KINETICS OF CURING OF A

VINYL ESTER RESIN

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ABSTRACT

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Differential Scanning Calorimetry (DSC) was used to study the kinetics of a vinyl ester resin catalysed with Methyl Ethyl Ketone Peroxide (MEKP). Kinetic equations were established for different ranges of temperature and degrees of conversion (or simply conversion) from an uncured liquid polymer solution to a fully cured polymer, and were used in a computer program to simulate curing under varying conditions. Outputs from the computer program list conversion and rate of reaction as a function of temperature and time, and are verified with the experimental results.

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1.0 INTRODUCTION

In the chemical and processing industries, pressure vessels and piping are often used to store and convey highly corrosive liquids under pressure. In increasing number of applications it is desirable to manufacture pressure vessels and piping from relatively low cost and corrosion resistant composite materials rather than resorting to expensive exotic materials and alloys.

Although composite materials have been in use for many years in the processing industries, the number of designs where these materials are specified remains limited. Much knowledge must be generated about the behaviour of composites during manufacturing of process equipment, in order to improve product quality and the level of confidence in their use as alternatives to conventional materials.

One important problem in the fabrication of Fiber Reinforced Plastic (FRP) process equipment is the pullback of connecting flanges. When pullback occurs in flanges, the mating surfaces are not flat (Fig. 1), and additional stresses are introduced to deform the flanges at bolt-up, which may result in resin cracking [15]. Pullback is the result of residual stresses which develop in the laminate as it cures. These residual stresses are caused by resin shrinkage or volume loss, and by temperature gradients in the laminate as it cures.

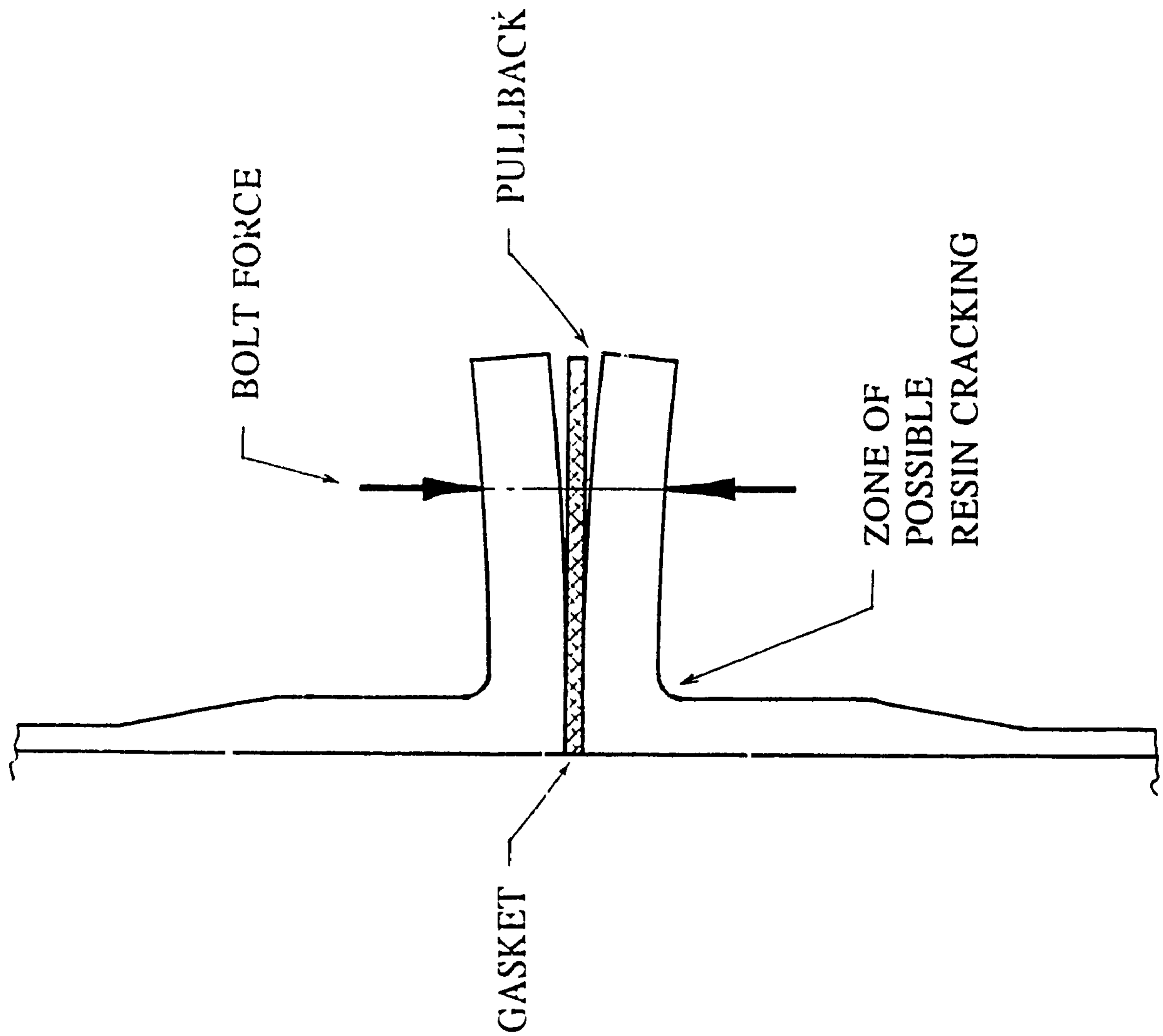

Figure 1 : Flange Pullback

Hand-layup is commonly used to fabricate non standard and large diameter FRP flanges, where the small lot sizes cannot justify the cost of tooling for injection molding. Laminate layup is done on a thermoplastic or wooden mandrel which carries the desired shape of the flange. Fiberglass mats and rovings are impregnated with thermoset resin, which may be epoxy, polyester or vinyl ester, and are stacked over the mandrel in successive layers until the desired flange thickness is achieved. Today, vinyl ester is the most commonly used resin for the fabrication of FRP process equipment.

The resin which was used in the present work was a Bisphenol-A Epoxy-based Methacrylate Vinyl Ester resin from Dow Chemicals, with the product designation Derakane 411-45. This is a high molecular weight resin which is supplied as a solution diluted in 45% by weight of styrene. Styrene is a co-reactive vinyl type comonomer.

Manufacturers may compensate somewhat for the pullback by using a layup mandrel where the vertical face is slightly tapered, hoping that upon completion of the layup and curing the vertical face will have shrunk into a near-vertical position. In practice however it has not been possible to accurately predict pullback, and significant lot to lot variations occur.

It is of great practical value to develop a method by which pullback may be predicted numerically, and this requires a better understanding of the manufacturing process. A complete analysis of the problem at hand should consist of three main parts, 1) a study of the resin kinetics, 2) a heat transfer analysis and 3) a structural analysis.

The objective of this work was to provide the data necessary for the thermal stress analysis of a curing vinyl ester laminate. A study of the resin kinetics, which the following work undertakes, should provide all the data necessary in order to predict the reaction rate at every moment in time and at any temperature within the range to which the laminate is subjected. In the hand-layup process, the FRP flange is placed in an ambient temperature environment and is left to cure by an autocatalysed reaction. As curing progresses, heat is generated from inside the laminate, which causes its temperature to rise, since the generated heat can only be dissipated by convection from its outer surfaces. The period during which the curing resin releases heat is referred to as the exotherm. Measurements have been performed on an occasional basis in the plant of an FRP flange manufacturer in Montreal (CPF Dualam Inc.) by introducing thermocouples into the curing laminate and recording the exotherm temperature throughout the cycle. According to the available data, using a resin mixture with Derakane 411-45 from Dow Chemicals, 1.5% Methyl Ethone Ketone Peroxide (MEKP), 0.2% Cobalt Naphtenate (CoNap) and 0.05% Dimethylaniline (DMA), at an ambient temperature of 25°C, a 3 mm laminate reaches a maximum exotherm temperature of approximately 35°C at mid-thickness, while a 6 mm laminate reaches a maximum exotherm temperature of approximately 70°C in the middle.

The mixture mentionned above was used for all the experiments of the present work and is a standard of the industry, with a processing range of 20 to 40 minutes between 25°C and 30°C, which is suitable for hand-layup [16]. For the manufacturing process under consideration a layup thickness of 6 mm is generally not exceeded, in order to avoid resin cracking [15] or excessive deformation when the curing rate becomes too rapid. If a thicker laminate is required, layup is done in succesive layers of

6 mm maximum thickness, with intermediate cooling periods. It can therefore be assumed that the actual exotherm temperature range is between 30°C and 70°C.

The heat generated by the resin during its exotherm is expressed as [6,7]

$$Q=\rho \Delta H_0 \frac{d\alpha}{dt} \tag{1}$$

where	Q	=	Heat generated	(kW/m^3)
	ρ	=	Density	(kg/m^3)
	α	=	Degree of cure or Conversion	(-)
	$d\alpha/dt$	=	Rate of Reaction	(1/sec.)
	ΔH_0	=	Total Heat of Reaction	(kJ/kg)

The kinetic analysis aims at determining the unknowns ΔH_0 and $d\alpha/dt$.

In the following text the notations α and C will be used interchangeably to represent the degree of cure, or conversion, whereas $d\alpha/dt$ and dC/dt represent interchangeably the rate of reaction.

Previous publications have proposed mathematical models for the kinetics of reaction of epoxy and polyester resin [1,2,3,4,5], which relate the reaction rate to temperature and conversion. These proposed kinetic models seem to be restricted only to some specific ranges of temperature and conversion. No publications have been found for the vinyl ester resin system of interest. After an extensive litterature search and consultations with the resin supplier, as well as with experts in this field of work, no similar publications or product data were found for the vinyl ester resin system under consideration.

In the present work, rather than to find a single equation to describe the entire temperature and conversion range of interest, which seemed difficult to obtain with a reasonable degree of accuracy, a set of data tables of equation parameters at different temperatures and conversions was constructed, which was used in a computer program to calculate the rate of reaction at every moment in time as the temperature changes. The data tables were obtained by performing isothermal DSC measurements at temperatures ranging from 30°C to 85°C in 5°C intervals. For each measurement, by integrating the heat flow curve, a table of conversion and reaction rate versus time was obtained and analysed with a curve fitting software in order to find equation parameters for different conversion ranges.

The results of this work establish the basis upon which a heat transfer analysis can be performed, by calculating the heat generation at each moment in time and at each point in the laminate while curing progresses. Once a method is found to determine temperature and conversion versus time at each location in the laminate, a complete structural analysis may be undertaken to study residual stresses and to predict pullback numerically. Some similar studies have been performed for temperature induced curing processes, using epoxy and polyester resins [6,7,8,9,10,11].

To the author's knowledge, the present work is the first of its kind for a low temperature curing resin system, and will hopefully contribute towards achieving a better understanding of residual stresses in composite materials and in particular in FRP flanges.

2.0 EXPERIMENTAL PROCEDURE

The aim of the following experiments was to obtain kinetic data for the resin at different temperatures or heating rates, which can be used in a computer program to simulate the curing process in varying temperature conditions.

Derakane 411-45 from Dow Chemicals with 45% styrene was used, promoted with 0.2% Cobalt Naphtenate (CoNaP) in 6% solution, accelerated with Dimethylaniline (DMA) in 100% solution, and catalysed with 1.5% Methyl Ethyl Ketone Peroxide (MEKP). All percentages are per weight of solution. This is a typical industry standard with a geltime of 20 to 40 minutes at 25°C to 30°C [16].

2.1 DSC Analysis

DSC analysis was performed on a model TA 912 from Dupont, with a dual sample cell base, as shown in Figure 2.

Figure 3 shows a cross section diagram of the standard DSC cell, which measures the differential heat flow between a resin filled sample pan and an empty reference pan. The sample and reference are subjected to heating or cooling in a controlled atmosphere.

Figure 2 : DSC Cell Base

The resulting differential heat flow is measured by a highly sensitive area thermocouple and recorded as illustrated in Figure 4. The ordinate of the curve in Figure 4 is the measured differential heat flow rate in mW. Since the specific heats of the uncured and cured resin are different, the differential heat flow at the right end of the curve (partially cured) is different from the left end (uncured). In order to integrate the curve a baseline is drawn, which is shown as a dotted line. The reaction rate $d\alpha/dt$ is obtained by dividing the differential rate of heat dH/dt at time t by the total heat of reaction of the fully cured resin, ΔH_0. The conversion α at any time t is obtained by dividing the partial heat of reaction ΔH_p up to time t (the area shown in black in Fig. 4) by the total heat of reaction ΔH_0 (obtained after 100% cure of the resin at a constant heating rate of 10°C/min, see Section 2.1.1.2).

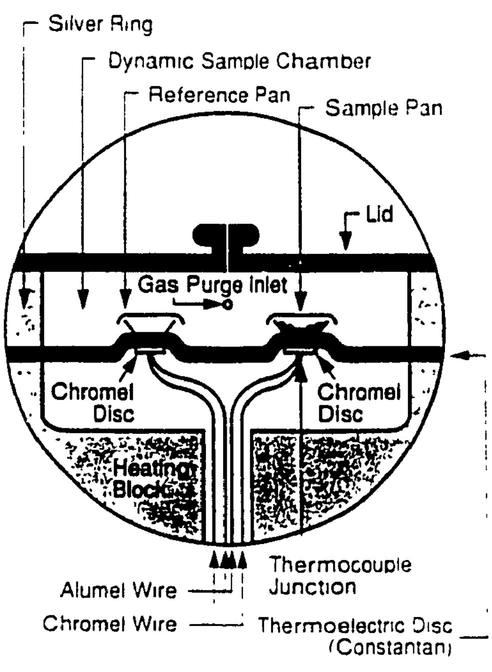

Figure 3 : Cross Section Diagram of DSC Cell

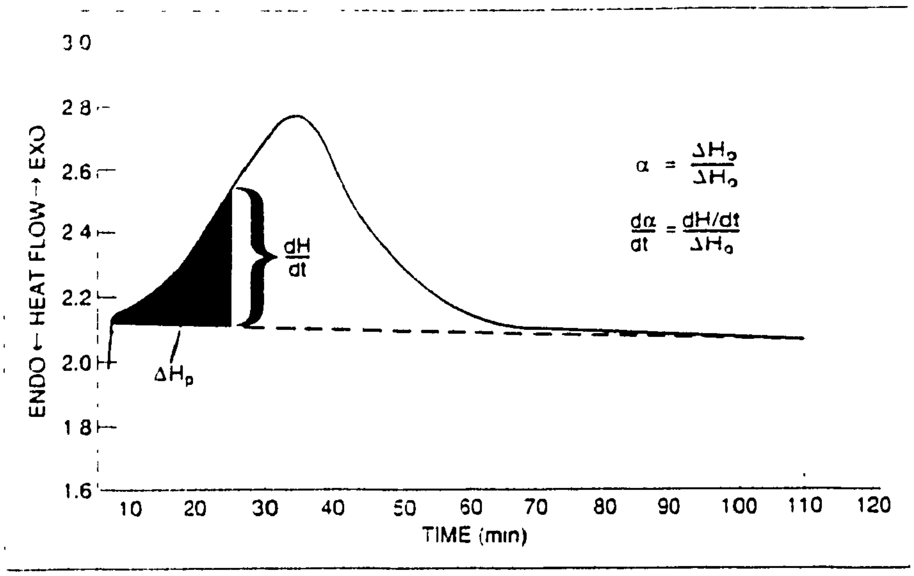

Figure 4 : Typical Exotherm Curve

2.1.1 Test Description

Fourteen (14) constant heating rate measurements were performed in order to calculate the average maximum heat of reaction, ΔH_0, and kinetic parameters n, Z and E_a to be used in Equation (2), and for comparisons in Section 3.2.2.

Twenty-four (24) isothermal measurements at temperatures from 30°C to 85°C provided the data necessary to obtain kinetic expressions relating the rate of reaction to conversion, temperature and time.

2.1.1.1 Procedure

Before each experiment, a new batch of resin mixture was prepared by adding accurately weighted amounts of catalyst to a premix of resin, promoter and accelerator. Two samples of the mixture, each with a mass of 5 to 10 mg, were dropped into aluminum pans, covered with a lid, and the walls of the pan were bent over the lid to seal the resin. Approximately 15 minutes after addition of the catalyst into the resin solution, the two pans (samples A and B) were placed simultaneously into the DSC cell and were heated at a constant temperature rate or isothermally, as described in Sections 2.1.1.2 and 2.1.1.3 respectively.

A Dupont 2100 Thermal Analyser records the heat flow into or out of the samples as they are exposed to a controlled thermal profile. The heat flow

flow curves shown in Appendices B and C were analysed with various softwares to obtain information on the curing characteristics of the resin system.

2.1.1.2 Constant Heating Rate Experiments

The resin was subjected to a constant heating ramp of 10°C/min., from 0°C to 200°C. After insertion of the sample pans at room temperature, the cell was initially cooled to -5°C using liquid nitrogen, and equilibrated at 0°C before startup of the program.

Seven consecutive experiments were performed under these conditions with different batches of resin mixture, providing a total of 14 heat flow curves, shown in Appendix B.

The Borchardt and Daniels DSC Kinetics Data Analysis Program [14] was used to analyse the heat flow curves, and to establish the total heat of reaction for each sample. The total heat of reaction, ΔH_0, is defined as the area under the exotherm peak, as illustrated in Figure 4, assuming that the resin is fully cured after completion of the thermal cycle. By running the experiment a second time on previously cured samples, it may be verified that no more exotherm heat is released during the thermal cycle, which indicates complete cure.

The results of the 14 samples and the calculated average ΔH_0 = 352 J/g are presented in Table 1.

For constant heating rate measurements at 10°C/min, the rate of reaction can be accurately represented by an equation of the form [12,13]

$$\frac{d\alpha}{dt} = k(T)\,(1-\alpha)^n \qquad (2)$$

where $k(T) = Ze^{-Ea/RT}$

Z = Constant

E_a = Constant

R = Gas Constant

Using the Borchardt and Daniels program for curve fitting the parameters Z, E_a and n were calculated for each experiment and the results are listed in Table 1 (columns 2 to 4 from the left). From the column containing the n values it is seen that a value close to 2.45 is obtained from 6 experiments (PE.011, PE.013, PE.014, PE.015, PE.018, PE.020). The Borchardt and Daniels program includes an option by which the values of Log(Z) and E_a may be recalculated by fixing the value of n, and by using n = 2.45 new values of E_a and Log(Z) were obtained for each trial. The resulting parameters are listed in the last 3 columns from the left, and the bottom right corner of the Table shows the calculated average Log(Z) and E_a values for n = 2.45. These data are used in Section 3.2.2 for comparative purposes.

In curing kinetics the value E_a is usually called the activation energy and may have a physical meaning, however in the following work E_a simply represents an equation constant which results from curve fitting trials.

Constant Rate Results

Trial No.	n	Ea	Log Z	dH0	n	Ea	Log Z
PE.008	1.6200	87 9000	12 2600	357 1000	2 4500	101 2000	14 3300
PE.009	0.3400	63.8000	8.6900	338.5000	2 4500	93 6000	13 4400
PE.010	3 2000	101 5000	14 2000	340 6000	2 4500	89 7000	12 4000
PE.011	2.4300	92.4000	12 8700	363 0000			
PE 012	3 5400	99 6000	13 9300	338 6000	2 5000	84 3000	11 5700
PE.013	2 4800	88 9000	12.3400	377 4000			
PE.014	2.4700	85.0000	11 7400	341 5000			
PE.015	2.3500	79 3000	10 9100	359 7000	2 4500	80 7000	11 1300
PE 016	3 4800	83 6000	11 4100	328 5000			
PE.017	1 1100	74.0000	10 0800	373 1000	2 4500	94 0000	13 1800
PE.018	2.1400	85.6000	11 8100	347 2000	2 4500	90 4000	12 5400
PE.019	1 5600	79 8000	10 9500	361 1000	2 4500	93 1000	13 [illegible]
PE.020	2 5100	91.8000	12 7200	336 0000	2 4500	91 0000	12 [illegible]
PE 021	1 8900	79 3000	10 8100	360 3000	2 4500	[illegible] 3000	12 [illegible]
.....			. .				
AVERAGES				352 0000	2 4500	90 5000	12 [illegible]

Table 1 : Constant Rate Results

2.1.1.3 Isothermal Experiments

Isothermal measurements were performed at temperatures varying from 30°C up to 85°C. The DSC cell was preheated to the set temperature and equilibrated for 5 minutes before insertion of the sample pans, in order to establish a clear integration baseline on the heat flow curve.

The running time of each experiment was varied according to the time required to complete the exotherm, over 3 hours at low temperature (30°C) and only 55 minutes at high temperature (85°C). 12 dual sample experiments provided a total of 24 heat flow curves, as shown in Appendix C.

The DSC Isothermal Kinetics Data Analysis Program [12,13] was used to analyse the heat flow curves and to obtain the partial heat of reaction at each temperature, calculated as the total area under the heat flow curve.

The maximum conversion at each temperature is expressed as

$$\alpha_{max} = \frac{\Delta H_r}{\Delta H_0} \qquad (3)$$

where ΔH_r = Total isothermal heat of reaction (total area under the heat flow curve)

ΔH_0 = Total maximum heat of reaction (obtained from the constant heating rate measurements)

Step by step integration of the heat flow curve yields the conversion at each moment in time

$$\alpha = \frac{\Delta H_p}{\Delta H_0} \qquad (4)$$

and the rate of reaction

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} \qquad (5)$$

where ΔH_p = Partial heat of reaction

dH/dt = Differential rate of heat at time t

(see Figure 4).

Appendix D lists the output data from the integration of each heat flow curve, and shows conversion versus time at constant temperature.

2.1.2 Results

2.1.2.1 Type of Equation

The curing kinetics of many thermoset resins can be modeled using either an expression such as Equation (2) which is used in the case of a constant heating rate, or such as Equation (6) [12,13]

$$\frac{d\alpha}{dt}=k(T)\,\alpha^{m}(1-\alpha)^{n} \tag{6}$$

where $d\alpha/dt$ = Reaction Rate

$k(T)$ = $Ze^{-Ea/RT}$

Z = Constant

E_a = Constant

R = Gas Constant

Under isothermal conditions (no external heat input to the curing sample), Equation (2) predicts that the maximum rate of reaction occurs near time = 0 ,as shown in Figure 5, whereas the expression of Equation (6) predicts that the maximum rate of reaction takes place at some time $t > 0$, as shown in Figure 6.

From the isothermal heat flow curves shown in Appendix C, it is seen that the reaction is similar to the example illustrated in Figure 6, and hence Equation (6) can be used to predict the rate of reaction for these isothermal cases.

Figure 7 shows the measured heat flow curve for a 50°C isothermal experiment and illustrates how the reaction rate increases up to a maximum after 35 minutes.

Table 2 lists both the conversion and the rate of reaction versus time after integrating the heat flow curve of Figure 7. It may be observed that the rate of reaction increases to its maximum at approximately 40% conversion, and then decreases.

Equation (6) very conveniently expresses $d\alpha/dt$ as a function of α and T, in such a way that if an expression can be found that agrees with the data of Table 2 at 50°C, the same expression is likely to remain valid for temperatures slightly below or above 50°C, where the rate variable $k(T) = Ze^{-Ea/RT}$ is an exponential function of temperature.

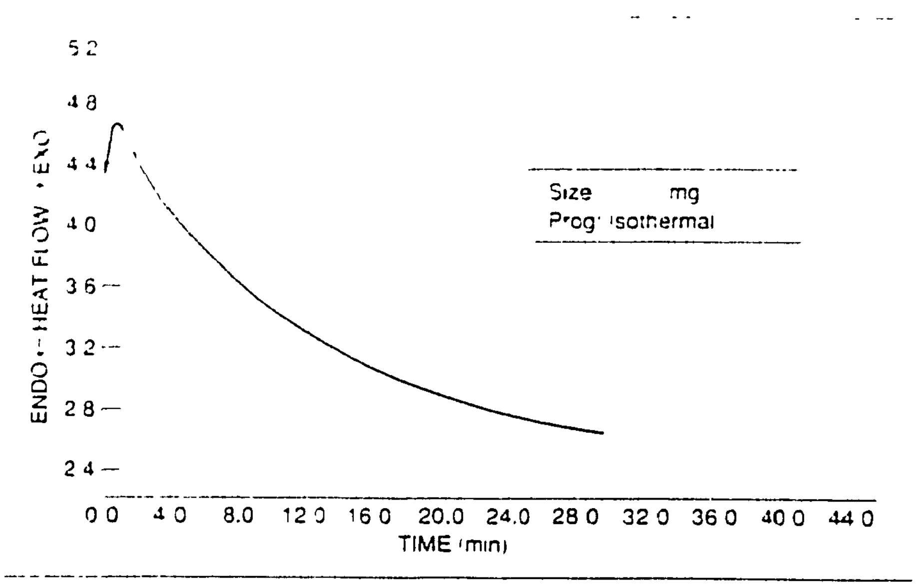

Figure 5 : Typical Heat Flow Curve corresponding to Equation (2) [12,13]

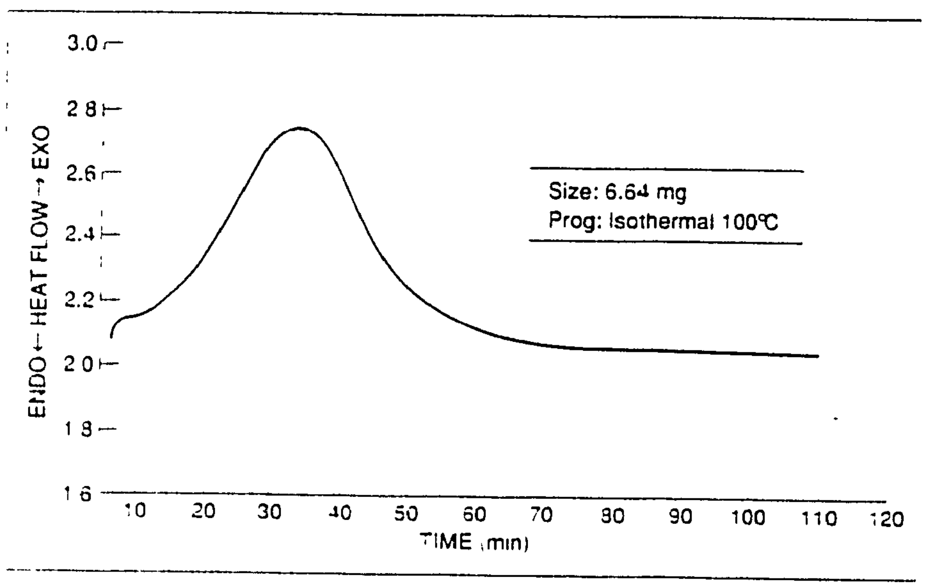

Figure 6 : Typical Heat Flow Curve corresponding to Equation (6) [12,13]

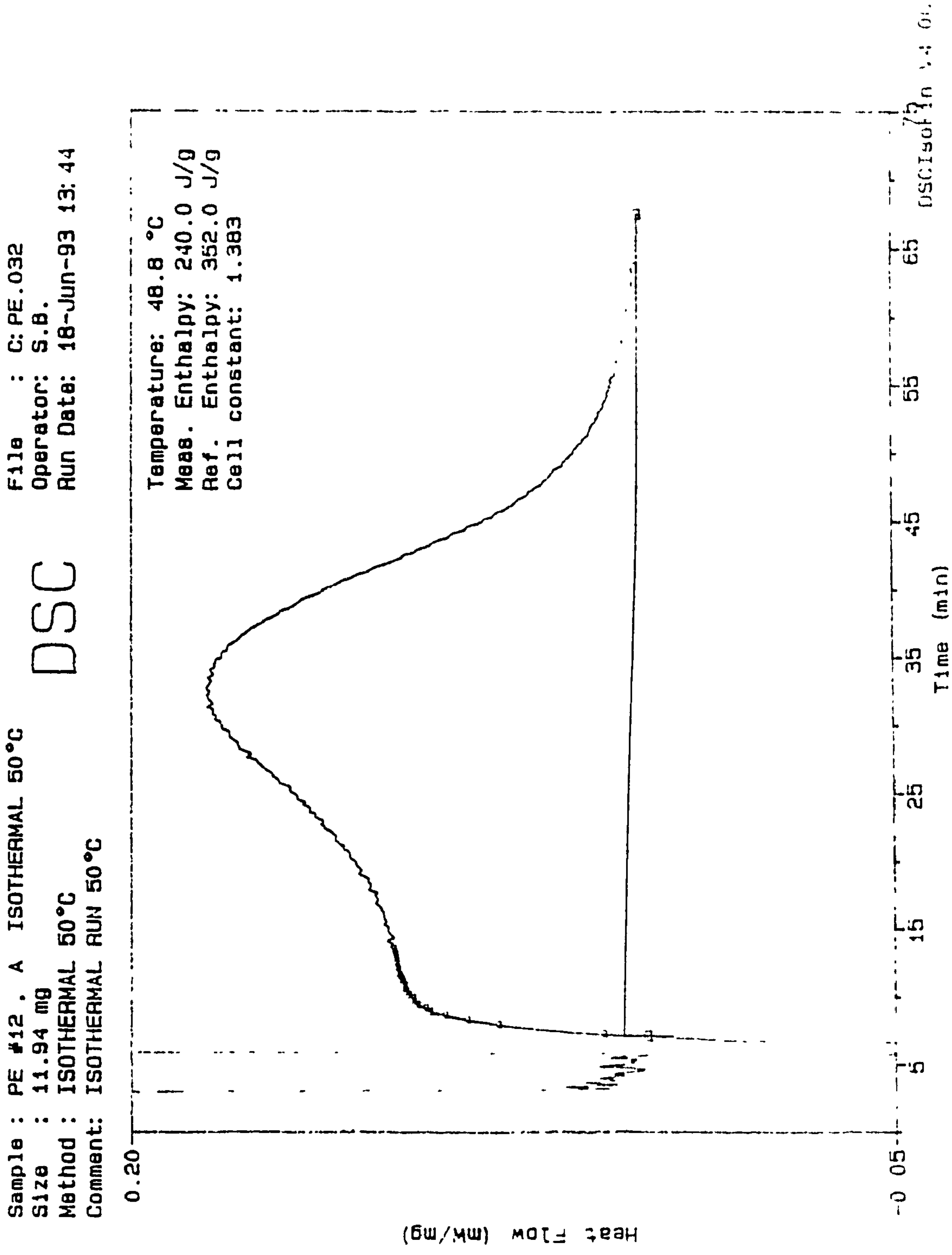

Figure 7 : Heat Flow Curve, T = 50°C

C and dC/dt
T = 50 Degrees C

Time (min.)	C	dC/dt
0.2060	0.0001	0.0016
3.2770	0.0285	0.0121
5.5700	0.0569	0.0126
7.7570	0.0851	0.0132
9.8640	0.1134	0.0138
11.8940	0.1419	0.0147
13.7870	0.1704	0.0156
15.5200	0.1985	0.0169
17.1470	0.2268	0.0181
18.6670	0.2553	0.0195
20.0800	0.2836	0.0207
21.4140	0.3119	0.0218
22.6940	0.3404	0.0228
23.9200	0.3688	0.0235
25.1200	0.3972	0.0238
26.2940	0.4250	0.0237
27.5200	0.4540	0.0234
28.7500	0.4823	0.0227
30.0300	0.5104	0.0214
31.4170	0.5388	0.0196
32.9370	0.5669	0.0174
34.7240	0.5951	0.0142
37.0700	0.6235	0.0101

Table 2 : Conversion (C) and Rate of Reaction (dC/dt) at 50°C

2.1.2.2 Single Temperature Equations

The DSC Isothermal Kinetics Data Analysis Program is used to find the best fit curve for each of the conversion data sets presented in Appendix D. The results are tabulated in Appendix E.

After several curve fitting trials, it was found that the data, as illustrated in Table 2, could not be fitted accurately with a single equation. Each data table was broken down into 10 conversion ranges, from the initial conversion $C=0$ to the maximum isothermal conversion $C=C_{max}(T)$, and for each conversion range the best fit parameters were calculated. $C_{max}(T)$ $(=\alpha_{max})$ is obtained from Equation (3) and the heat flow curve at constant temperature T.

The best fit parameters for $T=50°C$ are listed in Table 3.

Temperature = 50 Degrees C
Equation Parameters, Single Analysis

C	m	n	k
0.0000	0.3050	5.9100	4.31E-02
0.0680	-0.1250	-2.5400	7.65E-03
0.1360	-0.1290	-2.7700	7.40E-03
0.2050	0.5080	-0.2380	3.61E-02
0.2730	1.0200	1.1100	1.09E-01
0.3400	1.7200	2.4700	4.09E-01
0.4100	2.1000	3.0100	7.58E-01
0.4760	3.7700	4.8400	8.54E+00
0.5440	14.5000	13.4000	4.84E+06
0.6140	14.5000	13.4000	4.84E+06
0.6770	14.5000	13.4000	4.84E+06

Table 3 : Equation Parameters, T = 50°C

2.1.2.3 Multiple Temperature Equations

In Section 2.1.2.2 equation parameters were found that fit the conversion data from Appendix D at specific temperatures. In order to find parameters which satisfy a broader temperature range, and which can be used in a computer program, conversion data from three different temperature runs are analysed together. For the sake of accuracy, temperatures are selected 5°C apart.

Using the DSC Isothermal Kinetics Data Analysis Program, the following sets were analysed for 10 conversion ranges: 30°C/35°C/40°C, 35°C/40°C/45°C, 40°C/45°C/50°C, 45°C/50°C/55°C, 50°C/55°C/60°C, 55°C/60°C/65°C, 60°C/65°C/70°C, 75°C/80°C/85°C. The results from 30°C/35°/40°C were applied to T=30°C and are shown in Table 4. For T=35°C and T=40°C the results from 35°C/40°C/45°C were used, as shown in Tables 5 and 6. Tables 7 to 15 show the results for T=45°C to T=85°C.

The proposed computer program presented in Section 3.0 was used to calculate conversion and reaction rate versus time at each reference temperature from 30°C up to 85°C, using the equation parameters obtained by multiple temperature analysis (see the sets of three temperatures listed above). At some reference temperatures, for example at T=40°C, the equation parameters from two sets could have been used, either 35°C/40°C/45°C or 40°C/45°C/50°C. In this case the program was run twice at T=40°C, once using the parameters from the 35°C/40°C/45°C analysis, and a second time using the parameters from the 40°C/45°C/50°C analysis. The program produced an output table of C and dC/dt versus time for each case. Both output tables were compared to Tables D.5 and D.6 in Appendix D, and the parameters which produced the results closest to the experimental data shown in Tables D.5 and D.6 were selected. In the case T=40°C, the parameters from the set 35°C/40°C/45°C fit the experimental data more closely. The same procedure was followed for each reference temperature up to 85°C.

Among the analysis sets of three temperatures listed above two sets were omitted, 65°C/70°C/75°C and 70°C/75°C/80°C. This was due to a sudden change in the shape of the heat flow curves between 70°C and 75°C, which is seen by comparing Figures C.17 and C.18 to Figures C.19 and C.20 in Appendix C. The heat flow curves at 75°C are similar to those at 80°C and 85°C, but differ significantly from the heat flow curves at 70°C. Therefore it seemed logical not to perform multiple temperature analyses with temperature sets including both 70°C and 75°C.

Systems of equations are hereby available for 12 different reference temperatures at 5°C intervals from 30°C up to 85°C. For all intermediate temperatures, the equation parameters for the next lowest reference temperature are used. For example at T=43°C and C=0.26

$$\frac{dC}{dt}=Ze^{-E_a/RT}C^m(1-C)^n \tag{6}$$

where Z, E_a, n and m are the values at the reference temperature of 40°C and the reference conversion value of C=0.228

With this system of equations it is possible to simulate any varying time-temperature curve in the 30°C to 85°C range with a multiple step function, where the time increment of each step has a corresponding constant temperature.

Temperature = 30 Degrees C

Equation Parameters, Multiple Analysis

C	m	n	Ea	Log Z
0.0000	0.2050	-0.0799	63.1000	8.6800
0.0640	0.1210	-1.3600	55.0000	7.1400
0.1250	0.4350	-0.5440	53.8000	7.2800
0.1900	1.0000	1.1700	53.3000	7.7600
0.2530	0.7870	0.5620	53.0000	7.4800
0.3130	1.2300	1.5100	53.3000	7.9100
0.3760	0.3850	0.3840	54.3000	7.4600
0.4420	0.3300	0.7290	59.2000	8.3400
0.5010	1.0700	2.2800	76.2000	11.9000
0.5680	-4.5800	2.9600	155.0000	24.1000
0.6290	-4.5800	2.9600	155.0000	24.1000

Table 4 : Equation Parameters, T = 30°C

Temperature = 35 Degrees C
Equation Parameters, Multiple Analysis

C	m	n	Ea	Log Z
0.0000	0.2150	2.0300	42.3000	5.2500
0.0740	0.2920	-0.3080	43.2000	5.4000
0.1460	1.1000	2.5500	41.9000	6.0500
0.2200	2.0000	4.1200	42.2000	6.8500
0.2920	2.3200	3.8400	42.4000	7.0200
0.3680	2.9400	4.1500	41.7000	7.2200
0.4370	3.4000	3.8700	40.7000	7.1400
0.5150	4.4900	4.2700	41.0000	7.5900
0.5830	10.7000	8.3500	48.5000	11.8000
0.6560	10.7000	8.3500	48.5000	11.8000
0.7340	10.7000	8.3500	48.5000	11.8000

Table 5 : Equation Parameters, T = 35°C

Temperature = 40 Degrees C
Equation Parameters, Multiple Analysis

C	m	n	Ea	Log Z
0.0000	0.2150	2.0300	42.3000	5.2500
0.0760	0.2920	-0.3080	43.2000	5.4000
0.1500	1.1000	2.5500	41.9000	6.0500
0.2280	2.0000	4.1200	42.2000	6.8500
0.3030	2.3200	3.8400	42.4000	7.0200
0.3790	2.9400	4.1500	41.7000	7.2200
0.4550	3.4000	3.8700	40.7000	7.1400
0.5310	4.4900	4.2700	41.0000	7.5900
0.6070	10.7000	8.3500	48.5000	11.8000
0.6820	10.7000	8.3500	48.5000	11.8000
0.7550	10.7000	8.3500	48.5000	11.8000

Table 6 : Equation Parameters, T = 40°C

Temperature = 45 Degrees C
Equation Parameters, Multiple Analysis

C	m	n	Ea	Log Z
0.0000	0.2280	2.2800	44.7000	5.6600
0.0750	0.0387	-2.1100	37.2000	4.0800
0.1490	1.4200	3.9100	36.2000	5.4700
0.2260	2.7100	6.1100	37.9000	6.8200
0.3010	3.3900	6.1000	39.0000	7.3600
0.3720	3.4000	4.9800	40.0000	7.3200
0.4500	3.3000	4.0100	40.2000	7.0500
0.5250	3.8500	3.9900	37.1000	6.6800
0.5950	8.4900	6.9900	31.7000	7.9900
0.6810	8.4900	6.9900	31.7000	7.9900
0.7560	8.4900	6.9900	31.7000	7.9900

Table 7 : Equation Parameters, T = 45°C

Temperature = 50 Degrees C
Equation Parameters, Multiple Analysis

C	m	n	Ea	Log Z
0.0000	0.2280	2.2800	44.7000	5.6600
0.0680	0.0387	-2.1100	37.2000	4.0800
0.1360	1.4200	3.9100	36.2000	5.4700
0.2050	2.7100	6.1100	37.9000	6.8200
0.2730	3.3900	6.1000	39.0000	7.3600
0.3400	3.4000	4.9800	40.0000	7.3200
0.4100	3.3000	4.0100	40.2000	7.0500
0.4760	3.8500	3.9900	37.1000	6.6800
0.5440	8.4900	6.9900	31.7000	7.9900
0.6140	8.4900	6.9900	31.7000	7.9900
0.6770	8.4900	6.9900	31.7000	7.9900

Table 8 : Equation Parameters, T = 50°C

Temperature = 55 Degrees C
Equation Parameters, Multiple Analysis

C	m	n	Ea	Log Z
0.0000	0.2540	4.3000	35.4000	4.4100
0.0800	0.0606	-0.7650	28.1000	2.8700
0.1600	0.3030	-0.0942	22.6000	2.2600
0.2390	0.8530	1.2500	21.0000	2.5000
0.3180	1.3800	2.2300	21.5000	3.0200
0.3980	1.5000	2.2800	21.8000	3.1200
0.4770	1.3200	1.9500	20.2000	2.7100
0.5570	1.2100	1.7400	18.0000	2.2700
0.6360	1.0400	2.2300	20.1000	2.7600
0.7160	1.0400	2.2300	20.1000	2.7600
0.7950	1.0400	2.2300	20.1000	2.7600

Table 9 : Equation Parameters, T = 55°C

Temperature = 60 Degrees C
Equation Parameters, Multiple Analysis

C	m	n	Ea	Log Z
0.0000	0.2540	4.3000	35.4000	4.4100
0.0810	0.0606	-0.7650	28.1000	2.8700
0.1590	0.3030	-0.0942	22.6000	2.2600
0.2390	0.8530	1.2500	21.0000	2.5000
0.3170	1.3800	2.2300	21.5000	3.0200
0.3980	1.5000	2.2800	21.8000	3.1200
0.4780	1.3200	1.9500	20.2000	2.7100
0.5570	1.2100	1.7400	18.0000	2.2700
0.6330	1.0400	2.2300	20.1000	2.7600
0.7120	1.0400	2.2300	20.1000	2.7600
0.7880	1.0400	2.2300	20.1000	2.7600

Table 10 : Equation Parameters, T = 60°C

Temperature = 65 Degrees C
Equation Parameters, Multiple Analysis

C	m	n	Ea	Log Z
0.0000	0.2240	3.7400	54.6000	7.3300
0.0840	0.0223	-0.8140	57.5000	7.4000
0.1670	0.3650	0.3220	51.9000	6.9000
0.2500	1.2600	2.3400	44.6000	6.5600
0.3340	1.5000	2.4200	38.9000	5.8100
0.4180	1.4900	2.2500	34.7000	5.1300
0.5020	1.2600	1.9100	30.0000	4.2200
0.5840	0.4520	1.2800	26.8000	3.2800
0.6670	-1.6800	0.8320	36.0000	4.1100
0.7500	-1.6800	0.8320	36.0000	4.1100
0.8330	-1.6800	0.8320	36.0000	4.1100

Table 11 : Equation Parameters, T = 65°C

Temperature = 70 Degrees C
Equation Parameters, Multiple Analysis

C	m	n	Ea	Log Z
0.0000	0.2240	3.7400	54.6000	7.3300
0.0860	0.0223	-0.8140	57.5000	7.4000
0.1720	0.3650	0.3220	51.9000	6.9000
0.2580	1.2600	2.3400	44.6000	6.5600
0.3430	1.5000	2.4200	38.9000	5.8100
0.4300	1.4900	2.2500	34.7000	5.1300
0.5150	1.2600	1.9100	30.0000	4.2200
0.5990	0.4520	1.2800	26.8000	3.2800
0.6840	-1.6800	0.8320	36.0000	4.1100
0.7730	-1.6800	0.8320	36.0000	4.1100
0.8580	-1.6800	0.8320	36.0000	4.1100

Table 12 : Equation Parameters, T = 70°C

Temperature = 75 Degrees C
Equation Parameters, Multiple Analysis

C	m	n	Ea	Log Z
0.0000	0.2670	3.8200	36.6000	4.7000
0.0830	-0.2190	0.2750	21.2000	1.7600
0.1660	-1.0400	-3.8700	10.3000	-0.8540
0.2480	0.0863	-0.8870	8.6300	-0.1050
0.3300	0.3250	-0.4620	9.2700	0.1100
0.4130	2.1800	2.1500	9.1700	1.3300
0.4930	2.6500	2.2700	7.4000	1.1400
0.5790	2.6500	1.8100	4.1900	0.3800
0.6610	4.0500	2.1900	1.8100	0.3200
0.7440	4.0500	2.1900	1.8100	0.3200
0.8260	4.0500	2.1900	1.8100	0.3200

Table 13 : Equation Parameters, T = 75°C

Temperature = 80 Degrees C
Equation Parameters, Multiple Analysis

C	m	n	Ea	Log Z
0.0000	0.2670	3.8200	36.6000	4.7000
0.0850	-0.2190	0.2750	21.2000	1.7600
0.1700	-1.0400	-3.8700	10.3000	-0.8540
0.2530	0.0863	-0.8870	8.6300	-0.1050
0.3390	0.3250	-0.4620	9.2700	0.1100
0.4240	2.1800	2.1500	9.1700	1.3300
0.5080	2.6500	2.2700	7.4000	1.1400
0.5930	2.6500	1.8100	4.1900	0.3800
0.6780	4.0500	2.1900	1.8100	0.3200
0.7610	4.0500	2.1900	1.8100	0.3200
0.8470	4.0500	2.1900	1.8100	0.3200

Table 14 : Equation Parameters, T = 80°C

Temperature = 85 Degrees C
Equation Parameters, Multiple Analysis

C	m	n	Ea	Log Z
0.0000	0.2670	3.8200	36.6000	4.7000
0.0870	-0.2190	0.2750	21.2000	1.7600
0.1730	-1.0400	-3.8700	10.3000	-0.8540
0.2600	0.0863	-0.8870	8.6300	-0.1050
0.3470	0.3250	-0.4620	9.2700	0.1100
0.4340	2.1800	2.1500	9.1700	1.3300
0.5210	2.6500	2.2700	7.4000	1.1400
0.6080	2.6500	1.8100	4.1900	0.3800
0.6950	4.0500	2.1900	1.8100	0.3200
0.7780	4.0500	2.1900	1.8100	0.3200
0.8640	4.0500	2.1900	1.8100	0.3200

Table 15 : Equation Parameters, T = 85°C

3.0 COMPUTER SIMULATION

A program was written, which uses the parameters from Tables 4 to 15 in order to predict the advancement of cure throughout time with varying temperature. Because of its flexibility and user friendliness, but also in view of future applications, the problem was solved on a Lotus-123 spreadsheet.

3.1 Spreadsheet Layout

The program consists of 5 parts: inputs, data tables, computations, a macro program, and output tables.

3.1.1 Inputs

The inputs section includes selection of the type of analysis desired, such as isothermal, constant rate, varying temperature or temperatures as calculated with a heat transfer analysis for each time step (future work).

Other inputs are the time increment Δt (min.), limit time of the analysis t_{max} (min.), initial temperature T(0) (°C) and rate of heating (°C/min.), see Figure 8.

	INPUTS	ISO.	RAMP	VARYING	HEAT TRANSFER
YES/NO		0	1	0	0
t_{max}	6				
Δt	0.5				
T(0)	20				
Rate	10				

Figure 8 : Spreadsheet Data Inputs

Figure 8 shows the inputs for a constant heating rate of 10°C/min., starting at 20°C and finishing at 80°C after $t_{max}=6$ minutes. Calculations are performed at each 0.5 minute time increment.

3.1.2 Data Tables

Equation parameters as determined experimentally (see Section 2.1.2.3) at different temperature and conversion ranges are shown in Tables 4 to 15. These are also the tables which are used by the program for lookup of the parameters during computations at each time increment.

Temperatures from 30°C up to 85°C are listed in 5°C intervals. For intermediate temperatures and conversions, the next lowest data set is used. Below 30°C, the 30°C data are used. An input table of temperature versus time is also included on the spreadsheet for varying temperature runs. These are the exotherm temperatures measured with thermocouples during the cure of a laminate layup.

3.1.3 Computations

For each temperature and conversion value, equation parameters m,n,E_a and Log(Z) are extracted from the data table at the next lowest reference temperature and conversion values in the table.

The rate of reaction at each time increment is calculated as

$$\frac{dC}{dt}=Ze^{-E_a/RT}(1-C)^n C^m \tag{6}$$

The conversion for the following time increment is

$$\frac{dC}{dt}\Delta t+C_{old}=C_{new} \tag{7}$$

where

where	C_{old}	=	Conversion at time t
	C_{new}	=	Conversion at time t+Δt
	Δt	=	Time increment
	dC/dt	=	Rate of reaction at time t

For varying temperature runs, the new temperature at time t + Δt is extracted from the input data table. For constant heating rate runs, the temperature at time t+Δt is calculated as

$$T_{new}=T_0+t\cdot Rate \tag{8}$$

where T_o = Initial temperature

t = Cumulative time

3.1.4 Macro Program

The macro program, listed in Figure 9, initializes the spreadsheet and erases the output tables. The program increments time up to the limit requested in the input and stores the calculated conversion and rate of conversion at each increment.

```
/REH43.N243~
{LET A23,B8}
{LET B23,.0005}
{LET B25,.0005}
{LET B7,0}
{GOTO}Z25~
/C~I1~
{IF I1=30}{BRANCH T52}
{IF G23<I1}{BRANCH T55}
{DOWN 2}
/C{DOWN 10}~CL6~
{BRANCH T58}
{LEFT 1}
/C~I1~
{BRANCH T50}
{LET B23,B11}
{LET B25,B12}
{LET I43,G23}
/CB23~J43~
/CB25~M43~
{LET H43,A10}
{LET K43,C24}
{LET N43,C26}
/MH43.N243~H44~
{LET B7,A10}
{IF B7>B5}{BRANCH T70}
{BRANCH T48}
{QUIT}
```

Figure 9: Macro Program Listing

3.1.5 Output Tables

The output format is similar to the output tables of the DSC runs, shown in Appendix D, and is used for plotting of the results.

3.2 Results

Using the spreadsheet program, all the experiments of Section 2.0 were simulated, and the outputs were verified with the experimental results.

3.2.1 Isothermal Calculations

Using the computer program and the data Tables 4 to 15, graphs were printed which show conversion and reaction rate versus time at temperatures ranging from 30°C to 70°C, see Figures 10 to 19. Each graph shows a curve of the calculated values using the parameters from Tables 4 to 15 and the corresponding experimental curves for samples A and B (which were constructed directly from the data in Appendix D).

It is seen from Figures 10 to 19 that the calculated curves clearly follow the curves for samples A and B at all temperatures from 30°C to 70°C, which was to be expected since the equation parameters used for the calculations are based on the experimental data.

Although the majority of points on the calculated curves lie within 10% of the experimental values of samples A and B, local inaccuracies above 10% are encountered, as illustrated in Tables 16 and 17. These inaccuracies are mostly due to differences between samples A and B but also to the fact that the calculated results are based on an average between temperatures.

Figures 10 to 19 were not plotted for the complete time span of each experiment. For example Figures 10 and 11 show conversion and reaction rate up to 95 min. at 30°C, whereas the corresponding experiment at 30°C was stopped after approximately 200 min., as seen from the heat flow curves for sample A (Figure C.1) and sample B (Figure C.2) in Appendix C. This was due to a limitation in the DSC Isothermal Kinetics Data Analysis Program, through the use of which data tables of conversion and reaction rate could not be obtained for the complete time span of the heat flow curves. It is seen for example from Table D.2 in Appendix D that conversion and reaction rate for sample B at 30°C isothermal are listed only up to 96.461 min., which corresponds to approximately 0.46 conversion, whereas the conversion after 200 min. is approximately 0.63.

The approximate value 0.63 is obtained by dividing the average of the measured enthalpies (total area under the isothermal heat flow curve) shown in Figure C.1 (214.6 J/g) and in Figure C.2 (225.7 J/g) by the maximum (or reference) heat of reaction of the 100% cured resin (352 J/g).

However, using the same software, it was possible to establish equation parameters up to higher conversion ranges. This can be seen from Table 4 at T=30°C, where the parameters in the row beginning with C=.568 are valid from C=.568 to C=.629. From C=.629 onwards, that is up to time infinity, it was not possible to determine equation parameters, therefore the parameters of the previous row (C=.568) were listed in the last row, but these will not accurately predict conversion beyond the time span of the present experiment. Likewise at 70°C the parameters in the row containing C=.684 (Table 12) are valid from C=.684 to C=.773. Above C=.773 equation parameters could not be determined, and the row containing C=.684 was simply copied into the rows containing C=.773 and C=.858. Therefore the model can be used accurately only up to C=.773.

The problem at higher conversion ranges arises from the fact that the reaction becomes so slow that the differential heat flow rates cannot be measured, and the heat flow curve converges with its baseline, as illustrated in Figure 4. The maximum conversion which can be measured by DSC under isothermal conditions at 30°C is 0.63, but if the isothermal experiment were carried on beyond 200 min., the resin would continue curing at a very slow rate and the conversion may eventually reach 0.7 or more, however other methods of analysis would be required to obtain such data. The maximum conversion obtained at the end of each isothermal experiment ($\alpha_{max} = \Delta H_r / \Delta H_0$, see Equation (3), Section 2.1.1.3) is the maximum which can be measured with a single DSC isothermal run, however it is not the maximum attainable conversion at that temperature.

In the higher conversion ranges, approaching the maximum values for each temperature, it was not possible to find an equation which would be valid up to infinity, and therefore the upper limits of conversion (above 0.63 at 30°C or above 0.77 at 70°C) were neglected. This presented no problem for the suitability of the proposed model, since at higher conversion ranges the rate of reaction is small, and heat generation becomes negligible.

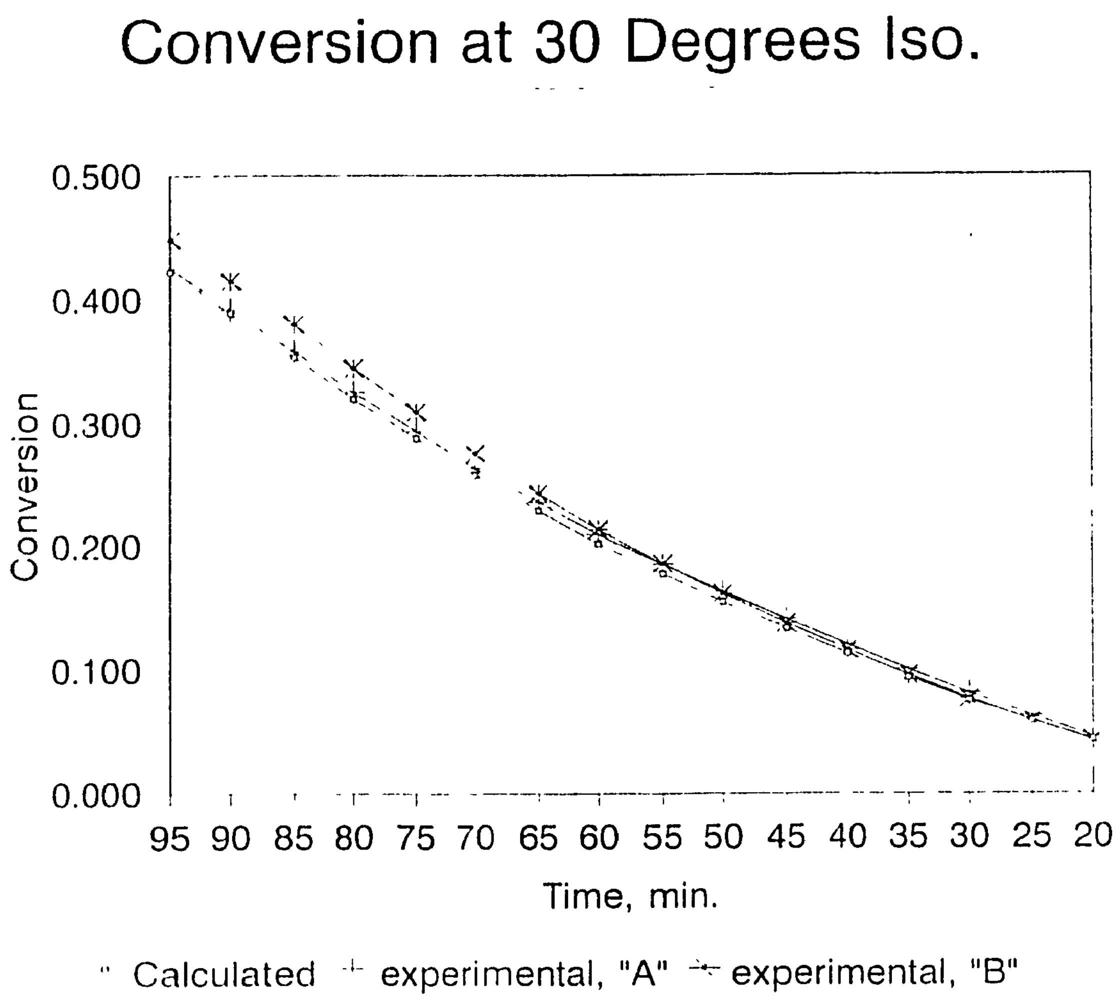

Figure 10 : Conversion at 30°C

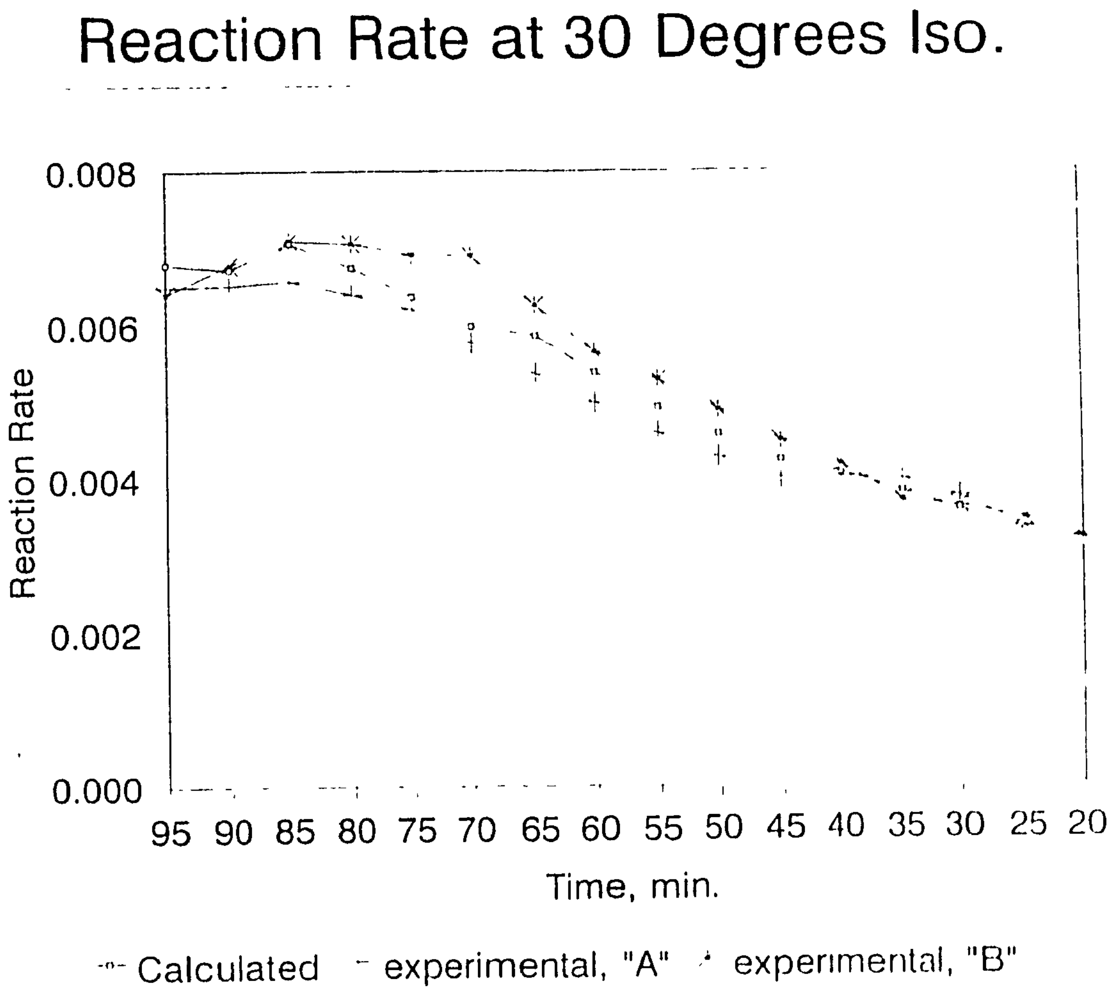

Figure 11 : Reaction Rate at 30°C

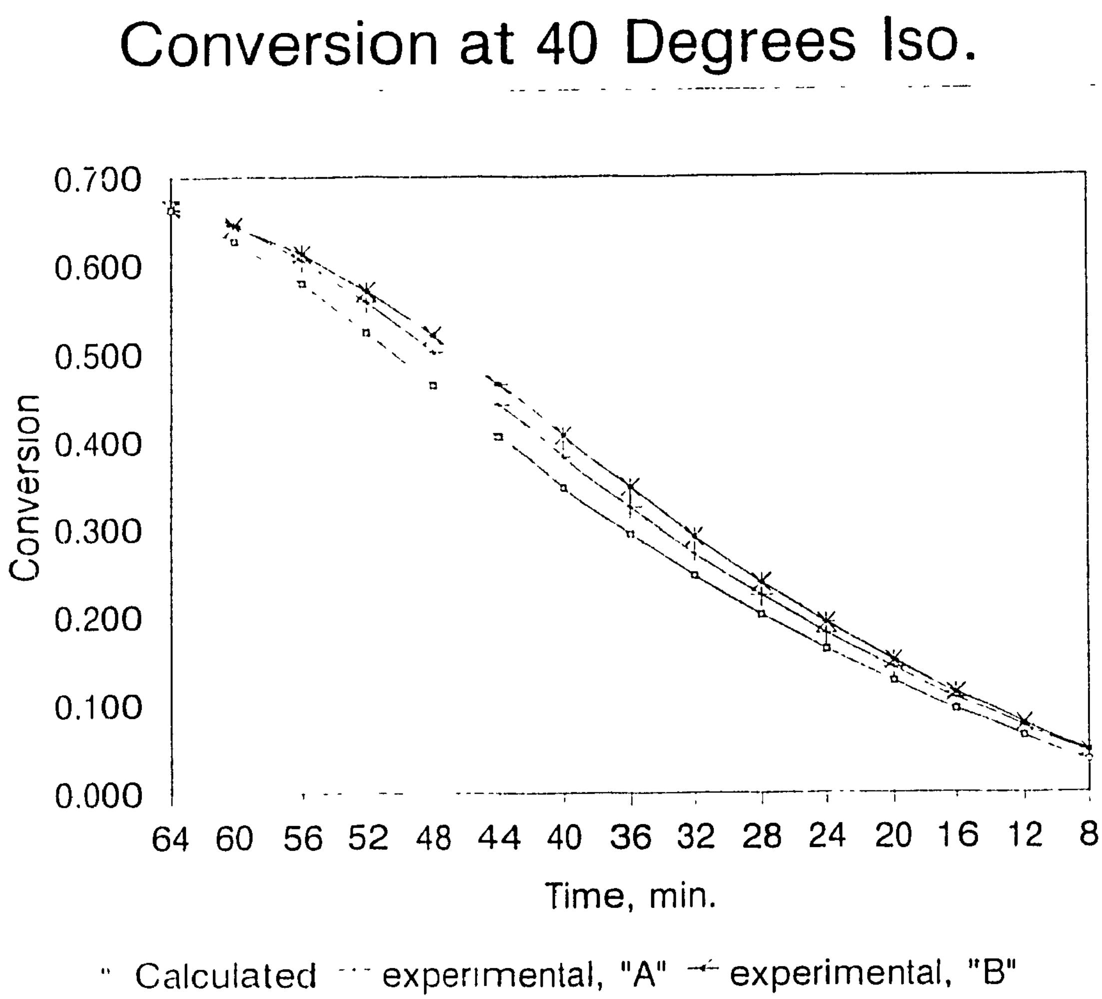

Figure 12 : Conversion at 40°C

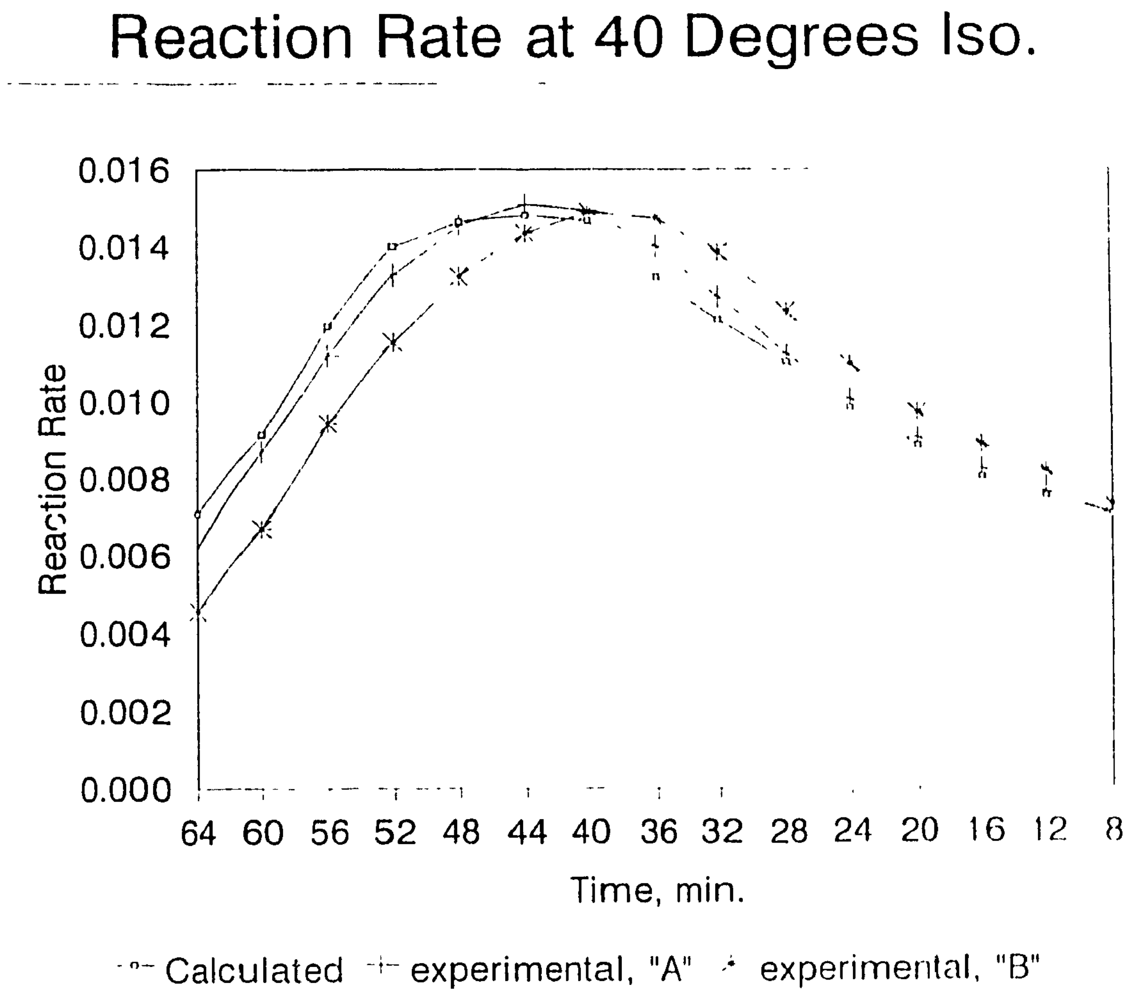

Figure 13 : Reaction Rate at 40°C

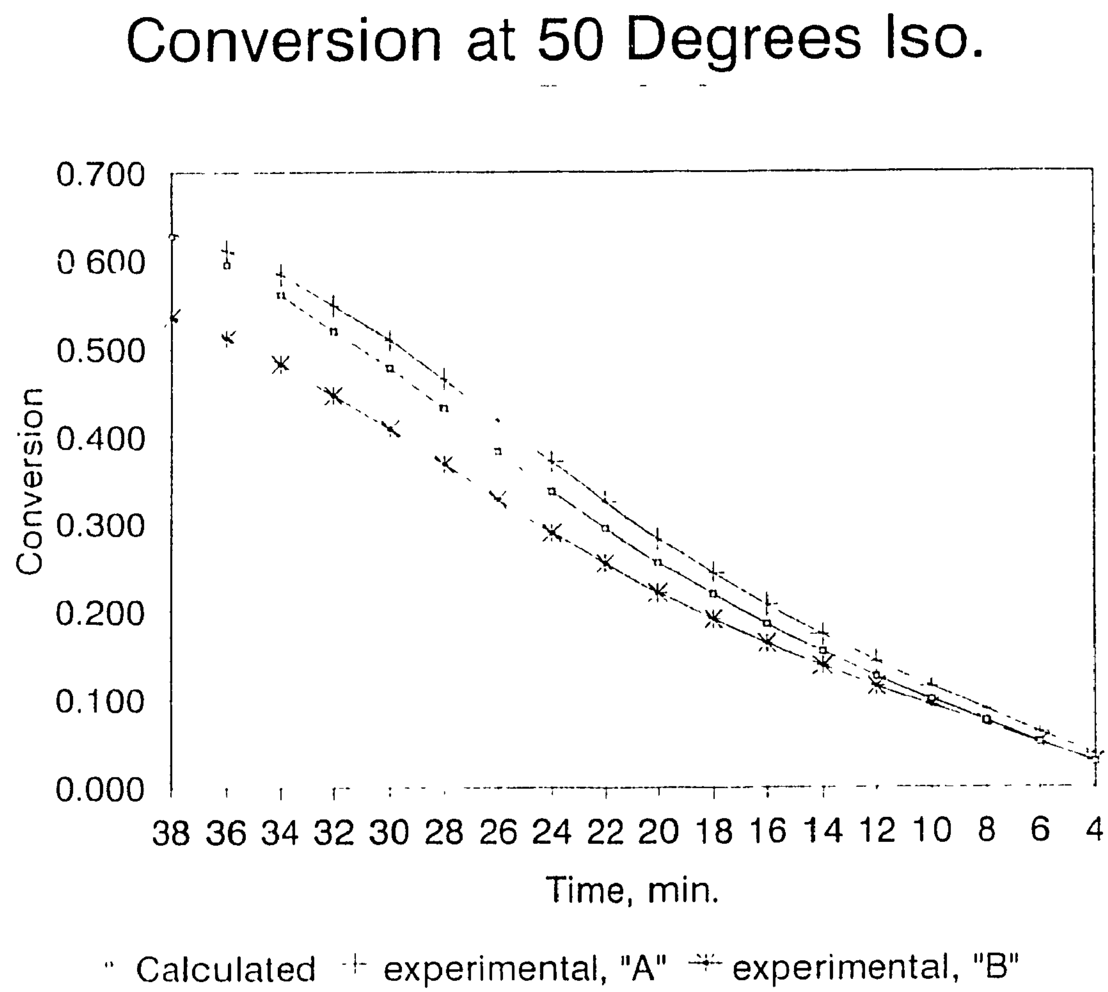

Figure 14 : Conversion at 50°C

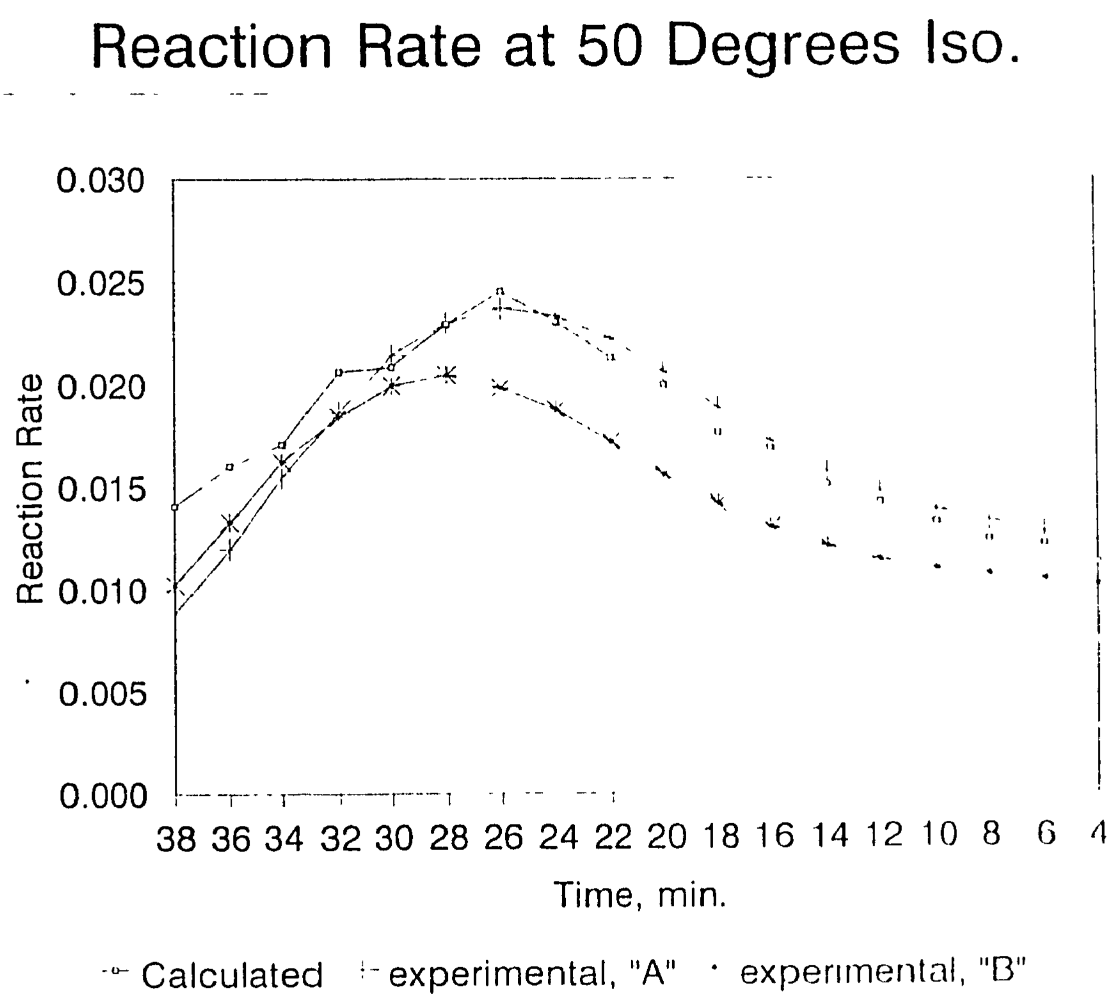

Figure 15 : Reaction Rate at 50°C

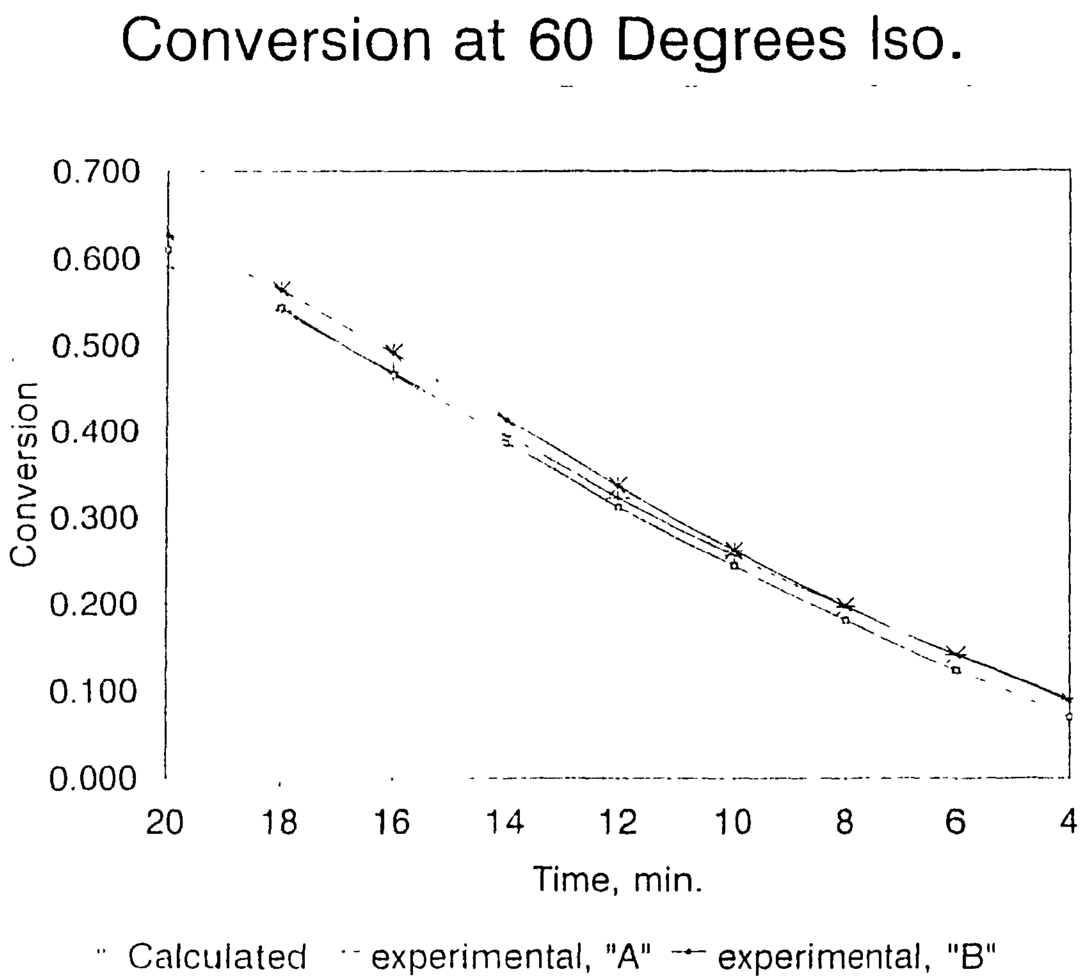

Figure 16 : Conversion at 60°C

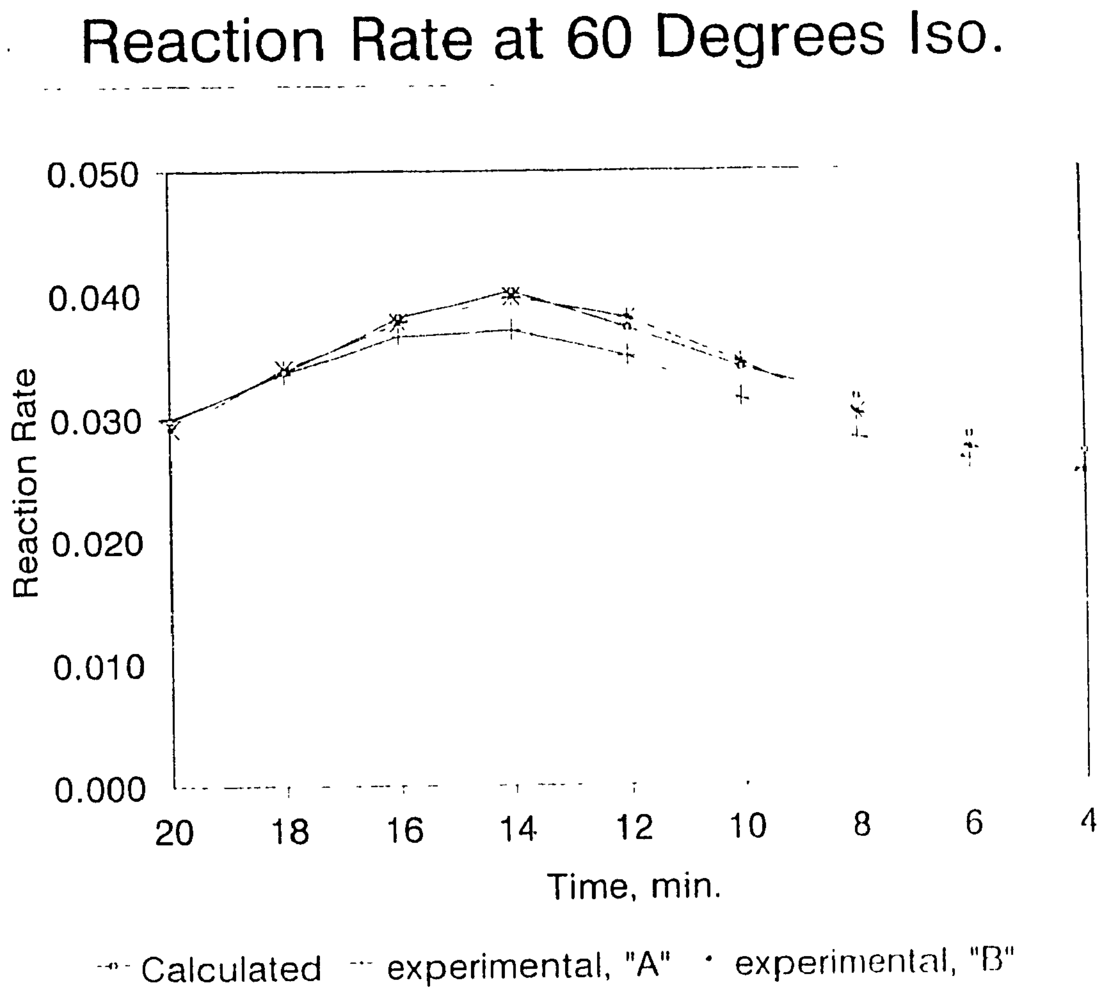

Figure 17 : Reaction Rate at 60°C

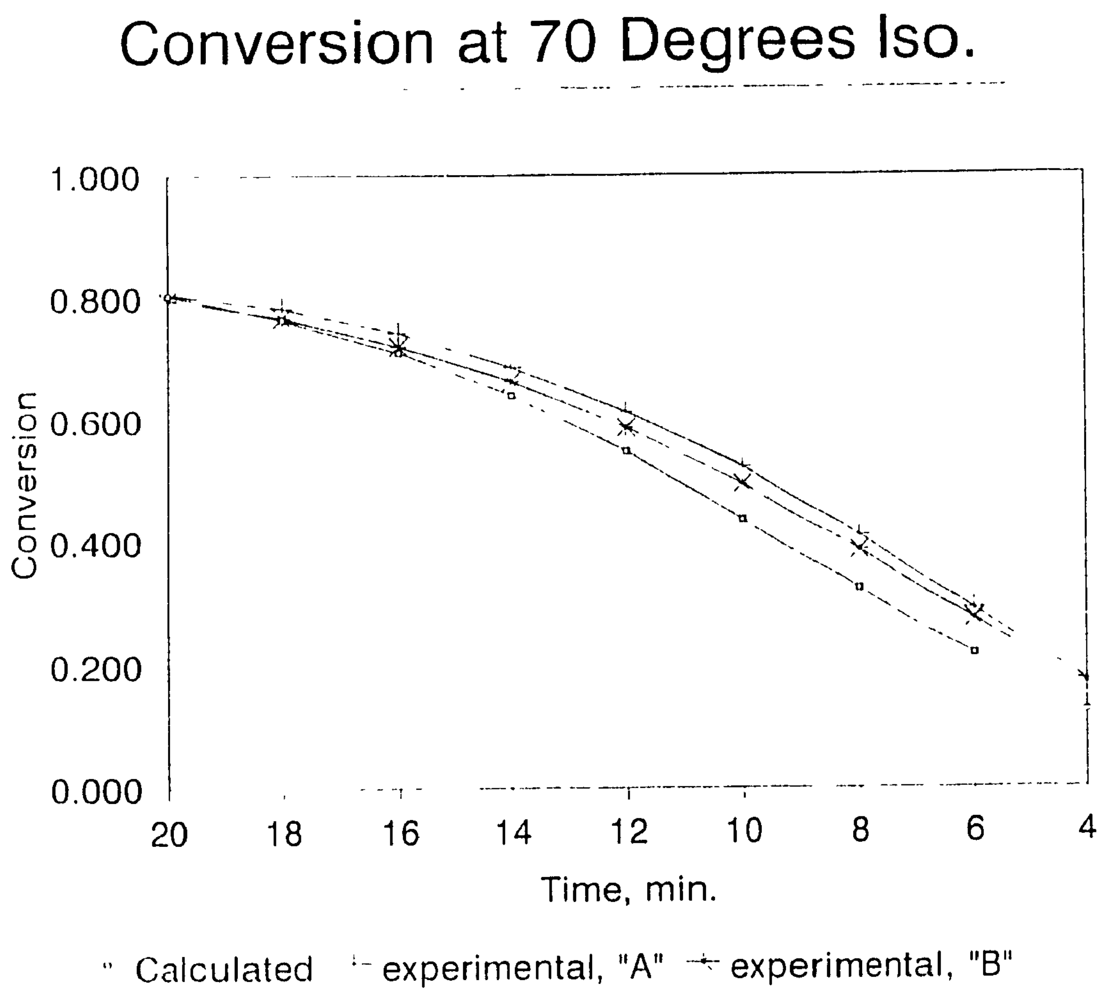

Figure 18 : Conversion at 70°C

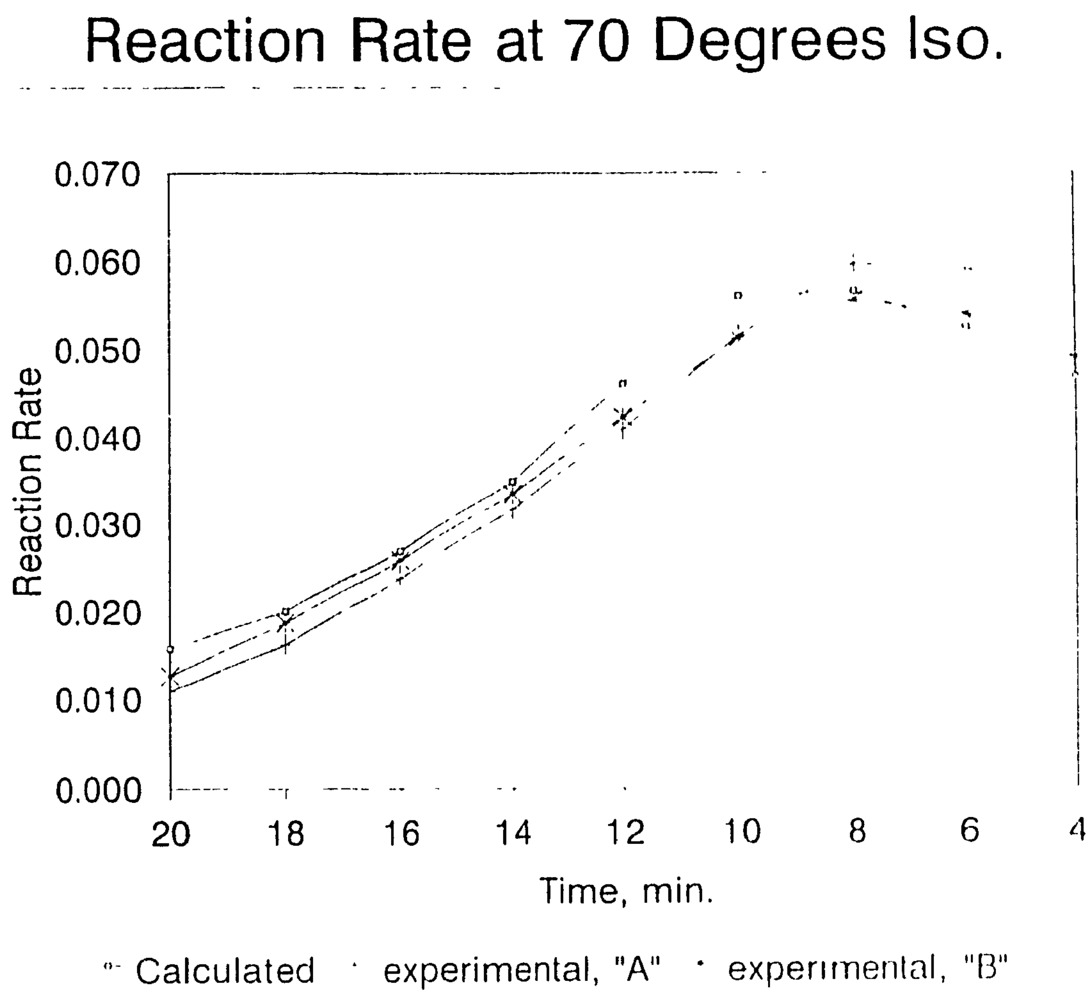

Figure 19 : Reaction Rate at 70°C

Temp. °C	Max. Error %	No.Points <10% %	No.Points <20% %
SAMPLE A			
30	7.3	100	100
40	27.5	77	93
50	31.5	63	88
60	28.6	78	89
70	41.5	43	57
SAMPLE B			
30	7.7	100	100
40	31.8	15	85
50	14.7	44	100
60	25.6	78	89
70	37.8	43	72

Table 16 : Error Analysis for Conversion in Figures 10 to 19

Temp. °C	Max. Error %	No.Points < 10% %	No.Points <20% %
SAMPLE A			
30	8.5	100	100
40	6	100	100
50	9.2	100	100
60	10	100	100
70	30.8	71	86
SAMPLE B			
30	15.4	6	100
40	14.4	77	100
50	23	31	88
60	6	100	100
70	19.6	86	100

Table 17 : Error Analysis for Reaction Rate in Figures 10 to 19

3.2.2 Constant Heating Rate Calculations

To complete the analysis and in order to demonstrate the validity of the method in varying temperature conditions, the proposed kinetic model was used to calculate conversion and reaction rate with a temperature ramp of 10°C/min. As discussed in Section 2.1.1.2, the experimental curve was constructed by using the equation

$$\frac{dC}{dt}=Ze^{-E_a/RT}(1-C)^n \qquad (2)$$

with the average equation parameters of the 14 trials at 10°C/min, obtained from Table 1. Figures 22 and 23 show plots of Equation (2) for conversion and reaction rate versus temperature with a heating rate of 10°C/min from 20°C up to 200°C.

The calculated results were obtained from the computer model with an input heating rate of 10°C/min and were plotted together with the experimental results, as seen in Figures 20 and 21. From these figures it is seen that the calculated curves follow the experimental results up to approximately 70°C, with an approximate error of 20% for the reaction rate and 10% for the conversion. Above 70°C, the experimental conversion and reaction rate (shown in Figures 22 and 23 up to 200°C) increase much faster than calculated, which suggests that the proposed model is valid only up to 70°C. The loss of accuracy of the model at higher temperatures may be explained as follows:

When performing an isothermal experiment at higher temperatures, upon introduction of the cold samples into the preheated cell, the temperature rise of the sample resin and the reaction of the resin become so quick that the equipment cannot accurately measure the initial heat flow. Once the heat flow curve stabilizes, the real conversion at each point of the curve is actually higher than the calculated conversion. Furthermore, it can be observed by looking at Tables D.1 to D.24 in Appendix D, that the maximum rate of reaction consistently occurs at approximately 40% conversion from 30°C up to 70°C. At 75°C suddenly the maximum rate occurs at 8% conversion. From the same tables it may be observed that the conversion after 50 minutes at 70°C is approximately 85%, which is identical to the results at 80°C. These facts suggest that the initial values of conversion measured at 80°C are incorrect, and that above 70°C the measured conversions are no longer accurate. As a result, using the proposed model to simulate a 10°C/min heating rate, the results are only valid up to 70°C. This limitation was however of no major concern, since in the applications for which this model is proposed a maximum exotherm temperature of 70°C should not be exceeded.

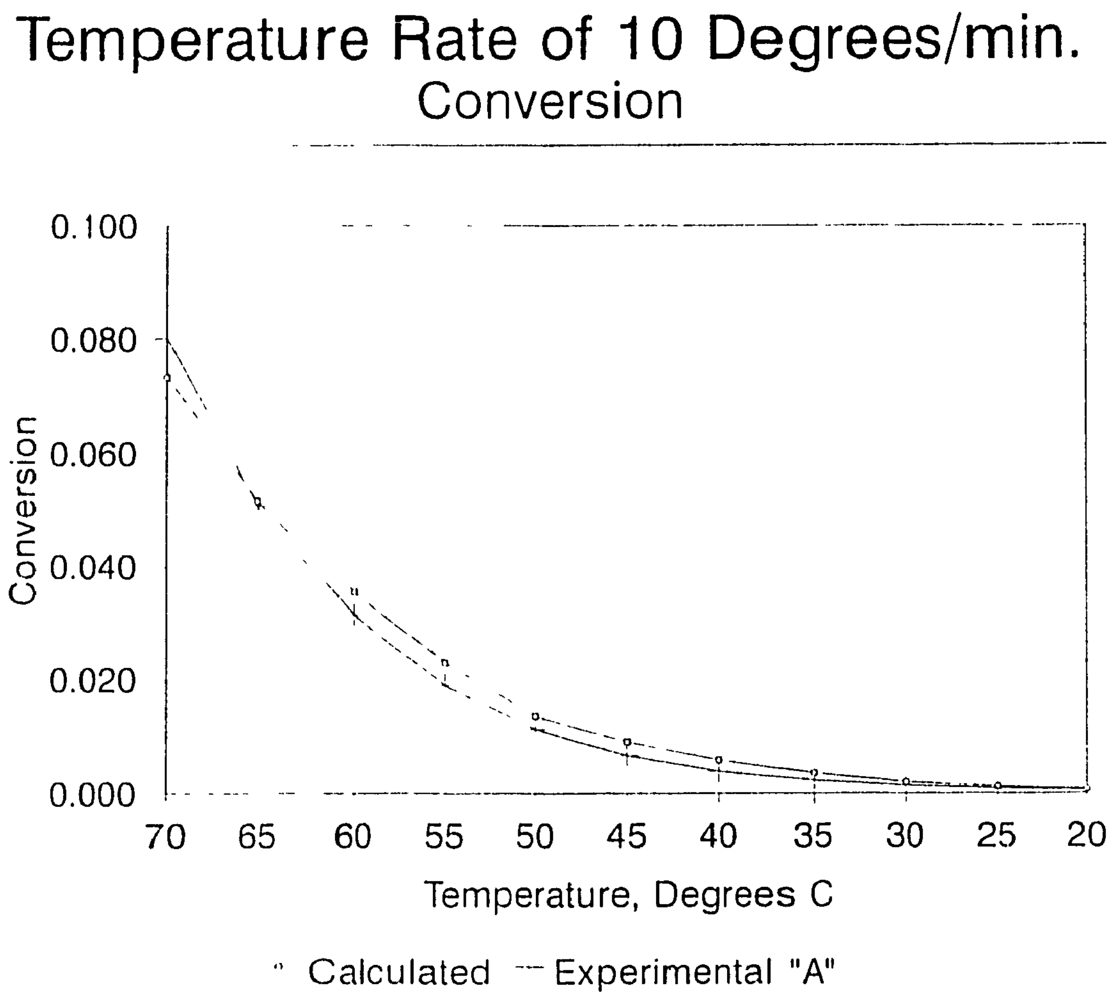

Figure 20 : Conversion at 10°C/min, Comparisons

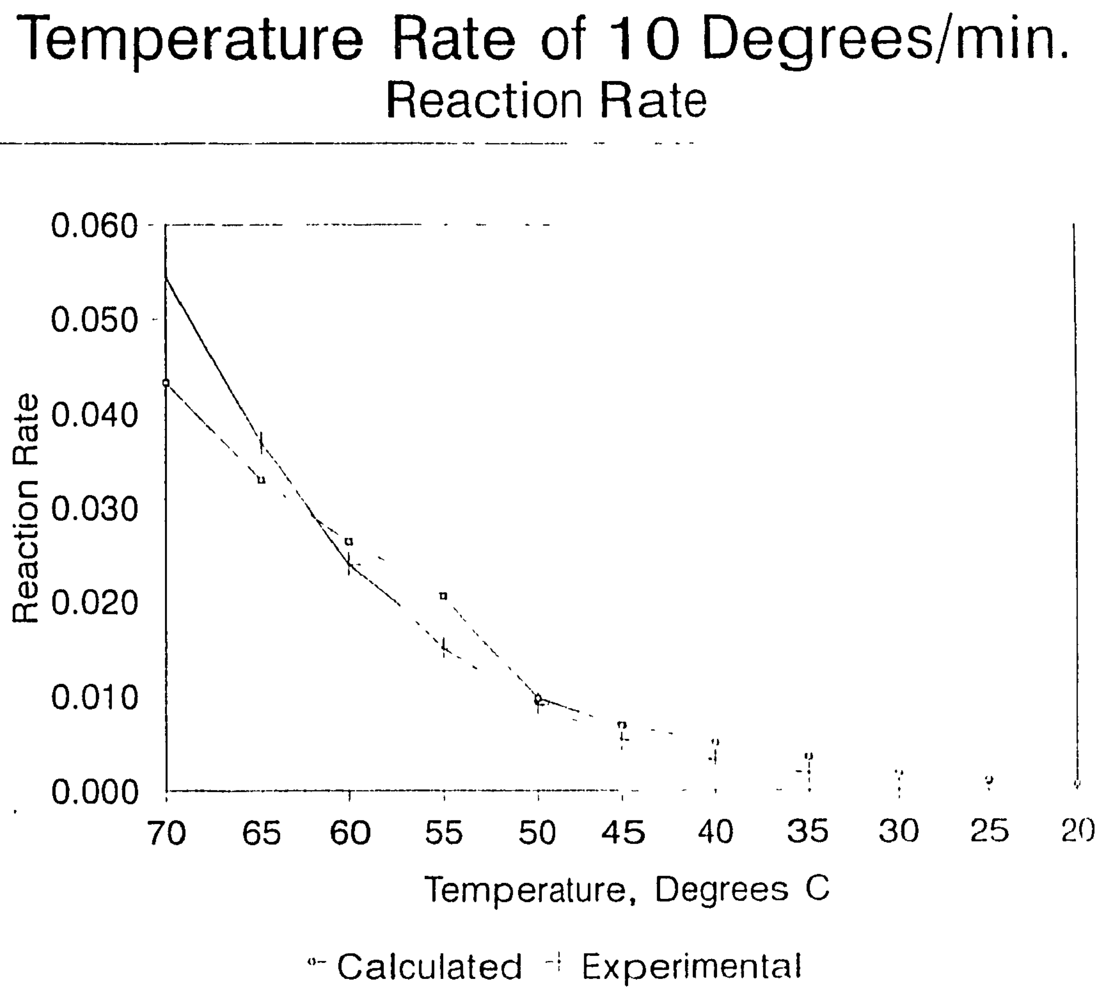

Figure 21 : Reaction Rate at 10°C/min, Comparisons

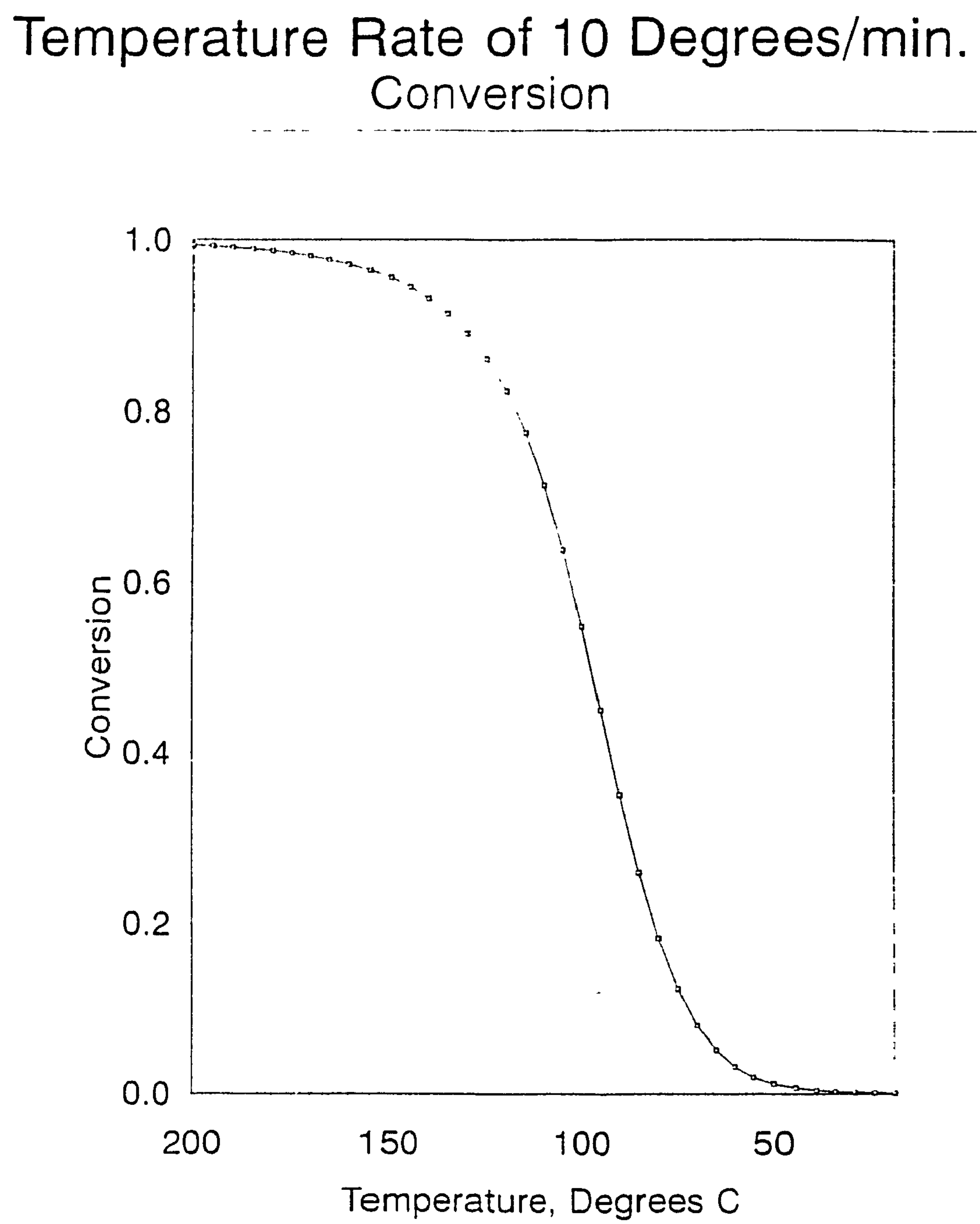

Figure 22 : Conversion at 10°C/min, 20°C to 200°C

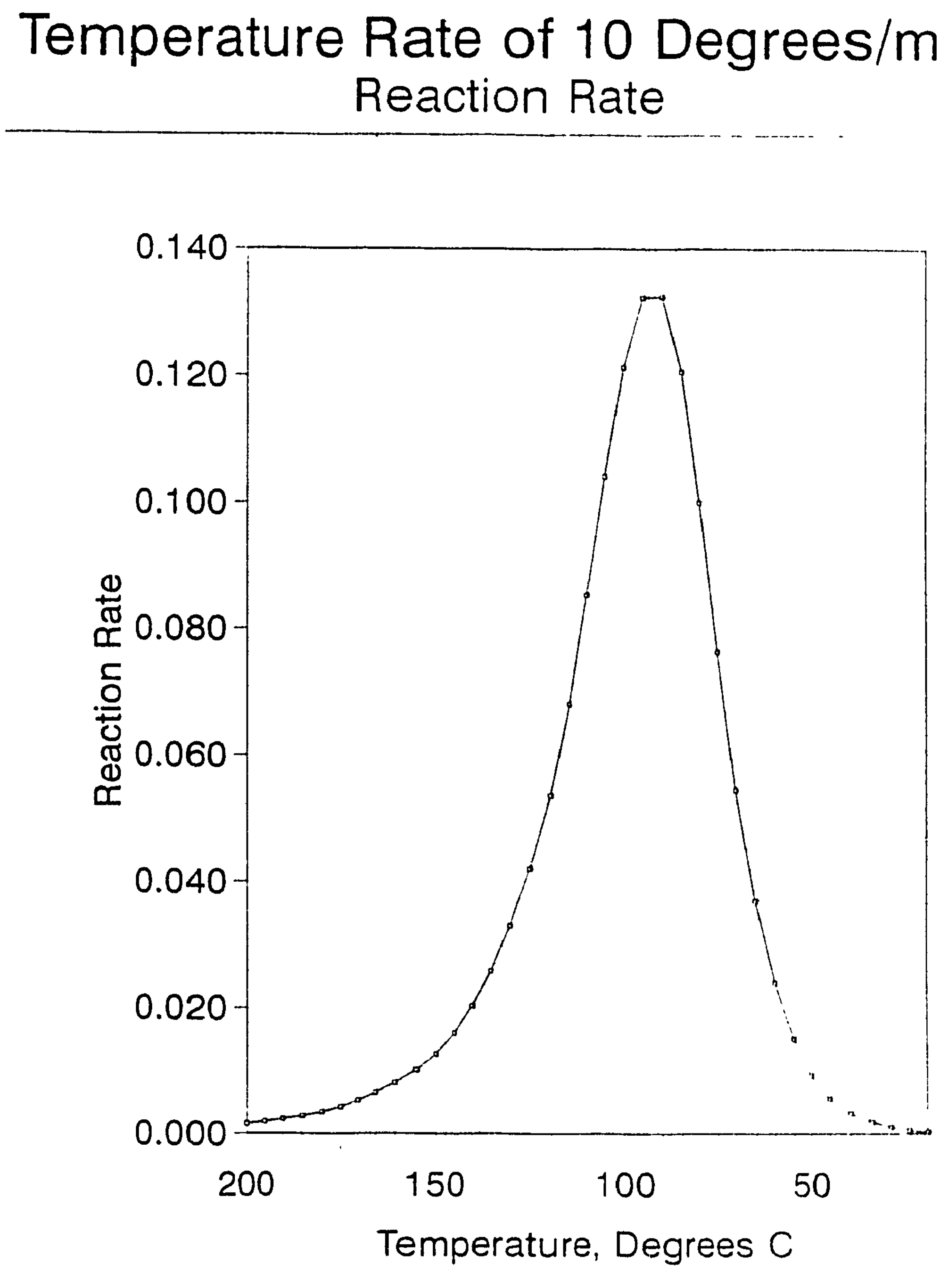

Figure 23 : Reaction Rate at 10°C/min, 20°C to 200°C

4.0 CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Summary

The kinetics of a vinyl ester resin system used for the hand-layup of FRP flanges were studied using DSC analysis, and kinetic data tables were constructed, which were used in a proposed computer spreadsheet model to calculate conversion and reaction rate with varying temperature. The data tables may also be used by any other computer program to predict the conversion and the reaction rate of the resin. It was found that for the vinyl ester resin under consideration the maximum reaction rate under isothermal conditions occurs at some time t > 0. This is predicted by the following equation, which the proposed model used to calculate conversion and rate of reaction

$$\frac{dC}{dt}=Ze^{-E_a/RT}C^m(1-C)^n \qquad (6)$$

The parameters Z, E_a, m and n were obtained by curve fitting of the results of DSC isothermal measurements from 30°C up to 85°C, in 10 ranges of conversion from the initial conversion at time t=0 (C=0), to the maximum isothermal conversion at temperature T ($C = C_{max}(T)$). Data tables of parameters for the above equation were created at each reference temperature by analysing simultaneously the results of three isothermal experiments at temperatures which were 5°C apart. These tables are used by the computer program to calculate conversion and reaction rate at each time increment.

Verification of the model was done in two steps, first by calculating isothermal conversion and reaction rate versus time at all reference temperatures, and comparing these to the experimental results. Comparative plots of calculated versus experimental results were presented in Figures 10 to 19, and confirm that the model predicts the majority of experimental isothermal data with an accuracy of 10% in the temperature range from 30°C to 70°C, as illustrated in Tables 16 and 17. Tables 16 and 17 also show local inaccuracies above 10%, which are due to differences between the experimental results of samples A and B and to the fact that the calculated results are based on an average between three isothermal experiments at temperatures which were 5°C apart. It was also found that different methods of analysis should be considered to obtain accurate measurements of isothermal conversion above 70°C, however since a maximum exotherm temperature of 70°C should not be exceeded in the practical problem under consideration, further analysis was not undertaken.

In the higher conversion ranges, difficulties were encountered in finding a model to simulate the experimental data. The upper limits of conversion, above 0.63 at 30°C and above 0.77 at 70°C, were therefore neglected, and this is believed to have no influence on the suitability of the model as a basis for heat transfer analysis, since the rate of reaction and hence the heat generation approach zero in these higher ranges.

Finally the model was used to simulate a 10°C/min temperature ramp from 20°C up to 70°C. The constant ramp is approximated by a multiple step temperature function, and isothermal calculations are performed at each time increment. The calculated conversion and reaction rate versus time were compared to the experimental results of 14 constant rate measurements, and it was found that the model simulates the experiments up to 70°C with an accuracy of approximately 20% for the reaction rate and 10% for the conversion, as illustrated in Figures 20 and 21.

The proposed model may be used to simulate any random temperature curve within the 30°C to 70°C range, and to obtain the rate of reaction at each moment in time up to 63% conversion at 30°C and 77% conversion at 70°C.

Conclusions

1) From a DSC analysis of a vinyl ester resin, Dow Chemicals Derakane 411-45, catalysed with MEKP, accelerated with DMA and promoted with CoNap, isothermal heat flow curves were obtained and kinetic data of conversion and reaction rate was generated.

2) Tables of equation parameters were constructed to simulate the curing process, and can be used to calculate reaction rate and conversion at any moment in time for temperatures up to 70°C.

3) A computer model of the curing process was developped using the tables of equation parameters. This model can be directly coupled with a heat transfer analysis to determine temperature gradients in curing vinyl

ester laminates.

No similar publications were found in literature on the curing kinetics of a vinyl ester resin. The present work also constitutes the first step in solving the problem of FRP flange pullback.

Future work

As future work, a heat transfer model can be created, based on the curing kinetics model, and a complete structural analysis of the pullback problem may be undertaken. Such an analysis also requires data on the mechanical properties of the resin during cure, which may be obtained by Dynamic Mechanical Analysis, and on the shrinkage of the resin.

By repeating the DSC experiments with new resin mixtures, varying the amounts of catalyst, accelerator or promoter, new data tables can be created, and using the kinetic model, valuable information may be obtained about the resin system which would support future studies of the problem of FRP flange pullback.

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APPENDIX A - SUMMARY OF RUNS

Constant Heating Rate

Test Number	Description
PE.008	10°C/min. Sample A
PE.009	10°C/min. Sample B
PE.010	10°C/min. Sample A
PE.011	10°C/min. Sample B
PE.012	10°C/min. Sample A
PE.013	10°C/min. Sample B
PE.014	10°C/min. Sample A
PE.015	10°C/min. Sample B
PE.016	10°C/min. Sample A
PE.017	10°C/min. Sample B
PE.018	10°C/min. Sample A
PE.019	10°C/min. Sample B
PE.020	10°C/min. Sample A
PE.021	10°C/min. Sample B

Isothermal

Test Number	Description
PE.O32	Isothermal 50°C Sample A
PE.033	Isothermal 50°C Sample B
PE.042	Isothermal 30°C Sample A
PE.043	Isothermal 30°C Sample B
PE.044	Isothermal 35°C Sample A
PE.045	Isothermal 35°C Sample B
PE.046	Isothermal 40°C Sample A
PE.047	Isothermal 40°C Sample B
PE.048	Isothermal 45°C Sample A
PE.049	Isothermal 45°C Sample B
PE.052	Isothermal 55°C Sample A
PE.053	Isothermal 55°C Sample B
PE.056	Isothermal 65°C Sample A
PE.057	Isothermal 65°C Sample B
PE.058	Isothermal 70°C Sample A
PE.059	Isothermal 70°C Sample B
PE.060	Isothermal 60°C Sample A
PE.061	Isothermal 60°C Sample B
PE.062	Isothermal 75°C Sample A
PE.063	Isothermal 75°C Sample B
PE.064	Isothermal 80°C Sample A
PE.065	Isothermal 80°C Sample B
PE.066	Isothermal 85°C Sample A
PE.067	Isothermal 85°C Sample B

APPENDIX B

HEAT FLOW CURVES
CONSTANT HEATING RATE

The following fourteen (14) curves, Figures B.1 to B.14, were obtained from seven (7) dual sample experiments with a constant heating rate of 10°C/min from 0°C up to 200°C. The DSC cell was cooled to -5°C using liquid nitrogen and stabilized at 0°C before starting the experiment. A list of all the experiments is found in Appendix A.

The Borchardt and Daniels Kinetics Data Analysis Program [14] was used to integrate the heat flow curves and to obtain the total heat of reaction and the parameters n (reaction order), E_a (constant) and Log(Z) (constant) for the equation

$$\frac{dC}{dt} = Ze^{-E_a/RT}(1-C)^n \qquad (2)$$

which is used to predict the reaction rate dC/dt and the conversion when the resin is subjected to a 10°C/min heating rate. The results of all the experiments are given in Table 1, Section 2.1.1.2.

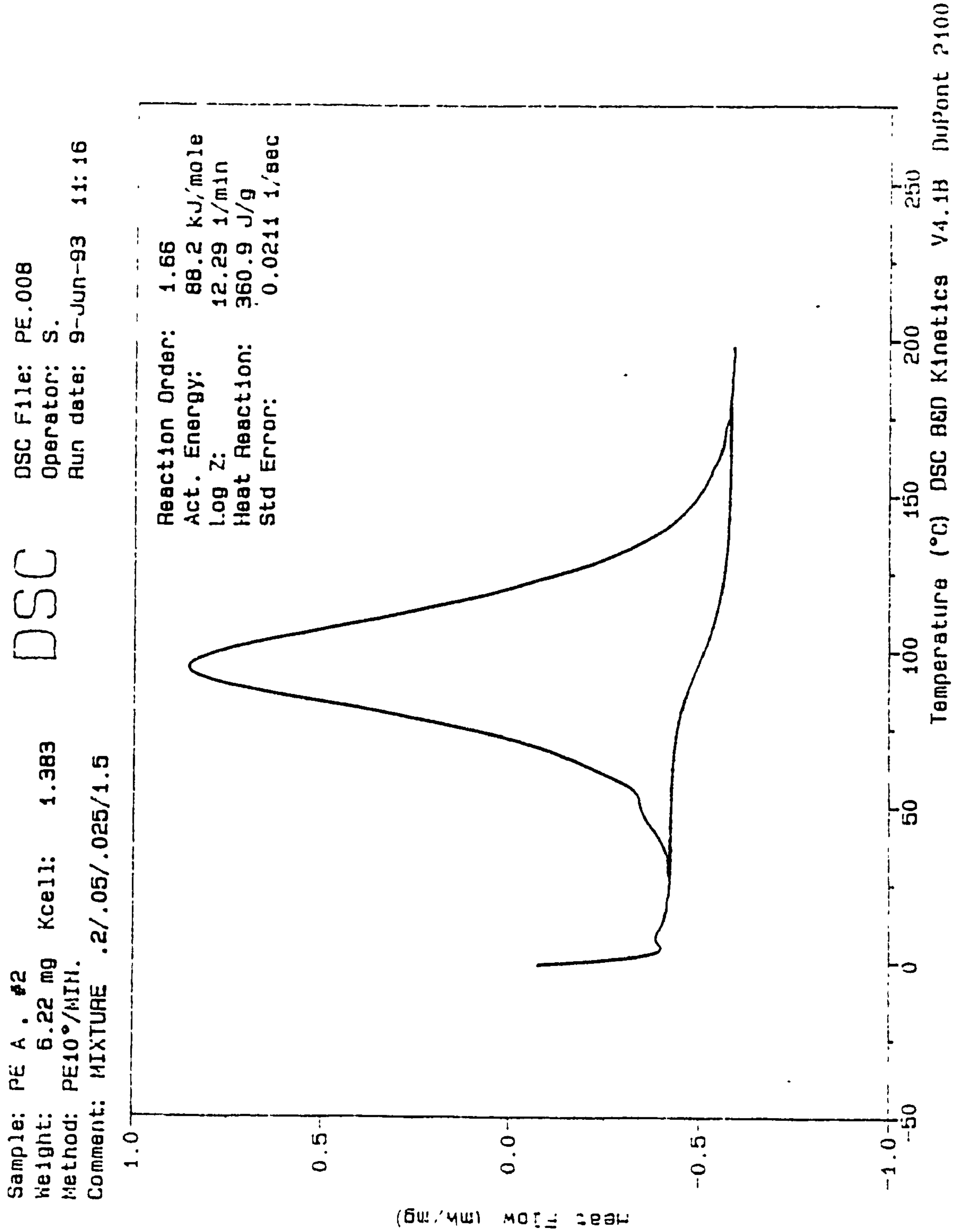

Figure B.1 : Heat Flow Curve. Trial PE.008

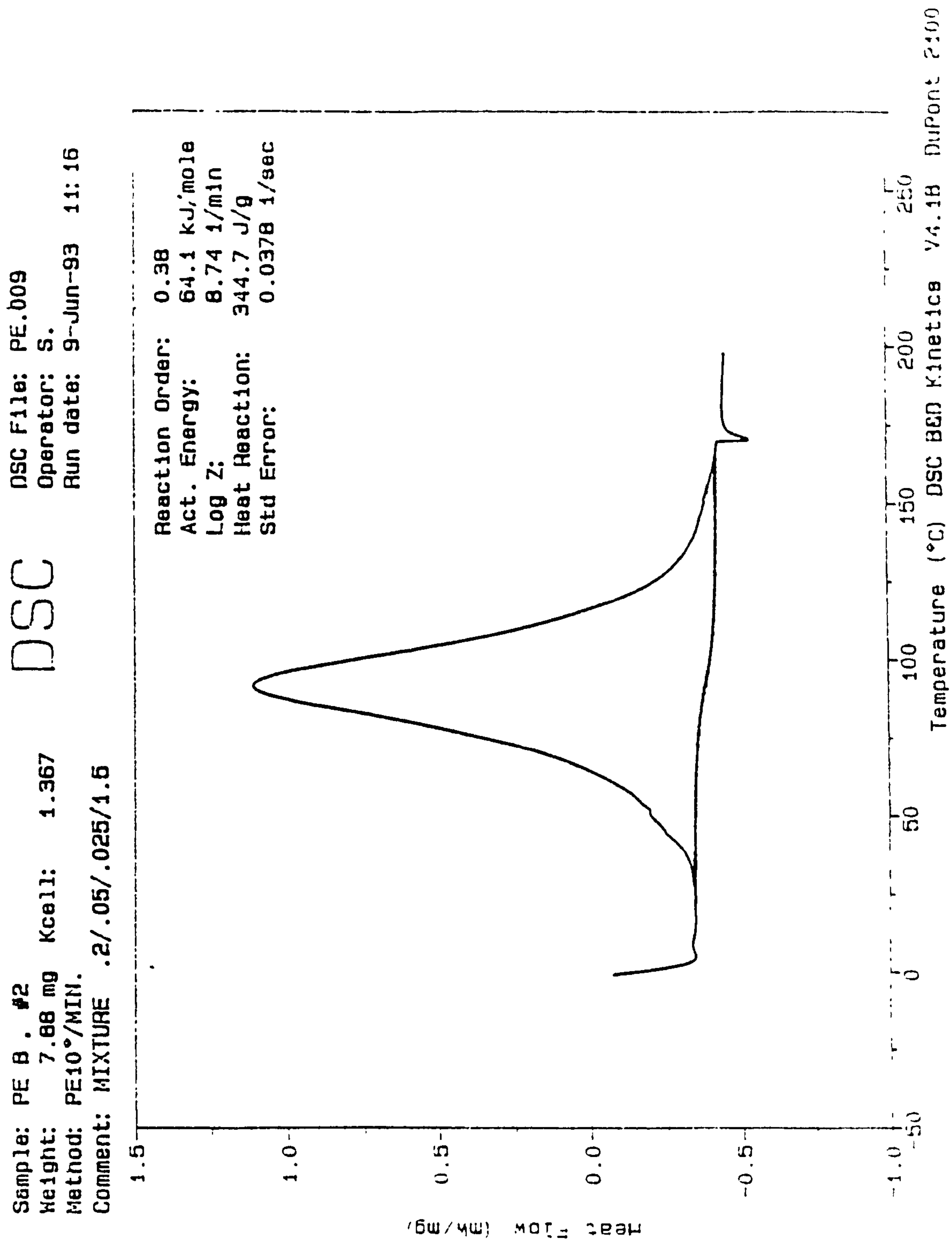

Figure B.2 : Heat Flow Curve, Trial PE.009

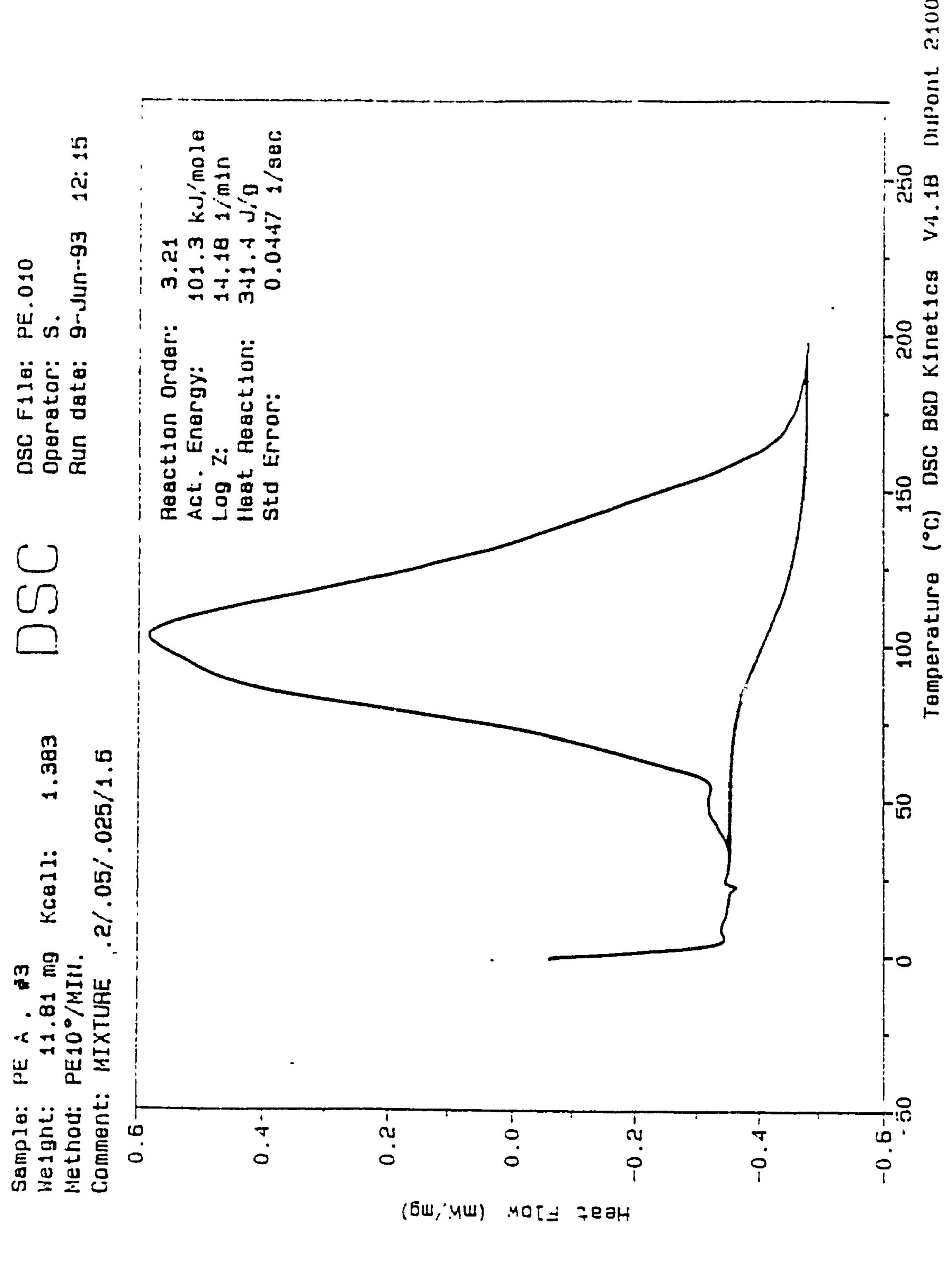

Figure B.3 : Heat Flow Curve, Trial PE.010

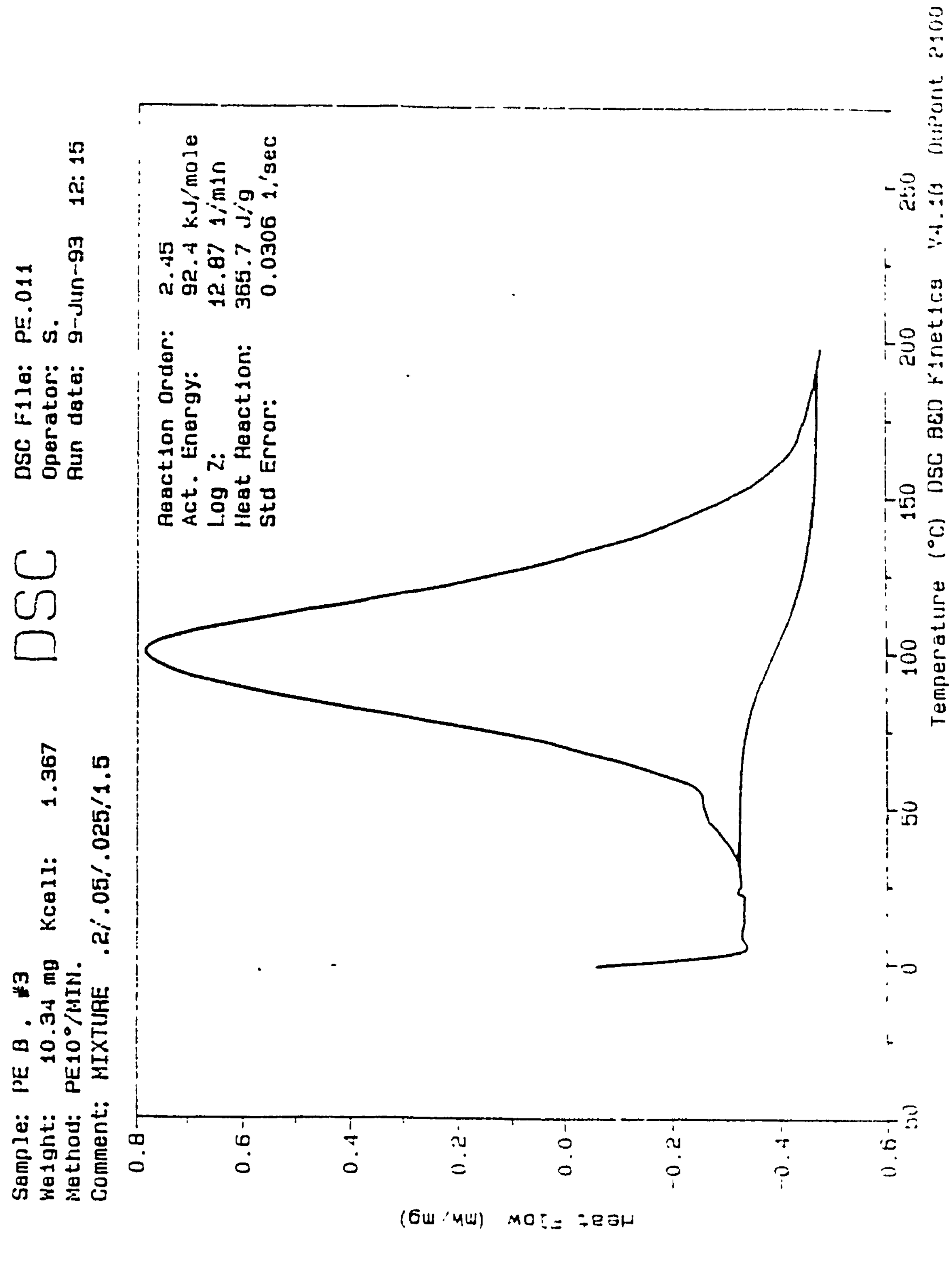

Figure B.4 : Heat Flow Curve, Trial PE.011

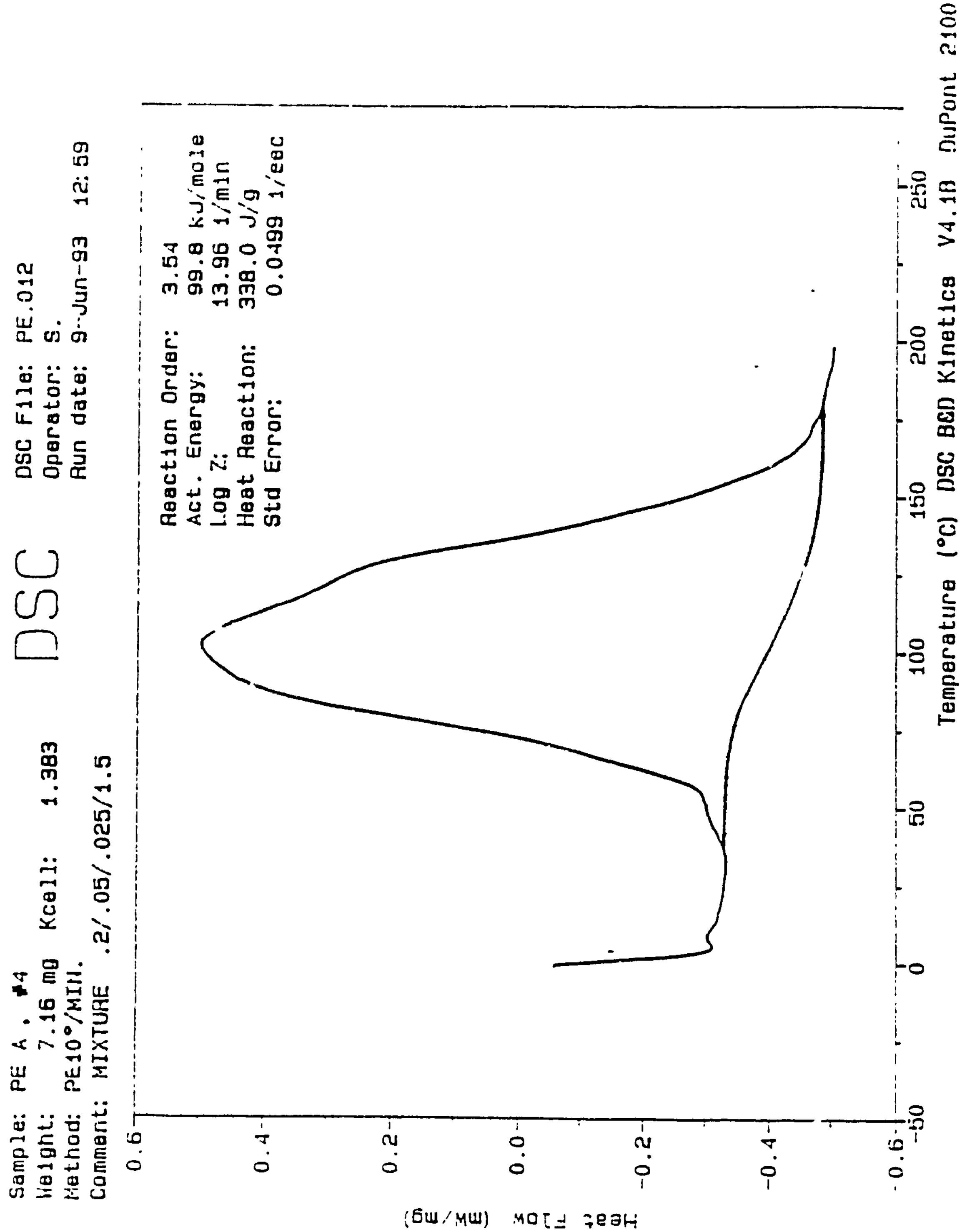

Figure B.5 : Heat Flow Curve, Trial PE.012

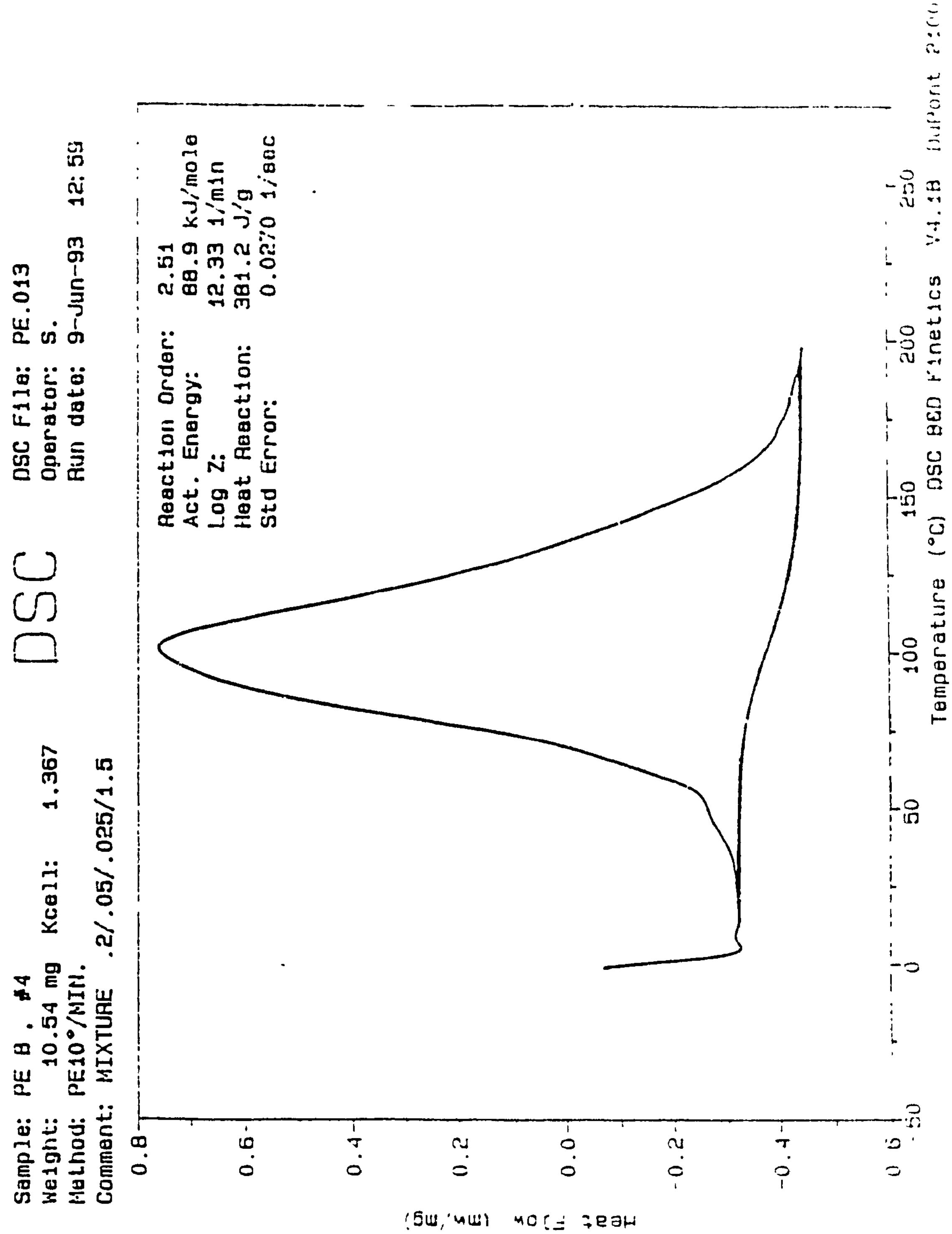

Figure B.6 : Heat Flow Curve, Trial PE.013

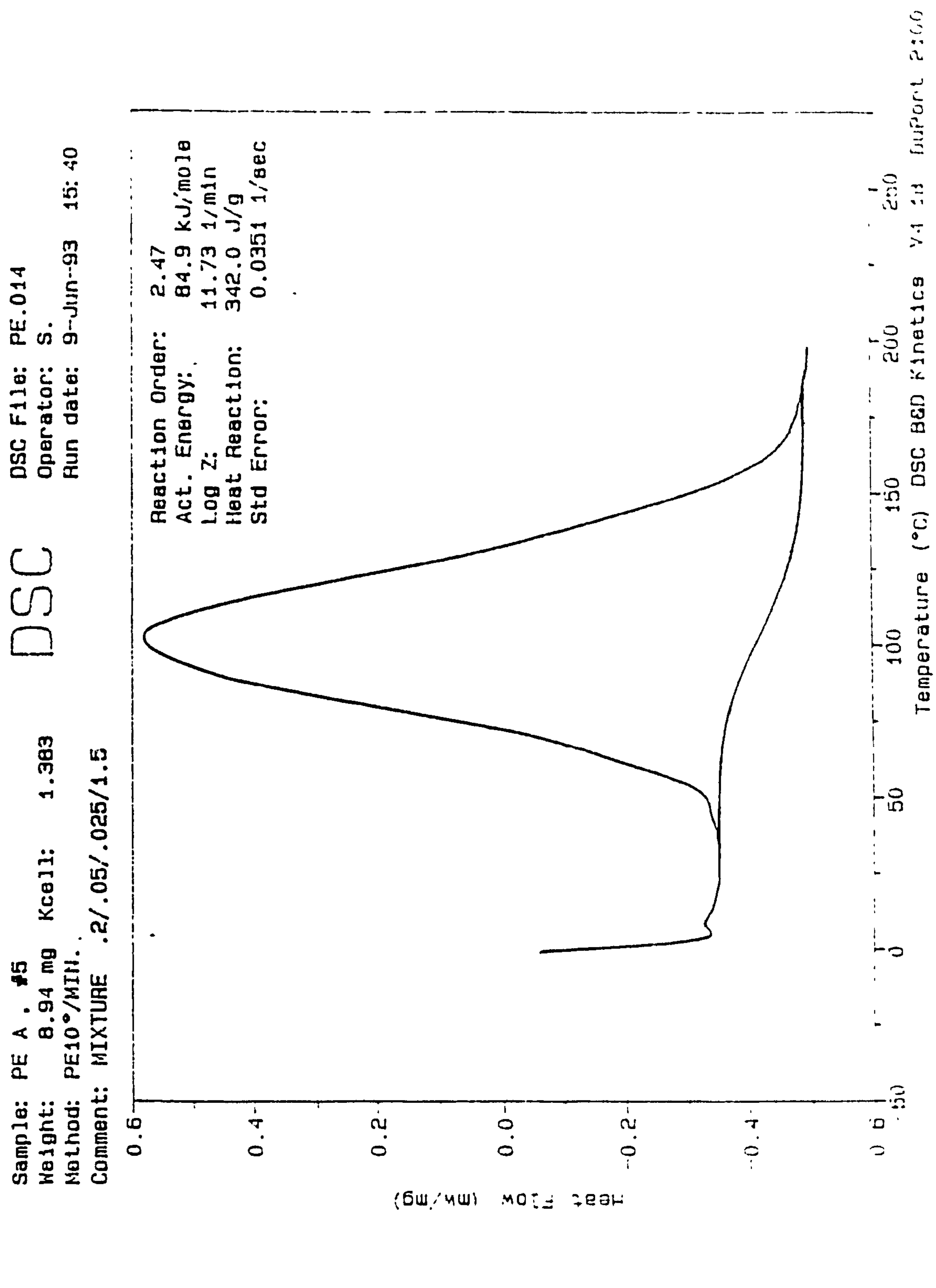

Figure B.7 : Heat Flow Curve, Trial PE.014

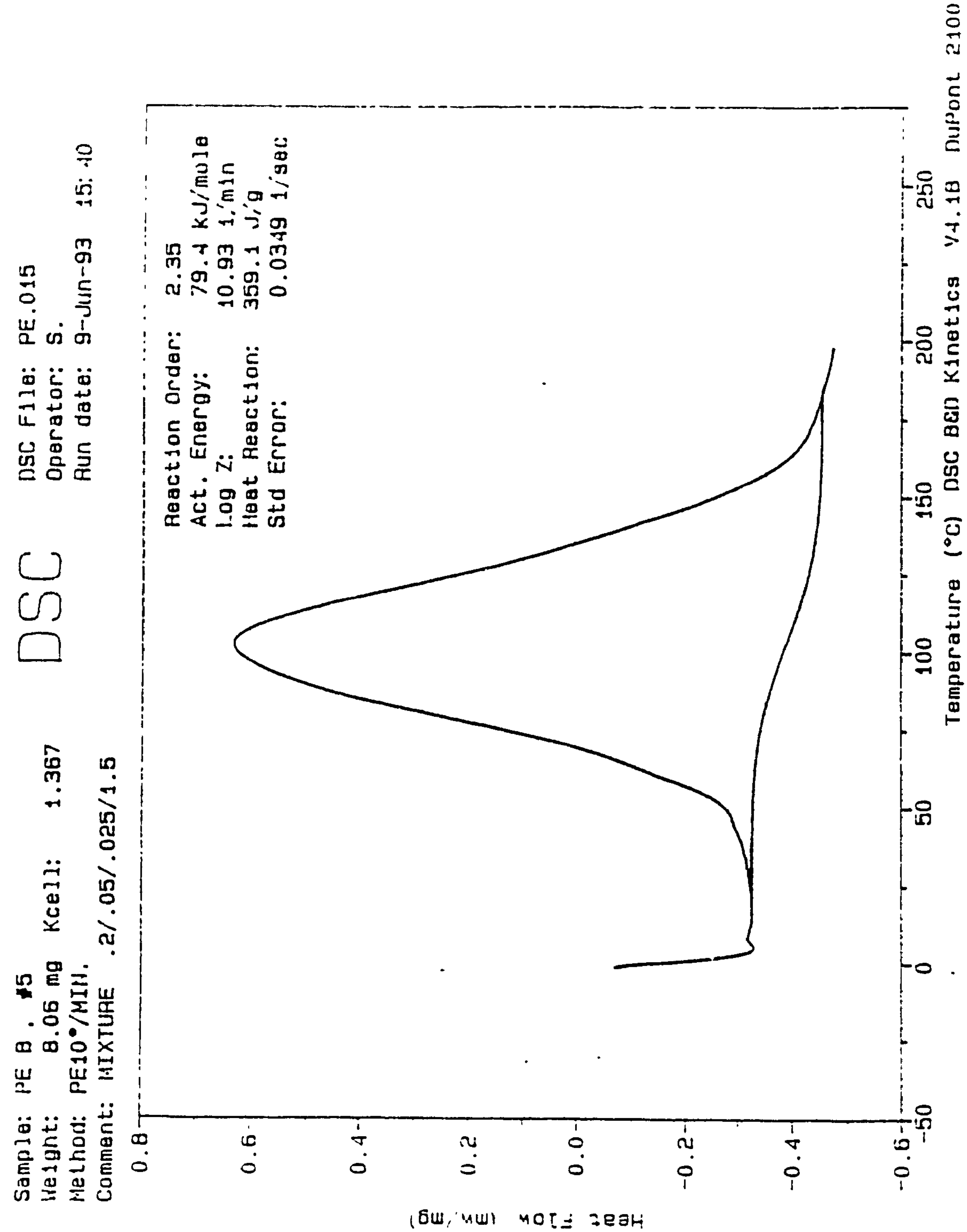

Figure B.8 : Heat Flow Curve, Trial PE.015

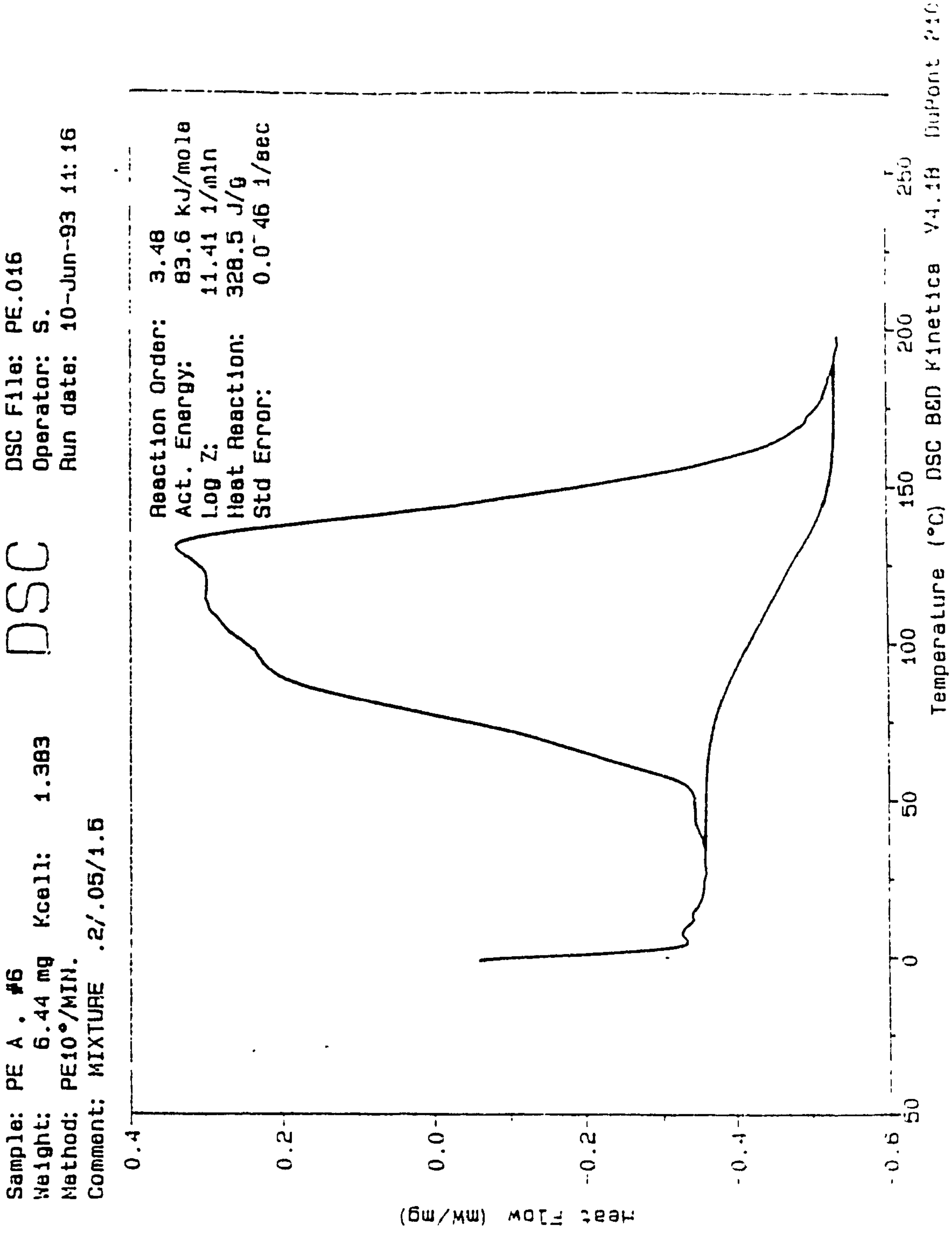

Figure B.9 : Heat Flow Curve, Trial PE.016

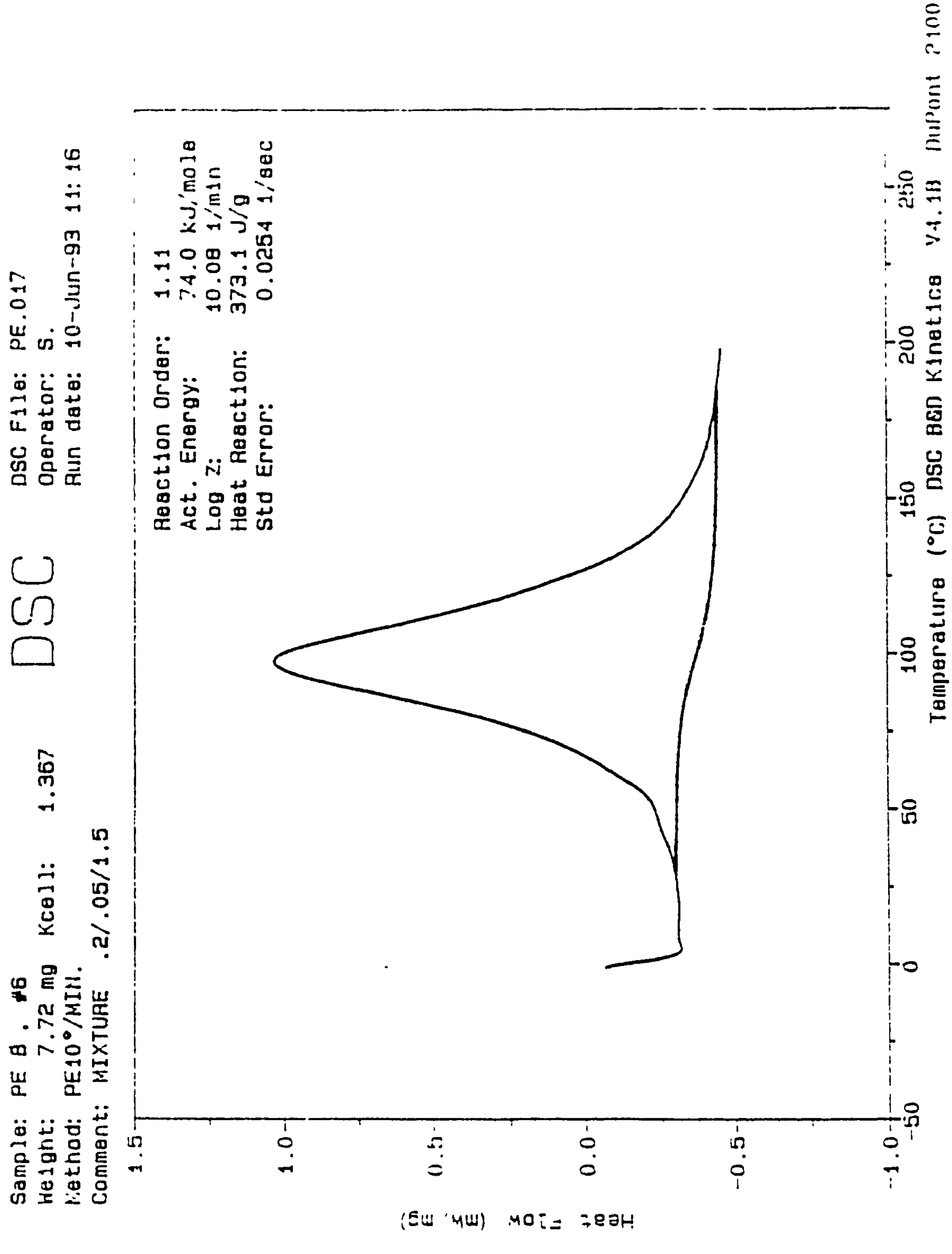

Figure B.10 : Heat Flow Curve. Trial PE.017

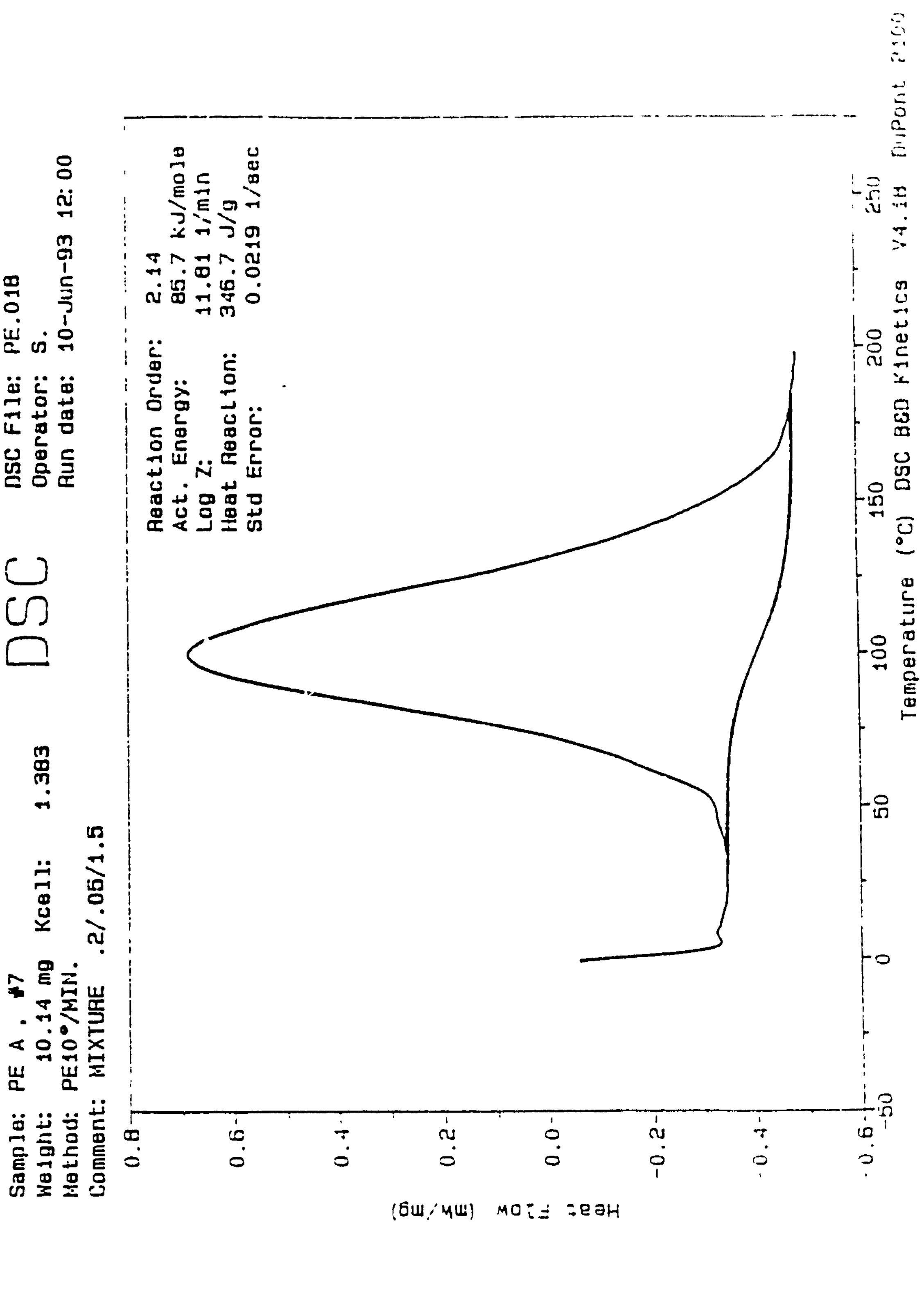

Figure B.11 : Heat Flow Curve, Trial PE.018

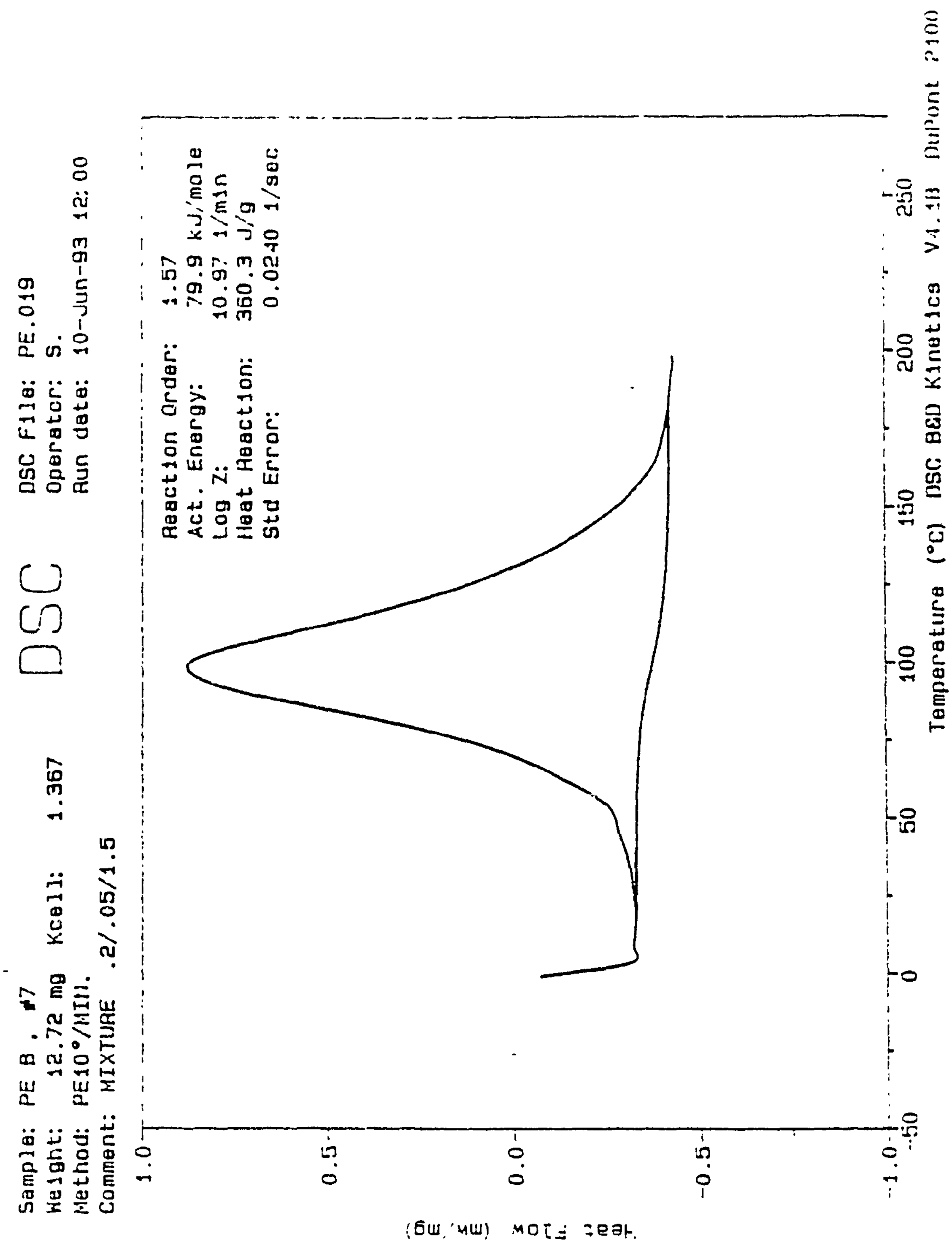

Figure B.12 : Heat Flow Curve, Trial PE.019

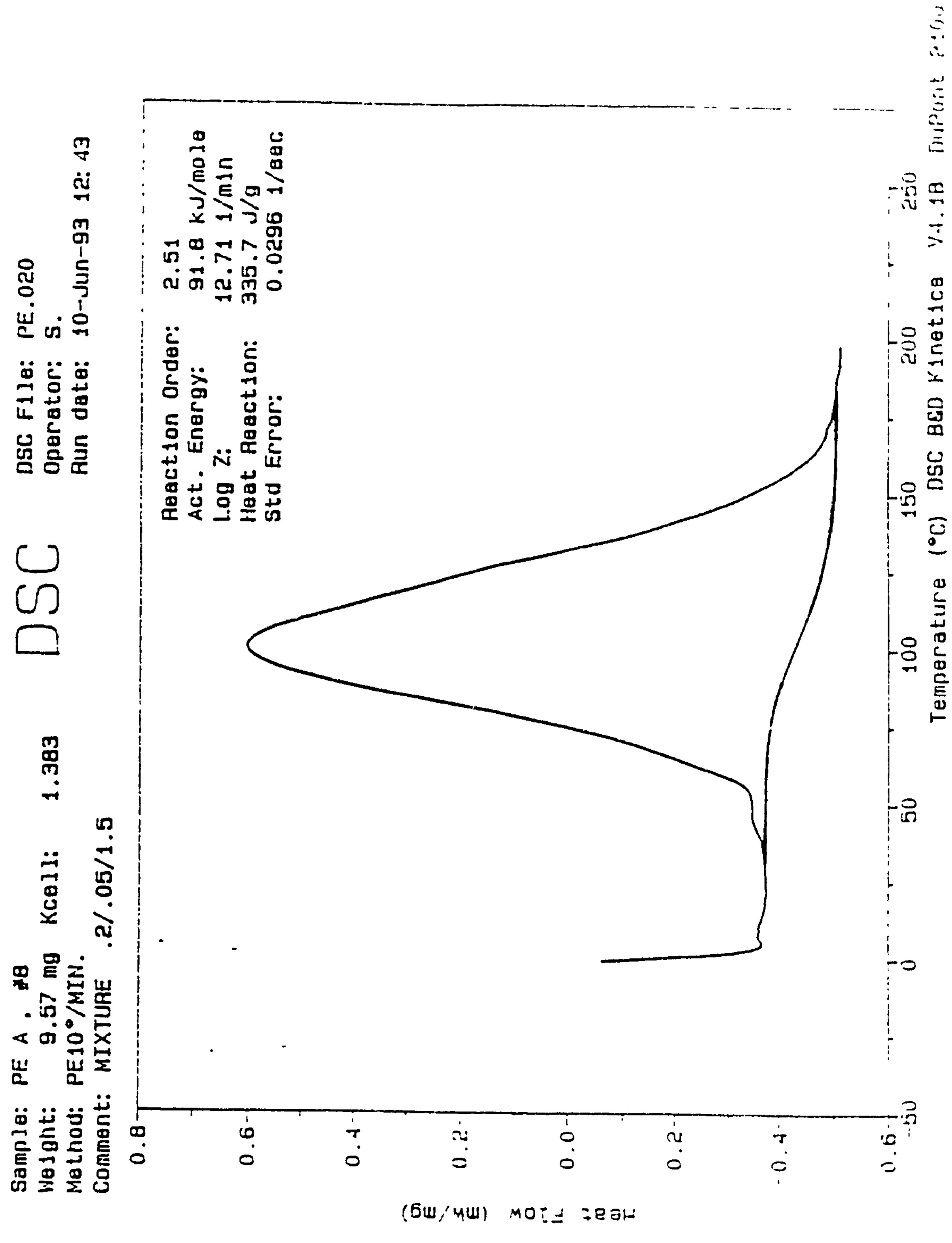

Figure B.13 : Heat Flow Curve, Trial PE.020

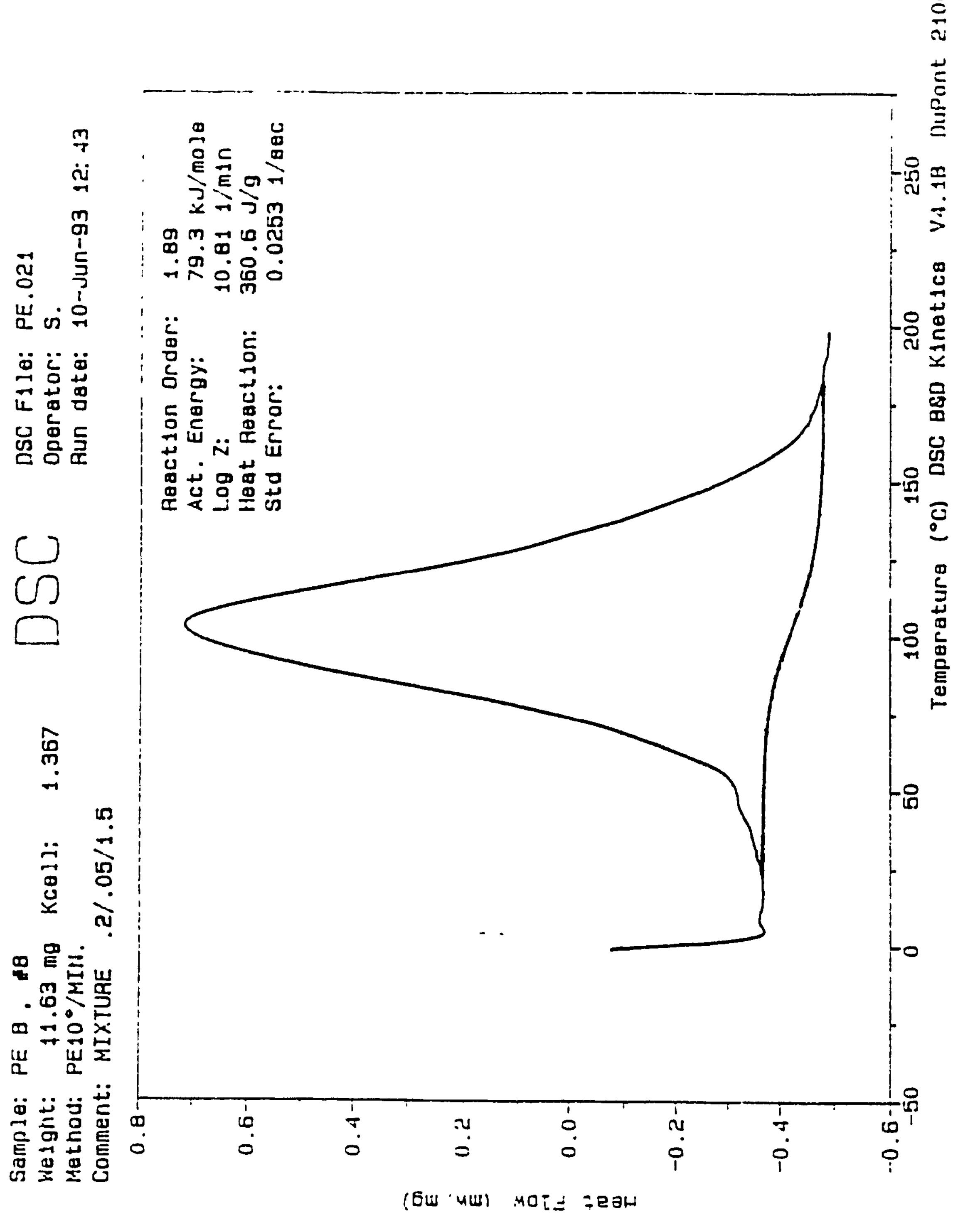

Figure B.14 : Heat Flow Curve, Trial PE.021

APPENDIX C

HEAT FLOW CURVES
ISOTHERMAL EXPERIMENTS

The following 24 curves, Figures C.1 to C.24, were obtained from 12 dual sample isothermal experiments at temperatures ranging from 30°C to 85°C. A list of all the experiments is found in Appendix A.

The DSC Isothermal Kinetics Data Analysis Program [12,13] was used to integrate the heat flow curves and to obtain the isothermal heat of reaction (written measured enthalpy in the following figures). The total heat of reaction (written reference enthalpy in the following figures) is input manually, and the value used is the average total heat of reaction (352 J/g) obtained from the constant heating rate experiments and listed in Table 1, Section 2.1.1.2. The Analysis Program divides the measured enthalpy by the reference enthalpy to determine the maximum isothermal conversion, and by stepwise integration the conversion and the rate of reaction are calculated at various moments in time, as discussed in Section 2.1.1.3. The results after integration (conversion and reaction rate versus time) are shown in Tables D.1 to D.24 in Appendix D.

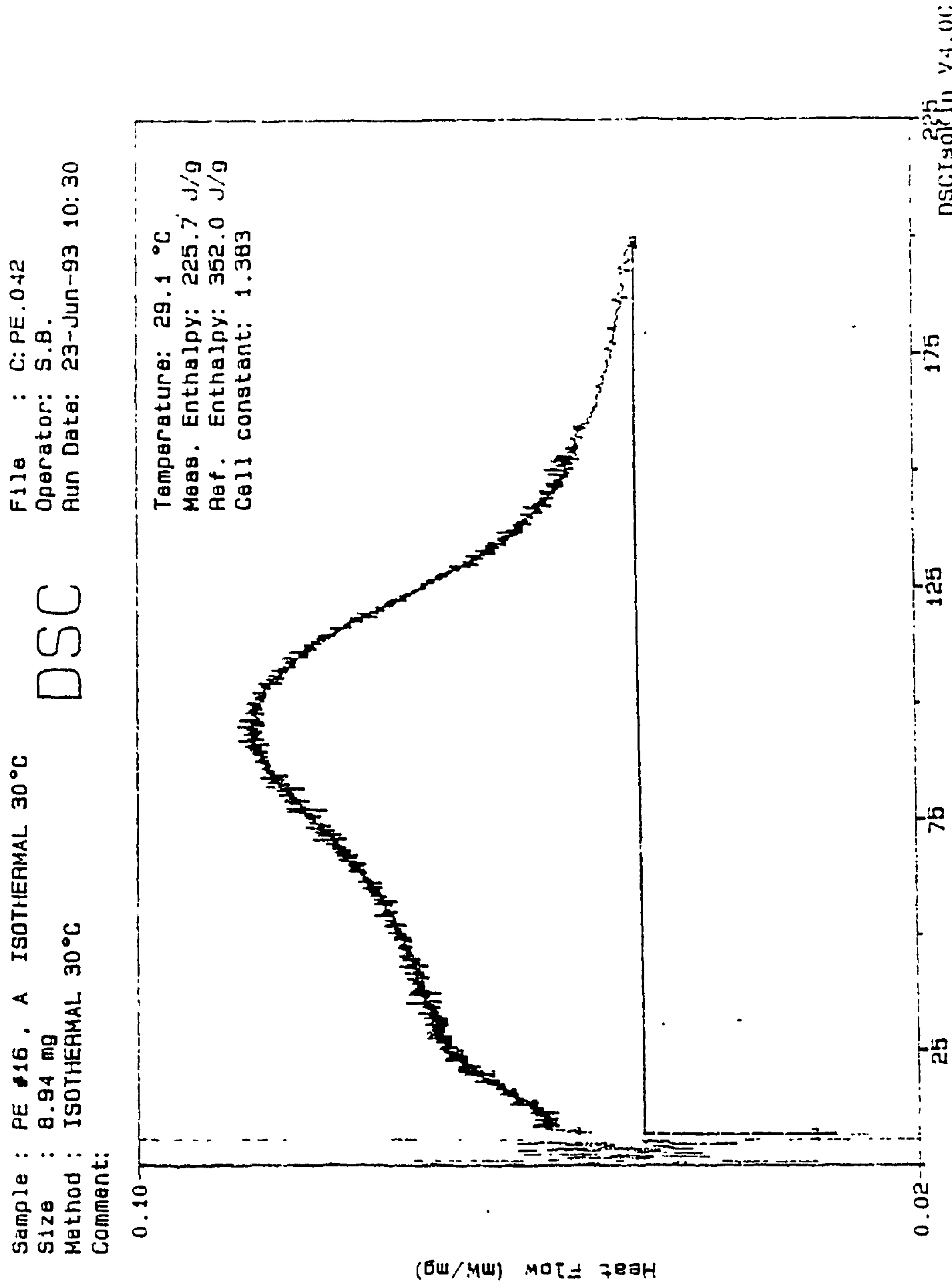

Figure C.1 : Heat Flow Curve Trial PE.042

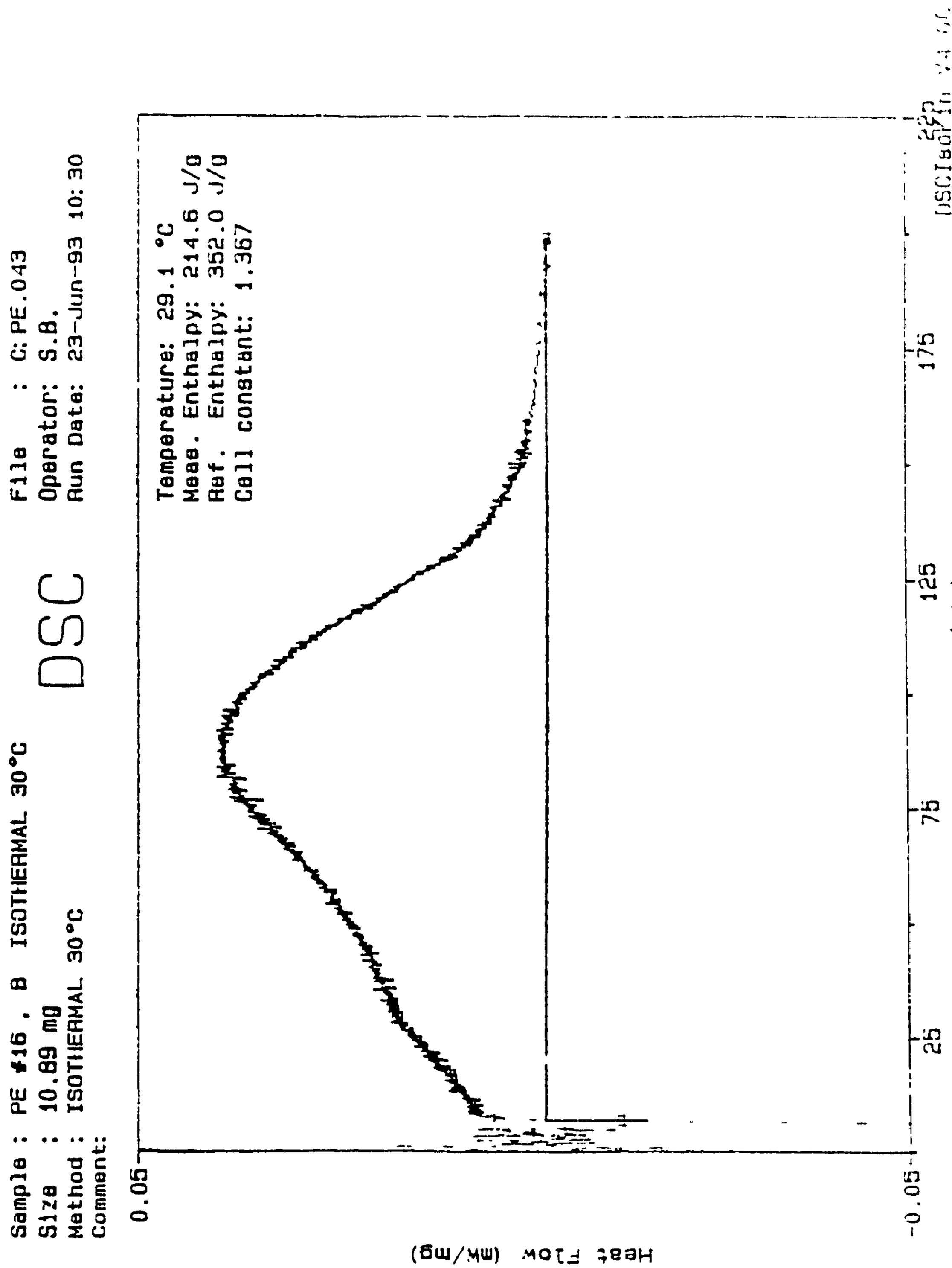

Figure C.2 : Heat Flow Curve, Trial PE.043

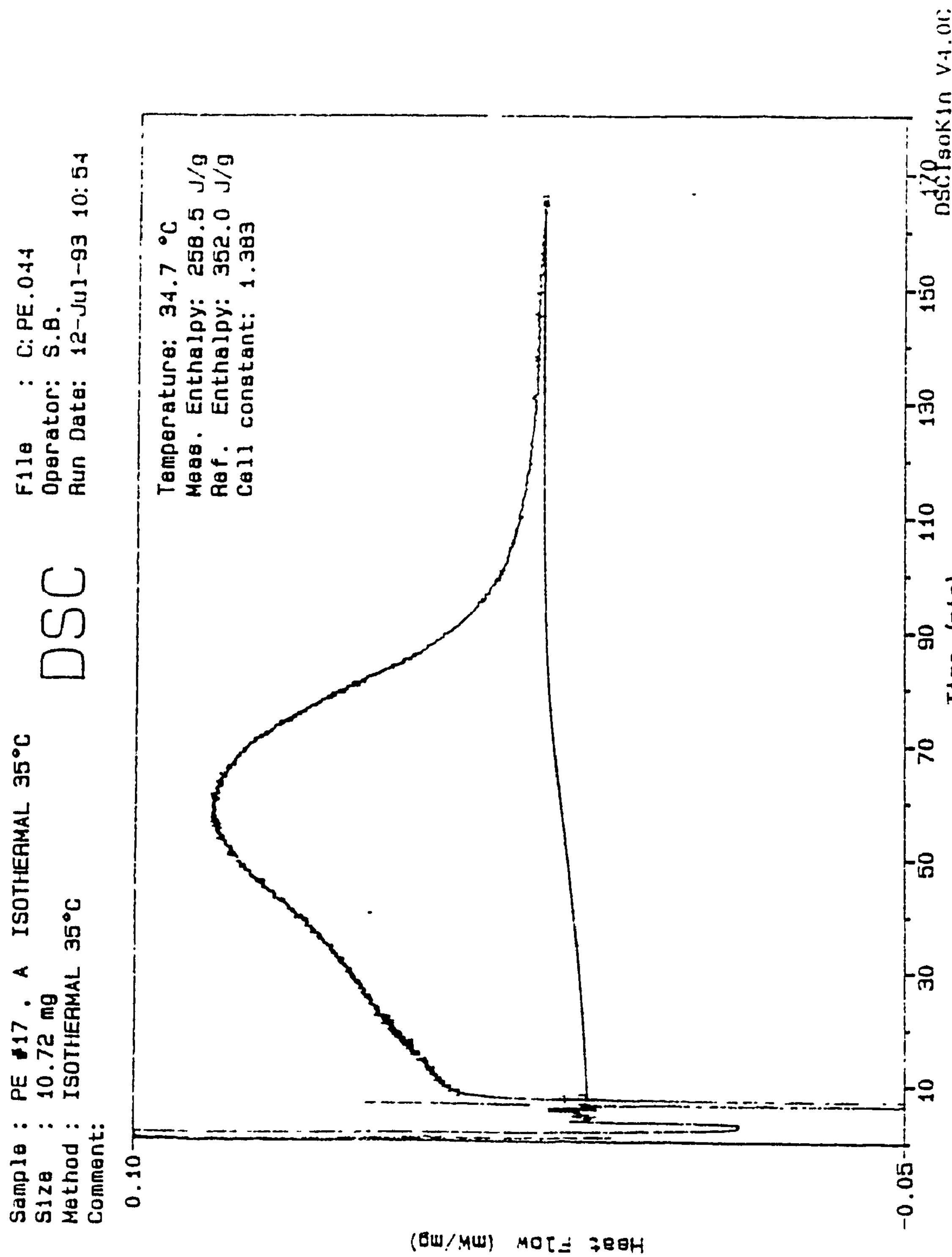

Figure C.3 : Heat Flow Curve, Trial PE.044

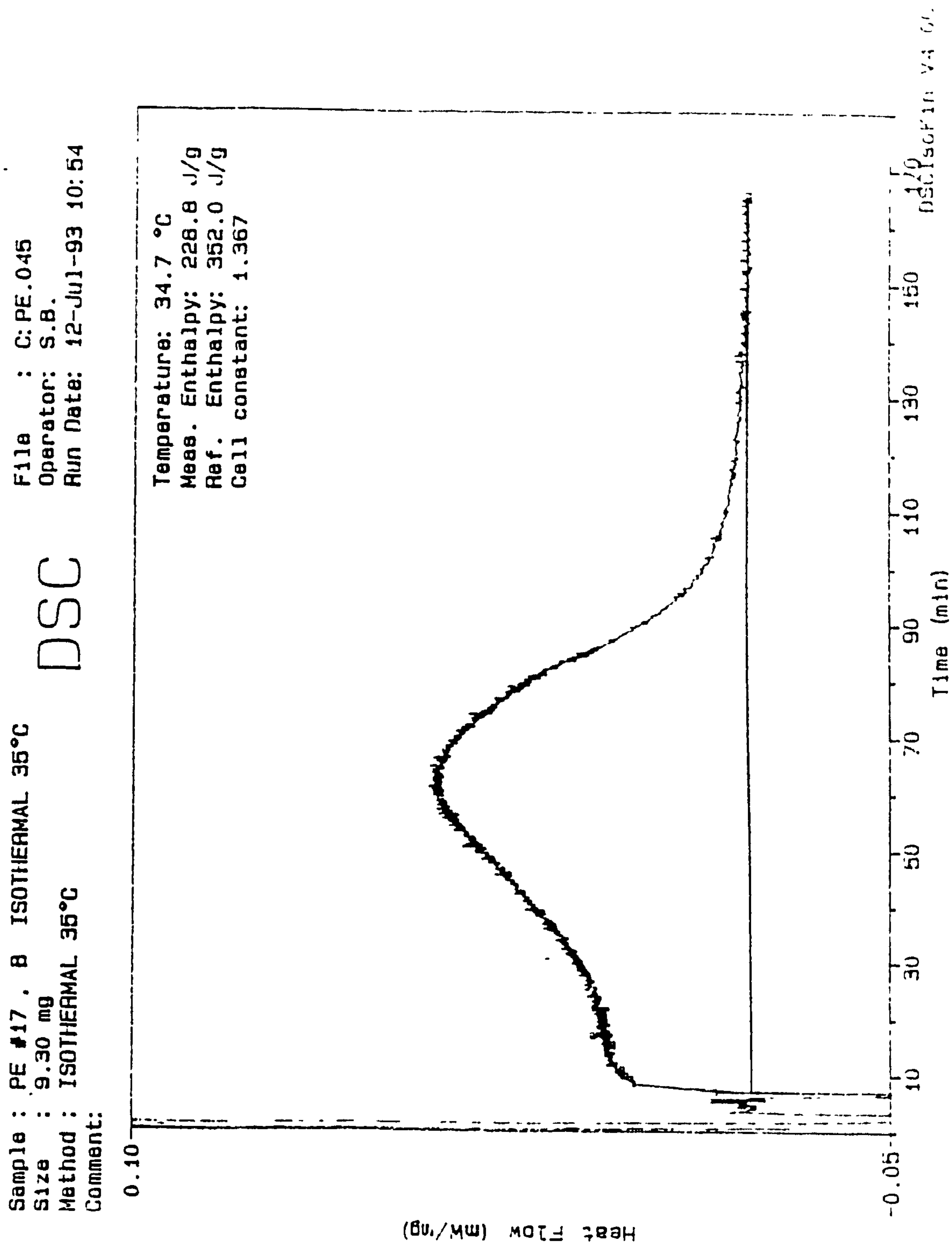

Figure C.4 : Heat Flow Curve, Trial PE.045

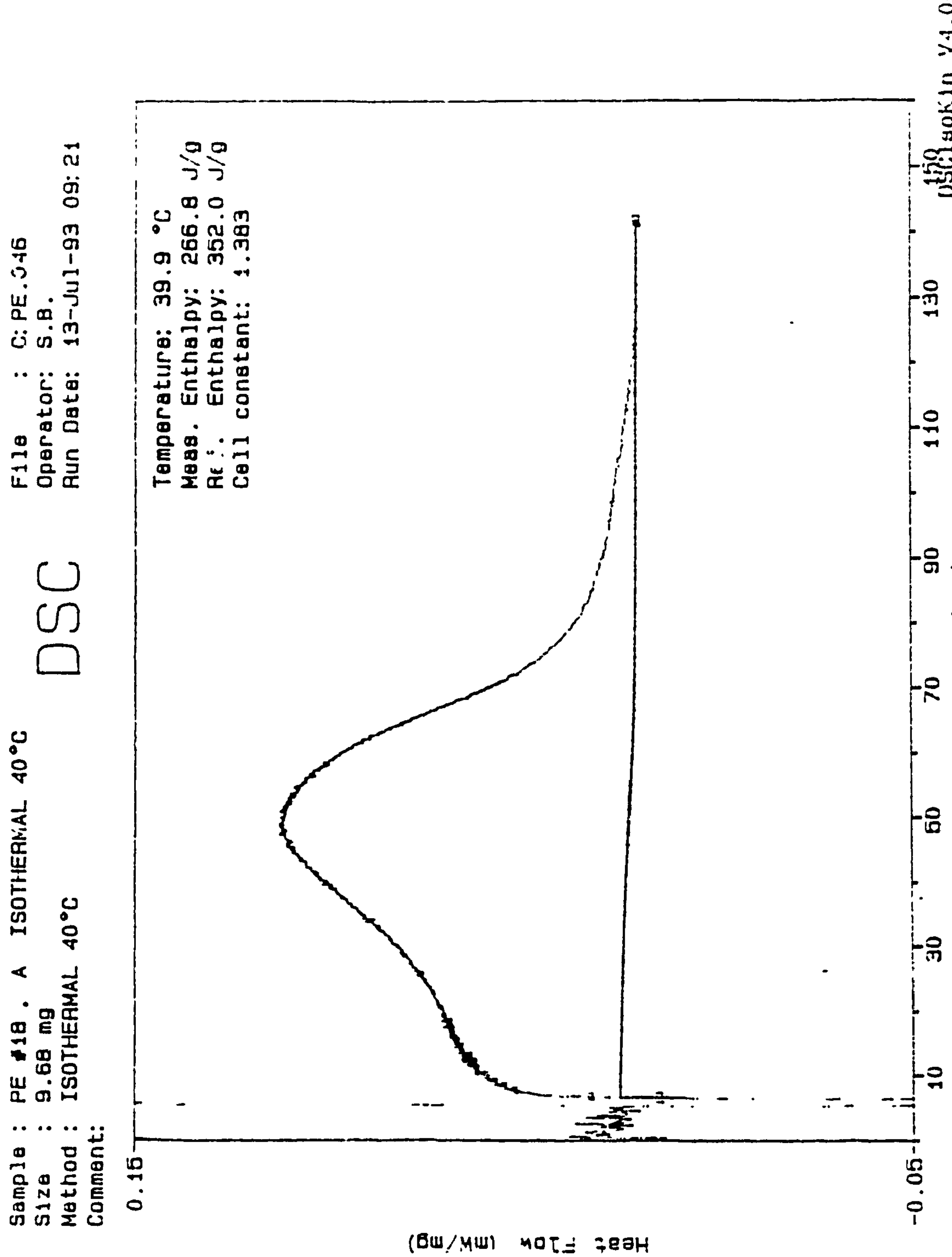

Figure C.5 : Heat Flow Curve, Trial PE.046

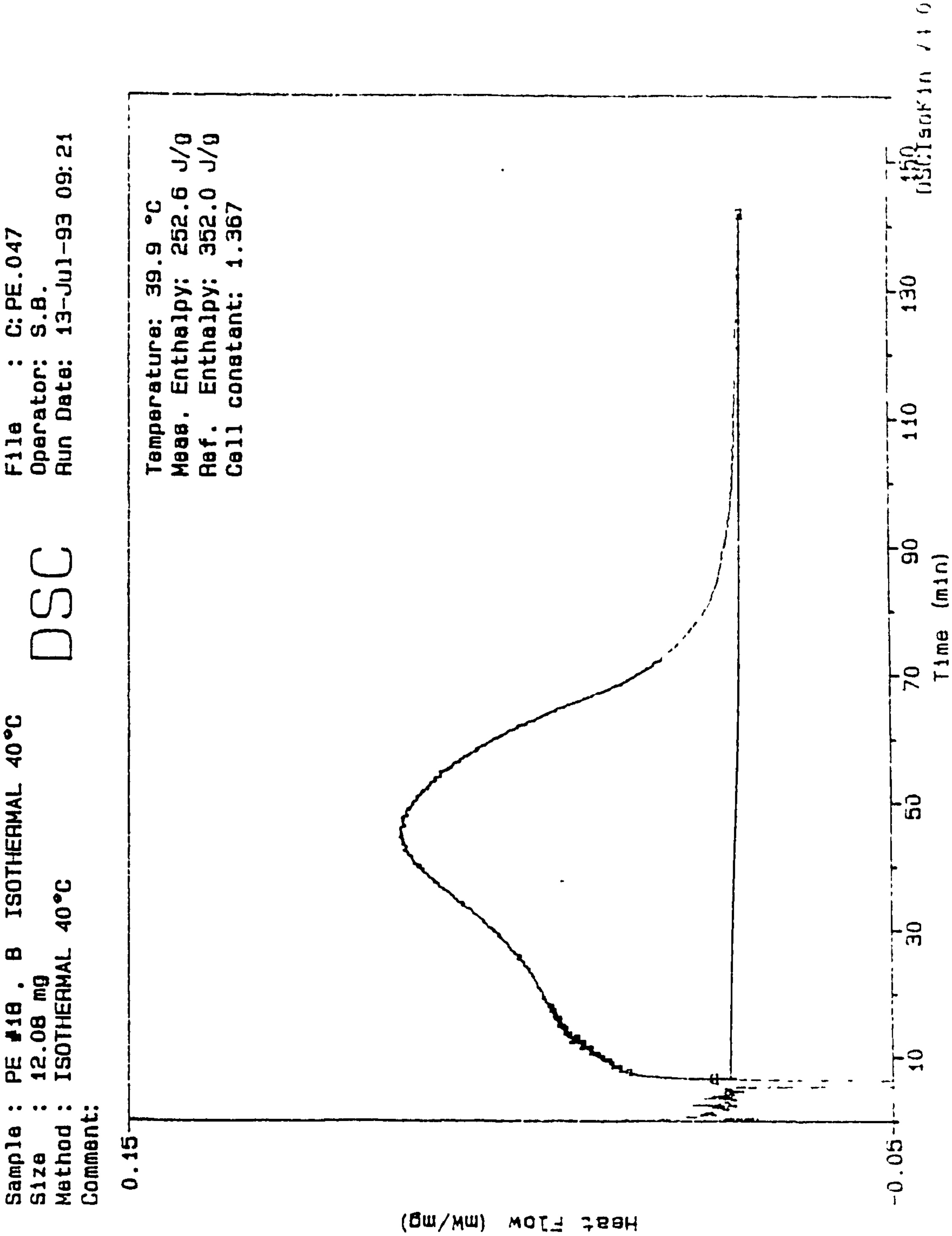

Figure C.6 : Heat Flow Curve, Trial PE.047

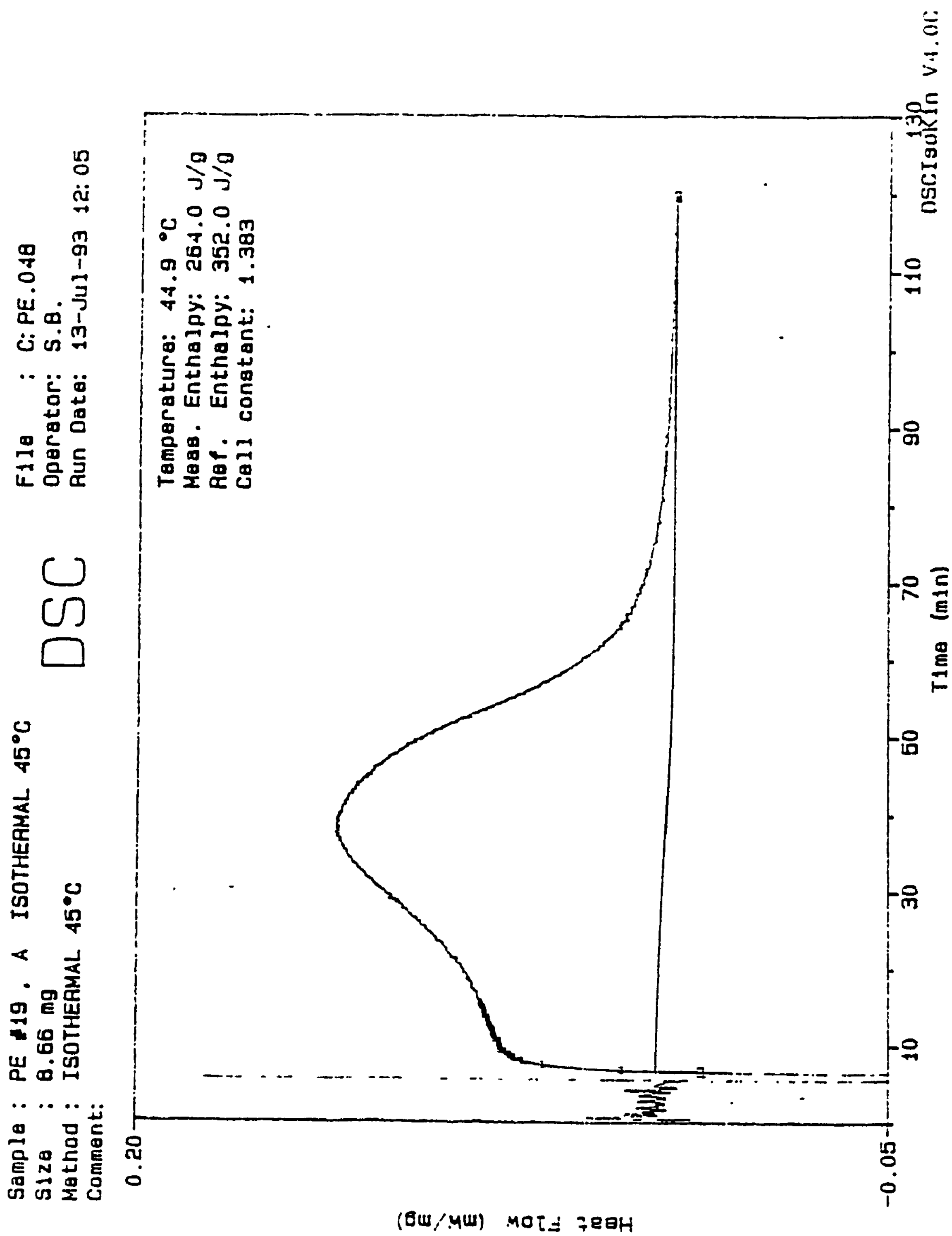

Figure C.7 : Heat Flow Curve, Trial PE.048

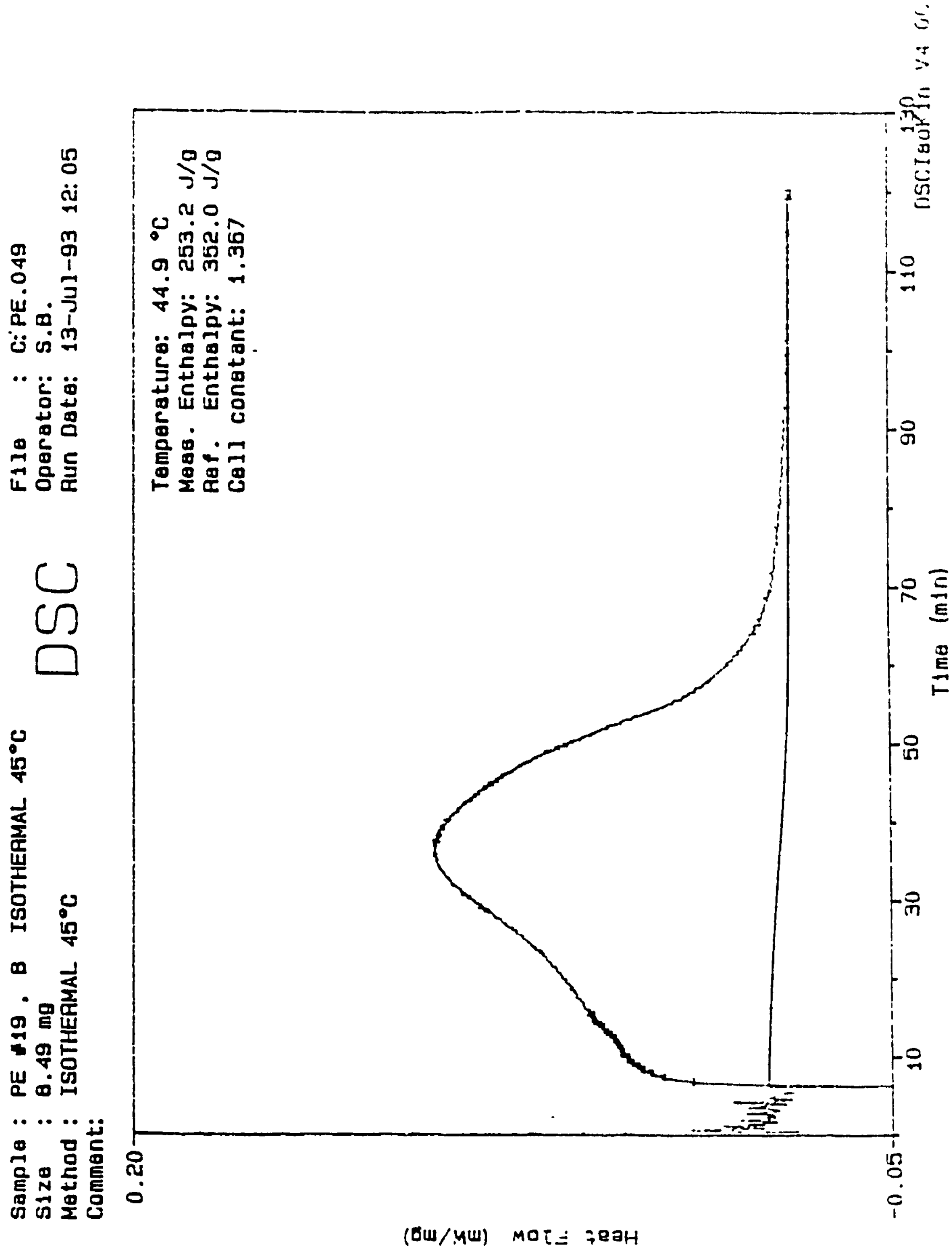

Figure C.8 : Heat Flow Curve, Trial PE.049

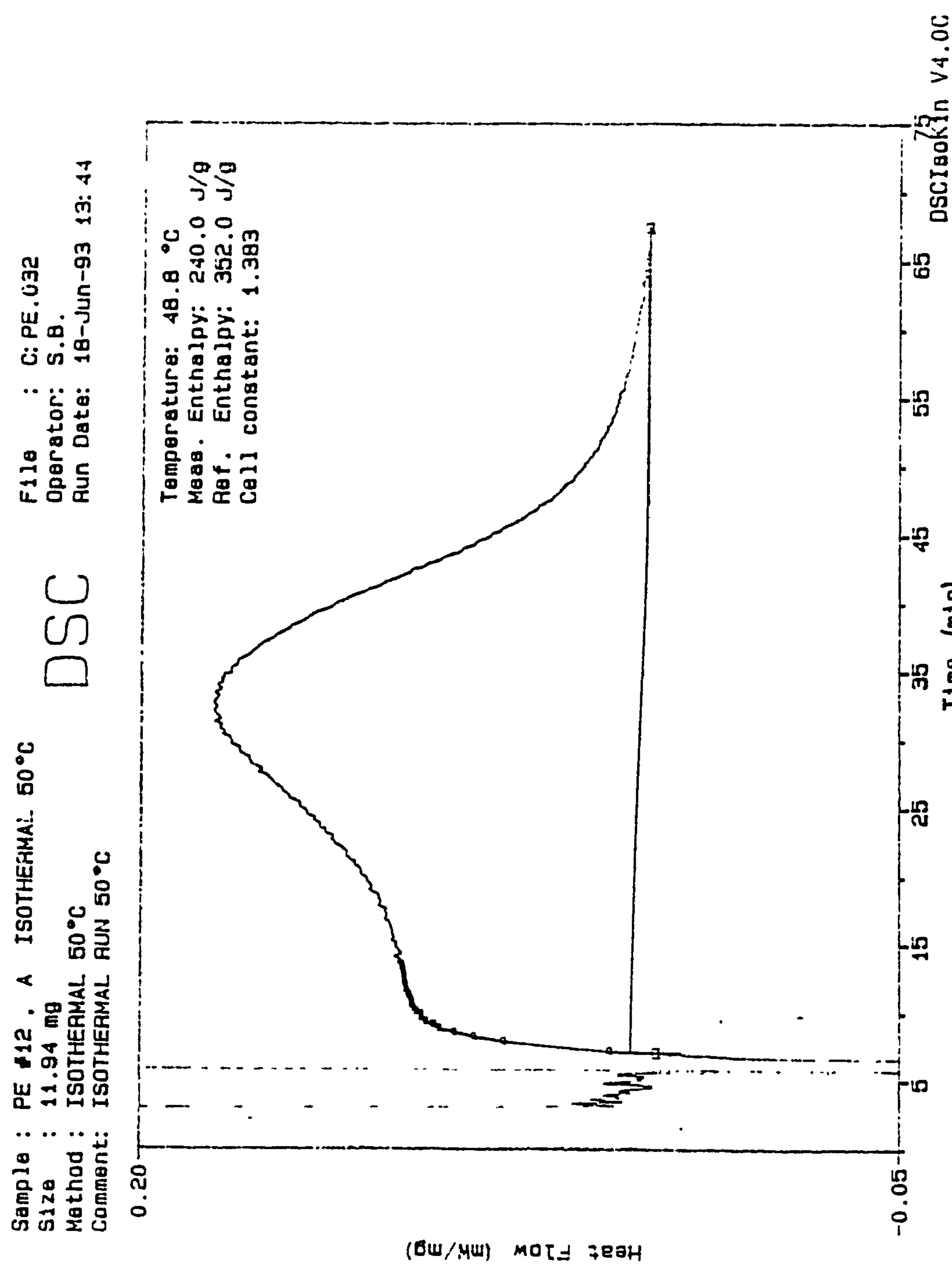

Figure C.9 : Heat Flow Curve, Trial PE.032

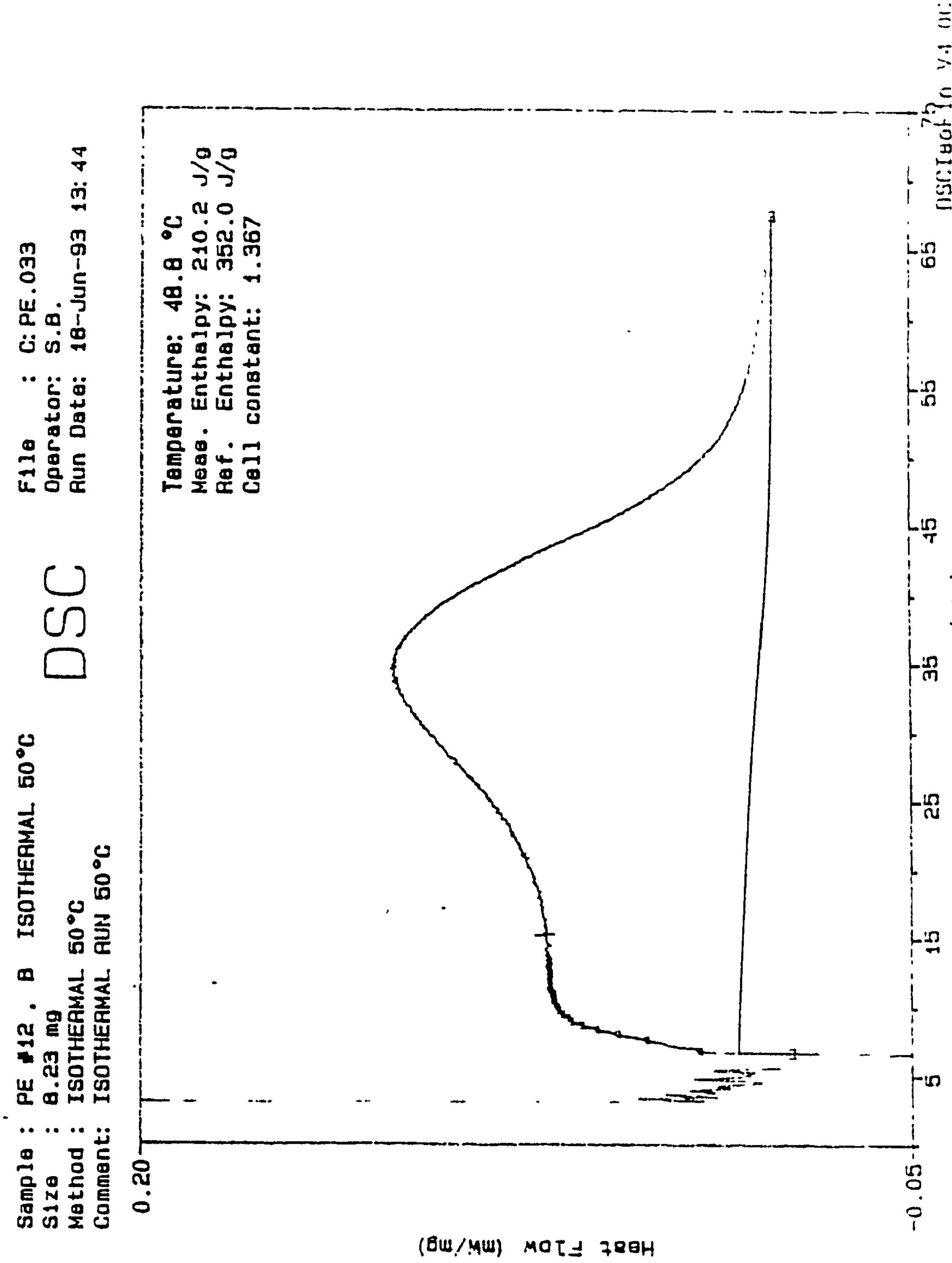

Figure C.10 : Heat Flow Curve, Trial PE.033

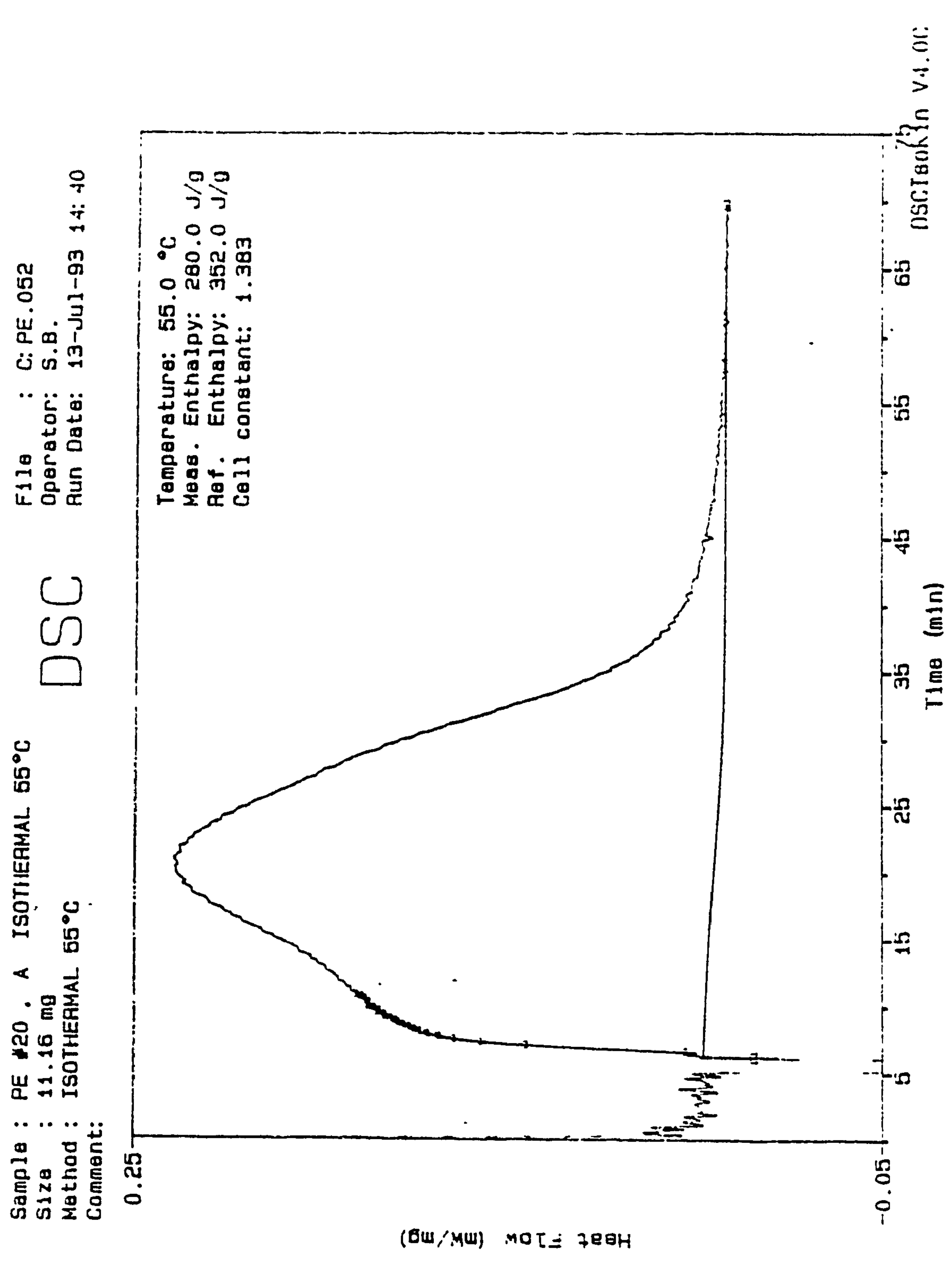

Figure C.11 : Heat Flow Curve, Trial PE.052

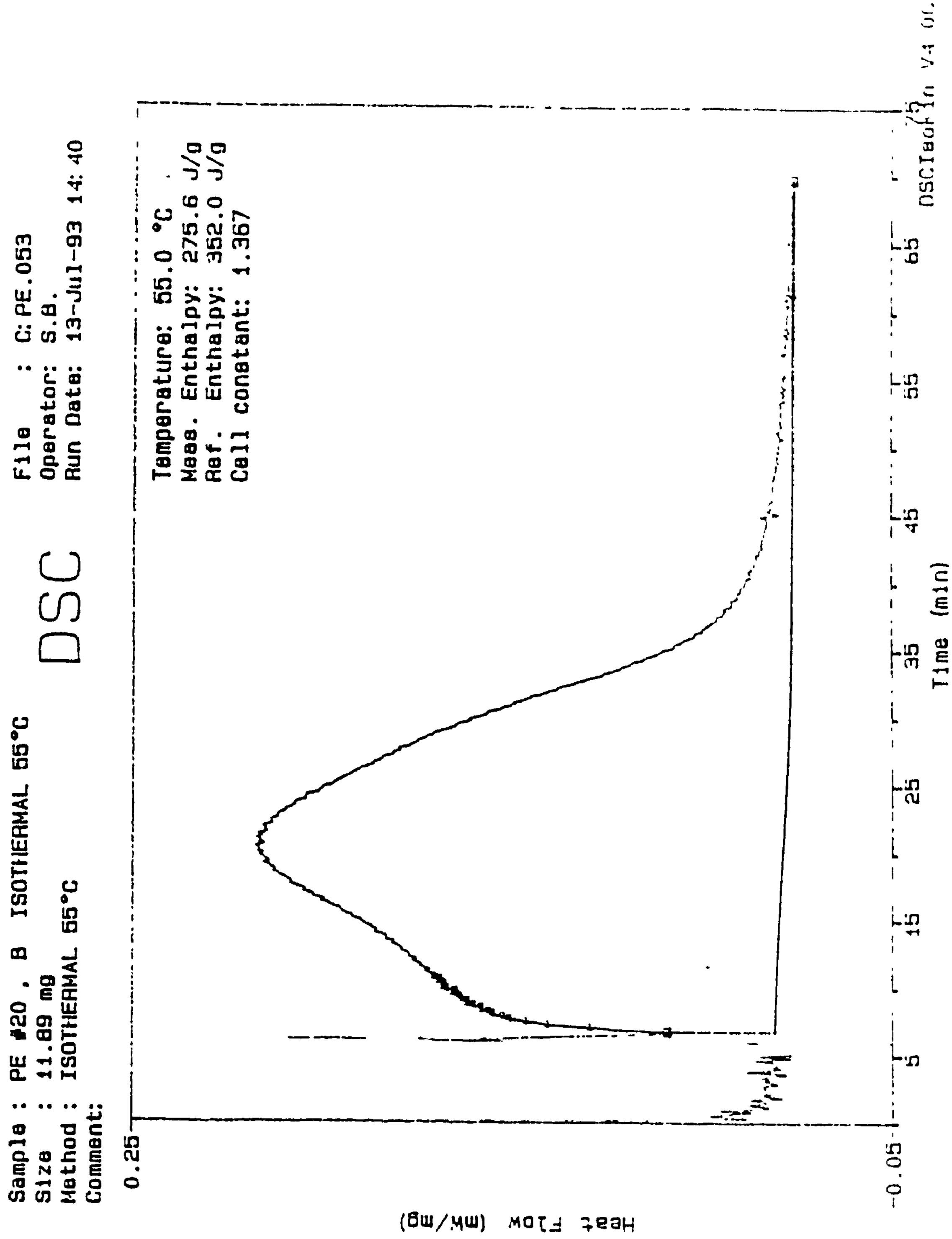

Figure C.12 : Heat Flow Curve, Trial PE.053

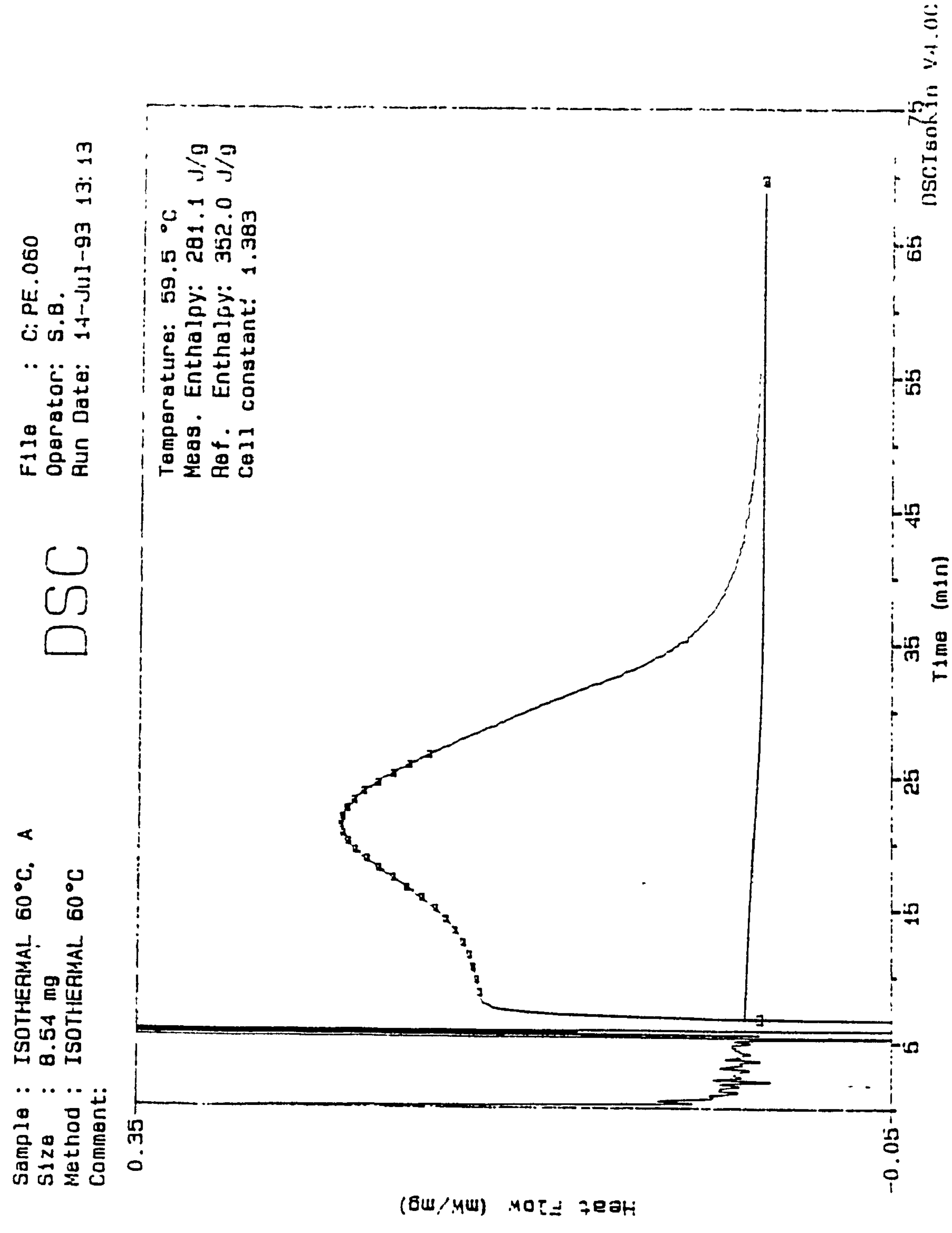

Figure C.13 : Heat Flow Curve, Trial PE.060

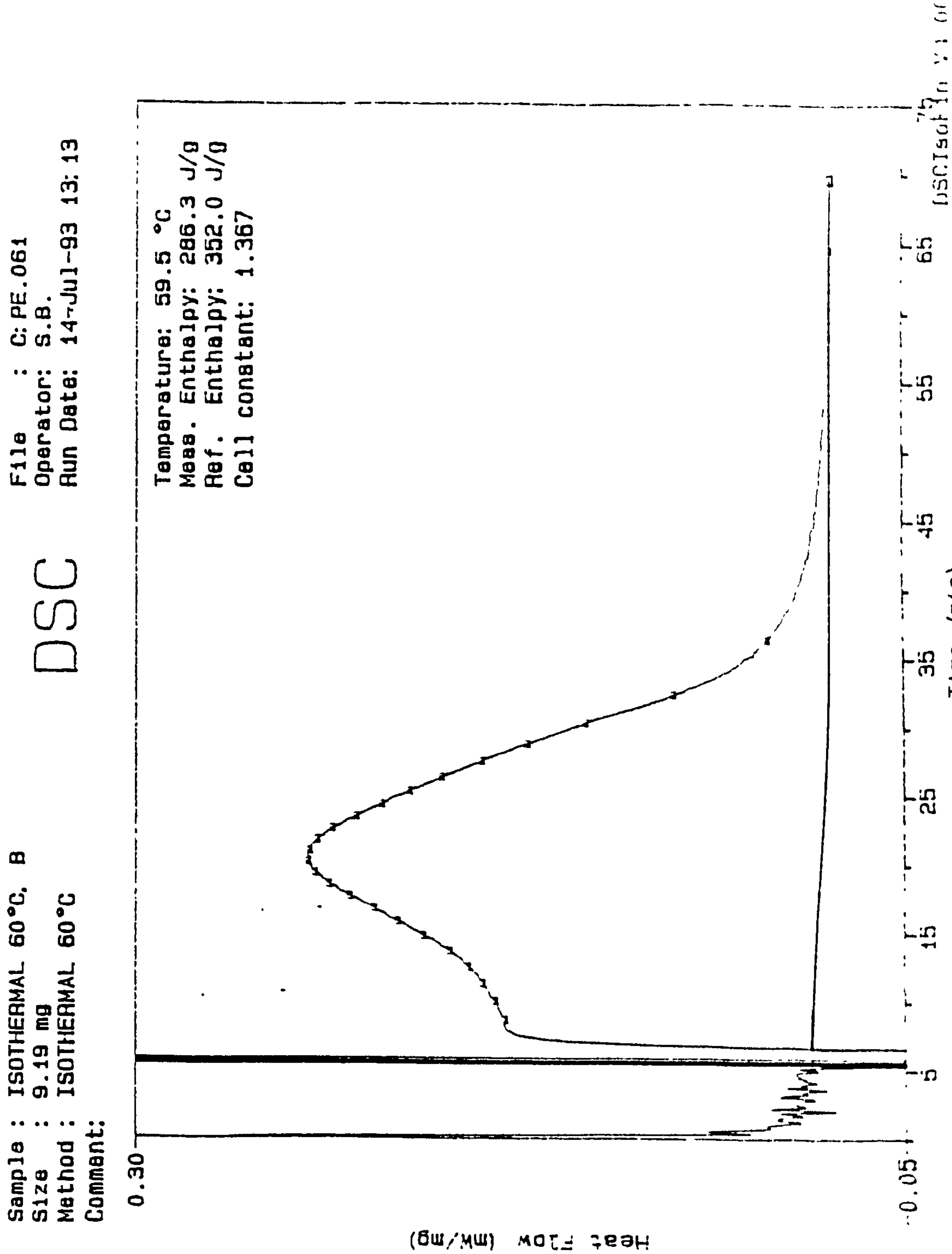

Figure C.14 : Heat Flow Curve, Trial PE.061

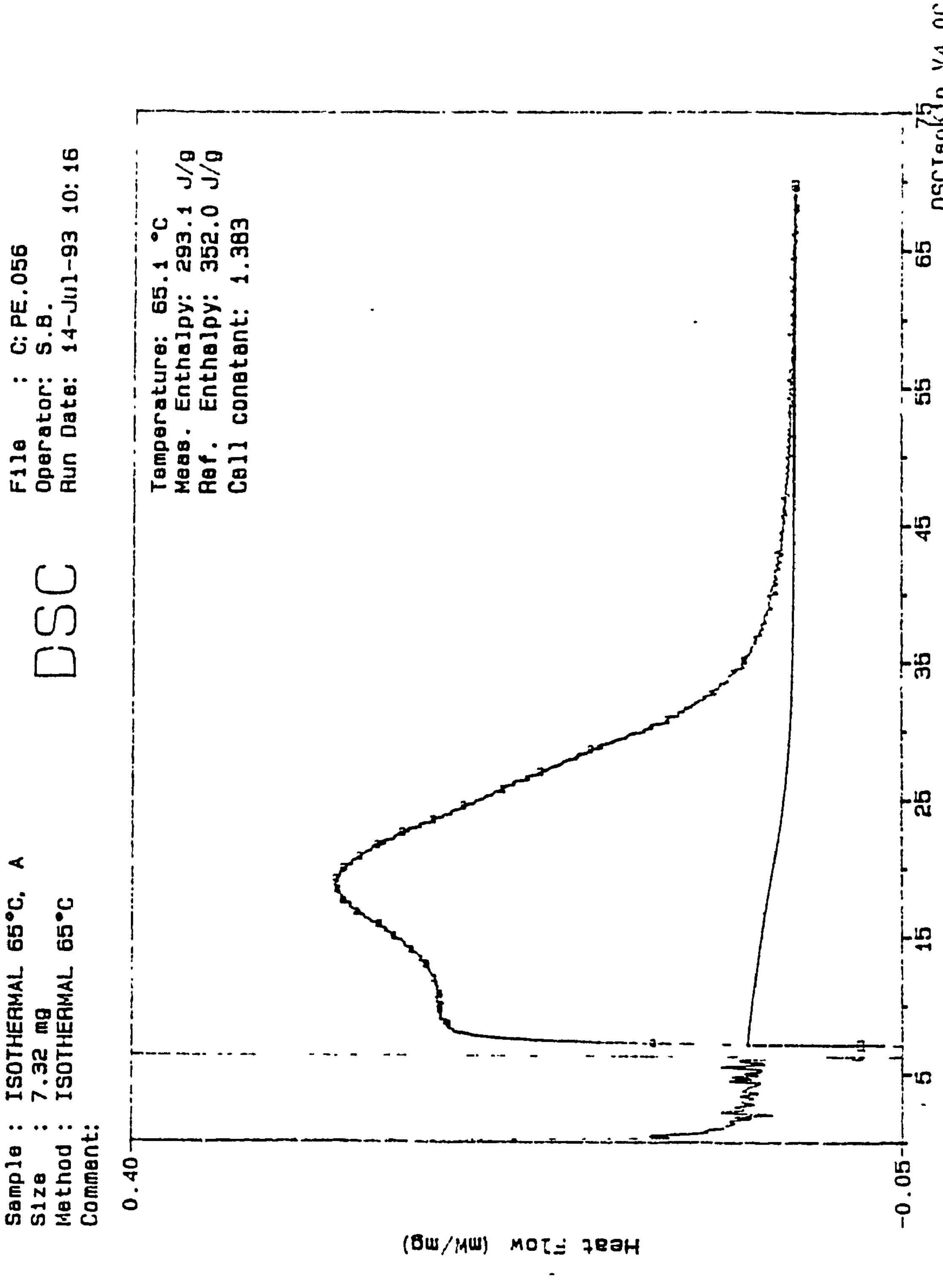

Figure C.15 : Heat Flow Curve, Trial PE.056

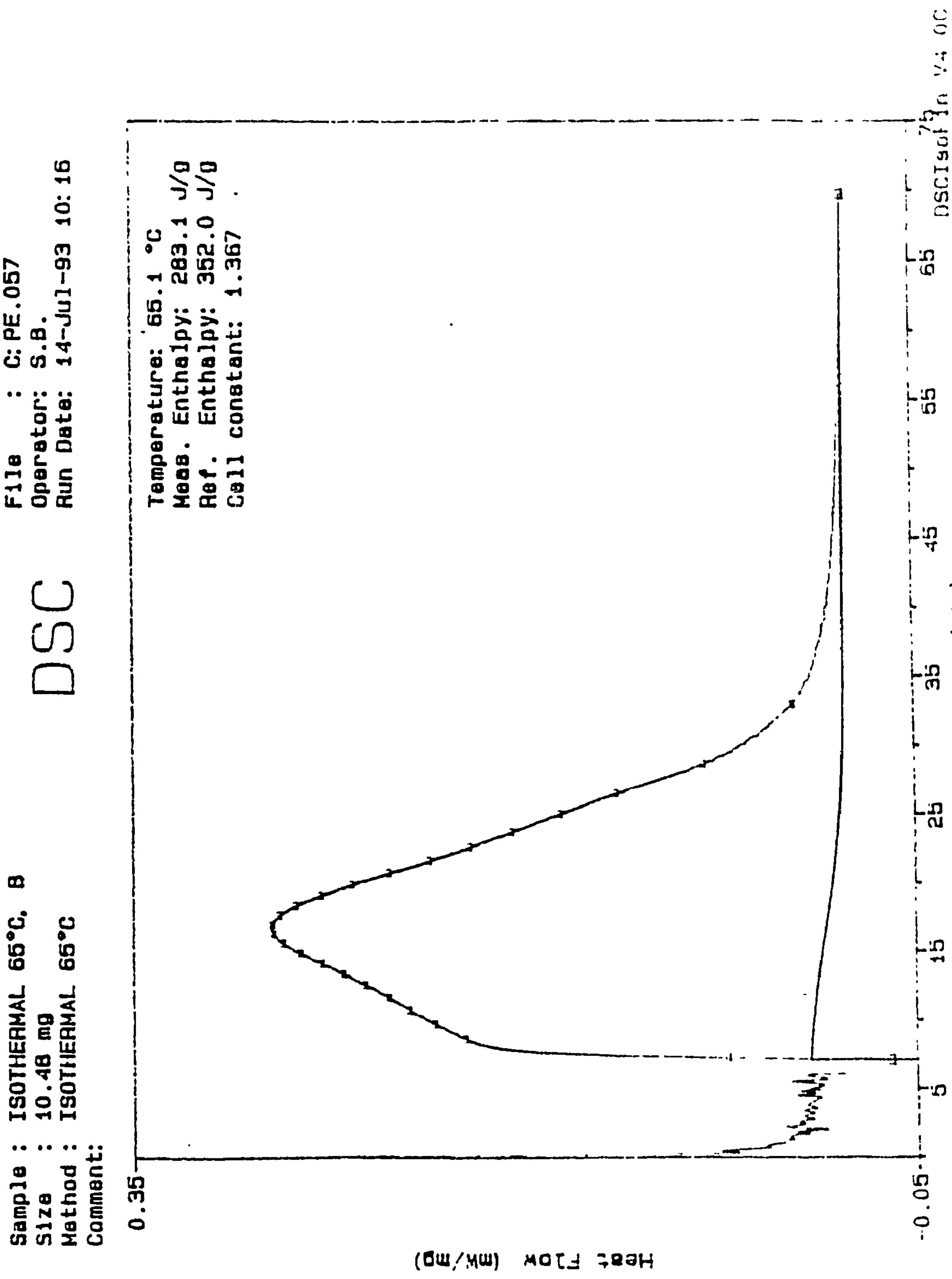

Figure C.16 : Heat Flow Curve, Trial PE.057

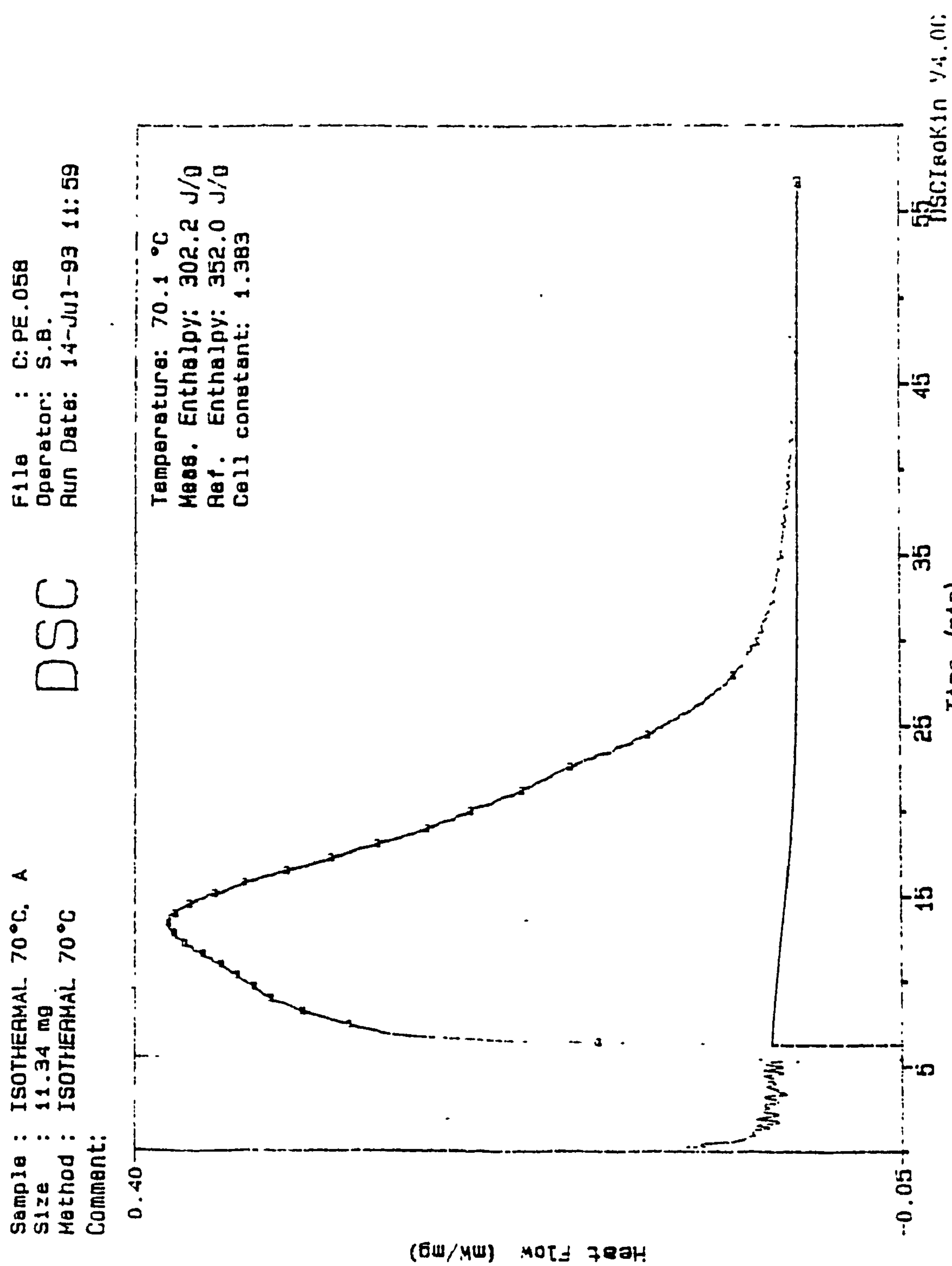

Figure C.17 : Heat Flow Curve, Trial PE.058

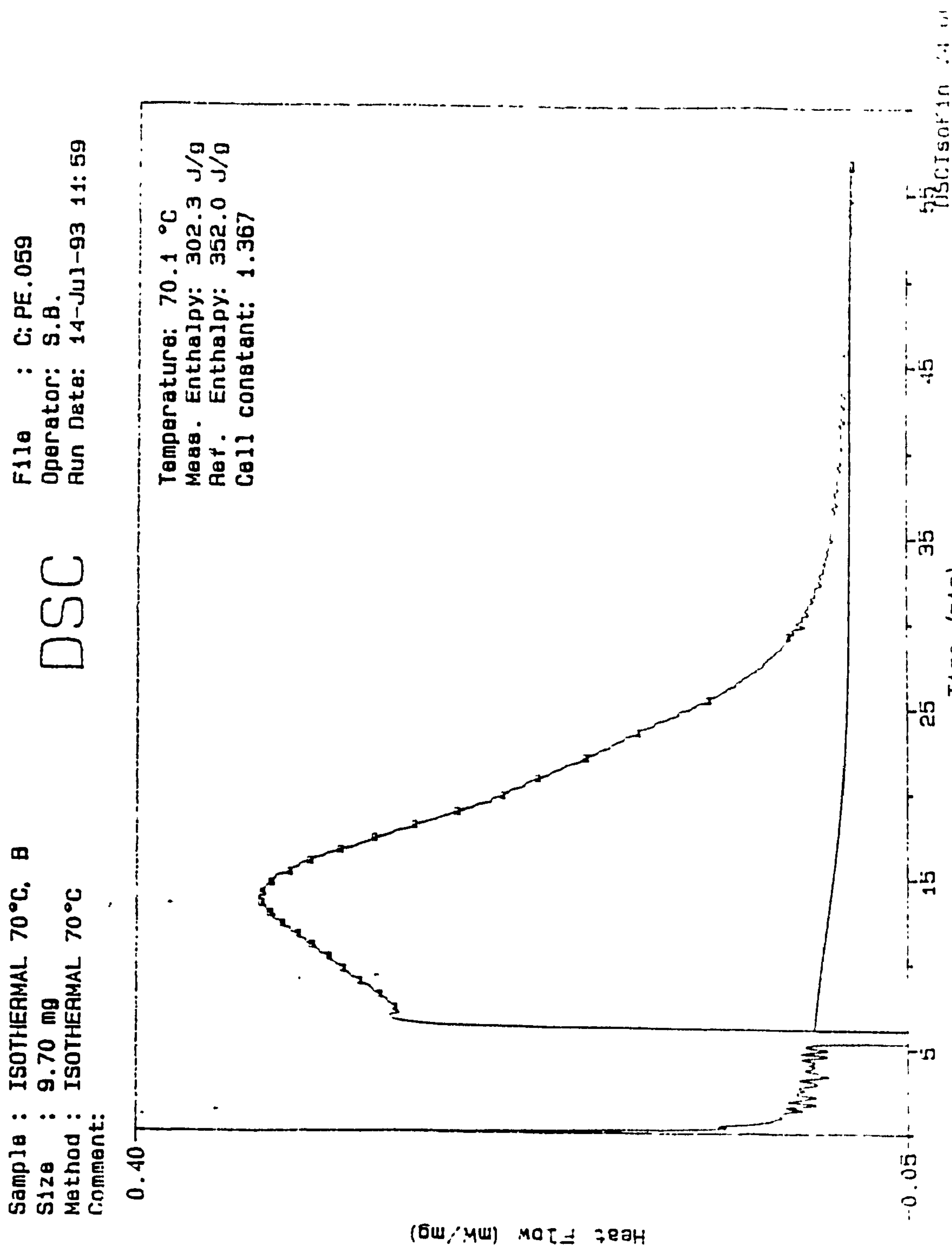

Figure C.18 : Heat Flow Curve, Trial PE.059

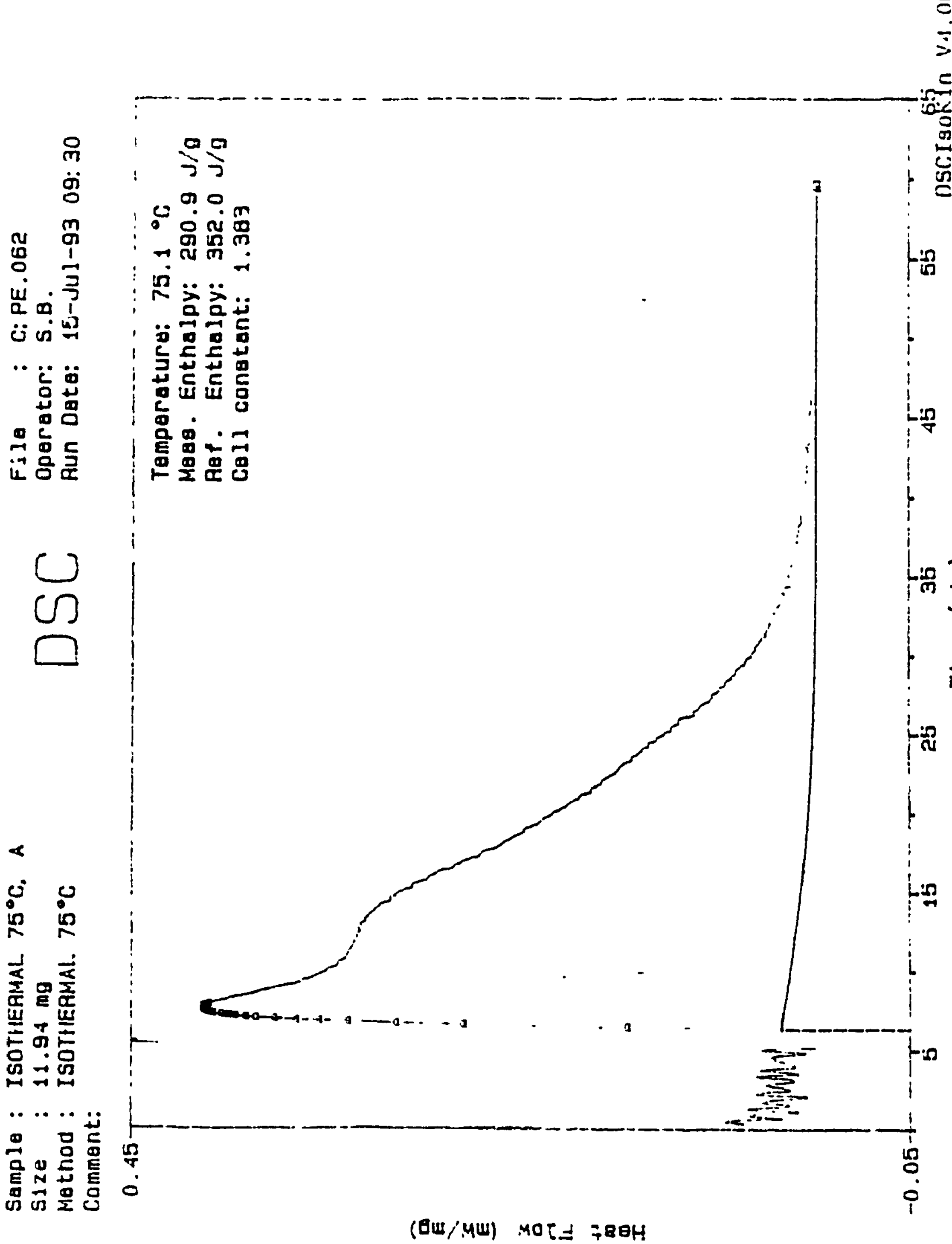

Figure C.19 : Heat Flow Curve, Trial PE.062

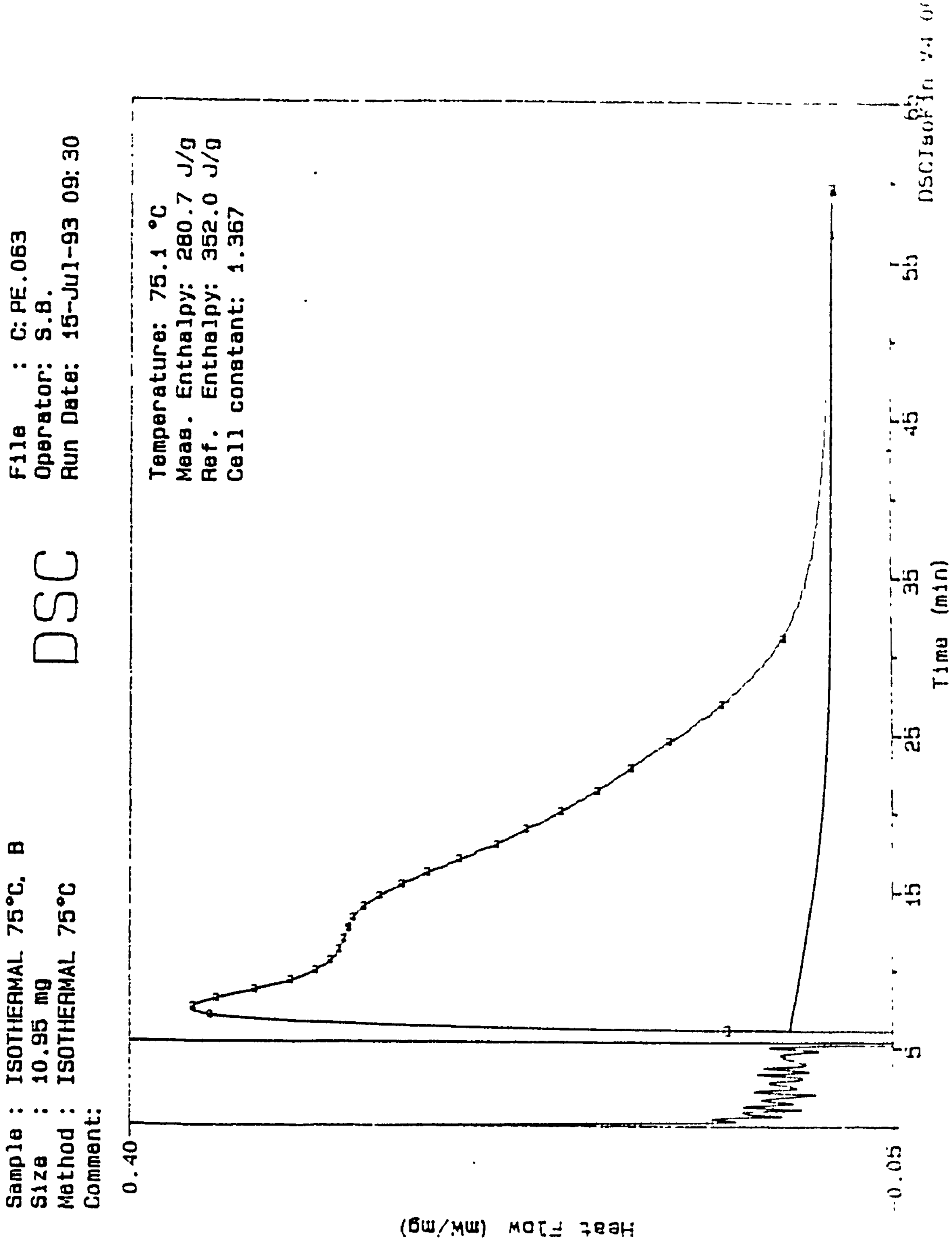

Figure C.20 : Heat Flow Curve, Trial PE.063

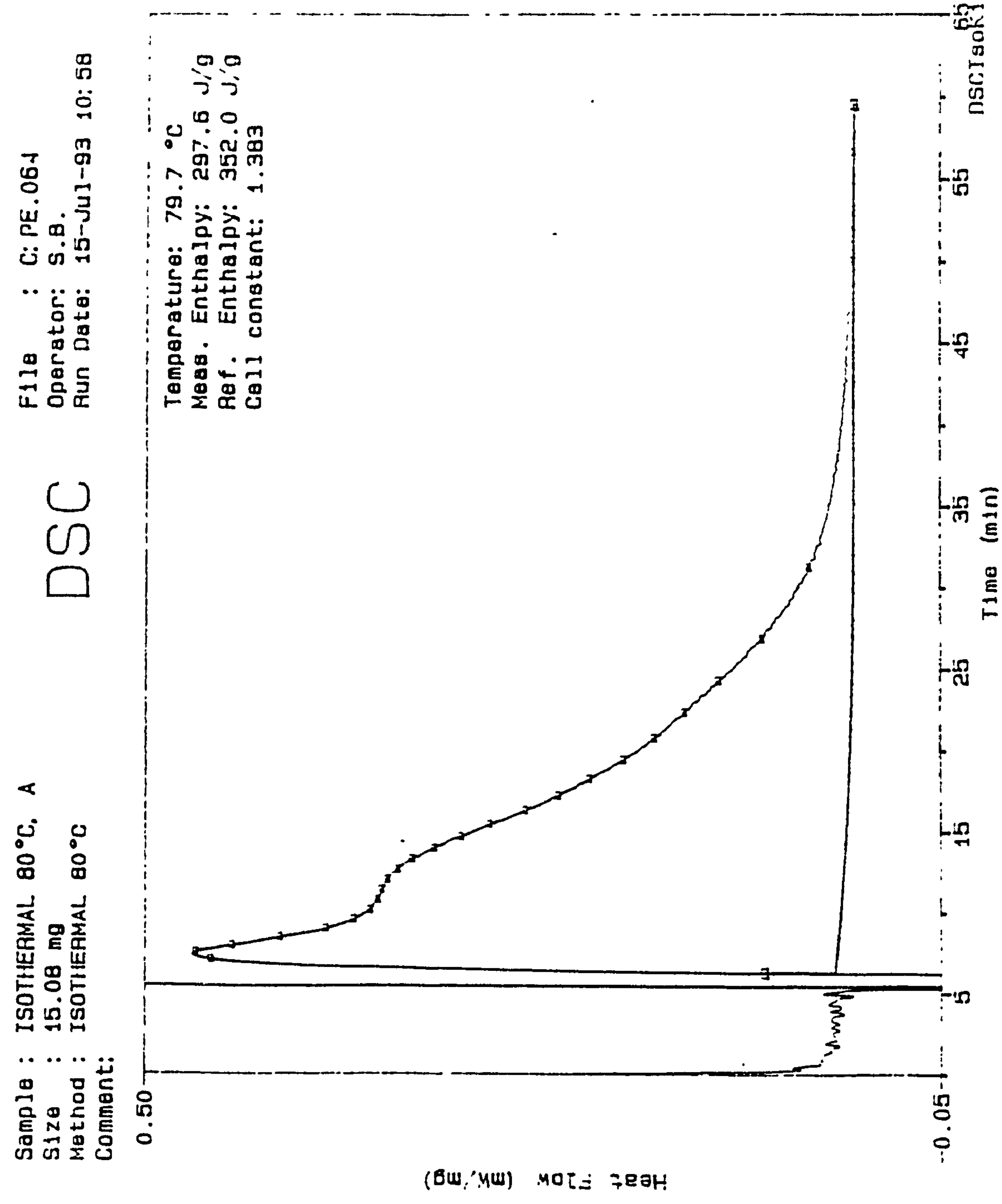

Figure C.21 : Heat Flow Curve, Trial PE.064

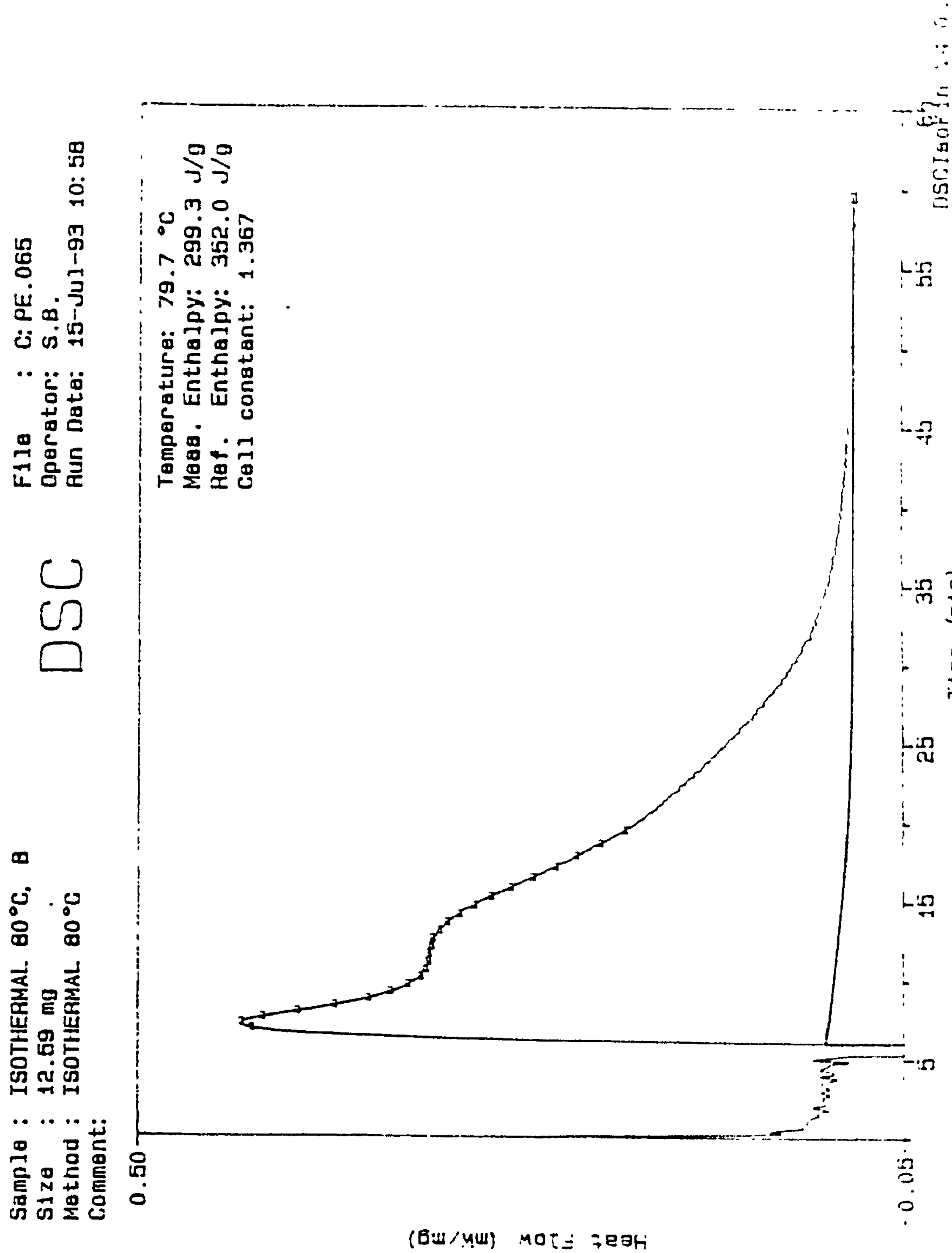

Figure C.22 : Heat Flow Curve, Trial PE.065

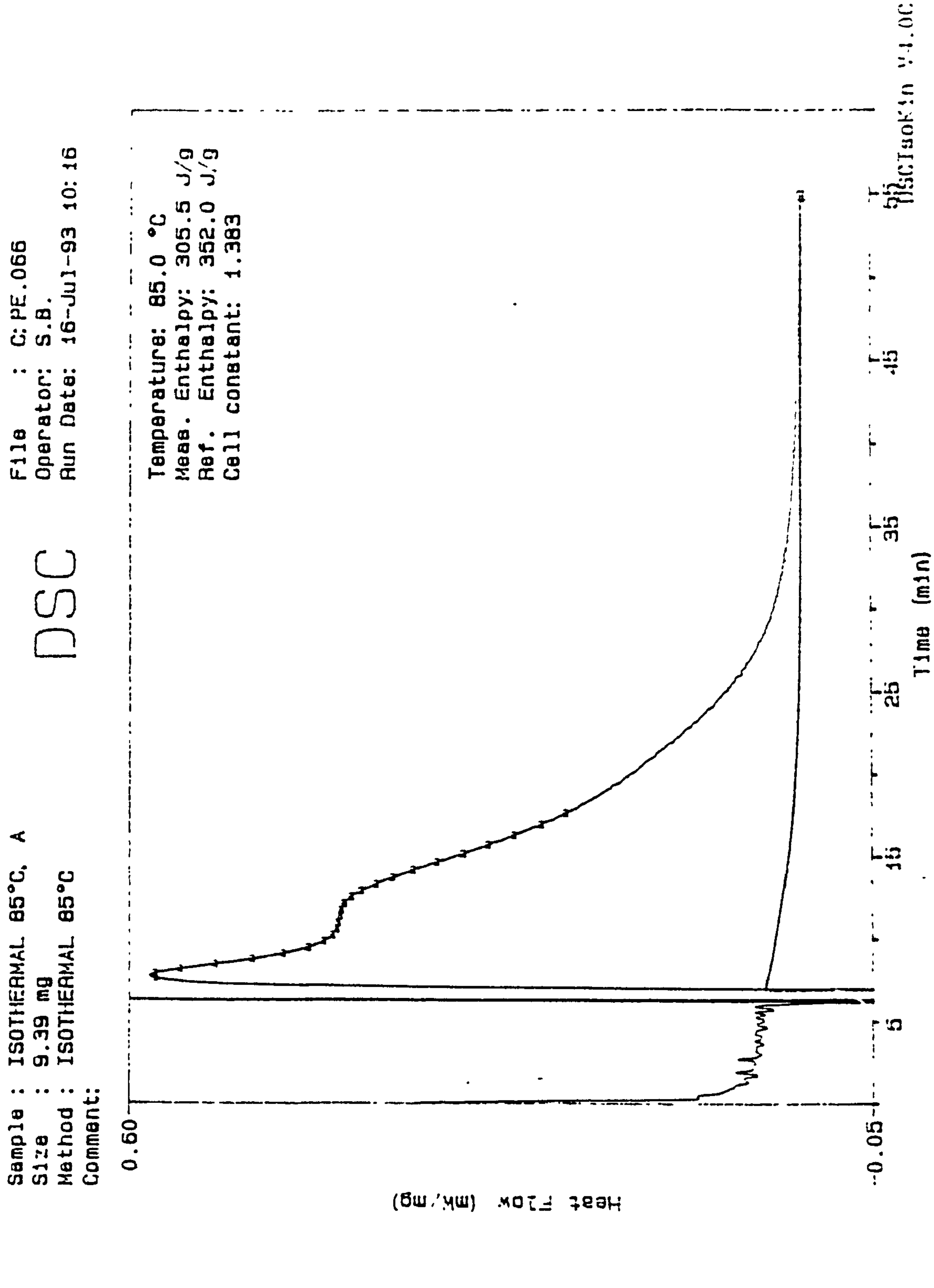

Figure C.23 : Heat Flow Curve, Trial PE.066

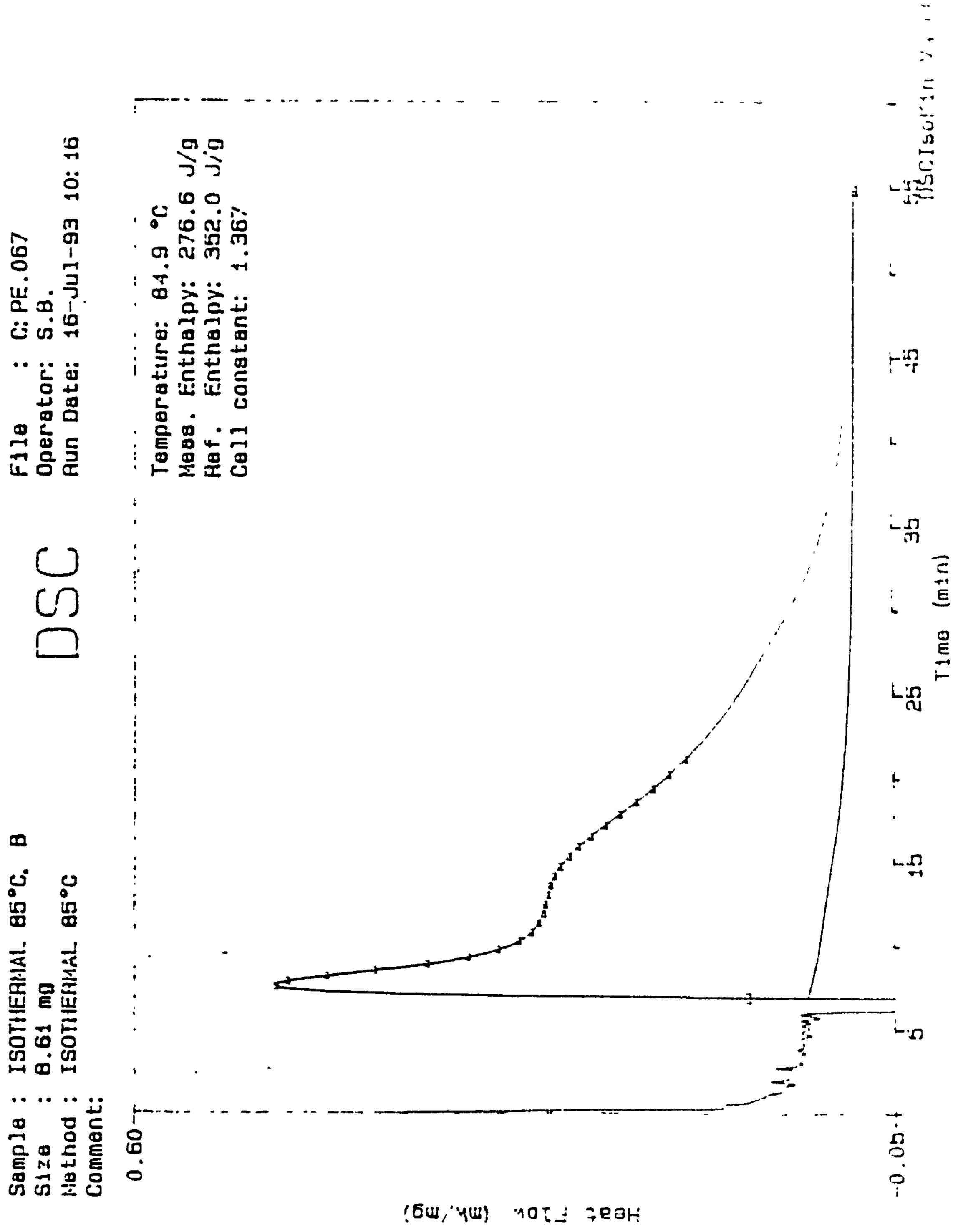

Figure C.24 : Heat Flow Curve, Trial PE.067

APPENDIX D - ISOTHERMAL RESULTS

The following 24 Tables, D.1 to D.24, were obtained by integration of the isothermal heat flow curves (Figures C.1 to C.24 in Appendix C) and list conversion C and rate of reaction dC/dt versus time at temperatures ranging from 30°C to 85°C for samples A and B at each reference temperature.

DSCIsoKin V4.0C 07/20/93 09:52:48 Page 1

DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.042 Run date: 23-Jun-93 10:30
Comment :

Sample : PE #16 , A ISOTHERMAL 30°C
Method : ISOTHERMAL 30°C
Operator : S.B.
Size : 8.940 mg
Cell constant : 1.383

Baseline type : Sigmoidal, horizontal
Reaction range : 6.77 -- 198.69 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.05
Maximum area fraction : 0.75
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 29.13 °C
Enthalpy : 222.16 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
15.571	0.0318	0.0031
21.204	0.0500	0.0032
26.504	0.0686	0.0034
31.521	0.0869	0.0039
36.327	0.1053	0.0041
40.982	0.1238	0.0042
45.408	0.1422	0.0040
49.625	0.1605	0.0044
53.726	0.1790	0.0045
57.625	0.1975	0.0048
61.283	0.2158	0.0051
64.819	0.2345	0.0056
68.246	0.2535	0.0056
71.271	0.2709	0.0059
74.329	0.2894	0.0061
77.347	0.3083	0.0066
80.119	0.3262	0.0064
82.986	0.3450	0.0066
85.667	0.3629	0.0066
88.464	0.3818	0.0066
91.158	0.3998	0.0065
93.912	0.4182	0.0065
96.722	0.4366	0.0065
99.682	0.4555	0.0062
102.605	0.4735	0.0060

Table D.1 : C and dC/dt vs t, Trial PE.042

DSCIsoKin V4.0C 07/20/93 10:09:02 Page 1

DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.043 Run date: 23-Jun-93 10:30
Comment :

Sample : PE #16 , B ISOTHERMAL 30°C
Method : ISOTHERMAL 30°C
Operator : S.B.
Size : 10.890 mg
Cell constant : 1.367

Baseline type : Sigmoidal, horizontal
Reaction range : 6.77 -- 198.69 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.05
Maximum area fraction : 0.75
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 29.12 °C
Enthalpy : 214.83 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
15.692	0.0306	0.0027
21.801	0.0485	0.0034
27.118	0.0664	0.0035
32.037	0.0842	0.0037
36.615	0.1020	0.0037
40.982	0.1198	0.0043
45.031	0.1373	0.0045
48.958	0.1555	0.0048
52.603	0.1732	0.0051
56.195	0.1919	0.0054
59.262	0.2088	0.0057
62.304	0.2265	0.0058
65.229	0.2444	0.0063
68.045	0.2624	0.0065
70.728	0.2801	0.0070
73.351	0.2979	0.0069
75.901	0.3156	0.0069
78.499	0.3339	0.0071
80.937	0.3513	0.0071
83.471	0.3693	0.0071
85.945	0.3869	0.0071
88.464	0.4045	0.0068
91.086	0.4225	0.0067
93.802	0.4408	0.0066
96.461	0.4580	0.0063

Table D.2 : C and dC/dt vs t, Trial PE.043

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C: PE.044   Run date: 12-Jul-93 10:54
Comment :

Sample : PE #17 . A ISOTHERMAL 35°C
Method : ISOTHERMAL 35°C
Operator : S.B.
Size : 10.720 mg
Cell constant : 1.383

Baseline type : Sigmoidal, horizontal
Reaction range : 7.50 -- 165.20 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.00
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 34.70 °C
Enthalpy : 256.58 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.040	0.0000	0.0006
6.609	0.0304	0.0053
11.821	0.0610	0.0063
16.416	0.0913	0.0069
20.652	0.1216	0.0073
24.650	0.1523	0.0079
28.354	0.1827	0.0085
31.770	0.2127	0.0090
35.075	0.2438	0.0096
38.054	0.2735	0.0102
40.971	0.3042	0.0109
43.709	0.3342	0.0110
46.448	0.3651	0.0114
49.054	0.3951	0.0114
51.802	0.4268	0.0115
54.325	0.4557	0.0113
57.078	0.4866	0.0111
59.859	0.5168	0.0106
62.789	0.5470	0.0100
66.000	0.5777	0.0090
69.522	0.6077	0.0078
73.780	0.6379	0.0063
79.813	0.6686	0.0041
81.056	0.6989	0.0017
157.260	0.7289	0.0000

Table D.3 : C and dC/dt vs t, Trial PE.044

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.045 Run date: 12-Jul-93 10:54
Comment :

Sample : PE #17 , B ISOTHERMAL 35°C
Method : ISOTHERMAL 35°C
Operator : S.B.
Size : 9.300 mg
Cell constant : 1.367

Baseline type : Sigmoidal, horizontal
Reaction range : 7.08 -- 165.20 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.00
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 34.69 °C
Enthalpy : 224.47 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.012	0.0000	0.0010
7.026	0.0270	0.0044
12.552	0.0532	0.0050
17.933	0.0800	0.0051
22.818	0.1063	0.0058
27.365	0.1333	0.0063
31.430	0.1598	0.0070
35.148	0.1864	0.0074
38.520	0.2128	0.0080
41.654	0.2392	0.0085
44.589	0.2657	0.0094
47.435	0.2928	0.0096
50.070	0.3190	0.0103
52.676	0.3456	0.0105
55.228	0.3721	0.0102
57.833	0.3991	0.0104
60.477	0.4260	0.0102
63.088	0.4519	0.0097
65.934	0.4788	0.0092
68.918	0.5052	0.0084
72.165	0.5315	0.0073
75.992	0.5581	0.0063
81.343	0.5857	0.0042
90.149	0.6113	0.0019

Table D.4 : C and dC/dt vs t, Trial PE.045

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.046 Run date: 13-Jul-93 09:21
Comment :

Sample : PE #18 . A ISOTHERMAL 40°C
Method : ISOTHERMAL 40°C
Operator : S.B.
Size : 9.680 mg
Cell constant : 1.383

Baseline type : Sigmoidal, horizontal
Reaction range : 6.67 -- 141.68 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.00
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 39.92 °C
Enthalpy : 266.81 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.166	0.0000	0.0013
5.938	0.0316	0.0068
10.432	0.0633	0.0074
14.524	0.0948	0.0080
18.320	0.1264	0.0086
21.818	0.1581	0.0095
25.097	0.1907	0.0103
27.948	0.2215	0.0112
30.632	0.2529	0.0121
33.142	0.2846	0.0132
35.475	0.3160	0.0139
37.715	0.3478	0.0145
39.848	0.3793	0.0149
41.928	0.4107	0.0153
44.008	0.4423	0.0151
46.115	0.4741	0.0148
48.248	0.5055	0.0145
50.462	0.5369	0.0139
52.833	0.5687	0.0130
55.394	0.6003	0.0118
58.285	0.6317	0.0099
61.982	0.6636	0.0073
67.845	0.6965	0.0041
78.686	0.7265	0.0019

Table D.5 : C and dC/dt vs t, Trial PE.046

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C: PE.047 Run date: 13-Jul-93 09: 21
Comment :

Sample : PE #18 , B ISOTHERMAL 40°C
Method : ISOTHERMAL 40°C
Operator : S.B.
Size : 12.080 mg
Cell constant : 1.357

Baseline type : Sigmoidal, horizontal
Reaction range : 6.67 -- 141.68 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.00
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 39.92 °C
Enthalpy : 252.56 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.015	0.0000	0.0010
5.559	0.0299	0.0066
9.657	0.0598	0.0078
13.418	0.0903	0.0084
16.788	0.1196	0.0090
19.988	0.1496	0.0097
22.991	0.1802	0.0106
25.701	0.2101	0.0115
28.201	0.2400	0.0124
30.464	0.2691	0.0132
32.660	0.2990	0.0141
34.755	0.3289	0.0145
36.808	0.3591	0.0149
38.808	0.3890	0.0149
40.782	0.4186	0.0149
42.808	0.4486	0.0146
44.888	0.4785	0.0142
47.048	0.5084	0.0137
49.315	0.5383	0.0128
51.755	0.5683	0.0117
54.425	0.5979	0.0104
57.643	0.6282	0.0084
61.927	0.6578	0.0053
70.670	0.6888	0.0022

Table D.6 : C and dC/dt vs t, Trial PE.047

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.048 Run date: 13-Jul-93 12:05
Comment :

Sample : PE #19 , A ISOTHERMAL 45°C
Method : ISOTHERMAL 45°C
Operator : S.B.
Size : 8.660 mg
Cell constant : 1.383

Baseline type : Sigmoidal, horizontal
Reaction range : 6.62 -- 119.67 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.00
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 44.94 °C
Enthalpy : 263.97 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.228	0.0000	0.0020
4.256	0.0313	0.0092
7.563	0.0627	0.0098
10.663	0.0941	0.0105
13.554	0.1253	0.0112
16.298	0.1573	0.0121
18.710	0.1878	0.0131
20.987	0.2191	0.0142
23.066	0.2501	0.0156
25.026	0.2815	0.0165
26.846	0.3125	0.0174
28.596	0.3437	0.0181
30.300	0.3751	0.0186
31.980	0.4065	0.0188
33.636	0.4375	0.0187
35.340	0.4690	0.0182
37.066	0.5000	0.0176
38.886	0.5315	0.0168
40.800	0.5626	0.0158
42.893	0.5941	0.0144
45.189	0.6249	0.0125
48.061	0.6566	0.0095
52.102	0.6876	0.0059
60.142	0.7189	0.0025
112.551	0.7499	0.0000

Table D.7 : C and dC/dt vs t, Trial PE.048

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.049 Run date: 13-Jul-93 12:05
Comment :

Sample : PE #19 . B ISOTHERMAL 45°C
Method : ISOTHERMAL 45°C
Operator : S.B.
Size : 8.490 mg
Cell constant : 1.367

Baseline type : Sigmoidal, horizontal
Reaction range : 6.62 -- 119.67 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.00
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 44.93 °C
Enthalpy : 251.37 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.012	0.0000	0.0018
4.488	0.0303	0.0081
7.835	0.0597	0.0096
10.776	0.0894	0.0106
13.464	0.1192	0.0117
15.929	0.1490	0.0126
18.210	0.1790	0.0137
20.299	0.2089	0.0150
22.177	0.2381	0.0159
23.976	0.2681	0.0171
25.656	0.2978	0.0181
27.266	0.3275	0.0188
28.830	0.3571	0.0191
30.393	0.3872	0.0192
31.933	0.4167	0.0192
33.520	0.4467	0.0187
35.130	0.4764	0.0182
36.810	0.5062	0.0172
38.560	0.5357	0.0164
40.450	0.5655	0.0151
42.532	0.5952	0.0136
44.993	0.6249	0.0108
48.419	0.6549	0.0070
55.190	0.6847	0.0027
112.882	0.7141	-0.0000

Table D.8 : C and dC/dt vs t, Trial PE.049

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C: PE.032 Run date: 18-Jun-93 13:44
Comment : ISOTHERMAL RUN 50°C

Sample : PE #12 , A ISOTHERMAL 50°C
Method : ISOTHERMAL 50°C
Operator : S.B.
Size : 11.940 mg
Cell constant : 1.383

Baseline type : Sigmoidal, horizontal
Reaction range : 7.12 -- 67.42 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.00
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 48.80 °C
Enthalpy : 239.36 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.206	0.0001	0.0016
3.277	0.0285	0.0121
5.570	0.0569	0.0126
7.757	0.0851	0.0132
9.864	0.1134	0.0138
11.894	0.1419	0.0147
13.787	0.1704	0.0156
15.520	0.1985	0.0169
17.147	0.2268	0.0181
18.667	0.2553	0.0195
20.080	0.2836	0.0207
21.414	0.3119	0.0218
22.694	0.3404	0.0228
23.920	0.3688	0.0235
25.120	0.3972	0.0238
26.294	0.4250	0.0237
27.520	0.4540	0.0234
28.750	0.4823	0.0227
30.030	0.5104	0.0214
31.417	0.5388	0.0196
32.937	0.5669	0.0174
34.724	0.5951	0.0142
37.070	0.6235	0.0101
40.983	0.6521	0.0050

Table D.9 : C and dC/dt vs t, Trial PE.032

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.033   Run date: 18-Jun-93 13:44
Comment : ISOTHERMAL RUN 50°C

Sample : PE #12 , B ISOTHERMAL 50°C
Method : ISOTHERMAL 50°C
Operator : S.B.
Size : 8.230 mg
Cell constant : 1.367

Baseline type : Sigmoidal, horizontal
Reaction range : 6.77 -- 67.42 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.00
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 48.78 °C
Enthalpy : 208.88 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.131	0.0000	0.0020
3.517	0.0247	0.0101
5.917	0.0495	0.0104
8.264	0.0743	0.0107
10.557	0.0991	0.0110
12.747	0.1238	0.0116
14.827	0.1487	0.0124
16.747	0.1734	0.0134
18.507	0.1979	0.0145
20.161	0.2228	0.0157
21.681	0.2476	0.0169
23.094	0.2723	0.0181
24.427	0.2970	0.0191
25.707	0.3219	0.0198
26.934	0.3465	0.0203
28.134	0.3710	0.0205
29.364	0.3961	0.0203
30.591	0.4207	0.0198
31.871	0.4454	0.0188
33.231	0.4700	0.0173
34.751	0.4949	0.0152
36.511	0.5194	0.0125
38.830	0.5443	0.0090
42.563	0.5689	0.0046

Table D.10 : C and dC/dt vs t, Trial PE.033

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.052 Run date: 13-Jul-93 14:40
Comment :

Sample : PE #20 , A ISOTHERMAL 55°C
Method : ISOTHERMAL 55°C
Operator : S.B.
Size : 11.160 mg
Cell constant : 1.383

Baseline type : Sigmoidal, horizontal
Reaction range : 6.25 -- 69.74 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.00
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 54.97 °C
Enthalpy : 281.32 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.292	0.0000	0.0009
2.492	0.0337	0.0212
3.972	0.0669	0.0232
5.352	0.1001	0.0249
6.652	0.1335	0.0264
7.872	0.1670	0.0284
9.012	0.2002	0.0301
10.072	0.2332	0.0322
11.092	0.2669	0.0337
12.052	0.3001	0.0354
12.972	0.3331	0.0366
13.892	0.3670	0.0371
14.792	0.4003	0.0373
15.692	0.4336	0.0370
16.592	0.4663	0.0359
17.552	0.5001	0.0345
18.532	0.5332	0.0330
19.572	0.5664	0.0310
20.692	0.5999	0.0288
21.892	0.6330	0.0263
23.232	0.6663	0.0233
24.792	0.6994	0.0192
26.872	0.7327	0.0129
30.678	0.7659	0.0056
59.571	0.7992	0.0001

Table D.11 : C and dC/dt vs t, Trial PE.052

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.053 Run date: 13-Jul-93 14:40
Comment :

Sample : PE #20 , B ISOTHERMAL 55°C
Method : ISOTHERMAL 55°C
Operator : S.B.
Size : 11.890 mg
Cell constant : 1.367

Baseline type : Sigmoidal, horizontal
Reaction range : 6.77 -- 69.74 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.00
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 54.96 °C
Enthalpy : 275.62 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.004	0.0000	0.0074
1.971	0.0330	0.0205
3.471	0.0654	0.0224
4.871	0.0979	0.0241
6.191	0.1306	0.0254
7.431	0.1633	0.0273
8.591	0.1960	0.0290
9.671	0.2284	0.0313
10.711	0.2615	0.0326
11.691	0.2942	0.0341
12.631	0.3267	0.0349
13.551	0.3592	0.0355
14.471	0.3919	0.0356
15.391	0.4244	0.0349
16.331	0.4569	0.0340
17.311	0.4896	0.0326
18.331	0.5221	0.0309
19.431	0.5551	0.0291
20.591	0.5877	0.0268
21.851	0.6202	0.0246
23.251	0.6525	0.0218
24.931	0.6853	0.0173
27.290	0.7182	0.0109
32.045	0.7508	0.0043

Table D.12 : C and dC/dt vs t, Trial PE.053

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.060 Run date: 14-Jul-93 13:13
Comment :

Sample : ISOTHERMAL 60°C, A
Method : ISOTHERMAL 60°C
Operator : S.B.
Size : 8.540 mg
Cell constant : 1.383

Baseline type : Sigmoidal, horizontal
Reaction range : 6.77 -- 69.66 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.05
Maximum area fraction : 0.75
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 59.50 °C
Enthalpy : 281.14 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
1.932	0.0400	0.0242
2.899	0.0635	0.0245
3.832	0.0866	0.0249
4.766	0.1100	0.0253
5.669	0.1332	0.0259
6.569	0.1568	0.0267
7.419	0.1797	0.0275
8.252	0.2030	0.0284
9.069	0.2268	0.0297
9.819	0.2496	0.0311
10.569	0.2734	0.0324
11.269	0.2965	0.0338
11.952	0.3200	0.0349
12.602	0.3430	0.0360
13.252	0.3667	0.0367
13.869	0.3895	0.0373
14.502	0.4131	0.0375
15.119	0.4362	0.0374
15.752	0.4597	0.0370
16.386	0.4830	0.0364
17.036	0.5063	0.0355
17.702	0.5296	0.0343
18.386	0.5527	0.0330
19.102	0.5759	0.0316
19.869	0.5995	0.0299

Table D.13 : C and dC/dt vs t, Trial PE.060

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C: PE.061 Run date: 14-Jul-93 13: 13
Comment :

Sample : ISOTHERMAL 60°C, B
Method : ISOTHERMAL 60°C
Operator : S.B.
Size : 9.190 mg
Cell constant : 1.367

Baseline type : Sigmoidal, horizontal
Reaction range : 6.60 -- 69.66 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.05
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 59.49 °C
Enthalpy : 286.30 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
2.056	0.0408	0.0238
3.389	0.0731	0.0246
4.673	0.1054	0.0257
5.893	0.1373	0.0268
7.059	0.1695	0.0284
8.159	0.2018	0.0305
9.193	0.2343	0.0326
10.143	0.2664	0.0347
11.043	0.2985	0.0367
11.909	0.3309	0.0383
12.726	0.3626	0.0394
13.543	0.3951	0.0400
14.343	0.4270	0.0399
15.159	0.4595	0.0394
15.993	0.4919	0.0384
16.843	0.5237	0.0366
17.743	0.5559	0.0346
18.709	0.5883	0.0324
19.743	0.6204	0.0299
20.876	0.6526	0.0269
22.159	0.6850	0.0234
23.676	0.7170	0.0188
25.751	0.7491	0.0123
29.789	0.7813	0.0050
58.031	0.8134	0.0000

Table D.14 : C and dC/dt vs t, Trial PE.061

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.056 Run date: 14-Jul-93 10:16
Comment :

Sample : ISOTHERMAL 65°C, A
Method : ISOTHERMAL 65°C
Operator : S.B.
Size : 7.320 mg
Cell constant : 1.383

Baseline type : Sigmoidal, horizontal
Reaction range : 7.12 -- 69.69 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.00
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 65.05 °C
Enthalpy : 293.14 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.142	0.0001	0.0095
1.475	0.0348	0.0302
2.609	0.0699	0.0312
3.709	0.1044	0.0315
4.792	0.1389	0.0322
5.859	0.1738	0.0331
6.875	0.2083	0.0348
7.859	0.2433	0.0367
8.775	0.2778	0.0384
9.659	0.3128	0.0409
10.492	0.3474	0.0424
11.309	0.3823	0.0431
12.109	0.4169	0.0434
12.909	0.4515	0.0429
13.725	0.4860	0.0415
14.575	0.5207	0.0400
15.475	0.5555	0.0376
16.425	0.5899	0.0348
17.475	0.6249	0.0321
18.625	0.6594	0.0281
19.942	0.6942	0.0245
21.537	0.7291	0.0195
23.706	0.7634	0.0124
28.062	0.7983	0.0050
60.943	0.8328	-0.0001

Table D.15 : C and dC/dt vs t, Trial PE.056

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.057 Run date: 14-Jul-93 10:16
Comment :

Sample : ISOTHERMAL 65°C, B
Method : ISOTHERMAL 65°C
Operator : S.B.
Size : 10.480 mg
Cell constant : 1.367

Baseline type : Sigmoidal, horizontal
Reaction range : 7.12 -- 69.69 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.00
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 65.05 °C
Enthalpy : 283.14 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.159	0.0001	0.0071
1.525	0.0337	0.0302
2.592	0.0674	0.0330
3.575	0.1010	0.0354
4.492	0.1342	0.0372
5.375	0.1680	0.0394
6.209	0.2017	0.0414
6.992	0.2349	0.0436
7.742	0.2684	0.0455
8.459	0.3016	0.0472
9.175	0.3358	0.0481
9.859	0.3689	0.0484
10.559	0.4026	0.0479
11.259	0.4357	0.0466
11.992	0.4692	0.0446
12.775	0.5031	0.0419
13.609	0.5368	0.0389
14.509	0.5703	0.0356
15.492	0.6036	0.0321
16.592	0.6369	0.0285
17.859	0.6706	0.0245
19.375	0.7040	0.0195
21.485	0.7375	0.0124
25.805	0.7715	0.0046

Table D.16 : C and dC/dt vs t, Trial PE.057

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.058 Run date: 14-Jul-93 11:59
Comment :

Sample : ISOTHERMAL 70°C, A
Method : ISOTHERMAL 70°C
Operator : S.B.
Size : 11.340 mg
Cell constant : 1.383

Baseline type : Sigmoidal, horizontal
Reaction range : 6.25 -- 56.72 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.00
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 70.10 °C
Enthalpy : 302.25 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.180	0.0001	0.0174
1.180	0.0364	0.0425
1.963	0.0717	0.0474
2.697	0.1076	0.0504
3.397	0.1436	0.0522
4.063	0.1791	0.0540
4.713	0.2149	0.0559
5.347	0.2510	0.0577
5.947	0.2862	0.0595
6.547	0.3223	0.0605
7.130	0.3579	0.0612
7.713	0.3936	0.0607
8.313	0.4297	0.0595
8.930	0.4658	0.0573
9.563	0.5011	0.0543
10.247	0.5368	0.0504
10.997	0.5729	0.0461
11.813	0.6086	0.0415
12.730	0.6446	0.0370
13.747	0.6798	0.0324
14.947	0.7160	0.0278
16.363	0.7516	0.0224
18.247	0.7872	0.0153
21.727	0.8231	0.0066
49.390	0.8587	0.0001

Table D.17 : C and dC/dt vs t, Trial PE.058

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.059 Run date: 14-Jul-93 11:59
Comment :

Sample : ISOTHERMAL 70°C, B
Method : ISOTHERMAL 70°C
Operator : S.B.
Size : 9.700 mg
Cell constant : 1.367

Baseline type : Sigmoidal, horizontal
Reaction range : 6.11 -- 56.72 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.05
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 70.09 °C
Enthalpy : 302.29 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
1.202	0.0434	0.0422
1.986	0.0771	0.0439
2.752	0.1116	0.0461
3.469	0.1453	0.0478
4.169	0.1793	0.0493
4.852	0.2136	0.0510
5.502	0.2474	0.0526
6.136	0.2813	0.0543
6.752	0.3153	0.0557
7.352	0.3490	0.0567
7.952	0.3830	0.0567
8.552	0.4169	0.0560
9.169	0.4512	0.0543
9.802	0.4851	0.0523
10.469	0.5192	0.0497
11.186	0.5535	0.0464
11.952	0.5874	0.0425
12.786	0.6211	0.0385
13.719	0.6551	0.0341
14.769	0.6890	0.0303
15.986	0.7231	0.0260
17.436	0.7571	0.0207
19.369	0.7908	0.0140
23.133	0.8259	0.0061
47.868	0.8588	0.0002

Table D.18 : C and dC/dt vs t, Trial PE.059

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.062 Run date: 15-Jul-93 09:30
Comment :

Sample : ISOTHERMAL 75°C, A
Method : ISOTHERMAL 75°C
Operator : S.B.
Size : 11.940 mg
Cell constant : 1.383

Baseline type : Sigmoidal, horizontal
Reaction range : 6.32 --- 59.55 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.05
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 75.11 °C
Enthalpy : 290.93 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.997	0.0420	0.0625
1.514	0.0749	0.0638
2.031	0.1071	0.0610
2.597	0.1404	0.0568
3.181	0.1724	0.0533
3.814	0.2053	0.0510
4.464	0.2377	0.0492
5.131	0.2703	0.0487
5.814	0.3034	0.0481
6.497	0.3363	0.0478
7.181	0.3688	0.0473
7.881	0.4015	0.0462
8.597	0.4340	0.0446
9.364	0.4673	0.0423
10.147	0.4994	0.0394
11.014	0.5322	0.0361
11.964	0.5653	0.0332
12.997	0.5979	0.0298
14.147	0.6303	0.0266
15.464	0.6632	0.0234
16.964	0.6959	0.0202
18.747	0.7284	0.0162
21.131	0.7611	0.0112
25.297	0.7938	0.0052
50.581	0.8265	0.0000

Table D.19 : C and dC/dt vs t, Trial PE.062

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.063 Run date: 15-Jul-93 09:30
Comment :

Sample : ISOTHERMAL 75°C, B
Method : ISOTHERMAL 75°C
Operator : S.B.
Size : 10.950 mg
Cell constant : 1.367

Baseline type : Sigmoidal, horizontal
Reaction range : 6.17 -- 59.55 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.05
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 75.10 °C
Enthalpy : 280.67 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.931	0.0406	0.0586
1.448	0.0717	0.0605
1.981	0.1035	0.0583
2.531	0.1346	0.0547
3.131	0.1664	0.0514
3.764	0.1981	0.0489
4.414	0.2294	0.0476
5.081	0.2608	0.0468
5.764	0.2927	0.0465
6.448	0.3244	0.0463
7.131	0.3559	0.0460
7.831	0.3878	0.0451
8.531	0.4188	0.0438
9.281	0.4509	0.0417
10.048	0.4819	0.0394
10.881	0.5133	0.0364
11.798	0.5451	0.0328
12.814	0.5769	0.0298
13.931	0.6081	0.0265
15.214	0.6399	0.0230
16.681	0.6713	0.0198
18.431	0.7027	0.0161
20.782	0.7343	0.0110
24.964	0.7661	0.0049
50.548	0.7974	0.0001

Table D.20 : C and dC/dt vs t, Trial PE.063

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.064 Run date: 15-Jul-93 10:58
Comment :

Sample : ISOTHERMAL 80°C, A
Method : ISOTHERMAL 80°C
Operator : S.B.
Size : 15.080 mg
Cell constant : 1.383

Baseline type : Sigmoidal, horizontal
Reaction range : 6.32 -- 59.54 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.05
Maximum area fraction : 1.00
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 79.70 °C
Enthalpy : 297.62 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.811	0.0435	0.0737
1.244	0.0761	0.0755
1.694	0.1093	0.0715
2.194	0.1435	0.0657
2.727	0.1771	0.0605
3.294	0.2104	0.0573
3.877	0.2432	0.0554
4.494	0.2771	0.0546
5.111	0.3106	0.0542
5.727	0.3438	0.0536
6.361	0.3774	0.0525
7.011	0.4111	0.0510
7.677	0.4443	0.0485
8.394	0.4781	0.0455
9.144	0.5109	0.0421
9.994	0.5449	0.0381
10.911	0.5780	0.0341
11.961	0.6116	0.0302
13.144	0.6450	0.0264
14.494	0.6782	0.0229
16.094	0.7119	0.0194
18.011	0.7453	0.0156
20.577	0.7787	0.0106
24.965	0.8121	0.0052
50.319	0.8455	0.0002

Table D.21 : C and dC/dt vs t, Trial PE.064

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.065 Run date: 15-Jul-93 10:58
Comment :

Sample : ISOTHERMAL 80°C, B
Method : ISOTHERMAL 80°C
Operator : S.B.
Size : 12.590 mg
Cell constant : 1.367

Baseline type : Sigmoidal, horizontal
Reaction range : 6.02 -- 59.54 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.05
Maximum area fraction : 0.75
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 79.68 °C
Enthalpy : 299.35 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.911	0.0428	0.0704
1.261	0.0678	0.0719
1.611	0.0926	0.0693
1.978	0.1173	0.0653
2.378	0.1425	0.0609
2.795	0.1670	0.0567
3.245	0.1919	0.0542
3.711	0.2167	0.0521
4.195	0.2415	0.0507
4.678	0.2659	0.0503
5.178	0.2910	0.0500
5.678	0.3160	0.0501
6.161	0.3402	0.0499
6.661	0.3651	0.0499
7.161	0.3898	0.0492
7.678	0.4150	0.0483
8.195	0.4396	0.0469
8.728	0.4643	0.0452
9.295	0.4894	0.0433
9.878	0.5140	0.0409
10.511	0.5391	0.0383
11.178	0.5638	0.0356
11.895	0.5883	0.0330
12.678	0.6131	0.0302
13.545	0.6380	0.0275

Table D.22 : C and dC/dt vs t, Trial PE.065

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C: PE.066 Run date: 16-Jul-93 10:16
Comment :

Sample : ISOTHERMAL 85°C, A
Method : ISOTHERMAL 85°C
Operator : S.B.
Size : 9.390 mg
Cell constant : 1.383

Baseline type : Sigmoidal, horizontal
Reaction range : 6.94 -- 54.87 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.05
Maximum area fraction : 0.75
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 84.96 °C
Enthalpy : 305.55 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.701	0.0440	0.0917
0.981	0.0698	0.0919
1.261	0.0951	0.0883
1.554	0.1203	0.0830
1.861	0.1449	0.0777
2.194	0.1700	0.0731
2.554	0.1957	0.0698
2.927	0.2213	0.0675
3.301	0.2463	0.0664
3.687	0.2719	0.0659
4.074	0.2973	0.0658
4.461	0.3227	0.0657
4.834	0.3472	0.0656
5.221	0.3726	0.0654
5.621	0.3986	0.0645
6.007	0.4233	0.0632
6.421	0.4490	0.0612
6.834	0.4739	0.0589
7.274	0.4991	0.0560
7.741	0.5245	0.0526
8.247	0.5502	0.0489
8.781	0.5754	0.0453
9.367	0.6008	0.0415
10.007	0.6262	0.0377
10.701	0.6511	0.0342

Table D.23 : C and dC/dt vs t, Trial PE.066

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DSC ISOTHERMAL KINETICS -- CURVE ANALYSIS REPORT

File : C:PE.067 Run date: 16-Jul-93 10:16
Comment :

Sample : ISOTHERMAL 85°C, B
Method : ISOTHERMAL 85°C
Operator : S.B.
Size : 8.610 mg
Cell constant : 1.367

Baseline type : Sigmoidal, horizontal
Reaction range : 6.94 -- 54.87 min
Reaction enthalpy : 352.0 J/g
Minimum area fraction : 0.05
Maximum area fraction : 0.75
Number of area fractions : 25
Heat flow smoothing window : 0.00 min

Temperature : 84.95 °C
Enthalpy : 276.59 J/g

Conversion and Rate of Conversion vs. Time

Time (min)	C	dC/dt (1/min)
0.634	0.0401	0.0783
0.927	0.0630	0.0768
1.234	0.0857	0.0712
1.567	0.1083	0.0642
1.954	0.1317	0.0571

Time (min)	C	dC/dt (1/min)
2.367	0.1541	0.051[illegible]
2.834	0.1770	0.0472
3.341	0.2001	0.0444
3.861	0.2227	0.0427
4.407	0.2457	0.0418
4.967	0.2690	0.0413
5.514	0.2915	0.0412
6.074	0.3145	0.0410
6.634	0.3374	0.0409
7.194	0.3602	0.0405
7.767	0.3832	0.0399
8.354	0.4064	0.0388
8.954	0.4294	0.0377
9.567	0.4520	0.0362
10.221	0.4751	0.0344
10.901	0.4979	0.0325
11.634	0.5209	0.0303
12.421	0.5439	0.0280
13.261	0.5665	0.0258
14.194	0.5895	0.0235

Table D.24 : C and dC/dt vs t, Trial PE.067

APPENDIX E

EQUATION PARAMETERS SINGLE TEMPERATURE ANALYSIS

The following Tables, E.1 to E.12, list parameters m, n and k which are used in the equation

$$\frac{dC}{dt} = kC^{m}(1-C)^{n} \qquad (6)$$

in various ranges of conversion C and at temperatures ranging from 30°C to 85°C. These parameters were determined using the DSC Isothermal Kinetics Data Analysis Program [12,13] for each temperature individually. The results of the single temperature analyses were analysed simultaneously in sets of three temperatures 5°C apart to obtain the results shown in Tables 4 to 15.

Temperature = 30 Degrees C
Equation Parameters, Single Analysis

C	m	n	k
0.0000	0.1230	-7.2100	3.43E-03
0.0640	0.0102	-1.7800	3.19E-03
0.1250	-0.4930	-4.7200	7.85E-04
0.1900	0.3180	-0.8790	6.74E-03
0.2530	1.6800	2.8300	1.29E-01
0.3130	3.3300	5.8300	2.70E+00
0.3760	2.1000	3.3500	2.53E-01
0.4420	7.4300	9.8500	8.52E+02
0.5010	30.4000	30.7000	1.34E+16
0.5680	30.4000	30.7000	1.34E+16
0.6290	30.4000	30.7000	1.34E+16

Figure E.1 : Parameters, Single Temperature Analysis, 30°C

Temperature = 35 Degrees C
Equation Parameters, Single Analysis

C	m	n	k
0.0000	0.2840	3.9300	1.78E-02
0.0740	0.0791	-1.4100	7.29E-03
0.1460	0.3220	-0.3950	1.36E-02
0.2200	0.3950	-0.2810	1.54E-02
0.2920	1.0900	1.5000	6.74E-02
0.3680	1.8300	2.7400	2.52E-01
0.4370	1.7300	2.3500	1.85E-01
0.5150	4.1900	4.6600	5.00E+00
0.5830	18.1000	14.0000	3.15E+07
0.6560	18.1000	14.0000	3.15E+07
0.7340	18.1000	14.0000	3.15E+07

Figure E.2 : Parameters, Single Temperature Analysis, 35°C

Temperature = 40 Degrees C
Equation Parameters, Single Analysis

C	m	n	k
0.0000	0.1840	0.6380	1.29E-02
0.0760	-0.0377	-2.6600	5.57E-03
0.1500	0.2170	-1.2600	1.14E-02
0.2280	0.4230	-0.4610	1.90E-02
0.3030	1.5400	2.1000	1.81E-01
0.3790	1.7700	2.4100	2.62E-01
0.4550	1.6000	2.1500	1.96E-01
0.5310	3.4200	3.7300	2.06E+00
0.6070	21.6000	15.1000	7.33E+08
0.6820	21.6000	15.1000	7.33E+08
0.7550	21.6000	15.1000	7.33E+08

Figure E.3 : Parameters, Single Temperature Analysis, 40°C

Temperature = 45 Degrees C
Equation Parameters, Single Analysis

C	m	n	k
0.0000	0.2470	4.1700	2.53E-02
0.0750	-0.1620	-3.3900	5.05E-03
0.1490	0.1600	-1.4700	1.27E-02
0.2260	1.0600	1.3700	9.95E-02
0.3010	1.3600	1.9800	1.79E-01
0.3720	1.4700	2.1500	2.17E-01
0.4500	1.5100	2.1500	2.23E-01
0.5250	2.6900	3.2400	1.06E+00
0.5950	18.6000	13.4000	4.66E+07
0.6810	18.6000	13.4000	4.66E+07
0.7560	18.6000	13.4000	4.66E+07

Figure E.4 : Parameters, Single Temperature Analysis, 45°C

Temperature = 50 Degrees C
Equation Parameters, Single Analysis

C	m	n	k
0.0000	0.3050	5.9100	4.31E-02
0.0680	-0.1250	-2.5400	7.65E-03
0.1360	-0.1290	-2.7700	7.40E-03
0.2050	0.5080	-0.2380	3.61E-02
0.2730	1.0200	1.1100	1.09E-01
0.3400	1.7200	2.4700	4.09E-01
0.4100	2.1000	3.0100	7.58E-01
0.4760	3.7700	4.8400	8.54E+00
0.5440	14.5000	13.4000	4.84E+06
0.6140	14.5000	13.4000	4.84E+06
0.6770	14.5000	13.4000	4.84E+06

Figure E.5 : Parameters, Single Temperature Analysis, 50°C

Temperature = 55 Degrees C
Equation Parameters, Single Analysis

C	m	n	k
0.0000	0.4010	6.9300	1.09E-01
0.0800	0.0152	-1.5800	2.17E-02
0.1600	0.1100	-1.1000	2.81E-02
0.2390	0.6410	0.7050	9.80E-02
0.3180	1.0100	1.5700	2.08E-01
0.3980	0.9920	1.6400	2.12E-01
0.4770	1.2900	1.9300	3.21E-01
0.5570	1.6700	2.1100	4.64E-01
0.6360	12.4000	7.8900	2.07E+04
0.7160	12.4000	7.8900	2.07E+04
0.7950	12.4000	7.8900	2.07E+04

Figure E.6 : Parameters, Single Temperature Analysis, 55°C

Temperature = 60 Degrees C
Equation Parameters, Single Analysis

C	m	n	k
0.0000	0.1780	3.1500	4.85E-02
0.0810	-0.1350	-1.8600	1.43E-02
0.1590	-0.1420	-1.9600	1.45E-02
0.2390	0.4860	-0.0229	6.03E-02
0.3170	1.4100	1.9900	3.74E-01
0.3980	1.3700	1.9300	3.51E-01
0.4780	1.2700	1.8500	3.08E-01
0.5570	1.8600	2.3600	6.57E+00
0.6330	11.7000	7.8300	1.41E+04
0.7120	11.7000	7.8300	1.41E+04
0.7880	11.7000	7.8300	1.41E+04

Figure E.7 : Parameters, Single Temperature Analysis, 60°C

Temperature = 65 Degrees C
Equation Parameters, Single Analysis

C	m	n	k
0.0000	0.2130	3.6200	7.15E-02
0.0840	-0.1220	-1.3900	2.06E-02
0.1670	-0.3570	-2.4700	1.11E-02
0.2500	0.3800	-0.1120	6.07E-02
0.3340	1.3700	1.9600	4.13E-01
0.4180	1.4600	2.0700	4.76E-01
0.5020	1.0300	1.6700	2.68E-01
0.5840	1.3600	1.9200	3.95E-01
0.6670	11.3000	6.5700	3.62E+03
0.7500	11.3000	6.5700	3.62E+03
0.8330	11.3000	6.5700	3.62E+03

Figure E.8 : Parameters, Single Temperature Analysis, 65°C

Temperature = 70 Degrees C
Equation Parameters, Single Analysis

C	m	n	k
0.0000	0.1430	-0.0821	6.84E-02
0.0860	0.1290	-0.0806	6.64E-02
0.1720	0.0576	-0.5170	5.40E-02
0.2580	0.4510	0.6640	1.30E-01
0.3430	1.1200	1.9700	4.64E-01
0.4300	1.2200	2.1300	5.52E-01
0.5150	0.6790	1.6600	2.74E-01
0.5990	0.4240	1.4600	1.99E-01
0.6840	7.4300	4.3500	8.02E+01
0.7730	7.4300	4.3500	8.02E+01
0.8580	7.4300	4.3500	8.02E+01

Figure E.9 : Parameters, Single Temperature Analysis, 70°C

Temperature = 75 Degrees C
Equation Parameters, Single Analysis

C	m	n	k
0.0000	0.2250	2.2700	1.38E-01
0.0830	0.0579	2.1700	8.82E-02
0.1660	-0.5910	-1.3700	1.45E-02
0.2480	-0.2330	-0.3840	3.18E-02
0.3300	0.9640	2.0300	3.15E-01
0.4130	1.1700	2.2700	4.27E-01
0.4930	0.8620	2.0000	2.86E-01
0.5790	-0.1810	1.2600	8.54E-02
0.6610	6.7200	4.5900	5.48E+01
0.7440	6.7200	4.5900	5.48E+01
0.8260	6.7200	4.5900	5.48E+01

Figure E.10 : Parameters, Single Temperature Analysis, 75°C

Temperature = 80 Degrees C
Equation Parameters, Single Analysis

C	m	n	k
0.0000	0.3390	4.4000	2.58E-01
0.0850	0.1200	2.9200	1.31E-01
0.1700	-0.6240	-1.3200	1.58E-02
0.2530	-0.1620	-0.1690	4.21E-02
0.3390	1.0000	2.1200	3.83E-01
0.4240	1.4900	2.7500	8.21E-01
0.5080	0.6570	1.9600	2.67E-01
0.5930	0.1350	1.5400	1.39E-01
0.6780	6.1000	4.1300	2.62E+01
0.7610	6.1000	4.1300	2.62E+01
0.8470	6.1000	4.1300	2.62E+01

Figure E.11 : Parameters, Single Temperature Analysis, 80°C

Temperature = 85 Degrees C
Equation Parameters, Single Analysis

C	m	n	k
0.0000	0.1680	2.4000	1.69E-01
0.0870	-0.0182	2.0900	1.04E-01
0.1730	-0.8860	-2.3900	9.70E-03
0.2600	-0.0669	-0.1120	5.83E-02
0.3470	1.1100	2.0900	5.20E-01
0.4340	1.6400	2.7500	1.17E+00
0.5210	0.9560	2.1000	4.65E-01
0.6080	-0.3620	1.2500	1.09E-01
0.6950	5.4700	3.6600	1.55E+01
0.7780	5.4700	3.6600	1.55E+01
0.8640	5.4700	3.6600	1.55E+01

Figure E.12 : Parameters, Single Temperature Analysis, 85°C