

Heat Capacities of Polyethylene from 2 to 360 K.

I. Standard Samples of Linear and Branched Polyethylene Whole Polymer

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(March 14, 1973)

Heat capacities of two well characterized polyethylene samples have been measured from 2 to 360 K in a precision vacuum adiabatic calorimeter. The two samples are derived from the same stocks from which NBS standard reference materials (SRM) 1475 and 1476 for linear and branched polyethylene whole polymers, respectively, were established. Both samples have been studied in the conditions as received. The branched polyethylene sample has also been studied following various thermal treatments in the calorimeter. The effect of thermal history on the behavior of branched polyethylene has also been studied by differential scanning calorimetry.

Key words: Branched polyethylene; calorimetry; glass transition; heat capacity; linear polyethylene; polyethylene; thermal analysis; thermodynamic properties.

1. Introduction

Polyethylene is the simplest hydrocarbon chain polymer composed of methylene groups. This basic polymer has been the most widely used and studied polymer. There are no less than twenty papers [1–21]¹ concerning the experimental heat capacity behavior of polyethylene of various origins and treatments. However most of the research papers present their results mainly or entirely in graphs [1, 2, 5, 6, 7, 10, 11, 13, 16, 18], in simple (linear or quadratic) analytical equations [1, 8, 12, 21] or in tables of smoothed values [3, 4, 9, 14, 15, 19, 20]. Hence even if the data is of high precision some fine features will be lost in the smoothing procedures and representations. Only one paper [17], concerning heat capacities of polyethylene samples below 30 K, listed the actual heat capacity data. Partial listing of the heat capacity data above 320 K appeared in another paper [21].

The present paper reports detailed investigations by precision adiabatic calorimetry from 2 to 360 K on two well characterized polyethylene samples in their as-received conditions. Over most of the temperature range investigated, the precision of the calorimetric measurement is better than 0.1 percent. These two samples are available as the National Bureau of Standards (NBS) standard reference materials (SRM) 1475 and 1476 for linear and branched polyethylene whole polymer, respectively. They are intended primarily as characterization standards for molecular weights and rheological properties.

Subsequent papers in this series will deal with the heat capacity behavior of densified linear polyethylene samples, the detection of the glass transformation in partially crystalline polyethylene, the deduction of heat capacity of 100 percent crystalline linear polyethylene, and a comparison of the heat capacity behavior of polyethylene from various origins and investigations.

2. Experimental Detail

2.1. Calorimetric Technique

Heat capacity measurements on the two polyethylene samples were performed in the vacuum adiabatic calorimeter described previously [22] with major modifications noted elsewhere [23]. The measuring procedures and methods of data treatment were discussed in more detail in another paper [24].

A calibrated platinum resistance thermometer was used to interpolate the temperature according to the International Practical Temperature Scale of 1968 [25, 26] above 13.81 K. Below 13.81 K the platinum thermometer was compared against a germanium resistance thermometer which has been calibrated in accordance with the NBS 1965 (2–20 K) provisional scale [27]. From this comparison, a fifth-degree polynomial [28] was generated to interpolate the temperature of the platinum thermometer below 13.81 K.

2.2. Material

Both calorimetric samples of the linear and of the branched polyethylene were taken from the stocks

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

from which NBS standard reference materials (SRM) 1475 and 1476, respectively, were established.

a. Linear Polyethylene

The Certificate for SRM 1475, Linear Polyethylene (Whole Polymer) gives the following information. The weight-averaged molecular weight, M_w , is 52,000 as determined by light-scattering in 1-chloronaphthalene at 135°C. Gel permeation chromatography gave a value of M_w as 53,070 with the ratio $M_z:M_w:M_n=7.54:2.90:1$. The methyl group content is 0.15 methyl groups per 100 carbon atoms. The limiting viscosity numbers (dl/g) are 0.890, 1.010, and 1.180 in 1-chloronaphthalene, 1,2,4-trichlorobenzene and decalin, respectively, at 130°C with a pellet to pellet coefficient of variation of 3 percent. This sample has an ash content of 0.002 percent. No volatiles were detected by a gas-chromatographic procedure capable of detecting 0.5 percent volatiles. The manufacturer of this sample added to the polymer 111 ppm of the anti-oxidant, *tetrakis*[methylene-3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)propionate] methane. The density reported in the certificate is $0.9784_4 \text{ g cm}^{-3}$ at 23°C, as determined by ASTM Method D1505-67 on a sample prepared by Procedure A, ASTM Method D1928-68. This density is obtained after a pretreatment of the sample and therefore differs from the density of the sample as received. Detailed reports on the investigations required for the certificate are described in a collection of papers [29].

The calorimetric sample for the linear polyethylene (SRM 1475) in the as received condition was composed of ellipsoidal pellets about 2-3 mm in diameter and about 3-5 mm in length. No treatment was applied to the sample before the heat capacity measurement. The density of the sample before the calorimetric measurement was 0.954 g cm^{-3} at 23°C with a variation of $\pm 0.001 \text{ g cm}^{-3}$ as determined by a flotation method in an ethanol-water mixture. After the heat capacity measurement, the density of the calorimetric sample was determined again. No change, greater than the initial variation, was found in the density from that of the sample before the calorimetric measurement. The variation in the density of the sample after the calorimetric measurement is however reduced to about 0.0005 g cm^{-3} . The density measurements were performed on no less than ten randomly chosen pellets from each of the samples.

The mass of the calorimetric sample was 78.572 g in vacuo, which corresponds to 5.6015 base mole or gram formula weight of methylene group, $-\text{CH}_2-$. The density values of 0.954 and $0.00117 \text{ g cm}^{-3}$ for the sample and for the air, respectively, were used to estimate the buoyancy correction. The top of the sample container was soldered on with In-Sn solder

while the container was surrounded with a water jacket, so that the sample was not heated above the ambient temperature during the soldering process. Helium gas at a pressure of 10 cm Hg was sealed in to facilitate the thermal conduction within the sample container.

b. Branched Polyethylene

The certificate for SRM 1476, Branched Polyethylene (Whole Polymer) gives the following information. The limiting viscosity numbers (dl/g) are 0.8132, 0.9024, and 1.042 in 1-chloronaphthalene, 1,2,4-trichlorobenzene and decalin, respectively, at 130°C. No pellet to pellet variation in limiting viscosity number was found. The melt index is 1.19 g/10 min. The density is 0.9312 g cm^{-3} at 23°C as determined by previously mentioned ASTM procedures. The manufacturer of this sample has added to the polymer 50 ppm of the antioxidant, 4,4'-thio-bis(6-*t*-butyl-3-cresol).

The calorimetric sample for the branched polyethylene was taken from the same stock from which SRM 1476 was established. The material was in the shape of cylindrical pellets, about 3 mm in diameter and 2-3 mm in length. The initial density of the sample before the calorimetric measurement was 0.9247 g cm^{-3} , at 23°C with a variation less than 0.001 g cm^{-3} by flotation method. The final density of the sample after the heat capacity measurement was 0.9272 g cm^{-3} with a variation of less than 0.0005 g cm^{-3} .

The mass of the calorimetric sample was 66.258 g in vacuo which corresponds to 4.7236 base mole or gram formula weight of methylene group, $-\text{CH}_2-$. The density values of 0.925 and $0.00117 \text{ g cm}^{-3}$ for the sample and for air, respectively, were used to estimate the buoyancy correction. Precautions were taken so as not to alter the condition of the sample from that as received. The top of the container was soldered on with In-Sn solder while the container was surrounded with a water jacket to prevent heating of the sample. Helium gas at a pressure of 10 cm Hg was sealed in to aid the thermal conduction within the container.

3. Results

The results of the heat capacity measurements are tabulated in table I and shown graphically in figure 1. The table is arranged in the order of increasing initial temperature of a series of heat capacity determinations. The series are numbered in chronological sequence in order to facilitate the tracing of thermal history of the sample. The temperature increment for a heat capacity determination may be inferred from the differences in the mean temperatures of the adjacent determinations within the series. Curvature corrections have been added to correct for the effect of the finite temperature rise of a determination [30].

TABLE 1. Heat capacities of polyethylene
(base mole $[-CH_2-] = 14.027$)

T, K	C_p , J/K mol	T, K	C_p , J/K mol	T, K	C_p , J/K mol
I. Linear Polyethylene (SRM 1475 As Received)					
SERIES VI		SERIES V		SERIES VIII	
2.32	.0020	47.15	4.259	253.16	21.07
3.12	.0055	51.16	4.774	SERIES IX	
4.20	.0143	55.89	5.359	262.66	22.01
5.29	.0291	61.44	6.008	272.24	23.03
6.33	.0492	67.41	6.662	SERIES IV	
7.40	.0770	SERIES II		SERIES IV	
8.53	.1136	73.12	7.252	265.49	22.33
9.69	.1599	79.78	7.890	SERIES X	
10.86	.2141	87.35	8.563	282.30	24.07
12.02	.2767	96.19	9.286	SERIES XI	
13.18	.3479	105.82	10.01	291.59	24.99
14.41	.4285	115.56	10.70	301.15	25.98
15.81	.5349	125.36	11.38	310.78	27.03
17.37	.6630	135.25	12.08	SERIES XII	
19.05	.8139	145.15	12.81	320.21	28.15
20.83	.9866	SERIES III		329.93	29.47
22.75	1.186	147.08	12.97	SERIES XIII	
24.96	1.430	157.14	13.71	339.34	30.73
27.47	1.722	167.25	14.42	348.93	32.43
SERIES VII		177.34	15.12	357.00	33.97
4.68	.0200	187.31	15.80	SERIES I	
5.56	.0335	197.20	16.47	212.27	17.52
6.35	.0497	207.01	17.14	222.16	18.26
7.18	.0709	SERIES I		231.95	19.08
8.20	.1017	212.27	17.52	241.73	19.99
9.17	.1380	222.16	18.26	251.40	20.89
10.16	.1804	231.95	19.08	260.88	21.83
11.21	.2321	241.73	19.99	SERIES I	
12.30	.2931	251.40	20.89	212.27	17.52
13.40	.3621	260.88	21.83	222.16	18.26
14.58	.4410	SERIES I		231.95	19.08
15.95	.5458	212.27	17.52	241.73	19.99
17.48	.6722	222.16	18.26	251.40	20.89
19.21	.8294	231.95	19.08	260.88	21.83
21.18	1.019	241.73	19.99	SERIES I	
23.33	1.247	251.40	20.89	212.27	17.52
25.73	1.516	260.88	21.83	222.16	18.26
28.38	1.828	SERIES I		231.95	19.08
31.21	2.178	212.27	17.52	241.73	19.99
34.29	2.575	222.16	18.26	251.40	20.89
37.73	3.024	231.95	19.08	260.88	21.83
41.45	3.513	SERIES I		212.27	17.52
45.55	4.049	212.27	17.52	222.16	18.26
50.06	4.630	222.16	18.26	231.95	19.08

TABLE 1. Heat capacities of polyethylene—Continued
(base mole $[-CH_2-] = 14.027$)

T, K	C_p , J/K mol	T, K	C_p , J/K mol	T, K	C_p , J/K mol
II. Branched Polyethylene (SRM 1476) II.a As Received					
SERIES VII		SERIES III		SERIES II	
2.29	.0031	74.66	7.469	233.46	20.68
3.06	.0074	81.87	8.144	243.62	22.12
3.95	.0172	90.03	8.855	253.36	23.63
4.80	.0315	99.41	9.616	262.87	25.10
5.72	.0532	109.38	10.38	SERIES VIII	
6.64	.0820	SERIES IV		265.72	25.53
7.56	.1160	114.88	10.79	275.32	26.92
8.47	.1568	124.43	11.49	SERIES IX	
9.37	.2024	134.11	12.19	284.78	28.29
10.31	.2558	143.95	12.92	294.45	29.48
11.36	.3220	153.84	13.67	304.10	30.97
12.56	.4064	163.81	14.43	313.59	33.30
13.91	.5080	SERIES V		SERIES I	
15.38	.6318	172.38	15.10	300.30	30.07
17.04	.7822	182.13	15.86	309.79	32.50
18.90	.9639	192.01	16.65	SERIES X	
20.91	1.173	201.89	17.47	317.85	33.79
23.03	1.406	211.68	18.35	328.02	36.71
25.24	1.661	SERIES VI		337.93	39.08
27.57	1.939	211.68	18.35	347.52	43.35
30.13	2.253	221.73	19.44	355.68	47.76
32.98	2.614	231.54	20.52	SERIES I	
36.25	3.033	SERIES VI		300.30	30.07
40.01	3.516	211.68	18.35	309.79	32.50
44.30	4.060	221.73	19.44	SERIES X	
49.08	4.659	231.54	20.52	317.85	33.79
54.31	5.294	SERIES VI		328.02	36.71
60.11	5.961	211.68	18.35	337.93	39.08
66.73	6.672	221.73	19.44	347.52	43.35
II.b. Stabilized at 360 K and then Quenched					
SERIES XI		SERIES XVII		SERIES XVIII	
25.46	1.680	203.28	17.67	298.63	30.66
28.04	1.990	213.11	18.54	308.09	32.16
30.93	2.345	223.06	19.51	317.88	33.97
34.17	2.758	232.98	20.58	327.73	36.18
37.74	3.217	242.74	21.92	337.54	37.90
42.03	3.765	252.30	23.35	346.43	38.71
46.94	4.395	261.76	24.78	352.88	40.09
52.16	5.038	271.05	26.14	357.72	42.51
57.77	5.690	280.37	27.36	SERIES XII	
63.77	6.356	289.70	29.06	304.59	31.66
70.55	7.059	SERIES XIV		314.17	33.36
78.18	7.797	206.63	17.92	323.86	35.53
SERIES XIII		216.56	18.86	333.48	37.35
87.07	8.607	226.49	19.84	343.21	38.48
96.56	9.385	233.45	20.60	SERIES XV	
106.47	10.16	237.44	21.13	316.39	33.91
116.25	10.89	241.41	21.68	326.30	35.92
SERIES XVI		245.38	22.30	336.17	37.66
154.85	13.75	249.32	22.85	346.02	38.63
164.67	14.51	253.24	23.47	355.35	41.43
174.37	15.26	260.14	24.52	SERIES I	
183.97	16.03	SERIES I		300.30	30.07
193.58	16.80	211.68	18.35	309.79	32.50

TABLE 1. Heat capacities of polyethylene—Continued

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

<i>T</i> , K	<i>C_p</i> , J/K mol	<i>T</i> , K	<i>C_p</i> , J/K mol	<i>T</i> , K	<i>C_p</i> , J/K mol
II.c. Annealed at 230 K					
SERIES XXI		SERIES XXII		SERIES XXIV	
2.17	.0024	65.55	6.551	201.74	17.34
2.79	.0057	71.45	7.155	211.65	18.27
3.65	.0129	78.60	7.843	221.54	19.22
4.66	.0282	87.31	8.619	231.40	20.34
5.66	.0505	96.91	9.411	241.17	21.63
6.63	.0794	SERIES XX		SERIES XIX	
7.57	.1140				
8.49	.1545	121.97	11.29	214.04	18.42
9.45	.2025	131.77	12.01	223.87	19.45
10.53	.2637	141.71	12.74	233.54	20.58
11.72	.3394	151.71	13.47	243.06	22.26
12.98	.4308	161.77	14.21	252.62	23.41
14.37	.5363	SERIES XXIII		262.23	24.81
15.91	.6685				
17.54	.8194	SERIES XXV		SERIES XXVI	
19.30	.9929				
21.24	1.195				
23.38	1.434				
25.81	1.716				
28.59	2.048				
31.68	2.434				
34.55	2.802				
37.31	3.157				
40.63	3.584				
44.68	4.100	142.99	12.82	250.22	22.99
49.43	4.695	152.83	13.54	260.04	24.62
54.78	5.344	162.63	14.28	269.86	26.06
60.68	6.021	172.41	15.03	279.72	27.27
		182.19	15.78	289.55	28.48
		192.09	16.55	299.26	30.31
				307.21	32.21
				317.04	34.18
				326.92	36.12
				336.76	37.87
				346.58	38.75
				355.85	41.33
II.d. Slow Cooled at 1 K/h					
SERIES XXVII		SERIES XXVIII		SERIES XXIX	
196.16	16.85	273.98	26.49	331.81	36.78
206.05	17.69	283.87	27.98	341.68	38.26
215.95	18.56	293.74	29.57	350.47	39.66
225.81	19.61	303.60	31.21	357.08	41.70
235.62	20.78	313.40	33.11		
245.32	22.19	323.21	35.16		
255.02	23.66				
264.77	25.19				

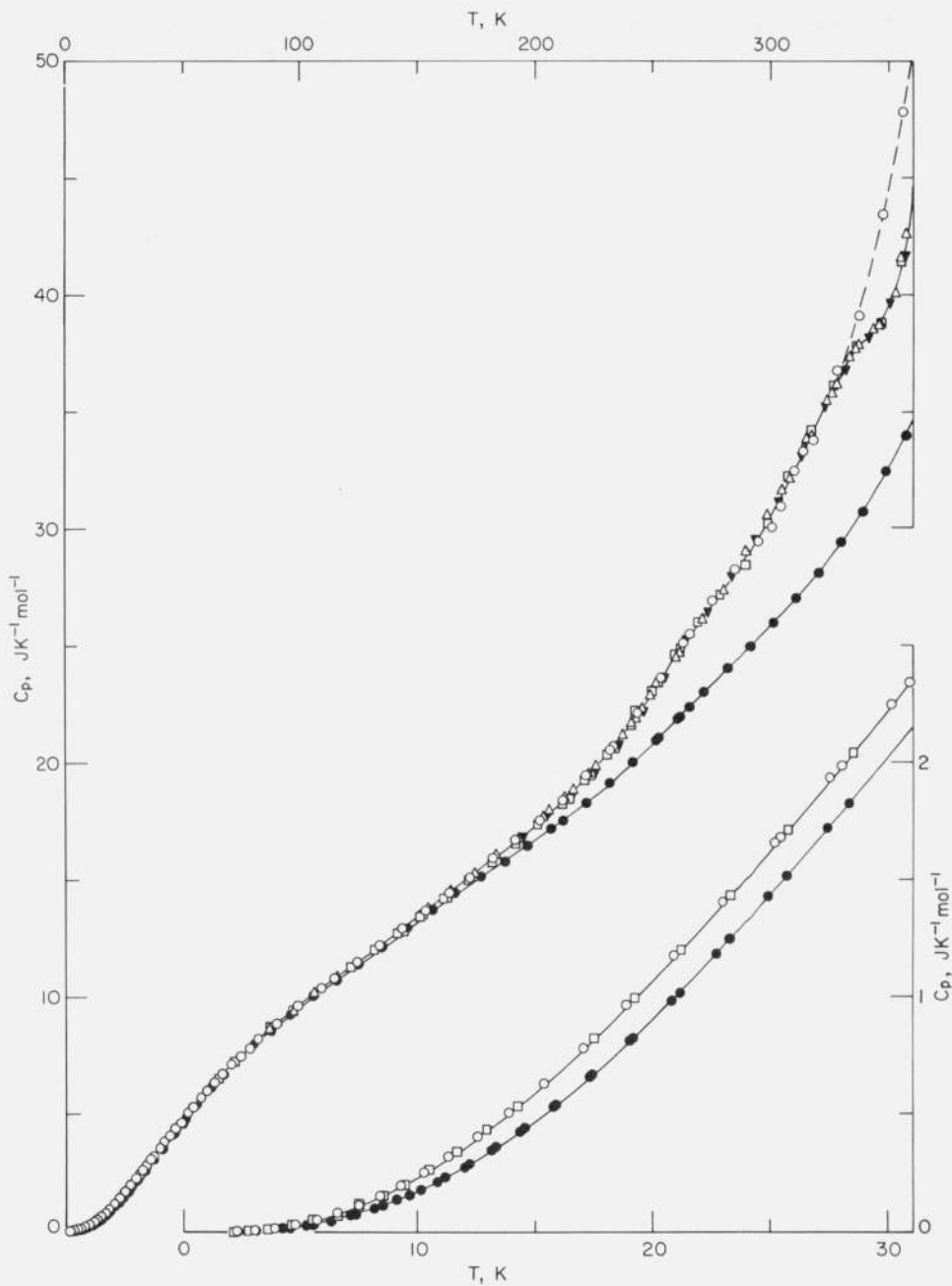


FIGURE 1. Heat capacity of polyethylene.

Linear, (SRM 1475 as received): ● Branched, (SRM 1476): ○ as received, △ stabilized at 360 K and then quenched, □ annealed at 230 K, ▼ slow cooled.

The precision of the measurement above 25 K is in the order of 0.05 percent. Below 25 K, the precision gradually changes to 1 percent at 5 K and about 5 percent at 2 K. The accuracy over most of the temperature range of the measurement is believed to be comparable to the precision as seen from the result of the heat capacity measurement on a Calorimetry Conference standard sample of sapphire [22].

Analytically smoothed heat capacity values at rounded temperatures along with values of other derived thermodynamic functions are listed in table 2. H_0 and S_0 refers to the zero point enthalpies and entropies of the individual samples. Since these samples are expected to have undetermined residual entropies at 0 K, Gibbs free energies for these samples are not given in table 2.

TABLE 2. *Thermodynamic functions of polyethylene*

(units in J, K and base mole $[-CH_2-]=14.027$)

Linear polyethylene (SRM 1475) As Received			
T	C_p	$H-H_0$	$S-S_0$
5	0.024	0.029	0.0076
10	.173	.46	.062
15	.473	2.01	.184
20	.904	5.41	.376
25	1.433	11.22	.633
30	2.027	19.85	.946
35	2.664	31.57	1.306
40	3.322	46.53	1.705
45	3.981	64.79	2.134
50	4.626	86.31	2.587
60	5.841	138.7	3.540
70	6.935	202.7	4.524
80	7.911	277.1	5.515
90	8.786	360.6	6.498
100	9.579	452.5	7.465
110	10.31	552.0	8.413
120	11.01	658.6	9.341
130	11.70	772.2	10.25
140	12.44	892.8	11.14
150	13.18	1021	12.03
160	13.91	1156	12.90
170	14.61	1299	13.77
180	15.30	1449	14.62
190	15.98	1605	15.47
200	16.66	1768	16.30
210	17.36	1938	17.13
220	18.10	2116	17.96
230	18.91	2301	18.78
240	19.80	2494	19.60
250	20.76	2697	20.43
260	21.76	2909	21.26
270	22.78	3132	22.10
280	23.80	3365	22.95
290	24.83	3608	23.80
300	25.87	3862	24.66
310	26.95	4126	25.53
320	28.11	4401	26.40
330	29.39	4688	27.29
340	30.86	4989	28.19
350	32.59	5306	29.10
360	34.65	5642	30.05
273.15	23.10	3204	22.37
298.15	25.68	3814	24.50

During the measurements from Series VIII to XIII for the linear polyethylene sample, relatively long negative temperature drifts were observed. These long drifts were probably due mainly to the slow responding adiabatic shield rather than due to thermal effects generated by the sample. Upon unloading the cryostat, it was found that the heater wires for the top and bottom of the adiabatic shield had partially been peeled off from the shield. Hence the shield was responding sluggishly to the controller. Since the density of the sample after the heat capacity measurement did not show significant change from that of the original sample, it may be concluded that little or no change in crystallinity had occurred during the course of heat capacity measurement up to 360 K.

TABLE 2. *Thermodynamic functions of polyethylene—Continued*

(units in J, K and base mole $[-CH_2-]=14.027$)

Branched Polyethylene (SRM 1476) As Received			
T	C_p	$H-H_0$	$S-S_0$
5	0.036	0.043	0.011
10	.238	.651	.088
15	.599	2.686	.248
20	1.077	6.835	.483
25	1.631	13.58	.782
30	2.233	23.22	1.132
35	2.871	35.97	1.524
40	3.511	51.93	1.949
45	4.151	71.09	2.400
50	4.773	93.40	2.869
60	5.945	147.1	3.845
70	7.008	211.9	4.842
80	7.971	286.9	5.842
90	8.849	371.1	6.832
100	9.662	463.7	7.807
110	10.43	564.2	8.764
120	11.16	672.1	9.703
130	11.89	787.4	10.63
140	12.63	910.0	11.53
150	13.38	1040	12.43
160	14.14	1178	13.32
170	14.91	1323	14.20
180	15.69	1476	15.07
190	16.49	1637	15.94
200	17.32	1806	16.81
210	18.22	1983	17.68
220	19.21	2170	18.55
230	20.32	2368	19.42
240	21.66	2577	20.32
250	23.14	2801	21.23
260	24.63	3040	22.17
270	26.08	3294	23.12
280	27.51	3562	24.10
290	28.96	3844	25.09
300	30.50	4141	26.09
310	32.23	4455	27.12
320	34.31	4787	28.18
330	36.92	5143	29.27
340	40.27	5528	30.42
350	44.62	5952	31.65
360	50.25	6425	32.98
273.15	26.53	3377	23.48
298.15	30.20	4085	25.91

TABLE 2. Thermodynamic functions of polyethylene—Continued

(units in J, K and base mole $[-\text{CH}_2-] = 14.027$)

Branched Polyethylene (SRM 1476) Annealed			
T	C_p	$H-H_0$	$S-S_0$
5	0.035	0.043	0.011
10	.233	.637	.086
15	.590	2.637	.244
20	1.065	6.732	.476
25	1.620	13.42	.772
30	2.223	23.01	1.120
35	2.859	35.71	1.510
40	3.503	51.61	1.934
45	4.142	70.73	2.384
50	4.766	93.01	2.853
60	5.943	146.6	3.827
70	7.012	211.5	4.825
80	7.974	286.5	5.825
90	8.846	370.7	6.816
100	9.652	463.2	7.790
110	10.41	563.6	8.746
120	11.15	671.4	9.684
130	11.88	786.6	10.61
140	12.60	909.0	11.51
150	13.34	1039	12.41
160	14.09	1176	13.29
170	14.84	1320	14.17
180	15.60	1473	15.04
190	16.38	1632	15.90
200	17.19	1800	16.76
210	18.06	1976	17.62
220	19.03	2162	18.48
230	20.13	2357	19.35
240	21.27	2564	20.23
250	22.90	2785	21.13
260	24.50	3022	22.05
270	25.92	3274	23.00
280	27.30	3541	23.96
290	28.84	3821	24.95
300	30.60	4119	25.95
310	32.59	4434	26.98
320	34.55	4770	28.04
330	36.33	5125	29.14
340	37.95	5497	30.24
350	39.74	5883	31.37
360	42.82	6295	32.52
273.15	26.35	3359	23.28
298.15	30.26	4064	25.74

The low temperature heat capacity of the linear polyethylene sample, SRM 1475 as received, agrees within 1 percent of that reported for Marlex 2,² one of the two linear polyethylene samples studied by Tucker and Reese [17]. This agreement may be expected, since the densities and hence the crystallinities of these two samples are very close to each other. The densities at room temperatures are 0.954 and 0.958 g cm⁻³ for SRM 1475 as received and Marlex 2, respectively. Below 30 K the heat capacity behavior of the branched polyethylene sample, SRM 1476, is similar to that of the

Low Density (L.D.) polyethylene sample also reported in reference [17]. The heat capacity of SRM 1476 is in general about 1–2 percent lower than that of L.D. This is in accord with the density differences of the two samples. The room temperature density of SRM 1476 at 0.925–0.927 g cm⁻³ is slightly higher than that of L.D. at 0.915. The lowering of the heat capacity due to the increase in density or due to annealing can also be detected when the results for SRM 1476 in the as received condition ($\rho = 0.925$) is compared with that in the annealed condition ($\rho = 0.927$). From 20 to 360 K, heat capacities of linear polyethylene samples from several previous works [3, 9, 21, 31] are within 5 percent of the values for the linear polyethylene sample reported here, irrespective of their origins and densities. Even the values for various branched polyethylene [3, 9, 14, 15, 31] do not differ more than 5 percent from the value of the linear polyethylene sample of this work in the temperature range from 40 to 230 K.

Figures 2a and 2b show the heat capacity differences between the branched polyethylene sample subjected to various thermal treatments and the linear polyethylene sample in the condition as received. These two figures also show approximately the degree of precision of the measurements reported here. A low temperature maximum in the heat capacity difference may be seen in figure 2a centering around 30 K. Similar features may also be observed if low temperature heat capacities of branched polyethylene from other sources [14, 17, 31] are compared against that of linear polyethylene. Maxima in heat capacity differences between the glass and crystal of the same substance have been observed to occur in the temperature range around 15 to 40 K in many substances. Such a feature has been attributed mainly to the volumetric differences between the two forms [32] and has also been correlated with Schottky functions [31].

A small irregularity in the order of 1 percent of the heat capacity at about 140 K is probably caused by the heat capacity behavior of the linear polyethylene sample in that region. In the temperature region of 230 to 260 K the heat capacity difference seems to increase more steeply than that in the regions immediately above or below. The abrupt increase in the heat capacity of branched polyethylene in the temperature region around 240 K is more pronounced in a calorimetric study [31] on a sample having lower density, 0.91 g cm⁻³, than that of SRM 1476, and in thin film calorimetric results [6] on an even lower density, 0.89 g cm⁻³, sample. The magnitude of this heat capacity irregularity, characteristic of a glass transition, increases as the density of the sample is decreased or as the amorphous content of the sample is increased. Hence the glass transition temperature of branched polyethylene is located around 235 to 240 K.

Below 250 K the heat capacity of the annealed or slow-cooled branched polyethylene samples is lower than that of the as received or the quenched sample. Above 250 K, however, the apparent heat capacity which may include any crystallization or premelting processes seems to be partially a function of where

²Certain commercial materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards.

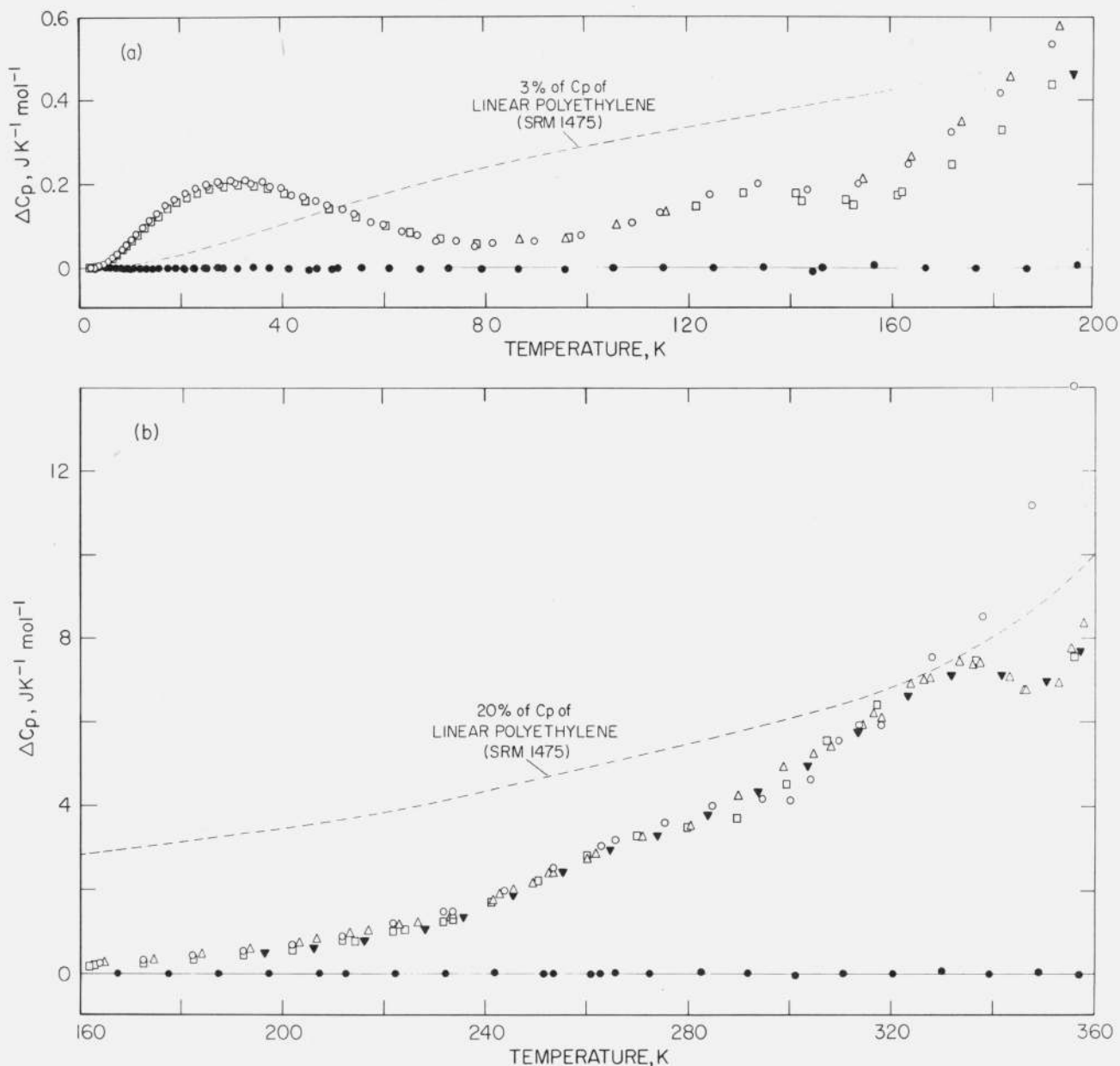


FIGURE 2. Comparison of heat capacity of polyethylene.

Baseline: smoothed values for linear polyethylene, SRM 1475 as received. All legends same as in figure 1. (a) Below 200 K. (b) Above 160 K.

the sample had been held previously at some higher temperature. When the sample is stored at temperatures above 250 K, the heat capacity is usually lowered in the vicinity of the storage temperature.

In order to assess the effect of the thermal history on the heat capacity of branched polyethylene and on the spontaneous temperature drift behavior (fig. 3) the following procedure was carried out. During the loading of the sample, a water-cooled jacket was used to surround the sample container, so that the sample would not be heated above room temperature during the process of soldering the container top. The sample

was cooled in the cryostat by radiation and conduction at a rate of about 5 K h^{-1} . The heat capacity of the as-received sample was measured below room temperature before the sample was heated above room temperature. No large spontaneous temperature drift was observed until the sample was heated above 330 K. Positive temperature drifts as high as 0.1 K min^{-1} were observed in the region 350 to 360 K, indicating that additional crystallization may have taken place. Figure 3 shows the spontaneous temperature drifts observed at about 30 min after the termination of the electrical energy input to the calorimeter. The sample

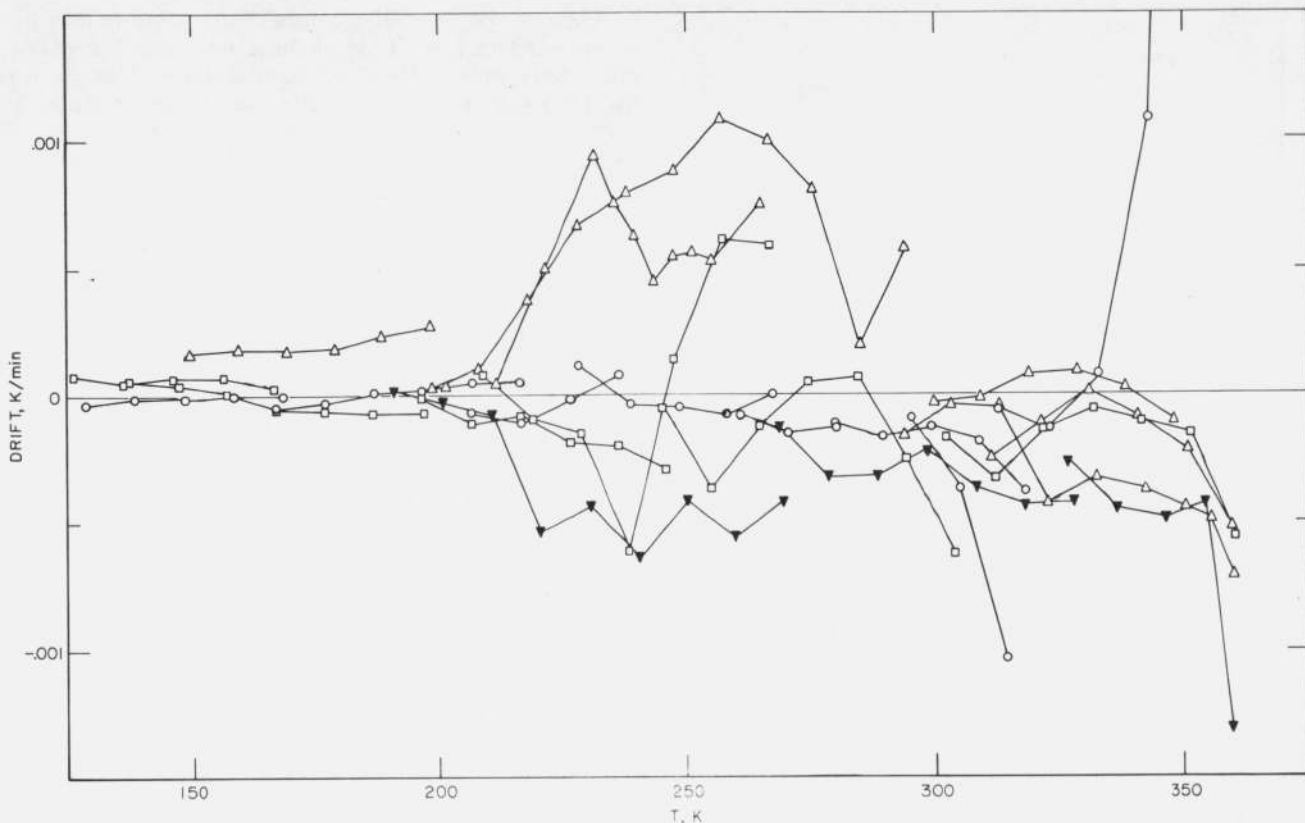


FIGURE 3. Spontaneous calorimetric temperature drift in branched polyethylene.

Data within a series are linked by straight lines. All legends same as in figure 1.

was then "stabilized" by maintaining the sample temperature at 360 K for 5 days. The sample was then quenched to temperatures below 100 K at a rate of about 5 K min^{-1} . Upon heating, a spontaneous warming trend starting around 210 K and reaching a peak around 230 K was observed. However large warming drifts persisted to about 300 K. The sample was again quenched from high temperature and then "annealed" at 230 K for 4 days. During the course of heat capacity measurement on the annealed sample, a spontaneous cooling peak was observed around 240 K. Upon further heating a large warming drift again showed up. Finally, heat capacity measurements were performed on the sample after it had been "slowly cooled" from 360 to 200 K at a rate of about 1 K h^{-1} . A rather broad region of spontaneous cooling drifts with a peak around 240 K was observed.

The first large warming drift peaks at about 230 K and the first cooling peaks at about 240 K due to quenching and annealing (or slow cooling), respectively, are probably associated with the glass transition phenomena. The large warming drifts seen above 250 K in both quenched samples and quenched samples followed by annealing are however due to crystallization of the polymer above the glass transition temperature.

A commercial differential scanning calorimeter (DSC) was also used to demonstrate qualitatively the behavior of the branched polyethylene sample. A sample of SRM 1476 weighing approximately 10 mg was subjected to various thermal treatments in the DSC and was then observed under identical operational conditions, such as the scanning rate, slope adjustment, temperature calibration adjustments, etc. The recorded traces of the DSC observations are reproduced in figure 4. Each trace was shifted vertically by a certain amount except trace (g) which was shifted a little more than the others. The vertical axis denotes the difference in the power inputs to the sample and to the reference, and hence is related to the difference in the heat capacity between the sample and the reference. The values on the abscissa are the readings of the temperature indicator of the DSC. The annealing temperatures for various traces were also read directly from the indicator. Neither the indicated programming temperature during a scan nor the isothermal temperature during annealing were corrected to the sample temperature. Under the operational conditions of the present observations, these corrections were less than 3 K.

All the curves are obtained with a scanning speed of 10 K min^{-1} from 310 to 420 K after the sample has

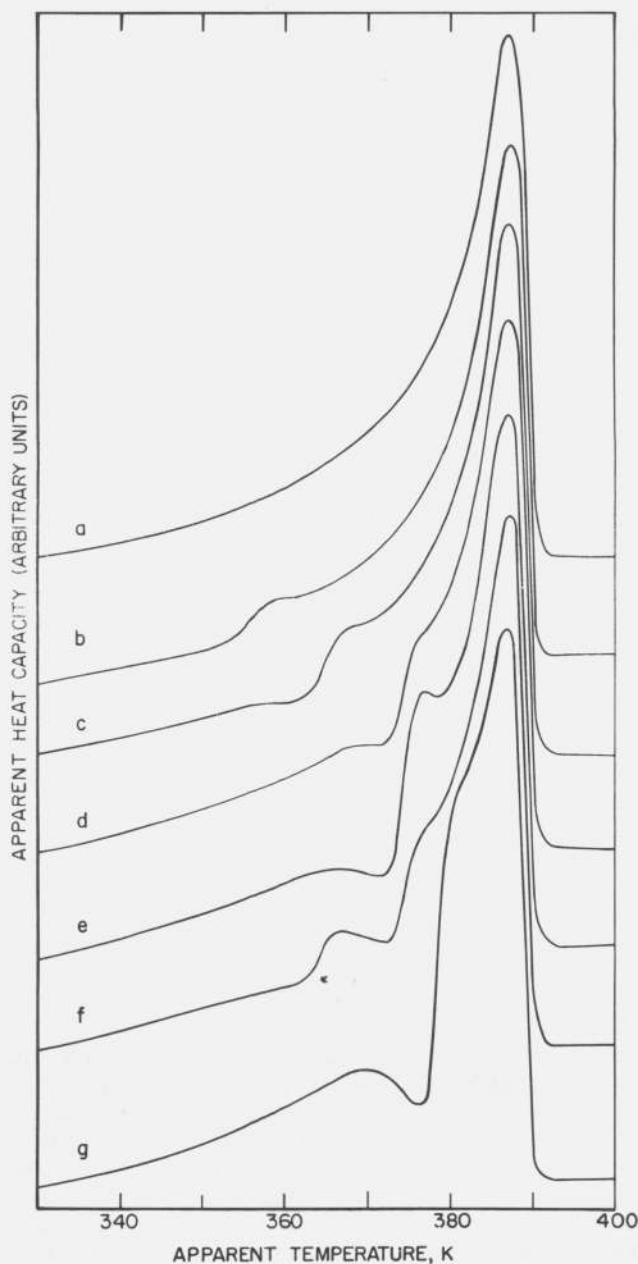


FIGURE 4. DSC melting curves of branched polyethylene.

All curves obtained with a scanning rate of 10 K min^{-1} after various thermal treatments: (a) cooled at -2.5 K min^{-1} . All other curves, cooled rapidly from the melt and then held at: (b) 350 K, (c) 360 K, (d) 370 K, (e) 360 and then at 370 K, (f) 370 and then at 360 K, (g) 350 and then at 5 K intervals to 375 K.

been cooled from the melt and received various thermal treatments. Curve (a) is a smooth trace obtained after cooling the sample continuously at a rate of 2.5 K min^{-1} from the melt. Curves (b), (c), and (d) show the effect of annealing or holding the sample in the DSC for 15 min at 350, 360, and 370 K, respectively. Annealing lowers the apparent heat capacity, including any premelting and recrystallization phenomena, near the annealing temperature. At 5 to

10 K above the annealing temperature a hump may be observed. The magnitude of these effects is increased with increasing annealing temperature. Curves (e) and (g) show the effect on the sample subjected to a multiple annealing process by successively raising the annealing temperature: (e) first at 360 and then at 370 K and (g) from 350 to 375 K at 5 K intervals. Both the dip near the highest annealing temperature, and the hump above that in these two curves are very pronounced. The apparent heat capacity below 370 K in curve (g) seems to be noticeably higher than the smooth curve (a). Curve (f) indicates the effect produced by annealing first at 370 K and then at 360 K. Two dips and humps may be seen on the same curve. The hump above 370 K is similar in magnitude to that in curve (d), however the hump between 360 and 370 K is somewhat smaller than that in curve (c). Similar phenomena have also been observed to occur in branched polyethylene by differential thermal analysis [33], and in high density polyethylene annealed within 15 K of its melting point by DSC [34].

Branched polyethylene, due to its geometrical irregularities, may form crystallites having a very wide range of melting points. As long as the cooling from the melt is continuous, the melting phenomena is also continuous. The smooth distribution of the crystallites, however, may be modified by discrete thermal treatments. By annealing or holding the sample at a particular temperature, the crystallites which melt near that temperature may either recrystallize or grow into less defective or larger crystallites. Thus the annealing process may deplete part of crystallites that melt near the annealing temperature and increase the amount of crystallites that melt at higher temperatures. Crystallites melting at much lower temperatures may not be affected by this process as they may not be incorporated into the high melting crystallites and may be formed again upon subsequent cooling. Therefore, in the DSC traces for the annealed samples, the apparent background heat capacity below the annealing temperature is similar to that of a smooth distribution. By correlating the more sensitive plot of heat capacity difference in figure 2b with the plot of observed calorimetric temperature drift in figure 3, one finds that the dips in the heat capacity curves at 290, 300, and 350 K are not associated with any large positive drifts. Therefore the dip in heat capacity curve near the annealing temperature is probably due to a depletion of crystallites which melt in that region.

The authors wish to thank C. H. Pearson in assisting with the calorimetric measurement.

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(Paper 77A4-779)