Low Temperature Thermal Expansivities of Polyethylene, Polypropylene and Their Mixtures

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I. INTRODUCTION

Because of the increasing interest in glass transition measurements and in improved methods of detecting them, measurements of length-temperature curves for several polymers and mixtures of two of these were made at low temperatures. Polymers studied include polyethylene, polypropylene and their mixtures and copolymers, polyurethanes and polystyrene.

A general object of this work was to ascertain if transitions other than the main glass transition temperature exist which can be detected by means of length-temperature measurements. If so, we wanted to determine the location and magnitude of the corresponding changes of the linear expansion coefficients in the range of +20 to -185°C. For the most part, multiple glassy transitions have been previously investigated by dynamic methods. More specific objectives were:

1. To compare the location and magnitude of any transitions noted in pure polyethylene and pure polypropylene with those found in their mixtures and copolymer, including the possibility of transitions not found in either pure polymer. From this an understanding of the relationship of the properties of the mixtures of two species and of their copolymers to the properties of the individual species might be obtained.

2. To determine the present practical limitations of length-temperature measurements for finding the locations and magnitudes of glassy transitions. This would include both repeatability of the length-temperature data and the available methods for analyzing the data.

3. To compare the results of length-temperature measurements on location and magnitude of glassy transitions with those using other techniques.

4. To determine the effect of thermal history on polyethylene properties.

II. Experimental

A. Materials

The polymer samples studied are listed in Table 1 below. Additional details on their composition are given in Reference (1).

Table I

Sample	Run Number	Polymer
A	1	Mobay Sample
B	2	Polyurethane Sample III-U-46-08(a)
C	3	Polystyrene(b)
D	4,5(c)	Polypropylene (see Table II)
E,F,G H,I	6-11(c) (d)	Mixtures of Polypropylene studied in Runs 4 and 5 with Polyethylene of Run 12 (See Table II)
J	12(c)	Polyethylene (see Table II)
K	13(c)	Non-crystalline random copolymer of ethylene and propylene (see Table II)
L	14(e)	Polyethylene test sample prepared by machining without heating or annealing of polymer
M	15(e)	Same polyethylene polymer as Run 14, but test sample prepared by casting

(a) prepared at the Jet Propulsion Laboratory, California Institute of Technology.

(b) prepared at the National Bureau of Standards, Sample 706 (with broad molecular weight distribution).

(c) prepared by Dr. E.G. Kontos, Naugatuck Chemical Company.

(d) all mixture samples were prepared from the polyethylene (Sample J) and polypropylene (Sample D) by Dr. E.G. Kontos. The procedure consisted of coagulation in a 50/50 mixture of methanol and isopropanol, containing a small amount of stabilizer, and drying under vacuum for 12 hours at 65°C.

(e) prepared by Union Carbide and Carbon Company.

Table II

Run Number	Polymer Designation	Polymer	Molar* Composition		Crystallinity* % by x-ray		Density g/ml* at 25°C
			%PP	%PE	%PP	%PE	
4,5	D	Polypropylene	100	0	18	0	$.87_1$
6	E	PP-PE mixture	91	9	16	8	$.87_0$
7	F	PP-PE mixture	68	32	13	14	$.87_9$
8,9	G	PP-PE mixture	52	48	12	23	$.88_8$
10	H	PP-PE mixture	36	64	10	28	$.89_7$
11	I	PP-PE mixture	12	88	6	42	$.90_6$
12	J	Polyethylene	0	100	0	54	$.92_9$
13	K	Copolymer PP-PE	50	50	0	0	$.85_4$

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*Data obtained from Dr. Kontos, Naugatuck Chemical Company

II. B. Procedures

The preparation of test specimens, description of the Linear Voltage Differential Transformer (Physical Sciences Transducer*) and the rest of the test apparatus and the test procedure are described in detail in References 1 and 2. Sample sizes were about 1½ inches long and ½ inch in diameter.

The LVDT was calibrated with a micrometer which could be read to 0.0001 inches. LVDT output could be read to 0.001 millivolts with a potentiometer. A length change of 0.0050 inches was equivalent to about 1.000 millivolts for all but the polystyrene run where the sensitivity was doubled. The average deviation from linearity was about ±3.0%.

The test runs reported here were performed by cooling the samples from room temperature to about -185°C by the slow introduction of liquid nitrogen over a period of about 7 hours. The output length voltage from the LVDT and the thermocouple voltages were read by a potentiometer to 0.001 millivolt and were recorded manually to avoid any recorder error. Readings of the output of a copper-constantan thermocouple were taken at intervals of 0.050 millivolts corresponding to temperature intervals of about 1.2°C at room temperature and 2.8°C at -185°C. LVDT output differences were generally greater than 0.040 mv (0.0002 inches). In the analysis of the data, the use of alternate points (.100 mv thermocouple output intervals) gave smoother results (see Section III). Thus, the minimum length difference used in the data analysis was 0.0004 inches.

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III. Analysis of Data

A. Analysis Techniques

Most of the previous data of this type, i.e., length or volume vs. temperature or specific heat vs. temperature, have been analyzed by passing a series of straight lines through the data and utilizing the slopes and intersections of the lines for any further calculations.

This procedure does not give clean cut results as different observers may fit the data in different ways. Furthermore, in some cases, the slopes are nearly equal above and below the suspected transition region, and a minor change in the positioning of a line can have a major effect on the positions of its intersections as well as on its slope. This will be particularly true in the case of apparently "weak" transitions.

An example of this procedure is shown in Figure 1 (Run 1) where LVDT voltage which is proportional to length is plotted against temperature for a polyurethane sample. It appears that the data can be best fitted with three linear regions, indicating two transitions.

In order to obtain the derivative of the length-temperature data directly, a moving arc method was selected. This yields a more accurate measure of the changes in slopes as a function of temperature. This method (3) is based on fitting local data points with least square polynomials and can be used conveniently on any data equispaced in one variable. The arc is moved through all of the data to obtain midpoint slopes at all but the last few points at each end. The latter are obtained by a similar procedure.

Results using this procedure on the data for Run 1 are shown in Figure 2 where $\frac{1}{L_o}(\frac{dL}{dT}) = \alpha'$ is plotted against temperature. Tangents to the curves were drawn on both sides of discontinuous sections which appear to be transitions. The point of maximum slope was determined by eye and was taken as the transition temperature. The difference in the height of the two tangents at that temperature was taken as the change in α' or $\Delta\alpha'$. Vertical arrows on Figures 2 and 5-15 indicate apparent transitions.

Comparisons of this technique with that described earlier for the data of Run 1 are shown below:

Comparison of Methods of Data Analysis

Table III

Transition* Designation	Direct Graphical Method Figure 1	Sloping Method Figure 2
T_G	-46°C	-46°C
$T_{g,g}^{a}$	---	-92°C
$T_{g,g}^{b}$	-132	-137

---

*Boyer(4a) has reviewed the literature on glassy transitions in high polymers and has offered the following proposals for designating transitions in polymers in which multiple transitions occur in the range of interest here. Classification III or γ refers to T_G, the glass transition temperature. Classification IV or δ refers to subgroup transitions below T_G. $T_{g,g}$ with an appropriate superscript letter would then refer to particular sub-group motions. Transitions between T_G and T_M are classified II or β and designated $T_{\ell,\ell}$ for liquid-liquid transitions.

The results obtained for T_G where the change in slope is large, are close for the two procedures. For $T_{g,g}{}^{b}$, where the slopes are almost the same, there is considerable uncertainty as to the correct temperature using the direct graphical method. The apparent transition at -92°C seen on Figure 2 is not predictable from Figure 1.

After trial calculations using 5-point cubics, 7-point cubics, 5-point parabolas and 7-point parabolas for the calculation of the derivatives, the 7-point parabola was selected. The cubics and, to a lesser extent, the 5-point parabolas are quite sensitive to minor variations in the data whereas 7-point parabolas give smoother derivative functions. The use of a still larger sample, e.g., 9 points, in the moving arc would reduce the sensitivity of the method.

The equation for the slope of the midpoint of a least squares parabola through 7 equispaced points is (3):

$$m_4 = \frac{1}{28(\Delta x)} [3\Delta y_1 + 5\Delta y_2 + 6\Delta y_3 + 6\Delta y_4 + 5\Delta y_5 + 3\Delta y_6]$$

where $\Delta y_n = y_{n+1} - y_n$;

for $1 \leq n \leq 6$

Δx = increment in x direction

Estimates of the slopes of the last 3 points at the ends of the curves are obtained from (3):

$$m_1 = \frac{1}{84(\Delta x)} [39\Delta y_1 + 45\Delta y_2 + 30\Delta y_3 + 6\Delta y_4 - 15\Delta y_5 - 21\Delta y_6]$$

$$m_2 = \frac{1}{84(\Delta x)} [29\Delta y_1 + 35\Delta y_2 + 26\Delta y_3 + 10\Delta y_4 - 5\Delta y_5 - 11\Delta y_6]$$

$$m_3 = \frac{1}{84(\Delta x)} [19\Delta y_1 + 25\Delta y_2 + 22\Delta y_3 + 14\Delta y_4 + 5\Delta y_5 - 1\Delta y_6]$$

$$m_5 = \frac{1}{84(\Delta x)} [-1\Delta y_1 + 5\Delta y_2 + 14\Delta y_3 + 22\Delta y_4 + 25\Delta y_5 + 19\Delta y_6]$$

$$m_6 = \frac{1}{84(\Delta x)} \left[-11\Delta y_1 + -5\Delta y_2 + 10\Delta y_3 + 26\Delta y_4 + 35\Delta y_5 + 29\Delta y_6\right]$$

$$m_7 = \frac{1}{84(\Delta x)} \left[-21\Delta y_1 - 15\Delta y_2 + 6\Delta y_3 + 30\Delta y_4 + 45\Delta y_5 + 39\Delta y_6\right]$$

The further the point from the center of the arc, the less reliable is the estimate of the slope at that point.

The raw data analyzed were output voltages of the LVDT, indicating length, vs. thermocouple voltages, indicating temperature. Changes in LVDT voltage are directly proportional to changes in the sample length. The relation between thermocouple output voltage and temperature is non-linear. Increments of 0.1 millivolts correspond to 2.5°C at room temperature and 5.6°C at -185°C, generally the low temperature limit. Over 60 data points were required to cover this range. Derivatives of the thermocouple output voltage-temperature function were computed using a 5-point moving arc parabola method. From this and the slope of the output voltages, the modified linear expansion coefficient, α', can be computed:

$$\alpha' = \frac{1}{L_o}\left(\frac{dL}{dT}\right) = \frac{C}{L_o}\left(\frac{\partial E_{LVDT}}{\partial E_{Thermocouple}}\right)\left(\frac{\partial E_{Thermocouple}}{\partial T}\right)$$

where

L = sample length

L_o = initial sample length at room temperature (in most cases above T_g)

C = proportionality factor between the change in EMF output of the LVDT and the change in sample length

T = temperature, °C

If the linear expansion coefficient is assumed equal to one third the volume expansion coefficient, α, then α' is closely equal to $\alpha/3$. It differs from $\alpha/3$ only in that L_o was not corrected for the decrease in sample length at low temperatures. Thus α' = α/3 at room temperature but may be as much as 2% lower than α/3 at the lowest temperature (-185°C).

Although data were available in thermocouple output increments of 0.050 millivolts, the use of alternate points (0.100 millivolt increments) smooths the output slopes, and this increment was used in all calculations. Figure 3 shows the smoothing effect of using alternate temperature readings on a polypropylene sample (Run 4).

The initial computations were performed on a desk calculator. After procedures were standardized, it took about 3 hours to analyze and plot the data for a single run. Later the procedure was programmed in Fortran II, and an IBM 1620 Model 2 computer was used. The program (CNZ001), including several optional subroutines, is on file at the University of Missouri at Rolla.

An examination of the plots of the raw data showed discontinuities in several runs. These were of three types:

1. The initial point in a new slope section of the curve;

2. A series of new points parallel to the original section of the curve, the point of discontinuity indicating either a human or an instrument error;

3. A series of new points shifted from the original section of the curve which drift back several points later to rejoin the original section of the curve.

Whenever the first or second cases occurred, the data points were "broken" at the point of discontinuity. Extrapolations of the preceding and succeeding data were used to estimate the values of α' on both sides of the break. In cases of the first type, the discontinuity was the start of a new level of α' values, and breaking "sharpened up" the transition point. In cases of the second type, reductions in erratic behavior of α' vs. T were obtained. All points where breaks were made are shown on the α' vs. T graphs with zigzag lines. Breaking could be accomplished up to 5 time through an optional sub-routine in the computer program. No breaks were made in cases of the third type of discontinuity in which the data drifted back. Here the smoothing techniques described below were helpful in smoothing out erratic data.

The computer program also included a data smoothing sub-routine which could be repeated on the raw data n times before sloping. This was particularly useful for smoothing discontinuities of the third type described above and also for damping out minor wiggles in the α' vs. T curves.

The smoothing technique is based on a least squares orthogonal polynomial method. Considerable smoothing occurs up to n of about 4. Beyond this, the changes are generally small as may be noted from Figure 4 which shows a comparison of 0, 4 and 10 smoothings for the polypropylene samples (Run 5). Hence, all of these data were smoothed four times before sloping. Excessive smoothing could "smear out" a sharp change in α'. However, this is most likely to occur at a discontinuity of the first type. The data were broken at these points as described above, and smoothing would have no "smearing out" tendencies.

III. B. Reliability of Results

In virtually all runs, data above about 0°C are erratic and inconsistent with the adjoining region. This is believed to be due to instabilities in the equipment which reached equilibrium after the run had progressed. Longer hold times at room temperature were not successful in eliminating the erratic results and they were generally discounted in drawing conclusions about the results.

One test of the reliability of the results is a comparison of these data with dilatometric results reported earlier. Polystyrene (Run 3) has no detectable transitions in the temperature range of these experiments as seen in Figure 6. The value of α' at 0°C is about 0.7×10^{-4} which is close to $(\alpha/3) = 0.6/^{\circ}C \times 10^{-4}$ below T_g, estimated from an equation given by Boyer(4b). The data show the same general shape as that of Martin, Rogers and Mandelkern(5). A small change in slope occurs at about -140°C in both sets of results.

The data for the two polyurethane samples (Run 1, Figure 2 and Run 2, Figure 5) show glass transitions at -46 and -54°C, close to the value of -60°C quoted by Simha and Boyer(6) for a polyurethane.

Another test is the repeatability of results obtained on the same sample. Two examples of this are shown. Figure 7 shows repeat runs on polypropylene, Sample D (Runs 4 and 5), and Figure 10 repeat runs on Sample G, a polypropylene-polyethylene mixture (Runs 8 and 9).

Runs 4 and 5 show general parallelism or overlapping throughout most of the range below 0°C except between -115 to -150°C where Run 5 shows a hump. This was caused by a discontinuity in the data for this run and the results for Run 4 are more reliable in this region and indicate a transition at -126°C. The location of the major transition, T_G, is virtually identical in the two runs.

Runs 8 and 9 exhibit about the same level of repeatibility. Again, the major transition temperature is identical on the two sets of data. Small discrepancies in the values of α' occur at lower temperatures. However, the apparent locations of the lower transition differ by about 15°C.

A third test is the internal consistency of the results. In general it was good, but discrepancies in the form of humps, dips and discontinuities did appear. The smoothings and breaks in the numerical analysis minimized these effects but did not eliminate all of them as can be seen from the curves. We believe that for the most part, they were caused by instabilities in the apparatus.

IV. Discussion of Results

A. Multiple Transitions in Single Component Systems

Plots of $\frac{1}{L_O}(\frac{dL}{dT})$ vs temperature are shown in Figures 2, 5, 6, 7, 13, 14, and 15 for Runs 1, 2, 3, 4, 5, 12, 13, 14, and 15, the single-component polymer samples. In most cases more than one transition appears to be present in the range of temperatures studied. Tabulations of temperatures of transitions, values of α' above the transitions, $\Delta\alpha'$ and $\frac{\Delta\alpha'}{\alpha'}$ are given in Table IV. As noted above, erratic fluctuations in the data for many of the runs in the 0 to 20°C range are probably due to settling or equilibrium of the system at the start of the runs and are not believed to be significant.

For the polyurethanes, there appear to be three transitions for Sample A (Run 1, Fig. 2) and two for Sample B (Run 2, Fig. 5). A discontinuity and erratic data were obtained for the latter in the -60 to -110°C range (drifting in the thermocouple readings was noted by the operator). Thus, the location of the second transition at -109°C is only a rough estimate and there is a possibility that the presence of a third transition has been masked.

The data for polystyrene (Sample C, Run 3, Fig. 6) do not show a definite transition in this range. However, as noted earlier, there is a drop in the α' values near -140°C, and a similar change in slope can be observed in the data from Reference 5. Illers claims to have observed a transition in polystyrene at about this temperature using a dynamic test method (7).

Polypropylene (Sample D, Runs 4 and 5, Fig. 7) shows a T_G of -13 or -14°C which is close to the value of -18°C reported

Table IV

Summary of Transition Data

Sample	Run No.	% PE	% Amorphous PE	% Amorphous PP	T °C	$\Delta\alpha'$ x 10^4	α'_ℓ x 10^4	$\frac{\Delta\alpha'}{\alpha'_\ell}$	T °C	$\Delta\alpha'$ x 10^4	α' (higher) x 10^4	$\frac{\Delta\alpha'}{\alpha'\text{ higher}}$	T °C	$\Delta\alpha'$ x 10^4	α' (higher) x 10^4	$\frac{\Delta\alpha'}{\alpha'\text{ higher}}$	Other Transitions °C
A	1	--	--	--	-46	1.25	2.10	0.60	-92	0.05	0.80	0.06	-137	0.07	0.65	0.11	
B	2	--	--	--	-54	1.85	2.75	0.67	-109	0.20	0.90	0.20					
C	3	--	--	--													
D	4	0	0	82	-14	1.01	1.90	0.53					-126	0.05	0.66	0.07	
	5	0	0	82	-13	1.07	2.00	0.54					Discontinuity near -120°C				
E	6	9	1	75	-12	0.90	1.70	0.53					-132	0.05	0.67	0.08	
F	7	32	18	55	-11	0.79	1.70	0.47					-137*	0.02	0.62	0.03	
G	8	48	25	40	-13	0.77	1.65	0.45					-110	0.06	0.73	0.08	<-135
	9	48	25	40	-14	0.62	1.50	0.41					-123	0.11	0.72	0.15	<-150
H	10	64	36	26	-11	0.40	1.40	0.29					-128	0.04	0.70	0.05	<-160
I	11	88	46	6	- 9	0.23	1.35	0.17					-125	0.05	0.82	0.06	<-160
J	12	100	46	0	- 2	0.10	1.30	0.08	-62*	0.04	0.98	0.04	-126	0.06	0.83	0.07	<-160
					-23	0.09	1.10	0.08									
K	13	50	50	50	-61												<-150
L	14	100	--	--	-10	0.08	1.65	0.05	-62	0.06	1.20	0.05	-122	0.05	0.83	0.06	<-160
					-33	0.22	1.50	0.14									
M	15	100	--	--	-10	0.13	1.70	0.07	Discontinuity near -67°C				Discontinuity near -137°C				<-160
					-40	0.07	1.30	0.05									

*Questionable transition

IV. A. (Continued)

by Reding (8) and by Manaresi and Giannella (9), and -15°C reported by Kontos and Slichter (10), all using dilatometry. The difference in α', the linear expansion coefficient, above and below T_G, is about $1 \times 10^{-4}\ {}^{\circ}C^{-1}$ for this 82% amorphous polypropylene sample. This compares with a value of $4 \times 10^{-4}\ {}^{\circ}C^{-1}$ for $\Delta\alpha$, the change in volumetric expansion coefficient, reported by Manaresi and Gianella (9) for 100% amorphous polypropylene (see also IV.B.).

The data of Run 4 also suggest another transition at about -126°C. A discontinuity in the data for Run 5 on the same sample at about -120°C gave a hump in the α' values in this region and the transition could not be verified. Boyer (4c) suggests a value of -70°C for this transition in polypropylene samples based on dynamic measurements of Flocke (11).

The three polyethylene samples tested (Samples J, L, and M, Runs 12, 14, and 15, Figs. 13 and 15) appeared to have two transitions in the range of 0 to -40°C. To some extent, the separation of these two transitions was arbitrary and a single larger transition in this range could also be postulated. However, the persistence of the apparent double hump in several runs on different samples strongly suggests that polyethylene has two transitions in this range. The data for Sample J (Fig. 13) also indicate a transition at -126°C and possibly one at -62°C (shown as a dotted arrow). Sample L (Run 14) appears to have transitions at -62 and -122°C. The data for Sample M (Run 15), which was cast from the same polymer sample as L, had discontinuities near -67°C and -137°C, and no conclusions can be drawn about lower temperature transitions in this sample. Because of this, a comparison of the effect of heat treatment (Run 15 was cast and Run 14 was machined to form the test samples) can only be made in the high and low ranges.

It is worth noting that extrapolations of dilatometric data of Kontos and Schlichter and of Manaresi and Gianella by Boyer (4b) on ethylene-propylene copolymers to 100% ethylene give glass transition temperatures of -87 and -83°C respectively. Boyer (4d) also shows that free volume concepts lead to an estimate of -93°C for T_G. At temperatures below -160°C all three samples show a fairly rapid drop in α' values suggesting another transition.

Transitions in the 0 to -40°C range in polyethylene have been ascribed to branching (4e) and those in the -122 to 126°C range to sub-group motion (4e, 12). Bohn (12) has found that the transition temperature in polyethylene around 0°C is lowered as branching increases (crystallinity decreases). Similar results were obtained by Tanaka (13). The lower transition temperatures found in this range for Samples L and M compared with J suggest that they are more branched and presumably less crystalline than J (54% crystalline). Furthermore, at temperatures above -140°C, α'-values for J are considerably lower than those for L and M as expected for a more crystalline sample. The differences between L and M in the high and low temperature regions are not large enough to draw meaningful conclusions about the effects of heat treatment on crystallinity, but the lower level of α' for the cast sample throughout most of the temperature range could mean that crystallinity is increased by casting.

The 50:50 propylene-ethylene copolymer (Sample K, Run 13, Fig. 14) gave erratic results above -40°C but shows a major transition at -61°C. Kontos and Schlichter (10), using dilatometry, reported a T_G value of -58°C for this composition, and Manaresi and Giannella's results on other copolymer compositions (9) predict a value of -57°C. Below -120°C, α'-values drop again but the change is small and it is questionable as to whether this is a transition. A further drop in α' begins at about -150°C. The erratic results obtained here above -40°C are believed due, at least in part, to trapped stresses in the sample. Similar fluctuating results were obtained in this temperature range on several other runs using a less sensitive LVDT (2).

IV. B. The Effect of Physical Mixtures of Polyethylene and Polypropylene on Glassy Transitions.

Figures 7 to 13 show the linear expansivities, α', for Runs 4 to 12 for a series of mixtures of polypropylene and polyethylene designated D, E, F, G, H, I and J. The per cent amorphous polyethylene and polypropylene in the mixtures were obtained from x-ray analysis of crystallinity by Dr. Kontos of the Naugatuck Chemical Company. These data and sample preparation information are summarized in Tables I and II. Tabulations of temperatures of transitions, values of α' above the transitions, $\Delta\alpha'$ and $\frac{\Delta\alpha'}{\alpha'}$, are given in Table IV.

In all of the samples except J which is 100% polyethylene, a major transition occurred in the range of -9 to -14°C and the magnitude of the change in the linear expansion coefficient, $\Delta\alpha'$, at this transition decreased with increasing polyethylene content. However, the ratio of $\Delta\alpha'/\alpha'_\ell$ diminished more slowly as α'_ℓ, the linear expansion coefficient just above the transition, also decreased with increasing polyethylene content.

It should also be noted from Figure 12 that data for Sample I (88% PE) are similar in shape to those of Sample J (100% PE) suggesting the possibility of transitions below -30°C and -60°C. However, the apparent transitions were so small that they were not shown in Table IV.

Estimates of the value of $\Delta\alpha'$ for 100% amorphous polypropylene in the temperature range of 0 to -15°C were made from the results on each sample containing polyethylene, and the calculations are summarized in Table V. The contributions by amorphous

Table V

Estimation of $\Delta\alpha'$ for 100% Amorphous Polypropylene

Sample	Run No.	% Amorphous PE	% Amorphous PP	*$\Delta\alpha'$ x 10^4, $^\circ C^{-1}$	**$\Delta\alpha''$ x 10^4, $^\circ C^{-1}$	Estimated $\Delta\alpha'$ x 10^4 100% PP
D	4	0	82	1.01	1.01	1.23
	5	0	82	1.07	1.07	1.30
E	6	1	75	0.90	0.90	1.20
F	7	18	55	0.79	0.75	1.36
G	8	25	40	0.77	0.72	1.80
	9	25	40	0.62	0.57	1.42
H	10	36	26	0.40	0.32	1.23
I	11	46	6	0.23	0.13	2.17
J	12	46	0	0.10	---	---

* Transition in range 0 to $-15^\circ C$.

** Adjusted $\Delta\alpha'$, reduced by contribution of amorphous PE in this same temperature range. Correction is based on data for Sample J.

$$\text{Correction} = \frac{(\%\text{ amorphous PE})}{46}(0.10)$$

$$= (0.00217 \times 10^{-4}) \cdot (\%\text{ amorphous PE})$$

polyethylene and amorphous polypropylene present in each sample were assumed to be additive, and the measured value of $\Delta\alpha'$ was reduced by the former. The estimated value of $\Delta\alpha'$ for 100% amorphous polypropylene was then obtained by dividing the adjusted $\Delta\alpha'$ (called $\Delta\alpha''$) for each sample by the fraction of amorphous polypropylene present.

The most reliable estimates are for Samples D, E and F with high amorphous polypropylene and low amorphous polyethylene contents as the correction term is smallest here and the results are less sensitive to small errors in the analyses of per cent amorphous polypropylene. These values of $\Delta\alpha'$ average about $1.3 \times 10^{-4}\ {}^{\circ}C^{-1}$, which is a close check on Manaresi and Giannella's (9) measured value of $4 \times 10^{-4}\ {}^{\circ}C^{-1}$ for $\Delta\alpha$, the change in the volumetric expansion coefficient, which was determined dilatometrically on amorphous polypropylene.

If the correction also included the $\Delta\alpha'$ value of 0.09 for polyethylene (-23°C transition), the estimates of $\Delta\alpha'$ for polypropylene from Samples G, H and I would be lowered, but the effect on the estimates from Samples D, E and F would be small.

In most of the same samples, a much smaller transition appeared to be present at -110 to -132°C. The magnitude of the change in the expansion coefficient here ranged from 4 to 22% of the higher temperature transition. Estimates of transition temperatures in this lower region are subject to larger errors because of the smaller changes in slope.

Run 4 on Sample D shows this transition but the discontinuity in the data for Run 5 on the same sample at about -120°C gave a hump in the α' values in this region and the transition could not be verified. The apparent transition in Sample F (Run 7) was so small that it is questionable as to whether it is actually present. It is therefore shown as a dashed arrow in Figure 9.

The trend of the data for Sample G in Run 8 suggest that another transition may be present below -135°C. This is also observed in Run 9 on Sample G but at a lower temperature (below -150°C), and on Samples H, I, and J which are the high polyethylene content samples, and also in the copolymer sample.

Plots of transition temperatures as a function of polyethylene content and of per cent amorphous polypropylene in the mixture are shown in Figure 16. The higher temperature transition is quite insensitive to polyethylene content until 100% polyethylene (and the double transition) is reached. The low temperature (-110 to -132°C) transition is also fairly insensitive to composition. However, this relative independence of transition temperatures with composition seems to occur because the transitions of the two polymers are so close to each other. There is no evidence of any transitions in the mixtures which are not found in the pure polymers.

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APPENDIX

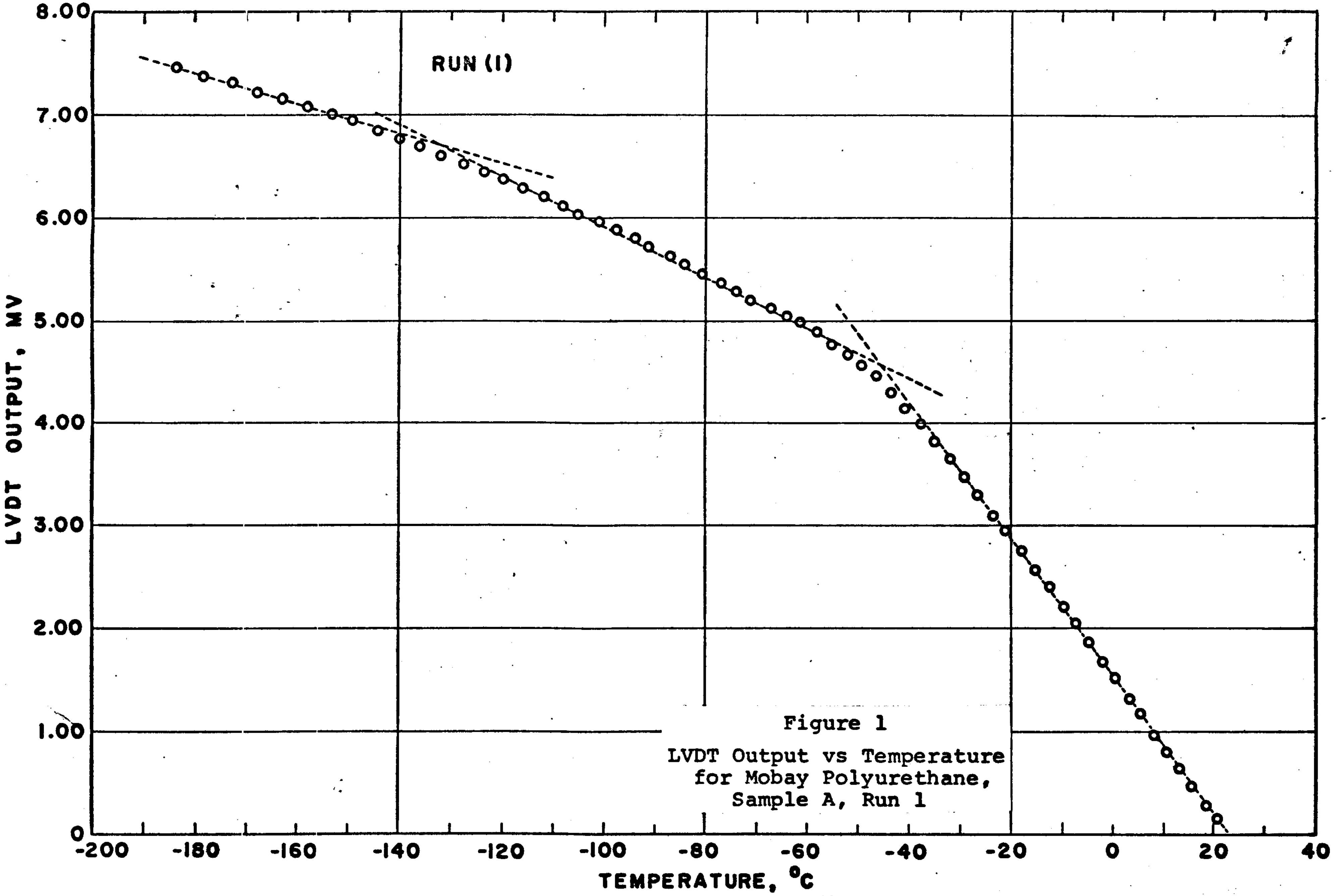

Figure 1
LVDT Output vs Temperature for Mobay Polyurethane, Sample A, Run 1

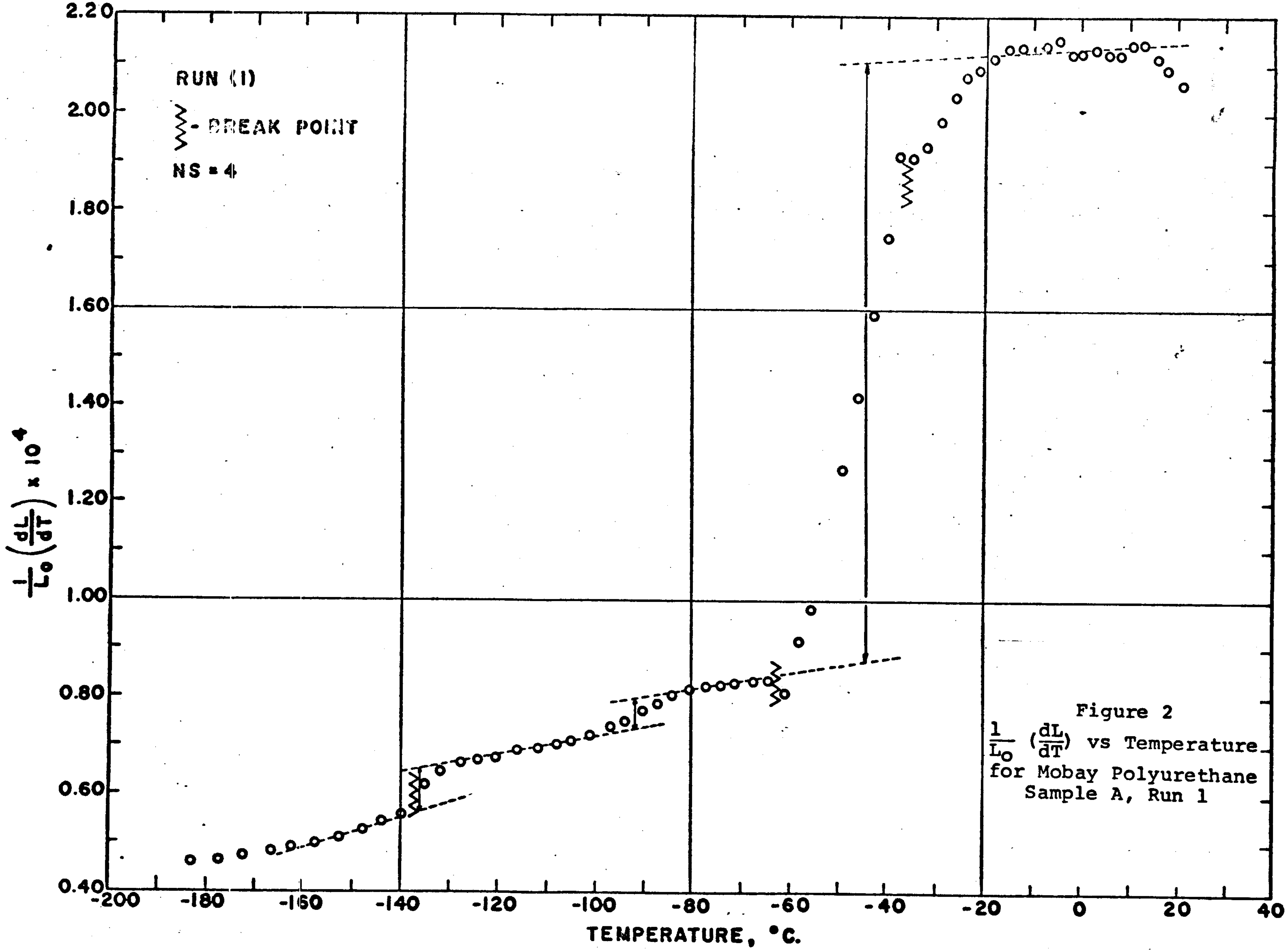

Figure 2
$\frac{1}{L_o}$ $(\frac{dL}{dT})$ vs Temperature
for Mobay Polyurethane
Sample A, Run 1

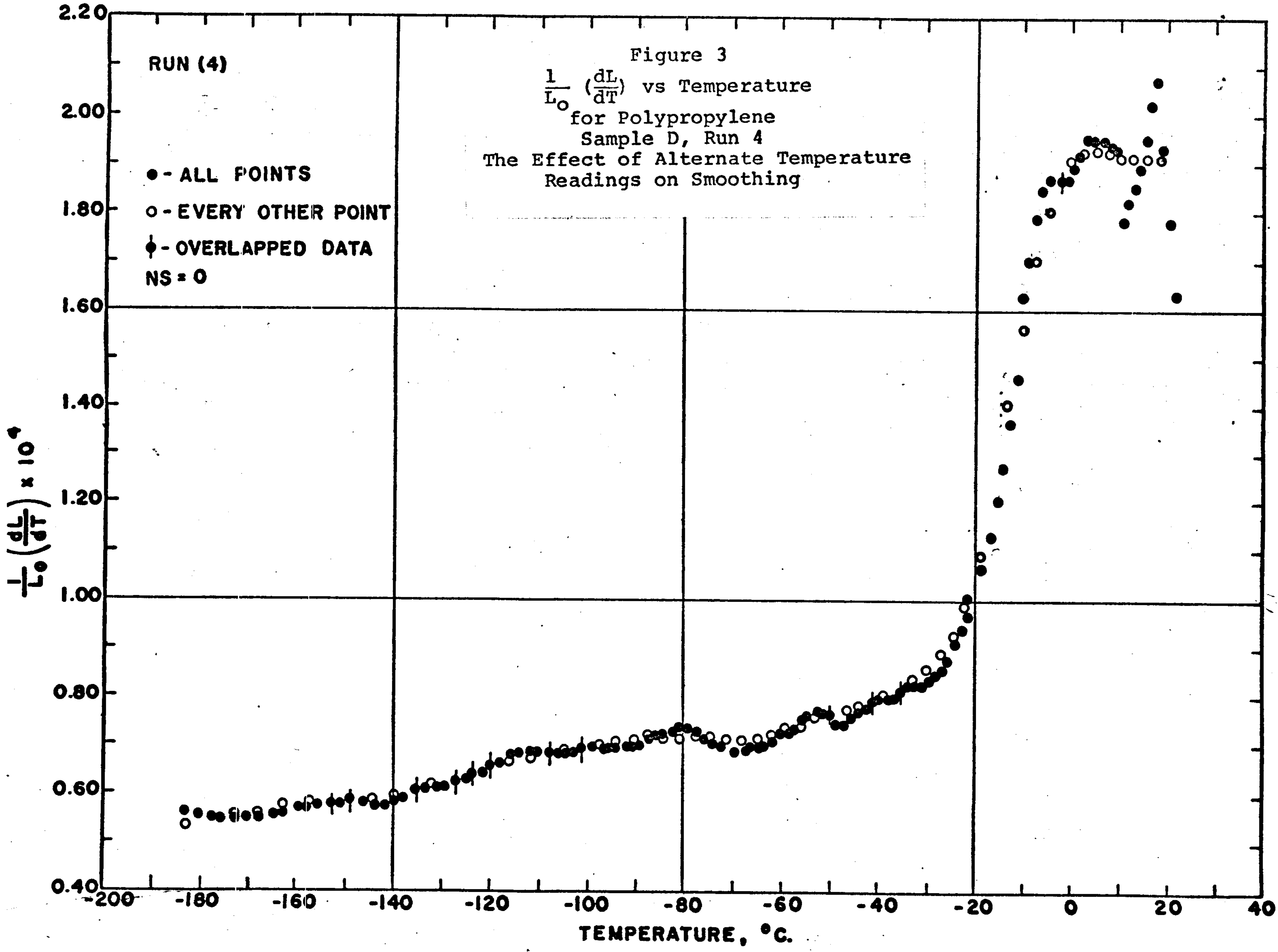

Figure 3

$\frac{1}{L_o}\left(\frac{dL}{dT}\right)$ vs Temperature
for Polypropylene
Sample D, Run 4
The Effect of Alternate Temperature
Readings on Smoothing

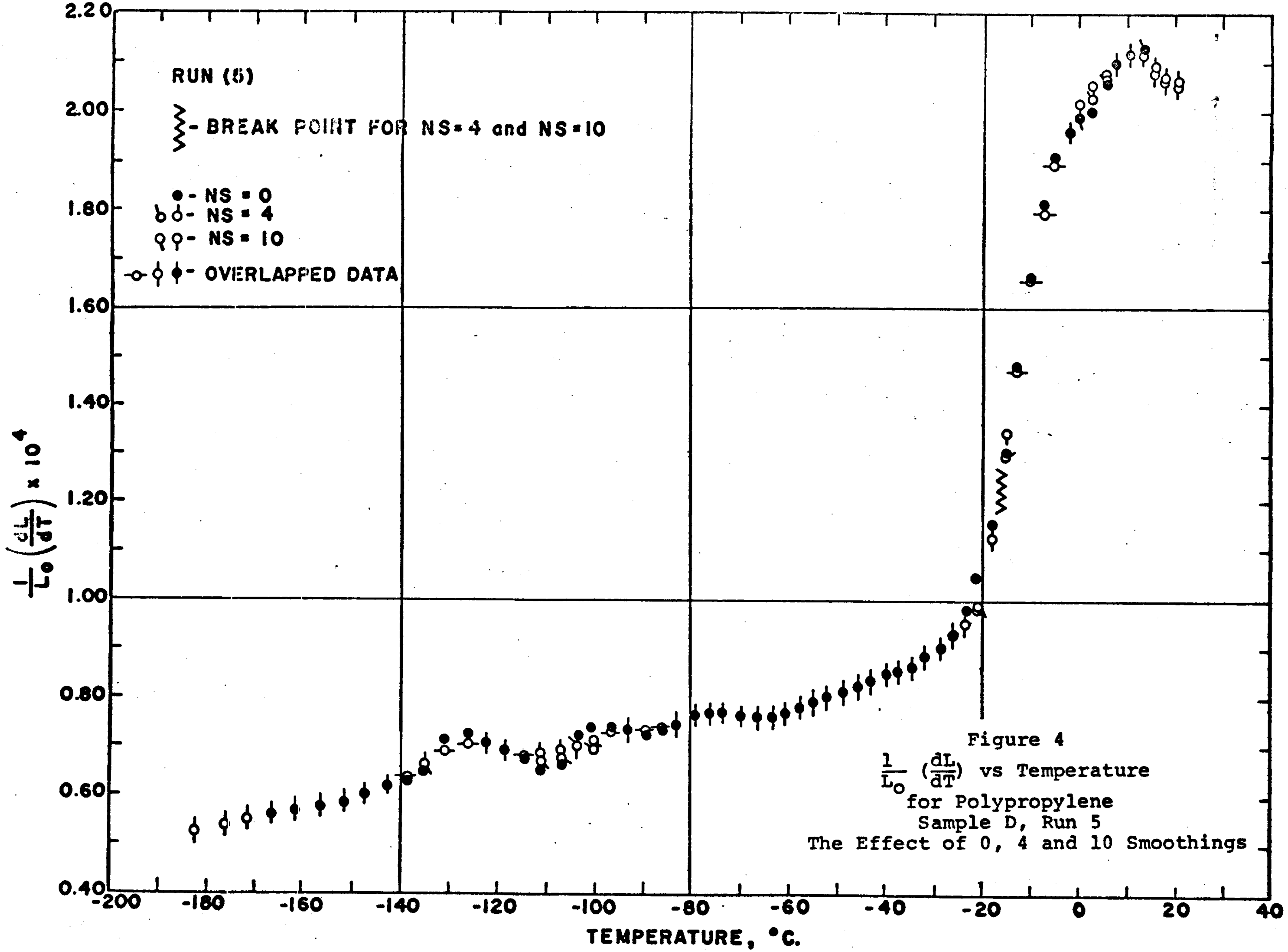

Figure 4
$\frac{1}{L_o}\left(\frac{dL}{dT}\right)$ vs Temperature
for Polypropylene
Sample D, Run 5
The Effect of 0, 4 and 10 Smoothings

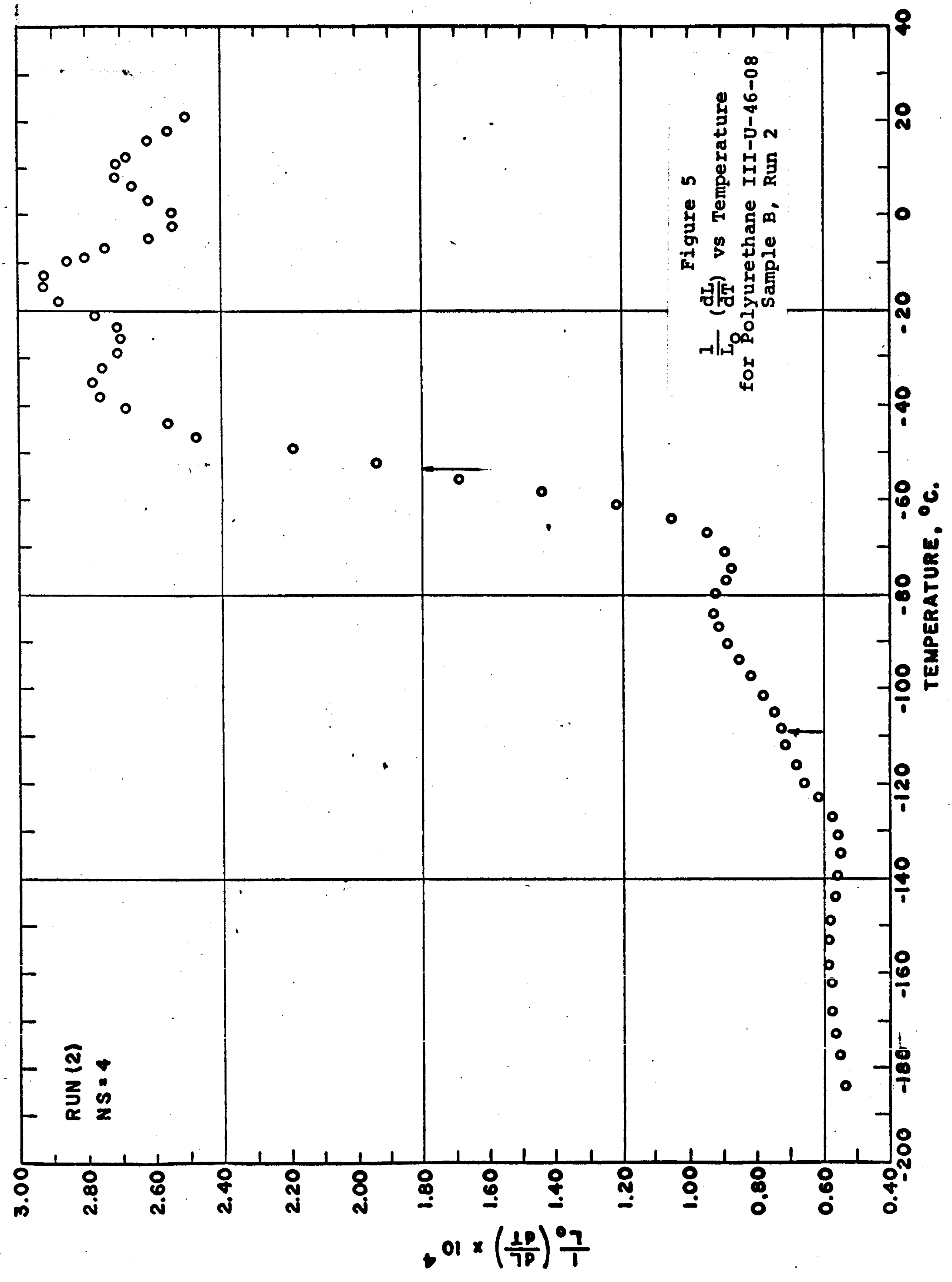

Figure 5

$\frac{1}{L_o}\left(\frac{dL}{dT}\right)$ vs Temperature

for Polyurethane III-U-46-08

Sample B, Run 2

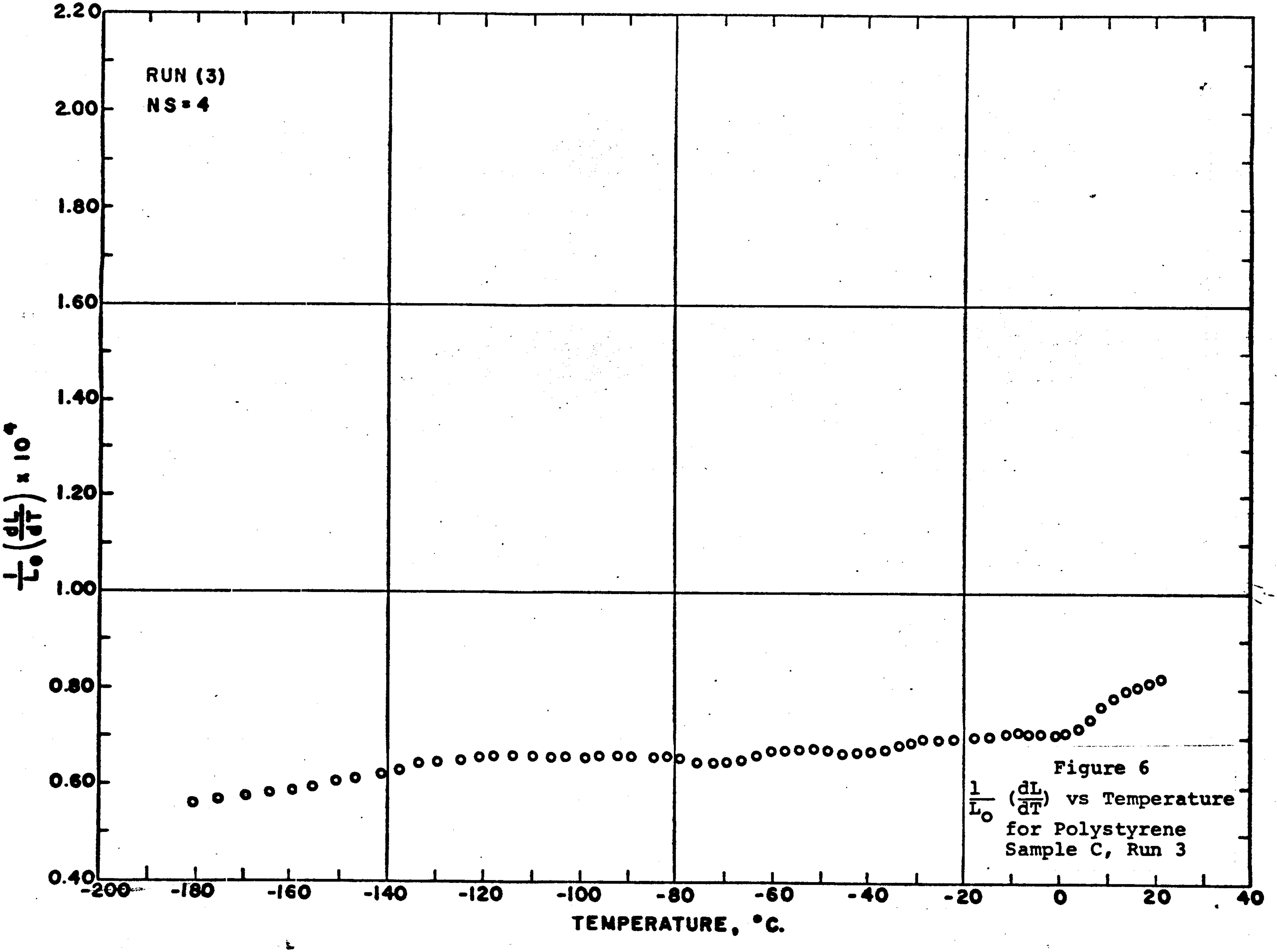

Figure 6
$\frac{1}{L_o}$ $(\frac{dL}{dT})$ vs Temperature
for Polystyrene
Sample C, Run 3

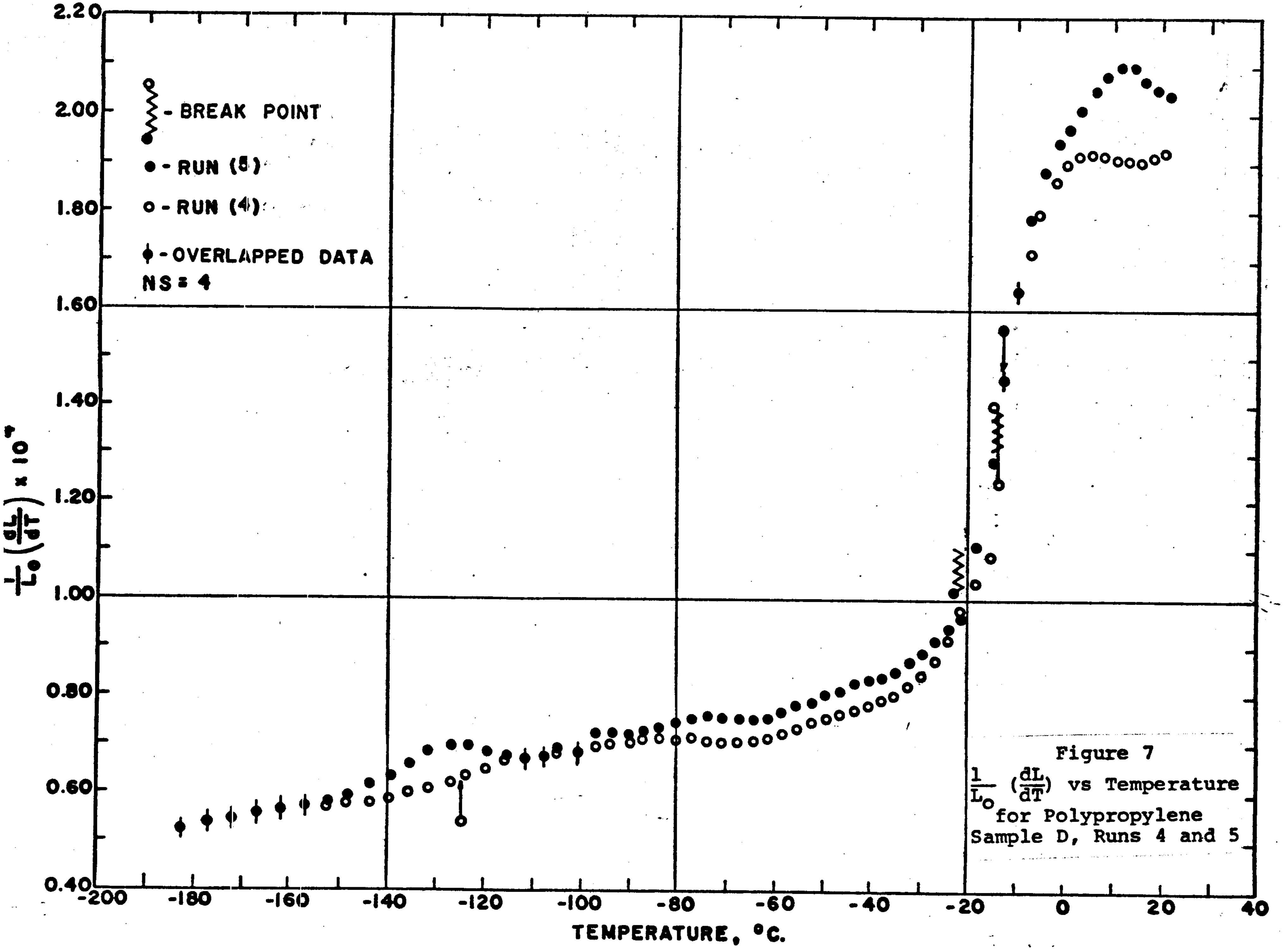

Figure 7
$\frac{1}{L_o}\left(\frac{dL}{dT}\right)$ vs Temperature for Polypropylene Sample D, Runs 4 and 5

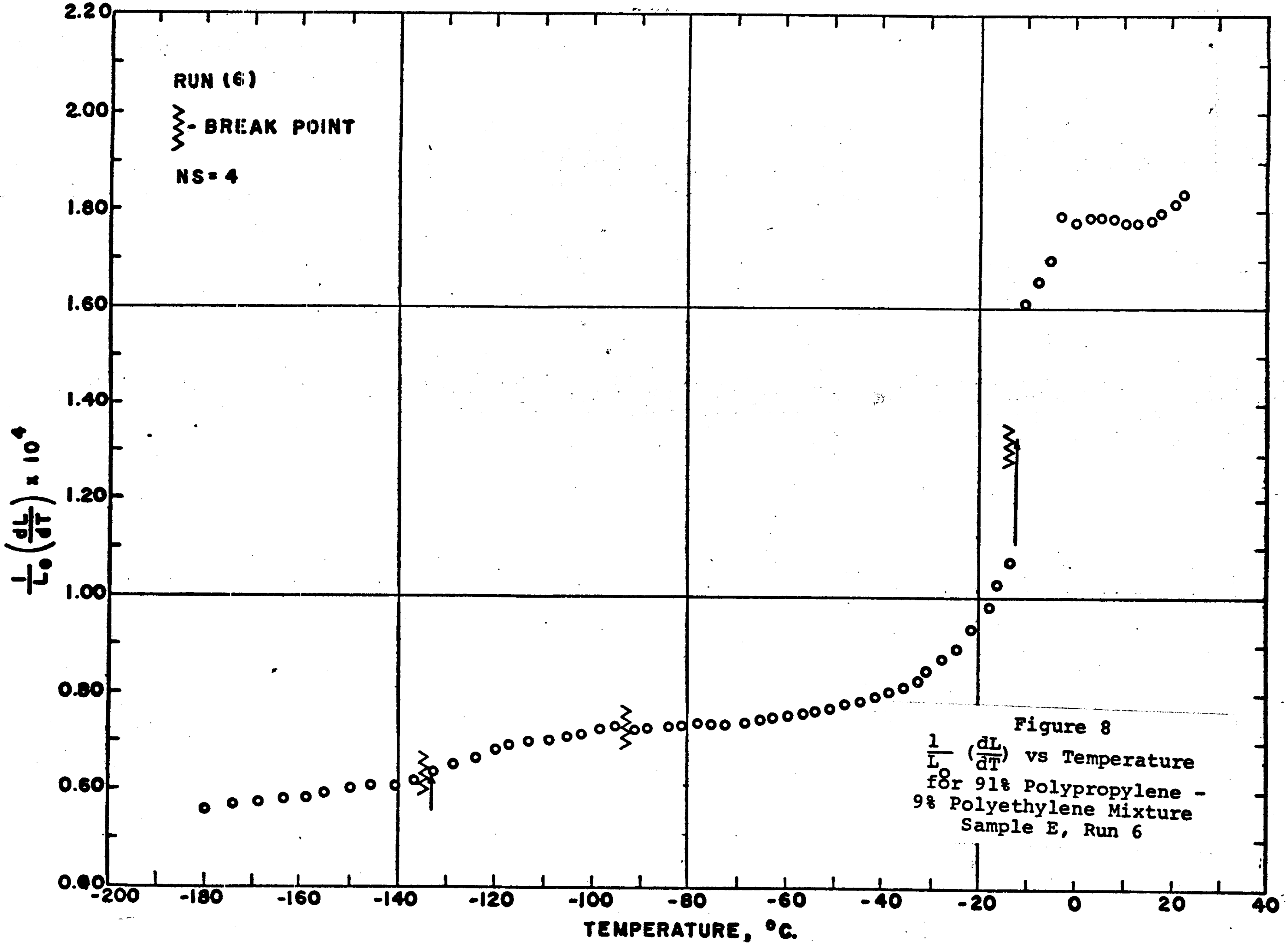

Figure 8

$\frac{1}{L_o}\left(\frac{dL}{dT}\right)$ vs Temperature
for 91% Polypropylene -
9% Polyethylene Mixture
Sample E, Run 6

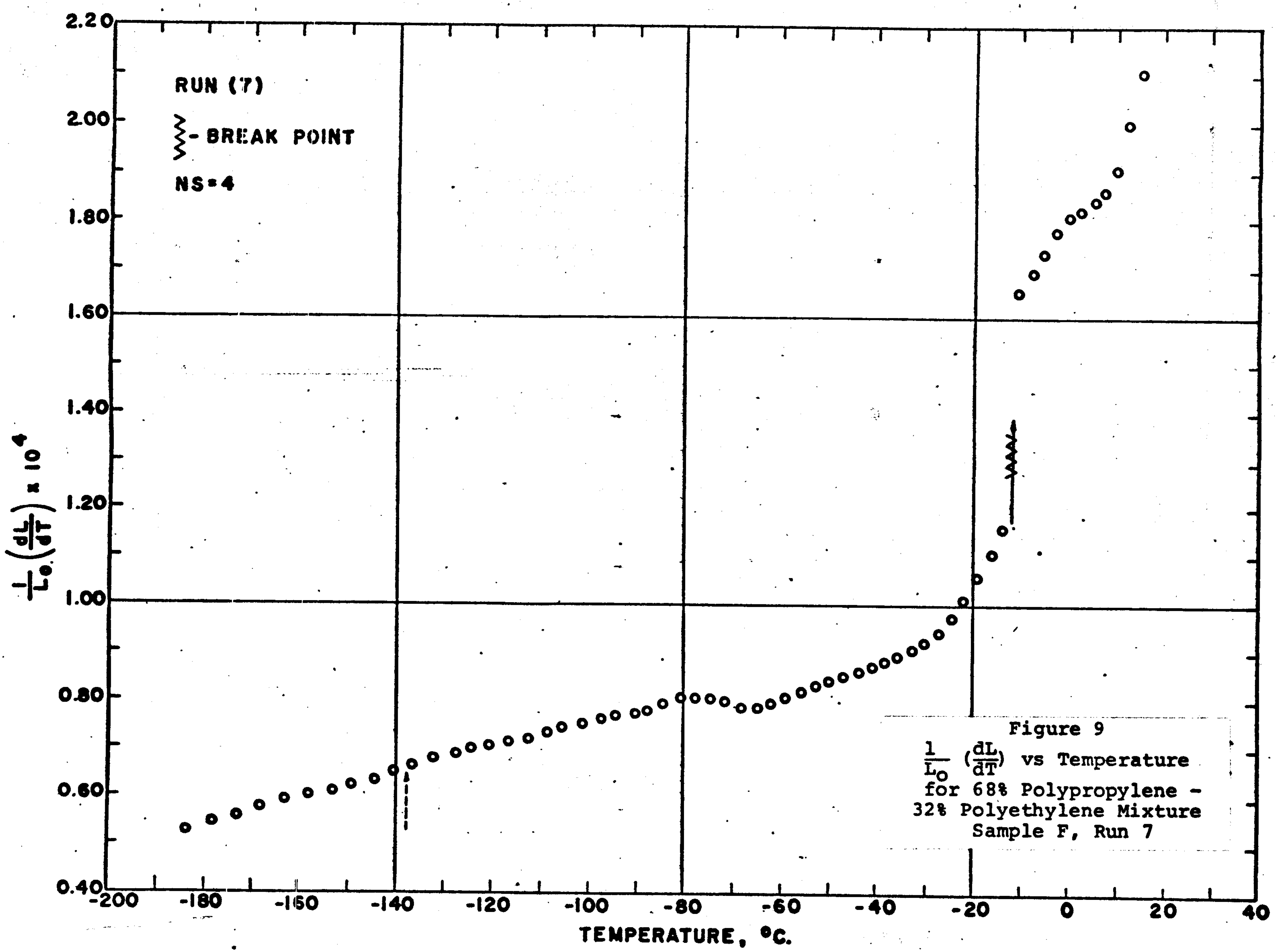

Figure 9

$\frac{1}{L_o}\left(\frac{dL}{dT}\right)$ vs Temperature for 68% Polypropylene - 32% Polyethylene Mixture Sample F, Run 7

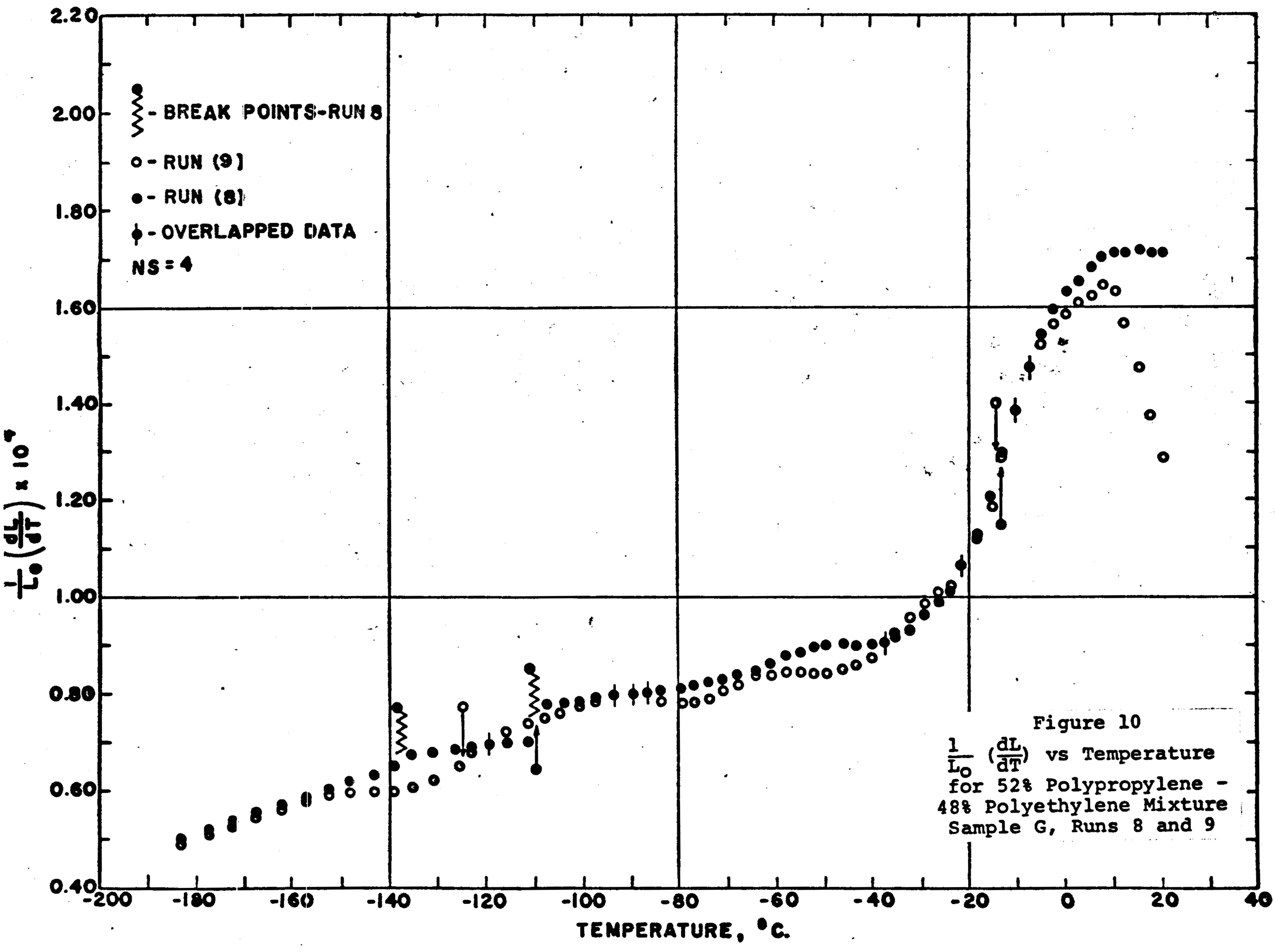

Figure 10

$\frac{1}{L_o}\left(\frac{dL}{dT}\right)$ vs Temperature for 52% Polypropylene - 48% Polyethylene Mixture Sample G, Runs 8 and 9

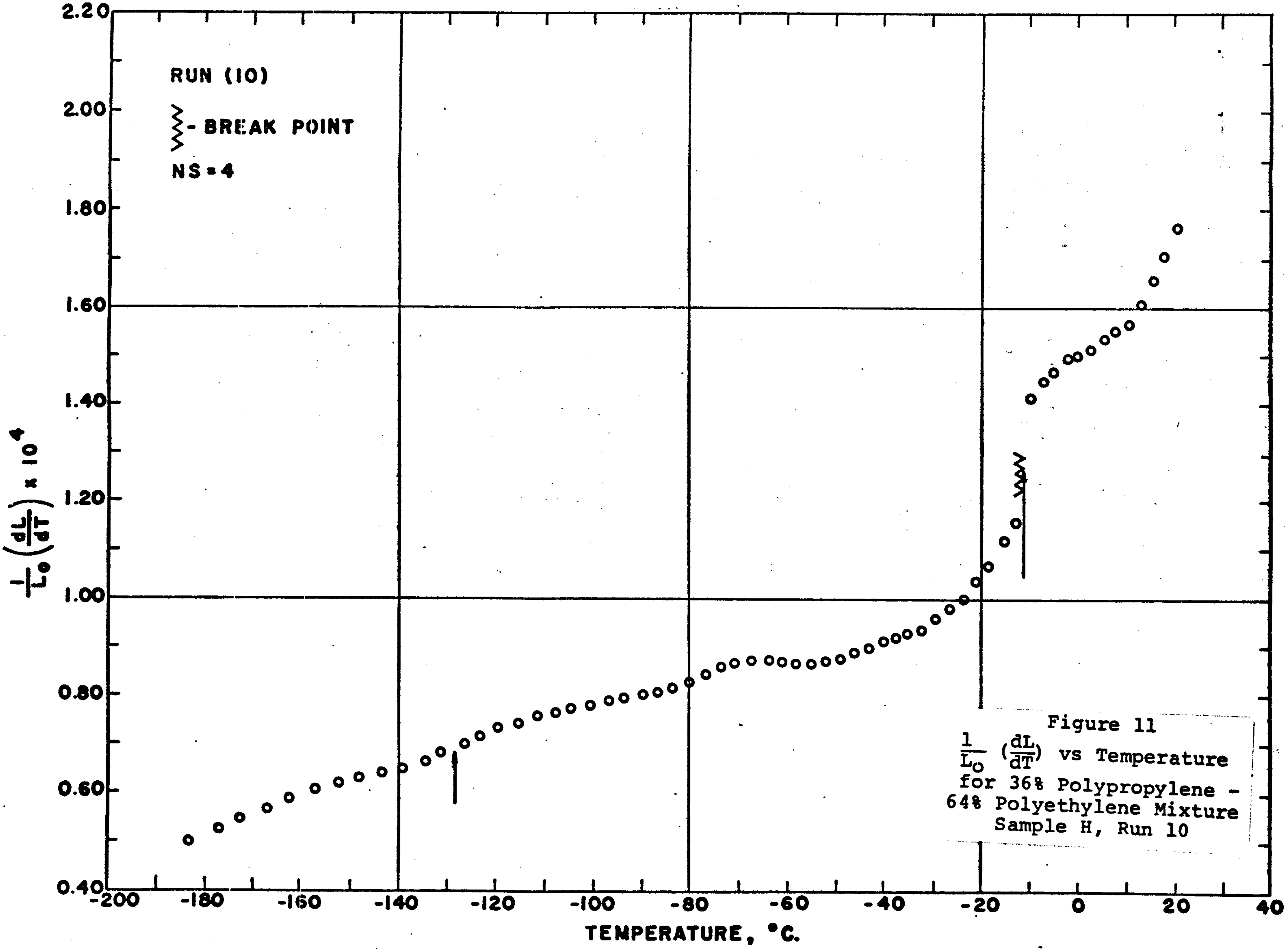

Figure 11

$\frac{1}{L_o}\left(\frac{dL}{dT}\right)$ vs Temperature for 36% Polypropylene - 64% Polyethylene Mixture Sample H, Run 10

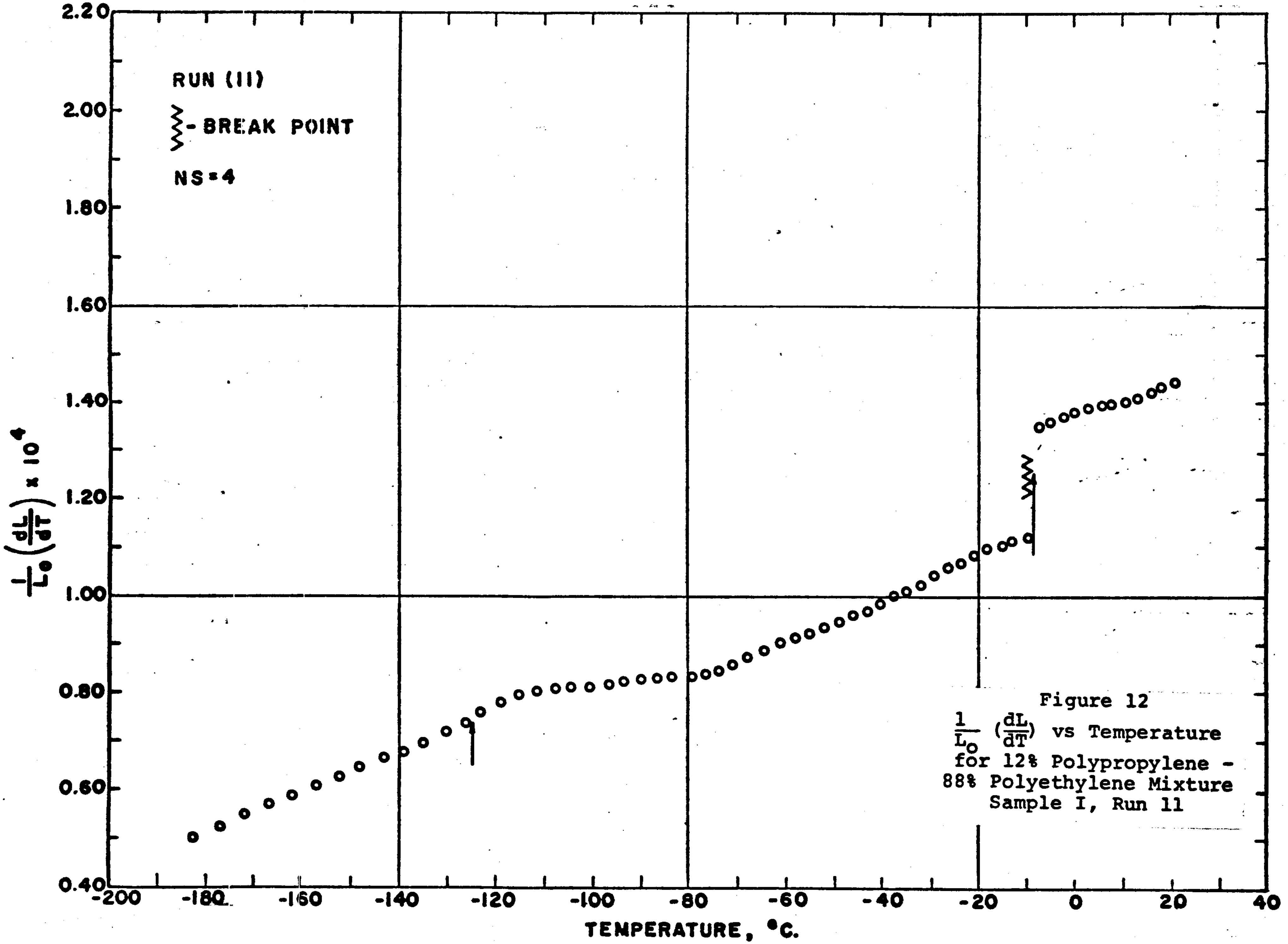

Figure 12

$\frac{1}{L_o}\left(\frac{dL}{dT}\right)$ vs Temperature for 12% Polypropylene - 88% Polyethylene Mixture Sample I, Run 11

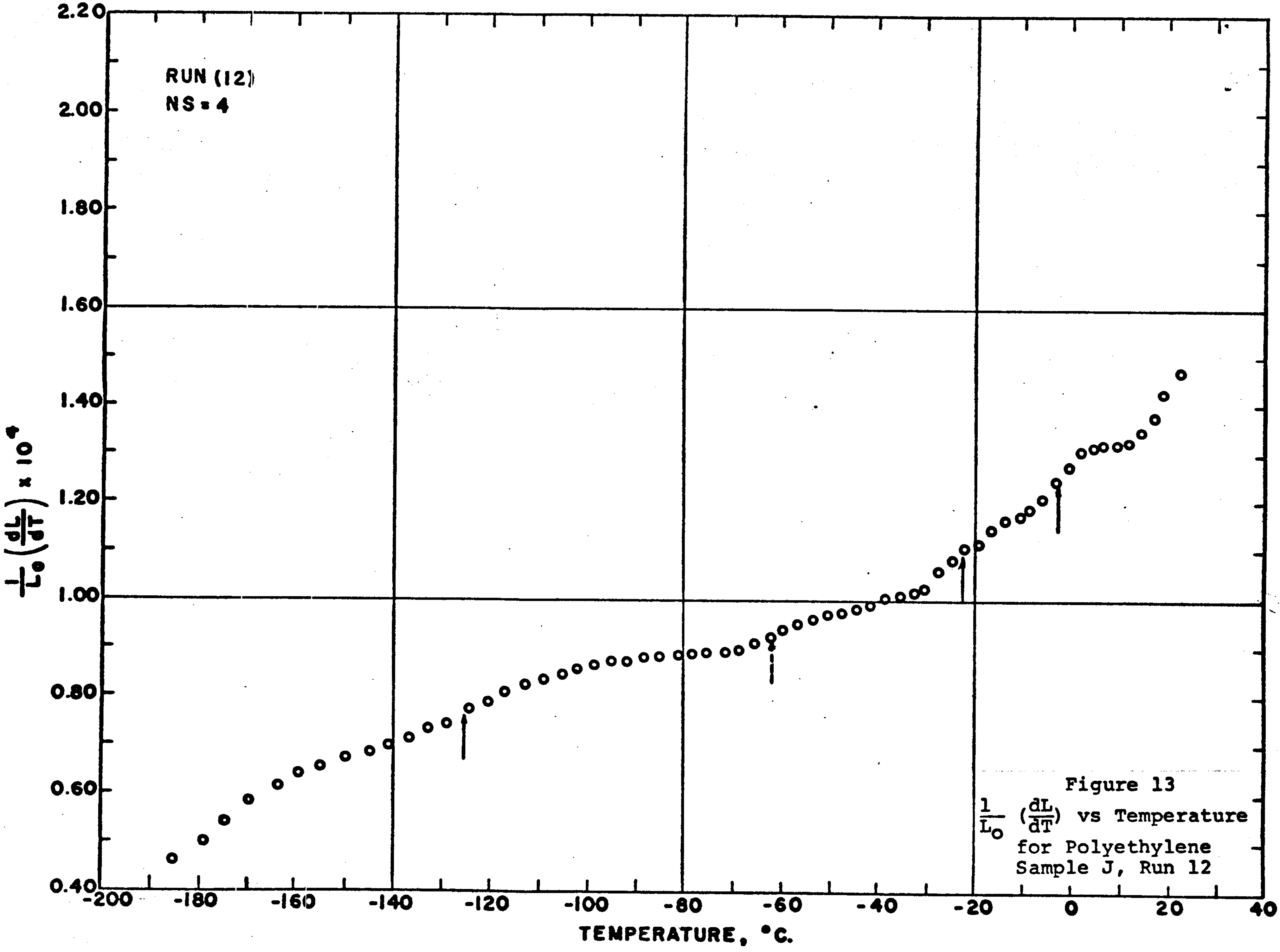

Figure 13

$\frac{1}{L_o}\left(\frac{dL}{dT}\right)$ vs Temperature for Polyethylene Sample J, Run 12

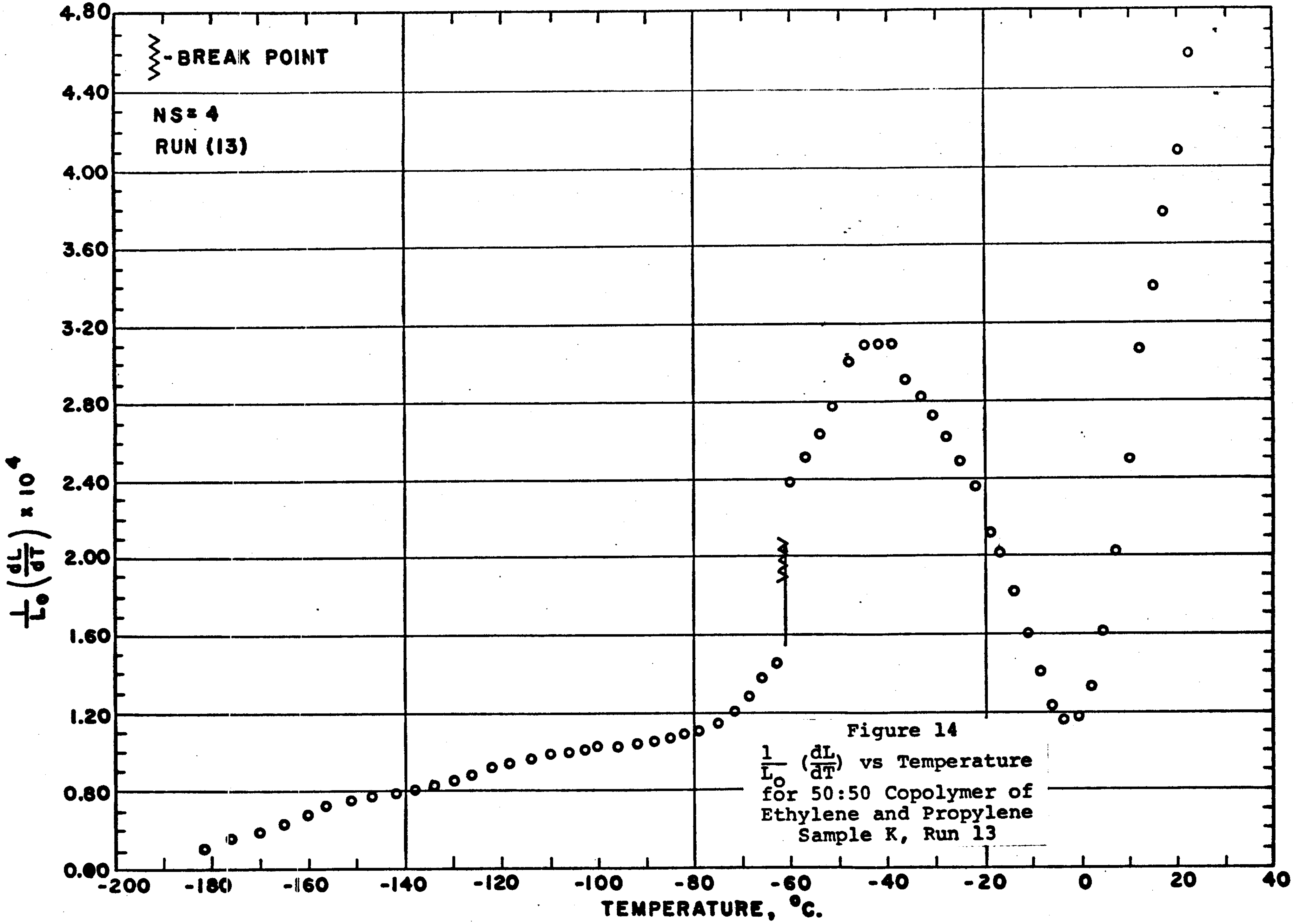

Figure 14

$\frac{1}{L_o}\left(\frac{dL}{dT}\right)$ vs Temperature for 50:50 Copolymer of Ethylene and Propylene Sample K, Run 13

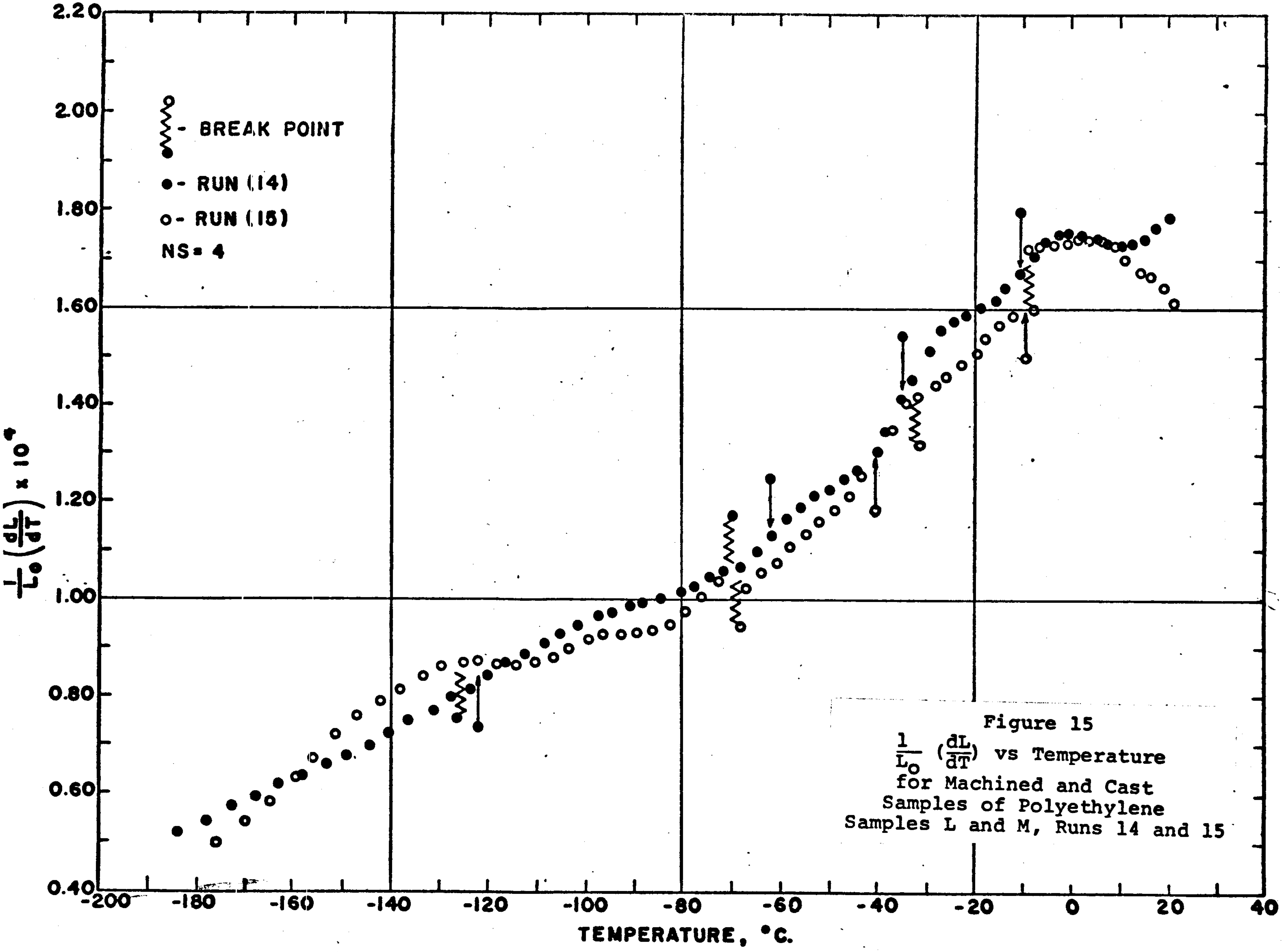

Figure 15

$\frac{1}{L_o}\left(\frac{dL}{dT}\right)$ vs Temperature for Machined and Cast Samples of Polyethylene Samples L and M, Runs 14 and 15

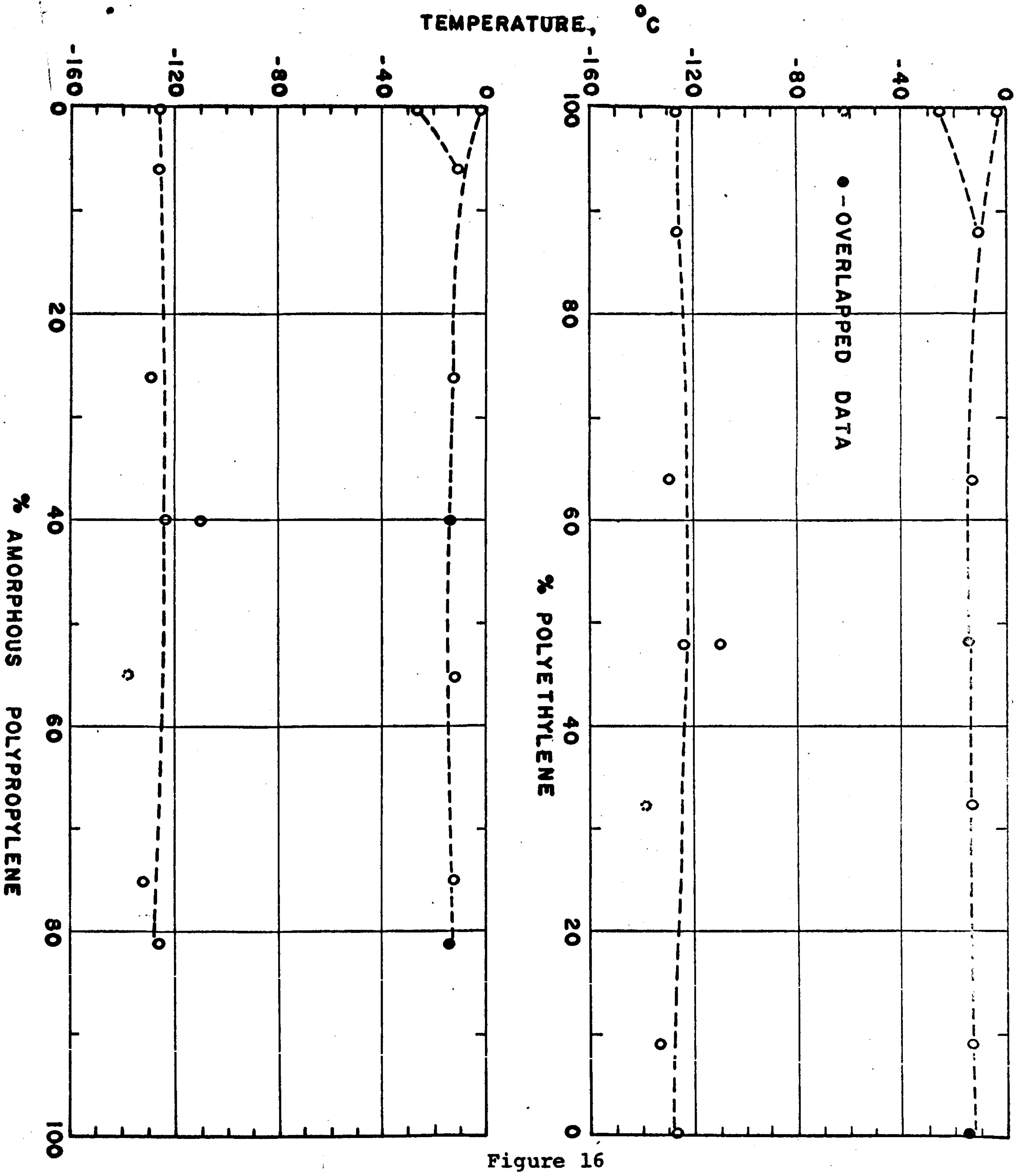

Figure 16

Transition Temperatures vs
Polyethylene Content and vs
Per Cent Amorphous Polypropylene
in the Mixture