

## The Heat Capacity of Linear and Branched Polyethylene

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### Introduction

In recent years, there has been a great deal of interest in the specific heat of chain and layer structures. It is well known that Debye-type calculations<sup>1,2</sup> for two-dimensional lattices leads to a specific heat which, at low temperature, varies as the second power of the absolute temperature, and this behavior has been observed experimentally.<sup>3</sup> Of even more interest to polymers, such considerations applied to a one-dimensional lattice or "linear continuum" lead to a specific heat which, at low temperatures, varies as the first power of the absolute temperature. For such a linear continuum it is easy to show that the specific heat is given by the expression

$$C_v = \frac{3 RT}{\theta_1} \int_0^{\theta_1/RT} \frac{x^2 e^x dx}{(e^x - 1)^2} \quad (1)$$

where  $x$  is  $h\nu/kT$  and  $\theta_1$  is  $h\nu/k$ , as usual. This expression clearly is linear in  $T$  for  $T \ll \theta_1$ , and this behavior is to be contrasted with the usual third power temperature dependence of the specific heat for most solids. It is to be expected that such a model would be a reasonable one for the behavior of such materials as selenium and tellurium and for some linear polymers, particularly polyethylene. Thus, a linear specific heat was observed experimentally by Anderson<sup>4</sup> for selenium, although later work by DeSorbo<sup>5</sup> showed that over a wider temperature range the specific heat of selenium deviated from strict proportionality to the temperature.

Indeed, it would be expected that for any material, as the temperature is lowered and hence the dominant phonons become of longer and longer wavelength, the interchain interactions would become important and these simple one-dimensional considerations would cease to apply. Thus, aside from the above-mentioned linear continuum theory, two other theoretical treatments of the specific heat of polymeric systems have been made. Realizing that at extremely low temperatures any solid must become a three-dimensional continuum, Tarassov<sup>6</sup> proposed that of the  $3N$  possible normal modes of the solid,  $3N_2$  were distributed according to the normal three-dimensional distribution, and  $3N_1$  according to a linear continuum. Thus Tarassov takes the frequency distribution to be

$$\begin{aligned}
 g(\nu) d\nu &= 9N_3 \nu_1^{-3} \nu^2 d\nu & (2) \\
 0 &< \nu < \nu_1 \\
 &= 3N_1 (\nu_m - \nu_1)^{-1} d\nu \\
 \nu_1 &< \nu < \nu_m
 \end{aligned}$$

where  $g(\nu)$  is the frequency distribution function,  $\nu_1$  is the frequency where the three-dimensional continuum goes into the linear continuum, and  $\nu_m$  is some cut-off frequency. With the further restriction that

$$N_3 = N \frac{\nu_1}{\nu_m} \quad (3)$$

one obtains for the specific heat,<sup>5</sup>

$$\begin{aligned}
 C_{1,3} &= \frac{3RT}{\theta_1} \int_0^{\theta_1/T} \frac{x^2 e^x dx}{(e^x - 1)^2} & (4) \\
 &- \frac{3RT}{\theta_1} \int_0^{\theta_1/T} \frac{x^2 dx}{(e^x - 1)^2} + \frac{9RT^3}{\theta_1 \theta_3^2} \int_0^{\theta_1/T} \frac{x^4 e^x dx}{(e^x - 1)^2}
 \end{aligned}$$

DeSorbo<sup>5</sup> found good agreement between this theory and the specific heat of selenium, but to our knowledge these considerations have never been applied to synthetic high polymers.

Stockmayer and Hecht<sup>7</sup> approached the problem in an entirely different manner. Using the Born-von Karman<sup>8</sup> technique they computed the frequency distribution of a cubic lattice with very high force constants (primary valence forces) in one direction, and weak force constants (van der Waals forces) in the other direction. As usual in such cases neither the frequency distribution nor the specific heat can be presented in closed form, but the specific heat is given as a function of only one parameter,  $T_m = h\nu_m/k$ . This computation, which was later extended by Genesky and Newell,<sup>9</sup> has recently been used by Dole<sup>11</sup> and Starkweather<sup>29</sup> for the analysis of polyethylene and polytetrafluoroethylene.

Synthetic polymers are good examples of highly anisotropic materials which indeed approach chain lattices. However, due to the structural complexities of the backbone they do not in general make very good systems with which to test the theories mentioned. Polyethylene, however, is an exception. One can argue that C-H vibrations are of such a high frequency that at low temperatures the CH<sub>2</sub> group acts essentially as a unit. One can also argue that the anisotropy in such a system is higher than any other. The backbone stretching or bending modes involve the deformation of carbon-carbon bonds and should thus have a very high Debye temperature, whereas the transverse vibrations of the lattice do involve only van der Waals forces. Thus polyethylene at low temperatures should be a good example of a chain lattice. Indeed, Wunderlich and Dole<sup>10</sup> found a linear portion in the specific heat temperature curve of polyethylene extending from -25 to 55°C., and Dole et al.<sup>12</sup> and Raine et al.<sup>13</sup> found similar behavior for high pressure polyethylene. Recently, however, Sochava<sup>14</sup> has

published data in the low temperature region (17–60°K.) which demonstrates that this linear behavior cannot be expected to continue to absolute zero.

The heat capacity of polymers over a wide range of temperature is desirable also for other reasons. Recent theoretical analysis of the glass transition by Gibbs and DiMarzio<sup>15</sup> indicates that the entropy of a glass should approach zero as the observed glass transition temperature approaches the temperature  $T_2$  of these authors, which is the glass temperature which would be observed in an infinitely slow experiment. A measurement of the absolute entropy in the liquid state of two polymers which are identical except for degree of crystallinity would allow one to draw some conclusions about the "zero-point" entropy of polymeric glasses. Assuming that at absolute zero the material is composed only of a glassy phase and a crystalline phase, and that the entropy of the liquids are comparable, the zero-point entropy of the glass is easily shown to be

$$S_0^g = \frac{S_{obs}^2 - S_{obs}^1}{f_2 - f_1} \quad (5)$$

where  $S_{obs}^2$  and  $S_{obs}^1$  are the observed entropies (integral of  $C_p/T$  of the higher and lower crystallinity species, respectively) and  $f_2$  and  $f_1$  are their degrees of crystallinity. High and low pressure polyethylene make reasonable systems to study this effect. The only difference in the entropy of the liquid would come from the degree of branching, and this difference is not expected to be large. To the extent, therefore, that this two phase concept can be applied to this system it makes a good system to test the Gibbs and DiMarzio<sup>15</sup> theory.

Although several measurements of the heat capacity of high and low pressure polyethylene exist<sup>10-13,16</sup> none is over a wide enough temperature range to make this analysis possible. We therefore have measured the heat capacity of two types of polyethylene from liquid air temperatures into the melt. The polyethylenes used were the low pressure type Marlex produced by the Phillips Petroleum Co. and also investigated by Wunderlich and Dole<sup>10</sup> and Sochava,<sup>14</sup> and which will hereafter be referred to as "linear," and a high pressure type DYNK produced by the Union Carbide Corp., for which no measurements seem to exist, and which will be referred to as "branched."

### Apparatus and Method

For the branched polyethylene a calorimeter based on the design used by Scott et al.<sup>17</sup> was used. The calorimeter itself was surrounded by a radiation shield, the temperature of which was electronically controlled to be 0.1°C. below that of the calorimeter. The temperature was measured by a calibrated platinum resistance thermometer. A constant current of 1 ma. was passed through the thermometer and the potential measured by a Leeds & Northrup type K potentiometer. The null sensing device was a

Liston-Becker d.c. amplifier. Energy input to the calorimeter was measured by determining the current to the iron-Constantan heater and the potential across it, and by determining the time with a high precision clock (manufactured by American Time Products, Inc. Power both for the heater and the thermometer was provided by well-stabilized storage batteries. The heat capacity was measured over 5°C. intervals, and the power was adjusted so that this temperature rise took place in approximately 15 min. During the melting region, of course, this could not be done, and much smaller temperature changes were used. With this system the power input could be measured to about 0.1%.

The method of operation was as follows. After balancing the potentiometer current and adjusting the thermometer current, heat was supplied to the calorimeter, the current and voltage being measured by a Rubicon potentiometer. The output of the Liston-Becker amplifier at low gain was then fed to an electronic recorder to give a graphic picture of the course of the heating cycle. At the end of the heating cycle, the thermometer current and potential were again balanced, and, at high gain (0.3  $\mu$  v per recorder division) any temperature drifts due to heat loss by the calorimeter were recorded. These were treated in the standard way, and this correction amounted usually to a maximum of 2% except during melting of the sample. The overall precision of this technique amounted to  $\pm 0.3\%$ .

It was found to be absolutely necessary to keep exchange gas in this calorimeter, or thermal equilibrium took a very long time to be established—sometimes as long as one-half hour—and a great deal of difficulty was experienced with leaks developing at low temperatures. Furthermore, the filling factor was such that the heat capacity of the polymer was only 15% of the total heat capacity so that the precision of the results for the polymer heat capacity was lowered to 3–4%. For these various reasons, for the linear polyethylene a much simpler and more direct system was used. A cylinder of the material containing Constantan heating coils was molded, and a hole drilled into it to receive the resistance thermometer. This cylinder was then suspended in an aluminum foil inside the radiation shield. The heat capacity of the aluminum, thermometer, and heating coil amounted to only 5% of the total heat capacity, and this could easily be corrected for without extensive calibration so that the precision of this system was greatly improved. The precision of these results is of the order of 0.5% and the overall accuracy probably about 1% (see below). This is essentially the same system used by Clement and Quinnell<sup>18</sup> for measurements on metals in the liquid helium region.

#### *Materials*

Both the linear and the branched samples were well-annealed. The linear had a density of 0.968 while the branched had a density of 0.924 at 20°C. Their molecular weights are unknown, but this is not considered important. The degree of branching of the linear is probably less than one per thousand, while that of the branched is approximately 2.5%.

### Results and Discussion

The results of the specific heat determinations are presented graphically in Figure 1, where only part of the data has been used. Smooth values are given in Table I. When plotted in this manner it is almost impossible to represent the specific heat through the melting region, because of the very high values obtained. For example, for the linear sample, values as high as

TABLE I  
Smoothed Values of Specific Heat  $C_p$  in Calories per Gram

$T$ , °K.	Linear	Branched	$T$ , °K.	Linear	Branched
90	0.152	—	370	0.625	—
100	0.167	0.160	370.7	—	1.227
110	0.179	0.174	377.7	—	1.463
120	0.192	0.185	380	0.709	—
130	0.203	0.196	383.7	—	2.22
140	0.214	0.208	385.5	—	2.74
150	0.224	0.219	387.5	—	0.819
160	0.234	0.228	389.2	—	0.557
170	0.244	0.239	390	0.891	—
180	0.254	0.252	395.2	—	0.530
190	0.265	0.265	399.2	1.337	—
200	0.277	0.277	401.2	—	0.530
210	0.287	0.293	401.5	2.21	—
220	0.298	0.310	403.2	4.39	—
230	0.311	0.330	403.6	6.24	—
240	0.324	0.350	404.1	8.34	—
250	0.337	0.371	405.4	15.1	—
260	0.349	0.394	405.6	31.5	—
270	0.365	0.417	405.8	22.7	—
280	0.381	0.443	406.8	19.7	—
290	0.398	0.469	407.2	—	0.536
300	0.417	0.497	408.5	1.466	—
310	0.437	0.529	409.8	1.070	—
320	0.460	0.565	413.2	—	0.541
330	0.485	0.609	414.6	0.950	—
340	0.509	0.670	415.	—	0.544
350	0.537	0.757	420.5	0.597	—
360	0.573	0.909	426.6	0.599	—
364.7	—	1.019	432.7	0.604	—

500 cal./mole degree were obtained. Furthermore, as pointed out by Dole et al.,<sup>12</sup> measurements in this region are hard to perform, and the specific heat curve is thus somewhat schematic between 375 and 388°K. for the branched and 390 and 412°K. for the linear. For this reason it is a little difficult to determine the melting point precisely from this kind of plot. In Figure 1 the values for Marlex obtained by Wunderlich and Dole<sup>10</sup> and the low temperature data of Sochava<sup>14</sup> were included, and both sets of data are seen to be in excellent agreement with the results. Also included were a few points from the data obtained by Dole et al.<sup>12</sup> on a sample of high

pressure polyethylene. The latter results are somewhat higher, which is to be expected from the slightly lower density of their material (0.912 as compared to 0.924). Data on the branched sample are also in excellent agreement with the results of Sochava and Trapenznikova<sup>16</sup> on an unidentified but presumably low density polyethylene. The heat capacity of the branched sample in the melt is lower than that of the linear material, the heat capacity of which is in excellent agreement with the data of Wunderlich and Dole<sup>10</sup> for the same material and of Dole et al.<sup>12</sup> and Raine et al.<sup>13</sup> for branched polyethylene. The last two points for the branched sample are almost certainly in error since the calorimeter developed a short circuit

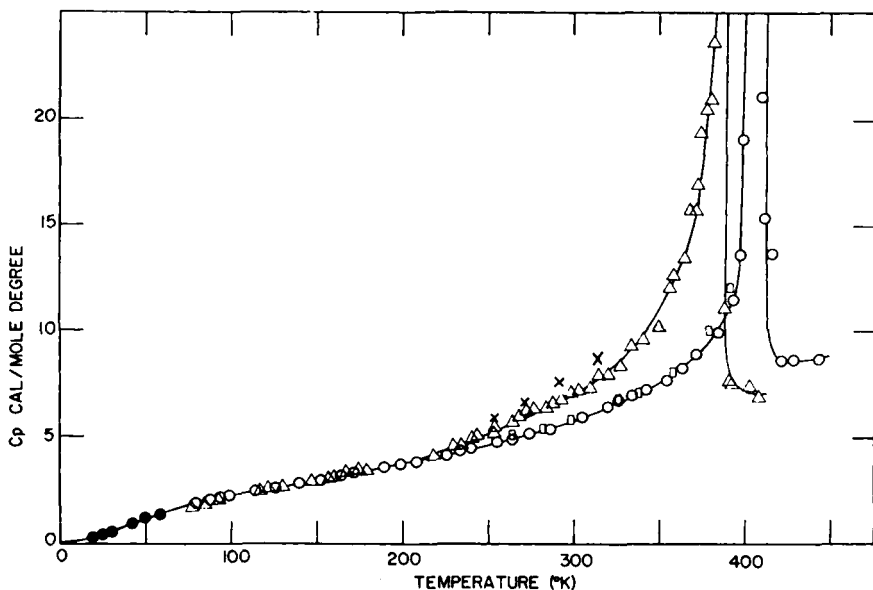


Fig. 1. The molar heat capacity of linear and branched polyethylene. (O) Linear; ( $\Delta$ ) branched; ( $\bullet$ ) data of Sochava (ref. 14); ( $\square$ ) data of Wunderlich and Dole (ref. 10) which are both for linear polyethylene; ( $\times$ ) measurements by Dole et al (ref. 12) on a sample of branched material of somewhat lower density than the authors'.

at this temperature, but the error does not vitiate the conclusions, so the results were not repeated.

There are several points of interest from these graphs. First it should be noticed that there is no clear-cut indication of a glass transition for either of these materials. There is perhaps a faint indication of a break in the curve for the branched samples at 160°K., where indeed mechanical measurements show a loss peak in polyethylene,<sup>19</sup> but there is none at 250°K. where the mechanical measurements indicate another loss peak. Experiments in the vicinity of 160°K. were accompanied by rather slow equilibrium, as occurs in the transition region,<sup>20</sup> but the effect on the specific heat was so subtle that a glass transition could not be unambiguously de-

terminated. Nothing of the sort was evident for the linear sample, and indeed this latter, except for the extended melting range, behaves like any normal crystalline solid. Perhaps this lack of a clear-cut indication of a glass transition should not be too surprising, for volume expansion measurements<sup>21</sup> also do not give an unambiguous indication of a transition. Only the more sensitive mechanical dispersion measurements indicate transitions.

Also of interest is the relative behavior of the two samples. Whereas above about 200°K. the specific heat of the branched is higher than that of the linear, below this temperature it seems actually to coincide with it or even be slightly below. Due to the relatively high error in the measurements for the branched sample it cannot, however, unambiguously be said that its specific heat is lower than that of the linear.

### Analysis

In order to compare these results with any of the theories of specific heat the values of  $C_p$  must be converted to  $C_v$ . This was done using the Nernst-Lindemann formula with a constant calculated to fit at 273°K. where data on the compressibility<sup>22</sup> and thermal expansion exist.<sup>21</sup> When comparing these results to the predictions of either the linear continuum (l.c.) theory or the Stockmayer-Hecht (S.H.) theory, both of which contain one parameter, it is customary to calculate the value of this parameter over a temperature range. Constancy of the parameter insures coincidence between theory and experiment. Results of these calculations are given in Table II,  $\theta$  being calculated from the l.c. theory and  $T_m$  from the S.H. theory. The behavior of the characteristic temperature is roughly the

TABLE II  
Characteristic Temperatures for Linear and Branched Polyethylenes

$T, ^\circ\text{K.}$	Linear		Branched	
	$\theta^a$	$T_m^b$	$\theta$	$T_m$
25	1270	833		
50	877	874		
80	829	889		
100	847	930	922	1010
120	889	984	958	1046
140	918	1004	986	1077
160	949	1032	986	1077
180	968	1051	981	1067
200	966	1053	971	1053
220	957	1050	989	978
240	923	1002	787	833
260	890	996	639	642
280	800	846		
300	667	685		

<sup>a</sup> Calculated from a one-dimensional Debye solid.

<sup>b</sup> Calculated from the Stockmayer-Hecht theory (ref. 7).

same for both theories. As temperature decreases from room temperature, the characteristic increases to a maximum then drops off again. For the S.H. theory it continues to drop, whereas in the l.c. theory it rises again. This is because this theory predicts a linear behavior at very low temperatures, and the S.H. theory must thus be considered to be a better representation at these temperatures. This is to be expected, for the S.H. theory takes into account interchain modes and is thus more realistic. It is comforting, however, that both theories give roughly the same value of characteristic temperature. This is not too surprising on inspection of the integral frequency distribution curve given by S.H. which, except at the lowest and highest frequencies, is very similar to the l.c. frequency distribution. No particular significance is attached to the difference between the two samples.

For both the linear and branched polyethylene the specific heat exceeds the Dulong and Petit value of 6 cal./mole long before the melting region is reached. This can be caused either by the structure of the  $\text{CH}_2$  unit or by some premelting. Although in the absence of reliable values for  $C_v$ , it is hardly worthwhile to pursue this point at great length, an attempt was made to fit the difference between the observed specific heat and that calculated by the l.c. theory with an Einstein function, which should closely approximate this situation. The results of this calculation are shown in Table III, where the values of the Einstein characteristic temperature  $\theta_E$  are given for a range of temperatures. Considering the crudity of the analysis, these values for the linear polyethylene are reasonably constant, and the wave numbers calculated from the characteristic temperature of 1800 for the linear sample are  $1250 \text{ cm.}^{-1}$ , which is not too far from the value of  $1460 \text{ cm.}^{-1}$  for the "scissors frequency" mode of  $\text{CH}_2$  vibration in polyethylene.<sup>23</sup> It is not, however, worthwhile to pursue this further.

TABLE III  
Einstein Characteristic Temperatures

$T, ^\circ\text{K.}$	Linear	Branched
220	2340	1583
240	1967	1446
260	1940	1376
280	1728	1299
300	1744	1293
320	1658	1077
340	1567	
360	1452	
380	1173	

An attempt also was made to fit the present data for the linear sample with the interaction theory for Tarassov.<sup>6</sup> Since this theory contains two parameters,  $\theta_2$  and  $\theta_1$ , it is not possible to carry out the same type of analysis as above. What was done was to compute values of the specific heat from



eq. (3) for various values of  $\theta_2$  and  $\theta_1$  and to determine what values give the best fit with the data. Using an electronic computer this is not too difficult. The results of this computation are shown in Figure 2, where the data of Sochava are also used. The best fit was obtained with values of  $\theta_1$

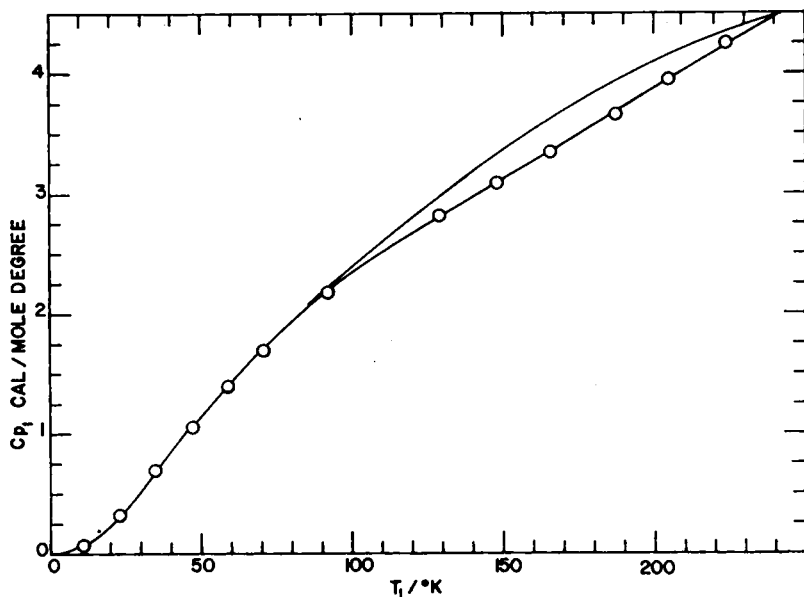


Fig. 2. A comparison of the Tarassov theory with experiment. The upper curve is theoretical with  $\theta_1 = 820$  and  $\theta_2 = 110$  while the lower curve is from the present data and those of Sochava.

of  $820^\circ\text{K.}$  and  $\theta_2$  of  $110^\circ\text{K.}$ , and the Tarassov function fits the data very well up to about  $100^\circ\text{K.}$ , deviates upward and then crosses the experimental data at  $250^\circ\text{K.}$  The data of Sochava and Trapenznikova<sup>16</sup> are also in good agreement with the result shown here. For purposes of comparison with other materials,<sup>5</sup> the values of  $\theta_1$  and  $\theta_2$  for selenium are  $370$  and  $75^\circ\text{K.}$ , respectively.

#### *Thermodynamic Analysis*

Using the data of Sochava<sup>14</sup> it is possible to determine the entropy and enthalpy referred to absolute zero of linear polyethylene and these values are given in Table IV, where values for the branched are also included. Because of the ambiguity in the low temperature values of the latter its entropy have been arbitrarily made to coincide with that of the linear at  $80^\circ\text{K.}$  Most of these data were taken from integrations of large plots of the appropriate specific heat data. However, in the melting region (above  $395^\circ\text{K.}$  for linear and  $362^\circ\text{K.}$  for branched) we have used the method of Dole et al.<sup>12</sup> and used the heats actually supplied to the calorimeter. No data exist in the literature with which these data may be compared directly. However,

TABLE IV  
 Entropy and Enthalpy Values

$T$ , °K.	Linear		Branched	
	$S_0$ , e.u./mole	$H_0$ , cal./mole	$S_0$ , e.u./mole	$H_0$ , cal./mole
20	0.1302	1.5		
40	0.447	12.2		
60	0.926	34.9		
80	1.402	68.7	1.402	68.7
100	1.876	111.4	1.876	111.4
120	2.330	161.6	2.312	157.9
140	2.765	218.3	2.729	211.3
160	3.184	281.2	3.133	270.8
180	3.588	349.6	3.521	377.9
200	3.979	423.9	3.920	412.1
220	4.362	504.4	4.312	494.1
240	4.739	591.6	4.732	586.5
260	5.118	685.9	5.124	690.6
280	5.497	789.2	5.551	807.6
300	5.881	900.8	6.016	939.1
320	6.276	1023.5	6.542	1087.4
340	6.688	1159.5	7.030	1258.8
360	7.119	1310.4	7.648	1473.8
380	7.592	1486.6	8.554	1822.8
385	7.725	1537.9	8.918	1968.3
390	7.867	1595.9	9.244	2057.9
395	8.027	1668.3	9.342	2095.0
400	8.228	1754.4	9.435	2132.1
405	9.011	2114.2	9.526	2169.6
410	10.30	2592.5	9.618	2207.2
415	10.42	2647.2	9.710	2245.1

an analysis of the data of Parks et al.<sup>24</sup> and of Finke et al.,<sup>25</sup> on normal paraffins indicates an entropy at 298.16°K. of about 6.0 e.u./mole of CH<sub>2</sub>, which is about 2.3% higher than our value of 5.863. This difference is not unreasonable.

In order to calculate the entropy of the glass at absolute zero from eq. (5), we used the data of Table IV and the degree of crystallinity. The latter may be calculated from the density, or from the specific heat measurements by methods previously outlined.<sup>10,12,13</sup> In addition, a variant of a method due to Hoffman<sup>27</sup> was used. The entropy curve for the linear sample between 250 and 375°K. was fitted with a second-order equation in the temperature, and this was used to extrapolate the enthalpy of the solid to the melting point. The difference between the liquid enthalpy and this extrapolated curve was taken as the heat of fusion of the material, which, when divided by the heat of fusion of pure crystalline polyethylene, gives the degree of crystallinity. The results for the degree of crystallinity for the linear sample computed from the equations of Wunderlich and Dole<sup>10</sup> are rather high but not impossible on the basis of recent results by Mat-

TABLE V  
Results for  $S_g^0$

	$f$ , linear	$f$ , branched	$\Delta f$	e.u./ $S_g^0$ , mole
Density, 25°C.	80.0	48.8	31.2	2.3
Specific heat <sup>a</sup>	87.5	47.5	40.0	1.8
Specific heat <sup>b</sup>	93.8	47.0	46.8	1.6

<sup>a</sup> Method outlined in text.

<sup>b</sup> Method used by Wunderlich and Dole (ref. 10).

suoka.<sup>28</sup> The results for  $S_g^0$  are given in Table V. There is quite a high error associated with these results (see below), but the value of 1.0–2.6 e.u./mole is not unreasonable in light of what has been observed for non-polymeric glasses.<sup>20</sup> The interpretation of this result in the absence of a clear-cut glass transition is open to question. Perhaps due to barriers to rotation, we have never reached a true glassy phase. Perhaps the true morphological picture of polyethylene is not that of a two-phase amorphous-crystalline material, but rather one of imperfect yet essentially completely crystalline material. Certainly any attempt to assess the validity of the glass transition theory of Gibbs and DiMarzio (which predicts the configurational entropy of a true glass to be zero) on the basis of the present results would be highly questionable. Nevertheless, it can be concluded from these results that the entropy is positive, and that for a hypothetical amorphous polyethylene it is somewhat larger than  $R \ln 2$  (1.38) e.u./mole. This implies that in the glass the fraction of bonds flexed is somewhat more than one-half.

### Conclusions

The lack of complete agreement between our results and theories of the specific heat of chain structure is perhaps not too surprising. Recent morphological studies indicate that polymers such as polyethylene even in the solid state are composed of highly crystalline lamellae approximately 100 Å thick. This unique morphology would make surface effects important, and perhaps these may be the source of the discrepancy. This would be particularly true for the theory of Stockmayer and Hecht which assumes essentially an infinite crystal, and to a lesser extent for the Tarassov theory. One would not, in any case, expect the linear-continuum theory to fit very well. This same morphology may be the basis for the lack of an observable glass transition.

### Errors

The average deviation of the experimental points from the smooth specific heat curve was 0.55% for the linear sample and 3.4% for the

branched sample. Because of the large number of points this leads to only a small error in the integrals. However, the absolute error or, what is more important, the difference in absolute error between the two samples is more difficult to assess. By comparison of these results with published values and the behavior of the curves themselves, it is concluded that the results for the branched sample may be low by as much as 2% and are probably not high. The results on the linear sample, particularly in the melt, may also be somewhat high. This was the basis for the error assignment in Table IV. It is felt that we have a maximum figure for  $S^0g$ , but the minimum may be somewhat lower than the results.

In addition to these experimental errors there was the difficulty of interpreting the meaning of thermodynamic measurements on what may be a nonequilibrium system such as a glass, as well as interpreting the meaning of a measured entropy change on a system as difficult to maintain at thermodynamic equilibrium as a polymer near the melting point. These are all errors which cannot be assessed, but it is felt that they will not change the qualitative nature of the conclusions.

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### Synopsis

The heat capacity of linear and branched polyethylene has been measured over the temperature range from 90°K. through the melting point. These and lower temperature data in the literature have been compared with the values calculated from a one-dimensional Debye model, the Stockmayer-Hecht calculation of the specific heat of polymers, and the two-parameter specific heat theory of Tarassov. The Stockmayer-Hecht calculation gives a better fit at very low temperatures than the one-dimensional Debye calculation, although the average characteristic temperatures are not too greatly different in the two cases. There is no appreciable difference between the linear and branched samples. The Tarassov theory gives an excellent fit at temperatures below 100°K. From the data the entropy and enthalpy referred to absolute zero were calculated. Although no obvious glass transition temperature was observed, the entropy difference between the two samples was used to calculate the residual entropy of "polyethylene glass" at absolute zero assuming a simple two-phase crystalline-amorphous model for the polymers. This residual entropy is  $1.7 \pm 0.7$  e.u./mole.

### Résumé

On a mesuré la capacité calorifique du polyéthylène linéaire et branché dans un domaine de température allant de 90°K jusqu'au point de fusion. On a comparé ces résultats et ceux de la littérature effectués à température plus basse avec les valeurs calculées, partir d'un modèle unidimensionnel de Debye, avec le calcul de Stockmayer-Hecht sur la chaleur spécifique des polymères et avec la théorie de la chaleur spécifique à deux paramètres de Tarassov. Le calcul de Stockmayer-Hecht donne une meilleure concordance pour les températures très basses que le calcul uni-dimensionnel de Debye, bien que les températures moyennes caractéristiques ne soient pas tellement différentes dans les deux cas. Il n'y a pas de différence appréciable entre les échantillons linéaires et branchés. La théorie de Tarassov donne un excellent accord pour des températures inférieures à 100°K. A partir des résultats on a calculé l'entropie et l'enthalpie rapportée au zéro absolu. Quoique nous n'ayons pas observé d'une façon évidente la température de transition vitreuse, nous nous sommes servis de la différence d'entropie entre les deux échantillons pour calculer l'entropie résiduelle du "polyéthylène vitreux" au zéro absolu en admettant un modèle simple à deux phases, cristallin amorphe, pour les polymères. Cette entropie résiduelle est de  $1.9 \pm 0.9$  e.u./mole.

### Zusammenfassung

Die Wärmekapazität von linearem und verzweigten Polyäthylen wurde im Temperaturbereich von 90°K bis zum Schmelzpunkt gemessen. Diese Daten und Literaturdaten bei tieferer Temperatur wurden sowohl mit den aus einem eindimensionalen Debye-modell berechneten Werten als auch mit der Stockmayer-Hecht-Berechnung der spezifischen Wärme von Polymeren und der zweiparametrischen Theorie der spezifischen Wärme von Tarassov verglichen. Die Berechnung nach Stockmayer und Hecht liefert bei sehr niedrigen Temperaturen eine besser Übereinstimmung als die Berechnung nach dem eindimensionalen Debye-Modell, obgleich die mittlere charakterische Temperatur in den beiden Fällen nicht allzu verschieden ist. Es besteht kein wesentlicher Unterschied

zwischen den linearen und verzweigten Proben. Die Theorie von Tarassov liefert bei Temperaturen unterhalb 100°K eine ausgezeichnete Übereinstimmung. Aus den Daten wurden Entropie und Enthalpie für den absoluten Nullpunkt berechnet. Es trat zwar keine beobachtbare Glasumwandlungstemperatur auf, doch wurde der Entropieunterschied zwischen den beiden Proben zur Berechnung der Nullpunktentropie des "Polyäthylenglases" unter Annahme eines einfachen zwei-Phasen-Modells, kristallin-amorph, für die Polymeren verwendet. Diese Nullpunktentropie beträgt,  $1,9 \pm 0,9$  E.U./Mol.

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