

Heat Capacities of Polyethylene III. One Linear and One Branched Sample from 5 to 350 K

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Heat capacities of two polyethylene samples, one linear with a density of 0.973 g cm^{-3} and one branched with a density of 0.91 g cm^{-3} , have been determined by adiabatic calorimetry from 5 to 360 K in a different experimental arrangement than employed for studies of other polyethylene samples in this series. The heat capacity behavior of these two samples confirms expectations for samples with corresponding densities.

Key words: Adiabatic calorimetry; branched polyethylene; calorimetry; cryogenic temperature; heat capacity; linear polyethylene; polyethylene; thermodynamic properties.

1. Introduction

Heat capacities of two polyethylene samples, one linear and one branched, were determined from 5 to 350 K by adiabatic calorimetry. The linear sample has been treated to yield a relatively high density value of 0.973 g cm^{-3} . The branched sample was one of the lowest density polyethylene sample available, its density value is 0.91 g cm^{-3} . The heat capacity behavior of these two samples, produced by different sources and measured with different experimental arrangements than that for four samples derived from two Standard Reference Materials [1, 2],¹ closely parallels the behavior (as a function of density) of the Standard Reference Materials [2].

2. Experimental Detail

2.1. Calorimetry

Heat capacities of the two polyethylene samples were measured with the Mark I cryostat in the Department of Chemistry, University of Michigan, Ann Arbor, Michigan. The design and the operational procedures of this aneroid-type adiabatic cryostat have been described elsewhere [3, 4], and are similar to a cryostat

described in more detail elsewhere [5]. The gold-plated copper sample container, laboratory designation W-9 [6], was used in the measurements of the branched polyethylene sample. Container, W-10, was used in the measurements of the linear polyethylene sample. Container W-10 is of similar design to W-9 except that there are no internal vanes for thermal conduction and the entire top of the container is made of copper and is removable for the admission of samples.

Temperatures were measured by a capsule-type platinum resistance thermometer, laboratory designation A-3, inserted in the axial well of the sample container. This thermometer has been calibrated by the National Bureau of Standards (NBS) according to the International Practical Temperature Scale (IPTS) of 1948 above 90 K; and to the NBS-1955 provisional temperature scale between 10 and 90 K. Below 10 K, a laboratory provisional scale was obtained by solving for the constants in the equation [7] $R = A + BT^2 + CT^5$ from the observed resistances at the boiling point of helium and at 10 K and the dR/dT value at 10 K.

To correct the original heat capacity data to temperatures expressed in terms of IPTS-1968 [8], the following procedures were used to provide adjustments between the several temperature scales.

Above 13.81 K, an approximate correction scheme was used to correct the heat capacities to values they

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¹ Figures in brackets indicate the literature references at the end of this paper.

would have if they were determined by a thermometer calibrated in accordance to the IPTS-1968 [8]. This procedure [9] involves the multiplication of each experimental heat capacity value by a factor of $1 + d(T_{68} - T)/dT$, where T is the temperature scale used in the experiment and $(T_{68} - T)$ is the difference between the IPTS-1968 and the experimental temperature scale. Tables of the differences between the IPTS-1968 and the IPTS-1948 or the NBS-1955 provisional scale are given in reference [10], and in more detail elsewhere [11].

Heat capacity values below 13.81 K may be corrected from the previously mentioned laboratory provisional temperature scale to a temperature scale which approximates the thermodynamic temperature scale or the NBS-1965 (2–20 K) temperature scale [12] based on acoustic thermometry. An improved thermometer calibration with an accuracy of about 0.02 K was obtained from a two-way structure analysis of the behaviors of a group of platinum resistance thermometers [13]. The differences between this improved calibration and the laboratory provisional scale were then used to correct the heat capacity values in a manner similar to the procedure described above for correcting heat capacity values at temperatures above 13.81 K.

2.2. Materials

a. Linear Polyethylene

A molded piece of Marlex 50² was supplied by Dr. Raymond L. Arnett of the Phillips Petroleum Co., Bartlesville, Oklahoma. This piece was machined as a cylinder with an axial hole (to accommodate the thermometer-heater wall) and was then loaded into the sample container, laboratory designation W-10, which has no thermal conducting vanes. The density of the machined sample was determined to be 0.973 g cm⁻³. The mass of the calorimetric sample was 87.121 g in vacuo. Helium gas at a pressure of 815 mm Hg (108 kPa) was sealed in to aid the thermal conduction within the sample container. Indium-tin alloy (50–50) was used to seal the top of the sample container. Apiezon.T grease was used to establish thermal contact between the sample container and the heater-thermometer assembly. In order to minimize the corrections, masses of both solder and grease were adjusted to approximately the values used when the heat capacity of the empty sample container was measured.

b. Branched Polyethylene

A sample with the designation DYNH CT-1660 was also supplied by Dr. Raymond L. Arnett of the Phillips Petroleum Co., Bartlesville, Oklahoma. This sample consists of cylindrical pellets about 5 mm diam and 5 mm length. The density was reported by Dr. Arnett to be 0.91 g cm⁻³. A sample mass of 45.122 g in vacuum was loaded in the sample container, laboratory

designation W-9. Dried and purified helium gas at a pressure of 190 mm Hg (25.2 kPa) was sealed in the calorimeter to aid the thermal conduction. Masses of indium-tin (50–50) solder and grease are adjusted to approximate the amounts used during empty sample container measurements.

3. Results

The experimental heat capacity determinations are listed chronologically in table 1 and are shown graphically in Figure 1. The approximate temperature

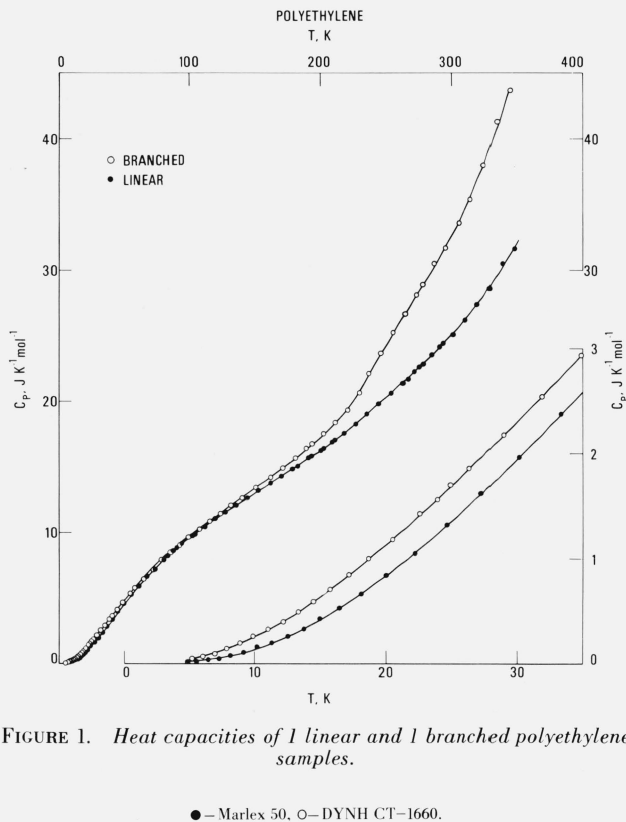


FIGURE 1. Heat capacities of 1 linear and 1 branched polyethylene samples.

increments of each determination may be inferred from the adjacent mean temperatures in a series of continuous determinations. An analytically determined curvature correction has been applied to the observed values of $\Delta H/\Delta T$ to correct for the finite size of the temperature increment used in the heat capacity determination. The molecular weight for the repeating methylene segment, $-\text{CH}_2-$, is taken as 14.027. Molal values of the heat capacity at constant pressure and the entropy and enthalpy increments generated by a least-square curve-fitting program are listed at selected rounded temperatures in table 2. The reported values of the heat capacities are believed to have probable errors less than 0.1 percent at temperatures above 25 K, about 1 percent at 10 K and 5 percent at 5 K. The probable error of the thermodynamic functions are considered to be less than 0.1 percent above 100 K. H_0 and S_0 refer to the zero point enthalpy

²Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

and residual entropy of individual samples. Gibbs energies for these samples are not given in table 2,

because these samples are expected to have undetermined residual entropies at 0 K.

TABLE I. *Heat Capacities of Polyethylene*

(base mole $[-CH_2-] = 14.027$)

A. Linear Polyethylene ($\rho = 0.973 \text{ g cm}^{-3}$)			
$T, \text{ K } C_p, \text{ J K}^{-1} \text{ mol}^{-1}$		$T, \text{ K } C_p, \text{ J K}^{-1} \text{ mol}^{-1}$	
SERIES I		SERIES VII	
80.41	7.953	4.83	0.016
83.41	8.242	5.58	0.022
89.78	8.841	6.44	0.035
SERIES II		7.25	0.054
SERIES III		8.16	0.081
104.13	9.856	9.15	0.122
111.84	10.41	10.21	0.176
119.96	11.07	11.31	0.210
128.03	11.51	12.52	0.265
136.03	12.09	13.77	0.341
144.31	12.64	15.06	0.429
152.99	13.21	16.48	0.533
161.82	13.78	18.15	0.667
170.27	14.32	20.07	0.841
178.43	14.83	22.25	1.055
SERIES IV		24.69	1.317
182.55	15.07	27.30	1.622
191.25	15.65	30.15	1.964
200.25	16.26	33.34	2.375
209.09	16.86	36.90	2.845
217.87	17.51	40.89	3.376
226.96	18.20	45.23	3.945
SERIES V		49.84	4.542
275.83	22.58	SERIES VIII	
284.92	23.48	50.12	4.574
293.96	24.40	55.46	5.236
SERIES VI		61.16	5.935
291.67	24.10	67.26	6.620
300.82	25.09	73.65	7.214
310.33	26.18	80.32	7.934
320.12	27.36	87.05	8.613
329.53	28.58	94.22	9.144
338.51	30.46	102.37	9.734
347.51	31.62	SERIES IX	
SERIES VII		193.27	15.80
SERIES VIII		202.14	16.36
SERIES IX		211.13	16.99
SERIES X		266.77	21.63
SERIES X		278.40	22.75

TABLE I—Continued

B. Branched Polyethylene ($\rho = 0.91 \text{ g cm}^{-3}$)			
$T, \text{ K } C_p, \text{ J K}^{-1} \text{ mol}^{-1}$		$T, \text{ K } C_p, \text{ J K}^{-1} \text{ mol}^{-1}$	
SERIES I		SERIES V	
5.20	0.039	193.89	16.74
6.05	.062	202.65	17.54
6.98	.098	211.45	18.38
7.87	.146	220.45	19.35
8.87	.200	229.57	20.60
9.90	.284	SERIES VI	
11.04	.331	237.06	22.08
12.20	.406	246.25	23.64
13.32	.499	255.39	25.18
14.51	.597	264.61	26.60
15.79	.712	273.75	28.08
17.16	.841	SERIES VII	
18.70	.997	278.37	28.92
20.52	1.184	286.74	30.43
22.63	1.422	295.89	31.67
24.93	1.708	305.57	33.52
SERIES II		314.85	35.34
23.94	1.563	SERIES VIII	
26.39	1.858	324.45	37.97
29.00	2.175	334.68	41.29
31.87	2.540	344.69	43.72
34.93	2.931	SERIES IX	
38.47	3.381	40.32	3.612
SERIES III		44.44	4.125
40.32	3.612	48.95	4.681
44.44	4.125	54.26	5.306
48.95	4.681	SERIES IV	
54.26	5.306	58.16	5.749
SERIES IV		64.59	6.473
58.16	5.749	71.56	7.331
64.59	6.473	78.46	7.661
71.56	7.331	85.47	8.506
78.46	7.661	92.32	9.068
85.47	8.506	99.62	9.621
92.32	9.068	107.66	10.23
99.62	9.621	115.56	10.83
107.66	10.23	123.49	11.42
115.56	10.83	131.71	12.03
123.49	11.42	151.04	13.45
131.71	12.03	161.99	14.22
151.04	13.45	171.15	14.93
161.99	14.22	180.32	15.66
171.15	14.93	189.54	16.39
180.32	15.66	SERIES X	
189.54	16.39	SERIES X	

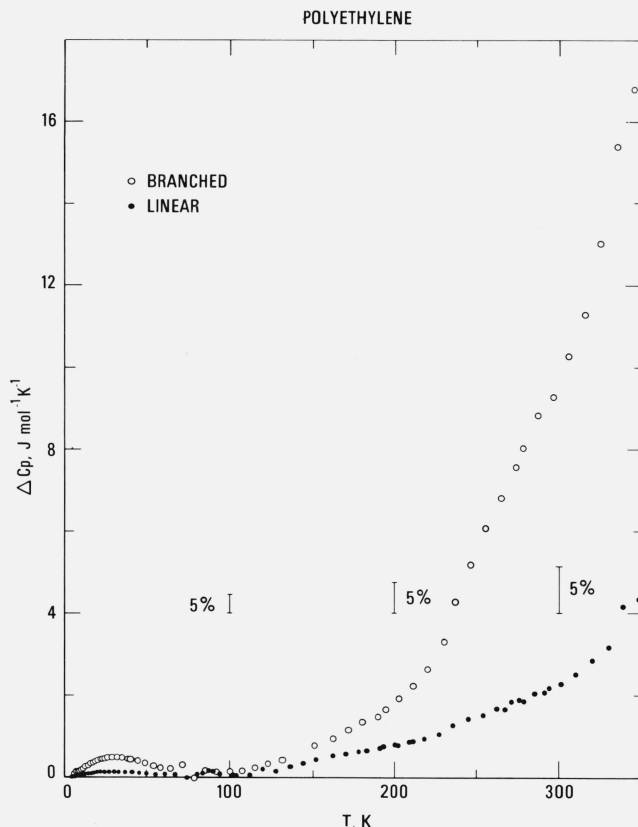
TABLE 2. *Thermodynamic Properties of Polyethylene*(Units in K, J and mole $[-\text{CH}_2-]=14.027$)

<i>T</i>	Linear (Marlex 50)			Branched (DYNH CT-1660)		
	<i>C_p</i>	<i>H-H₀</i>	<i>S-S₀</i>	<i>C_p</i>	<i>H-H₀</i>	<i>S-S₀</i>
5	0.020	0.03	0.007	0.038	0.05	0.013
10	0.155	0.38	0.050	0.273	0.72	0.097
15	0.422	1.77	0.160	0.636	2.94	0.272
20	0.833	4.85	0.334	1.134	7.32	0.521
25	1.357	10.29	0.574	1.696	14.39	0.833
30	1.941	18.51	0.872	2.303	24.36	1.195
35	2.595	29.84	1.221	2.944	37.48	1.599
40	3.254	44.46	1.610	3.570	53.77	2.033
45	3.911	62.38	2.031	4.187	73.16	2.489
50	4.557	83.55	2.477	4.798	95.63	2.962
60	5.789	135.4	3.418	5.988	149.6	3.943
70	6.912	199.0	4.396	7.092	215.1	4.950
80	7.915	273.2	5.386	8.063	291.0	5.962
90	8.801	356.9	6.371	8.901	375.9	6.961
100	9.592	448.9	7.340	9.651	468.7	7.938
110	10.31	548.5	8.288	10.39	568.9	8.893
120	11.00	655.1	9.215	11.17	676.7	9.830
130	11.67	768.4	10.12	11.92	792.2	10.75
140	12.36	888.5	11.01	12.62	914.8	11.66
150	13.02	1016	11.89	13.36	1045	12.56
160	13.67	1149	12.75	14.11	1182	13.45
170	14.30	1289	13.60	14.85	1327	14.32
180	14.93	1435	14.43	15.62	1479	15.19
190	15.57	1587	15.26	16.41	1639	16.06
200	16.23	1746	16.07	17.27	1808	16.92
210	16.93	1912	16.88	18.24	1985	17.79
220	17.67	2085	17.68	19.37	2173	18.66
230	18.48	2266	18.49	20.75	2373	19.55
240	19.35	2455	19.29	22.59	2590	20.47
250	20.23	2653	20.10	24.32	2825	21.43
260	21.11	2859	20.91	25.93	3076	22.42
270	22.00	3075	21.72	27.50	3343	23.42
280	22.93	3300	22.54	29.08	3626	24.45
290	23.92	3534	23.36	30.75	3925	25.50
300	24.99	3778	24.19	32.55	4241	26.57
310	26.15	4034	25.03	34.56	4577	27.67
320	27.43	4302	25.88	36.83	4933	28.81
330	28.84	4583	26.74	39.43	5314	29.98
340	30.41	4879	27.63	42.42	5723	31.20
350	32.16	5192	28.53	45.87	6164	32.48
273.15	22.29	3145	21.98	27.99	3430	23.75
298.15	24.79	3732	24.04	32.20	4181	26.37

In the course of determining the heat capacities of the linear polyethylene sample from Series I to IV, there was a loose connection in the circuit for the heater current measurement. Therefore, the energy input was calculated by adjusting the observed heater resistance values to the known resistance values obtained from previous measurements. These corrections ranged from 1 to 3 percent of the observed heat capacity values. After series IV, it was found that the top of the sample container was pushed out, apparently due to the large thermal expansion of the sample at higher temperatures. The measurements starting from Series V were made after the sample container top was resoldered and the container was sealed in with helium gas at a pressure of 719 mm (95.5 kPa).

The heat capacity of the calorimetric sample of Marlex 50 is about 2–3 percent lower than that of SRM-1475 in the as received condition [1]. The differences are probably due to the difference in the

densities and the degrees of crystallinity of the two samples. The density of SRM 1475 as received is 0.955 g cm^{-3} , which is slightly lower than that of the Marlex 50 sample, 0.971 g cm^{-3} , used in the present calorimetric study. The higher density indicates a higher crystalline content or a lower amorphous content. The heat capacity of crystalline polyethylene is lower than that of the amorphous phase over the entire temperature range of investigation. Below 300 K, the behavior of the present linear polyethylene sample agrees very well with the values obtained by interpolating to the corresponding density from the behaviors of three linear polyethylene samples of the same origin but of different densities in figure 2 of reference [2].

FIGURE 2. *Comparison of heat capacities of polyethylene samples versus estimated heat capacity of crystalline linear polyethylene.*

●—linear, Marlex 50, ○—branched, DYNH CT-1660.

When the heat capacity differences between the Marlex 50 and estimated completely crystalline linear polyethylene [2] are plotted in Figure 2, two regions of more abrupt rise in the heat capacity differences, around 150 and 250 K, may be noticed. The higher temperature rise has been ascribed to the glass transition phenomena on the basis of adiabatic temperature drift observations [14] and volume relaxation studies [15]. Heat capacity values for Marlex 50 based on IPTS-1948 and NBS-1955 scales were used in the difference plots in figure 7 of reference

[2]. After the values have been corrected to IPTS-1968 representation as described in previous section, the irregularities in the region 70-90 K due to the joining of the two scales [16] are diminished in magnitude but still noticeable.

The heat capacity behavior of the branched polyethylene used in this study is very similar to that of SRM-1476 branched polyethylene whole polymer [1]. Except in the region from 100 to 200 K, the heat capacities of these two samples and other branched polyethylene samples [17, 18, 19] are in general slightly higher than linear polyethylene results extrapolated to corresponding densities (cf. fig. 2 in reference [2]). Thus, the curves of the difference between the heat capacities, figure 2, of the branched polyethylene and 100 percent crystalline linear polyethylene show a more pronounced abrupt change in the region of 250 K than the corresponding curves for linear polyethylene and almost smooth curves in the region of 150 K.

Relatively large positive temperature drifts have been observed during the measurements of the branched polyethylene DYNH CT-1660 sample. In the 200 to 300 K region, a maximum drift of 0.01 K min⁻¹ was observed at around 255 K. This is probably similar to that which has been observed for the quenched, branched polyethylene, SRM 1476, in reference [1]. At temperatures above 300 K, the drift of DYNH CT-1660 gradually increased to about 0.15 K min⁻¹ at about 350 K. Similar behavior has been noted for SRM-1476 when it was heated above room temperature for the first time [1]. Calorimetric temperature drifts longer and larger than usual have also been observed for the linear polyethylene, Marlex 50, sample at temperatures above 220 K. Below 300 K, the maximum temperature drift observed at 30 min after the termination of heater input was less than 0.005 K min⁻¹. Near the highest measurement temperature the drift was still less than 0.01 K min⁻¹.

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