Transition-temperature differences on cooling for a monotropic liquid-crystal polyester observed in DSCs of different design

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Abstract

Most commercial differential scanning calorimeters (DSC) belong to two types of design, namely the power-compensation DSC and the heat-flux DSC. There have been some reports in the literature indicating differences in response between these two types of instrument. Most of these differences have been observed on heating, and it is often assumed that the response on cooling is symmetrical. In this work, we report on differences observed on cooling a monotropic liquid-crystal polyester in several DSCs of the two designs. The monotropic liquid-crystal polyester used here had two exothermic transitions under moderate cooling rates. It was found that the heat-flux instruments tended to give overlapping exothermic peaks, suggesting that the second transition started before the first was complete. The power-compensation instruments, on the other hand, showed completely separated peaks at the same cooling rates. A monotropic liquid-crystal polymer with appropriate crystallisation kinetics may be a good material to evaluate the DSC response on cooling. © 1998 Elsevier Science B.V.

Keywords: Heat-flux DSC; Monotropic liquid crystal; Power-compensation DSC; Peak separation

1. Introduction

The family of polyesters based on the condensation of 4,4′-biphenyl dicarboxylic acid and aliphatic diols HO–$(CH_2)_n$–OH (n=2–9, see below) shows meso- phase behaviour [1,2]. We have studied the polyester with n=8, namely poly(octamethylene bibenzoate) or BB8.

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The BB8 polyester has a *monotropic* liquid-crystal phase as the mesophase is only observed on cooling [2–4]. The phase sequence is K–I on heating, and I–S–K on cooling (K=crystal phase, S=smectic liquid-crystal phase, I=isotropic melt phase). We were puzzled at first, by the transition temperatures and mesophase windows which we found using the differential scanning calorimeter (DSC) when it was compared with those reported in the literature for BB8. According to Watanabe and Hayashi [2], BB8 has two transitions on cooling, the first at 171°C and second at 139°C (mesophase window of 32°C). According to Perez et al. [4], the I–S and S–K peaks are at 168° and 142°C, respectively, (mesophase window of 26°C). Krigbaum and Watanabe [1] did not show their DSC results explicitly, but listed the peaks for BB8 in table. On cooling of BB8, they reported peaks at 160°, 153° and 95°C, but these were not assigned. It is, however, probable that the DSC peaks at 160° and 153°C correspond to the isotropic mesophase transition and the second to the crystallisation transition; if this is correct, then their mesophase window on cooling was only 7°C wide. The third peak at 95°C, reported by Krigbaum and Watanabe [1], was not mentioned by the other invesigators of BB8 [2,4].

In our own investigation, we were even more puzzled because the mesophase window recorded on two different DSC instruments varied greatly for the *same sample of BB8*. We found that the heating scans of BB8 were similar on the two different calorimeters, but there were certain intriguing and striking differences in the cooling scans. One instrument showed, on cooling, two overlapping exothermic transitions at 170° and 161°C (i.e. a narrow mesophase window of 9°C). The second instrument showed two non-overlapping transitions with a wider window of (19°C peak-to-peak). Repeated experiments on both instruments confirmed this behaviour. Hence, it forced us to consider the possibility that the observed transitions on cooling are affected by the measuring instrument.

There were differences in the design of the two instruments. The first (Mettler DSC 30) was a 'heat-flux' instrument, whereas the second (Perkin–Elmer DSC 7) was a 'power-compensation' device. We suspected that the difference in instrumental design could affect the results to quite a significant extent in this particular example of a monotropic liquid-crystal polymer. In this work, we shall report how the instrument itself affects the transitions observed with BB8 and the apparent width of the mesophase window.

2. Experimental

The polymer was synthesised by transesterification [1] of 4,4′-biphenyl diethyl dicarboxylate ester with 1,8-octane diol using titanium isopropoxide as catalyst. The cream-coloured polymer was mechanically crushed and extracted with acetone and dried at 50°C. The polymer showed good extinction in the polarising microscope on isotropisation. The BB8 was run on a number of power-compensation and heat-flux calorimeters from different manufactures. These were: Mettler DSC 30 with a metal sensor, Setaram DSC 92 (heat flux) and Setaram DSC 141 (power compensation) and Perkin–Elmer DSC 7 (power compensation). All instruments were calibrated for temperature and enthalpy response with pure indium. The sample was held in a 30 µl aluminium crucible with a crimped lid, and the scan was conducted in an air atmosphere. The polymer was rapidly heated to isotropisation temperatures (200°C for 1 min) and the cooling scans were recorded at −10 and −5°C/min. Although, we shall mostly restrict ourselves to showing the results from these four calorimeters, the BB8 was also run on three other heat-flux instruments, namely, the Mettler DSC 820, Shimadzu DSC-50 and the Polymer Laboratories DSC Gold. In all experiments, the samples were contained in sealed aluminum pans.

3. Results and discussion

Before discussing the results, we shall briefly mention the salient features of the design of DSC instruments. *Most* commercial scanning calorimeters can be classified into two general categories: these are the power-compensation and heat-flux DSCs [5]. With the usual twin cell design of the power-compensation DSC, there are separate platinum resistance sensors for temperature measurement and individual platinum resistance heaters for the addition of heat. The sample S and reference R are placed in the two separate cells or furnaces [5]. The two calorimeters are mounted in a constant temperature block. The reference and sample

are heated separately, as required by their temperatures and temperature differences. The power-compensation instrument works on a null balance principle. In the power-compensation method, *no temperature difference* is allowed in theory to develop ($\Delta T=0$), even when an event like melting occurs. This is because extra power is pumped into the sample pan to compensate for the heat absorbed during melting, keeping the temperatures of the sample and reference identical. The difference in electrical power inputs to the two heaters directly gives $dQ_S/dt - dQ_R/dt = d\Delta Q/dt$ and the plot of this quantity vs. temperature is essentially quantitative for heats of phase transitions, heats of reaction, specific heat, etc. The temperature–time plot of such a calorimeter is supposed to be linear even through a phase transition. However, it has been pointed out that even with the power-compensation DSC, there is still a small temperature difference between sample and reference, although this is minimised by the control circuitry [6].

The heat-flux DSC [5,7] is an adaptation of the Boersma differential thermal aanlyzer (DTA) (1958). The parameter measured directly is not the heat flux but the temperature difference between sample and reference ($T_S - T_R = \Delta T$), as in DTA. In this design both, sample and reference pans are heated by a *single* furnace. The most popular design nowadays has a heat-flux plate (based on the Boersma DTA), whereby the conduction of heat goes through a metal bridge which acts as a controlled thermal leak. T and ΔT are measured by thermocouples. The heating block is often made of silver, copper or gold due to their high thermal conductivity and is programmed to give a linear temperature rise or fall.

The temperature vs. time profile through a phase transition in a heat-flux instrument is not linear. At a phase transition, or glass transition, there is a large change in the heat capacity of the sample and this leads to a difference in temperatures between the sample and reference container. The differential-heat flow is obtained from the temperature difference by a conversion (calibration) procedure [5].

Some authors have reported actual variations in results measured on DSC instruments of different designs, but such differences have been found mostly in studies of calorimeter response *during heating* [8]. A recent paper [9] reported the resolution and sensitivity of calorimeters (including all the instruments in this study) by examining the transitions of a molecular liquid crystal during heating. Much of the theory of DSC and DTA is based on endothermic events and the position is not as clear for exothermic events as observed on cooling [10]. In this work, we report on interesting differences between DSCs of the two designs *observed on cooling* of a monotropic liquid-crystal polymer.

The results for all the instruments are summarised in Table 1, but we shall illustrate the main findings with four calorimeters, two each belonging to the two DSC types mentioned above. Fig. 1(a) and Fig. 2 contrast the cooling curves recorded on a heat-flux and a power-compensation DSC, respectively. Fig. 1(a), recorded on a Mettler DSC 30 (heat-flux instrument) at $-10°C/min$, shows *partially overlapping* transitions (9°C window from peak-to-peak). There is also a large shift in the baseline after crystallisation (Fig. 1(a)). Fig. 2 in contrast was recorded at $-10°C/min$ on the Perkin–Elmer DSC 7, a power-compensation instrument. This shows *two distinct transitions occurring without overlap* (mesophase window of 19°C at $-10°C/min$). The sample weight (9.77 g) used was similar to that employed with the Mettler DSC 30 and the cooling rates are the same, hence, the conditions of the experiment are comparable.

For enhancing the resolution of multiple thermal events in the DSC, with usual materials, the normal practice is to use slower heating/cooling rates (this is, at the expense of sensitivity). Such a procedure could be used for improving the detection of closely spaced multiple transitions in enantiotropic liquid crystals, such as BB4 or BB6 (see reaction scheme with $n=4$ or 6) of this polyester family, where the liquid-crystal phase is indefinitely stable, whether the liquid-crystal state is achieved by heating from the crystalline state or by cooling from the isotropic. However, BB8 is a monotrpic liquid-crystal polymer [3,4]. This means that the liquid-crystal phase is only observed on cooling from the isotropic melt. In monotropic materials, the liquid-crystal phase is not thermodynamically stable and is only observed on cooling due to kinetic reasons. Thus, in a monotropic system, if the sample is held in the liquid-crystal phase, it will crystallise after some time; in a continuous cooling experiment, the width of the mesophase window will, therefore, depend on the cooling rate. As the cooling rate
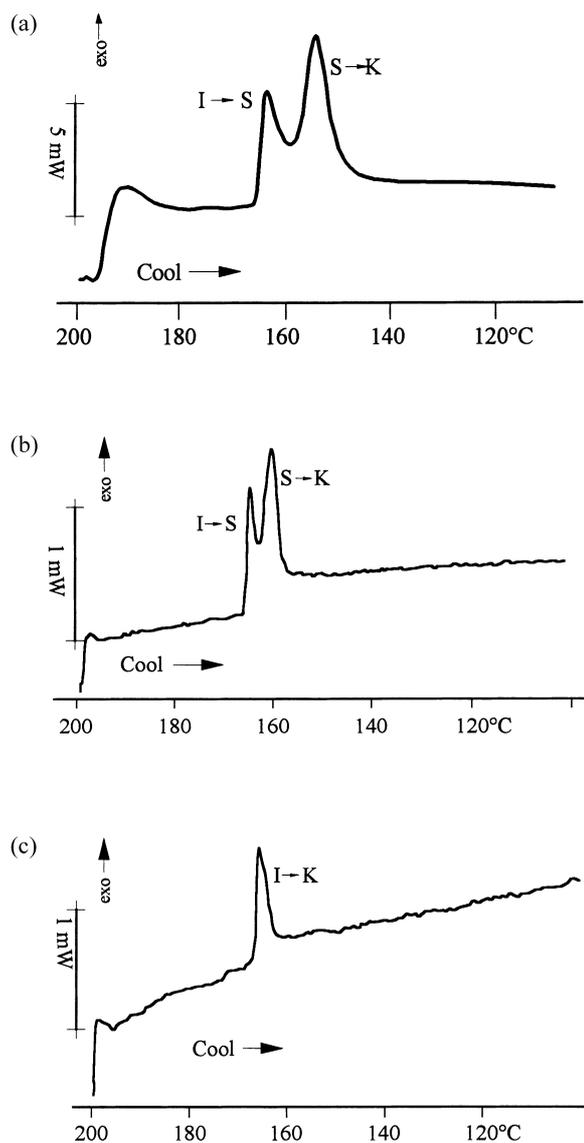
(a)

(b)

(c)

Fig. 1. (a) Cooling scan of BB8 at −10°C/min on the Mettler DSC 30 (wt. 9.00 mg). The peaks at 170° and 161°C and the I–S and S–K transitions, respectively. On this instrument, the two transitions are partially overlapping. (b) Cooling scan of BB8 at −2°C/min on the Mettler DSC 30 (wt. 9.00 mg). The peaks are at 168° and 163°C. (c) Cooling scan of BB8 at −0.5°C/min on the Mettler DSC 30 (wt. 9.00 mg). There is now only a single peak at 170°C (direct crystallisation without mesophase formation).

decreases, the crystallisation peak moves to higher temperatures and overlaps with the first transition; at very low cooling rates, the material may crystallise directly form the isotropic melt without forming a
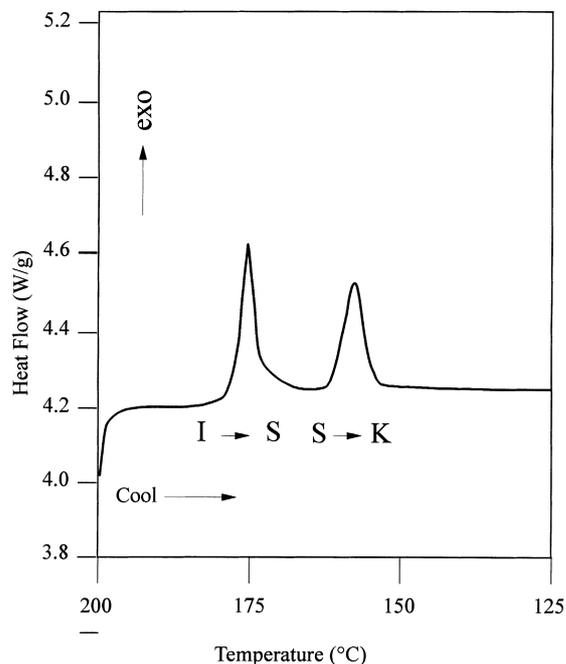
Fig. 2. Cooling scans of BB8 recorded on a power-compensation instrument (Perkin–Elmer DSC 7, 10°C/min). In the cooling scan, the transitions are well separated.

mesophase (Fig. 1(a–c)). Thus, one cannot improve the resolution of overlapping peaks by using slower cooling rates with monotropic liquid-crystal materials. On the other hand, using high cooling rates (−20°C/min) would allow the material less time to crystallise, but it causes broadening of the peaks and reduces resolution. Well-separated peaks can only be observed with monotropic liquid-crystal polymers at some intermediate cooling rates (such as, −10 or −5°C/min); the calorimeter design and response on cooling becomes particularly important in determining whether there is some range of cooling rates at which the transitions can be observed *without overlap*. Observing transitions without overlap is helpful in phase identification, because the relative enthalpy changes can give clues about the phases.

Setaram makes both, a power-compensation (Setaram DSC 141) and a heat-flux instrument (Setaram DSC 92). It was interesting to see how the BB8 would behave in two instruments of different designs from the same manufacturer. Fig. 3(a) shows the cooling scan (−10°C/min) of BB8 recorded on the
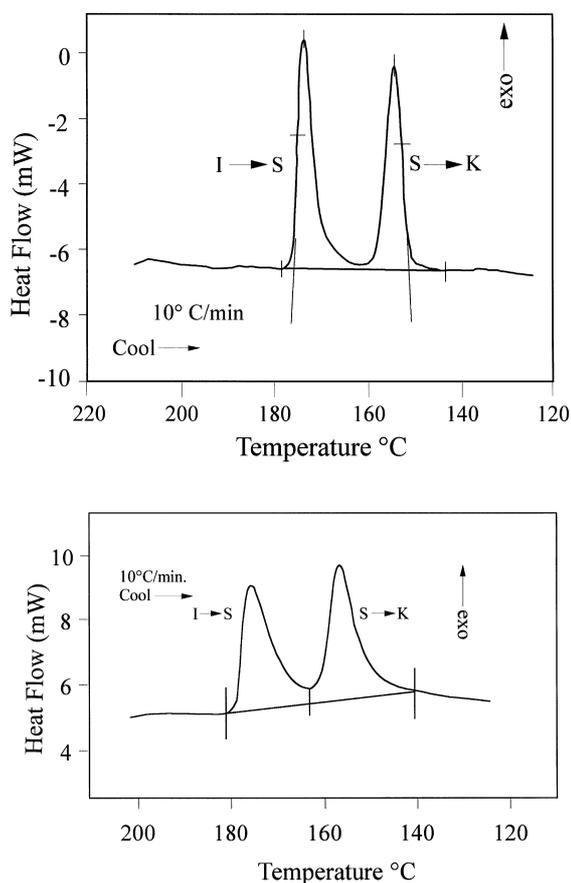
Fig. 3. (a) Cooling scan of BB8 at −10°C/min on Setaram DSC 141 (power-compensation instrument, wt. 8.98 mg). The transitions are well separated. (b) Cooling scan of BB8 on Setaram DSC 92 (heat-flux instrument, wt. 8.78 mg) at −10°C/min. There is some overlap.

power-compensation Setaram DSC 141. The sample mass used was 8.98 mg. From Fig. 3(a), at a glance, it can be seen that the two transitions do not overlap and the I–S transition is slightly bigger than the S–K transition. It can be seen that whereas the Mettler DSC 30 instrument suggests a mesophase window of ~9°C (peak-to-peak), the Setaram DSC 141, like the Perkin–Elmer DSC 7, indicates a window of ca. 20°C for our BB8. At −10°C/min, the enthalpy of the high-temperature peak (I–S) was 19.6 J/g and that of the low-temperature peak (S–K) was 17.9 J/g (Table 1). The typical repeatability of currently produced calorimeters is ca. ±0.2 J/g, hence, the difference in the two peak areas must be considered as real. At −5°C/min

(Table 1, thermograms not shown), the Setaram DSC 141 gave separated peaks with enthalpy values of 19.0 (I–S) and 17.2 J/g (S–K). Again, it is fair to compare the response of the Setaram DSC 141 (Fig. 3(a)) with Mettler DSC 30 (Fig. 1(a)), because the same cooling rates and similar sample weights were used (8.98 mg for the Setaram DSC 141 vs. 9.00 mg for the Mettler DSC 30).

Fig. 3(b) shows the cooling scan at −10°C/min of BB8 recorded on the *heat-flux* Setaram DSC 92. The sample mass used was 8.78 mg. From Fig. 3(b), it can be seen that the two transitions overlap to a certain extent, as the curve does not drop to the baseline, but the degree of overlap is not as much as on the Mettler DSC 30 (Fig. 1(a). The mesophase window was ca. 19°C (Table 1), which is similar to the results from the two power-compensation instruments (Perkin–Elmer DSC 7 and Setaram DSC 141). However, the enthalpy of I–S transition (21.3 J/g) was lower than S–K transition (22.2 J/g), but the situation is reversed at 5°C/min (Table 1).

Thus, from the two types of Setaram instruments, it is clear that the power-compensation instrument gives better resolution of peaks. The Setaram heat-flux instrument gives more overlap under the same conditions, but its performance is not grossly inferior. Several other heat-flux calorimeters (not shown here) were tried. Their performance was found to be variable: the Mettler DSC 820 gave overlapped peaks as in Fig. 1(a), the Shimadzu gave a performance similar to the heat-flux Setaram DSC 92 with some peak overlap, but the very best (Polymer Laboratories DSC Gold) approached a performance similar to the power-compensation DSCs (Table 1). With heat-flux calorimeters, such as the Mettler DSC 820, the response could be improved (i.e. non-overlapping peaks) by using smaller sample masses.

Oddly enough, we found that our observations of BB8 under the optical hot-stage microscope were more in accordance with the behaviour seen in the Mettler DSC 30 (i.e. overlapping transitions) than with the results observed with the power-compensation DSC. Thus, in the optical microscope, on cooling from the isotropic state, batonnets and conic focal domains of the S_A phase grow partially, but before they coalesce completely crystallisation starts. That is, the second phase transiton starts before the first is complete and we found that this makes the character-

Table 1
Heats of fusion, peak temperatures for BB8 measured on different DSCs

Instrument	DSC type[a]	dt/dt°C/min	Sample mass (mg)	Peak T_1 (I–S)	Peak T_2 (S–K)	ΔH_1 (J/g)	ΔH_2 (J/g)
Mettler DSC 30	HF	−10	9	170	161	peaks overlapped	peaks overlapped
Mettler DSC 820	HF	−10	10.73	172	162	peaks overlapped	peaks overlapped
Mettler DSC 820	HF	−10	8.61	172	152	less overlap	less overlap
Setaram DSC 141	PC	−10	8.98	173.6	154.1	19.6	17.9
Setaram DSC 141	PC	−5	8.98	175.7	158	19	17.2
Setaram DSC 92	HF	−10	8.78	175.3	156.5	21.3	22.2
Setaram DSC 92	HF	−5	8.78	175.7	158.9	19.5	18.5
Shimadzu DSC-50	HF	−10	1.7	176	157.4	not measured	not measured
Shimadzu DSC-50	HF	−5	1.7	176.6	158.5	not measured	not measured
PL-DSC Gold	HF	−10	5.48	177	157.8	18.5	17.6
PL-DSC Gold	HF	−5	5.48	178.4	161.3	17.5	15.9
Perkin–Elmer DSC 7	PC	−10	9.77	176	156	19.1	17.7

[a] HF: heat flux DSC; PC: power compensation DSC.

isation of BB8 difficult, both by optical microscopy and hot stage X-ray. This is unlike the case of BB6 which has a stable smectic mesophase and which shows non-overlapping transitions both, in the microscope and DSC. The reason for the similarity of the result for BB8 seen in the hot-stage optical microscope and the heat-flux DSC may be that, they cannot attain a linear cooling profile through a transition, which is possible with a power-compensation DSC instrument.

Finally, we must also consider whether the differences in the mesophase window of BB8 cited in the literature are affected by other factors apart from instrument design. For BB8, some authors have reported mesophase windows that are 26° and 32°C wide [1–4]. With monotropic molecular liquid crystals which are unimolecular, the crystallisation rates can be expected to be similar for products synthesized in different laboratories. However, with monotropic liquid-crystal polymers (as indeed with all crystallisable polymers), the crystallisation rate has a molecular weight dependence. Angelloni et al. [11] have shown that the width of the mesophase window in other types of monotropic liquid-crystal polymers is affected by the molecular weight due to its effect on the crystallisation rate. Two samples of BB8 synthesized in different laboratories can be different also, because of intrinsic differences in the crystallisation rate. Thus, the mesopase window of BB8 and the separation of transitions depends on molecular weight and crystallisation rate, the cooling rate and also on the instrument's detection capacity.

4. Conclusions

This work clearly illustrates the point that the DSC performance on heating and cooling may not be symmetrical (i.e. equally good). The response on cooling appears to be in general, better, with the power-compensation instruments. With a monotropic liquid-crystal polymer, such as BB8, the power-compensation instruments generally gave the best performance at −10 and −5°C/min, even with the use of relatively large sample masses (9 mg). That is, they showed complete separation of the two transitions. With most heat-flux calorimeters, the separation of transitions was inferior, and in some instruments it appears that the second transition starts before the first is complete. However, with heat-flux instruments, optomisation of instrumental design and testing conditions can improve matters when working with samples, such as monotropic liquid crystals. We believe that a monotropic polymer liquid crystal, such as BB8, which crystallises relatively fast, would be a good material to test the performance of a DSC instrument on cooling, in terms of its ability to separate the peaks.

Acknowledgements

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