reasons listed in the Results and discussion section).

– for the isotropic to nematic or cholesteric, and any liquid crystal to liquid crystal transition on cooling, the transition temperature was taken as the extrapolated onset of the exothermic peak due to reasons outlined in the Results and Discussion section.

The polarization optical microscopy observations were made using a Nikon Optiphot-2 Pol microscope fitted with a Mettler FP-80HT/82HT controller/hotstage combination.

Results and discussion

The relationship between real and indicated temperature of a Perkin Elmer type DSC is described by the following equation during a heating experiment [1, 15]:

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

where T_{real} is the real temperature during a heating or isothermal experiment, T_{ind} is the temperature displayed by the instrument, C_1 is the thermal lag constant (its value for aluminum pans was reported to be 0.085 [15]) and C_2 is the offset which can be calculated if the heating rate is known. Thus, when the instrument is calibrated on heating at 10 deg·min^{-1},

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

This equation was generally assumed to apply to both heating and cooling rates, but the data in the present work question its validity on cooling.

The DSC7 used in this work was calibrated on heating using high-purity In and Pb to an accuracy of ±0.1°C at different heating rates of interest (i.e., 2, 5, 10, 20, 40 and 80 deg·min^{-1}). Temperature calibration with such accuracy requires the precautions described in [1]. It is not recommended to use zinc as a melting point standard because its melting curve does not always give a straight leading edge, and 1°–2°C variation of its melting point was observed.

DSC curves of the CE-3, CE-8 and LC-1 liquid crystal standards on heating are shown in Figs 1, 3 and 5. The temperatures and heats of transitions of these liquid crystals are as follows:

1. CE-3

$Cr \rightarrow S_C^*$: $T_m = 66.0°\text{C}$, $\Delta H_f = 51.2$ J/g
$S_C^* \rightarrow Ch$: $T_m = 78.8°\text{C}$, $\Delta H_f = 3.35$ J/g
$Ch \rightarrow I$: $T_m = 163.5°\text{C}$, $\Delta H_f = 2.62$ J/g

2. CE-8

$Cr \rightarrow S_J^*$: $T_m = 55.8°\text{C}$, $\Delta H_f = 54.6$ J/g
$S_J^* \rightarrow S_I^*$: $T_m = 63.9°\text{C}$, $\Delta H_f = 0.15$ J/g
$S_I^* \rightarrow S_C^*$: $T_m = 69.2°\text{C}$, $\Delta H_f = 4.10$ J/g
$S_C^* \rightarrow S_A$: $T_m = 84.0°\text{C}$, not detectable by DSC, but seen by optical microscopy
$S_A \rightarrow Ch$: $T_m = 134.8°\text{C}$, $\Delta H_f = 5.7$ J/g
$Ch \rightarrow I$: $T_m = 140.7°\text{C}$, $\Delta H_f = 3.4$ J/g

3. LC-1

$Cr \rightarrow S_C$: $T_m = 39.2°\text{C}$, $\Delta H_f = 78.2$ J/g
$S_C \rightarrow N$: $T_m = 69.4°\text{C}$, $\Delta H_f = 2.57$ J/g
$N \rightarrow I$: $T_m = 89.2°\text{C}$, $\Delta H_f = 4.6$ J/g

An important precondition of using a liquid crystal standard for cooling calibration is that the liquid crystal must be thermally stable during the calibration runs. This means that the isotropic to nematic or cholesteric and the nematic

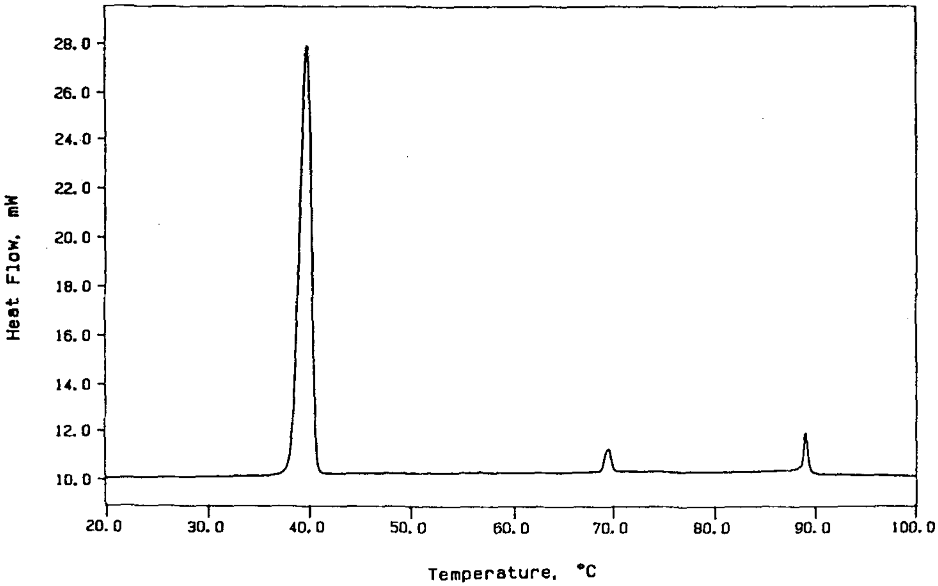

Fig. 1 DSC trace of liquid crystal LC-1 at a heating rate of 5 deg·min^{-1}. The transitions are: crystal to S_C, S_C to nematic and nematic to isotropic (endo up)

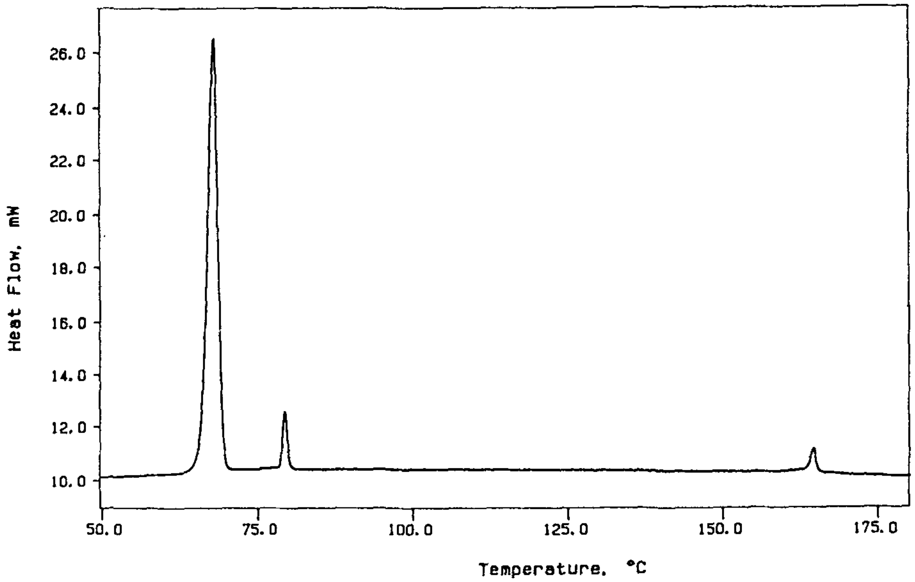

Fig. 2 DSC trace of liquid crystal CE-3 at a heating rate of 10 deg·min^{-1}. The transitions are: crystal to S_C^*, S_C^* to cholesteric, and cholesteric to isotropic (endo up)

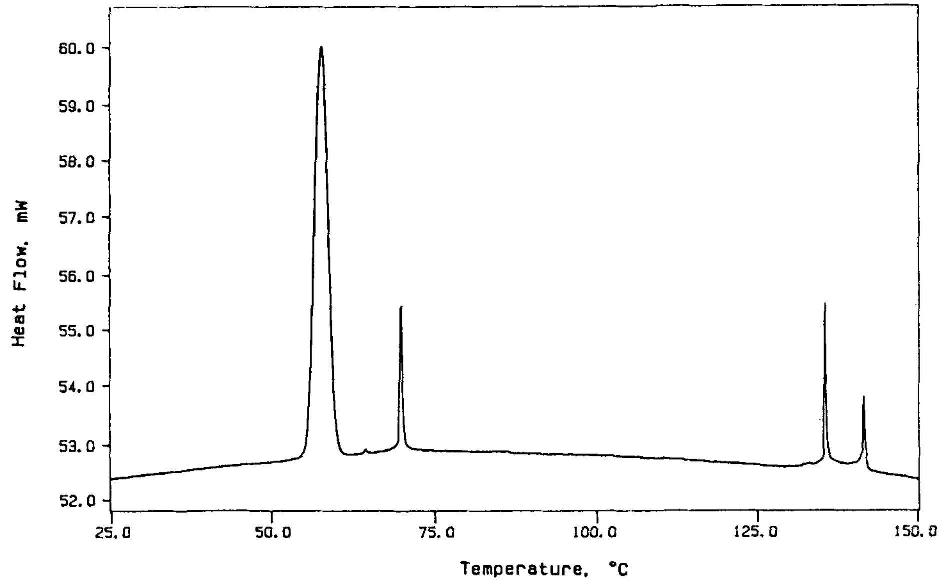

Fig. 3 DSC trace of liquid crystal CE-8 at a heating rate of 5 deg·min^{-1}. The transitions are: crystal to S_J^*, S_J^* to S_I^*, S_I^* to S_C, S_A to cholesteric, and cholesteric to isotropic (endo up)

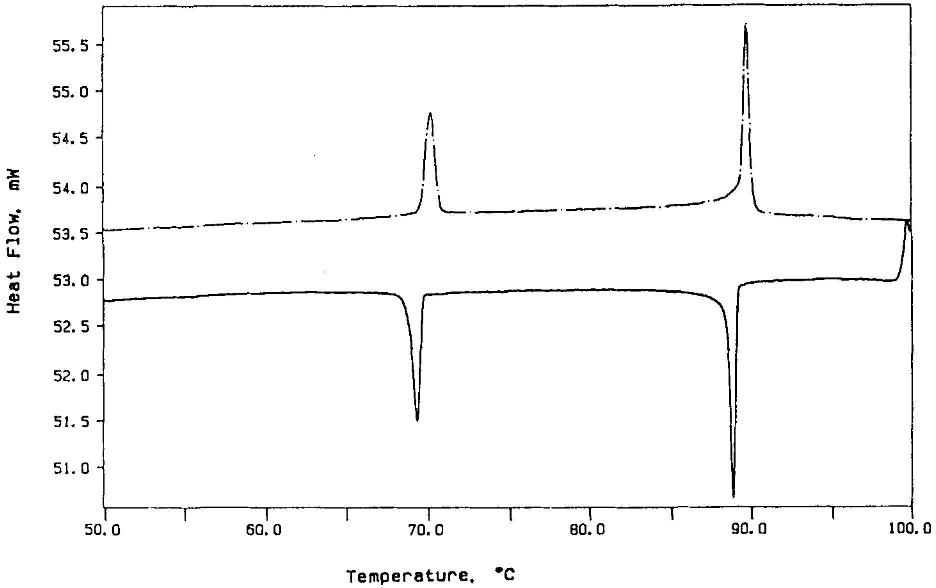

Fig. 4 Heating and cooling peaks of liquid crystal LC-1 used for calibration on cooling. Heating rate = 5 deg·min^{-1}, cooling rate = 5 deg·min^{-1} (endo up, exo down)

or cholesteric to isotropic transitions must occur at the same temperature during at least two subsequent cooling and heating runs. This condition was fulfilled with all three liquid crystals. Temperatures of the liquid crystalline transitions of all these liquid crystals did not change in two subsequent melting-crystallization cycles (both on heating and cooling), and decreased only ca. 0.1°C in four subsequent heating-cooling cycles. Thus, decomposition of fresh standards will not interfere with the accuracy of the calibrations.

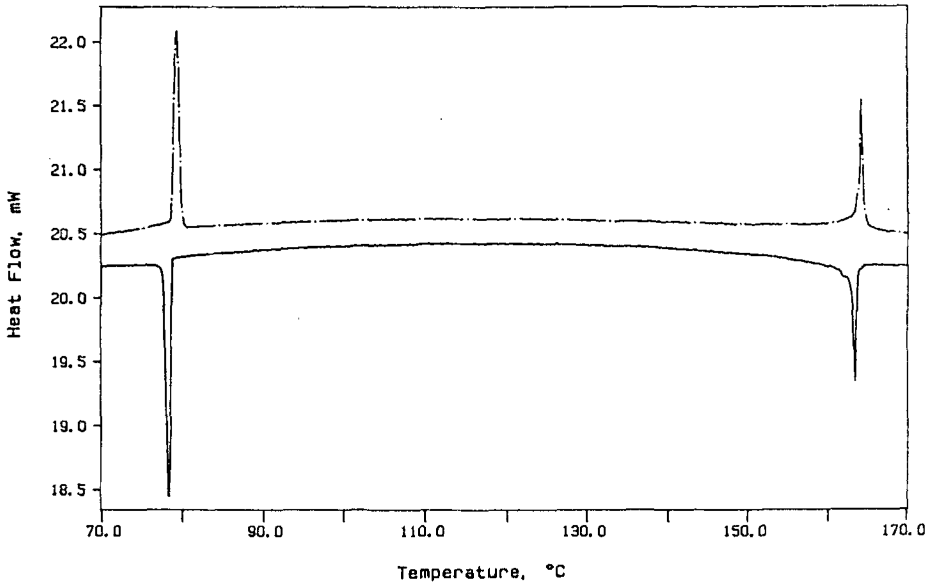

Fig. 5 Heating and cooling peaks of liquid crystal CE-3 used for calibration on cooling. Heating rate = 5 deg·min^{-1}, cooling rate = 5 deg·min^{-1} (endo up, exo down)

In the cooling calibration experiments the standars were melted, then cooled in order to record the isotropic to nematic (or cholesteric) and other liquid crystalline transitions, and finally, reheated to check the transition temperatures on heating again. The transition temperatures obtained during the cooling and second heating were always used. Fresh samples were used for each calibration. From the results obtained it became clear that none of the liquid crystal to liquid crystal transitions had any supercooling at any cooling rate used and therefore, in addition to the isotropic to nematic and the isotropic to cholesteric transitions, they can all be used for the cooling calibration.

The purity of the liquid crystal standard was determined by DSC using the van't Hoff method. When the van't Hoff equation was applied to the crystal to first liquid crystal phase transition, the purity of the as-received CE-3 and CE-8 liquid crystals was 96–98%. However, when the van't Hoff method was applied to any of the liquid crystal to liquid crystal transitions or to the nematic to isotropic or the cholesteric to isotropic transitions, 99.96–100.0% purity resulted. These transitions are very narrow, and are close to equilibrium transitions, and therefore the extrapolated onset should be chosen as the transition temperature for both the heating and cooling experiments. For moderately slow heating or cooling rates this is easy, because the isotropic to nematic or isotropic to cholesteric, or any of the liquid crystal to liquid crystal transitions are very narrow, and they are well separated (see Figs 2, 4 and 6). In these cases all the liquid crystalline transitions (i.e. 2 for LC-1, 2 for CE-3 and 4 for CE-8) could be used to calibrate the instrument. At higher heating or cooling rates, several transitions do overlap, and the exact transition temperature for these cannot be determined, as can be seen in Fig. 7 for the liquid crystal CE-8. In these cases the number of transitions usable for the calibration decreases.

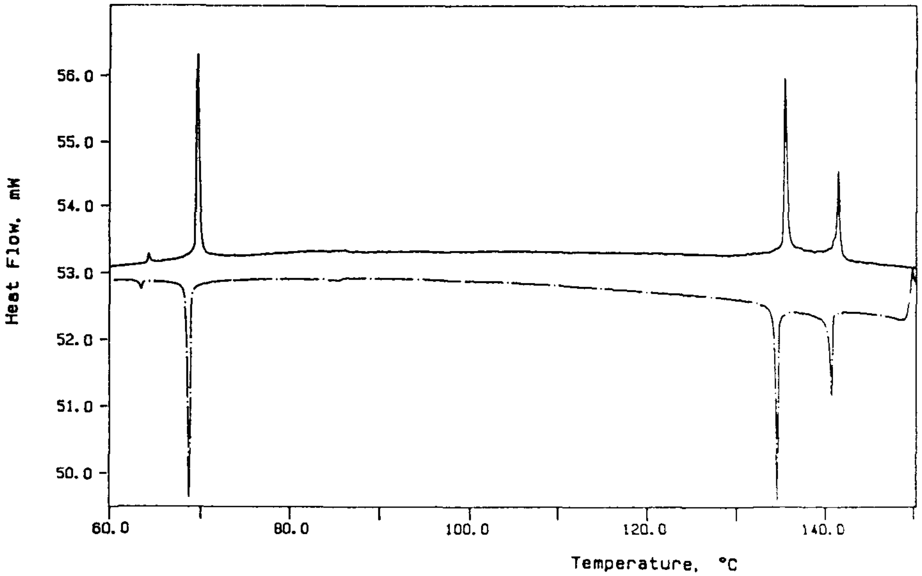

Fig. 6 Heating and cooling peaks of liquid crystal CE-8 used for calibration on cooling. Heating rate = 5 deg·min^{-1}, cooling rate = 5 deg·min^{-1} (endo up, exo down)

As described in [1], results were evaluated using the following equation:

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

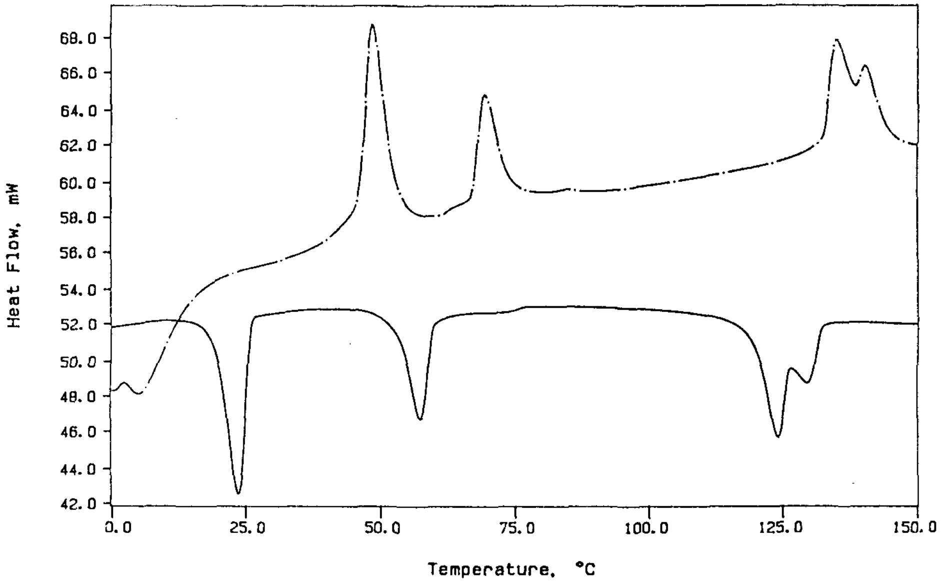

Fig. 7 Heating and cooling peaks of liquid crystal CE-8. Heating rate = 80 deg·min^{-1}, cooling rate = 80 deg·min^{-1}, (endo up, exo down)

Therefore, since T_{real} is the transition temperature measured by the calibrated instrument on heating (T_{cl}, the clearing point for the nematic or cholesteric to isotropic transition), and T_{cr} is the transition temperature measured on cooling,

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

enables calculation of ΔT. Also, when these equations are compared with Eqs (1) and (2),

$$\Delta T = -C_1(\mathrm{d}T/\mathrm{d}t) + C_2 \tag{5}$$

The results obtained for the three liquid crystals (for most data points this means 8 transitions) are presented in Table 1 together with the standard deviation for each point. As can be seen, the transition temperatures of three different liquid crystals lead to similar results with very good precision: the standard deviation of the data points below 40 deg·min^{-1} rates is ca. 0.3°C, and, even at 40 and 80 deg·min^{-1} cooling rates, the standard deviation is less than 1.0°C (this error arises due to the uncertainty in the determination of the extrapolated onset of the transition).

Table 1 $\Delta T = T_{\text{real}} - T_{\text{ind}}$ average results from heating-cooling of three liquid crystals

CR, deg·min^{-1}	1	2	5	10	20	40	80
HR, deg·min^{-1}							
2	–0.4 (±0.2)	–0.2 (±0.2)	–0.1 (±0.3)	0.1 (±0.1)	0.4 (±0.3)	1.2 (±0.5)	3.7 (±0.4)
5	–0.2 (±0.3)	0.1 (±0.3)	0.3 (±0.2)	0.5 (±0.2)	0.9 (±0.2)	1.8 (±0.1)	3.9 (±0.5)
10	0.0 (±0.1)	0.3 (±0.3)	0.5 (±0.2)	0.7 (±0.3)	1.3 (±0.3)	2.2 (±0.4)	4.5 (±0.7)
20	0.6 (±0.3)	0.7 (±0.3)	0.9 (±0.2)	1.2 (±0.4)	1.7 (±0.2)	2.5 (±0.4)	5.0 (±0.9)
40	1.1 (±0.3)	1.3 (±0.3)	1.4 (±0.3)	1.6 (±0.1)	2.1 (±0.2)	2.8 (±0.2)	5.2 (±0.6)
80	2.1 (±0.2)	2.3 (±0.3)	2.7 (±0.3)	3.0 (±0.3)	3.6 (±0.1)	4.3 (±0.2)	6.6 (±0.2)

The transition temperature values for the liquid crystals in heating experiments when measured at different heating rates have standard deviations of less than 0.3°C indicating that the temperature gradient in the samples at the applied heating rate range must be negligible. This can also be proven if one calculates the temperature gradient in the sample at the highest heating or cooling rate used (80 deg·min^{-1}) [16]. Since the sample weight of the liquid crystals was kept constant at ca. 4 mg, and the radius of the sample pan is ca. 0.3 cm, the temperature gradient in the samples at 80 deg·min^{-1} heating or cooling rate is 0.1°C.

Results are somewhat different from those reported in [1]. There are two possible reasons for this discrepancy. The first is that the purity of the CE-3 liquid crystal used in Ref. [1] was only ca. 98.0%. As indicated in Appendix 1, there is some residual carboxylic acid in the bulk ester material and, since the carboxylic acid is also liquid crystalline, this changes the transition temperatures. This problem can be overcome by thorough purification of the standard. The second problem is more complex. The results in Table 1 indicate that ΔT increases with increasing cooling rate for any heating rate calibration, as expected. However Perkin Elmer [15] reported the thermal lag constant for the DSC2, therefore also for the DSC7 sample holders, to be 0.085 when aluminum sample pans are used. Measuring the melting point of indium at different rates, it was found that different sample holders do have different thermal lag constants even when new, and the thermal lag constant changes with the age of the sample holder. For the sample holder used in this cooling calibration series of experiments the thermal lag constant was determined to be 0.06 by indium melting experiments. A value of 0.05 to 0.055 is obtained when the thermal lag constant is calculated from the results of the cooling calibraton reported in Table 1. Thus a reasonable agreement exists between the heating and cooling calibrations. If the heating or cooling rate does not exceed 20 $\mathrm{deg \cdot min^{-1}}$, the temperature for a cooling run can be calculated to a precision of ca. ±0.7°C using the thermal lag constant determined from indium melting experiments in a specific sample holder. Even for a sample holder calibrated at 80°C/min heating, the temperature for an 80 $\mathrm{deg \cdot min^{-1}}$ cooling experiment can be calculated to a precision of ca. ±1.5°C. Thus some discrepancy still exists between the results of these two calibrations. Therefore it is suggested that the cooling calibration is carried out for every occasion needed, and Eq. (1) should not be used to determine the temperature during cooling runs. It is also suggested that 0.085 should not be accepted as the thermal lag constant. Instead, C_l should be determined from indium melting experiments for a specific sample holder, and only then it can be used to determine isothermal temperatures or temperatures during experiments performed at different heating rates.

Conclusions

1. In addition to the isotropic to nematic, isotropic to cholesteric transitions, the nematic to smectic C, the cholesteric to chiral smectic C, the cholesteric to smectic A, the smectic chiral C to smectic chiral I, and the smectic chiral I to smectic chiral J transitions do not have supercooling.
2. Power compensation DSCs can be calibrated to a high degree of precision using the isotropic to nematic or cholesteric and all the liquid crystalline to liquid crystalline phase transitions described in this vork.
3. The purity of low molecular veight liquid crystals can be determined using the van't Hoff equation only by the crystal to first liquid crystalline phase transition.
4. The thermal lag constant of a specific sample holder should be determined using indium melting experiments before it is used to determine temperatures at different heating rates or isothermal mode. The value of 0.085 should not be automatically accepted for the thermal lag constant. The temperature for a cooling experiment can be calculated from the determined thermal lag constant if a ca. ±1°C

precision is sufficient. If higher precision is needed, the temperature should be determined by performing the calibration on cooling.

Appendix: Purification of the liquid crystal standards

All glassware was washed prior to use with concentrated sulphuric acid followed by three or four rinses with deionized water. The glassware was then dried in a convection oven at 110°C. All solvents used except ethanol were HPLC grade purchased from Aldrich and used without further purification. The ethanol was freshly opened anhydrous 'Tax Stamp' ethanol that was not denatured. The filter paper used for both hot filtration and collection of the recrystallized material was Whatman 541 hardened ashless filter paper. Purification of the liquid crystals for the cooling calibration was conducted as follows.

1. CE-3: The CE-3 was dissolved at room temperature in the minimum amount of hexanes and 50% more solvent added to the solution. The solution was filtered through a fluted filter paper by gravity and the filter paper washed with a minimum amount of fresh hexanes. The flask containing the hexanes solution of CE-8 was covered tightly with aluminum foil and placed in a foam ice bucket of dry ice. The ice bucket was kept covered to prevent water from condensing on the flask. After approximately 45 minutes, the flask was removed and the white solid filtered as quickly as possible by vacuum filtration. A large funnel connected to a supply of dry nitrogen had previously been placed over the filtration apparatus in order to purge moist air from the product to prevent water from condensing onto the cold product. The purity of the material was checked at the cholesteric to isotropic transition using hot-stage microscopy. It was evident that some impurity with a cholesteric to isotropic transition higher than the bulk of the mateial was present due to 'puddles' of cholesteric phase in the isotropic melt. The 'puddles' did not undergo the phase transition until the sample was heated almost 20°C higher than the bulk phase transition. This was an indication that the impurity is some residual carboxylic acid in the bulk ester material. The powder-like hexanes recrystallized CE-3 was then dissolved again in hexanes at room temperature. One gram of 70–230 mesh silica gel was added to the solution and the entire mixture warmed on a hot plate. The silica gel was used to preferentially adsorb any carboxylic acid in the mixture from the ester. The solution was filtered through a fluted filter paper by gravity and the filter paper containing the silica gel washed with a minimum amount of fresh hexanes and recrystallized as above. The powder-like hexane recrystallized CE-3 was then dissolved in the minimum amount of a mixture of 50/50 toluene/acetonitrile kept at 60°C and 10% more solvent added to the solution. The solution was not boiled since the nominal melting point of the material is 66°C. If the solution is heated above the melting point of the material, the liquid crystal will phase-separate from the solution in a liquid crystal phase. The liquid crystal phase can dissolve impurities just like a liquid and a true recrystallization is not accomplished leaving the material with the same purity as at the start. The CE-3 was not hot-filtered but simply allowed to cool to room temperature overnight and collected.

2. *CE-8*: The as-received CE-8 was dissolved at room temperature in the minimum amount of hexanes and 50% more solvent added to the solution. The solution was filtered through a fluted filter paper by gravity and the filter paper washed with a minimum amount of fresh hexanes. The flask containing the hexanes solution of CE-8 was covered tightly with aluminum foil and placed in a foam ice bucket of dry ice. The ice bucket was kept covered to prevent water from condensing on the flask. After approximately 45 minutes, the flask was removed and the white solid recovered as quickly as possible by vacuum filtration. A large funnel connected to a supply of dry nitrogen had previously been placed over the filtration apparatus in order to purge moist air from the product to prevent water from condensing onto the cold product. The powder-like hexanes recrystallized CE-8 was then dissolved in the minimum amount of boiling ethanol and 20% more solvent was added to the boiling solution. This was hot-filtered into another flask containing just enough boiling ethanol to keep the flask, funnel, and fluted filter paper wet with hot ethanol. The solution was allowed to stand overnight before filtering the product. The needles from the ethanol-recrystallized CE-8 was then recrystallized again from hexanes as described in the first step. The powder-like hexanes recrystallized product was then dissolved in the minimum amount of boiling acetonitrile and 10% more solvent added to the boiling solution. The solution was not hot-filtered but simply allowed to cool to room temperature overnight and collected.

3. *LC-1*: The yellow LC-1 was dissolved at room temperature in the minimum amount of hexanes and 50% more solvent added to the solution. The hexanes solution of LC-1 was very pale yellow to colourless. The presence of a yellow colour in the solution indicated there was a protic (water or alcohol) impurity in the solvent. This was solvatochromic which is almost colourless in nonpolar aprotic solvents. The solution was filtered through a fluted filter paper by gravity and the filter paper washed with a minimum amount of fresh hexanes. The flask containing the hexanes solution of LC-1 was covered tightly with aluminum foil and placed in a bucket of dry ice. This was kept covered to prevent water from condensing on the flask. After approximately 45 minutes, the flask was removed and the yellow solid recovered as quickly as possible by vacuum filtration. A large funnel connected to a supply of dry nitrogen had previously been placed over the filtration apparatus in order to purge away moist air from the product to prevent water from condensing onto the cold product. The powdery yellow hexanes recrystallized LC-1 was then dissolved in the minimum amount of boil-

ing ethanol and 20% more solvent was added to the boiling solution. This yellow solution was hot filtered into another flask containing just enough boiling ethanol to keep the flask, funnel, and fluted filter paper wet with hot ethanol. The solution was allowed to stand overnight before filtering the product. The yellow needles from the ethanol-recrystallized LC-1 was then recrystallized again from hexanes as described in the first step. The powder-like hexanes recrystallized LC-1 was then again recrystallized from the minimum amount of boiling ethanol with 10% more solvent added to the boiling solution. The solution was not hot-filtered but simply allowed to cool to room temperature overnight and collected.

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Zusammenfassung — Die Temperaturkalibrierung von DSC's erfolgt immer während des Aufheizens. Um die Temperatursteuerung auch bei Abkühlversuchen präzise zu steuern, muß die Kalibrierung beim Abkühlen erfolgen. Aus diesem Grunde wurden drei hochreine, thermisch stabile Flüssigkeitskristalle benutzt, um beim Abkühlvorgang die Temperaturkalibrierung eines elektrischen Kompensations-DSC auszuführen. Alle drei Flüssigkeitskristalle haben unterschiedliche flüssig-kristalline Phasen und alle besitzen die Reinheit von mindestens 99.9 %. Es wurden die Temperaturen für die isotropisch/nematische bzw. isotropisch/cholesterische beziehungsweise meso/meso-Phasenumwandlungen verwendet. Es wurde gezeigt, daß diese Flüssigkeitskristalle thermisch ausreichend stabil sind, um die Kalibrierung während des Kühlprozesses vorzunehmen. Für alle Aufheiz- und Abkühlgeschwindigkeitskombinationen von praktischem Interesse wurde die Abhängigkeit der tatsächlichen Temperatur von der angezeigten Temperatur ermittelt. Außerdem wurde gezeigt, daß die van't Hoffsche Gleichung nur bei Kristall/Flüssigkeitskristall-Umwandlungen, nicht aber bei Flüssigkeitskristall/Flüssigkeitskristall- oder bei Flüssigkeitskristall/isotrope Phase-Umwandlungen.