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Temperature calibration on cooling using liquid crystal phase transitions

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Abstract

Temperature calibration in heating and cooling mode is necessary in the case of power compensated differential scanning calorimeters for the accuracy in the temperature to be better thn 0.5 K on cooling. The smectic A to nematic transition of biphenyles fulfils the conditions required for verifying the symmetry of the temperature calibration in heating and cooling modes at at least one temperature. That is to say, there is a negligible supercooling of that transition combined with high thermal stability and reproducibility and a well defined determination of the transition temperature. 4-Cyano-4′-octyl-biphenyl is recommended for verifying the linearity of the temperature correction for heating and cooling rates in the case of power compensated DSC. The procedure for testing and correcting of apparative asymmetries is given.

INTRODUCTION

For heat flux DSC, symmetry in heating and cooling modes with regard to the thermal conditions is normally provided. In the case of power compensated DSC the symmetry of the calorimeter cell may be lost. In a previous paper [1] it was shown that there may be a discontinuity at zero heating rate for the temperature correction of the thermal lag due to heating and cooling runs [2]. The asymmetry in question arises from inexact adjustment of the electronic control circuits of the power compensation equipment. For precise measurements it is necessary to correct this asymmetry, and first of all to determine the dimension of the discontinuity.

Experiments with a sample of pure indium [1] with known supercooling (from independent measurements with a symmetric heat flux calorimeter) are very time consuming and not suitable for testing the calibration on cooling. Investigated second order phase transitions (showing no supercooling effects) cannot be used for such calibration procedures because of

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the lack of linearity between the transition temperature and the heating and cooling rates [1]. It was one aim of our investigations to find some substances suitable for testing the symmetry of the apparatus, that are in addition, commercially available to everybody.

SUBSTANCES

There are some arguments for the existence of first order phase transitions with negligible supercooling for some liquid crystals. The nucleation process seems to be rather easy because of the prebuild lamellar structure in both the smectic and the nematic phases, leading to only minor structural changes during transition. As shown in ref. 1, the supercooling is indeed rather small (some tenths of a kelvin) but even this is too much for accurate temperature calibration. Therefore, we searched for some special liquid crystals with negligible supercooling (i.e. <0.05 K) and commercially available to everybody.

There are some arguments supporting the use of special smectic–nematic liquid crystal transitions for temperature calibration on cooling:

(i) very low supercooling;

(ii) negligible change of heat conductivity during transitions;

(iii) very low heat of transition and thus small changes of heat flow during phase change;

(iv) sharp peaks and very well defined onset and maximum temperatures.

From points (ii) and (iii) it follows that there are only small changes in the stationary temperature profile within the sample during the transition and indeed also in that of the DSC. For this reason Richardson [3] recommended testing semectic A biphenyls [4] for calibration purposes.

EXPERIMENTAL

In this paper the results of testing two commercially available biphenyls (K24 and M24 [5]) are presented. The heating-rate and cooling-rate dependences of the smectic–nematic transition were studied on three power compensated differential scanning calorimeters (two DSC-2; one DSC-7 (Perkin-Elmer)) and on a heat flux differential scanning calorimeter (Du Pont TA 1090).

Figures 1 and 2 show the structure and known transitions of the

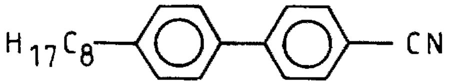

Fig. 1. 4-Cyano-4′-octyl-biphenyl (K24): crystalline, 294.5 K; smectic A, 306.5 K; nematic, 313.5 K isotrope [5].

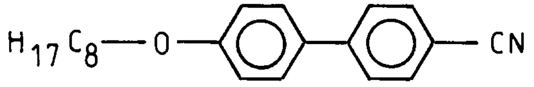

Fig. 2. 4-Cyano-4′-octyloxy-biphenyl (M24): crystalline, 327.5 K; smectic A, 340 K; nematic, 353 K isotrope [5].

compounds as received [5]. For the calorimetric investigations we used samples of about 3 mg of each compound as received. The calorimeters were calibrated on heating according to ref. 2 with the aid of gallium, indium and tin. Nitrogen was used as purge gas. The power compensating instruments were justified with regard to the symmetry on cooling according to the procedure described below.

Thermograms including the (multiple) melting T_m, the smectic A to nematic T_{S-N} and the nematic to isotrope T_{N-I} phase transitions are shown in Figs. 3 and 4. The two melting peaks in Fig. 4 are related to polymorphism depending on the thermal history. The sample under investigation was annealed for two days at room temperature. For samples measured immediately after cooling the relative intensity of the second peak T''_m increases.

As can be seen, the intensity of the smectic A to nematic transition is very small: $\Phi_{max} \approx 0.3$ mW at $\beta = 10$ K min^{-1}. (The zoomed inserts in Figs. 3 and 4 illustrate the relation between the peaks.) This leads to a very low "slope correction" [2] of the peak maximum temperature.

Taking into account a measured slope of a melting peak of pure indium of about 0.04 K mW^{-1} at 10 K min^{-1} heating rate, a correction of <0.01 K of the peak maximum temperature occurs. Thus a slope correction of the

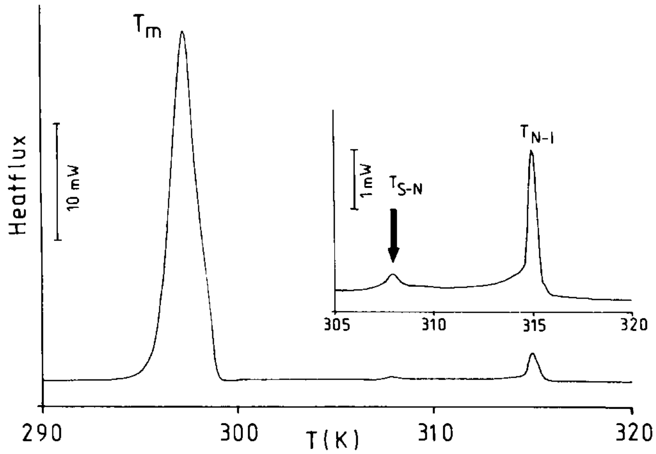

Fig. 3. Uncorrected DSC curve on heating ($\beta = 10$ K min^{-1}) of the liquid crystal K24 ($m_p = 3$ mg).

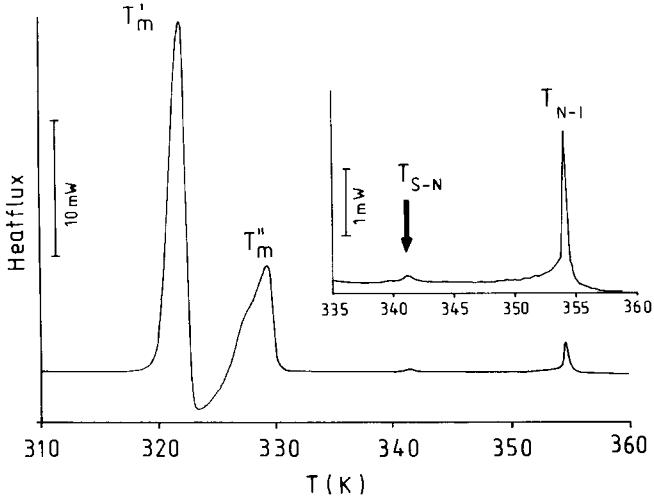

Fig. 4. Uncorrected DSC curve on heating ($\beta = 10\,\text{K min}^{-1}$) of the liquid crystal M24 ($m_p = 3$ mg).

peak maximum temperature was not necessary in the interesting range around zero heating rate.

The measured rate dependence of the maximum temperature of the smectic A to nematic transition of liquid crystal K24 is presented in Fig. 5, and that of M24 in Fig. 6. The samples where measured in the heating and cooling rates range from 20 K min^{-1} down to 0.3(0.1) K min^{-1}. In this range the dependence of the peak maximum temperature on heating and cooling rate is strictly linear. For clarity, only those parts of the curves around zero rate are shown.

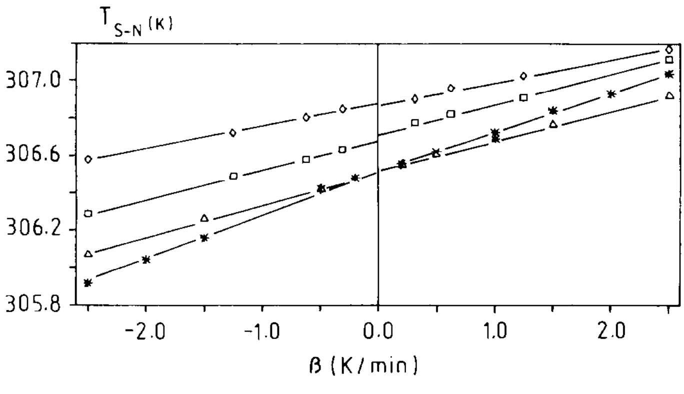

Fig. 5. Maximum temperature $T_{\text{S-N}}$ of the smectic A to nematic transition of K24 as a function of heating rate and cooling rate β. For the sake of clarity the successive curves are vertically shifted. Key: ◇, DSC-2 Güstrow; □, DSC-2 Ulm; *, DSC-7 Ulm 09.4.92; △, DSC-7 Ulm 13.4.92.

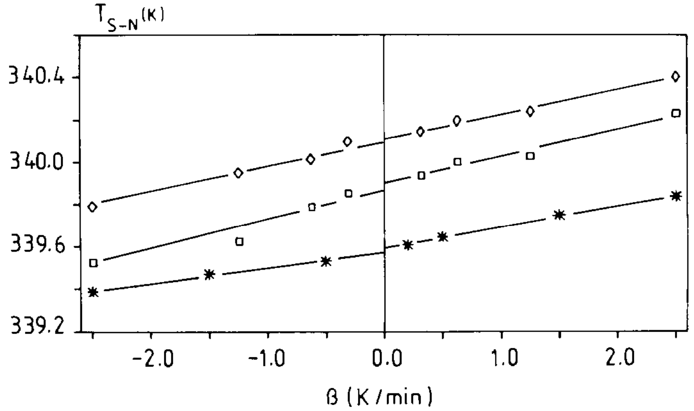

Fig. 6. Maximum temperature T_{S-N} of the smectic A to nematic transition of M24 as a function of heating- and cooling-rate β. For the sake of clarity the successive curves are vertically shifted. Key: ◇, DSC-2 Güstrow; *, DSC-7 Ulm; □, DSC-2 Ulm.

Fluctuation and uncertainty of the measuring points near zero heating rate are a consequence of the very low intensity of the peak (e.g. $\Phi_{\max} \approx 0.02$ mW for $\beta = 0.3125$ K min^{-1}). The interesting part of such a curve is shown in Fig. 7. As can be seen, the normal fluctuation (noise) of the measured signal has a periodicity of 3/100 K, the resolution limit of the temperature program of a DSC-2. Thus the determination of the peak temperature cannot be improved.

Figure 6 illustrates the influence of small changes of the measuring conditions. It shows two measurements (on 9 April 1992 and on 13 April

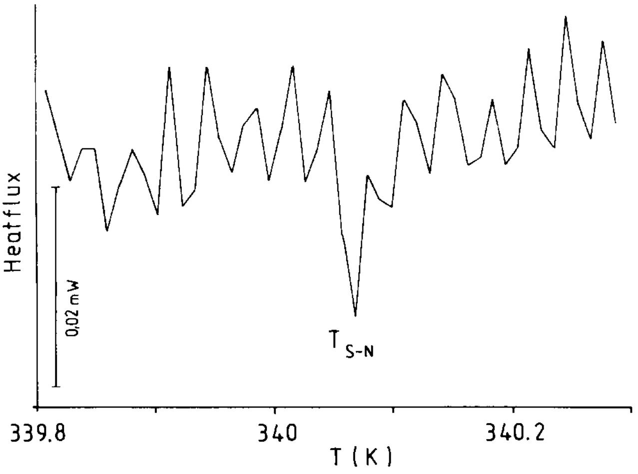

Fig. 7. DSC curve of M24 in the region of the smectic A to nematic transition ($\beta = -0.3125$ K min^{-1}; $m_p = 3$ mg); Perkin-Elmer DSC-2 Güstrow.

1992) with the same DSC-7, on two different samples of about the same weight. The slope of both curves is different (presumably a consequence of different heat resistances between oven and sample). As a result there are differences between the determined temperatures from both measurements (e.g. 0.2 K for $\beta = 2.5\ \mathrm{K\ min^{-1}}$). However, extrapolation to zero heating rate yields the same temperature. This strongly supports the recommendation to extrapolate the transition temperature to zero heating rate [2] or to correct the thermal lag in single measurements [6].

DISCUSSION

The results from the transition investigations of smectic biphenyls show the following.

(i) The supercooling of the smectic A to nematic transition of these substances is lower than 0.02 K (from heat flux DSC measurements).

(ii) The thermal stability of the compounds is sufficient. The results are reproducible for more than 50 heating–cooling cycles on the same sample.

(iii) There is no significant influence of the peak maximum temperature due to the temperature profile inside a sample of about 3 mg. A slope correction of the maximum temperature is for that reason not necessary.

As a result we recommend, using the smectic A to nematic transition of these substances to test the symmetry of temperature calibration on heating and cooling. It allows an easy determination of the discontinuity of the temperature correction at zero heating rate for all calorimeters. Unfortunately the transition temperature is rather low and the symmetry cannot be tested at other temperatures with these substances. There is, however, some evidence that an existing asymmetry does not depend on temperature.

CORRECTION OF THE ASYMMETRY

Because of the symmetry of the heat transport phenomena due to sign changes, the heat flux scanning calorimeter should not usually show any difference in temperature calibration in heating and cooling modes. However, in the event of an asymmetry it should be checked whether the temperature of the output plot (thermogram) is the measured temperature of the sample (with respect to the reference), or possibly the set value of the oven temperature, which may be different in heating and cooling modes, depending on the method used in generating it.

In the case of power compensated calorimeter, asymmetry of temperature calibration is rather common [1]. The cause of this must be supposed to lie within the electronic control circuits of the calorimeter in question. The widespread Perkin-Elmer DSC-2 produces the set value of the temperature via a linear voltage VP, with another voltage from the “lag compensator” added to correct the time constant of the smoothing integrator (IC 37). This additional voltage may be different for heating and cooling and should be adjusted (with the aid of R 35 and R 39) very carefully. This procedure is not easy, so the field service should usually be called in to do the work. It is also possible to obtain this programming voltage VP not from the electronics of the DSC-2 but from another item of modern external equipment (if, for example, the DSC is controlled from a PC [7]) and thus without any additional differences in heating and cooling mode; hence no significant asymmetry should appear.

In principle, the same situation may be found for the Perkin-Elmer DSC-7 because the principle of operation is almost the same. Unfortunately, the user of this calorimeter is not provided with the schematics of the electronics, so there is no other possibility but to call the field service to adjust the problem of asymmetry.

For other power compensated calorimeters, any measured asymmetry should be discussed individually with the field service. It may be helpful to mention, that the cause of it is probably to be found within the generation of the voltage for the set value of the temperature.

PRECISE MEASUREMENTS OF TEMPERATURES IN COOLING MODE

To carry out DSC measurements on cooling with a precision in the temperature better than 0.5 K the following procedure should be carried out.

Test and justification of symmetry between heating and cooling modes

A sample of about 3 mg K24 or M24 is to be located in the centre of the pan and the pan in the centre of the oven.

The rate dependence for the maximum temperature of the smectic A to nematic transition is to be determined in the rate range from $-10\,\mathrm{K\,min^{-1}}$ to $+10\,\mathrm{K\,min^{-1}}$, including the lowest rate for the apparatus in question. For all scans, steady state conditions at the beginning of the transition must be guaranteed. That means (in the case of the Perkin-Elmer calorimeters) that the time from the beginning of the scan to the transition should be more than two minutes. Thus, for a rate of $10\,\mathrm{K\,min^{-1}}$, for example, the starting temperature should be more than 20 K lower (or higher for cooling) than the expected transition temperature.

The maximum temperatures of the smectic A to nematic transition are to be plotted against the scan rate and a linear regression should be performed to determine the intersection at zero heating (cooling) rate.

If a discontinuity at zero heating rate occurs, a justification of the calorimeter must be carried out as described above. With a known discontinuity it is also possible to numerically correct the temperatures in cooling mode, avoiding a justification of the electronics.

Total temperature calibration

The procedure for temperature calibration in the heating mode with the aid of calibration substances is described in ref. 2. We support the recommendation of calibrating calorimeters for an (extrapolated) zero heating rate. In this case most of the problems concerned with thermal lag both from in the calorimeter oven and from the sample pan including the sample can be avoided. The temperatures on cooling can be extrapolated in the same manner to zero cooling rate and any discrepancies in temperature scales should not appear in a well justified calorimeter. The calorimeter is also calibrated in cooling mode.

Measuring in cooling mode

If it is also possible to measure the sample under investigation at different cooling rates, the determination of the exact temperature is easily done by extrapolation to zero cooling rate. Often this is not possible because of irreversible changes of the sample structure or other effects such as dependence of the transition temperature on the cooling rate (as is the case for supercooling and other kinetic effects).

For all such events the determination of the true temperature in cooling mode at one centain rate requires a knowledge of the thermal lag. Determining this requires the same conditions (heat capacity, heat transfer conditions, heat conductivity and shape of the sample) for calibration runs in heating or cooling mode with different rates, which is often not possible.

A method of correcting for the thermal lag from one measurement is described in refs. 6 and 8. The idea is to "desmear" the measured curve with the aid of the "Green's function" of the apparatus and the sample in question, which can be determined from the measuring curve itself.

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