Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules. II. Polyethylene

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The heat capacity of polyethylene from 0 K to 600 K is reviewed using measurements on 46 samples reported in the literature. The crystallinity dependence is evaluated critically and a set of recommended data for completely crystalline and amorphous polyethylene is derived. Entropy, enthalpy, and Gibbs energy functions are calculated. Polyethylene can serve as a standard material for the thermodynamic functions of a simple linear macromolecule. This paper is the second in a series which will ultimately cover all heat capacity measurements on linear macromolecules.

Key words: Crystal; crystallinity; density; enthalpy; entropy; fusion; Gibbs energy; glass transition; heat capacity; linear macromolecule; melt; polyethylene.

Contents

List of Tables

List of Figures

1. Introduction

This is the second paper in a series of discussions on the heat capacity of linear macromolecules. In the first paper [1][1], the heat capacity of selenium was analyzed. Selenium is a model compound for a monoatomic, linear macromolecule. In this paper the heat capacity of polyethylene, the simplest organic linear macromolecule has been critically analyzed. In subsequent publications, the analysis of heat capacities of groups of more complicated linear macromolecules will be reported. Since this is the first paper on a typically semicrystalline macromolecule, a brief general description of the heat capacity of such materials is given.

[1] Numbers in brackets refer to literature references in section 6.

2. Heat Capcity of Linear Macromolecules

Macroscopically most samples of linear macromolecules may be classified as either crystalline, semicrystalline, glassy, or molten. One considers the first three states as solid[2] and the last liquid. The crystalline and glassy states represent the limiting cases of order and disorder in the solid. In the liquid state, linear macromolecules reach internal equilibrium within a reasonably short time. On solidification, however, linear macromolecules rarely reach the equilibrium (fully crystalline) state [2]. Data on the fully crystalline state are often only accessible through extrapolation of properties of samples of various degrees of metastability.

The usual description of the crystalline state through crystal type and morphology is often complicated in the case of linear macromolecules because of the smallness of the crystals. As a result, a change of the thermodynamic functions of the crystals due to surface effects must sometimes be considered. In the case of the metastable, semicrystalline materials even greater complications can arise because the crystalline and amorphous portions of the sample may not be independent of each other due to the continuation of single molecules through several phase regions.

Microscopically a sample is described by the chemical composition and shape of its molecules. The shape is discussed in terms of the "macroconformation", a term which has been coined to distinguish the overall shape from the customary term "conformation" which refers to the structure of a small molecule, or small part of a large molecule achieved by rotation about one or several bonds.

The glassy, amorphous linear macroconformations represent randomly coiled, entangled chains. The glassy macroconformations are frozen-in on cooling through T_g and thus correspond approximately to the equilibrium macroconformation at the specific glass transition temperature experienced under the given cooling conditions. Above T_g, the samples are liquid and equilibrium macroconformations can be established.

The crystalline linear macromolecules are characterized by macroconformations of long, uninterrupted sequences of crystallographic motifs made up of the molecular repeating units. The limiting crystalline macroconformations are of the folded and extended chain types [2]. The crystal morphology is often of lamellar or fibrillar habit. Crystals with chain folded macroconformation are often lamellar and have usually a well defined thickness which ranges typically between 5–50 nm. Crystals with extended chain macroconformation are crystals of linear macromolecule which have an extended chain length of at least 200 nm in the molecular axis direction [2]. The term "fully extended crystals" is reserved for crystals where the complete extension of the linear macromolecule has been established. The chain folded macroconformations are usually found in metastable crystals. Extended or fully extended chain crystals are usually more stable than chain folded crystals and often represent a good approximation to equilibrium crystals. The upper temperature limit of existence of the crystalline phase is given by the melting temperature.

Many solid linear macromolecules are neither amorphous nor fully crystalline, but are semicrystalline. They show a glass transition as well as a melting transition. The molecular chains participate in both crystalline and amorphous regions of the sample. Their macroconformation can best be called "fringed micellar".

For most samples of these discussions the overall structure is approximated by a two phase model[3] characterized by one main parameter, the weight (mass) fraction crystallinity, w^c

$$w^c = \frac{W_c}{W} \tag{1}$$

where W_c and W are weights (masses) of the crystalline portion and total weight (mass) of the sample, respectively. It is usually calculated from density data

$$w^c = \left(\frac{\rho_c}{\rho}\right)\left(\frac{\rho - \rho_a}{\rho_c - \rho_a}\right) \tag{2}$$

where ρ, ρ_c, and ρ_a are densities of the semicrystalline, completely crystalline and completely amorphous states.

A typical schematic plot of the heat capacity vs temperature for linear macromolecules is given in figure 1. The measured heat capacity C_p, consists of appropriate fractions of the heat capacity of the crystalline polymer C_p^c and the heat capacity of the amorphous polymer C_p^a. In the temperature region of melting, rearrangement, or crystallization, a term representing the change of crystallinity is added.

$$C_p = w^c C_p^c + (1-w^c) C_p^a - \frac{dw^c}{dT} \Delta H_f. \tag{3}$$

In the temperature regions where crystalline order does not change ($dw^c/dT = 0$), eq (3) simplifies in the two phase model to

$$C_p - w^c C_p^c + (1-w^c) C_p^a. \tag{4}$$

Based upon this linear dependence, the heat capacities of completely amorphous and completely crystalline linear macromolecules can be derived through extrapolation from a series of measurements on various semicrystalline samples.

For amorphous linear macromolecules there is a significant increase in heat capacity at the glass transition temperature. According to Wunderlich's rule of constant ΔC_p^a which holds for many linear macromolecules [3], the heat capacity increase at the glass transition is given by

$$\Delta C_p = 11.3 \pm 2.1 \text{ J mol}^{-1} \text{ K}^{-1} \tag{5}$$

[2] In this connection a solid is defined as a crystal (range of existence from 0 K to the melting temperatures T_m) or as a glass (range of existence from 0 K to the glass transition temperature T_g). Semicrystalline samples are thus two-phase structures which show both a glass transition temperature and a melting temperature. Below T_g both phases are solid; above T_g, but below T_m, one phase is solid (crystal), the other is liquid.

[3] For poorly crystallized samples or for samples with excessive interphase dependence, a single parameter description is not possible (see data on ultrahigh molecular weight polyethylene). In this case the eqs (1) to (4) and (6) do not apply and the non-linearity of eqs (3), (4) and (6) can be used to identify the limit of the two phase model (crystallinity description).

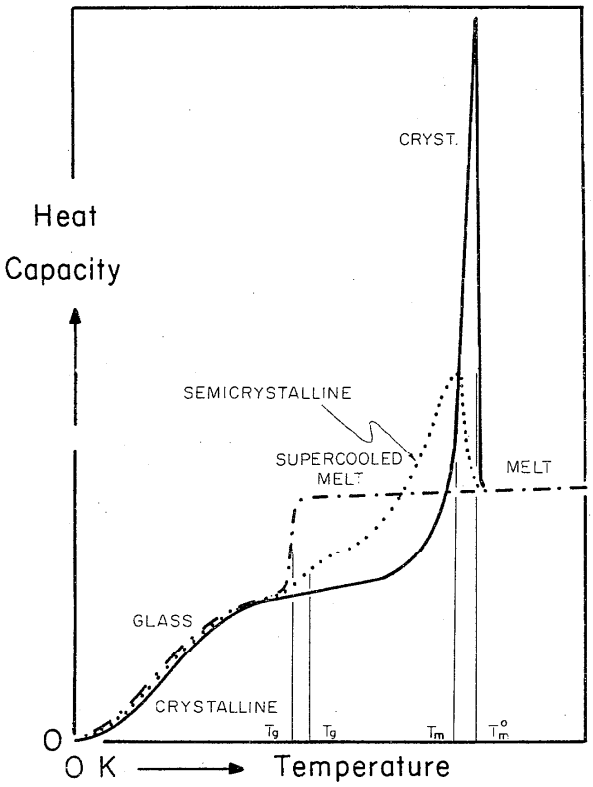

FIGURE 1. Typical schematic plot of the heat capacity vs temperature for linear macromolecules.

where the molar size is given by the smallest molecular unit whose movement may change the hole equilibrium (bead). No such jump in heat capacity is associated with crystalline polymers. The heat capacity change at T_g for a semicrystalline sample is smaller than for a completely amorphous sample, broadened, and usually shifted to higher temperature. One expects the change in heat capacity at T_g to be due to the amorphous regions of the semicrystalline sample only, so that it is related to its crystallinity by

$$\Delta C_p = (1 - w^c)\, \Delta C_p^a. \tag{6}$$

In the molten state, (i.e. above melting point for crystalline and semicrystalline samples or above T_g for amorphous samples), the heat capacity increases with temperature and can usually be represented by a single, linear function. This linearity of liquid heat capacities is surprising. It is largely based on a compensation of the decrease in heat capacity contribution of changes in free volume with temperature and an increase in heat capacity contributions from excitation of group vibrations. Heat capacities of macromolecules with monoatomic repeating units show thus a decrease with temperature in the liquid state (see selenium [1]). Also, one should expect that the accidental linearity is limited in temperature range.

The crystalline and semicrystalline linear macromolecules show an endotherm in the melting region. Only the equilibrium crystals of narrow molecular weight homopolymers give on slow heating (so that equilibrium is constantly maintained) a melting endotherm at a sharply defined temperature. Metastable samples of linear macromolecules usually show a broadened melting range which is often shifted to lower temperature. The interpretation of the melting under nonequilibrium conditions is complicated by time dependent crystal perfections, rearrangements, and recrystallizations. The usual broadening of the melting range of equilibrium crystals due to the presence of a second component is also observed for macromolecules. The second component may be in this case a different length, but otherwise identical molecule, a low or high molecular weight diluent molecule, or even internal copolymer units. In all cases the equilibrium melting range is difficult to separate from the nonequilibrium effects. A detailed accounting of melting is given in volume 3 of reference [2].

A review of the theory of heat capacities of linear macromolecules has been published earlier by Wunderlich and Baur [4]. In the present series of critical evaluations of the heat capacities of linear macromolecules, an effort will be made to discuss heat capacities and the derived thermodynamic functions as they relate to their macroscopic and microscopic structure.

3. Heat Capacity of Polyethylene

3.1. Introduction

Polyethylene is the most widely studied linear macromolecule (repeating unit CH_2-, formula weight 14.03). It crystallizes well from solution and melt. Large crystals of polyethylene which are close to equilibrium perfection and of high molecular weight have been grown [5, 6].

The stable crystal form of polyethylene contains planar zigzag chains (orthorhombic, for unit cell parameters see [7]). The crystalline density is 1.0030 Mg m^{-3} at 298 K (packing density 0.70) and 0.9962 Mg m^{-3} at the melting temperature (packing density 0.69) [8]. For other crystal modifications no heat capacities are known.

The amorphous density has been well established at 0.8519 Mg m^{-3} at 298 K from crystallinity and copolymer extrapolations [8]. At the melting temperature, it is 0.7835 Mg m^{-3}. The packing densities of the amorphous polyethylene at room temperature and at the melting temperature are 0.60 and 0.55, respectively.

On crystallization one obtains usually lamellar crystals with a typical crystal thickness in the c-direction of 7.5 to 15 nm on crystallization from solution and of 10 to 50 nm on crystallization from the melt. On low supercooling, slow melt crystallization lamallae as thick as 200 nm in the chain direction have been grown [9]. Under hydrostatic pressure of more than 300 MPa even larger, extended chain crystals of up to 10000 nm thickness were grown [6, 10, 11].

Melt crystallized polyethylene varies commonly in crystallinity from 40 to almost 100%. The low crystallinity samples are usually of branched molecules while the high crystallinity samples are more linear and of intermediate molecular weight (20,000–1,000,000). Low crystallinity samples can also be made from ultra-high molecular weight polyethylenes [12–14].

The equilibrium melting temperature of polyethylene has been established to be 414.6 ± 0.5 K [8, 10]. The heat of

fusion of equilibrium crystals of polyethylene is established reasonably well at 4.1 ± 0.2 kJ mol^{-1} at the melting temperature [8, 15]. Occasional reports of higher equilibrium melting points are most likely due to errors in extrapolation or may be caused by superheating effects [8].

The glass transition temperature of polyethylene continues to be a matter of controversy. Values ranging from 140 to 250 have been assigned by various investigators [4, 12, 14, 16–18, 20]. The heat capacity studies reported here and previously [19] agree only with a glass transition of 237 K. The difference in heat capacity between the extrapolated melt value at 237 K and the crystalline heat capacity is 10.48 J $mol^{-1}K^{-1}$, close to the expected value of eq (5). Extrapolating the heat capacity of the glass between 110 and 190 K to 237 yields a ΔC_p of only 6.15 J $mol^{-1}K^{-1}$. This is taken as a indication that the low temperature limit of the glass transition extends to relatively low temperatures. Only at 110 K does the amorphous heat capacity approach that of the crystal to within 4%.

3.2. Literature Data on Heat Capacity of Polyethylene

Forty-five investigations of the heat capacity of branched and linear polyethylene have been reported in the literature. Heat capacities of over one hundred samples of various crystallinities have been measured over wide ranges of temperature. Four discussions in terms of heat capacity of the completely crystalline and the completely amorphous polyethylene have also been reported in the literature [4, 17, 19, 21,].

All investigations were critically evaluated in terms of sample characterization, experimental technique used, error limits and accuracy of representation of the data. It was found that only 21 of the 45 investigations met our standards of acceptable data (discussed in ref. [1]). These investigations are listed in table 1. These contain heat capacity data on 46 samples of branched and linear polyethylene. These samples cover a broad range of molecular weights (25,000–8,000,000) and crystallinity (0.25–0.97). Twenty four investigations which did not contain acceptable data were not included in further analysis. These are listed in table 2, along with brief comments on the reasons for exclusion from this study.

Table 1 lists, chronologically, all the investigations from which data was retrieved. Each sample has been given a number, which is in accordance with the file numbers of our data bank. The temperature region over which the determination of heat capacity was carried out is given in kelvins. The experimental technique used by the investigators and their claimed experimental uncertainties are listed. A review of various experimental techniques used for measuring heat capacities of linear macromolecules was given in reference [1]. Sources of data (tables, graphs or curve-fitted functions) are also listed. If the data were in tabular form, but not in temperature intervals desired by us, (0.1 K intervals below 1 K, to 10 K intervals at higher temperatures), the data were interpolated. The spline function technique (discussed in ref. [1]) was used to determine the interpolated heat capacity values at desired temperatures.

Characterization of the samples is also given in table 1. Commercial names and origin of the samples are given. Molecular weight and brief thermal history of the sample, if reported by the investigators, is also listed. Key characterization parameter useful for our analysis is the crystallinity of the samples. If the density at 298 K was reported, the weight fraction crystallinity was recalculated using eq (2) and ρ_c = 1.0030 Mg m^{-3} and ρ_a = 0.8519 Mg m^{-3}. In investigations where density was not reported, crystallinities determined by other methods are listed. Crystallinities determined from heat of fusion were recalculated using ΔH_f = 4.1 kJ mol^{-1}.

As noted in reference [1], heat capacity measurements at temperatures below 25 K require specialized instrumentation and are associated with larger error limits (as high as 15% below 1 K). For the purpose of our analysis, the low temperature data of samples 1–8, 43–47, 51 and 52 were smoothed by fitting with an appropriate logarithmic function. The results of these fittings are given in table 1a.

The heat capacity data retrieved from the literature are given in tables 3 to 7. The low temperature data (below 30 K) for linear and branched polyethylene are given in tables 3 and 4, respectively. Tables 5 and 6 contain the high temperature data (30 K to melting) on linear and branched polyethylene. The data on molten, linear and branched polyethylene has been combined together and are given in table 7.

3.3. Recommended Data on Heat Capacity of Amorphous, Crystalline, and Molten Polyethylene.

To determine the heat capacity of the completely crystalline and the completely amorphous polyethylene (referred to thereafter as crystalline and amorphous polyethylene), the data on various linear and branched polyethylene samples were plotted as a function of crystallinity at each temperature (0.4 − 360 K). In the preliminary plotting, all the linear and branched samples fell on a straight line, with the exception of samples 19, 20, 8, and 29. All these four samples are ultrahigh molecular weight (UHMW) polyethylenes ranging in molecular weight from 3,000,000 to 8,000,000. These samples behaved drastically differently from samples of moderate molecular weight (20,000–1,000,000). The deviations of heat capacity of UHMW samples from lower molecular weight samples were erratic. Depending upon the temperature, the heat capacity of sample 8 was 1 to 29% lower. The values for sample 19 and 20 were 1 to 9% higher. Sample 29 showed negative deviations of as much as 12%. These deviations are significantly higher than the RMS deviations of all other samples.

These observations indicate that the two phase model (eq (3)) for linear extrapolation of heat capacities is not applicable to UHMW polyethylene. This situation seems to point to the need of investigations of UHMW samples with known structural parameters beyond crystallinity only.

The heat capacity data were then replotted excluding UHMW samples. AT 2 K the data on samples 1, 4, and 5 by Chang were excluded. These data points were 25–40% lower, possibly because Chang's calorimeter is designed primarily for measurements above 5 K, thus it is not surprising that the values at 2 K have a larger error. For the same reason, Chang's data on sample 6 at 5 K were excluded. Data on sample 12 at 180–220 K and sample 28 at 110–120 K were also excluded. Heat capacity for sample 12 was 5% higher and for sample 28, the data were 10% lower. Measurements on these samples

Table 1. Heat capacity measurements of polyethylene

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data[h]
Dole, Hettinger, Larson and Wethington (1952)[b] [22]	39. Branched; ρ_c = 0.912 Mg m^{-3} w^c = 0.44	260-470	Adiabatic (2%)	Table[a]
	40. Branched; Melt cryst. ρ_c = 0.917 Mg m^{-3} w^c = 0.47	260-470	Adiabatic (2%)	Table[a]
Wunderlich and Dole (1957) [23]	25. Linear; Marlex 50[f] w^c = 0.82 (enthalpy)	260-450	Adiabatic (1%)	260-310 K: Eq (1) 320-360 K: Table[a] 420-450 K: Eq (2)
	26. Linear; Marlex 50[f] Melt cryst.; slowly cooled w^c = 0.92 (X-rays; enthalpy)	250-450	Adiabatic (1%)	250-320 K: Eq (3) 320-350 K: Table[a] 420-450 K: Eq (4)
Issacs and Garland (1962) [24]	34. Linear; Marlex[f] ρ = 0.973 Mg m^{-3} w^c = 0.83	1.8-5.0	Isothermal vacuum (2%)	Eq (5) (uncertainty = 3%)
Hellwege, Knappe and Wetzel (1962)[c] [25]	21. Branched; Average data for 3 samples (Lupolen 18115, M, H)[f]	390-460	Adiabatic (1%)	Eq (6)
	22. Linear, Average data for 5 samples (Hostalen GC, GD, GF, GM, GU)[f] $\bar{M}_w$ = 60,000-1,000,000	390-460	Adiabatic (1%)	Eq (7)
Dainton, Evans, Hoare and Melia (1962) [26]	9. Linear; Rigidex 50[f] ρ = 0.964 Mg m^{-3} w^c = 0.77	22-310	Adiabatic (1%)	Table
	10. Linear; Marlex 50[f] w^c = 0.78 (IR, X-rays)	22-310	Adiabatic (1%)	Table
	11. Branched; WNC-18 (ICI) ρ = 0.921 Mg m^{-3} w^c = 0.50	100-300	Adiabatic (1%)	Table
Wunderlich (1965) [27]	12. Linear; Extended chains ρ = 0.997 Mg m^{-3} w^c = 0.97	180-410	DSC (5%)	Table
Gray and Brenner (1965) [28]	30. Linear ρ = 0.960 Mg m^{-3} w^c = 0.75	320-460	DSC (Unreported)	Graph
Reese and Tucker (1965) [29]	36. Linear; Marlex I[f] ρ = 0.964 Mg m^{-3} w^c = 0.77	1-4.5	Transient method (10%)	Eq (8)

Table 1. Heat capacity measurements of polyethylene --Continued

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data[h]
	37. Linear; Marlex II[f] ρ = 0.938 Mg m^{-3} w^c = 0.61	1-4.5	Transient method (10%)	Eq 9
	38. Branched; ρ = 0.917 Mg m^{-3} w^c = 0.47	1-4.5	Transient method (10%)	Eq 10
Richardson (1965)[d] [30]	23. Linear; Marlex 50[f]	400-470	Adiabatic (1%)	Eq 11
Tucker and Reese (1967) [21]	31. Linear; Marlex 1[f] ρ = 0.973 Mg m^{-3} w^c = 0.83	2.5-30	Adiabatic (3%)	Eq 12
	32. Linear; Marlex 2[f] ρ = 0.958 Mg m^{-3} w^c = 0.74	2.5-30	Adiabatic (3%)	Eq 13
	33. Branched ρ = 0.915 Mg m^{-3} w^c = 0.46	2.5-30	Adiabatic (3%)	Eq 14
Smit (1972) [31]	41. Linear; Carlona 65045[f] ρ = 0.965 Mg m^{-3}	420-570	DSC (Unreported)	Graph
	42. Linear; Carlona 50075 f ρ = 0.950 Mg m^{-3}	420-570	DSC (Unreported)	Graph
Bares and Wunderlich (1973) [32]	15. Linear; Marlex 50[f] $\bar{M}_w$ = 153,000 $\bar{M}_n$ = 85,000	420-630	DSC (1%)	Table
Scott, de Bruin, Giles and Terry, (1973) [33]	35. Linear ρ = 0.945 Mg m^{-3} w^c = 0.65	0.3-4.0	Pulsed heat-leak (Unreported)	Graph[e]
Chang and Bestul (1973) [34]	1. Linear; NBS-SRM 1475 $\bar{M}_w$ = 52,000 ρ = 0.954 Mg m^{-3} w^c = 0.65	2-360	Adiabatic (0.1%)	2-20 K: Eq 15 25-300 K: Table
	2. Branched; NBS-SRM 1476 ρ = 0.9247 Mg m^{-3} w^c = 0.52	2-360	Adiabatic (0.1%)	2-20 K: Eq 16 25-360 K: Table
	3. Branched; NBS-SRM 1476 Annealed at 230 K for four days ρ = 0.9272 Mg m^{-3} w^c = 0.54	2-360	Adiabatic (0.1%)	2-20 K: Eq 17 25-360 K: Table
Chang (1974) [17]	4. Linear; NBS-SRM 1475 $\bar{M}_w$ = 52,000 Pressure cryst. at 4.5 k bar and 210 K ρ = 0.993 Mg m^{-3} w^c = 0.94	2-360	Adiabatic (0.1%)	2-20 K: Eq 18 25-360 K: Table
	5. Linear; NBS-SRM 1475 $\bar{M}_w$ = 52,000 Slow melt cryst. cooling rate 0.75 K h^{-1} ρ = 0.981 Mg m^{-3} w^c = 0.87	2-360	Adiabatic (0.1%)	2-20 K: Eq 19 25-360 K: Table

Table 1. Heat capacity measurements of polyethylene --Continued

Investigator	Sample no. characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data[h]
Simon, Beatty and Karasz (1975) [12]	19. Linear $\bar{M}_V$ = 8,000,000 $w^c \simeq 0.50$	120-190	DSC, Adiabatic[g] (unreported)	Graph
	20. Linear $\bar{M}_V$ = 8,000,000 Irradiated with Co^{60} γ-radiation at 175°C, total dose 100 Mrad Quenched from 190°C to liq. nitrogen temp. $w^c \simeq 0.25$	120-190	DSC (Unreported)	Graph
Chang, Westrum and Carlson (1975) [35]	6. Linear; Marlex 50[f] ρ = 0.973 Mg m^{-3} w^c = 0.83	5-350	Adiabatic (0.1%)	5-20 K: Eq 20 25-350 K: Table
	7. Branched; DYNHCT-1660 (Phillips Petroleum) ρ = 0.91 w^c = 0.42	5-350	Adiabatic (0.1%)	5-20 K: Eq 21 25-350 K: Table
Chang (1976) [13]	8. Linear; 260-100 (Allied Chemicals) $\bar{M}_w$ = 3,000,000 w^c = 0.44 (ΔH_f)	5-380	Adiabatic (0.1%)	5-20 K: Eq 22 25-380 K: Table
Sakaguchi, Mandelkern and Maxfield (1976) [36]	27. Linear $\bar{M}_V$ = 200, 000 Melt crystallized w^c = 0.83	100-350	DSC (Unreported)	Graph
	28. Linear $\bar{M}_V$ = 28,500 Melt crystallized ρ = 0.986 Mg m^{-3} w^c = 0.90	110-350	DSC (Unreported)	Graph
	29. Linear, Hifax 28[f] $\bar{M}_w$ = 7,000,000 Quenched from melt to liq. nitrogen ρ = 0.921 Mg m^{-3} w^c = 0.50	110-360	DSC (Unreported)	Graph
Salinger and Cordell (unpublished) [37]	43. Linear; Marlex 6050[f] $\bar{M}_w$ = 92,500 Molded ρ = 0.957 Mg m^{-3} w^c = 0.73	0.4-4.4	Heat pulse (Unreported)	Eq 23
	44. Branched $\bar{M}_w$ = 300,000 Molded ρ = 0.924 Mg m^{-3} w^c = 0.52	0.6-3.8	Heat pulse (Unreported)	Eq 24
	45. Branched $\bar{M}_w$ = 555,000 Molded ρ = 0.921 Mg m^{-3} w^c = 0.50	0.4-4.4	Heat pulse (Unreported)	Eq 25

Table 1. Heat capacity measurements of polyethylene --Continued

Investigator	Sample no. characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data[h]
Salinger and Cieloszyk (unpublished) [38]	46. Linear; Marlex 6050[f] $\bar{M}_w$ = 92,500 Molded ρ = 0.975 Mg m^{-3} w^c = 0.84	0.4-4.4	Heat pulse (10%)	Eq 26
	47. Linear; Marlex 6050[f] $\bar{M}_w$ = 92,500 Molded ρ = 0.983 Mg m^{-3} w^c = 0.89	0.14-4.4	Heat pulse (10-15%)	Eq 27
	48. Linear; Marlex 6050[f] $\bar{M}_w$ = 92,500 Molded ρ = 0.972 Mg m^{-3} w^c = 0.82	0.19-0.8	Heat pulse (15%)	Eq 28
	49. Linear; Marlex 6001[f] $\bar{M}_w$ = 190,000 Molded ρ = 0.971 Mg m^{-3} w^c = 0.81	0.18-1.0	Heat pulse (15%)	Eq 29
	50. Linear; Marlex 55035[f] $\bar{M}_w$ > 300,000 Molded ρ = 0.969 Mg m^{-3} w^c = 0.80	0.16-1.20	Heat pulse (15%)	Eq 30
	51. Branched; Commercial (Cadillac Plastics) Molded ρ = 0.918 Mg m^{-3} w^c = 0.48	0.4-4.3	Heat pulse (10%)	Eq 31
	52. Branched Molded ρ = 0.931 Mg m^{-3} w^c = 0.56	0.4-4.3	Heat pulse (10%)	Eq 32

[a]Data were interpolated using the spline function technique to give heat capacities at every ten degree interval.

[b]Data on cold drawn polyethylene have also been reported by the authors.

[c]Data below the melting transition have also been excluded because of inaccurate representation.

[d]Heat capacities have also been reported for single crystals grown in xylene at 343 and 363 K; however, their values are 15-20% higher than our data for 100% crystalline polyethylene.

[e]Data reported in the form of a log-log plot. Error in reading the graph is about 7-8%.

[f]Trade name for linear polyethylene (Marlex: Phillips Petroleum Co.; Lupolen: BASF; Hostalen: Farbwerke Hochst; Rigidex: ICI; Carlona: Shell Chemical Co.; Hifax: Hercules).

[g]Adiabatic calorimeter and DSC were averaged.

[h]Equations cited as sources of data are listed separately in table 1a.

Table 1a Source of data[a]

Eq 1 $C_p = 0.383 + 2.0\cdot10^{-3}(T-273)$ cal g^{-1} K^{-1} (Av. dev. = 0.3%)[b]

Eq 2 $C_p = 0.545 + 5.3\cdot10^{-3}$ (T-273) cal g^{-1} K^{-1} (Av. dev. = 0.2%)[b]

Eq 3 $C_p = 0.373 + 1.81\cdot10^{-3}$(T-273) cal g^{-1} K^{-1} (Av. dev. = 0.4%)[b]

Eq 4 $C_p = 0.545 + 5.3\cdot10^{-3}$(T-273)cal g^{-1} K^{-1} (Av. dev. = 0.2%)[b]

Eq 5 $C_p = 1.13\cdot10^{-5}T^3$ Jg^{-1} K^{-1} (Uncertainty = 3%)[b]

Eq 6 $C_p = 0.482 + 8.3\cdot10^{-4}$(T-273)cal g^{-1} K^{-1} [b]

Eq 7 $C_p = 0.545 + 5.4\cdot10^{-4}$(T-273)cal g^{-1} K^{-1} [b]

Eq 8 $C_p = 143T^3$ erg cm^{-3} K^{-1} [b]

Eq 9 $C_p = 156T^3$ erg cm^{-3} K^{-1} [b]

Eq 10 $C_p = 193T^3$ erg cm^{-3} K^{-1} [b]

Eq 11 $C_p = 2.555 + 3.45\cdot10^{-3}$(T-403) J g^{-1} K^{-1} [b]

Eq 12 $C_p = 0.0748 + 0.1059T - 0.0586T^2 + 0.0253T^3 - 1.28\cdot10^{-3}T^4$
$+ 3.31\cdot10^{-5}T^5 - 3.47\cdot10^{-7}T^6$ mJ g^{-1} K^{-1} (RMS dev. = 1.5%)[b]

Eq 13 $C_p = -0.449 + 0.306T - 0.116T^2 + 0.0385T^3 - 2.36\cdot10^{-3}T^4$
$+ 7.16\cdot10^{-5}T^5 - 8.66\cdot10^{-7}T^6$mJ g^{-1} K^{-1} (RMS dev. = 1%)[b]

Eq 14 $C_p = -0.34 + 0.419T - 0.216T^2 + 0.071T^3 - 5.04\cdot10^{-3}T^4$
$+ 1.62\cdot10^{-4}T^5 - 1.97\cdot10^{-6}T^6$ mJ g^{-1} K^{-1} (RMS dev = 1%)[b]

Eq 15 $C_p = \exp[-8.46351\cdot10^{-3}(\ln T)^3 - 2.587\cdot10^{-1}(\ln T)^2$
$+ 3.93317\ \ln T - 9.3343$ J $mol^{-1}K^{-1}$(RMS dev. = 0.4%)[c]

Eq 16 $C_p = \exp[-4.53102\cdot10^{-2}(\ln T)^3 - 7.63945\cdot10^{-2}\ (\ln T)^2$
$+ 3.55878\ \ln T - 8.67761]$ J mol^{-1} K^{-1} (RMS dev. = 1.7%)[c]

Eq 17 $C_p = \exp[-2.52764\cdot10^{-2}(\ln T)^3 - 2.00106\cdot10^{-1}\ (\ln T)^2$
$+ 3.80232\ \ln T - 8.84804]$ J mol^{-1} K^{-1} (RMS dev. = 1%)[c]

Eq 18 $C_p = \exp[1.49809\cdot10^{-1}(\ln T)^3 + 8.79795\cdot10^{-1}\ (\ln T)^2$
$+ 1.20115\ \ln T - 7.74536]$ J mol^{-1} K^{-1} (RMS dev. = 2.2%)[c]

Eq 19 $C_p = \exp[-1.93153\cdot10^{-2}(\ln T)^3 - 1.0569\cdot10^{-1}\ (\ln T)^2$
$+ 3.55458\ \ln T - 9.41434]$ J mol^{-1} K^{-1} (RMS dev. = 0.9%)[c]

Eq 20 $C_p = \exp[-7.78624\cdot10^{-2}(\ln T)^3 + 7.95972\cdot10^{-2}\ (\ln T)^2$
$+ 3.74686\ \ln T - 10.0172]$ J mol^{-1} K^{-1} (RMS dev. = 5.3%)[c]

Eq 21 $C_p = \exp[3.12118\cdot10^{-1}(\ln T)^3 - 2.85027\ (\ln T)^2$
$+ 10.5626\ \ln T - 14.3393]$ J mol^{-1} K^{-1} (RMS dev. = 2.7%)[c]

Eq 22 $C_p = \exp[8.49711\cdot10^{-2}(\ln T)^3 - 9.50928\cdot10^{-1}\ (\ln T)^2$
$+ 5.53269\ \ln T - 10.4027]$ J mol^{-1} K^{-1} (RMS dev = 0.5%)[c]

Eq 23 $C_p = \exp[8.60481\cdot10^{-3}(\ln T)^3 + 1.55757\cdot10^{-1}\ (\ln T)^2$
$- 2.08958\cdot10^{-1}(\ln T) + 4.74195]T^3$ erg g^{-1} K^{-1}
(RMS dev. = 2.7%)[c]

Eq 24 $C_p = \exp[-6.36359\cdot10^{-1}(\ln T)^3 + 1.08779\ (\ln T)^2 - 3.33706\cdot10^{-1}(\ln T)$
$+ 5.10775]T^3$ erg g^{-1} K^{-1} (RMS dev. 2.0%)[c,d]

Eq 25 $C_p = \exp[1.89268\cdot10^{-1}(\ln T)^3 + 1.6739\cdot10^{-1}\ (\ln T)^2$
$- 3.06387\cdot10^{-1}(\ln T) + 5.1293]T^3$ erg g^{-1} K^{-1}
(RMS dev. = 3.4%)[c]

Table 1a Source of data[a]--Continued

Eq 26	$C_p = \exp[-1.44071 \cdot 10^{-1}(\ln T)^3 + 1.82529 \cdot 10^{-1}(\ln T)^2 + 2.90325(\ln T) + 4.76114]$ erg g^{-1} K^{-1} (RMS dev. = 5.9%)[c]
Eq 27	$C_p = \exp[-1.20758 \cdot 10^{-1}(\ln T)^3 + 1.75089 \cdot 10^{-1}(\ln T)^2 + 2.80894(\ln T) + 4.69289]$ erg g^{-1} K^{-1} (RMS dev. = 7.3%)[c,d]
Eq 28	$C_p = 11.7\ T + 90\ T^3$ erg g^{-1} K^{-1}[b]
Eq 29	$C_p = 9\ T + 92\ T^3$ erg g^{-1} K^{-1}[b]
Eq 30	$C_p = 10.4\ T + 96\ T^3$ erg g^{-1} K^{-1}[b]
Eq 31	$C_p = \exp[-1.20723 \cdot 10^{-1}(\ln T)^3 + 3.01787 \cdot 10^{-1}(\ln T)^2 + 2.77537(\ln T) + 5.23607]$ erg g^{-1} K^{-1} (RMS dev. = 4.5%)[c]
Eq 32	$C_p = \exp[-1.61765 \cdot 10^{-1}(\ln T) + 2.83651 \cdot 10^{-1}(\ln T)^2 + 2.90179(\ln T) + 5.15787]$ erg g^{-1} K^{-1} (RMS dev = 4.2%)[c]

[a] Equation numbers correspond to the equations in table 1.

[b] Equation reported by the authors

[c] Authors' tabulated data was curve fitted into the equation.

[d] Six data points were discarded during curve fitting because of large deviations (>30%).

Table 2. Investigations not included in this study

Reference	Reason(s) for exclusion
Raine, Richards and Ryder (1945) [39]	Sample characterization not reported; large error limits (5%).
Sochava and Trapeznikova (1957) [40]	Sample characterization not reported.
Warfield, Petree and Donovan (1959) [41]	Sample characterization not reported.
Sochava (1960) [42]	Sample characterization not reported.
Tautz, Glück, Hartmann and Leuteritz (1963, 1964) [43, 44]	Sample characterization not reported. Data could not be read accurately from too small graphs.
Passaglia and Kevorkian (1963) [45]	For unexplained reasons, their values for branched solid PE are 2-5% lower and for linear solid PE 0-3% higher than here reported. Branched melt data are 10% lower. These discrepancies seem to be based upon systematic errors.
Broadhurst (1963) [46]	Heat capacaties of polyethylene predicted from n-paraffin data. For melt, predicted values are 5% higher at 200 K to 2% lower at 420 K than the recommended data of this study.
Hager (1964) [48]	Data could not be read accurately from too small graphs.
Peterlin and Meinel (1965) [47]	Data on drawn samples (See also Fischer [57])
Chernobyl'skii and Tertyshnik (1966) [49]	Data could not be read accurately from too small graphs.
Mischenko, Samoilov and Buchatskii (1966) [50]	Data could not be read accurately from too small graphs.
Karasev (1967) [51]	Sample characterization not reported.
Rabinovich, Pavlinov and Krylova (1967) [52]	Heat capacity of deuteropolyethylene (93% D, w^c = 0.72) measured from 80 to 310 K. Complete replacement of H by D results in an increase in C_v by more than 20%. The change in frequency spectrum due to the isotope effect has been studied.
Samoilov (1967) [53]	Influence of irradiation with γ-rays on polyethylene was studied. After irradiation dose of 610 Mrad, C_p at 297 K decreases by 25% due to crosslinking.
Atkinson, Larkin and Richardson (1969) [54]	Heat capacity data on n-alkanes containing 19 to 48 carbon atoms has been extrapolated to evaluate C_p of infinite chain length. Their predicted values are within 1.5% of the best values evaluated in this study over the temperature range 230-420 K. An equation for molten polyethylene agrees within 2%.
Atkinson and Richardson (1969) [55]	Four samples (w^c = 0.78-0.9) have been studied over a limited temperature range (250-280 K). Their values agree within 1%.
Atkinson and Richardson (1969) [56]	Measurements have been reported on single crystals grown from 0.1% solution of polyethylene in xylene at 343, 353, 363 K, over the temperature range 240-340 K. Their values are 12-15% higher than heat capacity of completely crystalline polyethylene evaluated in this study.

Table 2. Investigations not included in this study --Continued

Reference	Reason(s) for exclusion
Gee and Melia (1970) [58]	Enthalpy changes due to crosslinking reported for polyethylene single crystals and melt crystallized samples of polyethylene, which had been subjected to different doses (0-1000 Mrad) of γ-radiation at 298 and 495 K.
Maeda and Kanetsuna (1970) [59]	Large error limits.
Dragan (1971) [60]	Data reported in arbitrary units.
Smola, et al. (1972) [61]	C_p used to study the effects of crystallization conditions.
Savina, Briskman and Bondarev (1972) [62]	Effect of γ-radiation (0-5000 Mrad) on heat capacity of polyethylene was studied. Only the melting range was investigated.
Anderson and Backstorm (1973) [63]	The pressure dependence of heat capacity of linear polyethylene was determined from simultaneous measurements of thermal conductivity and diffusivity at 300 K in the pressure range 0-25 kbar. The heat capacity decreases, most strongly at low pressures, and its value at 25 kbar is 0.8 times than at atmospheric pressure.
Dushchenko, et al. (1975) [64]	Heat capacity of linear polyethylene at 300 K reported for various molecular weights (10,000-106,000) at varying crystallinity.
Bashirov, et al. (1975, 1976) [65, 66]	Sample characterization not reported. Data could not be read accurately from too small graphs.
Karl, Amussen, Wolf and Ueberreiter (1977) [67]	Heat capacity of molten polyethylene measured at 451 K in the pressure range of 0.4-1.6 K bar. C_p was regarded as being independent of pressure in this range at 2.93 ± 0.09 J g^{-1} K^{-1}. $(dC_p/dP)_p$ = 2-4·10^{-5} J g^{-1} K^{-1} bar^{-1}.

Table 3. Heat capacity of various linear polyethylenes[a] at low temperature in mJ mol^{-1} K^{-1}

T(K)	34	36	37	31	32	35	1	4	5
0.2									
0.3									
0.4						0.0140			
0.5						0.0275			
0.6						0.0449			
0.7						0.0747			
0.8						0.0964			
0.9						0.136			
1.0		0.207	0.233			0.182			
1.2		0.357	0.403			0.357			
1.4		0.567	0.640			0.572			
1.6		0.847	0.956			0.779			
1.8	0.925	1.20	1.36			1.23			
2.0	1.27	1.65	1.87			1.70	1.19	1.45	0.905
3.0	4.28	5.58	6.30	4.25	4.07	5.07	4.81	3.84	3.47
4.0	10.15	13.23	4.93	10.31	11.91	13.29	12.26	8.34	8.73
5.0	19.82			20.35	24.25		24.49	15.64	17.46
6.0				35.05	41.88		42.16	26.50	30.32
7.0				54.93	65.23		65.69	41.57	47.84
8.0				80.34	94.56		95.34	61.40	70.41
9.0				111.5	129.9		131.2	86.48	98.35
10.0				148.5	171.2		173.3	117.2	131.9
12.0				240.4	271.3		275.8	196.6	216.4
14.0				355.8	393.8		401.8	300.7	324.7
16.0				494.5	537.8		549.7	429.6	457.0
18.0				656.2	702.9		717.7	582.8	612.8
20.0				840.6	889.0		904.0	756.5	791.7
25.0				1400•	1434.		1433.	1265•	1305•
30.0				2077•	1975.				

T(K)	6	8	43	46	47	48	49	50
0.2					0.0043	0.0043	0.0036	0.0040
0.3					0.0072	0.0083	0.0073	0.0080
0.4			0.0141	0.0149	0.0148	0.0146	0.0133	0.0145
0.5			0.0250	0.0251	0.0247	0.0240	0.0224	0.0241
0.6			0.0402	0.0398	0.0388	0.0371	0.0355	0.0378
0.7			0.0606	0.0600	0.0578	0.0548	0.0531	0.0564
0.8			0.0870	0.0867	0.0827	0.0778	0.0762	0.0804
0.9			0.120	0.121	0.114		0.105	0.111
1.0			0.161	0.164	0.153		0.142	0.149
1.2			0.269	0.280	0.257			0.250
1.4			0.419	0.442	0.400			
1.6			0.619	0.658	0.589			
1.8			0.877	0.935	0.828			
2.0			1.20	1.28	1.12			
3.0			4.22	4.10	3.53			
4.0			10.64	8.88	7.63			
5.0	16.49	27.13						
6.0	30.32	47.19						
7.0	49.86	73.44						
8.0	75.64	105.9						
9.0	107.9	144.3						
10.0	146.9	188.7						
12.0	244.2	294.5						
14.0	365.8	422.0						
16.0	508.5	570.2						
18.0	668.6	738.1						
20.0	842.3	925.1						
25.0	1357•	1463•						
30.0								

[a]Sample numbers correspond to the samples described in table 1.

Table 4. Heat capacity of various branched polyethylenes[a] at low temperatures in mJ mol^{-1} K^{-1}

T(K)	38	33	2	3	7	44	45	51	52
0.4							0.0200	0.0293	0.0245
0.5							0.0373	0.0463	0.0395
0.6							0.0610	0.0702	0.0609
0.7							0.0918	0.102	0.0905
0.8							0.131	0.144	0.130
0.9							0.179	0.197	0.180
1.0	0.295						0.237	0.264	0.244
1.2	0.510					0.389	0.390	0.441	0.417
1.4	0.810					0.628	0.602	0.691	0.664
1.6	1.21					0.966	0.890	1.03	0.998
1.8	1.72					1.43	1.27	1.46	1.43
2.0	2.36		1.91	1.81		2.01	1.77	2.00	1.98
3.0	7.97	7.29	7.30	7.11		6.94	7.19	6.82	6.72
4.0	18.90	18.12	18.10	17.80		13.87	22.65	16.01	15.26
5.0		35.85	35.55	35.01	32.67				
6.0		61.31	60.38	59.43	62.74				
7.0		94.73	92.95	91.35	102.4				
8.0		135.9	133.3	130.8	150.6				
9.0		184.4	181.3	177.7	205.9				
10.0		239.6	236.6	231.7	267.3				
12.0		367.5	367.4	359.5	405.4				
14.0		514.8	521.7	510.8	560.8				
16.0		679.1	695.2	682.0	732.0				
18.0		860.3	883.6	869.4	918.8				
20.0		1060	1083	1070	1122				
25.0		1639	1631	1620	1696				
30.0		2145							

[a]Sample numbers correspond to the samples described in table 1.

Table 5. Heat capacity of various linear polyethylenes[a] in J mol^{-1} K^{-1}

T(K)	25	26	9	10	12	30	1	4
30			2.051	2.062			2.027	1.854
40			3.327	3.346			3.322	3.168
50			4.669	4.671			4.626	4.502
60			5.881	5.869			5.841	5.750
70			6.929	6.904			6.935	6.870
80			7.871	7.865			7.911	7.860
90			8.755	8.774			8.786	8.736
100			9.569	9.580			9.579	9.522
110			10.32	10.31			10.31	10.24
120			11.05	11.04			11.01	10.90
130			11.78	11.77			11.70	11.52
140			12.49	12.51			12.44	12.11
150			13.22	13.24			13.18	12.70
160			13.96	13.95			13.91	13.27
170			14.68	14.68			14.61	13.84
180			15.38	15.42	15.57		15.30	14.42
190			16.06	16.12	16.15		15.98	15.00
200			16.77	16.82	16.74		16.66	15.60
210			17.50	17.58	17.33		17.36	16.22
220			18.24	18.41	17.62		18.10	16.86
230			19.01	19.29	17.92		18.91	17.54
240			19.85	20.23	18.21		19.80	18.26
250		19.46	20.82	21.20	18.80		20.76	19.00
260	20.96	20.52	21.89	22.22	19.09		21.76	19.76
270	22.14	21.58	22.95	23.29	19.68		22.78	20.56
280	23.31	22.65	24.03	24.34	20.56		23.80	21.39
290	24.48	23.71	25.13	25.42	21.15		24.83	22.26
300	25.66	24.77	26.22	26.49	22.03		25.87	23.14
310	26.84	25.84	27.36	27.58	22.62		26.95	24.05
320	28.05	26.91			23.50	28.90	28.11	24.99
330	29.56	28.05			24.67	29.84	29.39	25.97
340	31.00	29.67			25.55	31.49	30.86	27.04
350	33.30	31.31			26.73	33.37	32.59	28.26
360	35.00				27.90	35.72	34.65	29.72
370					29.37			
380					30.84			
390					32.31			
400					34.07			
410					36.13			

T(K)	5	19	20	6	8	27	28	29
30	1.895			1.941	2.062			
40	3.202			3.254	3.360			
50	4.526			4.557	4.656			
60	5.766			5.789	5.862			
70	6.882			6.912	6.946			
80	7.871			7.915	7.909			
90	8.747			8.801	8.769			
100	9.535			9.592	9.545	9.500		
110	10.26			10.31	10.26	10.36	9.700	9.300
120	10.94	10.94	11.19	11.00	10.94	11.05	10.74	10.16
130	11.59	11.78	12.02	11.67	11.59	11.72	11.52	11.05
140	12.22	12.72	13.03	12.36	12.22	12.34	12.08	12.09
150	12.86	13.91	14.26	13.02	12.86	12.91	12.95	13.11
160	13.49	14.98	14.69	13.67	13.50	13.55	13.46	13.77
170	14.12	15.84	15.84	14.30	14.15	14.25	14.03	14.19
180	14.74	16.72	16.96	14.93	14.81	14.78	14.77	15.27
190	15.37	17.59	17.80	15.57	15.47	15.39	15.36	15.96
200	16.01			16.23	16.14	16.10	16.05	16.77
210	16.66			16.93	16.82	16.67	16.57	17.55
220	17.33			17.67	17.52	17.45	17.27	18.07
230	18.04			18.48	18.27	18.25	18.09	18.64
240	18.79			19.35	19.09	18.98	18.81	19.53
250	19.59			20.23	19.96	19.77	19.45	20.37
260	20.42			21.11	20.90	20.35	20.42	21.03
270	21.31			22.00	21.87	21.29	21.08	22.14
280	22.24			22.93	22.89	22.44	22.06	22.99
290	23.18			23.92	24.00	23.41	23.29	23.92
300	24.14			24.99	25.20	24.24	23.93	25.04
310	25.10			26.15	26.51	25.21	24.91	25.90
320	26.10			27.43	27.90	26.16	25.67	26.99
330	27.16			28.84	29.38	27.14	26.32	28.65
340	28.33			30.41	30.91	28.20	27.43	30.02
350	29.67			32.16	32.46	29.92	28.57	31.53
360	31.23				34.00			33.56
370					35.44			
380					36.76			
390								
400								
410								

[a]Sample numbers correspond to the samples described in table 1.

Table 6. Heat capacity of various branched polyethylenes[a] in J mol^{-1} K^{-1}

T(K)	39	40	11	2	3	7
30				2.233	2.223	2.303
40				3.511	3.503	3.570
50				4.773	4.766	4.798
60				5.945	5.943	5.988
70				7.008	7.012	7.092
80				7.971	7.974	8.063
90				8.849	8.846	8.901
100			9.597	9.662	9.652	9.651
110			10.40	10.43	10.41	10.39
120			11.16	11.16	11.15	11.17
130			11.94	11.89	11.88	11.92
140			12.70	12.63	12.60	12.62
150			13.46	13.38	13.34	13.36
160			14.23	14.14	14.09	14.11
170			15.00	14.91	14.84	14.85
180			15.78	15.69	15.60	15.62
190			16.57	16.49	16.38	16.41
200			17.43	17.32	17.19	17.27
210			18.38	18.22	18.06	18.24
220			19.49	19.21	19.03	19.37
230			20.75	20.32	20.13	20.75
240			22.20	21.66	21.27	22.59
250			23.75	23.14	22.90	24.32
260	25.62	25.80	25.39	24.63	24.50	25.93
270	27.07	27.41	27.11	26.08	25.92	27.50
280	28.76	29.22	28.94	27.51	27.30	29.08
290	30.66	31.26	30.84	28.96	28.84	30.75
300	32.68	33.53	32.86	30.50	30.60	32.55
310	34.94	35.97		32.23	32.59	34.56
320	37.63	38.57		34.31	34.55	36.83
330	40.57	41.67		36.92	36.33	39.43
340	43.57	45.92		40.27	37.95	42.42
350	48.43	52.22		44.62	39.74	45.87
360				50.25	42.82	

[a]Sample numbers correspond to the samples described in table 1.

Table 7. Heat capacity of various molten polyethylenes[a] in J mol^{-1} K^{-1}

T(K)	39,40	25,26	21	22	30	23	41	42	15
390			34.01	35.72					
400	35.22		34.48	36.04	35.36	35.22			
410	35.70		35.01	36.36	35.48	35.70			
420	36.17	36.59	35.48	36.67	35.83	36.19	36.28	36.24	35.97
430	36.65	36.90	35.95	36.99	35.95	36.67	36.48	37.04	36.39
440	37.12	37.21	36.42	37.31	36.19	37.15	36.80	37.68	36.76
450	37.60	37.52	36.95	37.63	36.42	37.64	36.88	38.12	37.18
460	38.07		37.42	37.94	36.54	38.12	37.24	38.36	37.56
470	38.54					38.61	37.92	38.58	37.98
480							38.04	38.88	38.48
490							38.20	39.00	38.90
500							39.84	40.20	39.36
510							39.80	40.48	39.78
520							40.52	40.78	40.24
530							40.96	41.31	40.70
540							40.92	41.35	41.12
550							40.76	42.23	41.58
560							42.21	43.11	42.00
570							42.27	43.39	42.46
580									42.92
590									43.38
600									43.80
610									44.26
620									44.72
630									45.18

[a]Sample numbers correspond to the samples described in table 1.

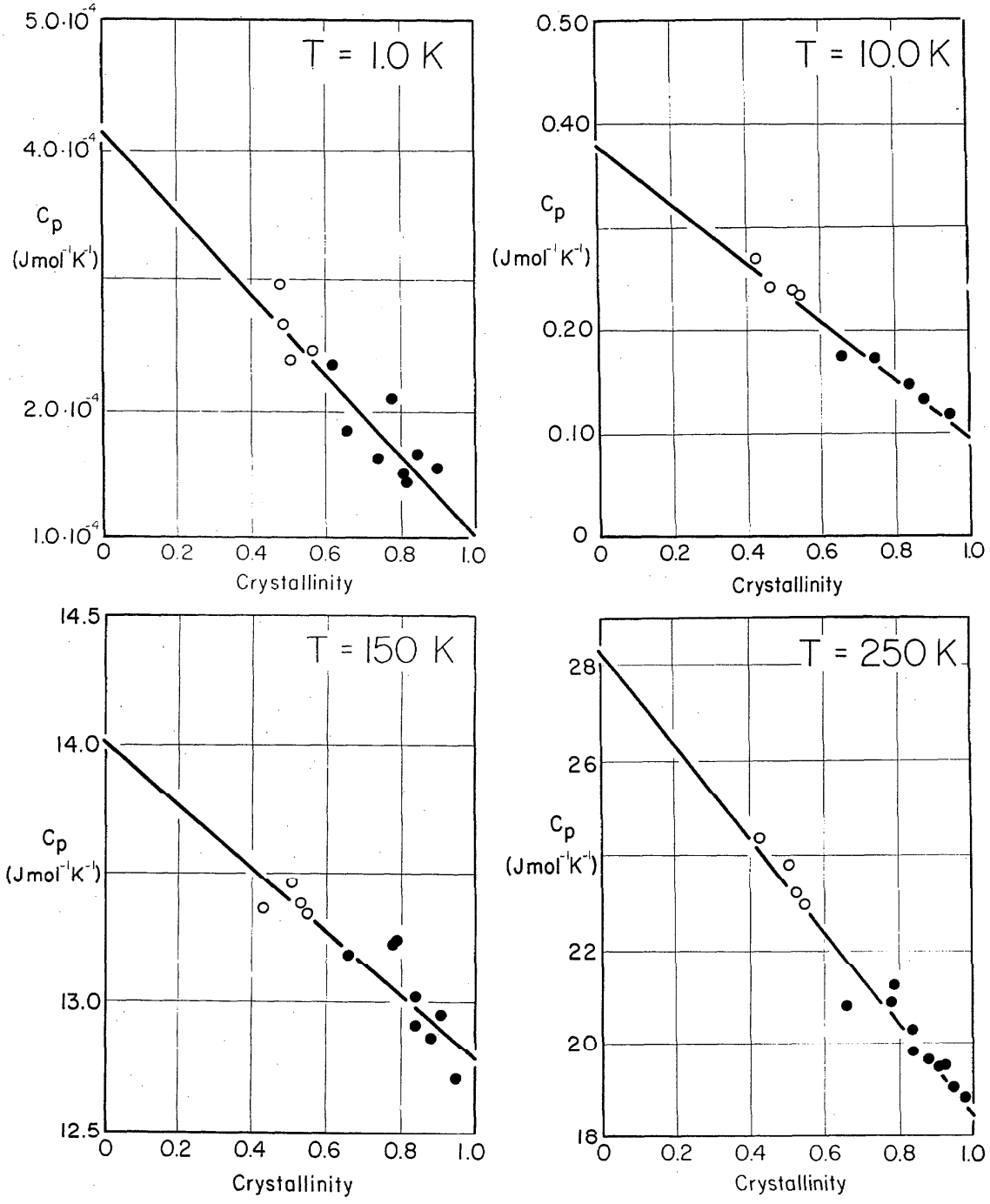

FIGURE 2. Heat capacity of polyethylene as a function of crystallinity at various temperatures.
Filled circles: Linear polyethylene.
Open circles: Branched polyethylene.

Table 8. Heat capacity vs. crystallinity[a]: Results of fitting data with the equation $C_p = Aw^c + B$

T(K)	C_p (crystalline) A + B	C_p (amorphous) B	RMS deviation (%)	Samples not included[b]
0.4	0.0000088	0.0000383	17.2	
0.5	0.0000149	0.0000652	11.0	
0.6	0.0000238	0.000102	9.4	
0.7	0.0000363	0.000152	8.0	
0.8	0.0000523	0.000213	8.8	
0.9	0.0000718	0.000290	8.9	
1.0	0.000102	0.000412	10.8	
1.2	0.000191	0.000676	10.4	
1.4	0.000321	0.00105	10.4	
1.6	0.000463	0.00158	11.0	
1.8	0.000655	0.00229	10.3	
2.0	0.000899	0.00313	9.6	1, 4, 5
3.0	0.00260	0.01153	10.5	
4.0	0.00582	0.02925	10.9	
5.0	0.01304	0.05388	6.9	6
6.0	0.02050	0.09708	6.3	
7.0	0.03242	0.1519	5.3	
8.0	0.04874	0.2178	5.0	
9.0	0.07017	0.2930	4.7	
10.0	0.09659	0.3765	4.5	
12.0	0.1698	0.5593	4.2	
14.0	0.2680	0.7589	3.9	
16.0	0.3916	0.9695	3.5	
18.0	0.5398	1.188	3.1	
20.0	0.7097	1.417	2.6	
25.0	1.218	2.031	2.0	
30.0	1.854	2.569	2.9	
40.0	3.124	3.902	1.0	
50.0	4.487	5.056	0.8	
60.0	5.731	6.176	0.5	
70.0	6.832	7.227	0.3	
80.0	7.818	8.168	0.3	
90.0	8.713	9.002	0.2	
100.0	9.506	9.766	0.3	
110.0	10.26	10.55	0.4	28
120.0	10.91	11.40	0.3	28

Table 8. Heat capacity vs. crystallinity[a]: Results of fitting data with the equation $C_p = Aw^C + B$ --Continued.

T(K)	C_p (crystalline) A + B	C_p (amorphous) B	RMS deviation (%)	Samples not included
130.0	11.52	12.29	0.5	
140.0	12.13	13.17	0.7	
150.0	12.78	14.00	0.8	
160.0	13.35	14.97	0.9	
170.0	13.95	15.90	1.1	
180.0	14.54	16.84	1.2	12
190.0	15.10	17.85	1.3	12
200.0	15.70	18.10	1.3	12
210.0	16.22	20.20	1.4	12
220.0	16.80	21.67	1.4	12
230.0	17.47	23.32	1.5	
240.0	17.90	25.74	1.7	
250.0	18.45	28.25	1.8	
260.0	18.96	(30.97)[c]	2.2	
270.0	19.64	(33.27)	2.4	
280.0	20.43	(35.59)	2.7	
290.0	21.16	(38.22)	3.1	
300.0	21.80	(41.18)	3.5	
310.0	22.50	(43.96)	3.8	
320.0	23.07	(47.69)	4.4	
330.0	23.69	(51.90)	5.0	
340.0	24.39	(56.89)	5.8	
350.0	25.08	(63.94)	7.2	
360.0	26.47	(65.39)	7.0	
360.0[d]	27.73			
370.0	29.23			
380.0	30.73			
390.0	32.23			
400.0	34.03			
410.0	36.14			

[a]Ultra-high molecular weight samples (#19, 20, 8, 29) have been excluded. See text.

[b]These data points were excluded because they were near the lower temperature limit of the instrument and showed large deviation in curve fitting.

[c]Heat capacities of amorphous polyethylene in the temperature range 260-360 K have not been accounted for change in crystallinity with temperature.

[d]Heat capacities 360-410 K were determined from data on extended chain crystals (sample no. 12)

$$C_p \text{ (Cryst.)} = \frac{C_p - 0.03\, C_p \text{ (melt)}}{0.97}$$

were made using a differential scanning calorimeter. These data points fall in the temperature region where the performance of the DSC used is of limited accuracy (see ref. [1]).

The plots of heat capacity vs crystallinity at several temperatures are given in figure 2. All branched and linear samples fit into the same straight line. The data were fitted into eq (4) using the method of least squares. The results of curve fitting to obtain heat capacity of crystalline and amorphous polyethylene are given in table 8. The RMS deviations are 10–20% at 0.4 to 5 K and decrease to 2% at 25 K. These RMS deviations are better than the errors associated with typical measurements below 25 K. The RMS deviations stay at 2% or better in the temperature 25 to 250 K. These deviations are comparable to routine accuracy of calorimeters (± 2%) in this temperature range. The RMS deviation increases beyond 250 K to 7% at 360 K. This increase is due to metastability of semicrystalline samples above the glass transition temperature. The crystallinity term in eq (3) would have to be evaluated for the plotting of the heat capacity as a function of crystallinity. Since a multitude of different metastable crystals is possible, detailed structure information, not available for the analyzed samples, would be needed in this temperature range for the heat capacity discussion.

The heat capacities of amorphous polyethylene obtained from crystallinity extrapolations and the molten polyethylene (discussed later in this section) match at 252 K. This temperature may be considered as the upper end of the glass transition region. The heat capacities of amorphous polyethylene obtained from crystallinity extrapolations were further smoothed as follows: Heat capacity values from 0.5 to 20 K were fitted into the equation

$$C_p = \exp[-0.135328(\ln T)^3 + 0.363949\,(\ln T)^2 + 2.85597(\ln T) - 7.84553]\ \mathrm{J\ mol^{-1}\ K^{-1}} \quad (7)$$

The RMS deviations were 2.2%. Data from 10 to 260 K in 10 degrees intervals were fitted in a seventh degree polynomial using the Chebyshev polynomial method.

$$C_p = \sum_{n=0}^{7} A_n T^n\ \mathrm{J\ mol^{-1}\ K^{-1}} \quad (8)$$

$A_0 = 1.0966333$

$A_1 = -1.1209575\cdot10^{-1}$

$A_2 = 9.3092851\cdot10^{-3}$

$A_3 = -1.7095906\cdot10^{-4}$

$A_4 = 1.5885817\cdot10^{-6}$

$A_5 = -7.931924\cdot10^{-9}$

$A_6 = 2.0248831\cdot10^{-11}$

$A_7 = -2.0616876\cdot10^{-14}$

The RMS deviation was 0.7%. The smooth values from 0.1 to 20 K, obtained from eq (7) and from 25 to 252 K, obtained from eq (8) are given in table 9. The smoothed data are compared to the extrapolated data of Chang [17] and Wunderlich and Baur [4] in figure 3.

The heat capacities of crystalline polyethylene as obtained from crystallinity extrapolations are listed in table 8. Although, at temperature beyond 252 K, linear extrapolation leads to inflated values for amorphous polyethylene (due to changes in crystallinity), the data obtained for crystalline polyethylene is acceptable. The last term in eq (3) which accounts for change in crystallinity, changes the slope of the $C_p - w^c$ extrapolated line, but does not effect the intercept at $w^c = 1$ significantly.

The heat capacity values for crystalline polyethylene in the temperature region 360–410 K were calculated using eq (4) and also from the data on extended chain crystals (sample 12) by correction for the small amorphous fraction using the extrapolated heat capacities of molten polyethylene (discussed later in this section). These values are also listed in table 8. The heat capacity at 360 K obtained from crystallinity extrapolations and from extended chain crystals differ by 5%. The latter was considered more reliable.

The extrapolated values of the heat capacity of crystalline polyethylene were further smoothed as follows: Data from 0.4 to 20 K were fitted into the equation

$$C_p = \exp[-1.07155\cdot10^{-2}\,(\ln T)^3 + 4.62622\cdot10^{-2}\,(\ln T)^2 + 2.89948\,(\ln T) - 9.12864]\ \mathrm{J\ mol^{-1}\ K^{-1}} \quad (9)$$

The RMS deviation was 5.8%. The heat capacities from 10 to 410 K to 10 degrees intervals were fitted with a ninth degree polynomial using the Chebyshev polynomial technique

$$C_p = \sum_{n=0}^{9} A_n T^n\ \mathrm{J\ mol^{-1}\ K^{-1}} \quad (10)$$

where

$A_0 = 1.1504009$

$A_1 = -1.9842302\cdot10^{-1}$

$A_2 = 1.2786634\cdot10^{-2}$

$A_3 = -2.4474207\cdot10^{-4}$

$A_4 = 2.593176\cdot10^{-6}$

$A_5 = -1.6647891\cdot10^{-8}$

$A_6 = 6.5926585\cdot10^{-11}$

$A_7 = -1.5679761\cdot10^{-13}$

$A_8 = 2.0474114\cdot10^{-16}$

$A_9 = -1.1252521\cdot10^{-19}$

The polynomial fits the data from 20 to 390 K with a RMS deviation of 1.2%.

To evaluate the heat capacity of superheated crystalline polyethylene, the data from 300–410 K were fitted into the equation

$$C_p = 4.1802 \cdot 10^6 T^{-2} + 0.32554 T - 122.15 \text{ J mol}^{-1} \text{K}^{-1} \quad (11)$$

The RMS deviation was 1.3%.

The smoothed values from 0.1 to 20 K, obtained from eq (9), from 25 to 390 K, obtained from eq (10) and drom 400–460 K obtrained from eq (11) are given in table 10. The smoothed data is compared to extrapolated data of Chang [17] and Wunderlich and Baur [4] in figure 4.

For molten polyethylene, all the reported data (390–600 K) for linear and branched samples have been plotted in figure 5. Agreement between linear and branched samples from various laboratories is very good. The data were fitted into the equation

$$C_p = 4.325 \cdot 10^{-2} T + 17.919 \text{ J mol}^{-1} \text{K}^{-1} \quad (12)$$

Maximum percent departure at any given temperature was less than 3.5%. The RMS deviation was 1.2%. Equation [12] was used to calculate the heat capacity of molten polyethylene down to 252 K, where the extrapolation with respect to crystallinity gives the same value. These values, from 260 to 600 K are listed in table 9.

Four sets of data on heat capacity of crystalline and amorphous polyethylene have been reported in the literature. The first set of data were reported by Wunderlich [19] in 1962. These were based upon data on samples 9–11, 25, 26, 34, 39, and 40. It was concluded that the crystalline and amorphous polyethylenes have practically identical heat capacities below 110 K. Above 110 K, crystallinity dependence of heat capacity was noted. These values lie in-between our data on amorphous and crystalline polyethylene.

Tuker and Reese [21] have reported extrapolated values for crystalline and amorphous polyethylene between 1 and 30 K. Their estimates were based upon their own measurements on samples 31–33 and 36–38. Tuker and Reese's extrapolated data below 5 K for the crystalline and amorphous polyethylene are about 30% higher than our values. Above 5 K, deviations from our values tend to decrease and above 15 K, their data is in good agreement with this work. Beyond 30 K, Tuker and Reese have reported estimated values to 150 K, with identical heat capacities between 60 and 150 K. Their estimates lie in-between our values for crystalline and amorphous polyethylene, but closer to crystalline values.

The more recent estimate by Wunderlich and Baur [4] over the temperature range 1 to 460 K was based upon data of 29 samples (9–11, 21–23, 25, 26, 30–34, 36–40, and data of Sochava et al. [40, 42], Raine, et al. [39], Warfield et al. [41], Passaglia and Kevorkian [45] and Tautz et al. [43,44]). It incorporated the estimate by Tucker and Reese [21] below 150 K and results of a differential scanning work on extended chain crystals [27]. Identical values for crystlline and amorphous polyethylene were reported between 60 and 210 K. These values also lie in-between our values for crystalline and amorphous polyethylene and are closer to the crystalline values. However, they are significantly lower than our new amorphous values (about 15% at 210 K). Below 60 K, agreement is good with our values. Wunderlich and Baur [4] also observed a pronounced dip in heat capacity around 250 K. This is not observed in this analysis.

The estimate of identical heat capacities for amorphous and crystalline polythylene at intermediate temperatures does not agree with the more extensive data base used in the present study. We conclude now that heat capacity of amorphous polyethylene is always higher than that of crystalline polyethylene up to temperatures close to the melting point. Below 10 K, the heat capacity of crystalline polyethylene is only about 20–30% of that of amorphous polyethylene. The differences get smaller above 10 K. At 20 K, heat capacity of crystalline polyethylene is about half the heat capacity of amorphous polyethylene. Between 60 and 150 K, the differences are less than 10%, the two heat capacities being closest at 110 K, where the difference is only 4%. Beyond 110 K, the differences tend to increase due to the glass transition effects in the amorphous phase and at 250 K, the heat capacity of crystalline polyethylene is about 65% of that of amorphous polyethylene.

In order to minimize the effects due to differences in laboratory techniques, Chang [17] estimated the heat capacity of crystalline and amorphous polyethylene over the temperature range of 5 to 360 K from the results obtained only on samples 1, 4, and 5 at National Bureau of Standards. Chang's crystalline data are in fair agreement with our crystalline values below 310 K. Above 310 K, Chang's values are higher (9% at 360 K). For amorphous polyethylene, Chang's data are in agreement with our values only below 150 K. However, his values are 2–6% higher from 140 to 220 K and 2–8% lower from 240 to 270 K. These deviations in heat capacities for amorphous polyethylene are not very surprising because Chang's extrapolations are based upon samples of fairly high crystallinity. Also, Chang's data beyond 260 K are erroneous because they do not account for change in crystallinity with temperature.

Heat capacity of liquid and supercooled polyethylene over the temperature range of 260 to 460 K had been reported by Wunderlich and Baur [4]. The data were based upon linear extrapolation to 260 K from the average of samples 21–23, 25, 26, 39, 40 and data of Passaglia and Kevorkian [45] and Tautz et al. [43, 44]. These values are 5% higher than our data at 260 K. The deviations decrease with temperature and tend to be negative. Their value at 460 K is 2% lower than our data.

Atkinson, Larkin, and Richardson [54] have based the estimates of molten polyethylene over the temperature range of 200 K to 450 K on their measurements on molten polyethylene and liquid n-paraffins data at low temperatures. Their values agree reasonably well (within ± 2%) with ours.

Broadhurst [46] has estimated the heat capacity of an ideal CH_2-chain. The estimates for the crystalline chain are higher than this study, although experimental n-paraffin values up to 200 K are slightly lower. Broadhurst [46] has also estimated heat capacity of ideal CH_2-chain liquid from n-paraffin data. The estimates deviate by as much as 5%.

4. Thermodynamic Functions of Polyethylene

Thermodynamic functions for amorphous and crystalline polyethylene have been derived from heat capacities. These are listed in tables 9 and 10. H_0 and S_0 refer to zero point enthalpy and residual entropy of the polymer.

At 0 K the residual amorphous entropy was found to be 2.59 J mol^{-1} K^{-1}. A value of 4.60 J mol^{-1} K^{-1} has been reported earlier by Wunderlich and Czornyj [8]. The higher residual entropy was arrived at because identical heat capacities were used for crystalline and amorphous polyethylene over the temperature range 60 to 210 K.

The heats of fusion at various temperatures can be calculated from derived enthalpies as

$$\Delta H_f = (H_T^a - H_0^c) - (H_T^c - H_0^c) = H_T^a - H_T^c. \quad (13)$$

These have been calculated from 260 to 460 K and are listed in table 11. The data has been plotted in figure 6. Based upon n-paraffin data, Atkinson and Richardson have derived the following equation for the Gibbs energy change on melting

$$\Delta G_f = 1.308 + 1.263 \cdot 10^{-2}T - 5.96 \cdot 10^{-5}T^2 + 5 \cdot 10^{-8}T^3 \text{ J g}^{-1}. \quad (14)$$

From eq (14) one can derive

$$\Delta H_f = 93.22 + 4.249 \cdot 10^{-3}T^2 - 7.413 \cdot 10^{-6}T^3 \text{ J g}^{-1} \quad (15)$$

Data for eq (15) are also plotted in figure 6.

Table 9. Recommended thermodynamic data of amorphous polyethylene

T(K)	C_p	$H_T^a - H_o^a$	$S_T^a - S_o^a$	$H_T^a - H_o^c$	S_T^a	$-(G_T^a - H_o^c)$
	($J\ mol^{-1}K^{-1}$)	($J\ mol^{-1}$)	($J\ mol^{-1}K^{-1}$)	($J\ mol^{-1}$)	($J\ mol^{-1}K^{-1}$)	($J\ mol^{-1}$)
0.0	0.0	0.0	0.0	2467.	2.59	-2467.
0.1	0.0000196	0.0000017	0.0000257	2467.	2.59	-2467.
0.2	0.0000178	0.0000034	0.0000375	2467.	2.59	-2466.
0.3	0.0000270	0.0000056	0.0000462	2467.	2.59	-2466.
0.4	0.0000431	0.0000090	0.0000560	2467.	2.59	-2466.
0.5	0.0000674	0.0000145	0.0000681	2467.	2.59	-2466.
0.6	0.000102	0.0000228	0.0000832	2467.	2.59	-2465.
0.7	0.000149	0.0000353	0.000102	2467.	2.59	-2465.
0.8	0.000211	0.0000531	0.000126	2467.	2.59	-2465.
0.9	0.000291	0.0000781	0.000155	2467.	2.59	-2465.
1.0	0.000391	0.000112	0.000191	2467.	2.59	-2464.
1.2	0.000666	0.000216	0.000285	2467.	2.59	-2464.
1.4	0.00106	0.000387	0.000416	2467.	2.59	-2463.
1.6	0.00160	0.000650	0.000591	2467.	2.59	-2463.
1.8	0.00231	0.00104	0.000819	2467.	2.59	-2462.
2.0	0.00323	0.00159	0.00111	2467.	2.59	-2462.
3.0	0.01170	0.00845	0.00378	2467.	2.59	-2459.
4.0	0.02880	0.02788	0.00925	2467.	2.60	-2457.
5.0	0.05667	0.06965	0.01845	2467.	2.61	-2454.
6.0	0.09649	0.1452	0.03212	2467.	2.62	-2451.
7.0	0.1485	0.2667	0.05075	2467.	2.64	-2449.
8.0	0.2123	0.4462	0.07461	2467.	2.66	-2446.
9.0	0.2869	0.6949	0.1048	2468.	2.69	-2443.

Table 9. Recommended thermodynamic data of amorphous polyethylene --Continued

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^a - H_o^a$ (J mol^{-1})	$S_T^a - S_o^a$ (J mol^{-1}K^{-1})	$H_T^a - H_o^c$ (J mol^{-1})	S_T^a (J mol^{-1}K^{-1})	$-(G_T^a - H_o^c)$ (J mol^{-1})
10.0	0.3709	1.023	0.1383	2468.	2.73	-2441.
12.0	0.5611	1.951	0.2224	2469.	2.81	-2435.
14.0	0.7703	3.280	0.3244	2470.	2.91	-2429.
16.0	0.9864	5.036	0.4414	2472.	3.03	-2424.
18.0	1.200	7.223	0.5699	2474.	3.16	-2417.
20.0	1.402	9.828	0.7069	2477.	3.30	-2411.
25.0	1.989	18.37	1.085	2485.	3.68	-2393.
30.0	2.605	29.83	1.502	2497.	4.09	-2374.
40.0	3.900	62.34	2.428	2529.	5.02	-2329.
50.0	5.145	107.7	3.434	2575.	6.02	-2273.
60.0	6.264	164.8	4.473	2632.	7.06	-2208.
70.0	7.250	232.5	5.514	2699.	8.10	-2132.
80.0	8.130	309.5	6.541	2776.	9.13	-2046.
90.0	8.949	394.9	7.546	2862.	10.14	-1950.
100.0	9.747	488.4	8.530	2955.	11.12	-1843.
110.0	10.56	589.9	9.497	3057.	12.09	-1727.
120.0	11.39	699.6	10.45	3167.	13.04	-1602.
130.0	12.26	817.8	11.40	3285.	13.99	-1466.
140.0	13.16	944.9	12.34	3412.	14.93	-1322.
150.0	14.06	1081.	13.28	3548.	15.87	-1168.
160.0	14.98	1226.	14.21	3693.	16.80	-1005.
170.0	15.89	1381.	15.15	3848.	17.74	- 831.8
180.0	16.83	1544.	16.08	4011.	18.67	- 649.7

Table 9. Recommended thermodynamic data of amorphous polyethylene--Continued

T(K)	C_p (J mol^{-1}K^{-1})	$H_T^a-H_o^a$ (J mol^{-1})	$S_T^a-S_o^a$ (J mol^{-1}K^{-1})	$H_T^a-H_o^c$ (J mol^{-1})	S_T^a (J mol^{-1}K^{-1})	$-(G_T^a-H_o^c)$ (J mol^{-1})
190.0	17.82	1717.	17.02	4184.	19.61	-458.3
200.0	18.92	1901.	17.96	4368.	20.55	-257.5
210.0	20.19	2096.	18.92	4563.	21.51	- 47.20
220.0	21.71	2306.	19.89	4773.	22.48	172.7
230.0	23.55	2532.	20.89	4999.	23.48	402.5
240.0	25.74	2778.	21.94	5245.	24.53	642.5
250.0	28.25	3047.	23.04	5514.	25.63	893.3
252.0	28.79	3105.	23.27	5572.	25.86	944.8
260.0	29.16	3336.	24.17	5803.	26.76	1155.
270.0	29.60	3630.	25.28	6097.	27.87	1428.
278.15	29.74	3724.	25.62	6191.	28.21	1518.
280.0	30.03	3928.	26.37	6395.	28.96	1713.
290.0	30.46	4231.	27.43	6698.	30.02	2008.
298.15	30.81	4481.	28.28	6948.	30.87	2257.
300.0	30.89	4538.	28.47	7005.	31.06	2313.
310.0	31.33	4849.	29.49	7316.	32.08	2629.
320.0	31.76	5164.	30.49	7631.	33.08	2954.
330.0	32.19	5484.	31.47	7951.	34.06	3290.
340.0	32.62	5808.	32.44	8275.	35.03	3636.
350.0	33.06	6136.	33.39	8603.	35.98	3991.
360.0	33.49	6469.	34.33	8936.	36.92	4355.
370.0	33.92	6806.	35.25	9273.	37.84	4729.
380.0	34.35	7148.	36.16	9615.	38.75	5112.

Table 9. Recommended thermodynamic data of amorphous polyethylene--Continued.

T(K)	C_p	$H_T^a - H_o^a$	$S_T^a - S_o^a$	$H_T^a - H_o^c$	S_T^a	$-(G_T^a - H_o^c)$
	($J\ mol^{-1}K^{-1}$)	($J\ mol^{-1}$)	($J\ mol^{-1}K^{-1}$)	($J\ mol^{-1}$)	($J\ mol^{-1}K^{-1}$)	($J\ mol^{-1}$)
390.0	34.79	7493.	37 06	9960.	39.65	5504.
400.0	35.22	7843.	37.95	10310.	40.54	5905.
410.0	35.65	8198.	38.82	10665.	41.41	6315.
414.6	35.85	8362.	39.22	10829	41.81	6506.
420.0	36.08	8556.	39.69	11023.	42.28	6733.
430.0	36.52	8919.	40.54	11386.	43.13	7160.
440.0	36.95	9287.	41.39	11753.	43.98	7596.
450.0	37.38	9658.	42.22	12125.	44.81	8040.
460.0	37.81	10034.	43.05	12501.	45.64	8492.
470.0	38.25	10414.	43.87	12881.	46.46	8953.
480.0	38.68	10799.	44.68	13266.	47.27	9421.
490.0	39.11	11188.	45.48	13655.	48.07	9898.
500.0	39.54	11581.	46.27	14048.	48.86	10382.
510.0	39.98	11979.	47.06	14446.	49.65	10875.
520.0	40.41	12380.	47.84	14847.	50.43	11375.
530.0	40.84	12787.	48.61	15254.	51.20	11883.
540.0	41.27	13197.	49.38	15664.	51.97	12399.
550.0	41.71	13612.	50.14	16079.	52.73	12923.
560.0	42.14	14031.	50.90	16498.	53.49	13454.
570.0	42.57	14455.	51.65	16922.	54.24	13992.
580.0	43.00	14883.	52.39	17350.	54.98	14538.
590.0	43.44	15315.	53.13	17782.	55.72	15092.
600.0	43.87	15752.	53.86	18219.	56.45	15653.

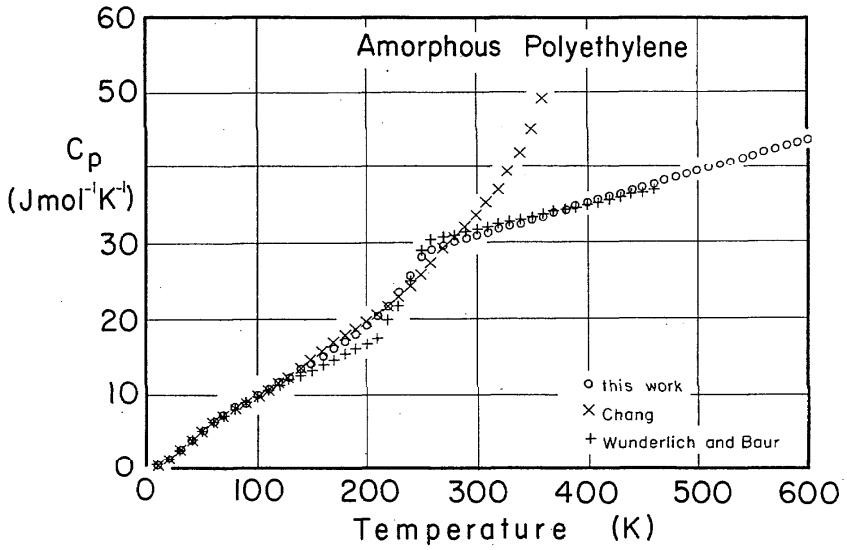

FIGURE 3. Heat capacity of amorphous polyethylene as a function of temperature.

Table 10. Recommended thermodynamic data of crystalline polyethylene

T(K)	C_p	$H_T^c - H_o^c$	S_T^c	$-(G_T^c - H_o^c)$
	(J mol^{-1}K^{-1})	(J mol^{-1})	(J mol^{-1}K^{-1})	(J mol^{-1})
0.0	0.0	0.0	0.0	0.0
0.1	0.0000002	0.000000005	0.00000007	0.000000001
0.2	0.0000012	0.00000007	0.0000005	0.00000002
0.3	0.0000036	0.0000003	0.0000013	0.0000001
0.4	0.0000080	0.0000009	0.0000029	0.0000003
0.5	0.0000149	0.0000020	0.0000054	0.0000007
0.6	0.0000250	0.0000039	0.0000090	0.0000014
0.7	0.0000388	0.0000071	0.0000138	0.0000026
0.8	0.0000570	0.0000119	0.0000201	0.0000042
0.9	0.0000799	0.0000187	0.0000281	0.0000066
1.0	0.000109	0.0000280	0.0000379	0.0000099
1.2	0.000184	0.0000569	0.0000640	0.0000200
1.4	0.000289	0.000104	0.0000999	0.0000362
1.6	0.000428	0.000175	0.000147	0.0000607
1.8	0.000605	0.000277	0.000207	0.0000959
2.0	0.000825	0.000420	0.000282	0.000145
3.0	0.00274	0.00208	0.000928	0.000708
4.0	0.00642	0.00648	0.00217	0.00220
5.0	0.01244	0.01569	0.00420	0.00531
6.0	0.02135	0.03232	0.00721	0.01093
7.0	0.03370	0.05954	0.01138	0.02011
8.0	0.05000	0.1010	0.01690	0.03413
9.0	0.07078	0.1610	0.02394	0.05442
10.0	0.09653	0.2443	0.03268	0.08258
12.0	0.1649	0.5017	0.05597	0.1699
14.0	0.2589	0.9209	0.08809	0.3123
16.0	0.3820	1.557	0.1303	0.5290
18.0	0.5378	2.471	0.1840	0.8413
20.0	0.7294	3.732	0.2502	1.273
25.0	1.223	8.498	0.4608	3.021
30.0	1.838	16.12	0.7370	5.990
40.0	3.188	41.19	1.449	16.77
50.0	4.523	79.82	2.305	35.45
60.0	5.745	131.3	3.240	63.13
70.0	6.829	194.3	4.209	100.4
80.0	7.790	267.4	5.185	147.3
90.0	8.656	349.7	6.153	204.0
100.0	9.453	440.3	7.107	270.3
110.0	10.20	538.6	8.043	346.1
120.0	10.92	644.3	8.962	431.1
130.0	11.60	756.9	9.863	525.3
140.0	12.25	876.1	10.75	628.3
150.0	12.87	1002.	11.61	740.1

Table 10. Recommended thermodynamic data of crystalline polyethylene--Continued.

T(K)	C_p	$H_T^C - H_o^C$	S_T^C	$-(G_T^C - H_o^C)$
	($J\ mol^{-1}K^{-1}$)	($J\ mol^{-1}$)	($J\ mol^{-1}K^{-1}$)	($J\ mol^{-1}$)
160.0	13.45	1133.	12.46	860.5
170.0	14.00	1271.	13.29	989.3
180.0	14.53	1413.	14.11	1126.
190.0	15.05	1561.	14.91	1271.
200.0	15.57	1714.	15.69	1424.
210.0	16.10	1873.	16.47	1585.
220.0	16.66	2036.	17.23	1754.
230.0	17.25	2206.	17.98	1930.
240.0	17.88	2382.	18.73	2113.
250.0	18.55	2564.	19.47	2304.
260.0	19.23	2753.	20.21	2503.
270.0	19.91	2948.	20.95	2709.
273.15	20.12	3012.	21.18	2776.
280.0	20.58	3151.	21.69	2922.
290.0	21.21	3360.	22.42	3142.
298.15	21.70	3535	23.01	3328.
300.0	21.81	3575.	23.15	3370.
310.0	22.38	3796	23.87	3605.
320.0	22.95	4022.	24.59	3848.
330.0	23.56	4255.	25.31	4097.
340.0	24.30	4494.	26.02	4354.
350.0	25.25	4742.	26.74	4618.
360.0	26.51	5000.	27.47	4889.
370.0	28.13	5273.	28.22	5167.
380.0	30.12	5564.	28.99	5453.
390.0	32.36	5876.	29.80	5747.
400.0	34.19	6209.	30.65	6049.
410.0	36.19	6560.	31.51	6360.
414.6	37.13	6729.	31.92	6506.
420.0	38.27	6933.	32.41	6680.
430.0	40.44	7326.	33.34	7008.
440.0	42.68	7742.	34.29	7347.
450.0	44.98	8180.	35.28	7694.
460.0	47.35	8642.	36.29	8052.

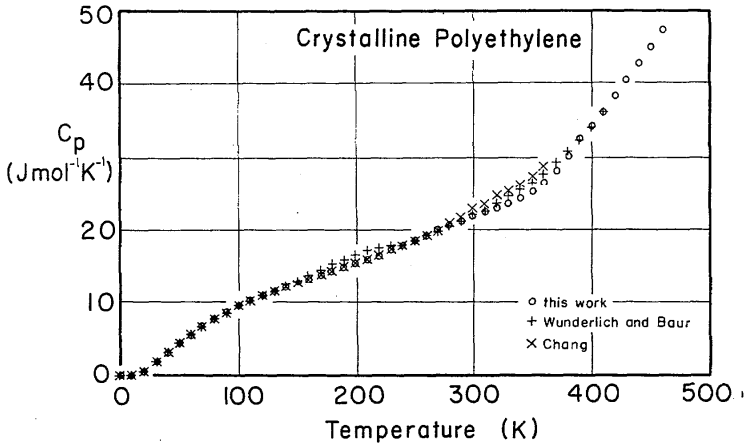

FIGURE 4. Heat capacity of crystalline polyethylene as a function of temperature.

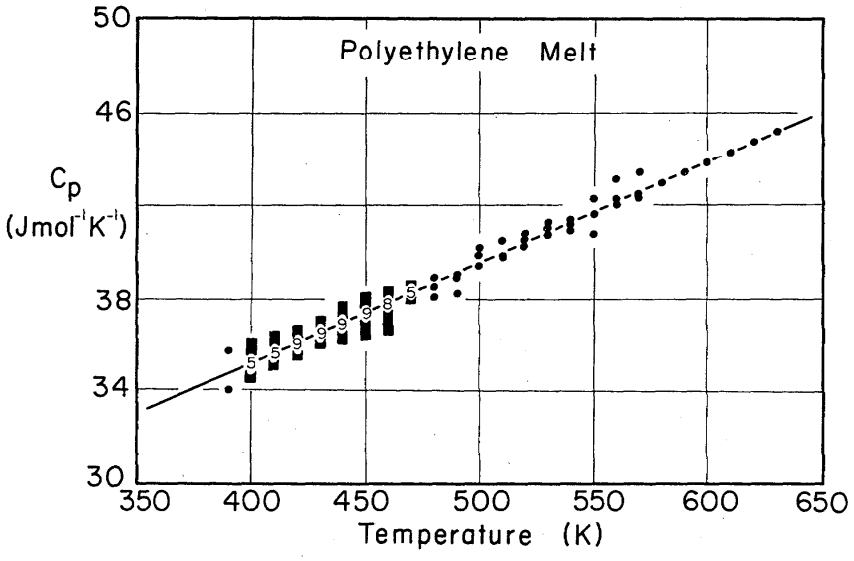

FIGURE 5. Heat capacity of molten polyethylene as a function of temperature (numerals in the figure denote number of overlapping points. Samples 15, 21–26, 30, 39–42. Drawn-out line represents eq (12)).

Table 11. Heat of fusion of polyethylene

T(K)	ΔH_f(kJ mol^{-1})
260	3.050
270	3.149
280	3.244
290	3.338
300	3.430
310	3.520
320	3.609
330	3.696
340	3.781
350	3.861
360	3.936
370	4.000
380	4.051
390	4.084
400	4.101
410	4.105
414.6	4.100±0.2[a]
420	4.090
430	4.060
440	4.011
450	3.944
460	3.859

[a]Reference [8]

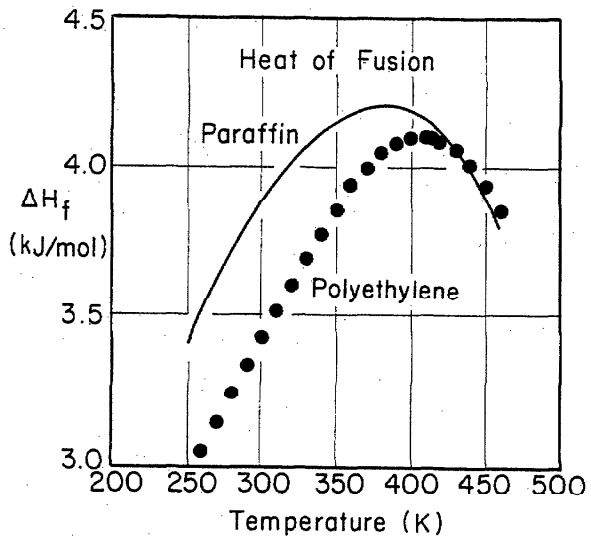

FIGURE 6. Heat of fusion of polyethylene as a function of temperature. Drawn-out curve as derived from paraffin data (eq (15)).

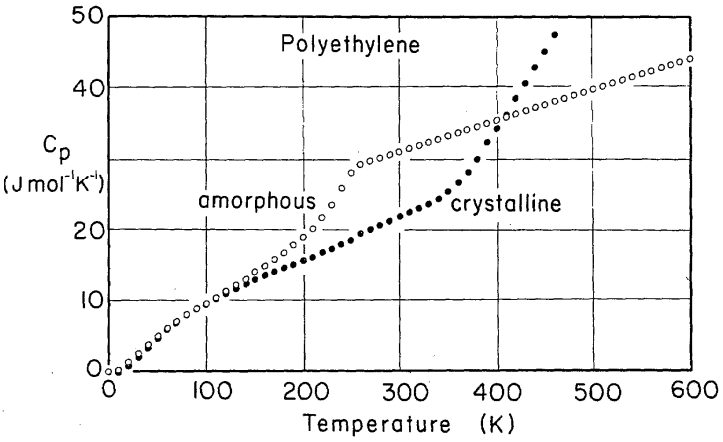

FIGURE 7. Recommended heat capacity data on amorphous and crystalline polyethylene as a function of temperature.

5. Conclusions

The heat capacity of polyethylene from 0 K to 600 has been reviewed using 46 measurements reported in the literature. The crystallinity dependence had been critically evaluated and sets of recommended heat capacity, enthalpy, entropy, and Gibbs energy data for completely crystalline and amorphous polyethylene have been derived. Recommended heat capacity data are plotted in figure 7. We have arrived in addition at the following conclusions:

1. The heat capacity of crystalline polyethylene is a smooth function of temperature from 0 to 360 K. The steeper slope above 360 K increases the heat capacity of the crystalline polyethylene to that of the amorphous at about 410 K. The heat capacity of amorphous polyethylene is also a smooth function of temperature from 0 to 200 K. The upward slope beyond 200 K can be associated with the glass transition. The heat capacity of molten polyethylene is a linear function of temperature to 600 K. Upon extrapolation below the melting temperature, it matches the extrapolated heat capacity of amorphous polyethylene at 252 K. Thus, 200 to 252 K may be considered the glass transition region ($T_g \approx 237$ K).

2. Up to temperatures close to the melting point, the heat capacity of amorphous polyethylene is higher than the heat capacity of crystalline polyethylene. Differences are, however, small over the temperature range from 60 to 150 K.

3 The two phase model for linear extrapolation of heat capacities is applicable to both linear and branched polyethylene, but not to ultrahigh molecular weight polyethylene. Beyond 250 K, the heat capacity of amorphous polyethylene obtained from linear extrapolation have to be corrected for changes in crystallinity with temperature.

4. At 0 K the residual amorphous entropy is 2.59 J mol^{-1} K^{-1}.

5. The heat of fusion has a surprising temperature dependence due to the different temperature dependencies of the heat capacities of amorphous and crystalline polyethylene.

6. The change in heat capacity of the amorphous polyethylene at the glass transition fits rule of constant ΔC_p, but the glass transition range is extended to very low temperatures.

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