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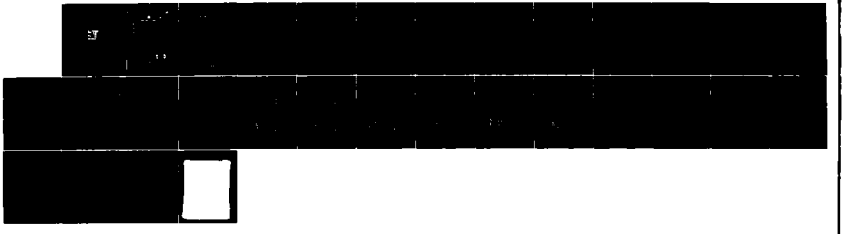

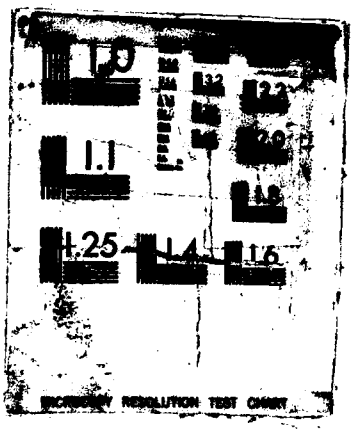
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MELBOURNE, VICTORIA

REPORT

MRL-R-1047

THE APPLICATION OF DIFFERENTIAL SCANNING CALORIMETRY TO IGNITION TRANSFER IN PYROTECHNIC DELAYS: TERNARY MIXTURES OF BORON, RED LEAD AND CHROMIC OXIDE

D.J. Whelan, L.V. De Yong, M. Maksacheff and B. Pletikapa

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ABSTRACT

In ignition transfer studies using the MRL Ignition Stand-Off Test Apparatus, it was found previously that some boron-fuelled pyrotechnic formulations based on boron - red lead - chromic oxide (BLC) sustained ignition while others did not. Differential scanning calorimetry has indicated that ignition can proceed by two different pathways, either by direct oxidation of boron by ~~Pb_3O_4~~ or by simple thermal decomposition of ~~Pb_3O_4~~, and it is sustained only in those red lead-rich formulations where direct oxidation of boron is the main reaction.

Lead oxide

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The application of differential scanning calorimetry to ignition transfer in pyrotechnic delays: ternary mixtures of boron, red lead and chromic oxide

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ANNOUNCEMENT

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KEYWORDS

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Reaction kinetics	Boron	Lead oxide
Ignition	Red lead	Solid state

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ABSTRACT

In ignition transfer studies using the MRL Ignition Stand-Off Test Apparatus, it was found previously that some boron-fuelled pyrotechnic formulations based on boron - red lead - chromic oxide (BLC) sustained ignition while others did not. Differential scanning calorimetry has indicated that ignition can proceed by two different pathways, either by direct oxidation of boron by Pb_3O_4 or by simple thermal decomposition of Pb_3O_4, and it is sustained only in those red lead-rich formulations where direct oxidation of boron is the main reaction.

CONTENTS

THE APPLICATION OF DIFFERENTIAL SCANNING CALORIMETRY TO IGNITION TRANSFER IN PYROTECHNIC DELAYS: TERNARY MIXTURES OF BORON, RED LEAD AND CHROMIC OXIDE

1. INTRODUCTION

Pyrotechnic delay compositions are used in many devices to provide a reliable, reproducible time interval between two events in an explosive train. They are formulated to undergo self-sustained combustion in the absence of air and often consist of only a fuel and an oxidant. Occasionally, however, materials are added to the formulation to assist in its initiation in a device, to moderate its reactivity or to improve its structural or mechanical integrity [1].

Such a range of formulations are the BLC pyrotechnic compositions (Table 1) which consist of an intimate mixture of amorphous boron (10% by weight) and varying amounts of red lead, Pb_3O_4 (oxidant) and chromic oxide, Cr_2O_3 (a compatible moderator, [2]). They are closely related to the gasless pyrotechnic composition BLC 190, originally proposed by Bentley and Elischer for use in M42 percussion cap assemblies [3,4], and were originally formulated for use as boron-fuelled acceptors in ignition transfer studies [5]. These studies, carried out in the recently-developed MRL Ignition Stand-Off Test Apparatus [5], established that ignition from M42 and from M42F1 filled percussion caps was sustained only by the first four members of this series (BLC 190, BLC 181, BLC 172 and BLC 163) and not by the next two members of the series (BLC 154 and BLC 145). This result was somewhat unexpected [6] as it had been found earlier that all of these formulations ignited at temperatures between 670 K and 695 K (Table 1) and that it was considered that there was sufficient oxidant (Pb_3O_4) available to sustain reaction in all these compositions once ignition commenced [6].

For this reason, it was decided to investigate the behaviour of these formulations under slow, controlled ignition conditions using the technique of differential scanning calorimetry. This report summarizes the results of this investigation and identifies the reason for the change in the observed ignition characteristics associated with these compositions.

Aspects of the chemistry of BLC 190 and the stoichiometry of the formulation have been discussed elsewhere [4]. Suffice it to say that, in these formulations as in most pyrotechnic formulations [1], the fuel (boron) is present in considerable excess compared to that of the oxidant, (Table 2).

2. EXPERIMENTAL

2.1 Thermochemical Measurements

Thermochemical measurements were obtained using a Perkin Elmer DSC-2C Differential Scanning Calorimeter operating in the non-isothermal mode and controlled by a Perkin-Elmer 3600 Data Station with appropriate DSC software.

All samples were accurately weighed on a Mettler ME-30 Microanalytical Balance directly into aluminium sample pans and lids placed (but not crimped) over the samples [7]. The mass of sample needed to obtain a satisfactory DSC trace depends on the rate of reaction of the sample and its energy output; in the present instance, it was necessary to use sample masses varying from 2 mg to 10 mg to achieve this.

The following conditions were used in the operation of the DSC apparatus:

Purge gas:	nitrogen (20 - 25 ml min^{-1})
Temperature calibration:	indium (429.8 K), tin (505 K), lead (600.6 K), K_2SO_4 (858 K)
Heat of Reaction standard:	indium (28.5 J g^{-1} or 6.80 cal g^{-1})
Temperature range scanned:	ambient to ca 850 K (577°C).

Selected samples of the various pyrotechnic compositions were weighed on the microbalance before and after each run in order to ascertain what overall mass changes occurred during the reactions observed in the DSC calorimeter.

Kinetic parameters from the DSC traces were determined from Kissinger's treatment of DSC data, as described by Hauser and Field [8]. This approach has been described in detail in previous publications [4,7]. It leads to (apparent) activation energies and Arrhenius pre-exponential factors [7].

2.2 Materials

The sample of boron used in these investigations was a technical grade, amorphous powder (ex Trona - Kerr McGee Corporation, Oklahoma,

U.S.A.). It was washed and dried before use [9]. Scanning electron microscopy revealed that the particle size of this material was "sub-micron" [4].

Red lead, Pb_3O_4, was an analytical grade reagent from May and Baker. It was ball-milled before use and found to have a median particle size of 6.8 μm [4].

The DSC traces from boron and from red lead have been previously described. Their contributions to the thermograms below 750 K from the BLC formulations are negligible [4].

Chromic oxide, Cr_2O_3, was also an analytical grade reagent from May and Baker. It was ball-milled before use and its median particle size found to be 10-12 μm . The DSC trace from chromic oxide is featureless over the temperature range studied in this work.

Batches of the various pyrotechnic compositions were prepared in a standard way by repetitive dry mix - sieving to produce homogeneous blends of the ingredients.

3. RESULTS

3.1 Differential Scanning Calorimetry

The non-isothermal DSC traces of all BLC formulations are characterised by a pre-ignition exotherm, occurring near 600 K, and an ignition exotherm, occurring near 690 K, at a heating rate of 5 K min^{-1}. However, the profile of the traces of this latter exotherm, measured at similar heating rates, and the energy output associated with it varies from composition to composition (Figs 1-12), the degree of complexity increasing as the relative amount of Cr_2O_3 increases.

The situation is best illustrated by comparing not only the traces from BLC 190 (Figs 1,2) with those from BLC 145 (Figs 11, 12) but also the tabulated kinetic and thermochemical data (Tables 3-5).

The DSC traces of the ignition exotherm of BLC 190 consist of a single, simple envelope associated solely with the oxidation of boron by Pb_3O_4 to yield lead tetraborate, $PbO.2B_2O_3$ [4]. On the other hand, the thermal output from BLC 145 over the temperature range 680 K - 850 K can be described in terms of the same ignition exotherm occurring in BLC 190 (around 690 K) and a post ignition exotherm (commencing around 800 K).

This post-ignition exotherm has characteristics very similar to those from the thermal decomposition of Pb_3O_4 [4],

$$2\ Pb_3O_4 \rightarrow 6\ PbO + O_2,$$

which suggests that, in BLC 145, the interaction between the fuel, B, and the oxidant, Pb_3O_4, is curtailed by Cr_2O_3, acting as either a moderator or diluent.

This interpretation is supported by thermogravimetry and comparison of the relative heat output from BLC 190 and BLC 145. When samples of BLC 190 are heated to ca 830 K, no loss of mass occurs; however, when BLC 145 is heated to this temperature, much less heat per unit mass is given out and an appreciable relative mass loss is observed (0.6 ± 0.1 per cent) suggesting that over 60 per cent of Pb_3O_4 in BLC 145 is decomposing directly with the liberation of oxygen.

These two reactions - viz. direct oxidation of boron and thermal decomposition of oxidant - occur to a greater or lesser degree in BLC 172, BLC 163 and BLC 154 (Figs 5-10 and mass loss experiments).

There is no reaction between boron and chromic oxide (BLC 109) over the temperature range 350 K - 800 K, (Fig. 13).

4. DISCUSSION

4.1 Relevance to Ignition Transfer

Ignition transfer in an explosive train relates both to the thermal energy transfer process which occurs between the ignition source and the acceptor and to the ability of the acceptor to sustain reaction. It requires an understanding of how the igniter operates, how its energy is transferred to the acceptor and how the acceptor responds [5,6].

As mentioned in the Introduction, it had been previously found that, when the BLC range of formulations were tested in the MRL Ignition Stand-off Test, ignition was sustained only by BLC 190, BLC 181, BLC 172 and BLC 163. The present DSC study has been instrumental in revealing why this has been so.

For the various BLC compositions, it can be seen that, once ignition commences, subsequent reaction can proceed by two independent pathways, viz. the low temperature oxidation of boron to B_2O_3 by Pb_3O_4 [4] and the high temperature thermal decomposition of Pb_3O_4 to PbO.

The DSC thermograms show that the latter assumes greater significance in those compositions containing relatively large amounts of diluent, Cr_2O_3, BLC 163, BLC 154 and BLC 145, and it is these last two formulations which failed to sustain reaction in the MRL Ignition Stand-off Test.

It is apparent that reaction of the fuel (boron) and oxidant (Pb_3O_4) is curtailed by moderator/diluent (Cr_2O_3) and this interaction adversely effects the propagation of the ignition reaction in these compositions, even though the fine particle sized boron is present in considerable excess (Table 2).

The situation is exacerbated by the relatively low exothermicity of compositions low in Pb_3O_4 compared to those like BLC 190 and BLC 181 which are richer in Pb_3O_4 (Table 5). While the measured heat of reaction per unit mass of oxidant, Pb_3O_4, does not vary appreciably from one composition to another, the total thermal output per unit mass of composition decreases considerably as chromic oxide content increases. Ultimately, it leads to a situation where the conditions sustaining ignition are not favourable.

Differential scanning calorimetry has proved to be the key to rationalizing these effects.

Footnote:-

This paper originally formed the basis of a presentation to the USA-UK-Canada-Australia Technical Cooperation Program TTCP - Panel W1 Key Technical Area KTA-16 Workshop (Ignition Transfer in Pyrotechnics) held in Melbourne, Australia, in November 1986.

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TABLE 1

The Composition and Temperature of Ignition
of Various BLC Compositions

Designation	Composition (by mass) B : Pb_3O_4 : Cr_2O_3	Ignition Temperature (K)
BLC 190	10 : 90 : 0	682
BLC 181	10 : 80 : 10	673
BLC 172	10 : 70 : 20	672
BLC 163	10 : 60 : 30	685
BLC 154	10 : 50 : 40	695
BLC 145	10 : 40 : 50	680

Ignition temperatures were determined on an instrument built to specifications for the Explosives Research and Development Establishment (now Royal Armaments Research and Development Establishment) Waltham Abbey, Essex, UK. Unconfined 50 mg samples were heated at $5^{o}C\ min^{-1}$ in an open test tube, the temperature of ignition being that tempeature at which the samples ignited to explosion or fast burn.

TABLE 2

The Stoichiometry of the Various BLC Compositions

DESIGNATION	MOLECULAR RATIO		
	B	: Pb_3O_4 :	Cr_2O_3
BLC 190	6.8	: 1.0 :	-
BLC 181	7.7	: 1.0 :	0.6
BLC 172	8.8	: 1.0 :	1.4
BLC 163	10.2	: 1.0 :	2.4
BLC 154	12.3	: 1.0 :	3.3
BLC 145	15.3	: 1.0 :	6.0

In determining these ratios, the following reagent purities were assumed [4]:

Boron 91%

Pb_3O_4 ..... 94% (6% PbO)

Cr_2O_3 ..... 99.5%

TABLE 3

Non-isothermal DSC Characteristics of the Exotherms Associated with the Thermal Decomposition of BLC 190, BLC 181, BLC 172 and BLC 145

BLC 190

Heating Rate ($K\ min^{-1}$)	Ignition Exotherm T_{onset} (K)	Ignition Exotherm T_{max} (K)	Post-ignition Exotherm T_{onset} (K)	Post-ignition Exotherm T_{max} (K)
20	707.4	728.2	-	-
10	699.5	720.2		
5	694.1	713.8		
2.5	690.0	707.6		

Heat of Reaction ($J\ g^{-1}$) 820 ± 29

BLC 181

Heating Rate ($K\ min^{-1}$)	Ignition Exotherm/ T_{onset} (K)	Ignition Exotherm/ T_{max} (K)	Post-ignition Exotherm T_{onset} (K)	Post-ignition Exotherm T_{max} (K)
40	714.2	745.1	-	-
20	707.0	736.9		
10	699.4	729.2		
5	692.9	723.9		
2.5	687.9	717.8		

Heat of Reaction ($J\ g^{-1}$) 728 ± 16

BLC 172

Heating Rate (K min^{-1})	Ignition Exotherm T_{onset} (K)	Ignition Exotherm T_{max} (K)	Post-ignition Exotherm T_{onset} (K)	Post-ignition Exotherm T_{max} (K)
20	706.5	747.3		
10	698.5	739.1	(just apparent)	
5	693.2	733.8	(just apparent)	
2.5	688.5	725.3	(just apparent)	
Heat of Reaction (J g^{-1})	704 ± 33			

BLC 145

Heating Rate (K min^{-1})	Ignition Exotherm T_{onset} (K)	Ignition Exotherm T_{max} (K)	Post-ignition Exotherm T_{onset} (K)	Post-ignition Exotherm T_{max} (K)
20	703	728	815	826
10	698	719	812	823
5	587	712	807	820
2.5	683	707	793	816
Heat of Reaction (J g^{-1})	347 ± 37			

TABLE 4

Kinetic Parameters from Kissinger Plots of Data from BLC 190 to BLC 145 [4,7]

Formulation	E^* (kJ $mole^{-1}$)	$\log_{10} A(s^{-1})$	Correl. Coeff.
BLC 190	420	28.66	0.995
BLC 181	435	29.28	0.980
BLC 172	420	27.80	0.992
BLC 145	405	22.94	0.986

It has been estimated [7] that errors in T_m lead to an uncertainty of ca ± 5 per cent in E^* and of ca ± 3 per cent in $\log_{10} A$. For this reason, the authors believe that there is little to be gained by commenting on the apparent differences in activation energies from formulation to formulation.

As discussed in Ref. 7, these are best regarded as "apparent" Arrhenius parameters.

TABLE 5

Exothermicities associated with the Ignition - Post Ignition Reactions for the Various BLC Formulations

Formulation	Total Heat Output (680 K - 850 K) J g^{-1}	J $(g,Pb_3O_4)^{-1}$
BLC 190	820 ± 29	910
BLC 181	728 ± 16	910
BLC 172	704 ± 33	1000
BLC 163	611 ± 31	1020
BLC 154	440 ± 38	880
BLC 145	347 ± 37	870

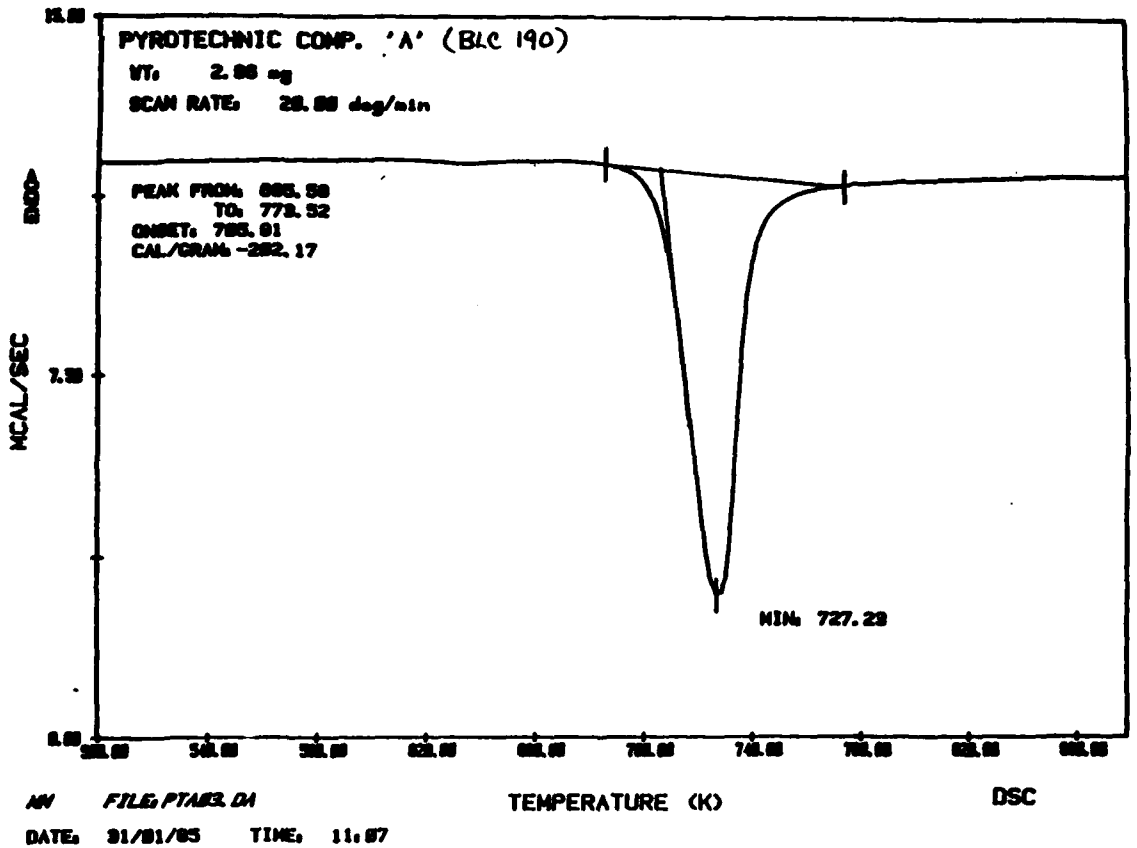

Figure 1 Non-isothermal DSC trace of BLC 190 run at a heating rate of 20K min^{-1} under nitrogen, in an aluminium sample pan.

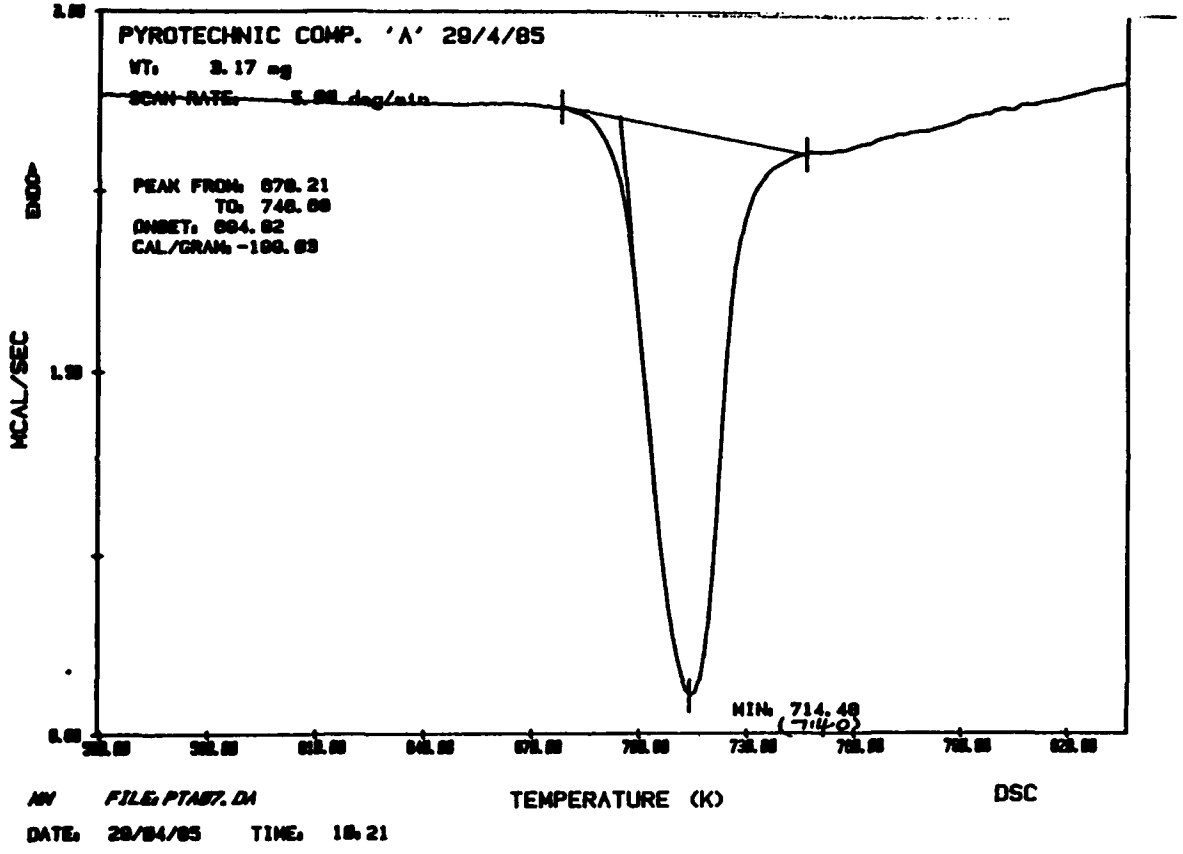

Figure 2 Non-isothermal DSC trace of BLC 190 run at a heating rate of 5K min^{-1} under nitrogen in an aluminium sample pan.

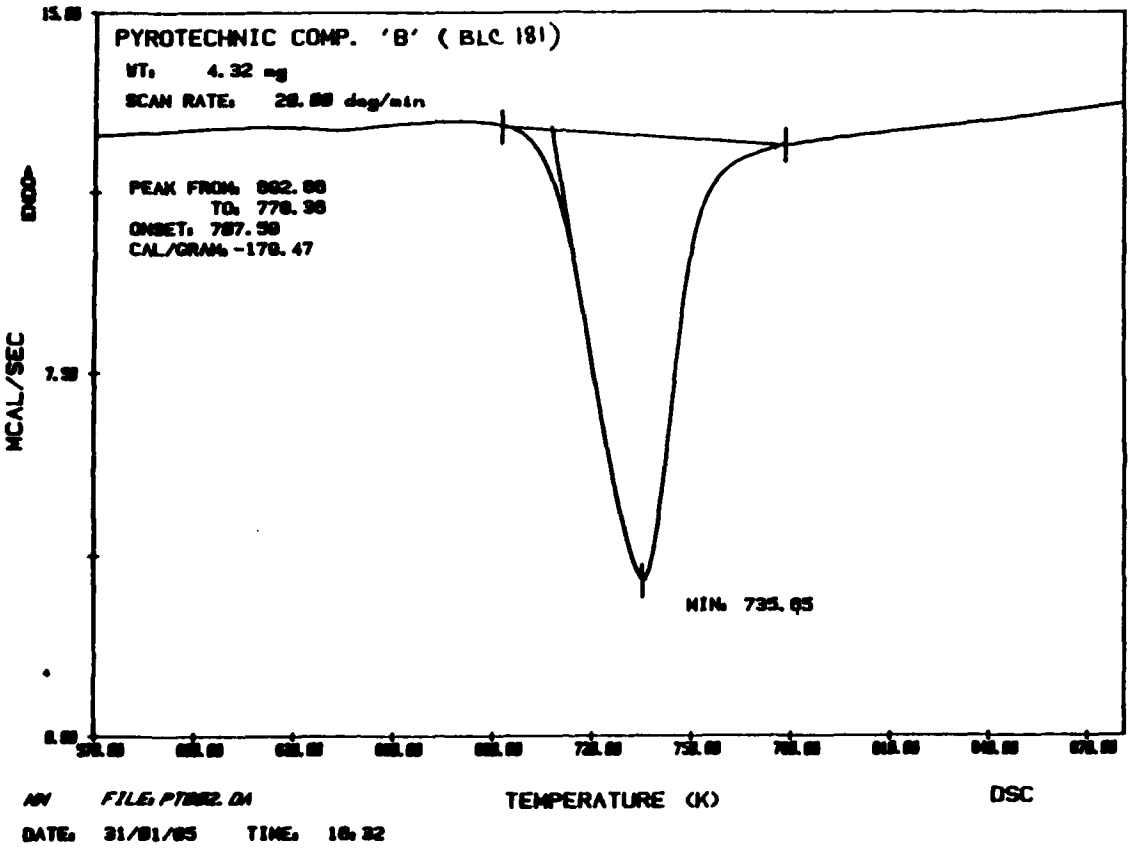

Figure 1 Non-isothermal DSC trace of BLC 181 run at a heating rate of 20K min^{-1} under nitrogen, in an aluminium sample pan.

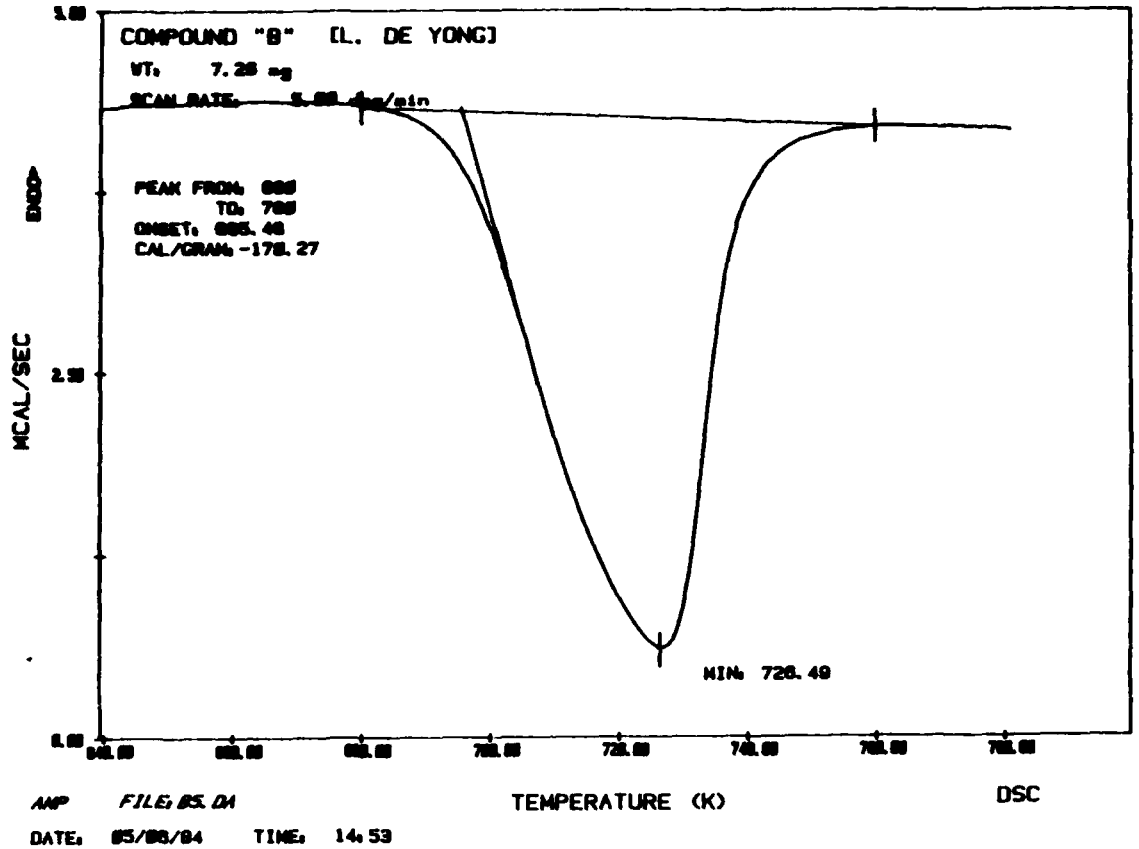

Figure 4 Non-isothermal DSC trace of BLC 181 run at a heating rate of 5K min^{-1} under nitrogen, in an aluminium sample pan.

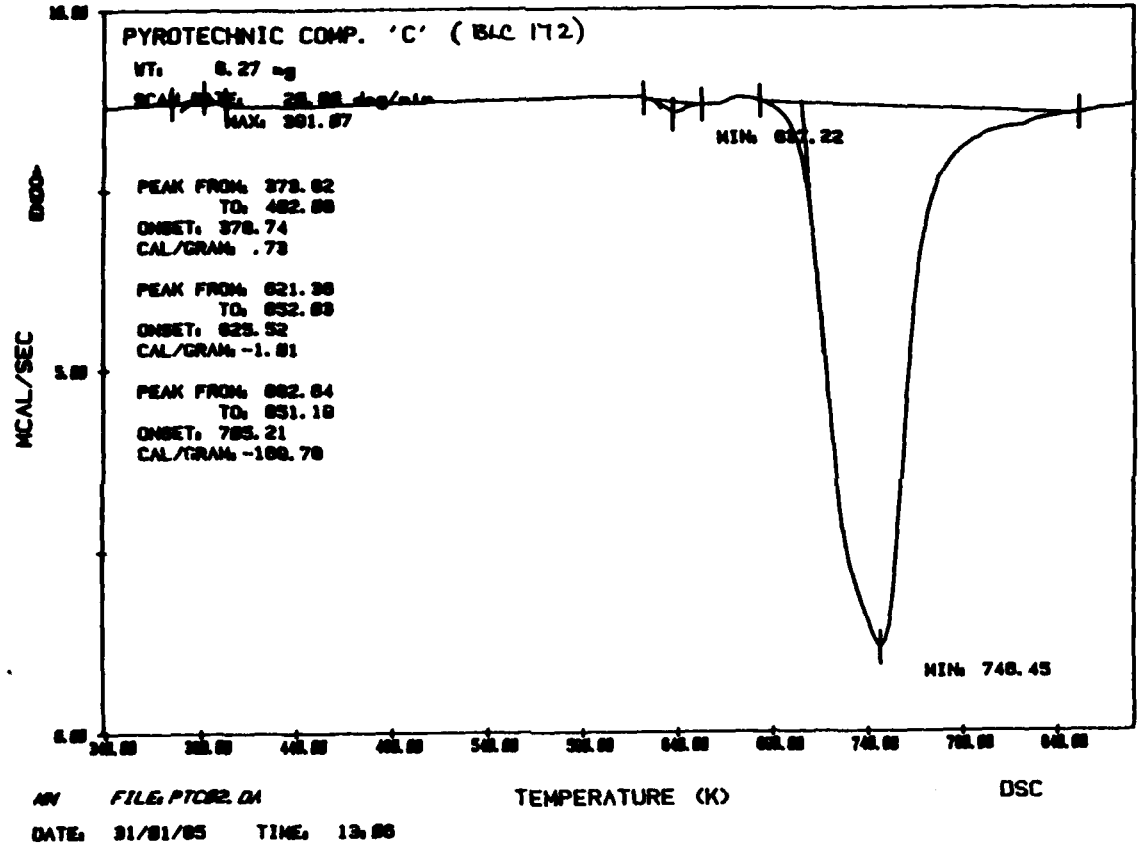

Figure 5 Non-isothermal DSC trace of BLC 172 run at a heating rate of 20K min^{-1} under nitrogen, in an aluminium sample pan.

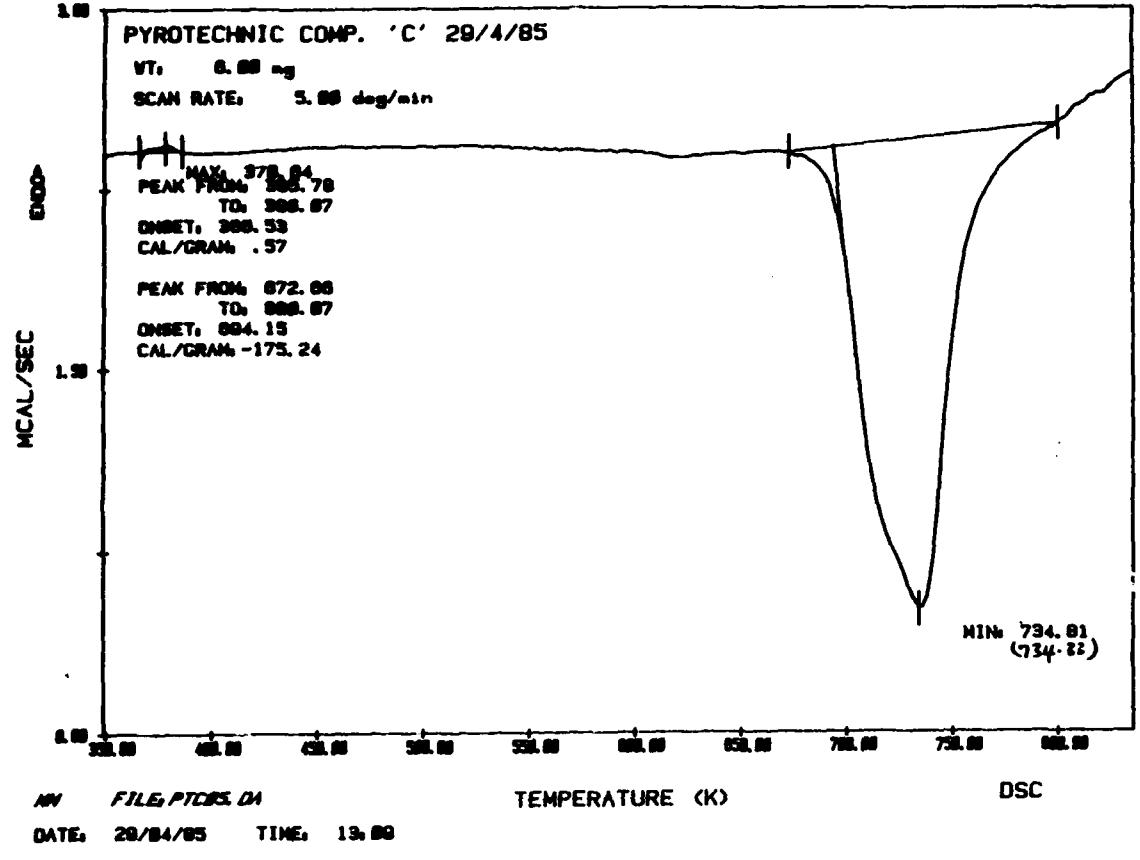

Figure 6 Non-isothermal DSC trace of BLC 172 run at a heating rate of 5K min^{-1} under nitrogen, in an aluminium sample pan.

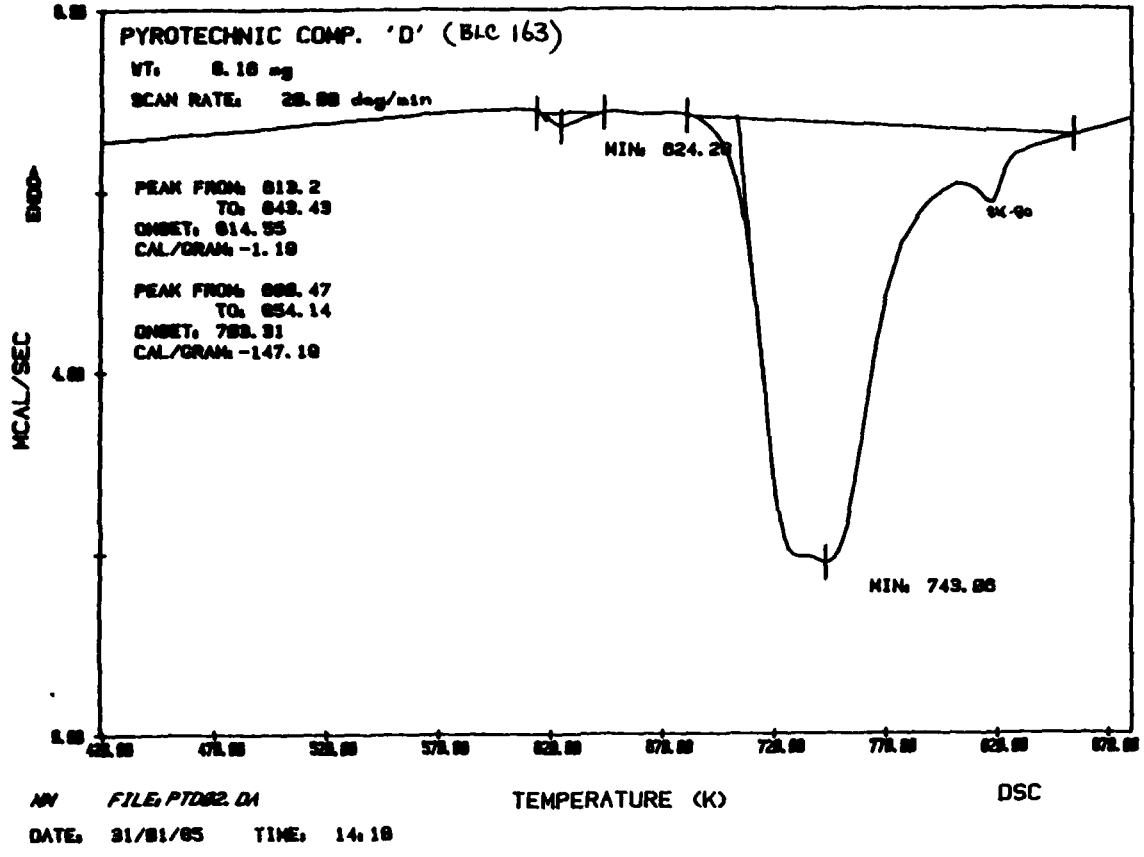

Figure 7 Non-isothermal DSC trace of BLC 163 run at a heating rate of 20K min^{-1} under nitrogen, in an aluminium sample pan.

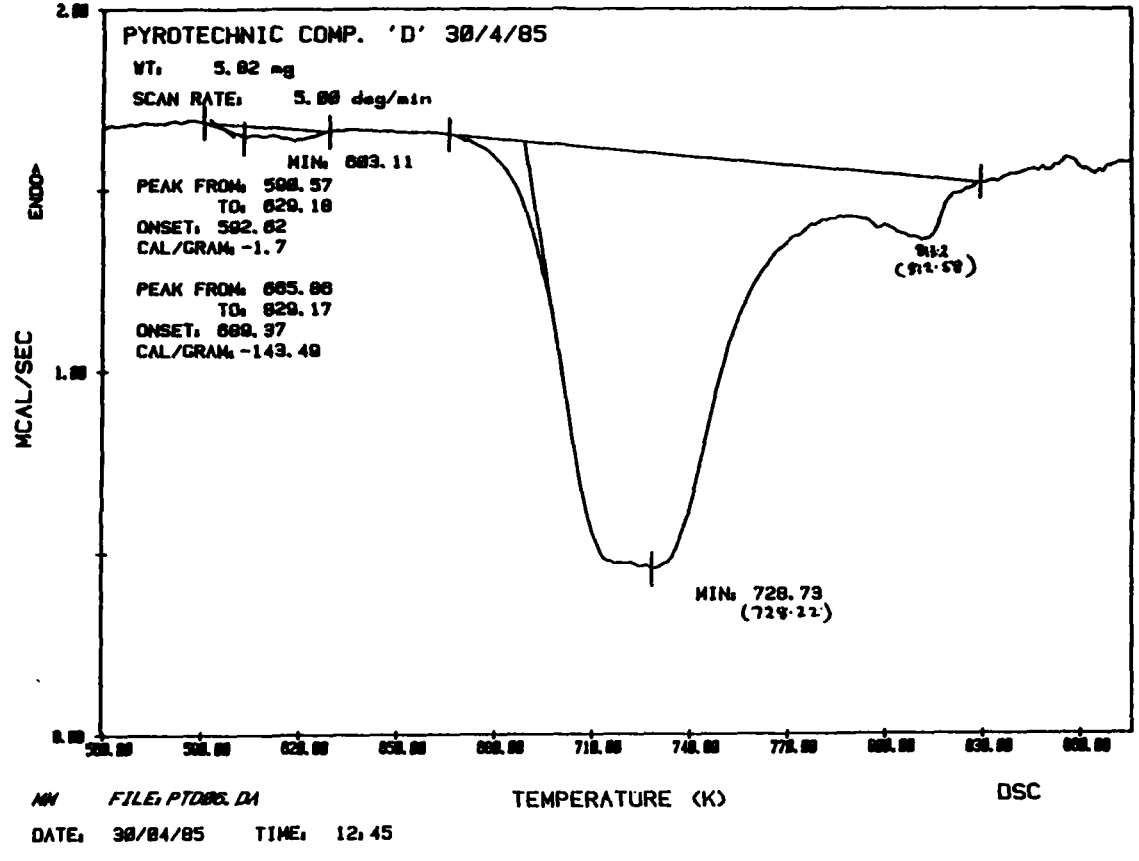

Figure 8 Non-isothermal DSC trace of BLC 163 run at a heating rate of 5K min^{-1} under nitrogen, in an aluminium sample pan.

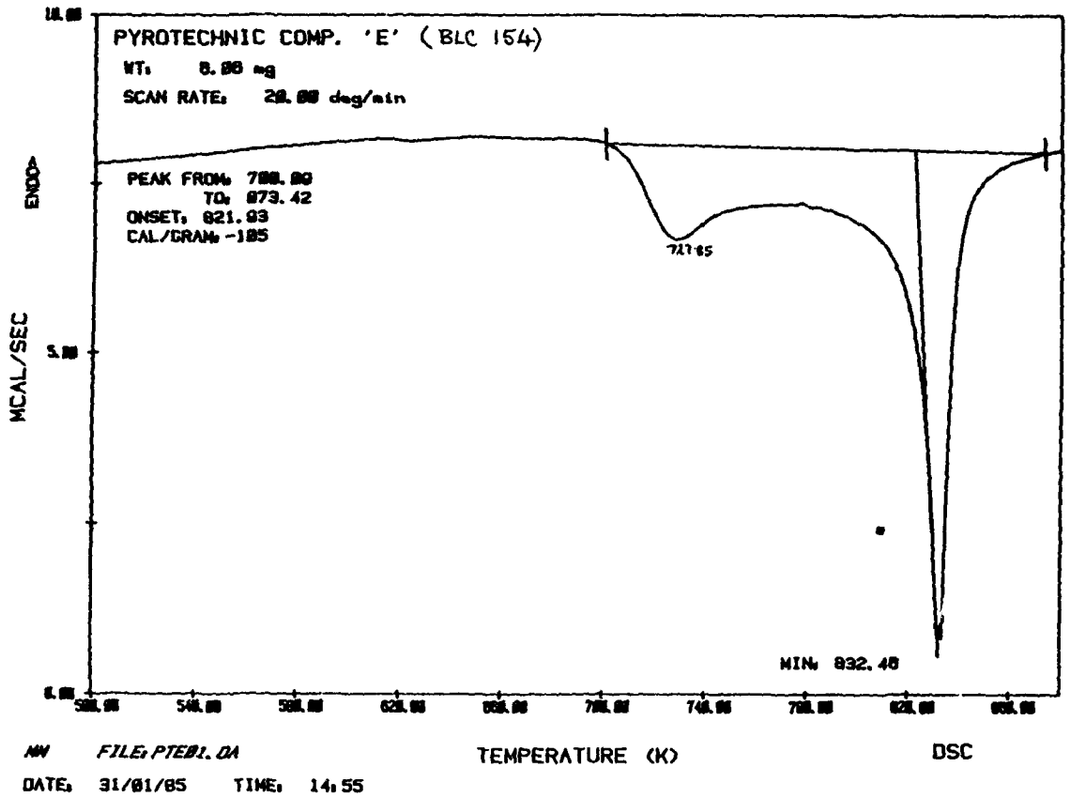

Figure 9 Non-isothermal DSC trace of BLC 154 run at a heating rate of 20K min^{-1} under nitrogen, in an aluminium sample pan.

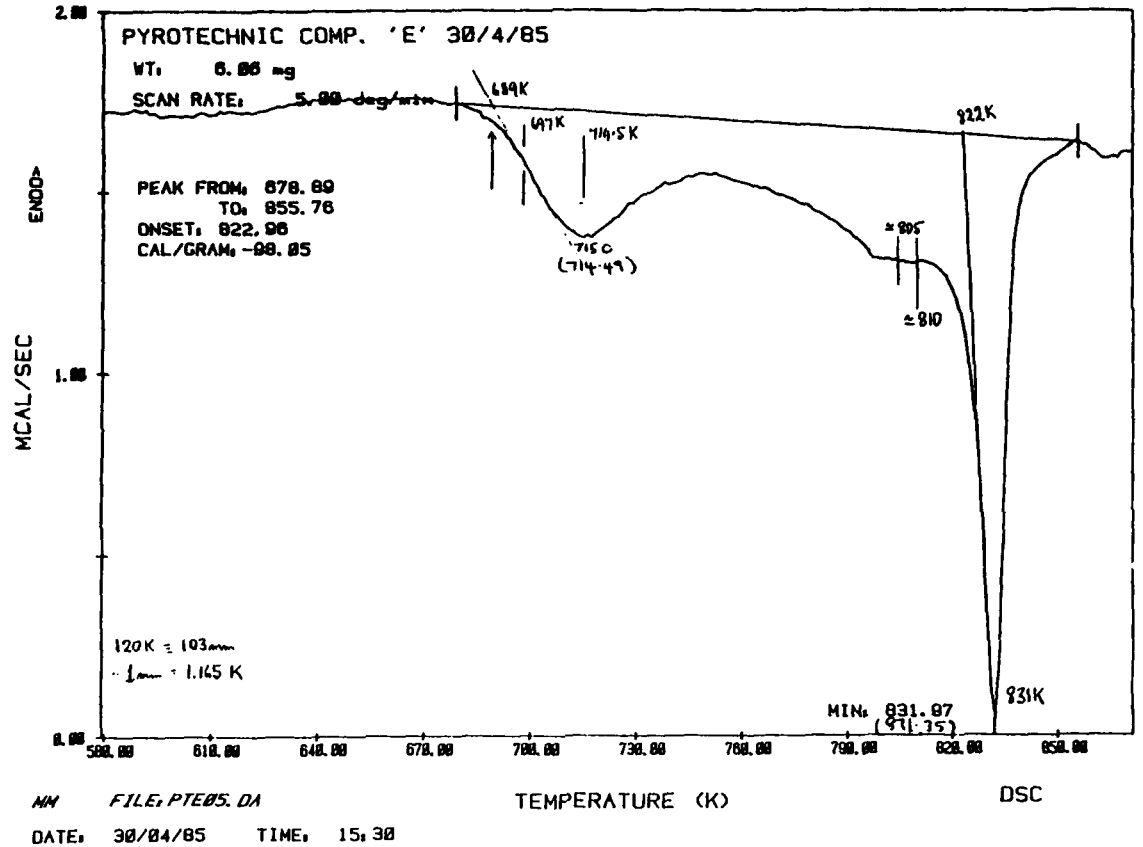

Figure 10 Non-isothermal DSC trace of BLC 154 run at a heating rate of 5K min^{-1} under nitrogen, in an aluminium sample pan.

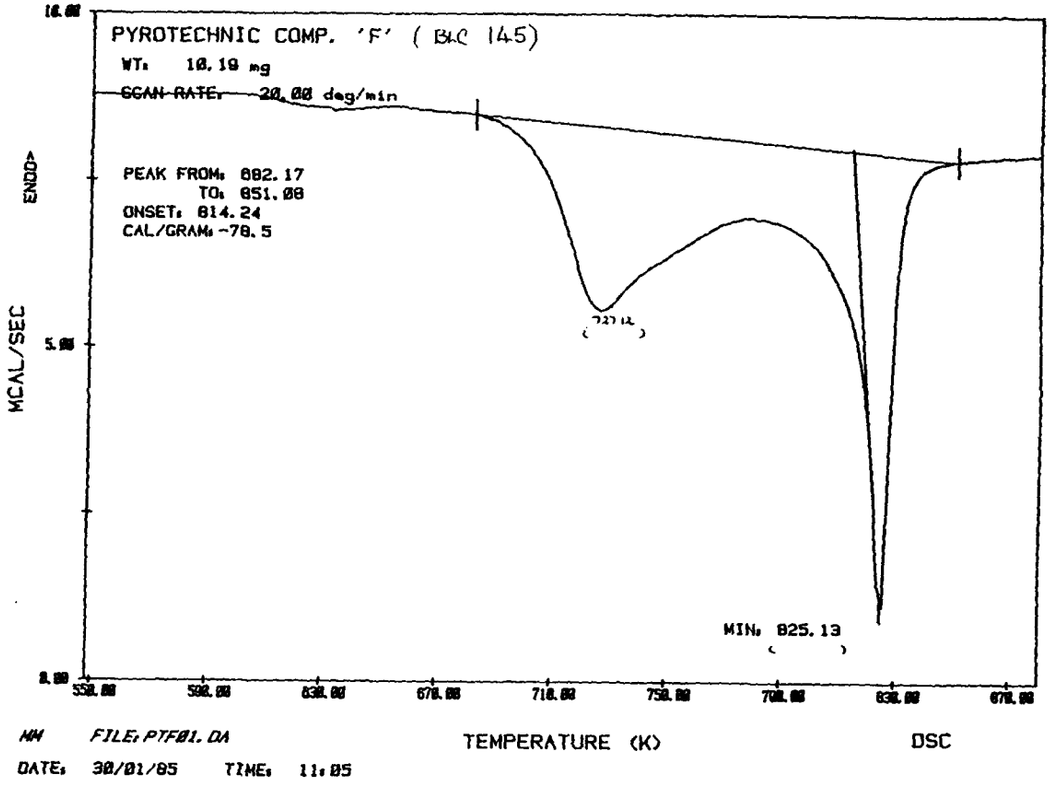

Figure 11 Non-isothermal DSC trace of BLC 145 run at a heating rate of 20K min^{-1} under nitrogen, in an aluminium sample pan.

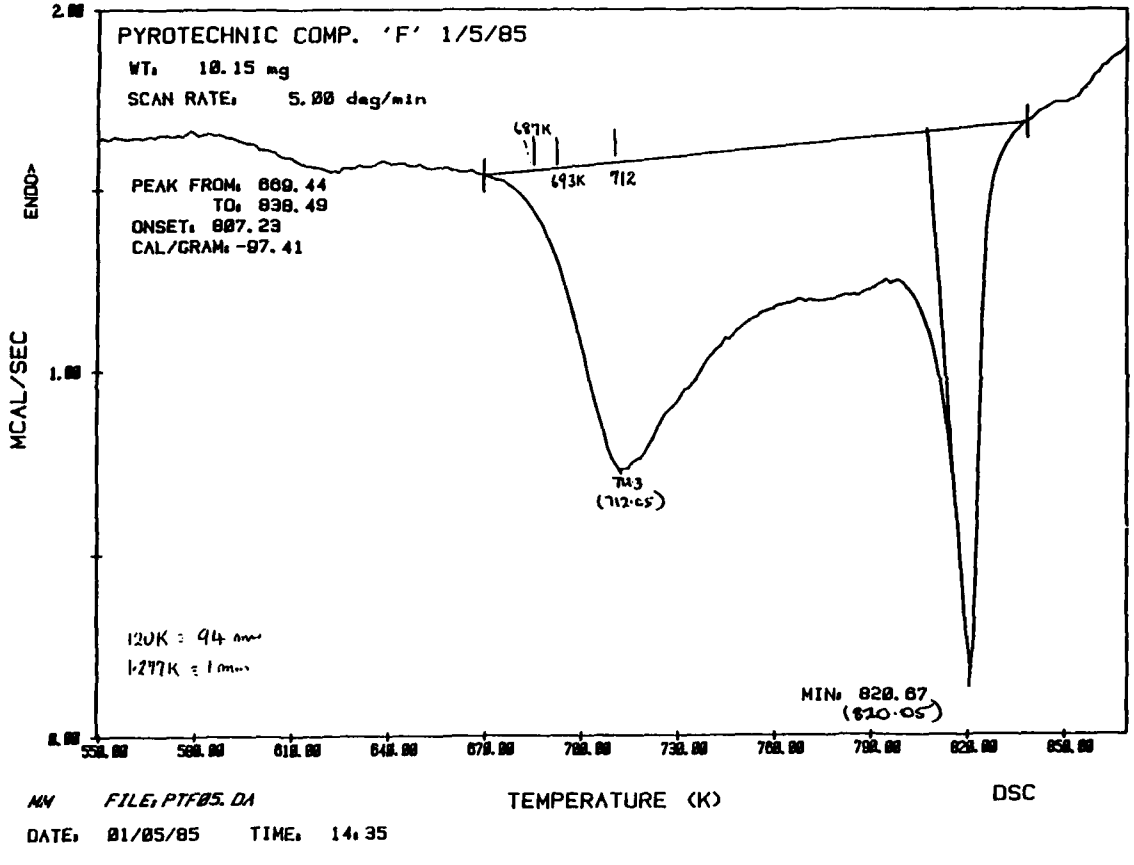

Figure 12 Non-isothermal DSC trace of BLC 145 run at a heating rate of 5K min^{-1} under nitrogen, in an aluminium sample pan.

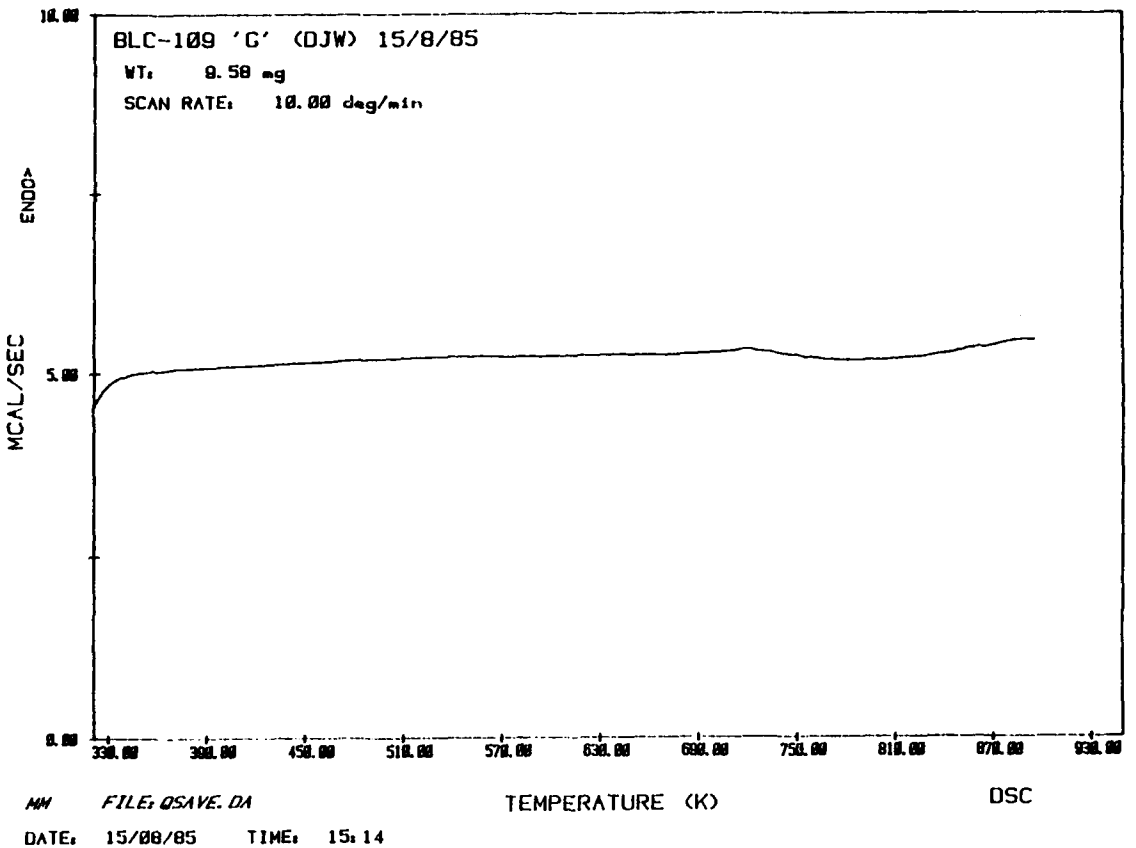

Figure 13 Non-isothermal DSC trace of BLC 109 run at a heating rate of 10K min^{-1} under nitrogen, in an aluminium sample pan.

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